Arsenate Adsorption Mechanisms at the Allophane–Water Interface

YUJI ARAI,^{*,†,‡} D. L. SPARKS,[‡] AND J. A DAVIS[†]

United States Geological Survey, MS 465 Middlefield Road, Menlo Park, California 94025, and Department of Plant and Soil Sciences, University of Delaware, Newark, Delaware 19717

We investigated arsenate (As(V)) reactivity and surface speciation on amorphous aluminosilicate mineral (synthetic allophane) surfaces using batch adsorption experiments, powder X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). The adsorption isotherm experiments indicated that As(V) uptake increased with increasing [As-(V)]_o from 50 to 1000 μ M (i.e., Langmuir type adsorption isotherm) and that the total As adsorption slightly decreased with increasing NaCl concentrations from 0.01 to 0.1 M. Arsenate adsorption was initially (0-10 h) rapid followed by a slow continuum uptake, and the adsorption processes reached the steady state after 720 h. X-ray absorption spectroscopic analyses suggest that As(V) predominantly forms bidentate binuclear surface species on aluminum octahedral structures, and these species are stable up to 11 months. Solubility calculations and powder XRD analyses indicate no evidence of crystalline Al-As(V) precipitates in the experimental systems. Overall, macroscopic and spectroscopic evidence suggest that the As(V) adsorption mechanisms at the allophane-water interface are attributable to ligand exchange reactions between As-(V) and surface-coordinated water molecules and hydroxyl and silicate ions. The research findings imply that dissolved tetrahedral oxyanions (e.g., $H_2PO_4^{2-}$ and $H_2AsO_4^{2-}$) are readily retained on amorphous aluminosilicate minerals in aquifer and soils at near neutral pH. The innersphere adsorption mechanisms might be important in controlling dissolved arsenate and phosphate in amorphous aluminosilicate-rich low-temperature geochemical environments.

Introduction

Allophane is a poorly crystalline aluminosilicate mineral consisting of hollow and spherical particles with diameters of 3.5-5 nm and with a molar Si/Al ratio of approximately 1:2 to 1:1 (1) and is commonly present in andisols and spodosols (2–5). Although the occurrence of allophane is commonly reported in soils with volcanic ash accumulated soils, it has been also identified in pumice deposits, stream sediments, and soils derived from igneous and sedimentary rock sandstones (5–7). Because of its high surface area, it has a great retention capacity for anions (i.e., nitrate, F, P, and chloride) over a wide pH range (4–8) (8, 9). We are

particularly interested in understanding tetrahedral oxyanion (e.g., P(V) and As(V)) adsorption mechanisms on allophane surfaces because it has environmental soil/geo chemical implications for (1) understanding the strong P fixation mechanism on allophane and imogolite (*10*) causing the reduction in plant-available P in agricultural and forest soils (e.g., andisols) and (2) predicting the As(V) transport processes in aquifer sediments that are dominated by amorphous aluminosilicate coatings.

Phosphate deficiency in allophatic soils has been well documented as major agronomic and forestry problems throughout the world. This phenomenon is attributed to a strong phosphate interaction with allophatic soil components (e.g., allophane and imogolite). Several researchers have investigated P adsorption reactions on allophane to understand the strong P fixation mechanisms in allophane and allophatic soils (10, 11). Slow Si release upon P adsorption on allophane has been indirectly linked to aluminum phosphate precipitation reactions (10, 12-14), however, there has been no conclusive in-situ experimental evidence that precipitation reactions were occurring at the mineral-water interface. Direct surface speciation via in-situ spectroscopic techniques would definitely add insight into our understanding of the nonlabile P fixation mechanisms on allophane surfaces. Such knowledge would also assist in more effectively managing P deficiencies in allophatic agricultural and forestry soils throughout the world.

At the U. S. Geological Survey field research sites on Cape Cod, Massachusetts, As(V) transport processes have been recently investigated via field scale tracer tests (*15*, *16*). The aquifer at the sites is composed of weathered and glacially deposited sediments whose coatings consist of polycrystalline materials enriched in Al and Si (*17*, *18*). To accurately predict As(V) transport processes at these sites, molecular scale data on As(V) reactions on aluminosilicate mineral surfaces are needed. While As(V) surface speciation has been extensively investigated on metal–oxide surfaces (*19–23*), As(V) adsorption mechanisms on aluminosilicate minerals are still poorly understood.

In this study, As(V) was chosen as an analogue of P(V) to gain an overall understanding of tetrahedral oxyanion reactivity and surface speciation at the amorphous aluminosilicate mineral–water interface. Specifically, the As(V) adsorption mechanism on allophane surfaces was investigated using batch adsorption experiments and As K-edge X-ray absorption spectroscopy (XAS), which provides better sensitivity than P K-edge XAS measurements at the current second and third generation synchrotron facilities. The As-(V) research findings can be extended to better understand important P geochemical processes since these two oxyanions have similar chemical properties (e.g., dissociation constants (p K_{a1-3} ; 2.1, 7.2, 12.3 for P and 2.2, 6.97, 13.4 for As(V)) (24).

Materials

Allophane (BET specific surface area of $369.69 \pm 1.51 \text{ m}^2 \text{ g}^{-1}$) was synthesized using the method described by Ohashi and co-workers (25). This method was chosen because the end products contain no bohemite and gibbsite impurities which were confirmed via XRD analyses. One hundred milliliters of 100 mM sodium orthosilicate was added to 100 mL 150 mM aluminum chloride solution. The mineral suspension was shaken for 1 h at room temperature. Precipitates were washed on a 0.25- μ m filter with deionized water to remove the entrained NaCl solutions. The precipitate was suspended in 200 mL of deionized water and then was treated at 80 °C for 5 days. The solids were recovered by filtration and kept

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^{*} Corresponding author phone: (650)329-4520; fax: (650)329-4327; e-mail: yarai@usgs.gov.

[†] United States Geological Survey.

[‡] University of Delaware.



FIGURE 1. Upper 2 θ portion of the synthetic allophane XRD patterns. Two broad peaks at 0.34 and 0.225 nm *d* spacing indicate the presence of allophane. Three additional patterns are aged allophane suspensions under the following reaction conditions: pH 6.5 \pm 0.3, I = 0.1 M NaCl, pCO₂ = 10^{-3.5} atm, and initial As(V) concentrations = 1 mM.

in suspension prior to batch adsorption experiments. For the XRD analyses, 20 mL of allophane suspensions (10 g L⁻¹) were filtered using 0.2- μ m filters and then rinsed twice with 10 mL of deionized water. Air-dried samples were finely ground using a mortar and pestle for the XRD analysis. Powder X-ray diffraction data were collected from 10 to 70° 2 θ with a Nicolet X-ray powder diffractometer (graphite monochromatized Cu K α radiation, 0.05° 2 θ step size, and 2-s count time per steps). The XRD analyses indicate that the synthesized material exhibits two broad peaks at 0.34 and 0.225 nm (Figure 1a) that correspond to diagnostic peaks for allophane. Similar peaks have been previously observed in allophatic materials by Parfitt (26). Electron micrograph observations indicate that synthetic allophane has small spheres varying from ~3 to 6 nm in diameter.

Ionic Strength Effects on As(V) Adsorption. Adsorption isotherm experiments were conducted in duplicate. First, the mineral suspensions (1.25 g L^{-1}) and As(V) stock solutions (5 mM NaH₂AsO₄) were prepared in 0.01 or 0.1 M NaCl background solutions. To facilitate atmospheric CO₂ equilibration of these solutions at pH 6.5, adequate amounts of 10 mM sodium bicarbonate solution were added and then preequilibrated for 24 h at pH 6.5 \pm 0.1 using a pH stat apparatus under a humidified air purge. Similarly, 0.01 or 0.1 M NaCl background and 10 mM organic buffer 2-[N-Morpholino]ethanesulfonic acid (MES) solutions at pH 6.5 were prepared. Twenty-four milliliters of the mineral suspensions was pipetted out in 35-mL polycarbonate highspeed centrifuge tubes, and then adequate amounts of As(V) stock solution, background electrolyte solution, and an MES stock solution were added to ensure $[As(V)]_0 = 50, 100, 300,$ 500 μ M, or 1 mM, a final suspension density = 1 g L⁻¹, a 1 mM MES, and a final volume of 30 mL for each ionic strength condition. The As(V) adsorption reactions were carried out on an end-over shaker at 14 rpm. After 48 h, pH values were measured in the suspension.

All samples were immediately centrifuged at 21 950g for 7 min at 20 °C. Aliquots were passed through 0.22- μ m Millex-GX filters (Millipore Corp., Bedford, MA). The reaction time of 48 h was chosen because the extent of adsorption after 48 h slows down significantly comparing to the initial 24 h, and this provides sufficient time to complete the consistent sampling processes. Arsenate concentrations were analyzed

using the molybdenum blue method (Cummings et al., 1999). The analytical uncertainties were about $\pm 2\%$. Dissolved Si and Al concentrations were measured using inductively coupled plasma-mass spectrometry (ICP-MS). The analytical uncertainties were about $\pm 3.5\%$ for Si and $\pm 2.5\%$ for Al. Because of possible C/N/O polyatomic interferences for total [Si] in the ICP-MS analyses, the dissolved Si concentrations were also measured using a silicomolybdic acid colorimetric method (27). The comparable results in both analytical methods suggest no polyatomic interferences for total Si concentrations in the ICP-MS measurements.

Adsorption Kinetics Experiments. Arsenate stock solutions and mineral suspensions (3.75 g L^{-1}) were prepared as described above, and kinetic experiments were conducted in 0.1 M NaCl background electrolyte without the use of the MES buffer. Mineral suspensions of 160 mL were preequilibrated at pH 6.5 for 24 h using a pH stat apparatus at 22 \pm 2 °C. Fifty milliliters of As(V) stock solution (5 mM sodium As(V) in 0.1M NaCl at pH 6.5) and 40 mL of 0.1 M NaCl solution were added to ensure an initial As(V) concentration of 1 mM, a final suspension density of 3 g L^{-1} , and a final volume of 250 mL. The As(V)-allophane mixed suspensions were stirred at 300 rpm. The pH was controlled at 6.5 ± 0.2 using a pH-stat apparatus up to 48 h. Thereafter, pH was manually adjusted every 5-10 days using 0.01-0.1 M HCl. Ten milliliters of suspensions were sampled periodically at 5, 15, and 30 min, 1, 3, 6, 10, and 24 h, 5, 15, and 30 days, and 3 months. Because of clogging problems due to fine allophane particles during filtration, all samples were initially centrifuged at 21 950g for 5 min at 20 °C, and then the aliquot was passed through 0.22-µm Millex-GX filters. Arsenate concentrations were analyzed using the molybdenum blue method. Dissolved Al and Si levels were measured using ICP-MS.

Arsenic K-Edge Extended X-ray Absorption Fine Structure Analyses. X-ray absorption spectroscopy was used to obtain in-situ chemical information on As(V) adsorption mechanisms at the allophane–water interface. All XAS samples were prepared under $_PCO_2 = 10^{-3.5}$ atm using the same experimental procedures described in the adsorption kinetics section. Thirty milliliters of the As(V) reacted allophane suspensions were collected and then centrifuged at 11 950g for 10 min at 20 °C. The paste was loaded in Teflon sample holders, which were then sealed with Kapton film/ tape (CHR Industries), and then kept at 5 °C. The data were collected within 36 h of the sample preparation. Arsenic K-edge (11867 eV) XAS spectra were collected on beamline X-11A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, NY. The electron storage ring was operated at 2.528 GeV with a current range of 130-250 mA. XAS spectra were collected in fluorescence mode with a Lytle detector filled with Krypton gas. EXAFS spectra were collected in 0.5-10 eV steps between the preedge to extended regions of the spectra. The ionization chamber (I_o) was filled with 90% N₂ and 10% Ar. The As K-edge energy was calibrated at 11874 eV using an As(V) standard (i.e., sodium arsenate salt), which was run simultaneously with adsorption samples to monitor potential energy shifts during the run. A Ge-filter was used to remove elastically scattered radiation from the fluorescence emissions. The monochromator consisted of two parallel Si(111) crystals with a vertical entrance slit of 0.5 mm. The sample holders were oriented at 45° to the unfocused incident beam. We performed data collection of the sorption samples at room temperature.

XAS data reduction and analyses were performed with Sixpack (28) using the following procedures. First, two to four spectra were averaged. The averaged spectra were normalized with respect to E_0 determined from the second derivative of the raw spectra, and then the total atomic crosssectional absorption was set to unity. A low-order polynomial function was fit to the preedge region and the postedge region. Next, the data were converted from *E*-space to *k*-space and weighted by k^3 to compensate for dampening of the XAFS amplitude with increasing k space. Fourier transformation was then performed over the k range of 1.6–12.8 Å⁻¹ to obtain the radial structural functions (RSF). Final fitting of the spectra was done on Fourier transformed k^3 weighted spectra in R-space. The FEFF702 code (29) was employed to calculate single-scattering theoretical spectra and phase shifts for As-O and As-Al backscattering using an input file on the basis of the structural refinement of mansfieldite (AlAsO₄ \cdot 2H₂O) (30). To reduce the number of degrees of freedom for the tetrahedral As(V) oxygen neighbors (i.e., four oxygen atoms), the best integer fit method was used by constraining the coordination number (CN) for As-O single-scattering shells to 4. The amplitude reduction factor, S_0^2 , was fixed to 0.9 to reduce the number of adjustable parameters (31). During fitting, the values of R of the As–O and As–Al shells were allowed to vary, as well as a single E_0 for all sets of backscattering atoms. The Debye-Waller factors of the As-O shells were also allowed to vary, but those of the As-Al shells were fixed at 0.005 Å². When allowed to vary, the Debye-Waller factors of the As-Al shells showed no trends for different samples (e.g., as a function of pH and loading levels). and we therefore used the average values (0.005 Å^2) in the final fitting procedure to reduce the number of free parameters. Accuracies for R and CN are ± 0.02 Å and $\pm 25\%$, respectively, for As–O shell and ± 0.03 Å and $\pm 30\%$, respectively, for the As-Al shell. Principal component analyses (PCA) were additionally conducted using k^3 weighted EXAFS spectra of five adsorption samples at $3.0-12.0 \text{ k}^{-1}$.

Results and Discussion:

Ionic Strength Effects on As(V) Adsorption Isotherm. The pseudo-equilibrium As(V) adsorption isotherms for allophane as a function of ionic strength are shown in Figure 2a. After 48 h of reaction time, pH values were stable at 6.5 ± 0.01 because of the use of the MES buffer. The As(V) uptake generally increased with increasing initial As(V) concentrations from 50 to 1000 μ M, showing Langmuir (or L-curve) type adsorption isotherm. Adsorption was not significantly affected by changes in ionic strength at the low C_{eq} (pseudo-equilibrium As(V) concentrations: $13.3-152.53 \mu$ M), but the

As(V) uptake slightly decreased with increasing NaCl concentrations from 0.01 to 0.1 M at the higher C_{eq} (>280 μ M). A one-site Langmuir isotherm model (C/q = 1/kb + C/b), where C is the pseudo-equilibrium concentrations of the adsorptive, q is the amount of adsorption (adsorbate per unit mass of adsorbent), *k* is the binding strength constant, and b is the maximum amount of adsorptive, was used to describe the isotherm data. The linear regression and Langmuir isotherm parameters are shown in Figure 3. The regression values > 0.987 indicate a good fit for both systems. The parameters for the 0.1 and 0.01 M NaCl systems indicate maximum monolayer coverage, b, of 0.83 and 0.98 μ M m⁻², respectively, and the binding strength constant, k, 87.56 and 122.05, respectively, consistent with the lower ionic strength system producing slightly stronger As(V) adsorption. This predicts the strong As(V) reactivity on amorphous aluminosilicate surfaces where ionic strength of soil solutions and porewater are below 0.1 M. Enhanced As(V) adsorption under the lower ionic strength condition might be associated with weakly complexed As(V) like outer-sphere surface species since the ionic strength dependent anion adsorption is often linked to distinguishing inner-sphere adsorption from outersphere adsorption mechanisms (32). However, it is difficult to elucidate the surface species without any spectroscopic evidence. Several spectroscopic studies have previously shown that ionic strength effect on inorganic contaminant adsorption cannot be simply related to the differences between outer- and inner-sphere surface species (33, 34). Although the adsorption maximum seems to be reached in the 0.1 M NaCl systems at C_{eq} (400–750 μ M), no mechanistic information can be suggested on the basis of the isotherm data. Veith and Sposito have previously demonstrated that both adsorption and precipitation reactions can be well fit using Langmuir isotherm data (35), meaning that the mechanistic hypotheses cannot be validated with the adsorption isotherm data.

We have subsequently monitored dissolved total Al and Si in the As(V) adsorption isotherm experiments. There was no trend in the dissolved total Al concentrations (below 0.5 μ M) with respect to the pseudo-equilibrium As(V) concentrations at either ionic strength, but Si release was significantly enhanced with increasing As(V) adsorption (Figure 2b) and with increasing in initial As(V) concentrations. The Si concentrations in the presence of As(V) (i.e., $100-450 \ \mu M$) are significantly higher than that of respective control systems (i.e., $<30 \,\mu$ M regardless of different *I*), indirectly suggesting that the Si release might be attributed to the As(V) adsorption. It is possible that weakly sorbed Si anions on allophane surfaces are exchanged via As(V) adsorption under different ionic strength, resulting in Si release. Enhanced Si release from these aluminosilicate minerals is important because it can affect the transport and reactivity of other inorganic and organic contaminants via competitive adsorption processes. Dissolved Si not only reduces chromate and arsenate adsorption on iron-based adsorbents (i.e., ferrihydrite and zerovalent iron) (36, 37) but also suppresses the degradation of 1,1,1-trichloroethane on granular iron surfaces (38).

Slow Si release from allophane has been observed during phosphate adsorption by several researchers (10, 12) as well as in soils and on natural clay minerals (i.e., kaolinite, natural allophane, and allophanic clay) (10, 39-41). Although several researchers have argued that Si release is attributed to phosphate isomorphic substitution for structural silicate in allophanic clays forming aluminum phosphate-like precipitates, it is difficult to elucidate the Si release mechanisms on the basis of macroscopic data observation alone.

Adsorption Kinetics Experiments. Long-term As(V) adsorption kinetic data are shown in Figure 4. Uptake of dissolved As(V) was initially (0–10 h) rapid, followed by a slow and continuous process up to 720 h. Although the



FIGURE 2. (a) Pseudo-equilibrium As(V) adsorption isotherm on the synthetic allophane (pCO₂ = $10^{-3.5}$ atm, pH 6.5 ± 0.1, I = 0.01-0.1 M NaCl + 1 mM MES buffer, initial As(V) concentrations = 50, 100, 300, 500, and 1000 μ M and suspension density = 1 g/L) as a function of ionic strength (0.01 and 0.1 M NaCl) and (b) dissolved total Al and Si during the As(V) adsorption isotherm shown in Figure 2a.



FIGURE 3. One-site Langmuir isotherm plots of As(V) adsorption on allophane derived from the data shown in Figure 2a.

dissolved As(V) concentrations varied only slightly between 720 and 7920 h, 80% of total As(V) was consistently retained on the allophane surfaces during the long-term experiments. This suggests an importance of long-term retention of As(V) on other geomedia containing aluminol and siloxane functional groups (e.g., aluminum (hydr)oxides and crystalline aluminosilicates). As observed in the previous As(V) adsorption isotherm experiments, Si release was also promoted via As(V) adsorption on allophane. The dissolved [Si] rapidly increased from ~ 50 to $\sim 400 \ \mu M$ during the fast As(V) adsorption (<10 h) and gradually decreased to \sim 325 μ M after 7920 h. Enhanced Si release during the As(V) adsorption is possibly creating the competitive mineral-water interfacial environments for unreacted (nonsorbed) As(V), possibly resulting in slow As(V) adsorption processes with increasing time. Dissolved [Al] ranged between 0.17 and 0.54 μ M, and there was no trend in the dissolved Al concentrations during the As(V) adsorption. It is possible that the fluctuating Al/Si concentrations might be attributed to reprecipitation of amorphous aluminosilicate minerals or aluminum arsenate minerals. We used X-ray absorption spectroscopic and XRD methods to investigate the effects of aging on (1) arsenate



FIGURE 4. Dissolved As(V) and total Si concentrations during As(V) adsorption kinetics on allophane (pH 6.5 \pm 0.3, *I* = 0.1 M NaCl, pCO₂ = 10^{-3.5} atm, initial As(V) concentrations = 1 mM).

surface speciation in aged arsenate reacted allophane and (2) the allophane structure.

Arsenic K-Edge Extended X-ray Absorption Fine Structure Analyses. Principal component analyses on k^3 weighted EXAFS spectra show that the first component that extracted from these spectra accounted for 82.4% of the total variance within the data (Table 2). While the significance of a single component was confirmed by visual inspection of each EXAFS component and a scree plot (not shown), it can be also validated by the indicator (IND) function. The primary component appears as the lowest IND value (0.643) in the entire analyses (Table 2) (42).

Figure 5a shows the k^3 -weighted EXAFS spectra of As-(V)-adsorbed allophane samples. The spectra show strong sinusoidal oscillations resulting from O-shell backscattering. The oscillation is similar to those of other As(V)-adsorbed aluminum oxides (20). Fourier transformed k^3 -weighted spectra (uncorrected for phase shift) show the quantitative estimation of interatomic distances between As and next neighboring atoms in the As(V) adsorption samples (Figure 5b). The structural parameters obtained from the linear leastsquares fits of the EXAFS data are shown in Table 1. Less than 1% R-factor (i.e., the absolute misfit between the theory and data) (43) in the linear least-squares fits of the EXAFS data indicates an excellent overall fit (Table 1). Interatomic distances of the As–O shell (\sim 1.69 Å) after correction for phase shifts (Table 1) indicate that AsO4 tetrahedral molecular structures are present in all samples. The interatomic distance of As-O is similar to reported values of sodium arsenate solutions and As(V) sorbed on metal oxides (19-22). In addition to the major As-O shell, there are As-Al shells as indicated by the vertical dotted lines (Figure 5b). Regardless of reaction times (1 day to 11 months), the As-Al shells were consistently present, suggesting the presence of predominant As(V) bonding environments on aluminol functional groups in allophane. Allophane generally forms small spherical aluminosilicate particles (3-5 nm diameter) that contain both aluminum octahedral and tetrahedral structures (44). The radial distance of the As-Al shells, ~3.19 Å, are the same as the As-Al radial distances reported in the As(V) bidentate binuclear coordination on aluminum octahedral structures of gibbsite (45) and slightly longer than the As-Al radial distances (i.e., 3.11-3.15 Å) on hydrated γ -Al(OH)₃ surfaces which contain Al tetrahedral structures (20, 46). On the basis of the information, it is reasonable to suggest the predominant bidentate binuclear AsO4 coordination environments on the

Al octahedral structure of allophane. In addition to the As-Al shells, two different As coordination states on Si tetrahedral structures (i.e., monodentate mononuclear coordination at \sim 3.4 Å and bidentate mononuclear coordination at \sim 2.6 Å) were considered in the fit. However, we were unable to incorporate these As-Si coordination environments. This suggests the absence of As(V) coordination with the Si tetrahedral structures. The absence of As-Si coordination can be also supported by the following evidence: (1) aluminol dominated chemical composition of allophane (i.e., SiO₂/ Al_2O_3 ratio < 2) and (2) a weak As(V) retention capacity on Si tetrahedral structures (i.e., quartz). Xu and co-workers previously reported that <1% of As(V) was adsorbed on quartz at pH 3-10 under the following reaction conditions ([As(V)] = 1 μ M, 0.1 M NaCl, 3-day contact times, and 25 g L⁻¹) (47). Overall, the results of nonlinear least-squares fits leastsquares fit and the PCA analyses suggest the presence of inner-sphere bidentate binuclear surface species on allophane surfaces.

As we discussed in the As(V) adsorption isotherm and kinetics sections, there was a positive correlation between total As(V) adsorbed and Si release and only minor Al dissolution ($\leq 0.54 \ \mu$ M). It may be possible that mixed Al-As(V)/Si precipitates were forming. The presence of a single As–Al shell at \sim 3.15 Å was previously reported in the XAS fit of mineral mansfieldite (AlAsO₄·2H₂O) (20). Considering the errors $(\pm 0.03\text{\AA})$ in the radial distance of As–Al shells, we cannot exclude the possibility of Al-AsO₄ precipitate formation in the As(V)-allophane system (Table 1 and Figure 4). However, we have a few lines of evidence supporting the absence of Al-As(V) precipitates during As(V) adsorption at the allophane-water interface. First, the negative saturation index values derived from the final Al and AsO₄ concentrations suggested that the systems were undersaturated with respect to am. Al(AsO₄)·2H₂O (Table 1). Second, the XRD analyses did not reveal any peaks corresponding to the mineral mansfieldite (e.g., 16.08 and 28.56 degree 2θ (Cu ka)), and the aging had no effect on the bulk mineralogy of allophane between 0 and 11 months of aging with/without As(V) (Figure 1a-d).

A similar tetrahedral oxyanion (i.e., P) adsorption mechanism on allophane has been previously hypothesized by (1) hydroxyl/water ligand exchange reactions and (2) displacement of structural Si (1). On the basis of the results of the in-situ XAS analyses on As(V) reacted allophane, it seems that the latter mechanism (i.e., tetrahedral anion isomorphic substitution mechanisms) is unlikely. Assuming that allophane is made up of halloysite- or imogolite-like structures as suggested by Parfitt and co-workers (48, 49), the As–Si backscatters should be observed from neighboring Si atoms if AsO₄ is isomorphically substituted for the structural SiO₄. However, there is no evidence of As–Si backscatters in aged As(V) sorbed allophane samples. Arsenate anions were probably adsorbed on aluminol functional groups via ligand exchange mechanisms.

Combining the macroscopic data (i.e., Si release during the As(V) adsorption isotherm and kinetic experiments) and the results of XAS analyses (i.e., presence of inner-sphere bidentate binuclear surface species on aluminum octahedral structures), we can include the displacement of surfacebound Si anions on aluminol functional groups in the ligand exchange mechanisms in addition to the displacement of hydroxyl ions and water molecules on aluminol functional groups. Silicate anions readily adsorb on variable charge mineral surfaces (50-55), and other oxyanion (e.g., phosphate and arsenate) adsorption may, in fact, replace the surfaceadsorbed Si anions on the mineral surfaces. Enhanced Si release that was observed during the As(V) adsorption was probably attributed to the replacement of surface-adsorbed SiO₄ ions on aluminol groups with As(V) ions.

| TABLE 1. Reaction | Conditions (pH | 6.5 ± 0.3 , 3 | Suspension | Density = 1 | 3 g L ⁻¹ , I | onic Strength | = 0.1 M NaCl, | and Initial | Arsenate |
|--------------------------|-----------------------|-------------------|------------|-------------|-------------------------|---------------|----------------|-------------|----------|
| Concentrations = | 1 mM) of XÄS | Samples and | Structural | Parameters | from the | Least-Squares | Analyses of As | K-Edge EX | AFS |
| spectra ^a | | - | | | | - | | • | |

| residence time | adsorption density Γ: adsorption density (μM m ⁻²). | | As-0 | As-Al | ΔE_0 (eV) | <i>R</i> -factor | saturation index Al(As 04)·2H20 |
|-------------------|---|---|-------------------------------|-----------------------------|-----------------------------------|------------------|------------------------------------|
| 1 d | 0.67 | CN R (Å) σ^2 (Å ²) | 4* 1.69(7) 0.0017 (4) | 2(1) 3.19(3) 0.005* | $\textbf{7.12} \pm \textbf{1.94}$ | 0.0437 | -3.411 |
| 1.5 mo | 0.75 | CN R (Å) σ^2 (Å ²) | 4* 1.69 (5) 0.0015 (3) | 2.1(9) 3.19(3) 0.005* | $\textbf{8.74} \pm \textbf{1.57}$ | 0.0321 | -3.809 |
| 3 mo | 0.75 | CN R (Å) σ^2 (Å ²) | 4* 1.69 (6) 0.0014 (4) | 2.4(9) 3.17(3) 0.005* | $\textbf{7.71} \pm \textbf{1.82}$ | 0.0381 | -3.651 |
| 7 mo | 0.82 | CN <i>R</i> (Å) σ² (Ų) | 4* 1.69 (5) 0.0015 (3) | 2.5(8) 3.19(2) 0.005* | $\textbf{8.54} \pm \textbf{1.47}$ | 0.0284 | -3.641 |
| 11 mo | 0.95 | CN <i>R</i> (Å) σ² (Ų) | 4* 1.69 (7) 0.0015 (4) | 2.5(1) 3.20(3) 0.005* | $\textbf{6.67} \pm \textbf{2.06}$ | 0.0467 | -3.435 |

^{*a*} CN: Coordination number. *R*: Interatomic distance *(Å). σ^2 : Debye–Waller factor (Å²). Fit quality confidence limit for parameters: Accuracies for *R* and CN for As–O shell are ±0.02 Å and ±25%, respectively, and for As–Al shell are ±0.03 Å and ±30%, respectively. * Fixed parameter. Saturation index values for am. Al(AsO₄)·2H₂O(s) were estimated using log K = -15.8, Minteqa version 3.11. Estimated standard deviations are given in parentheses.

TABLE 2. Results from Principal Component Analysis of As K-Edge EXAFS Analyses of Five As(V) Sorbed Allophane Samples

| component, <i>n</i> | eigenvalue | variance explained | cumulative % | IND functions ^a |
|---------------------|------------|-----------------------|--------------|-------------------------------|
| 1 | 165.416 | 82.4 | 82.4 | 0.643 |
| 2 | 17.326 | 8.6 | 91.1 | 0.713 |
| 3 | 9.122 | 4.5 | 95.6 | 1.122 |
| 4 | 5.468 | 2.7 | 98.6 | 3.230 |
| 5 | 3.230 | 1.6 | 100.0 | NA |

^{*a*} IND function is indicator error function proposed by Malinowski (1991).



FIGURE 5. (a) Normalized, background-subtracted k^3 -weighted As k-edge EXAFS spectra of As(V) adsorbed allophane samples are shown. Solid lines are the experimental data and the open circles represent the theoretical fit to the data. (b) Fourier transformed k^3 -weighted As k-edge EXAFS spectra of As(V) adsorbed allophane (solid lines) and nonlinear least-squares fits (open circles) are shown.

In summary, our research findings indicate that dissolved As(V) is rapidly adsorbed by allophane surfaces via ligand exchange mechanisms on the aluminol functional groups.

The inner-sphere bidentate binuclear surface species are stable at near neutral pH after months of reaction times under the relatively high (~1 mM) initial As(V) concentrations. This suggests that similar retention mechanisms might play an important role in controlling dissolved phosphate and As(V) concentrations on amorphous aluminosilicate coatings in aquifer and soils (e.g., andisols), as well as other geomedia containing aluminol functional groups (e.g., aluminum (hydr)oxides and crystalline aluminosilicates). Surface-bound Si on allophane surfaces and or its release (i.e., dissolved Si) could create the competitive mineral-water interfacial environment for the As(V)/P adsorption. Concentrations of silicic acid (Si(OH)₄) can be elevated as much as 100 mg L⁻¹ in groundwater because of the dissolution of naturally occurring minerals (e.g., quartz, feldspar, plagioclase, and orthosilicate) (56, 57), and silicate anion strongly reacts on metal oxide surfaces (50-55, 58). It is likely that the dissolved/ surface-bound Si anions become competitive ligands for P(V)/As(V), possibly resulting in the enhanced mobility of P/As. It may be also important to consider the environmental role of allophane-like nanoparticles with respect to As and P surface and subsurface transport processes. Several recent studies suggested the important colloid facilitated transport processes of other inorganic contaminants and nutrients (e.g., Cs, U, P) in the natural and synthetic systems (59-61). Dissolved allophane-like nanoparticles could possibly contribute to the rapid transport processes (e.g., surface runoff and preferential flow) of phosphate and As(V) in subsurface environments.

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