Effect of Phosphate on U(VI) Sorption to Montmorillonite: Ternary Complexation and Precipitation Barriers

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ABSTRACT

Phosphate addition is a potential treatment method to lower the solubility of U(VI) in soil and groundwater systems by causing U(VI) phosphate precipitation as well as enhancing adsorption. Previous work has shown that iron oxide surfaces may facilitate the nucleation of U(VI) phosphate minerals and, that under weakly acidic conditions, phosphate also enhances U(VI) adsorption to such phases. Like iron oxides, clays are important reactive phases in the subsurface but little is known about the interaction of U(VI) and phosphate with these minerals. The effect of aqueous phosphate on U(VI) binding to Wyoming montmorillonite (SWy-2) in air-equilibrated systems was investigated. Equilibrium U(VI) uptake to montmorillonite was determined at pH 4, 6 and 8 at discrete initial phosphate concentrations between 0 and 100 μM . The observed behavior of U(VI) indicates a transition from adsorption to precipitation with increasing total uranium and phosphate concentrations at all pH values. At the highest phosphate concentration examined at each pH value, a barrier to U(VI) phosphate nucleation is observed. At lower concentrations, phosphate has no effect on macroscopic U(VI) adsorption. To assess the mechanisms of U(VI)-phosphate interactions on smectite surfaces, U(VI) speciation was investigated under selected conditions using laser-induced fluorescence spectroscopy (LIFS) and extended X-ray absorption fine-structure (EXAFS) spectroscopy. Samples above the precipitation threshold display EXAFS and LIFS spectral signatures consistent with the autunite family of U(VI) phosphate minerals. However, at lower U(VI) concentrations, changes in LIFS spectra upon phosphate addition suggest that U(VI)-phosphate ternary surface complexes form on the montmorillonite surface at pH 4 and 6 despite the lack of a macroscopic effect on adsorption. The speciation of solid-associated U(VI) below the precipitation threshold at pH 8 is dominated by U(VI)-carbonate surface complexes. This work reveals that ternary complexation

64 may occur without a macroscopic signature, which is attributed to phosphate not appreciably
65 binding to smectite in the absence of U(VI), with U(VI) surface complexes serving as the sole
66 reactive surface sites for phosphate. This study shows that phosphate does not enhance U(VI)
67 adsorption to smectite clay minerals, unlike oxide phases, and that a barrier to homogeneous
68 nucleation of U(VI) phosphates was not affected by the presence of the smectite surface.

INTRODUCTION

Widespread uranium contamination of soil and groundwater across the United States has resulted in a need for remediation strategies to stabilize uranium in the solid phase (Palmisano and Hazen, 2003). One such strategy is the injection of phosphate into contaminated groundwater systems to promote the precipitation of U(VI) phosphate minerals (Lee et al., 1995; Wellman et al., 2006a,b, 2008; Vermeul et al., 2007). Phosphate addition can cause the formation of calcium phosphate solids, which may bind uranium through adsorption or coprecipitation (Fuller et al., 2002; Fanizza et al., 2013; Mehta et al., 2014). Phosphate may also promote adsorption of U(VI) to sediment minerals via ternary surface complexation (Payne et al., 1996; Cheng et al., 2004; Tang and Reeder, 2009; Tang et al., 2009; Singh et al., 2012). Uranyl phosphate precipitation has also been shown to take place in microbially-stimulated systems where the break down of organophosphate was facilitated by both aerobic and anaerobic bacteria (Beazley et al., 2007, 2009, 2011; Salome et al., 2013). Alternatively, uranium can be stabilized as $U^{IV}O_2$, which can be produced by microbially-mediated reduction of aqueous U(VI) (Anderson et al., 2003; Wu et al., 2007; Moon et al., 2010). Unlike, U(VI) phosphate minerals, UO_2 is susceptible to reoxidation and release if conditions become oxic, the natural condition in many contaminated shallow aquifers (Langmuir, 1997; Liu et al., 2005; Sani et al., 2005; Wu et al., 2006, 2007; Moon et al., 2007; Senko et al., 2007; Komlos et al., 2008; Wang et al., 2013). In addition to forming in amended systems, U(VI) phosphate minerals are known to occur naturally following the oxidative dissolution of primary U(IV)-containing ore in soils and rock (Murakami et al., 1997, 2005; Jerden et al., 2003). The occurrence of such minerals in natural systems suggests that U(VI) phosphates are stable in some environments.

The complex array of possible chemical interactions between U(VI) and phosphate makes it challenging to predict the reactions that will dominate under specific conditions because of competitive and cooperative interactions. The reactivity of sediments at contaminated sites is dominated by the fine fraction mineralogy, which often contains a mixture of iron oxide and clay minerals (Qafoku et al., 2005; Catalano et al., 2006; Zachara et al., 2007; Komlos et al., 2007; Hyun et al., 2009; Singer et al., 2009; Stubbs et al., 2009; Campbell et al., 2011). Oxide minerals such as goethite have been shown to display enhanced adsorption of U(VI) in the presence of phosphate because of ternary complexation and may also act to nucleate U(VI) phosphate minerals (Payne et al., 1996; Cheng et al., 2004; Singh et al., 2010, 2012; Munasinghe et al., 2015). U(VI)-phosphate ternary surface complexes have also been shown to form in the presence of alumina (Galindo et al., 2010). Such interactions have largely been studied at acidic conditions, not the circumneutral to alkaline conditions that dominate many groundwater systems. Smectite surfaces, like montmorillonite, are strong sorbents for U(VI) (Borovec, 1981; Tsunashima et al., 1981). U(VI) sorption onto montmorillonite occurs by cation exchange at low pH and by inner sphere complexation to Al, Fe, or Si polyhedral edge sites at neutral to high pH (Dent et al., 1992; Zachara and McKinley, 1993; Morris et al., 1994; McKinley et al., 1995; Sylwester et al., 2000; Chisholm-Brause et al., 2001, 2004; Catalano and Brown, 2005; Marques Fernandes et al., 2012). While the interaction between U(VI) and smectites has been widely studied, U(VI) and phosphate interactions on the surface of clay minerals have not previously been investigated. Such interactions on smectite surfaces are likely distinct from those occurring on iron oxides because of the different crystal structure of these substrates and the permanent layer charge of smectite.

The objective of this study was to investigate the effect of phosphate on U(VI) behavior in the presence of Wyoming montmorillonite SWy-2, a smectite clay mineral. Equilibrium U(VI) uptake behavior at pH 4, 6, and 8 and with a series of discrete initial phosphate concentrations was measured to investigate potential cooperative or competitive adsorption effects as well as to assess the conditions where U(VI) precipitation occurs. The mechanisms of U(VI) adsorption and the nature of the precipitates that form were identified using laser-induced fluorescence spectroscopy (LIFS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. An equilibrium speciation model that could account for U(VI) adsorption was then developed to investigate the saturation state required to induce the precipitation of U(VI) phosphate minerals in the presence of montmorillonite. Understanding U behavior under the investigated conditions can help to predict U behavior in the presence of phosphate and natural sediments and to provide an understanding for how mineral surfaces affect U mobility.

MATERIALS AND METHODS

Clay Preparation

Wyoming montmorillonite SWy-2 was obtained from the Source Clays Repository of the Clay Mineral Society. The carbonate component of the bulk sample was removed by extraction in a pH 5 sodium acetate/acetic acid buffer at 80°C (Soukup et al., 2008). The solid was then redispersed in DI water and size-fractionated to <2 µm via centrifugation (Soukup et al., 2008). The resulting suspension was mixed with a saturated NaCl solution, which ensures Na-saturation of the montmorillonite and flocculation. The excess salt was then removed by dialysis and the samples were freeze-dried for storage (Catalano and Brown, 2005). X-ray diffraction (XRD) analysis was performed on a Rigaku Geigerflex D-MAX/A diffractometer using Cu-K α radiation

at a power of 35 kV and 35 mA. The XRD pattern confirmed the isolated clay fraction to be primarily montmorillonite with a minor (<5 wt.%) content of quartz, in agreement with prior published work (Chipera and Bish, 2001). The cation exchange capacity for SWy-2 is 850 meq kg⁻¹ (Borden and Giese, 2001).

Uptake Experiments

To cover the wide range of initial U(VI) and phosphate concentrations used in the experiments, several stock solutions of varying concentrations were prepared from UO₂(NO₃)₂·6H₂O and Na₂HPO₄, respectively. Uranyl nitrate stock solutions of 10, 100, 1,000, 10,000 µM were used to prepare samples with starting U(VI) concentrations in the range of 0.025-0.1 µM, 0.25-1 µM, 2.5-10 µM, 25-100 µM, respectively. Na₂HPO₄ solutions of 1, 10, or 100 mM were used to prepare samples containing 1, 10, or 100 µM initial phosphate, respectively.

A stock suspension of 2.0 g/L montmorillonite in DI water was prepared fresh prior to the start of experiments. Experiments were conducted in the presence of 10 mM NaNO₃. Mineral loadings of 1.0 g/L montmorillonite at pH 4 and 0.20 g/L at pH 6 and 8 were used to account for the differences in the extent of U(VI) sorption on montmorillonite at each pH. For each phosphate concentration and pH, a 200 mL secondary stock solution at the desired montmorillonite loading was prepared. The pH of the suspension was adjusted using HNO₃ or NaHCO₃ stock solutions while air bubbling to reach a target pH of 4, 6, or 8 and to ensure a total CO₂ concentration in equilibrium with the atmosphere. The resulting suspension was then divided into 10 mL portions in 15-mL polypropylene tubes and spiked with the appropriate amount of U(VI) stock solution to reach the desired initial U(VI) concentration. When necessary,

pH was readjusted following U(VI) addition, while continually air bubbling. Samples were reacted for 48 hours while being rotated on an end-over-end rotator. pH was checked after 36 hours and readjusted to correct for drift during the experiments. This drift, when observed, was moderate (<0.1 pH units) and occurred only for the highest starting U(VI) concentrations, which are not the main focus of this paper. Final pH was within 0.1 pH units of the target pH.

After 48 hours, solids were separated by centrifugation. The decanted liquids were then further filtered using $0.22\ \mu\text{m}$ mixed cellulose ester (MCE) syringe filters (Fisher Scientific). The initial 2 mL of solution were discarded to minimize the effects of uranium adsorption onto the filter membranes. After adequate dilution and acidification with 2% HNO_3 , aqueous U(VI) and phosphate concentrations in the remaining supernatant were measured using an Agilent Technologies 7500ce inductively-coupled plasma mass spectrometer (ICP-MS). The detection limit was $1\ \mu\text{g/L}$ for uranium and $10\ \mu\text{g/L}$ for phosphorus. Select replicate samples at pH 8 were prepared to determine the effective CO_2 partial pressure because this strongly affects U(VI) speciation under alkaline conditions. Dissolved inorganic carbon was measured using a Shimadzu TOC-LCPH instrument and CO_2 partial pressure was calculated using the equilibrium thermodynamic model described below, yielding $370\pm 20\ \text{ppm CO}_2(\text{g})$. When preparing samples for extended X-ray absorption fine structure (EXAFS) spectroscopy and laser induced fluorescence spectroscopy (LIFS), larger suspension volumes were used to ensure that adequate material was available for analysis. A volume of 40 mL was used for each individual sample at pH 4, and 200 mL was used at pH 6 and pH 8. Samples were loaded into EXAFS and LIFS samples holders in the form of wet pastes.

Solid Phase Analysis

Selected samples from the batch experiments were chosen for solid phase analysis by laser induced fluorescence spectroscopy (LIFS) and extended X-ray absorption fine structure spectroscopy (EXAFS). The experimental conditions for this set of samples and the sample labels used from this point on are outlined in Table 1.

Instrumentation and experimental procedures for U(VI) laser induced fluorescence spectroscopy (LIFS) analysis have been described previously (Wang et al., 2004; Wang et al., 2005). Samples in quartz cuvettes were attached to the cold finger of a CRYO Industries RC152 cryostat with liquid helium vaporizing beneath the sample to reach a sample temperature of 8 ± 2 K. The samples were excited with a Spectra-Physics Nd:YAG laser-pumped Lasertechnik-GWU MOPO laser at 415 nm. The emitted light was collected at 85° to the excitation beam and detected with a thermoelectrically cooled Princeton Instruments PIMAX intensified CCD camera after spectral dispersion through an Acton SpectroPro 300i double monochromator spectrograph. The spectra were analyzed using the commercial software application IGOR (Wavematrix, Inc).

Uranium L_{III}-edge EXAFS spectra were measured at room temperature at beamlines 12-BM-B (Beno et al., 2001) and 20-BM-B (Heald et al., 1999; Heald, 2011) at the Advanced Photon Source (APS) at Argonne National Lab. Both beamlines employed Si(111) double-crystal monochromators as well as focusing and harmonic rejection mirrors. Spectra were collected in fluorescence-yield using 13-element energy-dispersive solid-state Ge detectors. Additional spectra were measured at beamline 11-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) using a Si (220) double-crystal monochromator and a collimating mirror before the monochromator for harmonic rejection. A 30-element energy-dispersive solid-state Ge detector was used to collect fluorescence-yield spectra at SSRL. The X-ray energy of the incident beam in

all measurements was calibrated using a Y metal foil, with the first inflection point in the Y K-edge set to 17038 eV.

Background subtraction and splining of the k^3 -weighted EXAFS data was performed using the SixPACK (Webb, 2005) and Athena (Ravel and Newville, 2005) interfaces to IFEFFIT (Newville, 2001). Phase-shift and backscattering amplitude functions were generated using FEFF 8.4 (Ankudinov et al., 1998) from the crystal structure of saleeite ($\text{Mg}(\text{UO}_2\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$) (Miller and Taylor, 1986). In the FEFF calculation, select Mg sites were replaced with Al and Fe, and a P site replaced with Si to provide backscattering paths for these elements (Catalano and Brown, 2005). The spectra were fit in R-space using a k range of 3-12 $\text{\AA}^{-1}$ and an R range of 1-4 $\text{\AA}$. All fits included three multiple scattering paths from the axial oxygen atoms of the uranyl cation (Hudson et al., 1996).

Equilibrium Speciation Calculations

Equilibrium speciation calculations were performed to determine aqueous speciation and to quantitatively examine the equilibrium partitioning of U(VI). Calculations were performed using MINEQL+ 4.6 (Schecher and McAvoy, 2007). A non-electrostatic, quasi-mechanistic thermodynamic sorption model was developed to provide a quantitative reaction-based framework for evaluating the effects of pH and phosphate concentration on U(VI) precipitation and adsorption in the presence of montmorillonite. This model included surface complexation and cation exchange reactions that were consistent with prior work (Table EA2) (Zachara and McKinley, 1993; Marques Fernandes et al., 2012; Wang and Giammar, 2013) and the spectroscopic analyses in the present study. Aqueous complexation reactions involving U(VI), carbonate, and phosphate (Table EA3) and precipitation reactions of U(VI) with phosphate and

hydroxide (Table EA2) were considered in calculations for interpreting the transition between U(VI) adsorption and precipitation. Precipitation reactions were used to examine the extent of solution supersaturation with respect to specific phases at given conditions for which there both was and was not experimental evidence of U(VI) phosphate precipitation.

RESULTS

Macroscopic U(VI) Uptake Behavior

At all pH conditions, the binding behavior of U(VI) to montmorillonite in the absence of phosphate resembles that of a Langmuir adsorption isotherm (Fig. 1A-C). The shape of the isotherms remains largely unchanged with the addition of 1 μM phosphate, and higher phosphate concentrations also have little effect at low final U(VI) concentrations. Upon addition of the highest phosphate concentrations investigated (100 μM for pH 4 and 8, 10 μM for pH 6), a break in the isotherms occurs, indicating precipitation. Experiments were not conducted at 100 μM phosphate for pH 6 because the onset of precipitation would occur near or below the detection limit for dissolved U(VI). At pH 4, precipitation appears as a sharp rise in U(VI) retention occurring at ~ 1 μM U(VI). In contrast, at pH 6 and 8 (dissolved U concentrations of 0.07 and 0.97 μM respectively), a back reflection in the isotherm, observed when final aqueous concentrations of U(VI) begin to decrease despite increasing initial concentrations, occurs at the onset of apparent precipitation.

The fraction of aqueous phosphate in solution at the end of the experiment was also measured (Fig. 1D-F). At the lower range of U(VI) concentrations, little phosphate uptake is observed at all pH values. In the absence of U(VI) no detectable phosphate adsorption occurred, i.e., final dissolved concentrations were within analytical error of their initial values (data not

shown). At the highest phosphate addition for each pH (100 μ M for pH 4 and 8, 10 μ M for pH 6), a steep drop in dissolved phosphate concentration is observed (Fig. 1D-F) that correlates with the sharp increase in U(VI) uptake at high initial uranium concentrations (5 μ M at pH 4, 0.5 μ M at pH 6, and 5 μ M at pH 8) (Fig. 1A-C), consistent with precipitation of a U(VI) phosphate mineral. At lower phosphate concentrations (10 and 1 μ M phosphate at pH 4 and 8 and 1 μ M phosphate at pH 6) a gradual decrease in aqueous phosphate is seen without a concomitant change in U(VI) uptake (Fig. 1D-F), suggesting that this may originate from co-adsorption behavior (e.g., ternary surface complexation).

Solid Phase Analysis

LIFS

LIFS spectra were collected on solids from selected sample points in the adsorption isotherms (Table 1). One sample from the highest phosphate concentration at each pH was selected at a U(VI) concentration above the onset of precipitation (8P100U10, 6P10U10, 4P100U100) to determine the identity of the precipitates (Fig. 2). The resulting spectra are similar to that of Na meta-autunite ($\text{NaUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$), confirming precipitation of a U(VI) phosphate mineral. A slight shoulder is observed on the peaks of the pH 8 sample spectrum; this may be due to partial dehydration prior to measurement.

LIFS spectra were also collected for samples at U(VI) concentrations below the threshold for precipitation in order to identify mechanisms of U(VI) adsorption (Fig. 3). The threshold for precipitation is the point at which the system is supersaturated with respect to Na autunite $[(\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2)]$ (Table EA2). Samples were chosen with the highest phosphate concentration for a given pH. For comparison, samples at the same initial U(VI) concentrations, but without

phosphate were also chosen. At pH 4, a shift in peak positions to longer wavelengths is observed upon addition of phosphate. This suggests that phosphate addition changes U(VI) surface speciation. In the spectrum of 4P100U5 (Fig. 3A), minor additional peaks can be observed at 505, 530, 550, and 575 nm, indicating the presence of a small amount of a U(VI) phosphate mineral. A LIFS spectrum (not shown) collected for a sample with a lower level of phosphate (4P10U5) resembled that of the phosphate-free sample 4P0U5, suggesting that changes in U(VI) surface speciation are only substantial at higher phosphate concentrations.

At pH 6 (Fig. 3B), the spectra of phosphate-free samples contain fluorescence peaks at different locations than for similar samples at pH 4. A shift in peak positions upon phosphate addition is again observed, but in this case the shift is to lower wavelengths. This indicates that U(VI) speciation at pH 6 is dominated by surface complexes that are different from those present at pH 4, both in the absence and presence of phosphate. In contrast, at pH 8 (Fig. 3C) the LIFS spectra do not change in response to phosphate addition and are consistent with adsorbed U(VI) that is complexed by carbonate (Waite et al., 1994; Wang et al., 2005). Differences in the relative peak intensities of the pH 8 spectra are likely the result of differences in the signal to background ratio associated with variations in U concentration from sample to sample. Residual free aqueous U(VI) species do not substantially contribute to the spectra; the solution concentrations and amount of retained solution suggest that at most ~0.5% of U in each sample is dissolved in the entrained fluid.

EXAFS Spectroscopy

While LIFS is an excellent technique for identifying the number of U(VI) species present and changes in U(VI) speciation with differences in pH or phosphate concentration, it does not

provide structural information beyond that obtained from comparison of similarities in spectral features. Uranium L_{III}-edge EXAFS spectra on select samples (Table 1) were thus collected to provide complementary information regarding the local structure of solid-associated U(VI). EXAFS spectra of the set of samples from conditions above the threshold for precipitation were analyzed to confirm the identity of precipitates (Fig. 4). These samples were selected from points above the deviation from linearity observed in the isotherms at the highest phosphate concentration for each pH (Figure 1). These spectra are nearly identical to that of Na-autunite in both k- and R-space, consistent with the LIFS spectra (Fig. 3A) and confirming the precipitation of an autunite mineral.

Spectra below the threshold of precipitation were also examined to investigate how adsorption mechanisms respond to phosphate addition. At pH 4, the EXAFS spectra change systematically with increasing phosphate concentration, with the Fourier transform feature near 2.0 Å associated with the equatorial oxygen shell (O_{eq}) broadening and a feature near 3.0 Å increasing in amplitude (Fig. 5). In the absence of phosphate, the spectrum is well reproduced with an O_{eq} shell and no second shell neighbors (Table 2); this is consistent with cation-exchanged UO₂²⁺ (Dent et al., 1992; Chisholm-Brause et al., 1994; Giaquinta et al., 1997; Sylwester et al., 2000; Catalano and Brown, 2005). Upon phosphate addition, the O_{eq} shell splits and features associated with Al, Si, or P second shell neighbors at ~3.1, ~3.3, and ~3.5 Å are apparent through fitting. Note that EXAFS cannot distinguish between adjacent elements on the periodic table, and modeling these shells as Al, Si, or P yields similar results. Based on coordination of U(VI) to these elements observed in crystal structures and prior studies, the ~3.1 Å neighbor is likely Si or P, the ~3.3 Å neighbor is likely P or Al, and the ~3.5 Å neighbor is likely Si or P. While the increase in amplitude of these features with increasing phosphate

concentration suggests one or more originate from P neighbors, features at similar distances in the absence of phosphate have been observed at higher pH to originate from Si and Al (Marques Fernandes et al., 2012). Based on these considerations, the ~ 3.1 , ~ 3.3 , and ~ 3.5 Å neighbors were modeled as Si, Al, and P, respectively. Despite this choice, the true coordination of phosphate to U(VI) at pH 4 is uncertain, although the change in spectra upon phosphate addition implies that a U(VI)-phosphate ternary complex has formed; such a complex would also explain the shift in LIFS spectra at this pH. To demonstrate the improvement of the fits with the inclusion of P as a nearest neighbor, results of the fitting without the P shell are also shown (Fig. EA1, Table EA1).

At pH 6, EXAFS spectra were collected on four samples, three with varying U(VI) concentrations in the absence of phosphate and a final sample that included phosphate (Fig. 6). The spectra show that U(VI) coordination does not change appreciably as surface coverage increases but is substantially altered upon phosphate addition. In the absence of phosphate, the local coordination environment of U(VI) included a split O_{eq} shell and two Al or Si second shell neighbors at ~ 3.1 and ~ 3.3 Å (Table 3), consistent with an inner-sphere surface complex. In the presence of phosphate an additional second shell neighbor at ~ 3.6 Å was required to reproduce the spectrum. This is assigned to originate from coordination by phosphate as U-P interatomic distances in most crystalline solid are ~ 3.6 Å (Locock and Burns, 2003; Catalano and Brown, 2004).

Equilibrium Speciation Modeling

A model was developed to assess the precipitation of U(VI) minerals and competition between precipitation and adsorption over the conditions examined by the macroscopic uptake

experiments. The isotherm data in the absence of phosphate was fit with three surface species: cation-exchanged UO_2^{2+} (UO_2X_2), a cationic surface complex ($\equiv\text{SOUO}_2^+$), and a U(VI)-carbonate ternary surface complex ($\equiv\text{SOUO}_2\text{CO}_3^-$). These species were selected based on prior studies and the speciation identified through spectroscopy in the present work (Zachara and Mckinley, 1993; Marques Fernandes et al., 2012; Wang et al., 2013); the model with these species could simulate the isotherm data well at all three pH values (Fig. EA2). Because of the strong pH dependence of U(VI) hydrolysis and complexation, the adsorption isotherm at each pH was dominated by a single surface complex: UO_2X_2 at pH 4, $\equiv\text{SOUO}_2^+$ at pH 6, and $\equiv\text{SOUO}_2\text{CO}_3^-$ at pH 8. In the absence of phosphate, supersaturation of schoepite was predicted above 1.3 μM dissolved U(VI) for pH 6 and above 62 μM dissolved U(VI) for pH 8, but the isotherms did not show evidence of schoepite precipitation and it was not further considered in the model.

After developing the model for systems in which adsorption was the only solid-water partitioning process that could occur, precipitation reactions of U(VI) phosphate minerals were then added. Model calculations showed that the relevant U(VI) phosphate minerals (i.e., those whose formation is thermodynamically favorable) are Na meta-autunite and U(VI) orthophosphate. Sodium meta-autunite was generally predicted to be the most thermodynamically stable solid phase, and recent work has shown that U(VI) orthophosphate does not readily form even when supersaturated (Mehta et al., 2014). Sodium meta-autunite was thus selected as the only U(VI) phosphate mineral in the model.

The model that included adsorption and precipitation reactions predicted the sharp rise in U(VI) binding at pH 4 and the associated drop in phosphate concentrations, indicating that these features are associated with U(VI) phosphate precipitation (Fig. 7). The model could also

simulate the rise and subsequent leveling off of the U(VI) solid-phase concentrations at pH 6, again confirming that this is the result of U(VI) phosphate precipitation. The level region in the U(VI) curve originates from the near complete consumption of phosphate, preventing further precipitation. However, the model does not reproduce the back reflection seen in the pH 6 isotherm, indicating that the system is supersaturated in this region. The model over predicts the extent of precipitation at pH 8 and also shows that the back reflection region again is more supersaturated than other conditions.

Although the spectroscopic data indicate the formation of U(VI)-phosphate ternary surface complexes at pH 4 and 6 when phosphate is present, no attempt was made to refine a surface speciation model that included such species. The regions of the isotherms dominated by adsorption do not change appreciably upon phosphate addition, making it challenging to obtain equilibrium constants for the formation of ternary complexes. In addition, refining such a model would not substantially improve the simulation of the isotherm data.

DISCUSSION

Effect of Phosphate on Sorption Mechanisms

The impact of phosphate on U(VI) interactions with montmorillonite can be explained by two mechanisms, U(VI)-phosphate ternary surface complexation and the precipitation of U(VI) phosphate minerals. Both LIFS and EXAFS data show a change in the local coordination environment of solid-associated U(VI) in the presence of phosphate at pH 4 and 6 before the onset of precipitation. The observed shift in LIFS spectra with phosphate addition (Fig. 3A and B) indicates a change in U(VI) surface complexation. Distortion of the equatorial oxygen shell indicates that U(VI) coordinates to a new ligand upon phosphate addition. Inclusion of a P shell

improves the fit to the EXAFS spectra and yields a surface complex consistent with the U(VI)-phosphate ternary complexes on goethite observed in prior studies (Singh et al., 2010, 2012). These three observations together strongly suggest that such ternary complexation occurs on smectite edges as well. This sorption mechanism is also supported by the gradual decrease in phosphate concentrations (Fig. EA2) with increasing U(VI) concentrations observed at lower phosphate concentrations, distinct from the sharp decline predicted by the model for U(VI)-phosphate precipitation. Although a mechanistic change was observed, phosphate did not affect the macroscopic sorption of U(VI) to montmorillonite (Fig. 1). Singh et al. (2012) could not distinguish between U-bridging and P-bridging ternary complexation on goethite using EXAFS spectroscopy, but U-bridging has been assumed in prior work examining other mineral systems (Bostick et al., 2002; Fuller et al., 2002). A U-bridging complex is most consistent with the macroscopic adsorption data because phosphate does not show detectable adsorption in the absence of U(VI), suggesting that interaction of phosphate with the smectite surface is unfavorable. This would indicate that phosphate surface coverage is limited by the number of surface sorption sites occupied by U(VI), with phosphate only adsorbing as a ternary complex with U(VI).

While we observe changes in the U(VI) adsorption mechanism upon addition of phosphate at the lower pH values, no such change is observed at pH 8. Unlike the pH 4 and 6 samples, the LIFS spectra had maxima at the same wavelength with and without phosphate present (Fig. 2C). The LIFS spectra at pH 8 are consistent with a carbonate complex (Waite et al., 1994; Wang et al., 2005), indicating that the U(VI)-carbonate ternary surface complex dominates surface speciation at pH 8. This is in agreement with a prior study that investigated such ternary complexation on montmorillonite (Marques Fernandes et al., 2012). Further

supporting this assignment of surface speciation, the macroscopic adsorption behavior at pH 8 is modeled well using a U(VI)-carbonate ternary surface complex (Fig. 7C).

U(VI) Phosphate Precipitation

While at low U(VI) concentrations, U(VI) uptake onto montmorillonite is only caused by adsorption, the precipitation of an autunite-like mineral takes place at elevated U(VI) and phosphate concentrations. The autunite-like mineral is predicted to be Na meta-autunite by thermodynamic modeling. Precipitation of this phase closely approaches predicted equilibrium solubility at pH 4 and 6 (Fig. 7A,B). At pH 8, a deviation of the experimental data from the thermodynamic model is observed and may have multiple possible origins. While dissolved inorganic carbon concentrations indicate air-equilibration, these were measured in replicate experiments conducted at a later date than the isotherm studies. The laboratory atmosphere may have had transiently higher CO₂(g) partial pressure during the isotherm experiments that increased U(VI) solubility. There could also be errors in the thermodynamic data, although the model is effective at lower pH values. Alternatively, U(VI) phosphates may not fully equilibrate with the fluid at alkaline pH conditions on the timescale of the experiments (Fig. 7C). Previous studies with U(VI) and goethite have observed the slow decrease in dissolved U concentrations, on the order of days to months, when experiments were supersaturated with respect to U(VI) oxyhydroxide and U(VI) phosphate minerals (Giammar and Hering, 2001; Singh et al., 2010). The overprediction of the extent of precipitation by the model suggests that precipitation rates of such solids are slow under alkaline conditions, raising the possibility that strong carbonate complexation inhibits precipitation of U(VI) phosphate minerals.

Separately, at the onset of precipitation a back reflection is observed in the experimental data at pH 6 and 8 rather than a sharp rise in U(VI) uptake into the solid phase (Fig. 7B,C). In these back-reflection regions, the saturation index of Na meta-autunite is approximately 2 (1.96 at pH 6, 2.00 at pH 8), indicating that substantial supersaturation is required to induce nucleation. For comparison, no back reflection is observed at pH 4, where the saturation index is -0.08 when precipitation is first observed. This suggests that a barrier to homogenous nucleation exists in the pH 6 and 8 systems and that this barrier persists in the presence of the montmorillonite surface. While previous work has shown that precipitation of U(VI) phosphates requires supersaturation at neutral to alkaline pH (Mehta et al., 2014), a barrier to homogenous nucleation has not been investigated. Consequently, the degree of supersaturation required for homogeneous nucleation of U(VI) phosphates is not known.

Environmental Implications

The present work indicates that the formation of U(VI) phosphate precipitates can be limited by several conditions. When designing remediation strategies in clay-rich soils or sediments, phosphate must be added at a concentration high enough to exceed the observed nucleation barrier and cause U(VI) phosphate precipitation. Below the barrier to nucleation, and when undersaturated, the formation of ternary U(VI)-phosphate sorption complexes did not enhance U(VI) uptake onto montmorillonite. Environmental conditions also determine the effectiveness of phosphate amendments as a method of U immobilization. For example, at uranium-contaminated sites with alkaline, high P_{CO_2} groundwater, such as at Rifle, Colorado (Campbell et al., 2012), we would not expect to observe an effect of phosphate on U(VI)

behavior due to the preferential formation of U(VI)-carbonate complexes and the inhibited precipitation and relatively high solubility of U(VI) phosphate minerals (Mehta et al., 2014). Although not examined in this study, the presence of calcium can also lead to the formation of highly soluble U(VI)-calcium-carbonate complexes under alkaline conditions (Stewart et al., 2010). Additionally, when calcium is present, precipitation of autunite $[\text{Ca}_2(\text{UO}_2)_2(\text{PO}_4)_2]$ and amorphous calcium phosphate precipitates, which may adsorb or incorporate U(VI), can occur (Mehta et al., 2014). It is unclear if the barrier to nucleation of U(VI) phosphate minerals seen in the present work is overcome at longer reaction times in the presence of smectites or how it is affected by dissolved calcium.

The results of this work also suggest that metals may affect the fate of phosphate in clay-bearing systems. Phosphate showed low adsorption to montmorillonite in the absence of U(VI), likely because of the fixed negative structural charge on the mineral. However, an increase in phosphate uptake was observed as U(VI) concentrations increased under conditions where a U(VI) phosphate solid did not precipitate (Fig. EA2). This finding implies that metal cations may also substantially increase phosphate adsorption to smectites via ternary surface complexation. While U(VI) is not widely abundant outside of contaminated sites, the presence of other metal cations may also promote ternary complexation. Such behavior must thus be accounted for if the migration of phosphate through clay-rich sediments or soils is to be correctly predicted.

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720

721 **TABLE 1.** Description of the samples used in spectroscopic analyses of the solid phase.

722

Sample label	pH	Initial U (μM)	Final U (μM)	Final adsorbed U ($\mu\text{mol/g}$)	Initial P (μM)	Final P (μM)
4P0U1	4	1	0.19	0.81	0	0
4P0U5	4	5	0.95	4.1	0	0
4P10U5	4	5	2.0	4.1	10	8.8
4P100U1	4	1	0.19	0.81	100	97
4P100U5	4	5	1.3	3.7	100	97
4P100U100	4	100	1.9	98	100	7.8
6P0U0.1	6	0.1	0.01	0.46	0	0
6P0U0.5	6	0.5	0.08	2.1	0	0
6P0U10	6	10	6.6	17	0	0
6P0U100	6	100	88	58	0	0
6P10U0.1	6	0.1	0.01	0.47	10	9.0
6P10U0.5	6	0.5	0.11	2.0	10	9.0
6P10U10	6	10	0.32	48	10	0.87
8P0U0.25	8	0.25	0.09	0.79	0	0
8P0U1	8	10	0.60	2.00	0	0
8P100U0.25	8	0.25	0.14	0.55	100	100
8P100U1	8	1	0.70	1.50	100	100
8P100U10	8	10	0.89	46	100	88

TABLE 2. U L_{III}-edge EXAFS fitting results for U(VI) adsorbed to montmorillonite at pH 4.

Shell		U-O _{ax}	U-O _{eq}	U-O _{eq}	U-Si	U-Al	U-P	ΔE_0 (eV) ^e	χ^2 ^f	R-factor ^f
4P0U5	N ^a	2	5(1)	—	—	—	—	4(2)	22.11	0.018
	R (Å) ^b	1.769(7) ^d	2.43(2)	—	—	—	—			
	σ^2 (Å ²) ^c	0.0016(5)	0.010(3)	—	—	—	—			
4P10U5	N	2	1.8(4)	3.7(5)	1.3(6)	2(1)	0.4(1.1)	4(1)	9.42	0.005
	R (Å)	1.764(6)	2.32(4)	2.47(2)	3.12(3)	3.33(5)	3.5(2)			
	σ^2 (Å ²)	0.0019(4)	0.004	0.004	0.003	0.003	0.003			
4P100U5	N	2	1.4(5)	4.3(5)	1.0(4)	2(1)	1(1)	3(2)	13.62	0.007
	R (Å)	1.763(9)	2.27(3)	2.46(2)	3.10(2)	3.36(3)	3.57(4)			
	σ^2 (Å ²)	0.0021(4)	0.004	0.004	0.003	0.003	0.003			

^a Coordination number. ^b Interatomic distance. ^c Debye-Waller factor. ^d The estimated standard deviations are listed in parentheses, representing the uncertainty in the last digit. Parameters with no listed uncertainties were not varied in the analyses. ^e Difference in the threshold Fermi level between the data and theory. ^f Goodness-of-fit parameters (Kelly et al., 2008).

TABLE 3. Summary of U L_{III}-edge EXAFS fitting results for U(VI) with montmorillonite at pH 6.

Shell		U-O _{ax}	U-O _{eq}	U-O _{eq}	U-Si	U-Al	U-P	ΔE_0 (eV) ^e	χ^2 ^f	R-factor ^f
6P0U0.5	N ^a	2	1.6(4)	4.6(4)	0.8(3)	0.9(4)	—	2(2)	3.32	0.008
	R (Å) ^b	1.758(6) ^d	2.27(2)	2.46(1)	3.10(3)	3.31(3)	—			
	σ^2 (Å ²) ^c	0.0020(4)	0.004	0.004	0.003	0.003	—			
6P0U10	N	2	1.5(8)	3.4(9)	1.5(4)	1.5(6)	—	5(1)	3.95	0.013
	R (Å)	1.769(6)	2.37(6)	2.50(3)	3.12(2)	3.36(2)	—			
	σ^2 (Å ²)	0.0016(5)	0.004	0.004	0.003	0.003	—			
6P0U100	N	2	1.7(4)	4.2(4)	0.9(3)	1.3(4)	—	3(1)	6.1	0.008
	R (Å)	1.758(5)	2.30(3)	2.47(1)	3.09(2)	3.33(2)	—			
	σ^2 (Å ²)	0.0015(3)	0.004	0.004	0.003	0.003	—			
6P10U0.5	N	2	2.6(4)	3.0(5)	1.6(7)	2(1)	0.4(1.0)	3(2)	5.55	0.007
	R (Å)	1.777(9)	2.28(2)	2.46(2)	3.13(2)	3.32(3)	3.5(1)			
	σ^2 (Å ²)	0.0018(4)	0.004	0.004	0.003	0.003	0.003			

^a Coordination number. ^b Interatomic distance. ^c Debye-Waller factor. ^d The estimated standard deviations are listed in parentheses, representing the uncertainty in the last digit. Parameters with no listed uncertainties were not varied in the analyses. ^e Difference in the threshold Fermi level between the data and theory. ^f Goodness-of-fit parameters (Kelly et al., 2008).

FIGURE CAPTIONS

Figure 1. U(VI) equilibrium uptake behavior at (A) pH 4, (B) pH 6, and (C) pH 8 and phosphate uptake (D) pH 4, (E) pH 6, (F) pH 8, on montmorillonite (1.0 g/L with pH 4, 0.20 g/L with pH 6, 8) with varying initial concentrations of phosphate (0-100 μM). Labels indicate samples with solid-phase analysis by EXAFS spectroscopy and LIFS and correspond to conditions described in Table 1.

Figure 2. Laser induced fluorescence emission spectra of U(VI) adsorbed to montmorillonite (1.0 g/L with pH 4, 0.20 g/L with pH 6, 8) in the presence of the highest initial phosphate concentration at each pH: 4 (blue, 10 μM U(VI), 100 μM PO_4^{3-}), 6 (red, 10 μM U(VI), 10 μM PO_4^{3-}), and 8 (green, 100 μM U(VI), 100 μM PO_4^{3-}). The spectrum of sodium autunite is plotted for comparison.

Figure 3. Laser induced fluorescence emission spectra of U(VI) adsorbed to montmorillonite (1.0 g/L with pH 4 and 0.20 g/L with pH 6, 8) with varying phosphate concentration below the onset of precipitation at (A) pH 4, (B) pH 6, and (C) pH 8. Blue indicates 100 μM phosphate, red indicates 10 μM phosphate, and black indicates 0 μM phosphate. Sample labels refer to sample conditions described in Table 1.

Figure 4. U L_{III} -edge extended X-ray absorption fine structure (EXAFS) spectra (left) and Fourier transforms (right) of samples at initial phosphate and U(VI) concentrations (sample labels in μM) above the precipitation threshold at pH 4 (1.0 g/L montmorillonite), 6 (0.20 g/L montmorillonite), and 8 (0.20 g/L montmorillonite). The spectrum of sodium autunite is plotted

for comparison.

Figure 5. U L_{III}-edge EXAFS (left) and Fourier transform (right) spectra (solid) and structural model fits (red dashed line) of samples with 5 μM initial U(VI) reacted with montmorillonite (1.0 g/L) and 0, 10, or 100 μM phosphate at pH 4. Structural model fits are shown as red dashed lines. Samples containing phosphate were also modeled without a P shell (blue dotted line).

Figure 6. U L_{III}-edge EXAFS (left) and Fourier transform (right) spectra (solid) and structural model fits (dashed) of samples with varying concentrations of U(VI) adsorbed on montmorillonite (0.20 g/L) with and without phosphate at pH 6. The sample containing phosphate was also modeled without a P shell (blue dotted line).

Figure 7. Macroscopic U(VI) uptake data (symbols) at (A) pH 4 with 100 μM phosphate with 1.0 g/L montmorillonite, (B) pH 6 with 10 μM phosphate, and (C) pH 8 with 100 μM phosphate with 0.20 g/L montmorillonite with corresponding equilibrium speciation model calculations (dashed lines).

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