Effects of calcium and phosphate on uranium(IV) oxidation: Comparison between nanoparticulate uraninite and amorphous U(IV)-phosphate

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Abstract

The mobility of uranium in subsurface environments depends strongly on its redox state, with U^{IV} phases being significantly less soluble than U^{VI} minerals. This study compares the oxidation kinetics and mechanisms of two potential products of U^{VI} reduction in natural systems, a nanoparticulate UO_2 phase and an amorphous U^{IV} -Ca- PO_4 analog to ningyoite ($\text{CaU}^{\text{IV}}(\text{PO}_4)_2 \cdot 1-2\text{H}_2\text{O}$). The valence of U was tracked by x-ray absorption near-edge spectroscopy (XANES), showing similar surface-normalized oxidation rate constants for $\text{U}^{\text{IV}}\text{O}_2$ and U^{IV} -phosphate in solutions equilibrated with atmospheric O_2 and CO_2 at pH 7.0 ($k_{\text{obs},\text{UO}_2} = 0.17 \pm 0.075 \text{ h}^{-1}$ vs. $k_{\text{obs},\text{U}^{\text{IV}}\text{PO}_4} = 0.30 \pm 0.25 \text{ h}^{-1}$). Addition of up to 400 μM Ca and PO_4 decreased the oxidation rate constant by an order of magnitude for both UO_2 and U^{IV} -phosphate. The intermediates and products of oxidation were tracked by electron microscopy, powder x-ray diffraction (pXRD), and extended x-ray absorption fine-structure spectroscopy (EXAFS). In the absence of Ca or PO_4 , the product of UO_2 oxidation is Na-uranyl oxyhydroxide (under environmentally relevant concentrations of sodium, 15 mM NaClO_4 and low carbonate concentration), resulting in low concentrations of dissolved U^{VI} ($<2.5 \times 10^{-7} \text{ M}$). Oxidation of U^{IV} -phosphate produced a Na-autunite phase ($\text{Na}_2(\text{UO}_2)\text{PO}_4 \cdot x\text{H}_2\text{O}$), resulting in similarly low dissolved U concentrations ($<7.3 \times 10^{-8} \text{ M}$). When Ca and PO_4 are present in the solution, the EXAFS data and the solubility of the U^{VI} phase resulting from oxidation of UO_2 and U^{IV} -phosphate are consistent with the precipitation of Na-autunite. Bicarbonate extractions and Ca K-edge x-ray absorption spectroscopy of oxidized solids indicate the formation of a Ca- U^{VI} - PO_4 layer on the UO_2 surface and suggest a passivation layer mechanism for the decreased rate of UO_2 oxidation in the presence of Ca and PO_4 . Interestingly, the extractions were unable to remove all of the oxidized U from partially oxidized UO_2 solids, suggesting that oxidized U is distributed between the interior of the UO_2 nanoparticles and the labile surface layer. Accounting for the entire pool of oxidized U by XANES is the likely reason for the higher UO_2 oxidation rate constants determined here relative to prior studies. Our results suggest that the natural presence or addition of Ca and PO_4 in groundwater could

slow the rates of U^{IV} oxidation, but that the rates are still fast enough to cause complete oxidation of U^{IV} within days under fully oxygenated conditions.

1. Introduction

Uranium is a toxic and radioactive element that has been used for energy generation and military purposes for several decades, resulting in stockpiles of spent fuel, mine tailings, and enrichment process waste stored at many locations around the world. Designing appropriate storage practices and predicting the effects of accidental release requires an in-depth understanding of the coupled chemical, physical, biological, and hydrological processes that control the mobility of U in oxic and anoxic environments. Developing this understanding is currently hindered by the limited availability of mechanistic information on the transformations and speciation of U under environmentally relevant conditions (Bargar et al., 2013; Burns et al., 2012; Newsome et al., 2014; Williams et al., 2013).

The solubility, and therefore the mobility, of uranium is strongly affected by its valence state. In oxidizing environments uranium is stable as U^{VI} . When equilibrium with schoepite ($UO_3 \cdot 2H_2O$) controls U^{VI} solubility, the resulting aqueous concentrations are on the order of 10^{-4} M at pH 7 (Jang et al., 2006). In reducing environments uranium is stable as U^{IV} . When equilibrium with uraninite (UO_{2+x}) controls U^{IV} solubility, the resulting aqueous concentrations are on the order of 10^{-8} M at pH 7 (Ulrich et al., 2008). The dramatic decrease in solubility in this simplified scenario is expected to significantly influence U mobility in the subsurface and has been the impetus for extensive research on (bio-) reduction of U^{VI} for the purpose of contaminated site remediation. However, uranium transformations in the subsurface occur in the presence of various surfaces and dissolved ions, which can affect the solubility, speciation, and outcome of reactions with U. For instance, carbonate forms strong, highly soluble complexes with U^{VI} and together with Ca^{2+} decreases the ability of U^{VI} to be reduced to U^{IV} (Brooks et al., 2003). Phosphate and phosphatase activity influences U^{VI} solubility through the formation of precipitates (Beazley et al., 2007), which can affect the rate of U^{VI} bioreduction (Rui et al., 2013). U^{VI} can interact with various mineral and biological surfaces to form stable adsorption complexes (Bargar et al., 1999; Kelly et al., 2002). The complexity in U^{VI} speciation described above is accounted for in most transport models. However, only an amorphous uraninite phase is typically used to model the behavior of reduced U^{IV} ,

under the assumption that the lowest solubility mineral controls U^{IV} dynamics (Li et al., 2010; Li et al., 2009; Yabusaki et al., 2007a). Research in the past few years has drawn this assumption into question, at least for processes occurring over the months-to-years timescale. Low levels of phosphate were shown to inhibit the formation of uraninite during U^{VI} reduction, resulting in non-uraninite, phosphate-complexed U^{IV} solid phases (Alessi et al., 2014b; Boyanov et al., 2011; Stylo et al., 2013). Investigations of U speciation in reduced sediments and soils also indicates the prevalence of non-uraninite U^{IV} species over uraninite, although the exact identity of U^{IV} species remains unclear (Alessi et al., 2014a; Bargar et al., 2013; Li et al., 2015; Wang et al., 2014). Recently, high-affinity mineral surface sites were shown to stabilize mononuclear U^{IV} adsorption complexes and thus inhibit uraninite formation (Latta et al., 2014). Subsequent work developed a surface complexation model and determined stability constants for such sites (Wang et al. 2015). These developments indicate a significant gap in the description of short-term U^{IV} dynamics in transport models and suggest the need for the study of non-uraninite U^{IV} reactions in model systems so appropriate reactions can be included in the more complex field-scale models (Long et al., 2015).

Of particular importance to U stability under the changing redox conditions in natural environments is the oxidation of U^{IV} phases, as U^{VI} species have a much higher potential for remobilization. Oxidation can occur due to the influx of dissolved oxidants, as well as due to water radiolysis under anoxic conditions (Ekeröth and Jonsson, 2003; Ulrich et al., 2008). A number of studies have addressed uraninite oxidation in batch and electrochemical experiments from the perspective of nuclear fuel corrosion, providing a detailed and mechanistic understanding of the process (Roth and Jonsson, 2008; Shoesmith, 2000) and references therein). Electrochemical studies coupled with surface sensitive x-ray photoelectron spectroscopy have shown that UO_2 oxidation proceeds via surface oxidation to $UO_{2.33}$, followed by accumulation of surface UO_2^{2+} layers as oxidation further progresses (Shoesmith, 2000; Shoesmith et al., 1989). Accumulation of surface U^V/U^{VI} hinders the interpretation of batch and flow UO_2 oxidation experiments. Surface layers of $UO_{2.33}$ do not form under high-bicarbonate conditions

because U^{VI} dissolves directly to solution (Shoesmith, 2000; Ulrich et al., 2009). Hence, most electrochemical studies have used high bicarbonate concentrations to provide meaningful results for UO_2 oxidation and dissolution. On the other hand, electrochemical studies only measure electron transfer reactions, and thus require supporting evidence such as spectroscopic or diffraction data to provide comprehensive information about non-redox phase transformations.

More recent studies have looked at the oxidation of uraninite from the perspective of U release following reductive remediation. Consistent with electrochemical studies on UO_2 spent fuel corrosion, several studies of UO_2 dissolution after reductive immobilization have found that carbonate increases the rate of oxidative UO_2 dissolution through promotion of U^V/U^{VI} surface layer detachment (Pierce et al., 2005; Ulrich et al., 2009). Interestingly, Ulrich and coworkers found that biogenic nanoparticulate uraninite dissolved at a similar surface-area-normalized rate as larger particles of synthetic UO_2 , but nanoparticulate UO_2 supported a higher concentration of U in solution during oxidation, presumably due to higher surface strain in the smaller particles. Several studies to date have shown that mass transport has important effects on the mobility of U in subsurface systems, and have found that the release of U^{VI} from UO_2 is slowed in diffusion limited and advective systems relative to mixed batch reactors (Campbell et al., 2011; Giammar et al., 2012).

In contrast to the extensive studies of UO_2 oxidation, very limited information is available on the stability and oxidation of non-uraninite U^{IV} phases. U^{IV} in biogenic, non-uraninite solids was found more labile to dissolution than uraninite in 1 M anoxic bicarbonate extractions (Alessi et al., 2012).

Interpretation of U^{IV} release in bicarbonate extractions, however, may be complicated by reversal of the electron transfer between U^{IV} and the oxidized reductant of U^{VI} (e.g., organic matter, electron shuttles, or Fe^{3+}) (Ginder-Vogel et al., 2006; Stoliker et al., 2013), leading to U^{IV} oxidation and release of U^{VI} .

Cerrato et al. (2013) studied the oxidation of a biogenic, non-uraninite phase at lower bicarbonate concentrations (100 mM) and concluded comparable oxidation rates for biogenic uraninite and non-uraninite U^{IV} species. A slight preference for oxidation of non-uraninite U^{IV} species relative to uraninite

was suggested in experiments with mixtures of these two phases. Sharp et al. (2011) investigated the oxidative release of U from non-uraninite U^{IV} species in sediments that have been previously subjected to reducing conditions and U^{VI} -containing influents. The authors concluded that these U^{IV} species were less stable than biogenic uraninite under both anoxic and oxic conditions. Despite these initial results, the knowledge about the stability of non-uraninite U^{IV} phases appears to be far from a state where specific reactions can be included in reactive transport models.

Here, we investigate the rates and products of the oxidation of a non-uraninite, amorphous U^{IV} -phosphate phase by dissolved oxygen (DO), under environmentally relevant conditions. The results are compared to the oxidation of nanoparticulate uraninite under the same conditions. The goal was to obtain insight on the oxidation mechanisms and to estimate the relative stability of the two U^{IV} phases in controlled experiments. We examined the effect of Ca^{2+} and HPO_4^{2-} on U^{IV} oxidation; both are ions that are ubiquitous and are typically in excess of U in natural environments, thus potentially affecting uranium geochemistry. Elevated Ca^{2+} and PO_4 concentrations also create conditions that inhibit U^{VI} dissolution, allowing for control of the surface dissolution step in the overall oxidation process and providing information on the mechanism of oxidation. Unlike previous studies, which determined the rate of U^{IV} oxidation from the rate of oxidant consumption or from the rate of U^{VI} dissolution, here we determined the change in U^{IV}/U^{VI} content over time from x-ray absorption spectroscopy measurements. This approach provides a direct measurement of U^{IV} oxidation in the hydrated solids under the conditions of interest, as well as information on the reaction products and intermediates. In such a way, the U^{IV} oxidation reaction was studied without potential interfering factors such as rate-limiting dissolution of the oxidized products or solution conditions that may favor oxidized U dissolution but alter U speciation and reaction dynamics. In addition, potential artifacts from drying of the samples or from unaccounted oxidant consumption in parallel reactions not related to U^{IV} oxidation are eliminated.

2. Methods and materials

2.1. Synthesis of U^{IV} solids

Uranium^{IV} solids were synthesized by chemical reduction of uranyl-carbonate solutions using 9,10-anthrahydroquinone-2,6-disulfonic acid (AH₂QDS). A 25 mM stock solution of AH₂QDS was prepared by reduction of 25 mM 9,10-anthraquinone-2,6-disulfonic acid (AQDS) by H₂ in the presence of a Pd catalyst (0.5 wt% on Al₂O₃ supports). AH₂QDS stock solutions were filtered prior to use. Uranyl chloride was used as the starting U^{VI} stock, and was synthesized by dissolving UO₃ in HCl to prepare a stock with an approximate uranium concentration of 0.1 M UO₂²⁺. All U^{IV} solids were synthesized inside an anoxic chamber with a 3% H₂/97% N₂ atmosphere with a Pd oxygen scrubbing catalyst (<1ppm O₂ at all times). Deionized water used in the anoxic chamber was deoxygenated by bubbling with N₂ for 2 hours, and left open overnight in the chamber to complete the removal of trace O₂.

2.1.1. Uraninite synthesis

Uraninite was synthesized from a uranyl-carbonate solution using AH₂QDS as a reductant for U^{VI}. A solution of 0.5 mM U^{VI} was prepared by adding 0.5 mL of 0.1 M uranyl chloride stock to 100 mL of 5 mM NaHCO₃ solution. After addition of the uranyl solution, the pH was adjusted to a value of 7.1 with 1 M NaOH. To initiate the reduction of U^{VI}, 9.6 mL of the 25 mM AH₂QDS stock was added to the uranyl-bicarbonate solution. The reactor was shaken to mix the reactants, then capped, and the pH was adjusted with 1 M NaOH or HCl and allowed to react for 24 hours. After a day of reaction time, the uranium solids were harvested by filtration (0.22 μm membrane filter). The filtered solids were resuspended in ~10 mL of deionized water in a serum vial and dispersed from the filter membrane using a bath-style sonicator. The total uranium content after digestion and oxidation of the suspension was measured by kinetic phosphorescence analysis (KPA-11, Chemchek Instruments, Inc.) using URAPLEX as the complexant. Kinetic phosphorescence analysis is specific to U^{VI}, and samples were prepared by dissolving 50 μL of the U^{IV} suspension in 200 μL 5 M H₂SO₄ for 1 hour, diluting to a total volume of 1

mL by addition of deionized (DI) water, and oxidizing the U^{IV} overnight (≈ 18 hours) in micro-centrifuge tubes removed from the anoxic glove box and exposed to air. Triplicate analyses indicated that the total U concentration in the uraninite suspension was 4.43 ± 0.113 mM (1σ).

2.1.2. U^{IV} -phosphate synthesis

A ningyoite-like (ningyoite: $CaU(PO_4)_2 \cdot H_2O$) U^{IV} -phosphate solid was synthesized from a uranyl-carbonate solution containing Ca^{2+} and PO_4^{3-} using AH_2QDS as a reductant. Here, a solution of 30 mM $NaHCO_3$ was prepared by adding 13.5 mL of 1 M $NaHCO_3$ to 410 mL DI water. U^{VI} was added using 0.45 mL of the 0.1 M uranyl chloride stock for a final concentration of 100 μ M. Then 1.35 mL of 0.1 M NaH_2PO_4 was added to the solution for a final concentration of 300 μ M PO_4^{3-} . A 1.05-mL aliquot of 0.043 M $CaCl_2$ was added last to minimize the possibility for $Ca-PO_4$ precipitation. The final Ca^{2+} concentration was 100 μ M. The pH of the $U^{VI}-Ca^{2+}-PO_4^{3-}-CO_3^{2-}$ solution was adjusted to 6.9, and 24 mL of 25 mM AH_2QDS stock was added to initiate the reduction reaction (final $[AH_2QDS] = 1.33$ mM). The pH was checked after AH_2QDS addition, and readjusted to a value of 6.9 with 1 M $NaOH$ and 1 M HCl . After 1 day of reaction time, the U^{IV} -phosphate solids were collected by filtration and the solids on the membrane were dispersed into DI water by sonication. As with uraninite, total U in the suspension was measured with the KPA after dissolution of 50 μ L of the suspension in 200 μ L 5 M H_2SO_4 , subsequent dilution to 1 mL, and oxidation of U^{IV} to U^{VI} in air. Analysis of triplicate samples indicated that the concentration of total U in the suspension was 3.12 ± 0.241 mM (1σ). Mean calcium concentration in the solids suspension (from two samples) measured by inductive coupled plasma-optical emission spectroscopy (ICP-OES) was 1.32 mM.

2.1.3. U^{VI} solids synthesis

Two U^{VI} samples were prepared to provide reference spectra of the possible oxidation endmember phases for the x-ray absorption spectroscopy (XAS) analysis. A U^{VI} oxyhydroxide sample

was prepared by adding 0.1 M U^{VI} -chloride stock to the 3-(N-morpholino)propanesulfonic acid (MOPS)/ $NaClO_4$ buffer for a nominal U^{VI} concentration of 0.5 mM, and adjusting the pH of the solution to approximately 7.0 with 0.5 M NaOH. A colloidal precipitate formed at this pH value and after 24 hours of reaction under stationary conditions the solution was filtered and the solids mounted as described above. A U^{VI} phosphate sample was prepared under solution conditions similar to those of the oxidation experiments: 100 μM U^{VI} , 400 μM Ca^{2+} , and 400 μM PO_4^{3-} at pH 7.2. Here, U^{VI} stock was added to the MOPS/ $NaClO_4$ buffer containing 400 μM Ca and PO_4^{3-} . The precipitate was filtered after 3 days of reaction and mounted for XAS analysis as with other samples.

2.2. Experimental procedures

2.2.1. U^{IV} oxidation experiments

Prior to the oxidation experiments, the phase identity of each batch of the starting U^{IV} materials was verified using EXAFS (Fig. EA-7). Oxidation of the two U^{IV} solids—uraninite and the ningyoite-like U^{IV} -phosphate—was performed in 5 mM MOPS buffer with 15 mM $NaClO_4$ as the background electrolyte and 100 μM of U^{IV} solids. The pH of the solution was set at pH 7.0 by using appropriate quantities of MOPS-acid and its sodium salt. The experiment consisted of a series of sacrificial batch reactors with each reactor representing a separate time point and treatment. Each reactor was prepared in a 60-mL glass serum bottle open to ambient atmosphere filled with 25 mL of the buffer/electrolyte solution. Initial dissolved oxygen in the buffer at 22°C was measured to be 237 μM O_2 using an Orion 3-Star Portable DO meter (Thermo Scientific).

Experiments with uraninite included uraninite oxidation without calcium and phosphate, and experiments that included 400 μM Ca^{2+} and/or 400 μM PO_4^{3-} . U^{IV} -phosphate oxidation experiments were done without added Ca or PO_4^{3-} , as well as with 100 μM and 400 μM added Ca^{2+} and PO_4^{3-} . Addition of the U^{IV} - PO_4 solid to the buffer added 42 μM Ca and 105 μM PO_4 . Immediately prior to initiation of the experiments, Ca and PO_4^{3-} were added from a 100 mM $CaCl_2$ stock and a 100 mM PO_4^{3-} stock prepared

from 0.062 M NaH_2PO_4 and 0.038 M Na_2HPO_4 to have a pH value near 7.0. Bottles were crimped with a butyl-rubber stopper to seal in an ambient atmosphere headspace, and transferred into the anoxic chamber.

Oxidation of U^{IV} was initiated by spiking the sealed oxygen-containing serum-vials with U^{IV} suspensions in the glove box. Aliquots of uraninite and U^{IV} -phosphate suspensions were measured out with a pipette into a micro-centrifuge tube, loaded into needle-tipped syringes, and injected into the serum vials to initiate the oxidation reaction. Reactors were shaken by hand to suspend the solids in the buffer, and transferred within 2 minutes to a shaker table operating at 175 rpm outside of the anoxic chamber. Nominal reaction times between 10 minutes and 72 hours were chosen to trace the kinetics of U^{IV} oxidation. Reaction time was recorded with a precision of 1 minute. Samples reacted for 10 and 30 minutes were not transferred out of the anoxic chamber, but were shaken vigorously by hand every 2–3 minutes to maintain oxygen equilibrium between the gas and liquid phase. The initial concentration of O_2 in the air-equilibrated solutions is 0.237 mM, which is sufficient to oxidize 0.948 mM of U^{IV} . The total reservoir of O_2 in the aqueous and gas phase was 1.45 mmoles, which is 290 times greater than the 5 μmoles of O_2 required to completely oxidize the amount of U^{IV} present. The oxidation reaction can therefore be assumed to be pseudo-first order with respect to the oxidant. Un-oxidized U^{IV} solids controls were prepared in a similar fashion, but in an anoxic buffer solution prepared by bubbling with Ar for 2 hours. Control vials were not removed from the anoxic chamber over the course of the experiments.

Prior to sampling, reactors were transferred back into the anoxic chamber and approximately 15 mL of suspension was filtered through a 0.22 μm membrane filter. The filtered solution was saved for Ca, PO_4^{3-} , and U analysis. The filtered solids were sealed together with the filter membrane between two layers of Kapton film for x-ray absorption spectroscopy analysis.

2.2.2. Bicarbonate extractions

A series of extraction experiments (100 mM NaHCO₃, pH 8.2) were conducted to probe whether a passivation layer of U^{VI} formed on the surface of UO₂ during oxidation in the presence of 400 μM Ca and PO₄. These experiments also tested whether removal of this oxidation layer affected subsequent U^{IV} oxidation. To start, a suspension of UO₂ was prepared and oxidized as described above: a 250-mL bottle filled with 150 mL of solution containing 5 mM MOPS, 15 mM NaClO₄, and 400 μM Ca, and PO₄ was equilibrated with 100 mL ambient atmosphere headspace. The sealed bottle was spiked with 100 μM U^{IV} as UO₂ and placed for 10 hours on an orbital shaker, then transferred back to the anoxic glove box and sub-sampled for analysis of U valence state prior to extraction. The remaining solids were collected by filtration through a 0.22 μm nylon membrane, suspended in 60 mL of anoxic 100 mM NaHCO₃ adjusted with HCl to pH 8.20, and sonicated to disperse the particles. The bottle was crimp-sealed and placed on an orbital shaker for 14.5 hours.

After extraction, an aliquot was filtered and mounted for XAS analysis of U valence state. The remaining solids were again collected by filtration, washed by passing approximately 20 mL of deoxygenated DI water over the filtered solids, and re-suspended in 4 mL deoxygenated DI water by sonication. Appropriate aliquots of the suspension were dispensed to reactors containing oxic 25-mL MOPS/NaClO₄ solutions for oxidation experiments identical to the ones described above with unextracted UO₂. Results were compared between reactors with and without added Ca and PO₄ in the solution phase.

2.3. Solids characterization

2.3.1. Electron microscopy

The U solids in some of the samples were imaged with scanning electron microscopy (SEM). Solids were centrifuged from 2-mL aliquots of the reactors and suspended in 0.1 mL of deoxygenated methanol. The suspensions were then spread onto 12.7-mm graphite stubs (Ted Pella, Inc.) and dried for 12 hours in the anoxic chamber in a sealed desiccator using calcium sulfate as a desiccant (Drierite). The

dried samples were only briefly exposed to oxygen when transferring them from an anoxic transport box to the SEM. Samples were imaged using a Quanta 400F Environmental SEM (FEI Company) operating under high-vacuum conditions and an accelerating voltage of 3 to 5 kV. Secondary electron images were collected using an Everhart-Thornley detector. Energy dispersive x-ray spectroscopy (EDS) fluorescence spectra were produced using an electron accelerating voltage of 20 kV and collected using a Revolution EDX spectrometer and software (4pi Analysis, Inc.). The x-ray fluorescence spectra were collected for 60 s while rastering the electron beam on the sample, resulting in spectra averaged over the imaged area.

Transmission electron microscopy (TEM) was used to determine the morphology and particle sizes of the uraninite and U^{IV}-phosphate starting materials, which were then used as a basis to calculate specific surface area. Samples were prepared as described above for SEM analysis, and dropped onto ultra-thin holey carbon copper supported TEM grids. Samples were imaged with a FEI CM30T microscope using an accelerating voltage of 200 kV and a Gatan charge-coupled device camera. For nearly spherical nanomaterials, TEM surface area is statistically similar to BET surface area (Bau et al., 2010).

2.3.2. X-ray absorption spectroscopy (XAS)

The hydrated solids from both unoxidized and oxidized reactors were analyzed by x-ray absorption spectroscopy to probe the oxidation state and the coordination environment of U and Ca using the x-ray absorption near-edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS) regions of the spectrum, respectively. Measurements at the uranium L_{III} edge (17,166 eV) were done at the MRCAT/EnviroCAT bending magnet and insertion device beamlines (sector 10-BM and 10-ID) at the Advanced Photon Source, Argonne National Laboratory. The experimental setup at these two beam lines is reviewed in prior work (Kropf et al., 2010; Segre et al., 2000). As described above, the filtered and hydrated solids were sealed between Kapton film and were maintained under anoxic conditions until measurement. Spectra were recorded at room temperature in transmission and

fluorescence modes using gas-filled ionization chambers. Samples were maintained in a N₂-flushed chamber during measurement to preclude oxidation by ambient O₂. Data consistency was confirmed by scanning three fresh locations on each sample, with at least two scans taken at each location. No evolution of oxidation state was observed in successive scans, indicating that beam-induced redox changes were negligible or absent. Spectra were averaged to produce the final data.

The raw spectra were normalized and background was subtracted using the program Athena (Ravel and Newville, 2005). Linear combination fits of the XANES and EXAFS spectra were carried out to quantify the proportions of U^{IV} and U^{VI} endmembers in the samples at different time points during oxidation. The statistical uncertainty from the numerical fits was reported by Athena as less than 2% for all fits; however, this estimate does not account for possible differences between the phases present in the sample and those used as endmembers in the fit. Due to the high quality of the data and the known endmembers we estimate an overall uncertainty of $\pm 5\%$ in the data reported in Fig. 1 and Table 2.

Calcium K-edge XAS spectra were collected at room temperature at the MRCAT/EnviroCAT bending magnet beamline in fluorescence mode using a four-element silicon drift detector. To maximize Ca fluorescence intensity, the sample and detector were placed in close proximity within a He purged chamber. Samples were mounted and sealed using Scotch (3M Corporation) brand tape, as preliminary measurements indicated that Kapton tape typically used to mount XAS samples contained a Ca contaminant. The energy was calibrated at 4038.5 eV to the inflection point of a spectrum from calcite (CaCO₃). Standards included a 1 M solution of CaCl₂ (as a standard of O-coordinated Ca²⁺) and calcium phosphate (hydroxyapatite). The latter was synthesized by mixing equal parts of 10 mM CaCl₂ and NaH₂PO₄ solutions and titrating the solution to pH 7.1. The turbid solution was allowed to age overnight, centrifuged and washed twice with DI water, then stored as a suspension in DI water for a month prior to use.

2.3.3 XRD measurements

Powder x-ray diffraction (pXRD) patterns were measured from selected UO_2 and U^{IV} -phosphate solids after oxidation. Data were collected using a Rigaku MiniFlex diffractometer using Cu K-alpha radiation with a Ni K-beta filter. Long scans (8 s per $0.02^\circ 2\theta$) were used because of the small amount of solids available. Samples were mounted on aluminum sample holders in the glove box and covered with a drop of glycerol and a thin layer of polyethylene film to prevent oxidation; pXRD was also used to confirm the identity of the calcium phosphate standard (hydroxyapatite).

2.4. Solution analysis

2.4.1. KPA analysis of total uranium

Solution samples from the uranium oxidation experiments were analyzed using kinetic phosphorescence analysis with a KPA-11 analyzer (Chemchek Instruments, Inc.). Total dissolved uranium was measured using a wet-ashing technique to remove interfering solution constituents (MOPS buffer and Cl^-). Glass sample vials (1 mL) were cleaned using a 1:1 dilution of trace-metals grade concentrated HNO_3 in water at 40°C for 12 hours, then washed with deionized water and dried. Each vial was filled with 500 μL of sample solution, 100 μL 30% H_2O_2 , and 400 μL trace-metals grade concentrated HNO_3 , and was evaporated to dryness in a heating block set to 90°C inside a fume hood. After wet-ashing, the samples were reconstituted to 1 mL with 1 M nitric acid (trace metals grade). A 250- μL aliquot of each sample was placed in a quartz cuvette and diluted to 1 mL with DI water, to which 1.5 mL of URAPLEX (Chemchek Instruments, Inc.) reagent was added. A 1 M nitric acid blank (1 mL) contained 4.25 ppb U, and uranium detections below this level were consistent with dilution of this quantity of U by 250 μL of sample. These are reported as less than the blank in Table 2.

2.4.2. ICP-OES analysis of total uranium, calcium, and phosphorus

Samples from oxidation experiments were analyzed concurrently for total uranium, calcium, and phosphorus (phosphate) using inductively coupled plasma-optical emission spectroscopy (Perkin-Elmer

4300DV ICP-OES). Samples were diluted into 10 mL of 5% HNO₃, to which 3 mL of a 1 ppm Y in 5% HNO₃ was added as an internal standard. Uranium was quantified using the emission line at 385.958 nm, calcium at 317.933 nm, and phosphorus at 213.617 nm.

3. Results and Discussion

3.1. Oxidation of U^{IV} solids by dissolved O₂

3.1.1 Oxidation of U^{IV} in nanoparticulate uraninite and in U^{IV}-phosphate

Here we present the results from the oxidation of nanoparticulate uraninite and amorphous U^{IV}-phosphate in closed systems with dissolved oxygen (O₂) and carbonate concentrations resulting from equilibrium of the initial solution with air (approximately 250 μ M O₂ and 100 μ M HCO₃⁻; air in the headspace). Suspensions with 100 μ M U^{IV} were oxidized at pH 7.0 buffered by 5 mM MOPS in 15 mM NaClO₄ background electrolyte. U in the solution phase of all systems was less than 0.3% of total U at all stages of the 72 h oxidation process (dissolved U < 0.22 μ M, Table 2). The changes in oxidation state of solid phase U were tracked by XANES. In all systems, the trend in the spectra with reaction time is a progressive shift of the absorption edge to higher binding energies, indicating an increase in the average valence state of U (Fig. EA1-EA5). The XANES overlays for the U^{IV}-phosphate system (Fig. EA3) exhibit isosbestic points, suggesting transformation between one U^{IV} and one U^{VI} endmember, without detectable (i.e., >5% of total U) intermediate phases. In contrast, experiments with uraninite do not show consistent isobestic points (Fig. EA1), suggesting that oxidation of uraninite may go through an intermediate phase prior to formation of the U^{VI} endmember. We discuss this result later in a discussion of the oxidized U products.

The kinetics of U^{IV} oxidation, shown as U^{IV}/U_{total} in the solids over time, are summarized in Fig. 1 and Table 1. The U^{IV}/U_{total} ratios were determined by linear combination fits of the XANES spectra using

the starting U^{IV} materials and the observed final U^{VI} phases as endmembers (U^{VI} -oxyhydroxide for uraninite and autunite for U^{IV} -phosphate, respectively). We assume that the kinetics of U^{IV} oxidation are pseudo-first order with respect to oxygen concentration (total oxygen in the system was 290 times the amount required for complete oxidation to U^{VI} , i.e., $\Delta O_2 < 0.3\%$). Using log-linear regression ($\ln(U^{IV}/U_{total})$ vs. time), we estimate the average rate constants for the initial oxidation (i.e. the first 4 points) of uraninite and U^{IV} -phosphate to be $k_{obs,UO_2} = 0.17 \pm 0.075 \text{ h}^{-1}$ (standard deviation of triplicate experiments) and $k_{obs,U^{IV}PO_4} = 0.30 \pm 0.25 \text{ h}^{-1}$ (duplicate experiments), which indicates that oxidation rate constants are similar for the two materials (Fig. 1 and Table 1). In experiments with different batches of U^{IV} solids, we found that the oxidation rate constants of both UO_2 and U^{IV} -phosphate vary over a factor of 2 to 4, most likely due to batch-to-batch variability in the morphology of the synthesized U^{IV} materials (the atomic structure as determined by EXAFS was the same between batches, Fig. EA-7).

We attribute some of the difference in apparent oxidation rate constants between UO_2 and U^{IV} -phosphate to differences in particle size between the two solids. The particle sizes of uraninite and U^{IV} -phosphate determined by TEM show that uraninite formed primary particles on average 3.5 nm in diameter, whereas U^{IV} -phosphate formed primary particles approximately 12–16 nm in diameter (Fig. EA6). Calculated surface areas (assuming a spherical particle) are $160 \text{ m}^2 \text{ g}^{-1}$ and 40 to $100 \text{ m}^2 \text{ g}^{-1}$ depending on the batch, respectively for UO_2 and U^{IV} -phosphate. Particle sizes on the second and third batches of uraninite were not measured. Given the uncertainties generally associated with rate constant and surface area determinations (e.g., batch-to-batch variability of the starting materials or differences in aggregation state modulating the reactive surface area), the difference of up to 4 times in rate constants suggests that, under the tested conditions, the oxidation rates of UO_2 and U^{IV} -phosphate are not greatly different and could be related to differences in particle sizes.

In order to compare our U^{IV} oxidation rates to previous work we estimated the initial oxidation rate of U^{IV} in our study from the slope of initial change of U^{IV}/U_{total} vs. time (Cerrato et al., 2013). Our average oxidation rates of $2.2 \times 10^{-7} \text{ mol (g U)}^{-1} \text{ s}^{-1}$ for U^{IV} -phosphate and $7.3 \times 10^{-7} \text{ mol (g U)}^{-1} \text{ s}^{-1}$ for

UO₂, are slower by a factor of approximately 4.5 relative to those determined in Cerrato et al., where biomass-associated U^{IV}-phosphate oxidized slightly faster ($9.9 \times 10^{-7} \text{ mol (g U)}^{-1} \text{ s}^{-1}$), but were similar for biogenic UO₂ ($6.2 \times 10^{-7} \text{ mol (g U)}^{-1} \text{ s}^{-1}$) (Cerrato et al., 2013). Our results are also consistent with those reported by Sharp and coworkers for oxidative release of U from sediment microcosms containing U^{IV} bound to phosphate or carbonate (Sharp et al., 2011). In that study, U^{IV} oxidation and release was modeled using two pools of U^{IV} with oxidative release rates of $5.5 \times 10^{-5} \text{ mol (g U)}^{-1} \text{ s}^{-1}$ and $8.1 \times 10^{-7} \text{ mol (g U)}^{-1} \text{ s}^{-1}$ (Sharp et al., 2011). In spite of different measurement methods of U^{IV} oxidation—U dissolution in the previous studies and solid U valence state by XANES here—the data from our study and those of Cerrato et al. and Sharp et al. are consistent. Overall, the additional data from our study confirms that under relatively simple solution conditions, U^{IV} oxidation in bulk precipitates of U^{IV}-phosphate and nanoparticulate UO₂ proceeds at rates that are within an order of magnitude of each other.

We also estimated initial surface-area normalized rate constants ($k_{SA} = k_{obs}/\text{surface area loading}$) in order to compare to those tabulated for large particulate UO₂ in Roth and Jonsson (2008). Here surface area normalized rate constants for UO₂ oxidation ($1 \text{ to } 2.7 \times 10^{-8} \text{ m s}^{-1}$) are 1 to 2 orders of magnitude higher than those tabulated for O₂-mediated oxidation of large UO₂ particles ($3 \times 10^{-9} \text{ to } 3.6 \times 10^{-10} \text{ m s}^{-1}$) (Roth and Jonsson, 2008). Although Cerrato et al. (2013) did not report specific surface area for the nanoparticulate solids used in their study, we calculated surface-normalized rate constants from the oxidation data (by using our TEM surface area for their similarly sized biogenic UO₂ particles of about 3.5 nm diameter). The data from Cerrato et al. suggests surface area normalized rates that are up to an order of magnitude greater for biogenic UO₂ with a particle of size of 3.5 nm ($\sim 2 \text{ to } 5 \times 10^{-9} \text{ m s}^{-1}$) than for chemogenic UO₂ ($1 \times 10^{-10} \text{ m s}^{-1}$) with a particle size of 100–200 nm. The differences in UO₂ surface-area normalized rates between our study, Cerrato et al.'s study, and the studies reviewed in Roth and Johnson (2008) may be due to a surface strain effect on reactivity resulting from the small particle size, as well as uncertainty in surface area estimation. Nanoparticulate UO₂ is likely more susceptible to oxidation, given that it also dissolves significantly faster than micron-sized UO₂ particles (Cerrato et al.,

2013; Roth and Jonsson, 2008; Ulrich et al., 2009). In addition, previous studies used (bi)carbonate extractions to solubilize oxidized U and assumed that U release was limited by U^{IV} oxidation (Cerrato et al., 2013; Roth and Jonsson, 2008). While the assumption of prompt dissolution of U^{VI} from the surface is likely a valid one, it is possible that U^V/U^{VI} present within the particles is released more slowly; this pool of oxidized U in the system is not captured by the bicarbonate extractions, but is observable in the x-ray spectroscopy measurements used here (discussed below).

3.1.2. Solution dynamics during oxidation

In addition to tracking U valence in the solids, we also measured dissolved U, Ca, and P (Table 2). We observed insignificant release of U to solution in all systems; dissolved U concentrations were below 2.5×10^{-7} M at all times ($<0.3\%$ of total U). The variability observed at these low concentrations is likely a separation artifact resulting from small amounts of solids passing through the filter and subsequently dissolving during the acidification of the aqueous samples. The range of measured U concentrations for each system is compared to equilibrium solubility calculations for several oxidized U phases in Fig. 2, with the understanding that the precipitated U^{VI} minerals may be in a metastable state.

Interestingly, the measured U concentrations for the UO_2 oxidation experiments are 3 orders of magnitude lower than those expected for U^{VI} in equilibrium with schoepite (calculation shown in Fig. 2A for our experimental conditions: 15 mM $NaClO_4$, pH 7.0, ~ 100 μ M dissolved bicarbonate from equilibrium with ~ 400 ppm CO_2 in the headspace air). Other U^{VI} precipitates considered for our 15 mM Na^+ systems were a low-temperature clarkeite-like solid studied by Giammar and Hering ($K_{sp} = [UO_2^{2+}][Na^+]/[H^+]^3 = 10^{8.81}$) and a Na-compreignacite phase studied by Gorman-Lewis et al. ($K_{sp} = [Na^+]^2[UO_2^{2+}]^6/[H^+]^{14} = 10^{39.4}$) (Giammar and Hering, 2004; Gorman-Lewis et al., 2008). The measured U^{VI} concentrations in our work are closer to those resulting from with the clarkeite-like solid than with schoepite or Na-compreignacite. The low solubility of sodium-containing uranyl phases may be of importance in oxic groundwater containing significant amounts of dissolved sodium and low bicarbonate

concentrations. For example, the U.S. Department of Energy (DOE) U-contaminated sites at Rifle, Colorado, and Oak Ridge, Tennessee, have approximately 10–30 mM dissolved Na^+ (Revil et al., 2013; Zachara et al., 2013). Such Na-bearing phases may control U solubility in rock salt formations used for U-bearing waste interment such as the Waste Isolation Pilot Plant (Goldstein, 2011), and during corrosion of UO_2 reactor fuel exposed to ocean water at the Fukushima nuclear incident site (Burns et al., 2012).

Oxidation of the U^{IV} -phosphate solids results in aqueous U concentrations below 7.3×10^{-8} M at all times (Table 2). Calcium concentrations in solution are relatively constant over the course of the experiment (16 to 23 μM). The Ca remaining in the solids after 72 hours of oxidation is 46% of the Ca present in the initial solids, suggesting that some calcium is retained in the oxidized solids. In contrast to Ca, aqueous phosphate concentrations increase from 10.5 μM in the control to 17.7 μM after 9 hours of oxidation but decrease to only 2.1 μM after 72 hours, suggesting a near-complete incorporation of the available 100 μM phosphate into the products of oxidation. Retention of Ca and PO_4 in the solids is consistent with the precipitation of autunite phases (autunites are $\text{X}_{1,2}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{--}11\text{H}_2\text{O}$, where X are mono- or di-valent metals). The measured concentrations of U in solution are within the range of calculated U solubilities from Na-autunite for the conditions in this study (2–18 μM PO_4 , 400 ppm CO_2 , and 15 mM Na^+ ; Fig. 2B). Overall, the solution dynamics of U, Ca, and phosphate suggest that oxidation of U^{IV} -phosphate results in low-solubility U^{VI} -phosphate phases; this is also supported by the spectroscopic and pXRD evidence discussed below.

3.1.3. Products of UO_2 and U^{IV} -phosphate oxidation

The solubility of U^{VI} in our study suggests the formation of Na-uranyl oxyhydroxides and Na-uranyl phosphates upon oxidation of UO_2 and U^{IV} -phosphate, respectively. The speciation of U in the solids is presented below, as determined by EXAFS, scanning electron microscopy with elemental dispersive x-ray analysis (SEM-EDX), and powder x-ray diffraction (pXRD).

The EXAFS spectra of the solids in all systems after 72 hours of oxidation are compared to spectra from U^{VI} -oxyhydroxide and U^{VI} -phosphate standards (Fig. 3). The EXAFS spectrum of UO_2 oxidized for 72 hours is the same as that of the U^{VI} oxyhydroxide precipitated from a U^{VI} solution under the solution conditions of our study. Scanning electron microscopy (Fig. 4A) indicates a morphology similar to sodium uranate type U^{VI} -oxyhydroxides, which have been observed to form round or hexagonal plates and rosettes (Buck et al., 2004; Díaz Arocas and Grambow, 1998). Less well-crystallized or agglomerated nanoparticulate material is also evident in the SEM image, which may be unoxidized UO_2 (~9% of the initial uraninite is still detected by linear combination fits of the EXAFS spectrum after 72 hours of oxidation). Results from pXRD of the solids (Fig. 5) indicate that the UO_2 has been oxidized primarily to Na-compreignacite ($Na_2(UO_2)_6O_4(OH)_6 \cdot 7H_2O$) (Gorman-Lewis et al., 2008). The XRD result is at odds with the measured U concentrations in our study, with the dissolved U concentration lower than the solubility of Na-compreignacite. However, we note that the presence of small amounts of UO_{2+x} (as suggested by the EXAFS and SEM data) may provide a sink for U^{VI} through sorption (Wang et al., 2015), lowering its concentration below the solubility of Na-compreignacite.

The EXAFS spectrum (Fig. 3) of the product resulting from 72 hours of U^{IV} -phosphate oxidation is similar to autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$). The same EXAFS spectrum is observed for the solid precipitated from aqueous U^{VI} through the addition of Ca and PO_4 (400 μM each) under the solution conditions of our study (i.e., U^{VI} concentration, buffer, electrolyte, and pH). SEM indicates the formation of a well-defined mineral after oxidation (Fig. 4C), with a morphology consistent with that of autunite (tabular, rectangular appearance) (Anthony et al., 2003). Analysis with SEM-EDX confirms that the solid product contains U and P (Fig. 6), as well as a small amount of Ca (inset, Fig. 6). Sodium is also likely present but is not detected in the SEM-EDX spectra because low-energy x-ray photons are absorbed by the Be window of the detector ($Na K_{\alpha} = 1,040$ eV). Results from pXRD of the U^{VI} phase formed (Fig. 5) indicate that the (002) peak of the diffraction pattern is closest to that of meta-natroautunite ($Na_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$). The slight shift of the (002) peak towards the smaller angle/greater d-spacing of

Ca-autunite indicates that the interlayer of the U^{VI} -product may contain some calcium, in agreement with the SEM-EDS spectrum and with the solution phase measurements. The pXRD and SEM results are also consistent with geochemical speciation calculations that suggest that Na-(meta)autunite is the predicted solubility-limiting phase in our systems (Fig. 2B).

3.2. Effect of calcium, sodium, and phosphate on U^{IV} -oxidation

Phosphate is present in many natural systems and can affect U speciation in several ways. A number of studies indicate that U^{IV} produced in U^{VI} reduction experiments often binds to inorganic phosphate present in the medium or to phosphoryl groups associated with biomass (Alessi et al., 2014b; Bargar et al., 2013; Bernier-Latmani et al., 2010; Boyanov et al., 2011; Fletcher et al., 2010; Sharp et al., 2011; Vecchia et al., 2010). Phosphate also plays a role in remediation strategies relying on the precipitation of U^{VI} -phosphate minerals or as U^{VI} adsorbed/incorporated into Ca-phosphate minerals such as apatite (Arey et al., 1999; Beazley et al., 2007; Fuller et al., 2002; Murakami et al., 2005; Singh et al., 2010). Although sparingly soluble, U^{VI} in phosphate minerals is not inert and can be reduced by metal-reducing bacteria to produce U^{IV} -phosphate minerals (Rui et al., 2013). U-phosphate interactions can also be important in field-scale remediation approaches, as phosphate was a non-negligible component of the emulsified vegetable oils mixture used in a recent bioremediation study (approx. 0.05 wt % $(NH_4)_3PO_4$, equivalent to ~ 0.7 mM PO_4^{3-} at injection) and could also be a component of the emulsifiers used in such mixtures through hydrolysis of phospholipids such as lecithin (Borden and Lee, 2008; Watson et al., 2013). Therefore, the unknown effect of phosphate on U^{IV} oxidation needs to be assessed in consideration of the potential for remobilization of reduced uranium. Here we have investigated the impact of varying phosphate and calcium concentrations on the oxidation of UO_2 or U^{IV} -phosphate. We hypothesized that uranium oxidation would be slowed by the presence of phosphate and calcium, primary through formation of passivating U^{VI} -phosphate surface layers. As above, we carried out experiments in oxalic 5 mM MOPS buffer and 15 mM $NaClO_4$ background electrolyte, adjusted to a pH value of 7.0.

3.2.1. *Effect of Ca and P on the rate of oxidation.*

We compared the oxidation of UO_2 in phosphate-free buffer to the oxidation of UO_2 in the presence of $400\ \mu\text{M}\ \text{Ca}^{2+}$ and PO_4^{3-} . The raw XANES spectra are shown in Fig. EA2. The proportions of U^{IV} over a 72 hour period were obtained from LC fits of the data and are plotted in Fig. 1. It is clear from Fig. 1 that the apparent rate and extent of UO_2 oxidation is decreased in the presence of added calcium and phosphate. The rate constants (k_{obs}) differ by an order of magnitude (Table 1) ($k_{\text{obs}} = 0.23\ \text{h}^{-1}$ vs $0.022\ \text{h}^{-1}$ with Ca and PO_4).

We also compared the rates of U^{IV} -phosphate oxidation in the presence and absence of additional 100 or $400\ \mu\text{M}\ \text{Ca}$ and PO_4 (Fig. 1). The raw XANES spectra are shown in Figs EA4 and EA5 in the Electronic Annex (EA). Addition of $100\ \mu\text{M}\ \text{Ca/PO}_4$ results in a rate constant decrease by a factor of 1.8 ($k_{\text{obs}} = 0.077\ \text{h}^{-1}$) relative to the U^{IV} -phosphate system without amendments, whereas addition of $400\ \mu\text{M}\ \text{Ca/PO}_4$ results in a rate constant decrease by a factor of 2.7 ($k_{\text{obs}} = 0.044\ \text{h}^{-1}$). Therefore, the relative decrease in the observed oxidation rate constant upon addition of Ca and PO_4 is greater for UO_2 than for U^{IV} -phosphate, with the oxidation rate constants differing by a factor of 1 to 2 between the UO_2 and U^{IV} -phosphate systems with added $400\ \mu\text{M}\ \text{Ca}$ and PO_4 .

To narrow down whether the decrease in oxidation rates was caused by Ca or PO_4 , or by their combined presence, we measured the rate of UO_2 oxidation only in the presence of $400\ \mu\text{M}\ \text{Ca}$, without phosphate addition. A new batch of UO_2 starting material was used for these experiments, which showed similar oxidation kinetics as the original batch of UO_2 in the absence of additions (Fig. 7). The determined oxidation rate constant for the new UO_2 batch is slightly lower ($k_{\text{obs}} = 0.087\ \text{h}^{-1}$, Table 1), possibly due to the coarser sampling of the initial kinetics. Addition of $400\ \mu\text{M}\ \text{Ca}$ to the UO_2 suspension had no effect on the rate or extent of oxidation over the course of the experiment (Fig. 7). Our observation that Ca has little impact on U^{IV} oxidation is in contrast with previous reports that Ca-containing U^{VI} minerals, including Ca- U^{VI} carbonates and silicates, form on the surface of UO_2 and inhibit its oxidative

dissolution (Cerrato et al., 2012; Giammar et al., 2012; Santos et al., 2006a). It is therefore likely that Ca affects U^{IV} oxidation only when present together with carbonate and/or silicate and that the lack of large quantities of carbonate (dissolved $HCO_3^- \sim 100 \mu M$) or silicate in our system precluded the formation of surface precipitates.

We also tested the impact of PO_4 addition on UO_2 oxidation in the absence of Ca. Addition of 400 μM PO_4 to the UO_2 suspension slowed the initial rate of oxidation ($k_{obs} = 0.068 h^{-1}$), but increased the extent of oxidation after 38 hours over that of the UO_2 alone and $UO_2 + Ca$ reactors. The slight inhibition of the oxidation rate initially may be due to precipitation of U^{VI} -phosphate surface layers (Shoesmith et al., 1988), which have been observed to partially passivate the UO_2 surface toward oxidation (Shoesmith et al., 1988). However, under conditions similar to our experiment (neutral pH and 10 mM $NaClO_4$ electrolyte), phosphate increased the rate of UO_2 dissolution above that observed for similar concentrations of carbonate by 1.5 orders of magnitude (Rey et al., 2008). It is possible that in our study passivation is balanced by PO_4 -promoted dissolution and subsequent re-precipitation as U^{VI} -phosphate. Overall, the data suggest that addition of Ca and PO_4 together is more effective in decreasing the rate of U^{IV} oxidation in suspensions of UO_2 than addition of either Ca or PO_4 alone.

3.2.2. Effect of Ca and P on solution dynamics

Measurable concentrations of dissolved U were present in systems without added Ca and PO_4 (Table 2). Addition of Ca and PO_4 to suspensions of UO_2 or U^{IV} -phosphate results in lower dissolved uranium concentrations down to the detection limit of ~ 17 nM U. The decrease in U solubility is consistent with thermodynamic calculations, which show 2–3 orders of magnitude decrease in solubility of Ca-autunite and Na-autunite when excess Ca or Na and PO_4 are present (Fig. 2B). Furthermore, solution measurements indicate that some of the added Ca and PO_4 is removed from solution during the oxidation process (Table 2). As discussed further below, the uptake of these species is consistent with the solid products formed.

3.2.3. Effect of Ca and P on the products of U^{IV} oxidation

Addition of calcium and phosphate to reactors with UO₂ as the starting U^{IV} phase results in a significant change in the oxidized U^{VI} product relative to UO₂ alone. In the absence of Ca and PO₄ the EXAFS spectra of the solids after 72 hours of oxidation closely match the spectra of U^{VI}-oxyhydroxides (Fig. 3). The product of UO₂ oxidation in the presence of 400 μ M Ca is the same as that without added Ca, and is consistent with the observed similarity in oxidation kinetics. In the presence of 400 μ M Ca and PO₄ during UO₂ oxidation, the resulting spectra match those of precipitated U^{VI}-phosphate and autunite.

The EXAFS results are corroborated by SEM images of the oxidized UO₂ products, where a significantly different morphology is seen in the absence (Fig. 4A) and presence of Ca and PO₄ (Fig. 4B). The U^{VI} product obtained in the absence of Ca/PO₄ has morphology similar to that of schoepite and other uranyl oxy-hydroxides, whereas a rectangular platy morphology typical of autunite-group minerals is observed in reactors with added Ca and PO₄ (Wellman et al., 2006). The pXRD results (Fig. 5) suggest that a mixture of two phases exists in the system with Ca/PO₄, as judged by the split (002) peak near 10°2 θ that is consistent with both meta-natroautunite or chernikovite and a phase similar to Ca-autunite. We suspect the monovalent autunite in our study is (meta-)natroautunite, rather than chernikovite, given that the concentration of Na⁺ is five orders of magnitude greater than that of H₃O⁺. Incorporation of Ca into the final products is corroborated by the SEM-EDS spectrum, where the Ca K α fluorescence line is observed (Fig. 6, inset). Overall, the EXAFS, pXRD, and SEM-EDS data suggest that the U^{VI} product from UO₂ oxidation in the presence of Ca and PO₄ is a mixture of Na- and Ca-autunites.

The products of U^{IV}-phosphate oxidation after 72 hours, both in systems with and without addition of 100 or 400 μ M Ca and PO₄, have the same EXAFS spectrum that corresponds to a U^{VI}-phosphate material (Fig. 3). The latter indicates that the U^{VI}-phosphate coordination in the autunite layer is the same regardless of the presence or absence of excess Ca/PO₄. There are minor differences in the SEM images of the U^{IV}-phosphate oxidation products produced in the absence and presence of added Ca

and PO_4 (Fig.s 4C, 4D, and 4E); however, overall the particles have a morphology consistent with sheets and plates of autunite minerals. In the absence of added Ca/PO_4 , the particles appear slightly larger and less aggregated. Diffraction lines for the U^{VI} -phosphate product in the reactors without addition of Ca and PO_4 are narrower than lines for the products formed with 100 or 400 μM Ca and PO_4 , also suggesting larger particle size in the absence of Ca and PO_4 . Elemental analysis using SEM-EDX (Fig. 6) shows that the oxidation products obtained in the presence of increasing aqueous Ca and PO_4 concentrations contain the same amount of U and PO_4 , but increasing amounts of incorporated or adsorbed Ca . The increase in Ca content in the oxidation products is corroborated by the pXRD data (Fig. 5), which show a progressive shift in the position of the (002) peak ($\sim 10^\circ$ 2θ) from that of metanatroautunite or chernikovite to that of Ca -autunite. In combination, the SEM-EDX and pXRD data suggest a progressive incorporation of Ca into the autunite interlayer during U^{IV} -phosphate oxidation at elevated Ca concentrations.

3.3. Mechanism of U^{IV} oxidation in the presence of Ca , PO_4 , and Na

The data presented to this point indicate that the oxidation rates of UO_2 and of U^{IV} -phosphate are slowed most significantly by the combined addition of Ca and PO_4 . Potential explanations for the effect of Ca and PO_4 include (i) influence on the solubility of the starting U^{IV} phases, (ii) influence on the thermodynamic driving force for oxidation to the end products, (iii) changes in aggregate status leading to reduced reactive surface area or O_2 diffusion into flocs, or (iv) passivation/encapsulation of the U^{IV} -surface by Ca-PO_4 or $\text{Ca/U}^{\text{VI}}\text{-PO}_4$ products formed during oxidation. Below we discuss each of these mechanisms in the context of the current results and the data available in the literature.

3.3.1. U^{IV} solubility and thermodynamic driving force

We can discount a role for differences in solubility driving the observed differences in oxidation rates of the U^{IV} phases in buffer alone versus Ca and PO_4 containing solution (Table 1). A dependence of oxidation rate on solubility would imply a mechanism whereby the dissolved U^{IV} species are oxidized to

U^{VI} . However, our U concentration measurements in the anoxic controls (samples at time 0 hours, Table 2) indicate dissolved U is at or near the detection limit of ~17 nM of the KPA method we used, and accounts for <0.02% of the total uranium in the system. This suggests that oxidation of U^{IV} is likely dominated by surface-mediated processes. Support for surface-controlled U^{IV} oxidation also comes from studies showing that oxidized U products (U^V and U^{VI}) accumulate on the UO_2 surface, as well as from studies that have demonstrated higher oxidant reduction rates with increasing U^{IV} solid surface area (Ekeröth and Jonsson, 2003; Hossain et al., 2006; Shoesmith et al., 1989; Sunder et al., 1991; Ulrich et al., 2009).

Another potential factor influencing oxidation rate is the thermodynamic driving force for oxidation to different U^{VI} products, which may be the reason for the observed slower rate of UO_2 oxidation in our systems with added Ca/PO_4 (end product autunite) relative to the systems without Ca/PO_4 (end product schoepite or Na-compreignacite). Thermodynamic calculations (details in EA) suggest that under the conditions of this study UO_2 oxidation to autunite is less favorable (-379 kJ/mol) than oxidation to Na-compreignacite (-1,009 kJ/mol). However, the calculation does not take into account any activation energy barriers that could limit the rate of reaction. Although the difference in energy suggests a larger driving force for oxidation to Na-compreignacite, the inability to account for the activation barrier precludes a conclusion on the cause for the larger oxidation rate constant without Ca and PO_4 . Therefore, the magnitude of the energy difference between the two reactions cannot be inferred to be the cause of the differences in oxidation rate with and without the presence of Ca and PO_4 .

3.3.2. Aggregation of UO_2 and U^{IV} -phosphate

Because the thermodynamic driving force or solubility considerations above were inconclusive, we tested the hypothesis that Ca and PO_4 cause different aggregation in the UO_2 and U^{IV} -phosphate suspensions. Aggregation is known to affect the reactivity of nanoparticulate oxides (Cwiertny et al., 2008; Lanzl et al., 2012; Stemig et al., 2014). In our system, aggregation could have limited the diffusion

of oxygen between the particles or could have occluded some of the surface sites. To test for aggregation, we compared the sedimentation rates of UO_2 and U^{IV} -phosphate suspensions in the absence and presence of 400 μM Ca and PO_4 . A decrease in absorbance was interpreted as a combined measure of aggregation and sedimentation, assuming that absorbance was due predominantly to scatter (Cwierny et al., 2008; Lanzl et al., 2012). The results from this experiment (Fig. 8) suggest that addition of Ca and PO_4 has an impact on aggregation in suspensions of UO_2 , but does not alter the sedimentation rates of the U^{IV} -phosphate particles used in the study. We obtained the same absorbance profiles for repeat settling after resuspension of both the UO_2 and U^{IV} - PO_4 suspensions, indicating that the particle size distributions are stable and that any flocculation is reversible.

While the initial settling rates for UO_2 are similar with and without amendments, over time the suspension with added Ca and PO_4 settles faster. Homogeneous precipitation of Ca- PO_4 particles can be excluded as the reason for increased sedimentation because there was no increase in light absorbance in 400 μM Ca and PO_4 containing solutions relative to a buffer-only control. It is possible that Ca and/or PO_4 caused compensation of surface charge or surface-catalyzed formation of Ca- PO_4 , leading to particle aggregation. The resulting decrease in exposed surface area may be one reason for the decreased oxidation rate in the presence of Ca and PO_4 relative to the system without amendments.

3.3.3. Surface passivation of UO_2 and U^{IV} -phosphate by Ca and PO_4

Based on several studies suggesting that passivation layers influence the oxidation of U^{IV} in UO_2 (Roth and Jonsson, 2008; Santos et al., 2006b; Shoesmith et al., 1988, 1989) and the subsequent release of U^{VI} (Cerrato et al., 2012; Giammar et al., 2012), we hypothesized that Ca and PO_4 promoted the formation of a surface layer during UO_2 oxidation and resulted in the observed slower U^{IV} oxidation rates. In an attempt to dissolve U^{VI} from the surface layer, we oxidized UO_2 in the presence of 400 μM Ca and PO_4 for 10 hours, followed by extraction of the solids in anoxic 100 mM NaHCO_3 (pH 8.2). The extracted solids were used as starting material in a new oxidation experiment without added Ca or PO_4 (i.e.,

resuspended to the same U concentrations but in a Ca- and PO₄-free buffer solution saturated with O₂ from air). The valence state of U over time from pre- and post-extraction solids are compared in Fig. 9 to a Ca- and PO₄-free UO₂ oxidation experiment for this new batch of UO₂.

The data in Fig. 9 show the same trend as the data in Fig. 1, namely that UO₂ with 400 μM Ca and PO₄ (red circles) oxidizes more slowly and less extensively than UO₂ alone (blue squares). We also find that bicarbonate extraction of the UO₂ solids that were oxidized for 10 hours in the presence of Ca and PO₄ did not remove all of the oxidized uranium, as the fit of the XANES data from the pre-extraction and post-extraction solids indicate similar U^{IV} content (67% vs. 72% U^{IV}/U_{total}, respectively). Solution measurements corroborate the XANES data (Table 3), with extraction of the UO₂ + Ca and PO₄ solids removing only 12% (12 μM U_{total}) of the U_{total} from the suspension, as well as 6.9 μM Ca and 20 μM PO₄. Control experiments indicate that autunite is more soluble in 100 mM bicarbonate than hydroxyapatite (91% vs. 28% extraction of PO₄), suggesting that bicarbonate dissolves more autunite than calcium phosphate phases, which together with the observed ratios of U, Ca, and PO₄ in the extract, suggest dissolution of an autunite layer on the UO₂ solids. Digestion of the post-extraction solids in oxic HNO₃ showed no detectable calcium or phosphate, suggesting that Ca and PO₄ were largely removed and due to dilution were below the detection limit of ICP-OES (but not x-ray fluorescence as seen in Fig. 10) in the extracted layer. Subsequent oxidation of the UO₂ solids after extraction follows a trend that is similar to the oxidation of the original UO₂ solids in systems without added Ca and PO₄ (Fig. 9, green circles). These data indicate that bicarbonate extraction removed a Ca, U^{IV}, and PO₄-containing passivation layer and that the lack of Ca and PO₄ in the post-extraction solution prevented a new layer from forming.

Our observation that 100 mM bicarbonate extraction does not remove all of the oxidized U present in the UO₂ nanoparticle is notable. Previous research indicates that 100 mM HCO₃⁻ solutions typically remove UO_{2.33} surface layers on bulk UO₂ minerals through UO₂²⁺ complexation (Shoesmith, 2000), resulting in stoichiometric UO₂ in the 5–10 nm surface layer as determined by x-ray photoelectron

spectroscopy. In contrast, the XANES results here are consistent with the oxidation of UO_2 nanoparticles resulting in conversion of the whole 3.5 nm particle to UO_{2+x} , in which the oxidized $\text{U}^{\text{V}}/\text{U}^{\text{VI}}$ species are relatively stable to bicarbonate extraction.

We also sought spectroscopic identification of the passivation layer using Ca K-edge XAS. The XANES spectra from the $\text{UO}_2 + 400 \mu\text{M Ca}$ and PO_4 system after 10 hours of oxidation are shown at the top of Fig. 10. The XANES spectra of the oxidized pre-extraction solids, the oxidized extracted solids, and the $\text{UO}_2 + \text{Ca}$ and PO_4 anoxic control are nearly identical and indicate the same Ca speciation in all three systems. When compared to those of hydroxyapatite, calcite (CaCO_3), synthetic Ca-autunite, and a 1 M solution of CaCl_2 , the spectra are most similar to those from the aqueous Ca^{2+} and the autunite standards. The EXAFS data of the UO_2 samples are also similar to those of the aqueous Ca^{2+} and autunite standards, but differ from the spectra of hydroxyapatite and calcite (Fig. 11). These results confirm the lack of significant hydroxyapatite or calcite precipitation in the system. The Fourier transforms of the data (Fig. 11B) lack features from outer coordination shells, similar to the Ca-autunite and the aqueous CaCl_2 solution standards. The lack of outer-shell peaks in these standards is due to the single-shell coordination of Ca in the inter-layer space of autunite and the disordered outer-hydration shell in dissolved Ca. The lack of second-shell coordination features in the oxidized UO_2 samples suggests that Ca is associated with the solids via outer-sphere complexation or by incorporation in the inter-layer space of a mineral (as in autunite). Taken together with the bicarbonate extraction results (showing the presence of U, Ca, and PO_4 in the dissolved layer), the Ca-edge spectroscopy results indicate the formation of a passivation layer with a structure similar to that of autunite.

In summary, our results indicate that the presence of calcium and phosphate in UO_2 suspensions induces a small change in particle aggregation and causes the formation of an autunite surface layer during oxidation. The extraction data and Ca XAS spectra suggest that a $\text{Ca-U}^{\text{VI}}\text{-PO}_4$ surface layer is formed. Removal of the $\text{U}^{\text{VI}}\text{-PO}_4$ layer returns the reactivity of UO_2 to that of UO_2 suspensions without added Ca and PO_4 . The results suggest that $\text{U}^{\text{VI}}\text{-PO}_4$ surface layers passivate nanoparticulate UO_2 and

slow the rate of U^{IV} oxidation, consistent with previous observations of passivation of bulk UO_2 electrodes in PO_4 -containing solutions (Shoesmith et al., 1988). As with bulk UO_2 , our results indicate that U^{VI} - PO_4 layers are quite thin, comprising 5 to 12% of the total U present in the suspensions. However, such layers slow down the rate of UO_2 oxidation and decrease the solubility of U^{VI} through formation of U^{VI} - PO_4 minerals.

4. Implications for Uranium Dynamics and Transport Modelling

The results of this work suggest that two of the U^{IV} species expected to form under reducing conditions in uranium contaminated sediments—nanoparticulate UO_2 and (Ca-) U^{IV} -phosphate—are likely to be oxidized by dissolved oxygen (O_2) at rates that are within an order of magnitude of each other. The relative oxidation rates determined here in systems at neutral pH and low bicarbonate content are consistent with the relative rates of oxidation of these two materials observed in recent work (Cerrato et al., 2013); however, the surface-normalized rates determined here for nanoparticulate UO_2 are greater by approximately one to two orders of magnitude relative to those measured for bulk UO_2 (Roth and Jonsson, 2008). The difference in our study is likely due to accounting for oxidized U remaining inside the solid phase, the stability of which will depend on the solution conditions. The oxidation rate constants will be useful in building comprehensive geochemical models for U fate and transport in the subsurface (Li et al., 2009; Yabusaki et al., 2007b). To date, development of numerical groundwater models has progressed to the point of including the kinetics of U reductive immobilization (e.g., (Li et al., 2010; Li et al., 2009; Yabusaki et al., 2007a). Future model development will aim to predict U^{IV} oxidation and mobilization on a more holistic level, coupling it to biological processes such as endogenous decay of biomass, respiration scavenging of O_2 and production of CO_2 , and abiotic reactions such as FeS oxygen scavenging (Bi and Hayes, 2013; Bi et al., 2013). Knowledge of the oxidation rates of relevant U^{IV} species will be essential in estimating the importance of different O_2 -consuming reactions in realistic systems.

Furthermore, our study shows that at low concentrations of bicarbonate and sodium, the oxidation of UO_2 leads to the formation of low-solubility sodium uranate type minerals such as clarkeite or Na-compreignacite. This finding may have implications for U speciation at several uranium contaminated sites where sodium concentrations are similar to those in our study (Revil et al., 2013; Zachara et al., 2013). Knowledge of the oxidized phase identity under various conditions is important in estimating the mobility of U following reductive immobilization.

Our results also indicate that the presence of phosphate can mitigate the oxidative dissolution of U^{IV} . Phosphate is now established as playing a significant role in binding U^{IV} during U^{VI} reduction (Bargar et al., 2013; Bernier-Latmani et al., 2010; Boyanov et al., 2011; Rui et al., 2013; Sharp et al., 2011; Sivaswamy et al., 2011; Veeramani et al., 2011) and will likely be a non-negligible component of many bioremediation influents (e.g., the emulsified vegetable oils used in a recent field-scale bioremediation study contained 0.05 wt% $(\text{NH}_4)_3\text{PO}_4$ (Watson et al., 2013)). In our study, the combination of calcium and phosphate slowed down the rate of UO_2 and U^{IV} -phosphate oxidation by up to an order of magnitude. However, the oxidation rates of U^{IV} were still fast enough to account for complete oxidation of U^{IV} within days under fully oxygenated conditions. Under the conditions of our study, we observed the formation of Na-autunite rather than Ca-autunite phases after oxidation of UO_2 and Ca- U^{IV} -phosphate. The lower solubility of Na-autunite relative to Ca-autunite maintained lower concentrations of dissolved U^{VI} in our system. Our work here, along with another recent study (Mehta et al., 2014), highlights the overall importance of dissolved Na^+ in mitigating the solubility of U^{VI} in the presence or absence of phosphate and indicates that solution conditions (e.g. dissolved cations, phosphate, and carbonate) will have a significant impact on the U^{VI} products formed from U^{IV} oxidation. The combined effects of alkali metals (Na^+ , K^+) as well as carbonate on U^{VI} solubility should be included in future U^{VI} reactive transport models.

Finally, our study provides mechanistic insight on the U^{IV} oxidation process, which informs how to control U^{IV} oxidation and which phases to consider in modelling the fate and transport of U. The

observed formation of $\text{U}^{\text{IV}}\text{-Ca-PO}_4$ surface layers during oxidation of UO_2 appears to passivate the surface from further oxidation and suggests that long-term immobilization of subsurface U contamination might be best achieved through a defense-in-depth methodology that combines reductive immobilization with concomitant additions of phosphate and calcium.

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Figures and Tables

Fig. 1. Oxidation of UO₂ (squares) and U^{IV}-phosphate (circles) with (open markers) and without (closed markers) amendments of 100 and 400 μ M Ca²⁺ and phosphate in neutral (pH 7.0) 5 mM MOPS buffer and 15 mM NaClO₄ supporting electrolyte. U^{IV} percentages are determined from linear combination fitting of XANES spectra using the starting U^{IV} material and U^{VI} precipitated in the presence or absence of Ca²⁺ and phosphate. In the case of UO₂ alone, a U^{VI} precipitate without added Ca²⁺ or PO₄³⁻ was used as the endmember.

Fig. 2. Semi-log plot of uranium solubility in (A) Na containing solutions with schoepite and sodium-uranate endmembers. The Na-uranate endmember is calculated for solubility product of $K_{\text{sp}} = 10^{8.81}$ (Giammar and Hering, 2004). Na-compreignacite solubility is calculated using the solubility constant in Gorman-Lewis et al (2008). (B) Na-Ca- PO_4 solutions relevant to the oxidation of U^{IV} -phosphate species used in this study as well as UO_2 oxidation in solutions containing added Ca and phosphate. Sodium and calcium bearing autunite solubility is calculated for systems with and without atmospheric CO_2 , and with and without fixed aqueous phase Ca and PO_4 concentrations. The grey bar indicates the range of measured U concentrations in the U^{IV} -phosphate oxidation experiments, and the hatched bar represents an upper estimate of U solubility in the UO_2 oxidation experiment with added Ca and PO_4 .

Fig. 3. Uranium L_{III} extended x-ray absorption fine structure spectra and the Fourier transformed spectra of U^{IV} products reacted with O_2 in the absence and presence of 100 and 400 μM Ca and/or PO_4 for 72 hours (determined to be predominantly U^{VI}). The experimental spectra are compared to a U^{VI} -oxyhydroxide precipitated from the MOPS/ NaClO_4 buffer used in this study, autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$), and 100 μM U^{VI} precipitated from a solution of 400 μM Ca and PO_4 in 5 mM MOPS buffer with a pH of 7.0 and 15 mM NaClO_4 background electrolyte. The dashed lines are an aid to the eye.

Fig. 4. SEM images of the products formed after oxidation of U^{IV} solids for 72 hours. (A) oxidized UO_2 with no additions of Ca or PO_4 . (B) Oxidized UO_2 with 400 μM added Ca and PO_4 . (C) Oxidized $\text{U}^{\text{VI}}\text{-PO}_4$ with no additions. (D) Oxidized $\text{U}^{\text{IV}}\text{-PO}_4$ with 100 μM added Ca and PO_4 . (E) $\text{U}^{\text{IV}}\text{-PO}_4$ with 400 μM added Ca and PO_4 . Scale bars are 5 μm .

Fig. 5. X-ray diffraction (Cu K-alpha radiation) showing the effect of solution composition and U^{IV} starting material on U oxidation products formed after 72 hours in 5 mM MOPS and 15 mM NaClO_4 buffer solution with a pH of 7.0. The bars at the bottom of the plot show reference powder patterns for Na-compreignacite ($\text{Na}_2(\text{UO}_2)_6\text{O}_4(\text{OH})_6 \cdot 8\text{H}_2\text{O}$), metanatroautunite ($\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$), and chernikovite ($(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$). The dashed line is a guide for the eye, showing the shift in the patterns of solids with and without added Ca.

Fig. 6. Energy dispersive x-ray (EDX) spectra of U^{IV} products oxidized for 72 hours in 5 mM MOPS/15 mM $NaClO_4$ solution buffered at pH 7.0. Spectra are normalized to the $U M_\alpha$ line. The top and bottom spectra are 100 μM U^{VI} precipitated from 400 μM Ca and PO_4 solution and 100 μM U^{VI} precipitated in the absence of Ca and PO_4 both in 5 mM MOPS/15 mM $NaClO_4$ solution buffered to pH 7.0, respectively. Inset: expanded view of U M and Ca K_α x-ray fluorescence lines.

Fig. 7. Oxidation of UO_2 alone (Batch 2: blue squares) and with addition of 400 μM calcium (green triangles) or phosphate addition (red circles) in neutral (pH 7.0) 5 mM MOPS buffer and 15 mM NaClO_4 supporting electrolyte. Data from this experiment with the Batch 2 UO_2 solids show excellent agreement with those from Fig. 1 for the Batch 1 UO_2 solids (grey circles). U^{IV} percentages are determined from linear combination fitting of XANES spectra using the starting UO_2 material and U^{VI} precipitated in the presence or absence of Ca^{2+} and phosphate. In the case of UO_2 alone, a U^{VI} precipitate without added Ca^{2+} or PO_4^{3-} was used as the endmember. $\text{U}^{\text{IV}}/\text{U}_{\text{total}}$ was determined using XANES LC fitting.

Fig. 8. Sedimentation of U^{IV}-phosphate and UO₂ suspensions at pH 7.0. Particles were suspended in 5 mM MOPS/15 mM NaClO₄ solution with and without 400 μM added Ca and PO₄. Normalized absorbance values (A/A_0) correspond to the amount of light ($\lambda = 500$ nm) absorbed by a 100 μM U_{solid} suspensions in 1-cm path-length cells.

Fig. 9. Comparison of UO₂ oxidation in the presence (red) and absence (blue) of 400 μ M added Ca/PO₄ to that of solids oxidized in the presence of 400 μ M Ca and PO₄ then extracted with 100 mM NaHCO₃ (pH 8.2) (green). Extracted solids were subsequently re-added to oxygen containing buffer not containing Ca and PO₄.

Fig. 10. Calcium K-edge XANES of UO_2 samples exposed to calcium and phosphate under anoxic conditions, after 10 hours of oxidation, and after extraction of the oxidized material with 100 mM bicarbonate. Samples are compared to standards of: calcium carbonate (calcite), calcium phosphate (hydroxyapatite), calcium autunite, and calcium chloride (1 M solution).

Fig. 11. Calcium K-edge EXAFS of UO_2 samples exposed to calcium and phosphate under anoxic conditions, after 10 hours of oxidation, and after extraction of the oxidized material with 100 mM bicarbonate. Samples are compared to standards of calcium carbonate (calcite), calcium phosphate (hydroxyapatite), calcium autunite, and calcium chloride (1 M solution).

Table 1 Rate constants for U^{IV} solids oxidation under various solution conditions.

Solid	Solution Conditions	Observed Oxidation Rate Constant, k_{obs}	Average Surface Area Normalized Rate Constant, k_{SA}
Nano-uraninite (batch 1)	Buffer ^a	$0.23 \pm 0.084 \text{ h}^{-1 \text{ b}}$	$1.4 \times 10^{-8} \text{ m/s}^{\text{c}}$
Nano-uraninite (batch 2)	Buffer ^a	$0.087 \pm 0.065 \text{ h}^{-1 \text{ b}}$	SA not determined
Nano-uraninite (batch 3)	Buffer ^a	$0.20 \pm 0.11 \text{ h}^{-1 \text{ b}}$	SA not determined
Average nano-uraninite	Buffer ^a	$0.17 \pm 0.075 \text{ h}^{-1 \text{ c}}$	
Nano-uraninite (batch 1)	400 μM Ca and PO_4^{a}	$0.022 \pm 0.0036 \text{ h}^{-1 \text{ b}}$	$0.14 \times 10^{-8} \text{ m/s}$
Nano-uraninite (batch 3)	400 μM Ca and PO_4^{a}	$0.074 \pm 0.043 \text{ h}^{-1 \text{ b}}$	SA not determined
Nano-uraninite (batch 2)	400 μM Ca ^a	$0.084 \pm 0.066 \text{ h}^{-1 \text{ b}}$	SA not determined
Nano-uraninite (batch 2)	400 μM PO_4^{a}	$0.068 \pm 0.0046 \text{ h}^{-1 \text{ b}}$	SA not determined
U ^{IV} -phosphate (batch 1)	Buffer ^a	$0.12 \pm 0.099 \text{ h}^{-1 \text{ b}}$	$0.9 \times 10^{-8} \text{ m/s}$
U ^{IV} -phosphate (batch 2)	Buffer ^a	$0.476 \text{ h}^{-1 \text{ d}}$	$2.7 \times 10^{-8} \text{ m/s}$
Average U ^{IV} -phosphate	Buffer ^a	0.30 h^{-1}	
U ^{IV} -phosphate (batch 1)	100 μM Ca and PO_4^{a}	$0.077 \pm 0.0098 \text{ h}^{-1 \text{ b}}$	$0.57 \times 10^{-8} \text{ m/s}$
U ^{IV} -phosphate (batch 1)	400 μM Ca and PO_4^{a}	$0.044 \pm 0.0056 \text{ h}^{-1 \text{ b}}$	$0.33 \times 10^{-8} \text{ m/s}$
U ^{IV} -phosphate (batch 2)	1 mM Ca and PO_4^{a}	$0.055 \pm 0.019 \text{ h}^{-1 \text{ b}}$	$0.32 \times 10^{-8} \text{ m/s}$
U ^{IV} -phosphate (batch 2)	1 mM Ca and $\text{PO}_4 + 10 \text{ mM NaHCO}_3$	$0.039 \pm 0.012 \text{ h}^{-1 \text{ b}}$	$0.22 \times 10^{-8} \text{ m/s}$

^a 5 mM MOPS buffer prepared with a pH of 7.0 and with 15 mM NaClO₄ background electrolyte.

^b Error term in fitting $\ln(\text{U}^{\text{IV}}/\text{U}_{\text{total}})$ vs. time (1 σ).

^c Error term, standard deviation of triplicate experiments.

^d Estimated from the slope at $t = 0$ and 2 hours.

^e $\text{m/s} = 1000 \text{ liters m}^{-2} \text{ s}^{-1}$.

Table 2. XANES and EXAFS fitting results and aqueous concentrations of U, Ca, and PO₄ for oxidation of UO₂ and U^{IV}-phosphate in 5 mM MOPS/15 mM NaClO₄ buffer with and without 400 μM added Ca and PO₄, as shown in Fig. 1.

Reaction Time (h)	Solids—XANES LC Fits			Solids—EXAFS LC Fits			Aqueous Phase		
	% U ^{IV}	% U ^{VI}	χ^2_v	% U ^{IV}	% U ^{VI}	χ^2_v	[U], μM	[Ca ²⁺], μM	[PO ₄ ³⁻], μM
UO ₂ with no added Ca ²⁺ or PO ₄ ³⁻									
0	100	0	-	100	0	-	b.d.l. ^a	b.d.l. ^c	n.m. ^d
0.2	76.3	23.7	4.00×10^{-4}	72	28	0.291	0.050 ^b	b.d.l.	n.m.
0.5	67.2	32.8	6.25×10^{-4}	73	27	0.301	b.d.l. ^a	b.d.l.	n.m.
1.0	75.1	24.9	3.66×10^{-4}	79	21	0.293	b.d.l. ^a	b.d.l.	n.m.
2.0	55.7	44.3	3.91×10^{-4}	66	34	0.324	0.25 ^b	b.d.l.	n.m.
5.2	52.4	47.6	3.95×10^{-4}	63	37	0.325	b.d.l. ^a	b.d.l.	n.m.
8.0	42.6	57.4	5.19×10^{-4}	56	44	0.414	0.19 ^b	b.d.l.	n.m.
23.6	40.8	59.2	4.71×10^{-4}	51	49	0.372	0.032 ^b	b.d.l.	n.m.
71.0	8.8	91.2	1.12×10^{-4}	12	88	0.148	0.003 ^b	b.d.l.	n.m.
UO ₂ + 400 μM Ca ²⁺ and PO ₄ ³⁻									
0	100	0	-	100	0	-	b.d.l. ^a	377	429
2.0	91.1	8.9	0.13×10^{-4}	91	9	0.138	b.d.l. ^a	349	340
4.5	88.3	11.7	0.19×10^{-4}	89	11	0.140	b.d.l. ^a	342	331
9.6	80	20	0.63×10^{-4}	85	15	0.216	b.d.l. ^a	349	356
24.2	73.8	26.2	1.71×10^{-4}	75	25	0.212	b.d.l. ^a	412	335
71.5	36.1	63.9	0.53×10^{-4}	33	67	0.095	b.d.l. ^a	327	301
U ^{IV} -phosphate with no added Ca ²⁺ or PO ₄ ³⁻									
0	100	0	-	100	0	-	0.005 ^b	16.1	10.5
1	75.2	24.8	0.13×10^{-4}	84	16	0.079	0.073 ^b	19.0	11.1
1.9	63.8	36.2	0.46×10^{-4}	74	26	0.102	0.012 ^b	18.6	14.5
4.3	58.6	41.4	0.21×10^{-4}	74	26	0.070	0.008 ^b	18.6	16.3
9.0	48.2	51.8	0.56×10^{-4}	64	36	0.113	0.050 ^b	17.4	17.7
16.8	34.1	65.9	0.69×10^{-4}	48	52	0.133	0.023 ^b	25.0	9.2
71.8	8	92	0.51×10^{-4}	14	86	0.043	0.009 ^b	23.0	2.1
U ^{IV} -phosphate + 100 μM Ca ²⁺ and PO ₄ ³⁻									
0	100	0	-	100	0	-	0.005 ^b	97.1	97.5
4.33	66.4	33.6	0.07×10^{-4}	67	33	0.020	0.005 ^b	95.6	91.5
8.8	50.8	49.2	0.04×10^{-4}	56	44	0.017	0.005 ^b	95.3	88.0
72.5	7	93	0.01×10^{-4}	10	90	0.038	b.d.l. ^a	92.1	80.8
U ^{IV} -phosphate + 400 μM Ca ²⁺ and PO ₄ ³⁻									
0	100	0	-	100	0	-	0.005 ^b	377	429
1.0	90.8	9.2	0.12	96	4	0.035	0.004 ^b	344	363
2.0	84	16	0.21×10^{-4}	86	14	0.028	0.003 ^b	352	349
4.0	79.6	20.4	0.02×10^{-4}	84	16	0.030	b.d.l. ^a	349	378
8.3	67.4	32.6	0.04×10^{-4}	75	25	0.042	b.d.l. ^a	344	356
72.2	9	91	0.11×10^{-4}	10	90	0.033	b.d.l. ^a	329	375

^a b.d.l. = below detection limit, equal to [U] in HNO₃ blank (0.017 μM U) used to prepare samples for KPA analysis.

^b [U] measured > detection limit of blank, the report concentration is the difference between the blank and the sample.

^c b.d.l. = below detection limit, <0.25 μM Ca²⁺.

^d n.m. = not measured.

Table 3 XANES and EXAFS fitting results and aqueous concentrations of U, Ca, and PO₄ for oxidation of UO₂ in 5 mM MOPS/15 mM NaClO₄ buffer with and without 400 μM added Ca and PO₄ and after 100 mM bicarbonate extraction as shown in Fig. 8.

Reaction Time (h)	Solids—XANES LC Fits			Aqueous Phase		
	% U ^{IV}	% U ^{VI}	χ_v^2	[U], μM	[Ca ²⁺], μM	[PO ₄ ³⁻], μM
UO ₂ without added Ca ²⁺ and PO ₄ ³⁻						
0	100	0	-	n.m. ^a	n.m. ^a	n.m. ^a
1.7	47	52.5	8.18×10^{-4}	1.15	b.d.l. ^b	b.d.l. ^b
4	43	53	8.51×10^{-4}	1.68	b.d.l. ^b	b.d.l. ^b
10.3	39	61	9.26×10^{-4}	4.66	b.d.l. ^b	b.d.l. ^b
75	26	74	6.31×10^{-4}	1.52	b.d.l. ^d	b.d.l. ^b
UO ₂ + 400 μM Ca ²⁺ and PO ₄ ³⁻ pre-extraction						
0	100	0	-	b.d.l. ^b	322	375
1.8	74	26	2.83×10^{-4}	b.d.l. ^b	322	381
4.3	72	28	2.83×10^{-4}	b.d.l. ^b	307	368
10	66	34	3.88×10^{-4}	b.d.l. ^b	317	371
73	43	57	4.15×10^{-4}			
100 mM anoxic bicarbonate extraction, pH 8.2						
14.5 ^c	-	-	-	12.2	6.9	20
UO ₂ + 400 μM Ca ²⁺ and PO ₄ ³⁻ post-extraction						
0 ^d	72	28	5.18×10^{-4}	n.m. ^a	n.m.	n.m.
2.1	51	49	9.22×10^{-4}	b.d.l. ^b	3.37	b.d.l. ^b
4.3	46	54	8.69×10^{-4}	0.78	1.97	b.d.l. ^b
10.1	44	56	8.20×10^{-4}	0.64	10.1	b.d.l. ^b
72	31	69	7.31×10^{-4}	3.37	2.20	b.d.l. ^b

^a n.m. = not measured.

^b b.d.l. = below detection limit, approximately <0.25 μM Ca²⁺, <0.4 μM U, <0.7 μM PO₄³⁻.

^c Solids were extracted for 14.5 hours.

^d t = 0 is defined here as the starting point of oxidation after anoxic bicarbonate extraction and washing.