

Formation of a U(VI)–Persulfide Complex during Environmentally Relevant Sulfidation of Iron (Oxyhydr)oxides

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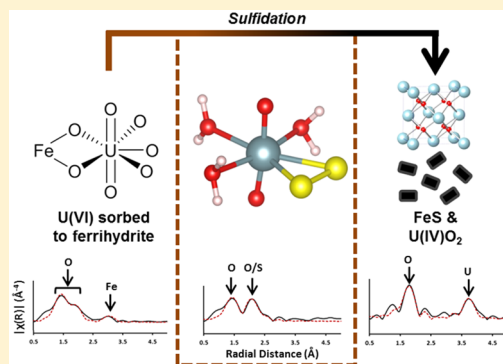
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Supporting Information

ABSTRACT: Uranium is a risk-driving radionuclide in both radioactive waste disposal and contaminated land scenarios. In these environments, a range of biogeochemical processes can occur, including sulfate reduction, which can induce sulfidation of iron (oxyhydr)oxide mineral phases. During sulfidation, labile U(VI) is known to reduce to relatively immobile U(IV); however, the detailed mechanisms of the changes in U speciation during these biogeochemical reactions are poorly constrained. Here, we performed highly controlled sulfidation experiments at pH 7 and pH 9.5 on U(VI) adsorbed to ferrihydrite and investigated the system using geochemical analyses, X-ray absorption spectroscopy (XAS), and computational modeling. Analysis of the XAS data indicated the formation of a novel, transient U(VI)–persulfide complex as an intermediate species during the sulfidation reaction, concomitant with the transient release of uranium to the solution. Extended X-ray absorption fine structure (EXAFS) modeling showed that a persulfide ligand was coordinated in the equatorial plane of the uranyl moiety, and formation of this species was supported by computational modeling. The final speciation of U was nanoparticulate U(IV) uraninite, and this phase was evident at 2 days at pH 7 and 1 year at pH 9.5. Our identification of a new, labile U(VI)–persulfide species under environmentally relevant conditions may have implications for U mobility in sulfidic environments pertinent to radioactive waste disposal and contaminated land scenarios.



INTRODUCTION

Globally, uranium (U) is of concern as a risk-driving radionuclide in geological disposal of radioactive wastes and clean-up of legacy nuclear sites and mines.^{1,2} The environmental behavior of U in the subsurface environment is dynamic, with changes in biogeochemical conditions leading to alterations in U speciation and mobility caused by complex interactions between dissolved species, mineral surfaces, and biological activity. Typically, the biogeochemical behavior of U is dominated by its oxidation state, with U(VI) existing as the relatively mobile uranyl (U(VI)O_2^{2+}) species and U(IV) as the largely immobile $\text{UO}_{2(s)}$ or noncrystalline U(IV) species.^{3–5} Additionally, in contaminated land and geodisposal systems, sorption to both iron (oxyhydr)oxides and sulfide minerals such as nanocrystalline ferrihydrite (FeOOH) and mackinawite (FeS) is a key factor controlling U mobility.^{6–10} Previous studies have clearly established that both abiotic and biotic sulfide sources can induce transformations of iron (oxyhydr)oxide minerals, resulting in significant impacts on environ-

mental U speciation and mobility.^{11–16} Furthermore, U-sulfide complexes have not been identified under environmentally relevant conditions, but if present, would provide a major new insight into our understanding of U biogeochemistry in the subsurface. To better predict the impact of iron (oxyhydr)oxide sulfidation on U environmental speciation and mobility relevant to radioactive waste disposal and contaminated land management, further information on the molecular-scale transformation pathways during sulfidation is required.

There has been significant research on U sorption to, and reaction with, iron (oxyhydr)oxides and sulfides as well as on the pathways of iron (oxyhydr)oxide sulfidation.^{17–25} The reaction of aqueous sulfide (HS^-) with the surfaces of iron (oxyhydr)oxides induces a transformation to iron sulfides such

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as nanocrystalline mackinawite (FeS).^{22,23,26} During sulfidation, sulfide reacts with the iron (oxyhydr)oxide to form FeS and elemental sulfur (S_8^0), via an intermediate sulfidized iron (oxyhydr)oxide surface.²³ In spite of the dominant speciation of aqueous sulfur under reducing conditions between pH 7 and 12 being reported as HS^- ,²⁷ recent work has shown that persulfide (S_2^{2-}) and polysulfide (S_n^{2-}) species form and accumulate at the iron (oxyhydr)oxide mineral surface during this intermediate stage of sulfidation.^{28–32} This has challenged past work, which assumed that polysulfides were only significant in the aqueous phase toward higher pH values (pH > 9).^{33–35}

The interactions of U(VI) with the surfaces of iron (oxyhydr)oxide and sulfide phases such as ferrihydrite and mackinawite have been extensively studied.^{17,19,36} Here, U(VI) has been shown to adsorb strongly to the surface of nanoparticulate ferrihydrite, forming a bidentate inner-sphere adsorption complex, with no change in the oxidation state.¹⁷ In contrast, sorption of U(VI) to an FeS surface or reaction with aqueous HS^- leads to reduction to U(IV) and results in the formation of nanocrystalline U(IV)O₂.^{20,25,37,38} During this process, the rate of reduction is strongly controlled by the pH with rapid reduction occurring at pH 7 and slower reduced reduction rates reported as pH increases.³⁷

Studies exploring sulfidation of iron (oxyhydr)oxides with sorbed U(VI) are sparse, although field studies have noted a enhanced U mobility under strongly reducing, sulfidic conditions which is counterintuitive.¹⁵ More recently, laboratory studies have explored the reaction of U(VI) adsorbed to iron (oxyhydr)oxide (lepidocrocite, hematite, and magnetite) surfaces with aqueous sulfide. Again, these studies have reported the transient release of U into the solution after sulfide addition despite the strongly reducing conditions.^{15,16,39} Overall, this work showed that the dominant product of sulfidation was U(IV)O₂, but no detailed mechanistic pathway explaining the transient U release during sulfidation was established.^{15,16}

Key to understanding the speciation and fate of U during sulfidation is determining the molecular-scale mechanisms of U release, sorption, reduction, and precipitation. Here, we have developed a methodology for controlled sulfidation of U(VI) adsorbed to ferrihydrite under environmentally relevant conditions (Supporting Information, Figures S1-1 and S1-2). In the chemostat experimental system, sulfide was added over several hours providing relevance to microbially induced sulfidation (where sulfide is produced in situ) and flow scenarios where sulfide may be supplied in groundwaters. We combined our controlled experiments with aqueous geochemical and spectroscopic analyses (X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS)) and with quantum chemical modeling to define the U reaction pathway in detail. Our findings provide a new mechanistic understanding showing strong evidence for U(VI)–persulfide species dominating during the earlier stages of sulfidation and where significant U release (up to 2.5% of total U) into the solution occurred. Our robust evidence for the presence of significant levels of transient U(VI)–persulfides in these aqueous systems provides important new insights into U biogeochemistry in engineered and natural environments.

■ EXPERIMENTAL METHODS

Ferrihydrite Preparation. Ferrihydrite (2-line) was synthesized following the method of Cornell and Schwert-

mann.⁴⁰ Briefly, iron (III) nitrate nonahydrate was dissolved in deionized water (DIW) before neutralizing to pH 7. The resulting red-brown precipitate was washed with deionized water five times. The product was then characterized using X-ray diffraction (XRD) and stored as a slurry in the refrigerator prior to use, typically within 1 week.

U(VI) Sorbed to Ferrihydrite Sulfidation. All experiments, sample collection, preparation, and manipulations for chemical and solid analysis were performed in an oxygen-free atmosphere using a nitrogen (95%) and hydrogen (5%) mix, either in a Coy Cabinet anaerobic chamber or in an airtight reaction vessel. All water and solutions used within the experiments were thoroughly degassed with N₂ gas prior to use under anaerobic conditions. The experiments were undertaken in an Applikon Bioreactor (chemostat) fitted with a bespoke polyether ether ketone (PEEK) head plate. The bioreactor controlled and monitored pH, Eh, temperature and reagent addition (see Figures S1-1 and S1-2). Degassed deionized water (400 mL) was added to the reaction vessel under nitrogen. Ferrihydrite slurry (1.25 mM Fe(III)) was then added to the reaction vessel and spiked with NaCl (10 mM) to control the ionic strength. Uranium was added as U(VI) from an acidified stock solution (pH 2 HCl) to a concentration of 12.6 μ M uranium. The ferrihydrite and uranium were left to equilibrate for 24 h under nitrogen. A stock solution of approximately 50 mM disodium sulfide was freshly prepared for each experiment by dissolving Na₂S·9H₂O in degassed deionized water. The stock solution concentration was standardized using the methylene blue assay prior to use.⁴¹ The sulfide solution (pH $\approx$ 10) was then added to the chemostat to a final concentration of 2.5 mM at a rate of approximately 0.055 mL/min over 6 h. Throughout the experiment, nitrogen was sparged into the reaction vessel and the pH was controlled using HCl (0.2 M) to pH 7 or 9.5.

Samples were taken periodically over 48 h under nitrogen, filtered to <0.22 μ m (polyethersulfone (PES) filter disks) in the pH 7 system and 3 kDa Nanosep centrifugation ultrafilters (PES) in the pH 9.5 experiment due to the presence of significant levels of colloidal FeS at pH 9.5. In both experiments, aqueous analyses were performed by inductively coupled plasma mass spectrometry (ICP-MS) for U and Fe and methylene blue assay for aqueous HS^- (using the calibration standard Radiello RAD171).⁴¹

Throughout the sulfidation reaction, solid samples (with an approximate U concentration of 3000 ppm) were collected at selected time points for analysis using filtration and/or centrifugation. Particle morphology was studied using transmission electron microscopy (TEM) (FEI Tecnai TF-30). For XAS, parallel samples were prepared at selected time points using filtration and the resultant solid was mounted and stored at -80 °C. Samples were then transported in a liquid nitrogen dry shipper to Diamond Light Source for analysis on either the I20-scanning or B18 beamlines. XAS spectra were obtained from the uranium L_{III} edge in the fluorescence mode at 80 K using 64-element (I20) and 36-element (B18) Ge detectors. Data reduction and fitting of the extended X-ray absorption fine structure (EXAFS) spectra were performed using Athena and Artemis with FEFF6.⁴²

Solid samples were prepared for XPS (X-ray photoelectron spectroscopy) by drop casting 0.1 mL of slurry onto silicon chips and thoroughly drying overnight under anaerobic conditions prior to analysis. Samples were then quickly transferred into the XPS loadlock. XPS spectra were recorded

with a SPECS NAP-XPS (operating under ultrahigh vacuum conditions) with a SPECS Focus 500 Monochromator and a SPECS Phoibos 150 NAP hemispherical analyzer. Samples were exposed to monochromatic Al $K\alpha$ X-rays. The detailed scans were collected at a pass energy of 30 eV. Spectra were analyzed using CASA XPS. Spectra were charge-referenced to the adventitious carbon peak at 284.8 eV. Analysis of the XPS spectra was performed quantitatively for iron oxide and iron sulfide species. Qualitative analysis of the U data, even at low (3000 ppm) concentrations, was also possible.

Computational Modeling. All calculations were performed using the Vienna Ab initio Simulation Package (VASP) version 5.4.4, a plane-wave density functional theory (DFT) code.^{43–46} DFT was used to help determine the nature of the ligands coordinated to U, particularly the U(VI)–persulfide species. Geometry optimization calculations were carried out on various candidate complexes, both surface bound and molecular, to produce models whose structure could then be compared with the scattering path distances and coordination numbers obtained from the EXAFS analysis. Further details on the DFT modeling are provided in the Supporting Information, Section S4.

RESULTS AND DISCUSSION

Uranium Mobility and Speciation during Sulfidation of Ferrihydrite. The controlled addition of sulfide to ferrihydrite with adsorbed U(VI) was studied at pH 7 (Figure 1) and 9.5 (Figures 2 and S1–5). Sulfide addition occurred over 6 h and by the end point of sulfide addition, the $\text{HS}^-/\text{Fe(III)}$ molar ratio was 2:1. Tracking the aqueous chemical data with time allowed three broad stages of reaction to be defined in both systems. Stage one was associated with a rapid reduction in Eh at the start of sulfide addition to the system. In stage two, there was a large increase in the aqueous HS^- concentration and a release of U (up to 2.5% of total U) to the solution. By the end of stage two, the XPS and TEM data confirmed that ferrihydrite had completely transformed to FeS. During stage three, after sulfide addition was complete ($\text{HS}^-/\text{Fe(III)}$; 2:1), both sulfide and uranium concentrations in the solution were low. We explored the transformation pathway of uranium in this complex dynamic environment by further characterizing these three stages of the reaction.

During stage one of the reaction for both pH 7 and 9.5 experiments, there was strong retention of U on the solid phase (Figures 1 and 2). At 1 h in the pH 7 system, the presence of U(VI) associated with the solid phases was confirmed by X-ray absorption near edge structure (XANES) and EXAFS analyses (Figure 3 and Supporting Information, Section S3). EXAFS analysis at 1 h showed that the U was present predominantly as a uranyl species adsorbed as an inner-sphere complex to the surface of ferrihydrite, consistent with the past work.¹⁷ Additionally, TEM imaging of the 1 h pH 7 sample showed ferrihydrite to dominate (Figure S1–3). Here, the 1 h time point confirms low levels of sulfidation as expected in conditions where only small amounts of sulfide have been added (Figures 1 and 2).

During stage two of the reaction at pH 7 (between 2 and 6 h), there was a notable release of U into the solution from 2 h (0.10 μM , 0.8% total U). A similar release occurred at 2 h in the pH 9.5 experiment, with less U released to the solution (0.03 μM , 0.2% total) compared to the pH 7 experiment. As time progressed, in both experiments, the U concentration in the solution peaked at 4 and 6 h with the release of 2.5 and

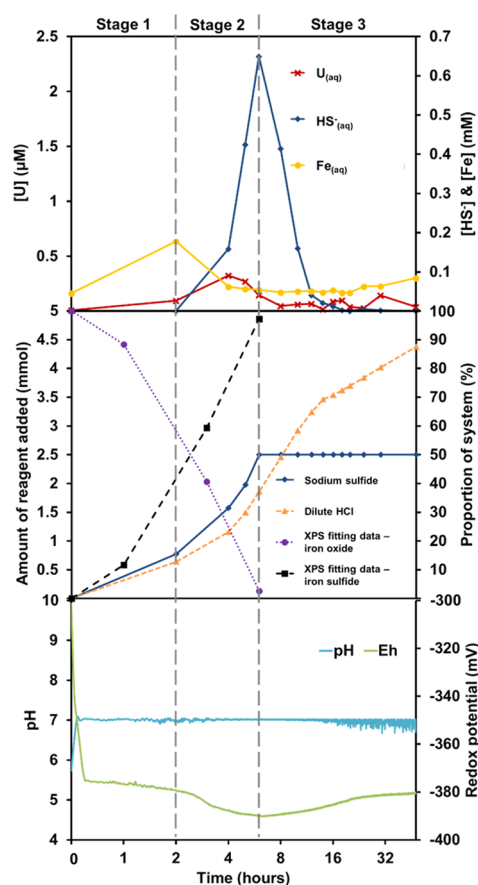


Figure 1. Chemical data for sulfidation of ferrihydrite with sorbed U(VI) at pH 7. The x-axis for time is shown as $\log_2$ after 0 h. The top panel shows the concentration of total aqueous uranium, iron, and sulfide. The middle panel shows the quantity, in moles, of sulfide and acid added and the proportion of different iron mineral phases produced from fitting of XPS data (Supporting Information, Section S2). The bottom panel shows the pH and Eh values.

1.8% of the total U for pH 7 and pH 9.5 systems, respectively (Figures 1, 2, and S1–5). This small but significant U release occurred despite the strongly reducing conditions and the presence of excess aqueous sulfide, which would be expected to reduce U(VI) to insoluble U(IV) O_2 (Figure 1).³⁸ A possible explanation for such a release may be due to the differing PHPZC of the ferrihydrite and FeS to U(VI). Alternatively, this may suggest that the U was chemically complexed in a form, which partially prevented its sorption, reduction, or precipitation.^{37,38} The release of U during the generation of sulfidic conditions is consistent with both field and laboratory observations,^{13,15,16,39} suggesting that our experimental methodology provides insight into these past observations. Additionally, TEM analysis of the particles in both systems shows a clear change in morphology from ferrihydrite to the sheet-like morphology of mackinawite over time (Figures S1–3 and S1–4). In the pH 7 system, this transformation was quantified further by the quantitative fitting of the XPS data (Figures 1 and S2–1). This showed that the proportion of iron (oxyhydr)oxide and iron sulfide present at 3 h was approximately 50:50% (Figure 1).

During this second stage, uranium XANES data collected on the solids at pH 7 (3 h) and pH 9.5 (6 h) were significantly different to the spectra from the end members of the experiments, U(VI) sorbed to ferrihydrite (stage one) or

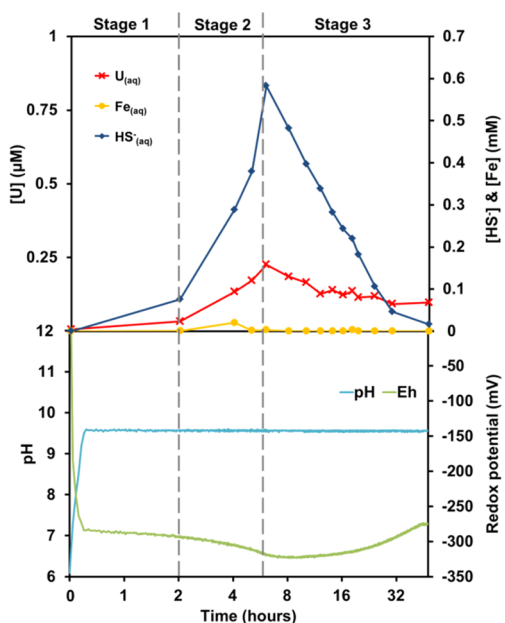


Figure 2. Chemical data for sulfidation of ferrihydrite with sorbed U(VI) at pH 9.5. The x -axis for time is shown as $\log_2$ after 0 h. The top panel shows the concentration of total aqueous uranium, iron, and sulfide. The bottom panel shows the pH and Eh values throughout the experiment up to 48 h. Additional long-term time points are shown in Figure S1–5.

nanoparticulate uraninite (stage three, see below). Indeed, the stage two samples could not be fitted with a linear combination of XANES spectra from the two end members. Specifically, in the XANES for both samples, the higher-energy resonance feature moved from 17 214 eV to approximately 17 205 eV (Figures S3–1 and S3–2). This indicates a significant alteration in the U local coordination environment when compared to either U(VI) sorbed to ferrihydrite or nanoparticulate uraninite. Further analysis of the EXAFS including exploration of models with only O_{eq} ligands and applying a backward Fourier Transform analysis confirmed that fits informed by the

end members alone were unsuccessful (Supporting Information, Section S3). Given the iron- and sulfide-rich environment, we then considered fits with U(VI) and sulfide present, which were informed by the past work on actinide–sulfide interactions^{19,47} and recent synthetic chemistry publications reporting U–sulfide species.^{48–51} Here, the best modeled fits to the two spectra (pH 7 and 9.5) were similar and included 1.5–1.8 axial oxygen (O) backscatterers at 1.84(1) Å, with a further shell of 3.2–4 O backscatterers at 2.50(1) Å, and 1.5–1.8 sulfur (S) backscatterers at 2.68 Å. This fit is consistent with U(VI) in uranyl coordination with 2 axial O_{ax} and 3–4 O_{eq} and 2 S_{eq} scatterers in the equatorial plane. The modest decrease in axial oxygen coordination number in the fits (1.5–1.8; Table 1) compared to the expected value of 2 in uranyl coordination

Table 1. Details of the U L_{III} edge EXAFS Fits from the pH 7 and pH 9.5 Experiment Compared to the Computational Modeling Structures for Free and Adsorbed Uranyl Persulfide Complex

	sample	path	coordination number	bond lengths (Å)
EXAFS data	pH 7, 3 h	O_{ax}	1.5	1.83
		O_{eq}	4.0	2.51
		S_{eq}	1.5	2.68
	pH 9.5, 6 h	O_{ax}	1.8	1.85
		O_{eq}	3.2	2.49
		S_{eq}	1.8	2.67
modeled structures	$UO_2S_2(H_2O)_3$	O_{ax}	2.0	1.79
		O_{eq}	3.0	2.59–2.61
		S_{eq}	2.0	2.69
	$UO_2S_2(H_2O)_3$ adsorbed to the FeS surface	O_{ax}	2.0	1.77
		O_{eq}	3.0	2.57–2.58
		S_{eq}	2.0	2.73

may suggest the presence of some U(IV) in the samples due to the dynamic and reducing nature of the system (Figure 3, Table 1, and Supporting Information, Section S3).

Uranium Persulfide Species. The combined geochemical and uranium XAS data from stage two of the reaction highlight

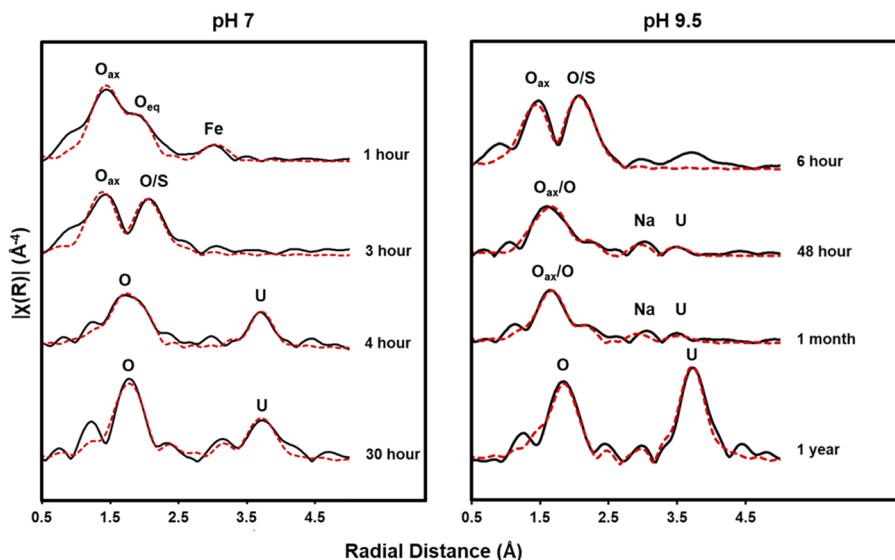


Figure 3. Fourier transform of k^3 -weighted uranium L_{III} edge EXAFS spectra from the pH 7 and pH 9.5 experiments, key peaks are labeled. Black lines are data and red lines are the best-fit models for the data (Table 1 and Supporting Information, Section S3).

that a novel U(VI), uranyl-sulfide species forms, which is associated with the transforming solid phase. The U(VI)–persulfide fits have both oxygen and sulfur directly bonded to U(VI) in the equatorial plane. Given the complexity of the experimental system, we further explored the structure and stability of potential sulfide complexes using computational modeling based on the plane-wave density functional theory (DFT). A range of U complexes were modeled, including both isolated molecular species and surface adsorbed complexes (Supporting Information, Section S4). For the latter, we used the mackinawite {001} surface as a representative model for ferrihydrite with a sulfidized surface layer. The predicted local coordination environment around the U in all uranyl (VI) complexes, featuring only oxygen-containing ligands in the equatorial shell and bonded directly to the mackinawite {001} surface, was inconsistent with the experimental data derived from EXAFS. We, therefore, further explored U(VI) molecular species in which S-containing ligands were introduced directly into the equatorial shell. The most stable of these was U(VI) coordinated with 3 oxygens from water ligands and by a persulfide (S_2^{2-}) (Figure 4). This local U environment was

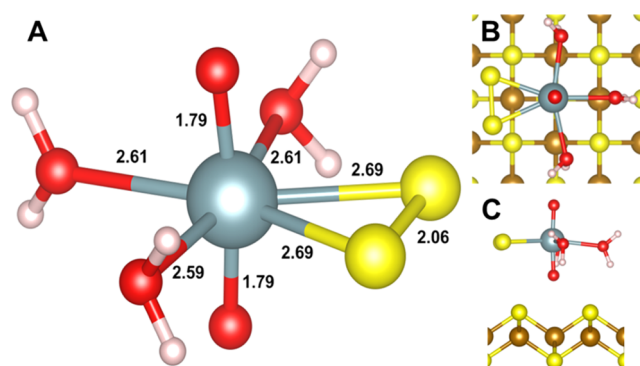


Figure 4. (A) Computed isolated uranyl(VI)–persulfide species with bond lengths shown in Ångström (Å). (B, C) Uranyl(VI)–persulfide complex adsorbed to the mackinawite {001} surface.

remarkably similar to that derived from the EXAFS fits from the pH 7, 3 h and pH 9.5, 6 h samples. We also investigated a U(V) analogue of this species using DFT, but the U(VI) complex described above provided the best match to the experimental data (Supporting Information, Section S4). Furthermore, the DFT modeling confirmed that outer-sphere adsorption of the U(VI)–persulfide complex to the mackinawite surface yields a modestly favorable adsorption energy of -102 kJ/mol suggesting that significant sorption of such a species is possible on the solid during the sulfidation process. Overall, the experimental and DFT modeling data suggest that the presence of a transient molecular U(VI)–persulfide species is associated with the sulfidizing surface via adsorption and/or occlusion during the transition from ferrihydrite to mackinawite.

Actinide sulfide species have occasionally been discussed in environmentally relevant scenarios,⁴⁷ and uranyl sulfide compounds have been formed synthetically with sulfide coordinated under various different configurations, including monodentate S^{2-} or bidentate persulfide S_2^{2-} .^{48–52} For the synthetic uranyl sulfide compounds, axial U=O bond lengths of between 1.85 and 1.89 Å and equatorial U–S bond lengths of between 2.65 and 2.80 Å are reported.^{48–51} These are consistent with the EXAFS best fits in this study, for axial U=

O (1.84 Å) and equatorial U–S bond lengths (2.67 Å and 2.68 Å, Tables 1 and S3–4). Furthermore, the calculated S–S bond length for the U(VI)–persulfide complex (2.06 Å) matches well with published synthetic persulfide complexes (2.08 Å)⁴⁸ and free persulfide bond lengths (2.06 Å).⁵³ It is noteworthy that the S–S distances in pyrite (FeS_2) are significantly longer (2.16 Å),⁵⁴ and, therefore, a pyrite-like surface-bound species seems inconsistent with both the experimental and modeling data.

Our results show strong evidence for the uranyl persulfide complex formation during sulfidation of ferrihydrite, as the uranyl unit ($U(VI)O_2^{2+}$) interacts with the solid phase during sulfidation. This is consistent with the accepted reductive dissolution mechanism for ferrihydrite during sulfidation whereby a sulfidized surface layer forms on the ferrihydrite during mineral dissolution and reprecipitation to FeS.^{23,26} In the context of U speciation, we propose that transient uranyl persulfide complex formation may be favored due to the presence of elevated concentrations of polysulfide species, in particular persulfides (S_2^{2-}), at the surface of the ferrihydrite during sulfidation.^{29–31} During stages one and two of the reaction, Fe(III) would be in stoichiometric excess compared to sulfide. These conditions favor polysulfide formation,^{29–31} suggesting that U(VI)–persulfide complex formation may be promoted under these conditions.

The U(VI)–persulfide complex we propose is important in explaining the transient release of uranium to the solution observed during stage two (Figures 1 and 2). Due to the low levels of U in the solution during this period (~ 0.3 μ M), direct spectroscopic determination of the U-solution species during the transient release period was not possible. However, under the dynamic sulfidation conditions in the experiments, the dominance of the U(VI)–persulfide complex, with its modest surface binding affinity, presumably favors desorption of a small but significant fraction of the uranyl species. Indeed, DFT calculations suggest that the U(VI)–persulfide association with the mackinawite surface is favorable (-102 kJ/mol); however, the adsorption energy is relatively weak compared to inner sphere U(VI) adsorption to, for example, quartz and amorphous silica (greater than -1000 kJ/mol).⁵⁵ The relatively weak surface association of the U(VI)–persulfide complex predicted from computational modeling is consistent with the observed transient release of uranium into the solution during sulfidation in our experiments. Overall, the experimental and modeling data suggest the presence of a transient molecular U(VI)–persulfide species, which is partially associated with the sulfidizing surface during the transition from ferrihydrite to mackinawite.

Uranium Behavior during Aging. A solid EXAFS sample taken at 4 h in the pH 7 experiment, during the transition from stage two to three, showed a significant change in U speciation. While the XANES edge position and structure were indicative of both U(IV)/U(VI) in the sample (Figures S3–1 and S3–2), the EXAFS could best be fitted with a split O shell at 2.25 Å and 2.39 Å and a U shell at 3.85 Å, consistent with a uraninite-like coordination environment (Table S3–1). This suggested a clear progression from U(VI) to U(IV) with time. This trend was further reinforced by EXAFS of the final time point of 30 h (in stage three) showing a similar best fit, with a split O shell at 2.29 Å and 2.46 Å and a U shell at 3.84 Å, again consistent with a uraninite-like coordination environment. The coordination numbers of the O and U shells (7 and 5, respectively) were somewhat lower than expected in both fits (8 and 12,

respectively)⁵⁶ suggesting that the uraninite reaction product was nanocrystalline.⁵⁷ The EXAFS data were in agreement with the qualitative XPS analyses for uranium, which confirmed reduction of U(VI) to U(IV) as sulfide reached excess concentrations in the reaction (Figure S2-2). This is consistent with the past work reporting reduction of U(VI) to nanoparticulate uraninite by both Fe(II) and aqueous sulfide.^{25,37,38,58–63} We suggest that the decrease in S_2^{2-} concentration in the solution leads to the dissociation of the U(VI)–persulfide complex leaving U(VI) then available for reduction to U(IV) by reducing agents such as Fe(II) or HS^- .^{38,62} Interestingly, direct reduction by sulfide can occur in solution, whereas Fe(II)-mediated reduction takes place primarily at iron (oxyhydr)oxide and sulfide mineral surfaces. Overall, the latter stages of the pH 7 experiment were dominated by strongly reducing conditions and U was strongly partitioned to the solid phase as nanoparticulate uraninite.

At pH 9.5, the U remained elevated in the solution from midway through stage two and up to 1 month (Figure S1-5). To explore this further, PHREEQC modeling was performed using the aqueous chemical data obtained from the reaction profile.⁶⁴ Here, thermodynamic modeling showed that from 2 h to 1 month, the solution was oversaturated with respect to the sodium uranate phase, clarkite ($Na_2U_2O_7$) (Figure S1-5). This implies that a clarkite-like or uranate-like phase may be present as a solid and, if so, may be the reason for the persistent low levels of U present in the solution at pH 9.5. Additionally, alkaline pH values are known to slow the rate of reduction of U(VI) in the solution,³⁷ and so this may play a role in the persistent and elevated aqueous U concentrations observed. The presence of a uranate-like phase was supported by the XANES, which are consistent with U(VI) in uranate-like coordination (Figure S3-2),⁶⁵ and fits to the EXAFS data for the pH 9.5 solid at 48 h are consistent with the presence of U(VI) uranate-like phases. The best fits included 2 axial O at 1.82 Å, a split equatorial O shell at 2.25 Å and 2.41 Å, a sodium (Na) shell at 3.34 Å, and a U shell at 3.71 Å (Supporting Information, Section S3). Likewise, the 1 month solid sample produced a similar fit to the 48 h sample, again consistent with a uranate-like phase, and in agreement with the past work.⁶⁶ Additional TEM observations on particles at 48 h showed a mixture of mackinawite and aggregates of nanoparticles (~10–20 nm), with EDS of the aggregates highlighting the presence of discreet areas of Na, U, and O (Figure S1-4). Both the morphology and composition of these particles are consistent with the uranate-like phase.⁶⁶ XRD confirmation of this uranate-like phase was not possible due to the U concentration being below the detection limit.

For the pH 9.5 experiment, a 1 year sample was also analyzed and confirmed that the end product of the reaction was nanoparticulate uraninite, almost identical to the species observed at 30 h in the pH 7 experiment. Overall, this indicates that at pH 9.5, the persistent elevated levels of U in the solution during stage three are likely explained by the presence of uranate-like formed during the early stages of the reaction (stages one and two), when U(VI) was released from the ferrihydrite. Following formation, the uranate-like phases presumably gradually dissolve with subsequent U(VI) reduction then occurring. Clearly, this is a slow process and provides insight into the elevated U-solution concentration up to 1 month in the pH 9.5 experiments.

In summary, by combining our controlled experimental methodology with quantum chemical calculations, we provide

strong evidence for the formation of a novel U(VI)–persulfide complex during iron (oxyhydr)oxide sulfidation, which facilitates the transient release of U into the aqueous solution. This speciation is newly observed under aqueous conditions and provides new insight into U behavior in environments where sulfide is present. Furthermore, the existence of a U(VI)–persulfide under environmentally relevant conditions provides the intriguing potential for U–S complexes to be used in a range of applications, from actinide separations in nuclear fuel reprocessing to U materials chemistry and potential catalytic reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.9b03180>.

Additional information on the experimental set-up; geochemical data; X-ray photoelectron spectroscopy (XPS); X-ray absorption spectroscopy (XAS); computational modeling (PDF)

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L.T.T., S.S., and K.M. designed the research and experimental program, collected XAS data, and wrote the paper. L.T.T. and T.S.N. performed the sampling throughout the experiments. N.E.R.O. and N.K. performed the computational modeling. A.S.W. collected the XPS data and performed the corresponding analyses. L.T.T., S.S., K.M., and J.F.W.M. performed XAS data analysis. All authors reviewed the manuscript prior to submission.

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Notes

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