This is an author produced version of Stable U(IV) Complexes Form at High-Affinity Mineral Surface Sites.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/127224/

Article:

https://doi.org/10.1021/es4047389

(c) 2014, American Chemical Society. This document is the Accepted Manuscript version of a Published Work that appeared in final form in Environmental Science & Technology, copyright (c) American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see:
https://doi.org/10.1021/es4047389
Stable U(IV) complexes form at high-affinity mineral surface sites

Drew E. Latta*, 1 Bhoopesh Mishra, 2 Russell E. Cook, 3 Kenneth M. Kenner, 1 and Maxim I. Boyanov* 1

1 Biosciences Division, Argonne National Laboratory, Argonne, IL 60439

2 Physics Department, Illinois Institute of Technology, Chicago, Illinois, IL 60616

3 Electron Microscopy Center, Argonne National Laboratory, Argonne, IL 60439

*Corresponding authors

Dr. Maxim I. Boyanov
Biosciences Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 203
Argonne, IL 60439-4843
Phone: (630) 252-8242
Fax: (630) 252-9793
E-mail: mboyanov@anl.gov

Dr. Drew E. Latta
Biosciences Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 203
Argonne, IL 60439-4843
Phone: (630) 252-3985
Fax: (630) 252-9793
E-mail: dlatta@anl.gov

KEYWORDS: uranium, reduction, non-uraninite products, molecular speciation
Abstract. Uranium (U) poses a significant contamination hazard to soils, sediments, and groundwater due to its extensive use for energy production. Despite advances in modeling the risks of this toxic and radioactive element, lack of information about the mechanisms controlling U transport hinders further improvements, particularly in reducing environments where U⁴⁺ predominates. Here, we establish that mineral surfaces can stabilize the majority of U as adsorbed U⁴⁺ species following reduction of U⁶⁺. Using x-ray absorption spectroscopy and electron imaging analysis, we find that at low surface coverage U⁴⁺ forms inner-sphere complexes with two metal oxides, TiO₂ and Fe₃O₄ (at <1.3 U nm⁻² and <0.04 U nm⁻², respectively). The uraninite (UO₂) form of U⁴⁺ predominates only at higher surface coverage. U⁴⁺-TiO₂ complexes remain stable for at least 12 months and U⁴⁺-Fe₃O₄ complexes remain stable for at least 4 months under anoxic conditions. Adsorbed U⁴⁺ results from U⁶⁺ reduction by Fe²⁺ or by the reduced electron shuttle AH₂QDS, suggesting that both abiotic and biotic reduction pathways can produce stable U⁴⁺-mineral complexes in the subsurface. The observed control of high-affinity mineral surface sites on U⁴⁺ speciation helps explain the presence of non-uraninite U⁴⁺ in sediments and has important implications for U transport modeling.
Introduction

The fate of uranium is an important consideration in the impact of energy systems on environmental quality. Long-term stewardship of spent nuclear fuel and radionuclide waste is an active issue of concern, and several countries have embarked on projects that will entomb spent fuel in geologic repositories. Current environmental issues associated with uranium include releases during the Chernobyl and Fukushima Daiichi accidents, as well as uranium accumulation near former mines and sites of nuclear fuel and weapons production. Uranium contamination is also a concern in emerging energy-related cycles, such as the use of uraniferous black shales for hydrocarbon production and the development of rare earth element ores for renewable energy production and storage. Besides environmental issues, detailed knowledge of U chemistry is necessary for understanding uranium ore genesis and for interpreting the U decay series and associated geochronometers.

The behavior of U in the subsurface is controlled by its interactions with minerals, bacteria, and soluble groundwater constituents, yet limited mechanistic understanding of these reactions hinders broad efforts to predict and model U transformations and mobility. A particular knowledge gap is the behavior of U under reducing conditions that are naturally occurring or induced as part of remediation activities. Reduction of U\(^{6+}\) (the stable valence state in equilibrium with oxygenated water) to U\(^{4+}\) can result in a dramatic decrease of U solubility due to precipitation of the mineral uraninite, UO\(_{2+x}\). Previous studies have shown that both bacteria and abiotic reductants can reduce U\(^{6+}\) to U\(^{4+}\), resulting in uraninite formation. Extensive research has consequently focused on characterization of the stability of uraninite phases. However, recent spectroscopic evidence suggests that U\(^{4+}\) in sediments does not form uraninite on the time scale of months to years. Laboratory studies indicate that phosphate or
phosphoryl groups complex $\text{U}^{4+}$ and inhibit uraninite formation.^{21-24} Phosphate-bound $\text{U}^{4+}$ was found subsequently to be more labile to dissolution or reoxidation than uraninite.$^{17,25}$ Additionally, bacterial strain and physiology appear to have an effect on the nature of $\text{U}^{4+}$ produced during respiration on $\text{U}^{6+}$, most likely through control of the chemical conditions at the location of electron transfer.$^{21}$ The identification of various $\text{U}^{4+}$ species with stabilities different from that of uraninite has profound implications for prediction of U transport, yet none of the current field-scale models account for $\text{U}^{4+}$ species other than a uraninite phase.$^{26-27}$ Indeed, there is a pressing need to characterize the factors controlling the formation of non-uraninite $\text{U}^{4+}$ species, their molecular-scale structures, and their stability to solubilization and oxidation.

In contrast to (bio)mineralization of $\text{U}^{4+}$, the role of mineral surfaces in $\text{U}^{4+}$ speciation has been largely overlooked. Subsurface environments may not always contain high phosphate or high biomass concentrations, but typically they have high mineral surface:U ratios. The abundance of mineral surface sites in natural systems suggests a potentially significant role for them in controlling $\text{U}^{4+}$ speciation and stability. Although the low solubility of uraninite suggests that it may be the thermodynamically stable $\text{U}^{4+}$ state in many systems, the potential of high-affinity mineral sites to complex $\text{U}^{4+}$ atoms for significant periods of time and thus affect U transport has not been examined. Previous investigations of $\text{U}^{6+}$ reduction in phosphate-free mineral suspensions have consistently observed the formation of nanoparticulate uraninite.$^{23,28-32}$ To date, only one study has identified complexed $\text{U}^{4+}$ species on the surface of a mineral (Ti-doped magnetite).$^{33}$

Here we establish that model minerals can bind $\text{U}^{4+}$ in inner-sphere surface complexes that are stable with respect to uraninite formation over extended periods of time. We used synchrotron x-ray spectroscopy and high-resolution transmission electron microscopy to
investigate the speciation of U$^{4+}$ produced (a) in the presence of rutile (α-TiO$_2$) after reduction of U$^{6+}$ by the soluble electron shuttle AH$_2$QDS and (b) by the solid-phase reductant magnetite (Fe$_3$O$_4$). In both cases, we observed the stabilization of adsorbed U$^{4+}$ species at low U:surface ratios that are more typical of environmental conditions. These findings provide a framework for explaining the observations of non-uraninite U$^{4+}$ in sediments and necessitate a paradigm shift in the modeling of U transport, namely the inclusion of U$^{4+}$ surface complexation reactions in addition to uraninite and U$^{4+}$-biomineral formation. The findings also indicate a need for extensive new research on U$^{4+}$ speciation and stability to constrain appropriate reaction pathways for reactive transport models.

Experimental

Magnetite synthesis and characterization

Details on the synthesis and characterization of the magnetite (Fe$_3$O$_4$) nanoparticles are provided in the SI text and in previous work. Briefly, a stirred solution of 0.2 M FeCl$_3$·6H$_2$O and 0.1 M FeCl$_2$·4H$_2$O was titrated under anoxic conditions to a pH of ~9.5 with 10 M NaOH to precipitate magnetite. Characterization showed only stoichiometric magnetite (Fe$_3$O$_4$, Fe$^{2+}$/Fe$^{3+}$ = 0.48 ± 0.02) with a particle size of 13.3 ± 5.7 nm (1 σ) and Brunauer-Emmett-Teller (BET) surface area of 67.1 m$^2$/g. The magnetite suspensions were stored under anoxic conditions until use.

Rutile characterization

The rutile form of TiO$_2$ (α-TiO$_2$) was purchased from Alfa-Aesar. Characterization by x-ray diffraction confirmed the presence of only rutile. The particles size measured by scanning electron microscopy (SEM) was 787 ± 479 nm, and the BET surface area was 4.1 m$^2$ g$^{-1}$. 
Reaction of U⁶⁺ with Fe₃O₄

Fe₃O₄ suspensions of 5, 30, 60 and 120 g L⁻¹ were prepared under strict anoxic conditions by centrifuging the stock Fe₃O₄ suspension and resuspending the particles in 5 to 15 mL of 2 mM NaHCO₃ buffer or 50 mM MOPS buffer, both prepared in deoxygenated deionized (DI) H₂O (18 MΩ·cm). Except for the centrifugation step, the Fe₃O₄ solids were not washed to prevent significant changes in the Fe²⁺/Fe³⁺ ratio in the solids.

The pH of the Fe₃O₄ reactors was adjusted to a value of 7.2, as needed, with 0.5 M HCl and 0.5 M NaOH. The reactions with U⁶⁺ were initiated by spiking with 0.5 mM uranyl acetate from a 0.1 M stock dissolved in 0.1 M HCl. The solution pH was readjusted to 7.2 after addition of U. Reactors were shaken periodically over the initial reaction time of 2 to 5 days. Samples for the x-ray absorption measurements were collected by centrifugation after 2 to 5 days and again after 4 or 6 months of aging at room temperature in the anoxic chamber.

Reaction of U⁶⁺ with TiO₂ and AH₂QDS.

Suspensions of 10, 30, and 60 g L⁻¹ TiO₂ were prepared under strict anoxic conditions by adding TiO₂ to 15 mL of deoxygenated 2 mM NaHCO₃ buffer or 50 mM MOPS buffer, followed by a spike of 0.5 mM U⁶⁺. The solution pH was adjusted to 7.2, and U⁶⁺ was allowed to sorb to the solids for 2 h. U⁶⁺ reduction was initiated by adding 2 mM AH₂QDS from a 25 mM stock (details in SI text). Reactors were shaken by hand, sealed, and covered with aluminum foil to prevent light-induced redox reactions. Solid samples were collected for x-ray absorption measurements after 3 to 5 days of initial reaction and then after 11.8 months.

Transmission electron microscopy.

Samples for TEM imaging were prepared by centrifuging subsamples of the Fe₃O₄ and TiO₂ suspensions and resuspending them in deoxygenated DI water. Drops of the new suspensions
were immediately placed on carbon-coated 400 mesh Cu grids with holey carbon supports and
dried under anoxic conditions. The samples were kept anoxic until mounting onto the TEM
sample holder and insertion into the column of the microscope (<1 min exposure to air). Images
were acquired at 200 kV with a FEI CM30T TEM and an FEI Tecnai F20ST scanning TEM.
Further details can be found in the SI text.

X-ray absorption spectroscopy.

U L_{III} edge (17,166 eV) x-ray absorption spectroscopy was done at the MR-CAT/EnviroCAT
insertion device beamline (Sector 10-ID, Advanced Photon Source). The beamline utilizes a
LN_{2}-cooled Si (111) double-crystal monochromator and a Rh harmonic rejection mirror.
Fluorescence-mode spectra were collected using an Ar-filled ionization chamber. Samples were
kept at -100 °C to prevent photochemical reactions. Sample preparation and analysis procedures
are described in detail in the SI text.

Results and Discussion

The conditions and samples are summarized in Table 1. In the first series of experiments,
we chose TiO_{2} as a redox-inactive substrate and reduced U^{6+} with the soluble reductant 9,10-
anthradihydroquinone-2,6-disulfonate (AH_{2}QDS). The AH_{2}QDS molecule is widely used as a
two-electron transfer mediator to simulate the electron shuttle compounds used by
microorganisms (oxidized form, AQDS, E_{pH=7}^{0} = -0.184 V).^{35} Ti^{4+} sites are relevant to U
speciation in many soils, sediments, and rocks where Ti is typically found in higher
concentrations (e.g., ~0.2 % by mass in soils) than known uranophile elements such as P (~0.06
%);^{36} U^{6+} was adsorbed to TiO_{2} in suspensions varying from 10 to 60 g L^{-1} (average surface
density of 7.5 to 1.3 U nm^{-2}; Table 1), and AH_{2}QDS was added subsequently. In the second
series of experiments, magnetite (Fe$_3$O$_4$) was used as both the reductant and the source of binding sites for U. Fe$_3$O$_4$ is a common iron oxide found in geological materials, produced by iron metal corrosion or through microbial respiration of Fe oxy-hydroxide minerals. 23, 28 Fe$_3$O$_4$ conducts and stores electrons in its structure and exchanges them with redox-active solution components (including U$^{6+}$) via interfacial electron transfer reactions. 28, 30, 33-34, 37-38 We studied the reaction of U$^{6+}$ with Fe$_3$O$_4$ in suspensions of 5 to 120 g L$^{-1}$ (U surface density of 0.9 to 0.04 U nm$^{-2}$). We also varied the reaction time (from 2 days to 12 months) and the presence/absence of bicarbonate (a strong complexant for U). In all reactors, >99% of the added U$^{6+}$ was removed from solution after <2 days.

Table 1. Experimental conditions and sample list

<table>
<thead>
<tr>
<th>Solids Concentration</th>
<th>Buffer</th>
<th>Surface area loading, m$^2$ L$^{-1}$</th>
<th>Surface uranium coverage, U nm$^{-2}$</th>
<th>Reaction time, day (months)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (rutile)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>40</td>
<td>7.5</td>
<td>3.2</td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>120</td>
<td>2.5</td>
<td>4.2</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>240</td>
<td>1.3</td>
<td>3.7</td>
</tr>
<tr>
<td>TiO$_2$ (rutile)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>40</td>
<td>7.5</td>
<td>2.8</td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>120</td>
<td>2.5</td>
<td>3.7</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>240</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>TiO$_2$ (rutile)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long Term</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>120</td>
<td>2.5</td>
<td>358 (11.8)</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>240</td>
<td>1.3</td>
<td>358 (11.8)</td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>300</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>1800</td>
<td>0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>3600</td>
<td>0.08</td>
<td>1.7</td>
</tr>
<tr>
<td>120 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>7200</td>
<td>0.04</td>
<td>5.0</td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>300</td>
<td>0.9</td>
<td>4.7</td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>1800</td>
<td>0.2</td>
<td>4.8</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>3600</td>
<td>0.08</td>
<td>2.1</td>
</tr>
<tr>
<td>120 g L$^{-1}$</td>
<td>50 mM MOPS</td>
<td>7200</td>
<td>0.04</td>
<td>3.3</td>
</tr>
<tr>
<td>Magnetite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long Term</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>1800</td>
<td>0.2</td>
<td>190 (6.3)</td>
</tr>
<tr>
<td>60 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>3600</td>
<td>0.08</td>
<td>190 (6.3)</td>
</tr>
<tr>
<td>120 g L$^{-1}$</td>
<td>2 mM HCO$_3$</td>
<td>7200</td>
<td>0.04</td>
<td>116 (3.8)</td>
</tr>
</tbody>
</table>

$^a$ Reaction time in months in parentheses is calculated by using an average of 30.44 days/month
Electron transfer to U⁶⁺ was verified by x-ray absorption near-edge spectroscopy (XANES) at the U L₃-edge (17,166 eV). Complete reduction to U⁴⁺ (>95% of solid-phase U) occurred under the experimental conditions in all Fe₃O₄ and TiO₂/AH₂QDS systems (Fig. S1). A control reactor with U⁶⁺ and TiO₂ but no added AH₂QDS did not produce U⁴⁺ (Fig. S1). These results are consistent with previous studies where U⁶⁺ was reduced to U⁴⁺ by Fe₃O₄ or AH₂QDS, resulting in uraninite formation.²¹, ²³, ²⁸, ³⁰, ³² However, the average speciation of U⁴⁺ in our systems exhibited an unexpected dependence on U:surface ratio, as discussed below.

**Effect of TiO₂ surface area on U⁴⁺ speciation**

We characterized the molecular structure around U⁴⁺ by using extended x-ray absorption fine-structure (EXAFS) spectroscopy (experimental details in SI text). Trends in the Fourier-transformed EXAFS data with changing TiO₂ mineral loading are illustrated in Figs. 1A and S2A.

**Fig. 1.** Fourier transform (FT) of the U L₃-edge EXAFS data from U⁴⁺ produced by reactions of U⁶⁺ with (A) TiO₂ and 2 mM AH₂QDS and (B) Fe₃O₄ as a solid-phase reductant. Data are from reactors with 2-mM NaHCO₃ at pH 7.2. Lines in color show the data from samples at different U surface densities. Standards are nanoparticulate uraninite and an aqueous solution of U⁴⁺ in 0.5 M H₂SO₄ (dotted and dashed lines, respectively). Arrows show trends with decreasing U density.
(increasing surface area). The molecular model illustrates the U-U coordination in uraninite. FTs are done over $k = 2.2$-10.4 Å$^{-1}$ with a Hanning window sill 1 Å$^{-1}$ wide.

The salient feature is the doublet peak corresponding to the dioxo-bridging bonds between the U$^{4+}$ atoms in uraninite (labeled U-U). The presence and amplitude of the U-U peak indicate that the predominant form of U$^{4+}$ at the high average surface density of 7.5 U nm$^{-2}$ is nanoparticulate uraninite, whereas the lack of amplitude at 1.3 U nm$^{-2}$ indicates the predominance of adsorbed non-uraninite U$^{4+}$ species. The spectral features of the adsorbed U$^{4+}$ species are different from those of non–uraninite U$^{4+}$ observed in bacterial systems and in sediments, indicating the sensitivity of EXAFS to this distinct form of U$^{4+}$. The molecular structure derived from fits of the data indicates inner-sphere complexation between U$^{4+}$ and Ti$^{4+}$ centers (details in SI text; Fig. S3). Adsorption geometries on the surface of TiO$_2$ that are consistent with the EXAFS data are illustrated in Fig. 2A.
**Fig. 2.** Molecular models of U⁴⁺ adsorption. (A) U⁴⁺-TiO₂ complexes. The fragment shows the edge-sharing Ti-O₆ octahedra (gray) in rutile. T1 depicts adsorption of U⁴⁺ (yellow) to the edge of a terminal Ti octahedron. T2 depicts adsorption of U⁴⁺ to the corners or the free edges of two edge-sharing Ti octahedra. (B) U⁴⁺-Fe₃O₄ complexes. The fragment shows the (111) surface of Fe₃O₄, with some Fe centers removed to illustrate possible adsorption sites. Fe octahedra are in orange; Fe tetrahedra are in green. The light-orange Fe octahedra are situated in the layer below the dark-orange octahedra. The symmetric sites M1-M3 were found to be inconsistent with the distances obtained in the EXAFS fits. The likely sites for U⁴⁺ adsorption (M4 and M5) are shown.

The findings from the EXAFS analysis are corroborated by transmission electron microscopy...
(TEM). Fig. 3A reveals the formation of particles sized 2-4 nm in samples with U:surface density of 7.5 U nm$^{-2}$. The particles have lattice fringe spacing of 0.32 nm (Fig. S4), consistent with the (111) lattice spacing in uraninite (0.316 nm)$^{41}$. Selected-area electron diffraction (SAED) patterns are also consistent with those of uraninite (Fig. S4). In contrast to the 7.5 U nm$^{-2}$ sample, uraninite particles are absent at the lower 1.3 U nm$^{-2}$ coverage (Fig. 3B). Taken together, our EXAFS and TEM results suggest that U$^{4+}$ is stabilized as an adsorbed species when the TiO$_2$ surface loading is high enough to provide a sufficient number of high-affinity binding sites.

Fig. 3. Transmission electron microscopy images from the TiO$_2$/AH$_2$QDS and Fe$_3$O$_4$ reactors with U$^{6+}$ at high and low U surface density. (A) A bright-field image of a TiO$_2$ suspension with 7.5 U nm$^{-2}$ showing 2- to 4-nm particles with lattice fringe spacing of 0.32-nm, which are more clearly displayed in Fig. S4. (B and inset) Bright-field images of TiO$_2$ particles containing 1.3 U nm$^{-2}$. No UO$_2$ nanoparticles are observed. (C) High-angle annular dark-field (HAADF) STEM, showing Z-contrast between Fe$_3$O$_4$ and brighter uraninite (red arrows) nanoparticles (0.9 U nm$^{-2}$).
(D) Representative bright-field image of 0.04 U nm$^{-2}$ sample, indicating the absence of uraninite nanoparticles. Additional TEM images are included in the SI.

**Effect of Fe$_3$O$_4$ surface area on U$^{4+}$ speciation**

The trends in the U$^{4+}$ EXAFS spectra with changing U:Fe$_3$O$_4$ surface loading are illustrated in Figs. 1B and S2B. At the highest average density of 0.9 U nm$^{-2}$, the EXAFS spectrum is identical to that of the uraninite standard (Fig. 1B). Formation of UO$_2$ during U$^{6+}$ reduction by Fe$_3$O$_4$ has been observed consistently in previous studies carried out at similarly high U:surface ratios.$^{23,28,30,32}$ Upon decreasing the average U surface coverage to 0.2, 0.08, and 0.04 U nm$^{-2}$ we observe significantly smaller amplitudes of the U-U doublet (Fig. 1B and S2B). This trend is accompanied by an increase in the amplitude and distance of the peak corresponding to O coordination ($R + \Delta \sim 1.8$ Å; Fig. 1B). Consistent and significant changes with U surface density can also be observed in the $k^3 \chi(k)$ data (Fig. S5B). Fits of the data from the sample at the lowest coverage (0.04 U nm$^{-2}$) indicate a larger O coordination number (10 vs. 8) and a larger U$^{4+}$-O distance (2.43 vs. 2.35 Å) relative to uraninite (SI text; Figs. S5, S6; Table S1). Coordination numbers of 9-10 and longer U$^{4+}$-O bonds of 2.41-2.45 Å have been determined previously for non-uraninite U$^{4+}$ species in solution and in solids.$^{42-43}$ The longer U-O bonds observed here at 0.04 U nm$^{-2}$ coverage suggest a predominantly non-uraninite U$^{4+}$ speciation. Shell-by-shell fits of the features up to $R + \Delta = 4.2$ Å produced a best fit with 10 O atoms around U$^{4+}$ at 2.43 Å, ~1.5 Fe atoms at 3.59 Å, and ~5 O atoms at 4.30 Å (Table S1). Models with a U shell at $R \sim 3.9$ Å resulted in lower-quality fits and inconsistent reproduction of the data at different k-weights of the Fourier transform (SI text; Figure S6).
Despite the presence of a peak where the U shell contributes in uraninite (Fig. 1B), the analysis above indicates that this peak is not due to U-U coordination in uraninite for samples with low U coverage. The peak from the Fe shell and its distance from U$^{4+}$ suggest inner-sphere, bidentate complexation of U$^{4+}$ to $\equiv$FeO sites. Possible edge-sharing complexes at the (111) surface of Fe$_3$O$_4$ are illustrated in Fig. 2B. The low surface coverage at which these U$^{4+}$ complexes are predominant (0.04 U nm$^{-2}$) suggests that these mononuclear U$^{4+}$ species are formed at defect sites or at lattice step/kink sites on the Fe$_3$O$_4$ surface, possibly in chelate-type complexes (e.g., M5 in Fig. 2B).

TEM corroborates the presence of UO$_2$ nanoparticles at 0.9 U nm$^{-2}$ average surface density (Fig. 3C). Images collected in high-angle annular dark-field mode emphasize high-Z elements in the sample and indicate that the sub-10 nm particles of uraninite form clusters with other uraninite particles. Our observation of uraninite clusters detached from the iron oxide is unusual. Previous studies observed association of individual uraninite particles with the edges of green rust$^{\text{31}}$ or with large crystals of Fe$_3$O$_4$. Reasons for the segregation of uraninite may relate to the mechanisms of reduction, which we discuss further down, together with other findings. In contrast to the samples at high U:surface ratio, extensive TEM imaging of the 0.04 U nm$^{-2}$ sample revealed no evidence for U-rich particles (Fig. 3D), supporting the conclusion of adsorbed U$^{4+}$ from the EXAFS analysis.

**Effect of bicarbonate on U$^{4+}$ speciation**

Our experimental design included parallel systems with and without bicarbonate to test for its effects on redox reactivity or on U$^{4+}$ speciation. An additional consideration was to test whether carbonate associated with the adsorbed U$^{4+}$ atoms and was thus responsible for the stabilization of the non-uraninite U$^{4+}$ species. Carbonate has been shown to complex U$^{4+}$, but at
significantly higher carbonate:U ratios than we used. Fig. S7 compares spectra between our systems with and without bicarbonate for different U surface densities on TiO$_2$. The presence of 2 mM bicarbonate has little or no effect on the EXAFS spectrum of the reduced U$^{4+}$ species. At the U:mineral loading of 7.5 U nm$^{-2}$ in the TiO$_2$ system, the features corresponding to uraninite appear slightly more pronounced in the absence of bicarbonate and indicate a slightly more abundant or a slightly more ordered uraninite phase in that sample. For the lower surface coverages of 2.5 and 1.3 U nm$^{-2}$ the spectra with or without bicarbonate are identical.

As for the TiO$_2$ system above, the absence of bicarbonate in the Fe$_3$O$_4$ reactors results in slightly larger amplitude of the U-U features relative to the corresponding systems with added bicarbonate (Fig. S7). Although these spectral trends appear consistently for loadings of 0.9, 0.2, and 0.08 U nm$^{-2}$, numerical analysis of the data could not establish a statistically significant increase in the average O or U coordination numbers, suggesting that bicarbonate does not have a significant effect on the average U$^{4+}$ speciation at the surface (i.e., <10% of total U may be affected).

The results indicate that carbonate does not affect the adsorption mechanism of U$^{4+}$ to TiO$_2$ or Fe$_3$O$_4$ surfaces and that carbonate is not the reason for the stabilization of non-uraninite U$^{4+}$. Indeed, both shell-by-shell modeling of the EXAFS and the independence of the spectra on bicarbonate suggest that the non-uraninite U$^{4+}$ species are stabilized by inner-sphere complexation to binding sites on the TiO$_2$ or Fe$_3$O$_4$ surfaces.

**Stability of adsorbed U$^{4+}$ over time**

We investigated the stability of surface-complexed U$^{4+}$ species under anoxic conditions by characterizing a subsample of the reactors after ~3 days of reaction and then after several months (Table 1). Only the sample series with 2 mM bicarbonate was examined. The EXAFS
data from the TiO$_2$ reactors with 3.5 and 1.2 U nm$^{-2}$ (low U coverage) (Fig. 4A) show identical spectra after 3 days and after 11.8 months of reaction, suggesting that the TiO$_2$-complexed U$^{4+}$ species are not transformed to uraninite over at least a year, even with a minor uraninite component present in the 3.5 U nm$^{-2}$ sample to provide nucleation sites. Notably, the non-uraninite U$^{4+}$ species are stable in the presence of bicarbonate, which presumably accelerates solubilization of monomeric U$^{4+}$ and facilitates migration between sites on the TiO$_2$ surface and the sites of uraninite nucleation.$^{25}$

**Fig. 4.** U L$_{III}$-edge EXAFS showing the effect of aging on the U$^{4+}$ speciation in (A) TiO$_2$ suspensions and (B) Fe$_3$O$_4$ suspensions. TiO$_2$ suspensions were allowed to react for 3 days (dotted line) and 11.8 months (solid line). Fe$_3$O$_4$ suspensions were aged for 2-5 days (dotted lines) and 6 months (solid lines, 0.2 U nm$^{-2}$ and 0.08 U nm$^{-2}$) or 4 months (solid line, 0.04 U nm$^{-2}$) in 2-mM NaHCO$_3$ solution, pH 7.2. U$^{4+}$ standards are shown in the lower portion of panel A for comparison. Arrows indicate the growth of the U-U peak with time in the magnetite samples with higher U coverage.
To test whether formation of uraninite in the TiO$_2$ system was kinetically or thermodynamically inhibited, we reacted pre-formed uraninite with TiO$_2$ at the same U$^{4+}$:mineral ratios as in the 1.2 U nm$^{-2}$ sample (details in SI text). We did not observe evolution of the starting uraninite to U$^{4+}$ adsorbed to TiO$_2$ after 1 month at 70 °C (Fig. S8). The question of kinetic or thermodynamic limitation therefore remains open. Regardless of whether uraninite or the TiO$_2$-adsorbed U$^{4+}$ species is thermodynamically more stable, progress towards equilibrium appears to be slow.

The U$^{4+}$ species in the Fe$_3$O$_4$ system exhibit different stabilities relative to the TiO$_2$ system (Fig. 4B). The non-uraninite U$^{4+}$ species in the 0.04 U nm$^{-2}$ system (low U coverage) remained unaltered after 4 months, indicating significant stabilization of adsorbed U$^{4+}$ at high-affinity binding sites on the Fe$_3$O$_4$ surface. In contrast, the predominantly non-uraninite U$^{4+}$ speciation in the 0.08 and 0.2 U nm$^{-2}$ system shifted toward nanoparticulate uraninite after 6 months of reaction time, suggesting that the U$^{4+}$ species on the Fe$_3$O$_4$ surface are less stable than non-uraninite U$^{4+}$ stabilized on the TiO$_2$ surface. The growth of uraninite in the Fe$_3$O$_4$ system may be due to a weaker bond between the U$^{4+}$ atoms and the Fe$_3$O$_4$ surface relative to the surface of TiO$_2$. An alternative explanation may be the known role of Fe$_3$O$_4$ as a reservoir for electrons, which would allow for temporary oxidation of U$^{4+}$ to U$^{5+}$ or U$^{6+}$. The consequent increase in U mobility and transport to a U$^{6+}$ reduction site that is closer to a uraninite nucleation site could promote uraninite growth over time (Fig. 5).
Fig. 5. Conceptual model for U$^{6+}$ reduction at TiO$_2$ and Fe$_3$O$_4$ surfaces. The soluble shuttle (for TiO$_2$) and interfacial electron transfer (for Fe$_3$O$_4$) pathways are illustrated with the U$^{6+}$ atom to the top left. The initially adsorbed U$^{6+}$ atoms are depicted at the top, the reduced U$^{4+}$ species at the bottom. At low surface coverage, reduced U$^{4+}$ atoms are stabilized individually at the high-affinity sites (left). At high surface coverage, the more labile U$^{4+}$ atoms at the low-affinity sites combine to form uraninite (right). A possible U$^{5+}$ disproportionation pathway is also illustrated. The axial O atoms of U$^{6+}$ or U$^{5+}$ are emphasized in dark blue. 

Uranium dynamics at the mineral surface

Uranium is known to undergo two single-electron transfer steps during reduction: UO$_2^{2+}$ to UO$_2^{+}$ and UO$_2^{+}$ to U$^{4+}$. Depending on solution conditions, two UO$_2^{+}$ (U$^{5+}$) molecules can undergo a disproportionation reaction, producing U$^{4+}$ and UO$_2^{2+}$. Ample evidence exists to suggest that U$^{5+}$ disproportionation reactions are kinetically hindered at the surface of Fe-bearing minerals. However, reports are conflicting as to whether the formation of U$^{4+}$ involves (a) disproportionation of U$^{5+}$ at the surface or (b) two subsequent electron transfers from Fe$^{2+}$ (shown conceptually in Fig. 5). In either case, the processes operative in our systems must be consistent with the observed valence state, localization, and speciation of U, as well as the observed aging of U$^{4+}$ surface complexes to uraninite.
While it is tempting to conclude that the segregated nanoclusters of uraninite (Fig. 3C) observed in the Fe$_3$O$_4$ sample with 0.9 U nm$^{-2}$ result directly from U$^{5+}$ disproportionation reactions (Fig. 5, right side), our observation of U$^{4+}$-Fe surface complexes aging to uraninite suggest that precipitation of uraninite may be due to solubilization of adsorbed U$^{4+}$ in the Fe$_3$O$_4$ samples with 0.2 and 0.08 U nm$^{-2}$. Alternatively, formation of uraninite nanoparticles from adsorbed U$^{4+}$ may also be explained through a dynamic redox equilibrium between U$^{4+}$/U$^{5+}$ and Fe$^{2+}$/Fe$^{3+}$, whereby the electron exchange between Fe$^{3+}$ and U$^{4+}$ controls the solution activity of U$^{5+}$ and hence the formation of uraninite via the disproportionation pathway (Fig. 5). Another possible mechanism for uraninite formation may be Ostwald ripening on the surface of Fe$_3$O$_4$, with subsequent detachment and agglomeration of the uraninite particles. Regardless of the pathway for uraninite formation, our results suggest that the process begins with single U$^{4+}$ atoms complexed at the Fe$_3$O$_4$ surface and that the predominant U$^{4+}$ speciation is controlled by the availability of high-affinity surface sites.

Significant stabilization of adsorbed U$^{4+}$ is observed when TiO$_2$ is present as the mineral substrate. Soluble AH$_2$QDS has been shown to reduce U$^{6+}$ in solution, leading to nanoparticulate uraninite.$^{21}$ This result, together with the lack of reaction between TiO$_2$ and pre-formed UO$_2$ in our aging experiments, suggests that TiO$_2$-sorbed U$^{4+}$ is not formed after reduction of aqueous U$^{5+}$ species. Instead, electron transfer likely occurs between AH$_2$QDS and adsorbed U$^{6+}$ species (left side, Fig. 5). Studies of U$^{6+}$ adsorption to TiO$_2$ have shown that U$^{6+}$ forms primarily inner-sphere complexes at low U coverage ($\sim$1 U nm$^{-2}$) and outer-sphere complexes at higher U coverage.$^{48}$ The correlation with the dependence of U$^{4+}$ speciation on U surface coverage determined in our study (adsorbed U$^{4+}$ at 1.3 U nm$^{-2}$ and nanoparticulate uraninite at 7.5 U nm$^{-2}$) suggests that reduction of outer-sphere-sorbed U$^{6+}$ results in uraninite, whereas reduction of
inner-sphere-sorbed $U^{6+}$ results in surface-complexed $U^{4+}$. The lack of aging of the $U^{4+}$-Ti complexes indicates that sorption to high-affinity Ti sites (left side, Fig. 5) provides significant stabilization of $U^{4+}$ against desorption or Ostwald ripening and subsequent uraninite formation.

Environmental implications

This study significantly expands the diversity of $U^{4+}$ species that may control the transport of $U$ in environmental systems and underscores the need for improved description of $U^{4+}$ speciation. Although several studies have now observed non-uraninite $U^{4+}$ species in sediments and soils,\textsuperscript{18,20,49} the molecular structure and the mechanisms leading to these $U^{4+}$ species remain uncertain. Transformations in sediments are governed by highly coupled biotic-abiotic interactions, and the pathway through which an observed $U^{4+}$ species is produced can be difficult to ascertain. Our study demonstrates that $=\text{TiO}$ and $=\text{FeO}$ sites can stabilize non-uraninite, surface-adsorbed $U^{4+}$ species, which are distinct chemically and spectroscopically from the carbonate- or phosphate-bound $U^{4+}$ complexes observed during enzymatic reduction of $U^{6+}$.\textsuperscript{21-22,24,50} It is likely that many other subsurface minerals have high-affinity sites (e.g., at steps or kinks on their surface) that can stabilize adsorbed $U^{4+}$ at sufficiently low U coverage. Our results also suggest that $U^{4+}$ can be stabilized on mineral surfaces both as a result of abiotic reduction by $\text{Fe}^{2+}$ (e.g., $U^{6+}$ reduction by $\text{Fe}_2\text{O}_4$) and in coupled biotic-abiotic reduction pathways involving an electron shuttle (e.g., $U^{6+}$ reduction by $\text{AH}_2\text{QDS}$ in the presence of $\text{TiO}_2$). These observations provide a basis for establishing a connection (or lack thereof) between observed $U^{4+}$ speciation and reduction pathways of $U^{6+}$ in future studies.

The discovery of an array of non-uraninite $U^{4+}$ species here and in previous studies\textsuperscript{18,20-22,24,49-50} points to significant gaps in our understanding of $U^{4+}$ biogeochemistry. Such gaps have
immediate bearing on the ability of geochemical models to predict the behavior of U over the
short and long term. If U$^{4+}$ surface-complexes are less stable than uraninite, then the common
assumption of reductive precipitation of U$^{4+}$ as uraninite will under-predict the mobility of U in
groundwaters and vice versa. The lack of thermodynamic parameters (e.g., $\Delta G^0$ or $E^0$) for the
formation of U$^{4+}$-mineral complexes hinders modeling efforts focused on determining U stability
with redox conditions, and additional complications arise for modeling the kinetics of these
reactions. While our study suggests that U$^{4+}$-Fe complexes are a relatively stable but likely a
transitory phase in the formation of uraninite, the lack of U$^{4+}$-Ti complex transformations over
nearly a year indicates that U$^{4+}$-Ti complexes may be important in U dynamics over time scales
relevant to the remediation of contaminated sediments. U$^{4+}$ complexes to $=\text{TiO}$ sites may be
precursors to the naturally-occurring mineral brannerite (U$^{4+}\text{Ti}_2\text{O}_6$) and help explain its
formation. Also lacking is information on the stability of U$^{4+}$ surface complexes to oxidation by
common groundwater oxidants such as dissolved O$_2$ and nitrite (NO$_2^-$). Uraninite and U$^{4+}$
complexes to $=\text{FeO}$ sites are likely to be less susceptible to oxidation when in contact with
Fe$_3$O$_4$, given that Fe$_3$O$_4$ is capable of U$^{6+}$ reduction even when its Fe$^{2+}$/Fe$^{3+}$ ratio is significantly
more oxidized than the stoichiometric 0.5.\textsuperscript{28, 51}

The strong complexation between U$^{4+}$ and $=\text{TiO}$ sites may be useful for technological
applications related to water purification. The TiO$_2$ surface appears to have high density of sites
for U$^{4+}$ complexation (~1 U nm$^{-2}$). If reduction of U$^{6+}$ to U$^{4+}$ leads to lower aqueous U
concentrations regardless of the speciation of U$^{4+}$, sequestering U as adsorbed U$^{4+}$ species rather
than nanoparticulate uraninite might be advantageous. Strong adsorption of U$^{4+}$ to large TiO$_2$-
coated particles can lower the risk of colloidal U transport.
Acknowledgements

We thank Michael McCormick at Hamilton College for graciously providing BET surface area analysis for the materials used in this study. We also thank Edward O’Loughlin for insightful discussions and Karen Haugen for editing. This research is part of the Subsurface Science Scientific Focus Area at Argonne National Laboratory supported by the DOE Subsurface Biogeochemical Research Program, Office of Biological and Environmental Research, Office of Science. Use of the Electron Microscopy Center at Argonne and the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. MRCAT/EnviroCAT operations are supported by DOE and the MRCAT/EnviroCAT member institutions. All work at Argonne was under Contract DE-AC02-06CH11357.

Supporting Information. More details on the experimental methods, TEM imaging, and EXAFS data analysis are included in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.
Table of Contents (TOC) Art
References


