Reaction of U^{VI} with Titanium-Substituted Magnetite: Influence of Ti on U^{IV} Speciation

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S Supporting Information

ABSTRACT: Reduction of hexavalent uranium (U^{VI}) to less soluble tetravalent uranium (U^{IV}) through enzymatic or abiotic redox reactions has the potential to alter U mobility in subsurface environments. As a ubiquitous natural mineral, magnetite (Fe_3O_4) is of interest because of its ability to act as a rechargeable reductant for U^{VI} . Natural magnetites are often impure with titanium, and structural Fe^{3+} replacement by Ti^{IV} yields a proportional increase in the relative Fe^{2+} content in the metal sublattice to maintain bulk charge neutrality. In the absence of oxidation, the Ti content sets the initial bulk Fe^{2+}/Fe^{3+} ratio (R). Here, we demonstrate that Ti-doped magnetites ($Fe_{3-x}Ti_xO_4$) reduce U^{VI} to U^{IV} . The U^{VI} – Fe^{2+} redox reactivity was found to be controlled directly by R but was otherwise independent of Ti content (x_{Ti}). However, in contrast to previous studies with pure magnetite where U^{VI} was reduced to nanocrystalline uraninite (UO_2), the presence of structural Ti ($x_{Ti} = 0.25$ – 0.53) results in the formation of U^{IV} species that lack the bidentate U – O_2 – U bridges of uraninite. Extended X-ray absorption fine structure spectroscopic analysis indicated that the titanomagnetite-bound U^{IV} phase has a novel U^{IV} –Ti binding geometry different from the coordination of U^{IV} in the mineral brannerite ($U^{IV}Ti_2O_6$). The observed U^{IV} –Ti coordination at a distance of 3.43 Å suggests a binuclear corner-sharing adsorption/incorporation U^{IV} complex with the solid phase. Furthermore, we explored the effect of oxidation (decreasing R) and solids-to-solution ratio on the reduced U^{IV} phase. The formation of the non-uraninite U^{IV} –Ti phase appears to be controlled by availability of surface Ti sites rather than R . Our work highlights a previously unrecognized role of Ti in the environmental chemistry of U^{IV} and suggests that further work to characterize the long-term stability of U^{IV} phases formed in the presence of Ti is warranted.

INTRODUCTION

Uranium, a ubiquitous constituent of Earth's crustal material, is generally distributed at low levels (parts per million) in rocks and soil. Redox reactions drive the element's natural cycling. Uranium accumulates in both unconformity and roll-type ore bodies through continual migration of U^{VI} -bearing groundwater through a reducing zone resulting in precipitation of sparingly soluble U^{IV} . Conversely, U^{IV} can be oxidized to U^{VI} by environmental oxidants (O_2 , NO_3^- , etc.) forming mobile U^{VI} species such as U^{VI} –carbonate complexes.^{1,2} Other important drivers of U geochemistry are precipitation of U^{VI} –phosphates, –vanadates, and –carbonates.³ In addition to natural U cycling, contamination of soils, sediments, and groundwaters with U has occurred during U refining for use in weapons and energy production. Research into ways to immobilize U contamination has focused on the stimulation of native microbial communities capable of reducing polyvalent metals.^{4–8} The relatively mobile $U^{VI}O_2^{2+}$ uranyl species is reduced to the less mobile U^{IV} valence state through various direct microbial enzymatic pathways^{9–12} or through indirect reduction by solid or dissolved Fe^{2+} and S^{2-} species resulting from dissimilatory iron and sulfur reduction.^{13–17} Reduction of U^{VI} to U^{IV} by either microbial or abiotic processes results in the production a range of U^{IV} species.

Microbially produced U^{IV} species include commonly observed uraninite (UO_2) with its bidentate U – O_2 – U bonds^{10,18–20} as well as U^{IV} complexed with phosphate, carbonate, and Fe ligands.^{5,11,21–24} The latter U^{IV} solid phases discussed in this work, referred to as non-uraninite species, can be represented by individual U^{IV} atoms adsorbed to surfaces or U^{IV} incorporated into minerals other than uraninite. Non-uraninite species are of considerable interest because of the paucity of data for predicting their stability in terms of dissolution and oxidation despite recent evidence for their formation under environmentally relevant conditions.^{5,25,26}

Considerable research has focused on the mechanisms of sorption and reduction of U^{VI} by structural Fe^{2+} in the iron oxide mineral magnetite, $Fe^{2+}Fe^{3+}_2O_4$,^{27–31} and references therein primarily because of its role as a common product of dissimilatory iron reduction and corrosion product in iron-bearing waste containers.^{32–36} The broad base of knowledge available on the crystal chemistry and aqueous geochemistry of

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magnetite makes it an attractive model mineral for exploring environmental Fe redox chemistry.^{29,37–42} In addition, magnetite is ubiquitous in igneous rocks and sediments derived from them. Recent studies have advanced our knowledge of the geochemical factors controlling magnetite reactivity with U. Primary among the factors that influence magnetite reactivity with U^{VI} are the magnetite bulk stoichiometry (Fe²⁺/Fe³⁺ ratio, *R*) and the resulting differences in redox potential.³¹ Other geochemical factors that drive magnetite reactivity with U^{VI} include solution pH,^{29,30} the presence of Ca²⁺,^{27,28} the resupply of electrons at the surface by electron hopping and diffusion of Fe²⁺ through the solid,^{29,40,43–45} and the nature of the crystallographic faces and surface defects exposed to solution.^{27,28}

Natural magnetites often contain structural impurities with substitution of Ti for Fe being common.^{46,47} Typical (titano-) magnetite concentrations are between 10 and 100 g kg^{−1} in igneous rocks, and concentrations in sediments and sedimentary rocks range from very low (in carbonates) to Fe ore-grade (in black sands).⁴⁷ Such Ti-substituted magnetites have been observed in the magnetic fraction of sediment from the U.S. Department of Energy (DOE) Hanford site, and they also may be important in hard rock radionuclide repositories, where (titano-)magnetite is present as an accessory mineral in granite.^{48–50} The substitution of Ti in magnetite enables a rich mineral chemistry, which can vary in both the amount of Ti (*x*) and the amount of structural Fe²⁺ in the inverse spinel structure of magnetite. In basaltic rocks and sediments derived from basaltic rocks, *x*_{Ti} is approximately 0.6.⁵¹ Under such conditions, titanomagnetites can incorporate a significant fraction of the Ti present in the rocks and sediments (average crustal Ti-content ~0.5 wt %).⁵² The formula for Ti-substituted magnetite/maghemite (titanomagnetites/titanomaghemites) can be written as⁵³

where *x* varies between 0 and 1, between magnetite (*x* = 0) and ulvöspinel (*x* = 1), and *y* varies from 0 to 1 depending on the amount of oxidation of Fe²⁺ in the magnetite structure. The Ti content is defined by *x*, whereas *y* is the oxidation parameter. At *x* = 0 (no Ti), variation of *y* (0 ≤ *y* ≤ 1) describes the magnetite–maghemite solid solution, whereas at *x* = 1 (Ti saturated) variation of *y* describes the ulvöspinel–titanomaghemite solid solution. In either case, as well as for intermediate values of *x* (i.e., titanomagnetites), oxidation, that is, *y* > 0, occurs by charge-balanced diffusion of Fe and electrons out of the structure at a rate of 3Fe²⁺_(oxide) → 2Fe³⁺_{oxide} + Fe³⁺ + 3 electrons. Hence, for every three structural Fe²⁺ cations oxidized, one Fe atom is removed leaving behind a cationic vacancy (□).⁴⁴ In previous work, the parameter *x* (*x* = Fe²⁺/Fe³⁺) was used to define the extent of oxidation between stoichiometric magnetite (*x* = 0.5) and maghemite (*x* = 0).^{31,40,54,55} Here, we adopt the notation of *R* = Fe²⁺/Fe³⁺ to avoid confusion with other articles in this series studying the effects of Ti substitution in magnetite on its properties and reactivity, and we use *x* and *y* as defined in eq 1.^{44,45}

We have studied the reaction between aqueous U^{VI} and nanoparticulate titanomagnetites with varying amounts of Ti-for-Fe substitution. We focused on the resulting solid-phase speciation of U using X-ray absorption spectroscopy. The goals were to determine the combined effects of Ti impurities and varying Fe²⁺ content in magnetite on its redox reactivity with

U^{VI}. Magnetite Ti contents (*x*_{Ti}) were varied from 0 to 0.5, and Fe²⁺ oxidation extents (*R*) were varied over the range 0.08–1.2 at fixed Ti content (0.5). A series of U^{VI}/Fe²⁺/Ti^{IV} coprecipitation samples was synthesized and used in extended X-ray absorption fine structure (EXAFS) analysis of the U phases. In cases where reduction to U^{IV} was observed, we discuss the possible factors leading to the formation of uraninite and non-uraninite U^{IV} species.

MATERIALS AND METHODS

Experimental Procedures. Titanomagnetite nanoparticles (~10 nm) were synthesized previously by Pearce et al.⁴⁴ Extensive characterization indicated that Fe and Ti were incorporated into the structure of titanomagnetite for *x*_{Ti} ≤ 0.37. Minor Fe(OH)₂ and amorphous TiO₂ phases were observed for titanomagnetite syntheses with *x*_{Ti} > 0.4.⁴⁴ Solids were separated by centrifugation and washed twice prior to use. The Fe²⁺ content, Fe³⁺ content, and ratio *R* of the solids used here were determined after the washing step using the methods described in the Supporting Information.

Reactor setup and all procedures were performed under strict anoxic conditions. Bottles containing 15 mL of 2 mM NaHCO₃ solution with a nominal U^{VI} concentration of 500 μM were prepared by adding U^{VI} from a 0.1 M uranyl acetate stock dissolved in 0.1 M HCl. After U^{VI} addition, the solution pH remained above 6.0, and no CO₂ evolution was observed. Prior to addition of the solids, the solution pH was adjusted to 7.2 with 0.1 M NaOH. The (titano-) magnetite solids were suspended in the 15 mL of NaHCO₃ solution to achieve a solids loading of 5 g L^{−1}. Additional experiments were done with *x*_{Ti} = 0.50 magnetite at a lower solids loading of 0.75 g L^{−1} with all other parameters the same. The solution pH was adjusted to 7.2 with 0.1 M NaOH or 0.1 M HCl. A comparative experiment was done in carbonate-free solution by suspending titanomagnetite (5 g L^{−1}, *x*_{Ti} = 0.37) in 15 mL of 3-(*N*-morpholino)propanesulfonic acid buffer (MOPS, p*K*_a = 7.2) prepared with a pH value of 7.2. Here, U^{VI} was added in 5 aliquots of 100 μM to the titanomagnetite suspension for a nominal U^{VI} concentration of 500 μM, with mixing between each addition to avoid momentary oversaturation of dissolved U^{VI} before adsorption to the solids. Reactors were sampled after 3 days; previously, complete reduction of U^{VI} by pure magnetite was observed after 1 day.^{21,28,31} Aqueous uranium concentrations were measured after filtration (0.22 μm) by inductively coupled plasma optical emission spectrometry (PerkinElmer 4300DV). Sufficient Fe²⁺ was available in all experiments for the stoichiometric reduction of all the added U^{VI} to U^{IV} (i.e., [Fe²⁺]/[U^{VI}] > 2). Total Ti/U ratios were 0 (pure magnetite), 11 (*x*_{Ti} = 0.25), 16 (*x*_{Ti} = 0.37), and 23 (*x*_{Ti} = 0.53).

X-ray Absorption Spectroscopy. The average valence state and local atomic coordination of U in the hydrated solid phases were determined by X-ray absorption near edge structure (XANES) spectroscopy and by EXAFS spectroscopy at the U L_{III}-edge (17 166 eV). The measurements were carried out in a cryostat (−100 °C) at the MRCAT/EnviroCAT sector 10-BM bending magnet and 10-ID insertion device beamlines,^{56,57} Advanced Photon Source (APS), Argonne National Laboratory, Argonne, Illinois. Details on the sample preparation, synchrotron measurement, and data analysis procedures are provided in the Supporting Information.

Table 1. Experimental Variables and Results from Linear Combination Fitting of U L_{III} XANES and k^3 -Weighted EXAFS of U-Reacted Ti–Magnetites

								linear combination EXAFS		
								% % UO_2^d	% monomeric U^{IVd}	% sorbed $U^{VI d}$
Ti content (x_{Ti})	bulk $R =$ Fe^{2+}/Fe^{3+}	total Fe^{2+} (mM)	BET specific surface area ($m^2\ g^{-1}$)	surface Ti/ Fe^a	surface Ti sites (mM) ^b	$Ti_{surface}/U$	XANES % U^{IV}/U_{Total}^c			
Vary Ti Content (5 g L ⁻¹ solids loading)										
0	0.50	25.7 ^e	98.2	0	0	0	100	83	17	0
0.25	0.68	26.4 ^e	153.4	0.05	0.62	1.2	100	25	75	0
0.37	0.82	28.0 ^e	224.4	0.12	2.2	4.4	100	19	81	0
0.53	1.2	29.5 ^e	157.0	0.19	2.4	4.8	100	3	97	0
Vary Fe^{2+} Content (5 g L ⁻¹ solids loading)										
0.50	0.08	3.00 ^f		0.19	2.4	4.8	6	0	0	100
0.50	0.21	4.54 ^f					6	0	0	100
0.50	0.53	8.90 ^f					59, 94 ^g	29, 0 ^g	50, 80 ^g	21, 20 ^g
0.50	1.1	20.1 ^f					100	0	100	0
Bicarbonate-Free MOPS Buffer (5 g L ⁻¹ solids loading) ^h										
0.37	0.82	28.0 ^e	224.4	0.12	2.2	4.4	100	68	32	0
Vary Solids Loading (0.75 g L ⁻¹ solids loading)										
0.50	1.1	3.0 ^e		0.19	0.36	0.72	76	49	35	16

^aSurface Ti-to-Fe ratio calculated from the integrated area of the XA spectra for the Fe and Ti $L_{2,3}$ -edges as described by Liu et al.⁴⁵ The error is approximately 2% sample-to-sample variation in Ti/Fe. ^bEstimated on the basis of the density of octahedral Fe sites in magnetite parallel to the (111) plane (~ 10 Fe atoms nm^{-2}), the Fe/Ti ratio measured by using Fe and Ti $L_{2,3}$ -edge XAS, and the measured specific surface area. If (100) or (110) faces are assumed to be present, then the surface Ti concentration would be lower due to the lower metal site densities of ~ 6 and ~ 4 Fe atoms nm^{-2} , respectively. ^c U^{IV} end member, nanoparticulate UO_2 ; ³¹ U^{VI} end member, UO_2^{2+} sorbed to maghemite. XANES LC fit range: 17 150 to 17 165.8 eV. Uncertainty in valence state determination is approximately $\pm 5\%$. ^dEnd members for EXAFS fitting, nanoparticulate UO_2 ; ³¹ U^{IV} from the titanomagnetite sample with $x_{Ti} = 0.5$ and $Fe^{2+}/Fe^{3+} = 1.2$; U^{VI} end member, UO_2^{2+} sorbed to maghemite. ³¹ EXAFS LC fit range, 2.2 to 10.0 Å⁻¹. Uncertainty in the spectral components content is approximately $\pm 5\%$. ^eCalculated from the formula $Fe_{3-x}Ti_xO_4$. ^fMeasured by dissolving an aliquot of the starting suspension in 5 M H_2SO_4 or HCl. Typical error is $\sim 5\%$ based on replicate dissolutions. ^gReplicate measurements. ^hBicarbonate-free 50 mM MOPS buffer, pH 7.2.

RESULTS AND DISCUSSION

Effect of Titanium Content on U^{VI} Reduction. The four samples used to explore the effect of Ti doping on the redox reactivity between magnetite and U^{VI} are listed in the top section of Table 1. Titanium doping in the range $0 \leq x \leq 0.53$, with Fe^{2+}/Fe^{3+} ratios of $0.5 \leq R \leq 1.2$, resulted in reduction of U^{VI} to U^{IV} by titanomagnetite over the 3 days of reaction. The U L_{III} -edge XANES spectra of U^{VI} reacted with the magnetite and titanomagnetite overlaid the U^{IV} standard spectra (part A of Figure 1). Linear combination (LC) fits of the XANES data with U^{IV} and U^{VI} end member spectra indicate complete reduction to U^{IV} (Table 1). Closer examination of the XANES spectra reveals a trend with increasing Ti content in the postedge region shape relative to the nanoparticulate uraninite (nano- UO_2) standard (arrow in part A of Figure 1). The postedge region is similar to that noted for non-uraninite U^{IV} species²² suggesting that the U^{IV} product formed with Ti-substituted magnetite is distinct from nanoparticulate uraninite. The trend in the XANES data is consistent with the EXAFS data discussed below.

The EXAFS spectra of U^{IV} species produced are also significantly different in the presence and absence of Ti substitution in magnetite (parts A and B of Figure 2). In the absence of Ti substitution ($x_{Ti} = 0$), the Fourier transform (FT) of the spectrum shows a pronounced peak at $R + \Delta \sim 3.7$ Å (dashed vertical line, part A of Figure 2).^{10,18,24} The presence and amplitude of this peak indicate nanoparticulate uraninite formation in the Ti-free system in agreement with previous results.^{14,21,27,31} The FT peak at $R + \Delta \sim 3.7$ Å in the FT spectrum is due to the bidentate U – O₂ – U links in the structure of uraninite, and the amplitude of this U–U feature is smaller in 2 to 5 nm particles of uraninite because of the

increased proportion of under-coordinated U^{IV} atoms at the surface.²⁴ Increased amounts of Ti in the magnetite lattice result in decreased amplitude at $R + \Delta \sim 3.7$ Å (part A of Figure 2).

Linear combination (LC) fitting of the k^3 -weighted EXAFS spectra using nanoparticulate uraninite, U reacted with $x_{Ti} = 0.50$ Ti–magnetite, and U^{VI} sorbed to maghemite as end-members shows that the amount of non-uraninite U^{IV} increases with increasing Ti content (Table 1, LC fit quality illustrated in Figure S1 of the Supporting Information). The pure magnetite end member in this study has the highest amount of UO_2 as determined by the LC fit (83% UO_2 and 17% non- UO_2 U^{IV}). The UO_2 content decreased to only 25% and 20% when the Ti content increased to $x_{Ti} = 0.25$ and 0.37, respectively. A UO_2 component was mostly absent in the spectra at the higher Ti contents of 0.50 and 0.53. The approximately 17% non- UO_2 spectral component in the $x_{Ti} = 0$ spectrum is consistent with the previously observed coexistence of a labile U^{IV} phase dissolved by a 1 M bicarbonate solution and nanoparticulate uraninite.⁵⁸ A non-uraninite U^{IV} phase might be present as $\sim 20\%$ of the U^{IV} in our $x_{Ti} = 0$ system; however, its proportion in the sample could be lower than was determined by LC fits of the EXAFS data because of possible differences in uraninite particle sizes between the sample and the standard. Smaller uraninite particle sizes result in smaller amplitude of the U–U features in the spectrum¹⁰ and would result in overestimation of the actual amount of non-uraninite U^{IV} present.

Effects of the Fe^{2+}/Fe^{3+} Ratio. We attempted to determine whether the observed non-uraninite U^{IV} speciation was related to the presence of Ti or the increased Fe^{2+} content in titanomagnetites by varying the Fe^{2+}/Fe^{3+} ratio, R , at a fixed level of Ti doping ($x_{Ti} = 0.50$). We varied R by oxidizing

Figure 1. (A) U L_{III}-edge XANES showing the effect of Ti content x_{Ti} on the reaction of U^{VI} with titanomagnetite ($Fe_{3-x}Ti_xO_4$). The spectra of the $x_{Ti} = 0.37$ and $x_{Ti} = 0.53$ are overlapping. The arrow denotes a change in the postedge feature with increasing Ti content (discussed in the text). (B) U L_{III}-edge XANES showing the effect of Fe^{2+}/Fe^{3+} content on the reaction of U^{VI} with $x_{Ti} = 0.50$ titanomagnetite. Spectra are compared to U^{VI} and U^{IV} standards: non-uraninite U^{IV} -carbonate produced during U^{VI} respiration by *A. dehalogenans*, nano- UO_2 produced by stoichiometric magnetite in previous work, and U^{VI} sorbed to maghemite.^{22,31} Solution conditions: 500 μM U^{VI} , 5 g/L solids loading in 2 mM $NaHCO_3$, pH 7.2.

structural Fe^{2+} with a controlled amount of H_2O_2 and allowed the resulting oxidized titanomagnetites to react with U^{VI} as above. Reduction of U^{VI} to U^{IV} was observed only when R was greater than or equal to ~ 0.5 (part B of Figure 1, Table 1). When R was less than 0.5, only sorbed U^{VI} was observed after 4 days of reaction. The trend in U^{VI} reduction reactivity with the Fe^{2+}/Fe^{3+} ratio is similar to that observed previously with Ti-free magnetite (Figure 3).³¹ The lack of U^{VI} reduction by oxidized titanomagnetite is consistent with the previously observed effect of R on the bulk redox potential of magnetite.^{31,44,45,55} The similarity observed here between undoped magnetite and titanomagnetite in the transition from reduction of U^{VI} at high R to sorption of U^{VI} at lower R (Figure 3) indicates that the redox reactivity of magnetite with respect to U^{VI} reduction is not directly linked to Ti doping but only indirectly through its influence on the initial value of R .

We found that, under conditions where reduction of U^{VI} by titanomagnetite was observed ($x_{Ti} = 0.5$, $R \geq 0.5$), titanomagnetite with different Fe^{2+}/Fe^{3+} ratios produced predominantly non-uraninite U^{IV} (note the lack of a U–U

Figure 2. U L_{III}-edge k^3 -weighted Fourier transform EXAFS data, $\Delta k = 2.0$ – $10.4 \text{ \AA}^{-1}$. The EXAFS data itself is included in the Supporting Information. (A) Effect on U coordination of varying Ti content from $x_{Ti} = 0$ to 0.50. (B) Effect of varying Fe(II) content at fixed Ti content of $x_{Ti} = 0.50$, from $Fe^{2+}/Fe^{3+} = 1.18$ to 0. (C) Effect of varying solids loading at Ti content of $x_{Ti} = 0.5$, for samples with 5 g L⁻¹ and 0.75 g L⁻¹, are shown, and the effect of bicarbonate-free buffer (50 mM MOPS) on 5 g L⁻¹ $x_{Ti} = 0.37$ titanomagnetite. Standards (in black or gray) are non-uraninite U^{IV} produced during U^{VI} respiration by *Desulfitobacterium spp.* in phosphate-free carbonate-containing media, nano- UO_2 produced by stoichiometric magnetite, and U^{VI} sorbed to maghemite.^{22,31} The position of the peak resulting from U–U coordination in uraninite is indicated by the vertical dashed lines. Peaks corresponding to the presence of U^{VI} are denoted in part B as $U^{VI}-O_{ax}$ for the axial $O_{ax}=U=O_{ax}$ bonding in the uranyl cation and $U^{VI}-O_{eq}$ for the U–O coordination in the equatorial plane.

peak in part B of Figure 2). The formation of uraninite by pure magnetite ($R = 0.50$) and of non-uraninite U^{IV} species by oxidized titanomagnetite with $R \approx 0.5$ indicates that the presence of Ti is the determining factor in the formation of the non-uraninite U^{IV} product rather than the increased Fe^{2+} content of titanomagnetite.

Figure 3. Comparison of U^{IV}/U_{total} from linear-combination fitting of XANES data for 5 g L⁻¹ magnetite³¹ and for 5 g L⁻¹ titanomagnetite systems (this work). The Ti content of the titanomagnetites used is noted as text labels on the graph. The lines are visual aids only. The solid line connects samples of U^{VI} reacted with unoxidized titanomagnetite, and the broken line connects samples of U^{VI} reacted with $x_{Ti} = 0.50$ titanomagnetite samples that were oxidized at a controlled extent. Error bars represent a 10% estimated uncertainty of valence state determination.

Speciation of U^{IV} in the Presence of Ti. In lieu of a significant effect of increased R in titanomagnetites on U^{VI} reduction to non-uraninite U^{IV}, we explored ways that Ti might influence U^{IV} speciation. One possible effect of Ti in the system is to suppress uraninite formation by promoting the precipitation of a U^{IV}- and Ti-bearing mineral. Brannerite (U^{IV}Ti₂O₆) is a common mineral found in U ore deposits and is of technological interest because of its stability in titanate ceramics for high-level radioactive waste immobilization.^{59,60} A sample of brannerite was synthesized by using a high-temperature, solid-state reaction method (details in the Supporting Information)⁶¹ and analyzed by synchrotron X-ray diffraction (XRD) and EXAFS (Figures S2–S6 of the Supporting Information). The EXAFS spectrum of brannerite is reproduced well by using the published crystal structure (details in Figure S6 of the Supporting Information).⁶⁰ Comparison of the brannerite spectrum to that of U^{IV} in the titanomagnetite system, together with LC fits (Figure S1 of the Supporting Information), shows that brannerite is not a significant component (<10%) of the spectrum. In addition, separate U phases or Fe oxidation products could not be identified by transmission electron microscopy (Figure S7 of the Supporting Information). The absence of secondary products argues against the formation of discrete U^{IV} phases, which have been observed in other studies,^{29,30} and against the incorporation of reduced U into secondary Fe phases such as goethite.^{62,63} In addition, U was fully reduced to U^{IV} in our study, whereas U incorporated into goethite (and possibly magnetite) has been interpreted as a U^V phase as supported by atomistic simulations of U incorporation into Fe oxides.^{62–64} These arguments suggest that the U^{IV} species in the titanomagnetite systems are present as surface or occluded complexes rather than incorporated into the structure of a U or Fe mineral.

To further address U^{IV} coordination in the titanomagnetite system, a series of U^{VI}/Fe²⁺/Ti^{IV} coprecipitation samples were prepared for EXAFS analysis. The soluble reactants (U^{VI}/Fe²⁺/Ti^{IV} = 0.1/1.0/0, 0.1, 0.2, 0.5 mM) were mixed in anoxic and carbonate-free aqueous solutions under acidic conditions (pH

0–1) and slowly titrated with NaOH to pH 8.4 (Supporting Information). On the basis of the known pH dependence of Ti^{IV} solubility, the aqueous concentration of Ti^{IV} in the coprecipitation system would be expected to decrease to roughly 10⁻⁸ to 10⁻⁹ M above pH 3 because of the precipitation of Ti^{IV} presumably as an amorphous hydrated oxide.⁶⁵ U^{VI}–Fe²⁺ redox reactivity was observed at pH > 8.0 similar to the results of previous work with carboxyl-functionalized beads as the substrate.²⁴ Figure S8 of the Supporting Information shows XANES and XRD analyses of the hydrated solid phases in the coprecipitation reactors demonstrating reduction of U^{VI} to U^{IV} at pH 8.4 coupled to the formation of magnetite from Fe²⁺ oxidation. Crystalline TiO₂ was not observed in the XRD pattern of the coprecipitates suggesting that the U^{VI}–Fe²⁺ redox reaction occurred in the presence of an amorphous, presumably TiO₂-like, phase.

The U-edge EXAFS data for the coprecipitates indicate that the presence of Ti^{IV} at or above 1:1 molar ratio with U inhibits uraninite formation and results in the formation of a non-uraninite U^{IV} phase (Figure S9 of the Supporting Information). Features corresponding to atomic shells combine linearly in the real part of the Fourier transform (FT), which, in certain cases, makes them easier to observe than those in the magnitude of the FT (Figure S6 of the Supporting Information). The real part of the FT data are shown in part C of Figure 4. The near-neighbor O shell feature ($R + \Delta = 1.5$ – 2.0 Å) in Ti-containing samples occurs at a larger distance than that in brannerite (part D of Figure 4) and at a distance similar to that for the uraninite U^{IV} species. Fits of the data determined a U–O distance of 2.32 Å for both the uraninite and non-uraninite coprecipitate samples (Table S1 of the Supporting Information). The longer U^{IV}–O distance suggests the presence of the U^{IV}O₈ polyhedra found in uraninite rather than the U^{IV}O₆ octahedra found in brannerite (parts A–C of Figure 5). The amplitudes of the features at $R + \Delta = 2.5$ – 3.2 Å increase consistently with increasing Ti^{IV} concentration suggesting that they are due to U^{IV}–Ti coordination. Analysis of the EXAFS data shows that these FT features can be explained by U^{IV}–Ti coordination at 3.43 Å (Figure S10 and Table S1, discussion in the Supporting Information). This U^{IV}–Ti distance is shorter than that in brannerite, in which case U^{IV} binds to the corners of TiO₆ octahedra and results in a U^{IV}–Ti distance of 3.55–3.70 Å (part C of Figure 5). The shorter U^{IV}–Ti distance of 3.43 Å can be accommodated in a corner-sharing binuclear binding mechanism between a U^{IV}O₈ and two TiO₆ octahedra by rotation of the U^{IV}O₈ unit around an axis through the corner O atoms (part D of Figure 5). Such a U–Ti bonding geometry would require minimal distortions of only the bond angles between the U^{IV}–O and the Ti^{IV}–O polyhedra found in the respective binary oxides. An undistorted edge-sharing U^{IV}O₈–TiO₆ complex results in a maximum U^{IV}–Ti distance of 3.20 Å and will require more distortion to accommodate the determined 3.43 Å distance.

The U^{IV}–Ti binding geometry and the EXAFS signatures obtained from the U^{VI}/Fe²⁺/Ti^{IV} coprecipitation samples provide a framework for the analysis of the U^{IV} formed by titanomagnetite. The spectral maximum near $R + \Delta = 1.7$ Å in Figure 4 occurs at the same distance as in the coprecipitate samples. This was confirmed by the refined U^{IV}–O distance (Figure S11 and Table S2 of the Supporting Information) suggesting the presence of U^{IV}O₈ polyhedra. Parts B and C of Figure 4 also indicate small but significant differences in the real part of the FT EXAFS between U^{IV} in the titanomagnetite

Figure 4. Real part of the Fourier transform (FT) of the k^3 -weighted experimental EXAFS data. Contributions from atomic shells add linearly in the real part of the FT – the spectral regions where the O, Ti, and U shells contribute in the brannerite standard are shown as a guide. The EXAFS data, the magnitude of the FT, and details on fitting the spectra are shown in Figures S3–S11 of the Supporting Information. The FT range is $k = 2.2$ – $10.4 \text{ \AA}^{-1}$ using $1.0 \text{ \AA}^{-1}$ wide Hanning window sills. Lowercase letters correspond to spectral features discussed in the text, and vertical dashed lines delineate their positions. The vertical arrow labeled Ti shows the trend in spectral features with increasing Ti content in the coprecipitate sample series. The horizontal arrow shows the difference in position of the Ti shell feature between brannerite and all other Ti-containing samples. (A) Non-uraninite U^{IV} from Boyanov et al.²² Blue, phosphate-free system; red, phosphate present at 0.3 mM. The feature corresponding to the P shell is noted. See Boyanov et al.²² for details. (B) Non-uraninite U^{IV} from titanomagnetite in this work. Blue: $x_{\text{Ti}} = 0.37$, $R = 0.82$; red: $x_{\text{Ti}} = 0.5$, $R = 0.9$. (C) U/Fe/Ti coprecipitate samples. Gray: Ti = 0 mM; blue: Ti = 0.1 mM; green: Ti = 0.2 mM; red: Ti = 0.5 mM. The contribution from a U shell in the Ti = 0 mM sample is noted. (D) Brannerite standard (UTi_2O_6). Fit of these data is shown in Figure S6 of the Supporting Information.

system and in the coprecipitates. The spectral minimum near $R + \Delta = 2.0$ – $2.3 \text{ \AA}$ is centered at a different distance and has a different shape in the two systems (Figure 4, features a, b, c). This spectral region is also dominated by signals from the O atoms around U^{IV} ; the differences indicate different near-neighbor O coordination in the two systems. The spectral differences mimic those observed between non-uraninite U formed in the presence and absence of phosphate from U^{VI} reduction by *Desulfitobacterium* spp. or AH_2DS (a reduced form of anthraquinone-2,6-disulfonate (AQDS), feature d in part A of Figure 4).²² The spectral differences were explained previously by U^{IV} –phosphate versus U^{IV} –carbonate complexation.²² Shell-by-shell fits indicate larger disorder in the near-neighbor O shell of titanomagnetite samples relative to the coprecipitate samples or possibly the presence of more than one U–O coordination shell (Figure S11 and Table S2 of the Supporting Information). The Ti shell feature observed in the coprecipitation samples at $R + \Delta = 2.5$ – $3.2 \text{ \AA}$ is not as pronounced in the titanomagnetite spectra (Figure 4) and could not be confirmed in the shell-by-shell fits.

Overall, the analysis of the EXAFS data from the titanomagnetite samples could not definitively establish the binuclear corner-sharing U^{IV} –Ti coordination that was observed in the coprecipitate samples. A possible explanation

Figure 5. Coordination environments of U^{IV} . (A) Polyhedral structure of brannerite. Yellow, $\text{U}^{\text{IV}}\text{O}_6$; gray, $\text{Ti}^{\text{IV}}\text{O}_6$. The edge-sharing chains of $\text{U}^{\text{IV}}\text{O}_6$ bind together the sheets of $\text{Ti}^{\text{IV}}\text{O}_6$. (B) Local atomic environment of U^{IV} in brannerite. (C) Binding model of $\text{U}^{\text{IV}}\text{O}_6$ to the $\text{Ti}^{\text{IV}}\text{O}_6$ sheet in brannerite. (D) Combination of binuclear corner-sharing and mononuclear edge-sharing adsorption complex of $\text{U}^{\text{IV}}\text{O}_6$. The U^{IV} –Ti distance determined from the EXAFS data is consistent with the corner-sharing geometry and not with the edge-sharing geometry (denoted by the red cross). (E) Type I adsorption complex of U^{IV} –carbonate on a TiO_2 surface (U atom bridging). Green, C atom. (F) Type II adsorption complex of U^{IV} –carbonate on a TiO_2 surface (carbonate group bridging).

for the difference is that in the coprecipitate system a TiO_2 -like phase is formed before the occurrence of U^{VI} reduction and of magnetite formation, so U^{IV} speciation is potentially influenced by distinct TiO_2 and Fe_3O_4 surfaces. In contrast, extensive evidence suggests that Ti is incorporated into the structure of titanomagnetites.^{44,45} Our results suggest that the presence of Ti binding sites on the surface of titanomagnetite controls the formation of the non-uraninite U^{IV} species. It is possible that Ti sites on the surface of titanomagnetite could have different coordination geometries than a site on a TiO_2 surface resulting in slightly different U^{IV} –Ti complexes. Carbonate groups, if present, might also bind to the back side of the adsorbed U^{IV} atom resulting in overlap of the spectral contribution from Ti atoms and the carbonate group (part E of Figure 5).

In attempting to address the possibility of carbonate binding by preparing samples under carbonate-free conditions, we obtained an unexpected result. Titanomagnetite ($x_{\text{Ti}} = 0.37$) reacted with U^{VI} in bicarbonate-free 50 mM MOPS buffer resulted in the formation of nanoparticulate uraninite (part C of Figure 2 and Table 1). In contrast, previous results with Ti-free magnetite under the same conditions indicated that nanoparticulate uraninite formed in both bicarbonate-free MOPS buffer and in 2 mM bicarbonate solutions.³¹ Possible

mechanisms for the observed dependence of U^{IV} speciation on the presence of bicarbonate in the titanomagnetite system may be the stabilization of a U^{IV} –carbonate complex over uraninite with Ti^{4+} providing a binding site for a U^{IV} –carbonate moiety or for a bridging carbonate group (parts E and F of Figure 5). Another possibility is that carbonate promotes the initial sorption of negatively charged U^{VI} –carbonate complexes to more positive Ti^{4+} sites (relative to Fe^{2+} or Fe^{3+}) before the electron transfer step with the U^{IV} atoms resulting from reduction near Ti sites stabilized as carbonate-free U^{IV} –Ti complexes.

As a further test of whether Ti binding sites control U^{IV} speciation in titanomagnetite suspensions, we evaluated binding site saturation by decreasing the solids loading from 5 g L^{-1} to 0.75 g L^{-1} . In this experiment, we reduced the solids loading to 0.75 g L^{-1} of unoxidized $x_{\text{Ti}} = 0.50$ titanomagnetite ($\sim 3 \text{ mM Fe}^{2+}$ in the system) for reaction with $0.5 \text{ mM U}^{\text{VI}}$. Nearly complete reduction to U^{IV} and the formation of nanoparticulate uraninite was observed (U–U peak in the FT EXAFS shown in part C of Figure 2). The LC fits of the EXAFS data showed that most of the added U^{VI} was reduced to U^{IV} (84%, Table 1), whereas a significant amount of U^{IV} formed nanoparticulate uraninite (49%). The rest of the reduced U (35%) was fitted with the non-uraninite U^{IV} component observed in the 5 g L^{-1} $x_{\text{Ti}} = 0.50$ titanomagnetite suspension. The oxidized U fraction determined from the EXAFS data is also indicated from the shift in edge position in the XANES toward higher energy (Figure S12 of the Supporting Information). The amount of U^{VI} reduced in the lower-solids-loading experiment determined by the LC analysis (76%, Table 1) is consistent with the oxidation of the titanomagnetite to a value of $R \sim 0.4$ or less with consequent loss of reactivity to the remaining portion of the U^{VI} .

The differences in U^{IV} speciation between the reactors with 0.75 and 5 g L^{-1} solids loading, along with the increase in non-uraninite U^{IV} with increasing Ti content in magnetite (previous section), suggest saturation of the Ti sites available for U^{IV} binding. We calculated Ti surface site densities for the measured ratio of Ti to Fe derived from Fe and Ti $L_{2,3}$ -edge XAS of the nanoparticles, as described by Liu et al.,⁴⁵ and used these values to estimate the ratio of surface-exposed Ti to U ($\text{Ti}_{\text{surface}}/\text{U}$ in Table 1). A trend of increasing non-uraninite U^{IV} with increasing $\text{Ti}_{\text{surface}}/\text{U}$ ratios is suggested by the data, with 35% non- UO_2 U^{IV} present in the 0.75 g L^{-1} experiment having a $\text{Ti}_{\text{surface}}/\text{U}$ ratio of 0.72, increasing to 75% non-uraninite U^{IV} in the $x_{\text{Ti}} = 0.25$ system having a $\text{Ti}_{\text{surface}}/\text{U}$ ratio of 1.2. At $\text{Ti}_{\text{surface}}/\text{U}$ ratios of 4.4 and above, predominantly non-uraninite U^{IV} is observed under the experimental conditions.

These results support the conclusion that U binding to Ti surface sites controls the formation of the non-uraninite U^{IV} phase observed but uncertainties associated with the estimation of exposed $\equiv\text{TiO}$ sites preclude a more definitive determination of the stoichiometry. We suspect that $\equiv\text{FeO}$ surface sites are not a factor in determining the formation of the non-uraninite U^{IV} phase under our experimental conditions. The surface area loading and experimental conditions used in our titanomagnetite experiments (0.4 to $1 \mu\text{mole L m}^{-2}$, 2 mM bicarbonate, pH 7.2) are not greatly different from those in previous studies with pure magnetites (1 to $1.2 \mu\text{mole L m}^{-2}$, 1 to 2 mM bicarbonate, pH 7.0 to 7.2) where nanoparticulate UO_2 was the only product of U^{VI} reduction.^{21,31} Although the lack of non-uraninite U^{IV} species at high surface area loadings of magnetite suggests that $\equiv\text{FeO}$ sites do not control U^{IV}

speciation under our experimental conditions, it is also possible that Ti doping above a certain level modifies the $\equiv\text{Fe}-\text{O}$ surface site coordination or affinity causing the formation of non-uraninite U^{IV} . Experiments with well-characterized TiO_2 and Fe oxide surfaces are underway to constrain the surface controls on non-uraninite U^{IV} formation.

Implications for Contaminant Reduction by (Titanomagnetite). We found that Ti substitution in magnetite up to $x_{\text{Ti}} = 0.5$ does not directly affect the ability of magnetite to reduce dissolved U^{VI} under near-neutral pH conditions other than through its influence on the initial bulk R . Rather, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ stoichiometry of Ti-doped magnetites itself directly controls the reduction of U^{VI} in a way similar to that observed with Ti-free magnetite.³¹ The trend of U^{VI} reduction to U^{IV} at $R \sim > 0.4$ and no reduction for $R < 0.4$ is consistent with the idea that the bulk redox potential of magnetite is directly controlled by the solid $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio.^{31,55} The change in (titano-)magnetite reactivity with respect to U^{VI} reduction,³¹ Te^{VII} reduction,⁴⁵ and nitroaromatic reduction⁵⁵ from high reactivity to lower or no reactivity at $R \sim 0.4$ might alternatively indicate the onset of a rate-limiting step. Below this value of R , limitations in the diffusivity of Fe^{2+} through the magnetite lattice, as opposed to the fast electron-hopping rate that generally occurs between octahedral Fe chains, could be responsible for the decreased reactivity.^{29,42} The diffusion of Fe and electrons through the lattice has been postulated to explain the continued resupply of reactive Fe^{2+} to the surface of titanomagnetites and to explain isotope exchange between aqueous Fe^{2+} and structural Fe^{2+} in magnetite.^{43–45} Such a diffusion-limited step might ultimately control the reactivity of magnetite in natural and engineered systems.

Our current work expands on the importance of non-uraninite U^{IV} phases in the environmental chemistry of U suggested in previous work.^{21–23,26,66} Here, we have found that the presence of Ti has significant control on the U^{IV} speciation resulting from U^{VI} reduction by structural Fe^{2+} with uraninite U^{IV} formed in Ti-free systems and a novel U^{IV} surface complex formed in Ti-bearing systems. An association of U^{IV} with Ti might be predicted on the basis that the mineral brannerite (UTi_2O_6) is a relatively common U mineral in ores.⁶⁷ Formation of U^{IV} –Ti phases during reduction by Ti-doped magnetite, and possibly during (bio)reduction in the presence of other Ti-bearing minerals such as anatase and rutile (TiO_2), could be important to overall mobility of U under reducing conditions in the subsurface. We note that typical titanium concentrations in rocks and sediments are on the order of $0.5 \text{ wt } \%$, that is $\sim 10\%$ of iron concentrations, and 3 orders of magnitude higher than average U concentrations.⁵² Additionally, our observations of U^{VI} reduction by the nanoparticulate titanomagnetites in this study suggest that natural micrometer-sized titanomagnetites in Hanford sediments exposed to reducing conditions ($x_{\text{Ti}} = 0.15$, $R = 0.49$), as well as elsewhere, may be active reductants for U^{VI} .⁵⁰ On the basis of previous reports detailing the oxidative and ligand-promoted (carbonate) dissolution of brannerite,^{59,68} we speculate that U^{IV} –Ti phases might be more resistant than uraninite to oxidation and dissolution. Further work to determine the relative reactivity of uraninite and non-uraninite phases is needed to provide information on the stability of U^{IV} phases observed during abiotic and biotic U^{VI} reduction.

■ ASSOCIATED CONTENT

■ Supporting Information

As mentioned in the text, additional text, tables, and figures are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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