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Influence of Chelating Agents on Biogenic Uraninite Reoxidation by Fe(III) (Hydr)oxides

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ABSTRACT: Microbially mediated reduction of soluble U(VI) to U(IV) with subsequent precipitation of uraninite, UO₂(s), has been proposed as a method for limiting uranium (U) migration. However, microbially reduced UO₂ may be susceptible to reoxidation by environmental factors, with Fe(III) (hydr)oxides playing a significant role. Little is known about the role that organic compounds such as Fe(III) chelators play in the stability of reduced U. Here, we investigate the impact of citrate, DFB, EDTA, and NTA on biogenic UO₂ reoxidation with ferrihydrite, goethite, and hematite. Experiments were conducted in anaerobic batch systems in PIPES buffer (10 mM, pH 7) with bicarbonate for approximately 80 days. Results showed EDTA accelerated UO₂ reoxidation the most at an initial rate of 9.5 $\mu\text{M day}^{-1}$ with ferrihydrite, 8.6 $\mu\text{M day}^{-1}$ with goethite, and 8.8 $\mu\text{M day}^{-1}$ with hematite. NTA accelerated UO₂ reoxidation with ferrihydrite at a rate of 4.8 $\mu\text{M day}^{-1}$; rates were less with goethite and hematite (0.66 and 0.71 $\mu\text{M day}^{-1}$, respectively). Citrate increased UO₂ reoxidation with ferrihydrite at a rate of 1.8 $\mu\text{M day}^{-1}$, but did not increase the extent of reaction with goethite or hematite, with no reoxidation in this case. In all cases, bicarbonate increased the rate and extent of UO₂ reoxidation with ferrihydrite in the presence and absence of chelators. The highest rate of UO₂ reoxidation occurred when the chelator promoted both UO₂ and Fe(III) (hydr)oxide dissolution as demonstrated with EDTA. When UO₂ dissolution did not occur, UO₂ reoxidation likely proceeded through an aqueous Fe(III) intermediate with lower reoxidation rates observed. Reaction modeling suggests that strong Fe(II) chelators promote reoxidation whereas strong Fe(III) chelators impede it. These results indicate that chelators found in U contaminated sites may play a significant role in mobilizing U, potentially affecting bioremediation efforts.

By the end of the cold war, uranium (U) contamination in the U.S. was present at one hundred and twenty nuclear weapon production sites covering 7280 km².¹ At these sites, U is the most common radionuclide,² making it a primary target for remediation by the Department of Energy (DOE). Understanding the stability and mobility of U-bearing compounds is critical to the DOE remediation effort. In general, U(VI) compounds are considered more soluble, and thus more mobile, than U(IV) compounds, such that the oxidation of U(IV) to U(VI) is regarded as mobilizing U. Conversely, reduction of U(VI) to U(IV) is considered to decrease the mobility of U through the formation and precipitation of U(IV) minerals primarily as UO₂.^{3,4}

In oxygen rich environments, U(VI) dominates and is primarily present as uranyl (UO₂²⁺) species, including uranyl complexes with hydroxide, phosphate, calcium, carbonate, and solid surfaces. In sufficiently reduced environments, U(IV) may remain stable^{5,6} and often resides as the relatively insoluble mineral UO₂(s), uraninite. Redox reactions and complexation to organic and inorganic compounds often control U mobility

and ultimate fate in surface and subsurface systems. While certain bacteria are known to reduce U(VI) to U(IV),^{7–12} microbial respiration increases bicarbonate concentrations that form strong complexes with U(VI), favoring mobilization.^{13–15} In microbial U reduction remediation scenarios, it is important to characterize microbial and environmental factors that dictate U oxidation state to ultimately understand and control the environmental fate and transport of U.

To ensure effective immobilization, reduced U must remain stable and resist reoxidation to its soluble and more mobile form.¹ Numerous studies have shown biogenic UO₂ reoxidation is affected by a variety of environmental factors.^{12,16–25} Previous studies have demonstrated Fe(III) (hydr)oxides can play a significant role in biogenic UO₂ reoxidation,^{13,18,19,26,27,36} with the Fe(III) and U(IV) electron transfer mechanism shown in eq 1:

Biogenic UO_2 reoxidation in the presence of Fe(III) (hydr)oxides has also been shown to proceed even under sulfate-reducing and methanogenic conditions.^{13,18,19,27} Thermodynamically, oxidation of biogenic UO_2 in the presence of Fe(III) (hydr)oxides is favorable only under specific and limited geochemical conditions. For example, ferrihydrite is predicted to promote UO_2 oxidation with elevated bicarbonate levels and low concentrations of Fe(II) and U(VI), while goethite and hematite generally are not expected to promote UO_2 oxidation.^{21,25}

In addition, iron-binding organic compounds have been shown to impact U transformations. Chelating compounds including citrate, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid (NTA) were demonstrated to inhibit bacterial production of UO_2 through formation of soluble U(IV)-organic complexes upon reduction of U(VI) by *Shewanella putrefaciens*.^{14,28,29} Additionally, chelating agents were found to impact reduction and oxidation kinetics of uranium and in some cases influence dissolution of U-bearing minerals.^{30–32} These chelators are present in certain U contaminated settings due to their use as complexing agents in radioactive waste streams,^{33,34} yet the complete nature of their role in U stability remains unclear.

This study examines the effects of Fe(III) (hydr)oxides (ferrihydrite, goethite, and hematite) on reoxidation of biogenically reduced U in the presence of desferrioxamine B (DFB), citrate, NTA, and EDTA. The Fe(III) (hydr)oxides studied vary in reactivity³⁵ and thus drive the reoxidation of UO_2 to different degrees.^{21,36} In addition, the role of bicarbonate on U–Fe(III)–chelator systems was investigated both experimentally and through numerical modeling, due to previous reports of its influence on the reoxidation of UO_2 by Fe(III).¹³ Results presented here provide significant additional insight into U(IV) stability and the potential role of metal chelating agents in long-term U immobilization efforts.

MATERIALS AND METHODS

Biogenic Uraninite. All experiments were performed in an anaerobic chamber (Coy Laboratory Products Inc.) containing a premixed gas of 90% N_2 , 5% H_2 , and 5% CO_2 (by volume). Biogenic UO_2 was synthesized using a slightly modified version of Ulrich et al.²² through the reduction of uranyl chloride (UO_2Cl_2) by *Shewanella putrefaciens* CN32 coupled to lactate oxidation at pH 7. Medium components consisted of the following per 1 L: 30 mmol KHCO_3 , 1.5 μL Wolfe's minerals,³⁷ 10 mmol PIPES, 0.067 mmol KCl, 0.42 mmol MgSO_4 , 0.5 mmol NaCl, 18.7 mmol NH_4Cl , 7.35 mmol KH_2PO_4 , and 30 mmol sodium lactate. Uraninite was produced by adding CN32 cells and 1.375 g UO_2Cl_2 to 1 L of medium in an anaerobic chamber. After 5 d, 10 mmol additional sodium lactate was added to enhance reduction. Following reduction for 12 d, the uraninite product was purified and washed following the method described by Ulrich et al.²² Briefly, the solution was centrifuged and then treated with 1 M NaOH to destroy intact cells, followed by incubation with anoxic hexane to separate any remaining organic matter. Lastly, reduced U was resuspended in 100 mM anoxic KHCO_3 to remove any remaining U(VI) adsorbed on the UO_2 particles and stored in the anaerobic chamber until needed. The U concentration was measured by oxidizing unfiltered samples with concentrated HNO_3 over-

night and analyzing on a kinetic phosphorescence analyzer (Chemcheck Instruments, KPA-11).

Fe(III) (Hydr)oxide Preparation. Ferrihydrite was synthesized as described by Brooks et al.³⁸ Briefly, the pH of a 0.06 M ferric chloride solution was adjusted to 7.5 with 0.4 N NaOH over a period of several hours. Goethite was prepared as described by Atkinson et al.,³⁹ where 1 M NaOH was added to a ferric nitrate solution while being continuously stirred over 3 to 4 h until a pH of 12 was reached. This iron slurry was placed in a 60 °C oven for 24 h, and the salts were removed by dialysis over a period of approximately two weeks. Hematite was synthesized as described by Schwertmann and Cornell,⁴⁰ where 1 M ferric nitrate was slowly added to boiling distilled water over a period of 4 h. The salts were removed by dialysis for approximately two weeks. The goethite and hematite slurry were stored at 4 °C.

Each Fe(III) (hydr)oxide sample was prepared individually. Each iron slurry was then poured onto quartz sand (Iota 6 Quartz Sand, Unimin Corp., 75–300 μm) in separate plastic trays and mixed by hand as described by Brooks et al.³⁸ The sands dried for at least 48 h, after which they were rinsed with nanopure water. Rinsing was repeated until the water being decanted was clear. After rinsing, the iron-coated sands were allowed to dry for at least 12 h. Hematite and goethite were stored at room temperature until needed, while ferrihydrite was stored at room temperature and used within 2 weeks of preparation.

Fe(III) concentrations on the sand were measured by adding concentrated HNO_3 to the iron-coated sand to allow Fe(III) to dissociate from the quartz. Aqueous Fe concentrations were measured on an inductively coupled plasma mass spectrometer (ICP-MS, Agilent). Iron(III) concentrations were approximately 6 ± 0.7 g of Fe(III) per mg of sand.

Aqueous U(VI) and Total Aqueous U. To measure aqueous U(VI) concentrations, samples were extracted from bottles by syringe in the anoxic chamber and filtered (0.2 μm , Fisher). The filtered sample was placed in a scintillation vial and the lid was tightly fastened to prevent air entering the vial. Samples were taken out of the glovebag in groups of approximately seven to ensure no UO_2 oxidation occurred due to atmospheric oxygen (small groups of samples decreased the amount of time outside of the glovebag prior to analysis). The samples were mixed with 0.1 M H_2SO_4 and then added to dilute uraplex (Chemcheck Instruments). H_2SO_4 was used for U(VI) analysis instead of HNO_3 to avoid possible oxidation by nitrate. To minimize exposure time, samples were placed manually in the KPA-11 (Chemcheck Instruments). Calibration curves for the KPA-11 were made with a U standard solution in 5% nitric acid ($1000 \text{ ppm} \pm 10 \mu\text{g mL}^{-1}$, GFS Chemicals, Inc.) diluted in 0.1 M H_2SO_4 ranging from concentration values of 0 μM to 150 μM . All samples and standards were diluted by a factor of 200. Negative KPA-11 responses were regarded as zero. With these conditions, the U(VI) detection limit was 0.2 μM .

To measure total aqueous U concentrations ($\text{U(VI)aq} + \text{U(IV)aq}$), samples were filtered (0.2 μm) and placed in a 3 KDa Nanosep centrifugal device (Pall Life Sciences) in a glovebag and centrifuged (14 565 g) on the benchtop for 15 min to eliminate any solid U that passed through the 0.2 μm filters under anoxic conditions. The filtered sample was then added to concentrated HNO_3 and incubated for at least 1 h to allow any aqueous U(IV) to oxidize to U(VI). The samples were then measured on the KPA-11. The total aqueous U was

measured, and aqueous U(IV) concentrations were calculated by difference. A separate calibration curve was used for total U measurements with the U standard diluted in 0.1 M HNO₃ at concentrations ranging from 0 μ M to 150 μ M. Negative KPA-11 responses were regarded as zero and detection limit was 0.2 μ M (lowest consistent measurable concentration). In reoxidation experiments, the difference between dissolution without oxidation and actual oxidation was determined by measuring U(VI) and U(total) (U(VI)+U(IV)) and calculating U(IV) by the difference. The presence of U(VI) indicated oxidation.

Total Dissolved Iron. Soluble iron concentrations were measured by ICP-MS. Samples were diluted in a 5% trace metal grade HNO₃ (Fisher Scientific) and stored at 4 °C until analysis. Iron standards in 5% HNO₃ were made using an iron reference standard solution (1000 ppm $\pm$ 1) at concentrations ranging from 0 μ M to 895 μ M with a calculated detection limit for iron of 0.179 μ M. Iron(II) measurements using ferrozine were attempted but did not yield any measurable amounts.

UO₂ Dissolution Experiments. Uraninite dissolution experiments investigated the effects of various chelators on dissolution rates of UO₂. Uranium and chelator concentrations were selected based on midrange values found in some contaminated settings. Serum bottles (50 mL) initially contained biogenic UO₂ (125 μ M), 50 mL of 10 mM PIPES buffer at pH 7 with 0.0, 0.1, or 0.2 mM chelator (DFB, citrate, EDTA, or NTA). All media and experimental constituents were purged with N₂ gas until no oxygen remained (approximately 2 h, confirmed by measurement with dissolved oxygen probe). Potassium bicarbonate was added to a final concentration of 10 mM following N₂ purging. Conditions throughout experiments and sampling were maintained as reducing and oxygen-free as possible. Systems with no chelator were used as controls for these experiments. Samples were filtered (0.2 μ m) and analyzed for U(VI). Then, the filtered sample was measured for total dissolved U to calculate aqueous U(IV) concentrations by subtraction (as described above). Separate experiments were conducted in triplicate for each chelator (DFB, citrate, EDTA, and NTA). Error bars represent standard deviation among triplicates. A second set of dissolution experiments investigated the effects of various chelators on solubilization of Fe(III) (hydr)oxides (details are provided in the Supporting Information).

UO₂ Reoxidation Experiments. To investigate the effects of chelating agents on UO₂ reoxidation in the presence of Fe(III) (hydr)oxides, batch experiments were conducted in the same way as the UO₂ dissolution experiments with the addition of 1 g iron-coated sands (approximately 2.5 mM of Fe(III) in each serum bottle). Samples were filtered (0.2 μ m) and analyzed for U(VI) concentrations using the KPA-11 over 80 d. Separate experiments were run with each of the three Fe(III) (hydr)oxides (ferrihydrite, goethite, and hematite) and each chelator (DFB, citrate, EDTA, and NTA). Additional experiments were conducted with each of the chelating agents and Fe(III) chloride to compare the oxidizing behavior of an aqueous form of Fe(III) to that of the Fe(III) (hydr)oxides.

RESULTS AND DISCUSSION

Dissolution Experiments. In these experiments, increased U(VI) concentrations may result from reoxidation of UO₂ or extraction of U(VI) from UO₂ surfaces. Approximately 4% of U in the biogenic UO₂ remained as U(VI) in this study (determined through nitric acid digestion followed by total U and U(VI) measurement as described in the methods section),

consistent with the findings of Ginder-Vogel et al.²¹ In chelator-free control systems, total dissolved U concentrations were below 1 μ M, with virtually no difference between U(VI) and total dissolved U concentrations. Systems with citrate yielded similar results suggesting that citrate did not promote significant UO₂ dissolution nor was it able to appreciably extract adsorbed U(VI). As in the case of experiments with citrate, U(VI) and total dissolved U concentrations in systems with NTA were the same with a maximum value of approximately 3 μ M, suggesting that NTA also did not promote significant U(IV) dissolution. However, comparing chelator-free U(VI) concentrations to systems with NTA shows that NTA slightly increased aqueous U(VI) concentrations. These results suggest that NTA increased the amount of aqueous U(VI) primarily through extraction of U(VI) adsorbed to UO₂ particles and not through dissolution of U(IV) in the UO₂ mineral structure. Figure 1 shows that, in systems with

Figure 1. Dissolution of biogenic UO₂ (black) and ferrihydrite (gray) by citrate, NTA, or EDTA in 10 mM bicarbonate solutions after approximately 80 days showing that both NTA and EDTA promote UO₂ and ferrihydrite dissolution, while citrate promotes ferrihydrite dissolution but not UO₂ dissolution. The extent of dissolution was significantly less with NTA compared to EDTA. Error bars represent the standard deviation of triplicates.

EDTA, U(VI) and total U concentrations increased with increasing concentrations of EDTA. With EDTA, because total dissolved U concentrations were greater (~6 μ M after 80 d) than U(VI) concentrations (~3 μ M after 80 d), it appears that EDTA promoted UO₂ dissolution as U(IV) and also increased aqueous U(VI) concentrations. The addition of either NTA or EDTA promoted some dissolution of U(IV) in the UO₂ mineral with initial rates of 5.5×10^{-2} μ M U d⁻¹ and 2.8×10^{-1} μ M U d⁻¹ for 0.2 mM NTA and EDTA respectively (Table 1).

When comparing the chelator-promoted dissolution of Fe(III) (hydr)oxides and UO₂ in dissolution experiments, the amount of soluble Fe was much greater than soluble U in all cases. In systems with 0.2 mM EDTA, total soluble Fe concentrations were approximately 150 μ M compared to total soluble U concentrations of approximately 6 μ M (Figure 1). When compared to the chelator-free control, EDTA and NTA increased both total dissolved Fe and U.

UO₂ Reoxidation Experiments. The ability of ferrihydrite, goethite, and hematite to reoxidize biogenic UO₂ in the presence of citrate, NTA, or EDTA was investigated. In chelator-free control experiments, UO₂ reoxidation by ferrihy-

Table 1. Average Initial Rates for UO_2 Dissolution Experiments with EDTA and NTA (0, 0.1, or 0.2 mM) with 10 mM Bicarbonate

	avg initial rate (μM total U d^{-1})
0 chelator	0.0×10^0
0.1 citrate	0.0×10^0
0.2 citrate	0.0×10^0
0.1 NTA	7.3×10^{-02}
0.2 NTA	5.5×10^{-02}
0.1 EDTA	1.6×10^{-01}
0.2 EDTA	2.8×10^{-01}

drite was observed with approximately $15 \mu\text{M}$ of U(VI) detected after 80 d, consistent with the results of Ginder-Vogel et al.,²¹ who proposed a mechanism that involves ferrihydrite solubilizing and promoting UO_2 reoxidation through an aqueous Fe(III) intermediate.²⁵

Figure 2 shows the initial rate of UO_2 reoxidation by ferrihydrite in the presence of citrate was 0.88 and $1.8 \mu\text{M}$

Figure 2. Average initial rates for UO_2 reoxidation by ferrihydrite, goethite, or hematite in the presence of no chelator, citrate (cit), EDTA, or NTA (0.1 or 0.2 mM), 10 mM bicarbonate, and PIPES (pH = 7).

$\text{U(VI)} \text{ d}^{-1}$ in systems containing 0.1 and 0.2 mM citrate respectively. Figure 3 expands upon citrate results and shows that citrate did not promote dissolution of UO_2 , suggesting that the reoxidation rate accelerating step is citrate promoting

Figure 3. UO_2 reoxidation in the presence of citrate and ferrihydrite with 10 mM bicarbonate and PIPES (pH = 7) showing that citrate increases the rate of UO_2 reoxidation but not the extent. Error bars represent the standard deviation of triplicates.

dissolution of ferrihydrite, which in turn allows soluble Fe(III) to react with UO_2 , thus promoting U reoxidation. Limited reoxidation was observed with goethite and hematite in the citrate-free control, and U concentrations remained below $2 \mu\text{M}$ with citrate (results not shown). In comparison to ferrihydrite, goethite and hematite are less reactive toward U, likely due to their not being as easily solubilized by citrate, and did not play a significant role in citrate-mediated UO_2 reoxidation.

UO_2 reoxidation in the presence of NTA was more appreciable than with citrate (Figure 4 and 5). NTA solubilized

Figure 4. UO_2 reoxidation in the presence of NTA and ferrihydrite with 10 mM bicarbonate and PIPES (pH = 7) showing that NTA increases the rate of UO_2 reoxidation. Error bars represent the standard deviation of triplicates.

Figure 5. UO_2 reoxidation in the presence of NTA and hematite (▲) or goethite (■) with 10 mM bicarbonate and PIPES (pH = 7) showing that NTA increases the rate of UO_2 reoxidation. Error bars represent the standard deviation of triplicates.

ferrihydrite at an initial rate of $1.1 \mu\text{M Fe d}^{-1}$ but did not solubilize goethite or hematite as efficiently with a maximum initial rate of only $0.029 \mu\text{M Fe d}^{-1}$ (Table S1, Supporting Information). After 80 d with 0.2 mM NTA and ferrihydrite, U(VI) concentrations were approximately $50 \mu\text{M}$ with an initial reoxidation rate of $4.81 \mu\text{M U(VI) d}^{-1}$, while with either goethite or hematite U(VI) was below $20 \mu\text{M}$. In all systems, increased NTA concentration resulted in greater U(VI) values. Heterogenous reaction modeling simulations suggest that this results from a stronger complexation of Fe(II) with NTA than with citrate, favoring reoxidation by lowering the activity of Fe^{2+} in solution (reaction 1), with the formation of Fe(III) chelates computed to be insignificant relative to the Fe(II)

chelates. U(VI) concentrations were highest in systems with ferrihydrite, indicating that (similar to citrate) NTA-promoted reductive iron dissolution as an Fe(II) chelate appears to play a key role in determining the U reoxidation rate.

The rate and extent of UO_2 reoxidation by Fe(III) minerals with EDTA was significantly higher than in systems with either NTA or citrate. During the first week of incubation with 0.2 mM EDTA, aqueous U(VI) concentrations rose to approximately 60 μM . Figure 2 shows initial reoxidation rates of 9.54, 8.56, and 8.81 $\mu\text{M U(VI) d}^{-1}$ for ferrihydrite, goethite, and hematite, respectively. As initial rates with all three minerals were similar, reoxidation in the presence of EDTA appeared independent of the Fe(III) (hydr)oxide present. This could be explained by the complete dissolution of available solid Fe(III) with all three minerals, as suggested by modeling calculations, or by surface passivation of Fe(III) minerals and/or UO_2 particles with Fe(II) and/or U(VI). The maximum observed concentration of soluble U(VI) was dependent on the concentration of EDTA present, with increased EDTA leading to greater U(VI) concentrations. As compared to citrate and NTA, Figure 2 shows EDTA reoxidized UO_2 at a faster initial rate than citrate (initial rate = 1.82 $\mu\text{M U(VI) d}^{-1}$) or NTA (initial rate = 4.81 $\mu\text{M U(VI) d}^{-1}$).

When comparing the three Fe(III) (hydr)oxides in Figure 6, U(VI) concentrations were similar for a given EDTA

Figure 6. UO_2 reoxidation in the presence of EDTA and ferrihydrite (◆), hematite (▲), or goethite (■), with 10 mM bicarbonate and PIPES (pH = 7) showing that EDTA increases the rate of UO_2 reoxidation.

concentration, indicating that EDTA likely dissolved some UO_2 in addition to solubilization of Fe(III) (hydr)oxides. These results support the findings of Ginder-Vogel et al.²⁵ where the authors hypothesized that the rate controlling step in UO_2 reoxidation by Fe(III) (hydr)oxides is interaction through a soluble U(IV) intermediate. Since EDTA increased dissolution rates of both UO_2 and Fe(III) (hydr)oxides (Figure 1), UO_2 reoxidation was more extensive than with citrate, where only iron was solubilized, or with NTA, where iron was solubilized and U(VI) extracted from UO_2 particles.

Iron(III) (hydr)oxide minerals were also tested for their ability to reoxidize biogenic UO_2 in the presence of the siderophore desferrioxamine B (DFB), with 10 mM bicarbonate at pH 7. No reoxidation was observed in any system that contained DFB (results not shown) and Fe(III) (hydr)oxides. A possible explanation for this observation is the high thermodynamic stability of DFB-Fe(III) complexes, which

could tie up Fe(III) such that it is essentially unreactive toward UO_2 . An additional experiment with aqueous Fe(III) and DFB showed no reoxidation with 1:1 Fe(III)_(aq)/DFB and ~25% reoxidation with 2:1 Fe(III)_(aq)/DFB. Note that the other chelators in this study bind less strongly with Fe(III) compared to DFB, which allows more uncomplexed Fe(III) to be available to interact with UO_2 in systems with these chelators.

Of the chelators tested in this study, EDTA promoted the greatest amount of UO_2 reoxidation, followed by NTA. EDTA solubilized all three Fe(III) (hydr)oxides as well as biogenic UO_2 , allowing for over half the total U present (approximately 4 μmol) to be reoxidized within the first week of incubation. Reaction modeling results presented below suggest that the observed progressively stronger UO_2 reoxidation with citrate, NTA, and EDTA at pH 7 results from the formation of progressively stronger complexes of these chelators with Fe(II), and not with U(VI). This could allow for either aqueous Fe(III) or an Fe(III)–EDTA complex to react with the solid uraninite, aqueous U(IV), and/or an U(IV)–EDTA complex. Conversely, citrate and NTA appear more limited in interacting with the Fe(III) minerals (ferrihydrite in most cases), promoting U reoxidation through formation of Fe(II) chelates, and either aqueous Fe(III) or an Fe(III)–chelator complex interacting with solid UO_2 . Additional reoxidation experiments were conducted with Fe(III) chloride and each of the chelating agents to compare the reoxidation trends of a soluble Fe(III) source to those of the Fe(III) (hydr)oxides. Results followed a similar trend as with the Fe(III) (hydr)oxides, where greater rate and extent of reoxidation were observed in the presence of EDTA and NTA compared to citrate and DFB (Figure S2, Supporting Information).

Numerical Modeling. Multicomponent heterogeneous reaction modeling simulations were performed to investigate the oxidation of UO_2 by hematite in systems containing citrate, NTA, and EDTA at equilibrium under a range of pH conditions (Figure 7). These simulations indicate that the increased UO_2 reoxidation near pH 7 in the presence of chelators, 10 mM bicarbonate, and hematite results from the formation of strong Fe(II)–chelator and U(VI) carbonate complexes, rather than from U(VI)–chelator species, following the reactions:

The progressively increasing $\log_{10}(K)$ values of these reactions ($\Delta G = -2.3RT \log_{10}(K)$) imply that on the basis of thermodynamics alone, UO_2 reoxidation at pH ~ 7 should be progressively higher in the citrate, NTA, and EDTA systems, respectively, which is consistent with experimental observa-

Figure 7. Simulated uraninite (as $\text{UO}_2(\text{cr})$) reoxidation by hematite (as $\text{Fe}_2\text{O}_3(\text{cr})$) in systems containing 0.2 mM of either citrate, NTA, or EDTA, and 10 mM KHCO_3 at equilibrium, showing resulting U and Fe speciation, redox conditions (pe) and solution CO_2 partial pressure (P_{CO_2}) as a function of pH. Symbols represent experimental U solubilities at pH 7 for systems containing either hematite (lowest values), goethite, or ferrihydrite (highest values). Dotted lines represent computed total dissolved U and Fe concentrations for systems containing ferrihydrite instead of hematite, resulting in mostly similar speciation (not shown for clarity).

tions. Also, the computed total dissolved U concentrations at pH 7 for the hematite and ferrihydrite systems encompass measured concentrations reasonably well, given the fact that these concentrations span ranges of one or more orders of magnitude depending on pH and the type of Fe(III) solid involved. It should be noted that simulations for a system without chelators were also conducted and indicate solubilities about 1 order of magnitude lower than in the citrate system. Modeling results including input thermodynamic data are further discussed in the Supporting Information.

Implications for U Mobility. Our results reveal important UO_2 reoxidation mechanisms that appear to depend on the thermodynamic stability of chelating agents primarily with Fe(III) and Fe(II). UO_2 reoxidation with DFB was inhibited with ferrihydrite and was undetectable with goethite or hematite, most likely as the result of strong DFB–Fe(III) complexes tying up soluble Fe(III) available for reaction. Such Fe(III) chelated species were predicted to play an insignificant role with the other chelators, except for EDTA at $\text{pH} < 6.5$. In contrast, progressively stronger complexes of citrate, NTA, and EDTA with Fe(II) appear to be driving the progressively more favorable reoxidation by these chelators. Thus, the rate and extent of dissolution of Fe(III) (hydr)oxides and complexation with Fe(II) are likely key mechanisms in UO_2 reoxidation by Fe(III) (hydr)oxides. The rate of UO_2 reoxidation by ferrihydrite increased with citrate (relative to no chelator), but the extent of reoxidation ($< 15 \mu\text{M}$) was not affected. Additionally, with citrate, no UO_2 reoxidation occurred with goethite or hematite. The greatest initial rate and extent of UO_2 reoxidation was observed with EDTA ($\sim 80 \mu\text{M}$ U(VI) detected) and was independent of Fe(III) (hydr)oxide type. NTA had the next highest rate of reoxidation by ferrihydrite with approximately $50 \mu\text{M}$ U(VI) detected. Consistent with our

experimental results and numerical simulations, strong Fe(II) chelators appear to promote the most reoxidation, whereas strong Fe(III) chelators actually promote UO_2 stability. Note that if a chelator was able to facilitate the release of available U(IV) in solution, as suggested by our experimental results for the case of UO_2 dissolution by NTA and EDTA without Fe(III), this could also be a primary contributor to UO_2 dissolution. However, our modeling results suggest that when both UO_2 and Fe(III) are present, chelated U(IV) does not play a significant role in the reoxidation. Additional studies involving more chelating agents (e.g., catechol, additional siderophore compounds) and varying pH values would help to expand on our understanding of these systems. These results demonstrate that it is critical to understand how complexing agents found at U contaminated sites impact the stability of reduced U minerals and ultimately help to predict the fate of U in these settings.

■ ASSOCIATED CONTENT

📄 Supporting Information

XRD analysis, results from aqueous Fe(III)-chelator experiments, table of stability constants, and a more detailed thermodynamic analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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