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U(VI) Reduction by Biogenic and Abiotic Hydroxycarbonate Green Rusts: Impacts on U(IV) Speciation and Stability Over Time

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ABSTRACT

Green rusts (GRs) are redox active Fe^{II}-Fe^{III} minerals that form in the environment via various biotic and abiotic processes. Although both biogenic (BioGR) and abiotic (ChemGR) GRs have been shown to reduce U^{VI}, the dynamics of the transformations and the speciation and stability of the resulting U^{IV} phases are poorly understood. We used carbonate extraction and XAFS spectroscopy to investigate the products of U^{VI} reduction by BioGR and ChemGR. The results show that both GRs can rapidly remove U^{VI} from synthetic groundwater via reduction to U^{IV}. The initial products in the ChemGR system are solids-associated U^{IV}-carbonate complexes that gradually transform to nanocrystalline uraninite over time, leading to a decrease in the proportion of carbonate-extractable U from ~95% to ~10%. In contrast, solid-phase U^{IV} atoms in the BioGR system remain relatively extractable, non-uraninite U^{IV} species over the same reaction period. The presence of calcium and carbonate in groundwater significantly increase the extractability of U^{IV} in the BioGR system. These data provide new insights into the transformations of U under anoxic conditions in groundwater that contains calcium and carbonate, and have major implications for predicting uranium stability within redox dynamic environments and designing approaches for the remediation of uranium-contaminated groundwater.

INTRODUCTION

Uranium (U) is a contaminant at numerous uranium mining, ore processing, nuclear energy, and weapons-related sites. Indeed, nearly 70% of U.S. Department of Energy facilities report groundwater contamination by uranium.[1] The predominant valence states of uranium in groundwater are U^{VI} and U^{IV},[2] and the reduction of soluble uranyl ($U^{VI}O_2^{2+}$) to sparingly soluble U^{IV} forms such as uraninite and non-uraninite U^{IV} species has been explored as a basis for managing uranium mobility at contaminated sites. Past studies have indicated that mixtures of uraninite and non-uraninite U^{IV} species can form as products of U^{VI} reduction in reduced sediments.[3-5] Although some of the factors controlling the formation and stability of non-uraninite U^{IV} species have been determined,[6-8] much remains unknown concerning the effects of ligands and mineral surfaces on U^{IV} speciation and the stability and transformation of the U^{IV} products. Understanding the structure and transformation of these U^{IV} products is crucial for understanding their long-term stability and the processes controlling the fate and mobility of U in natural and engineered environments.

Green rusts (GRs) are mixed-valence Fe^{II}-Fe^{III} minerals found in redox transition zones in a variety of suboxic and anoxic environments including surface waters,[9] groundwater,[10, 11] soils,[12-14] and sediments.[15-17] GRs are redox active and may play a role in the fate and transformation of many organic[18, 19] and inorganic contaminants,[20-23] including uranium. GRs can form via various microbial and abiotic processes under circumneutral to alkaline conditions in suboxic environments.[24-31] Biogenic (BioGR) and abiotic (ChemGR) GRs have different surface properties, attributed largely to sorption of extracellular polymeric substances (EPSs) on BioGRs that passivate their surface, thereby inhibiting their reactivity toward contaminants such as nitrate and methyl red.[32, 33] However, Remy et al. found no significant difference in reactivity between BioGR and ChemGR with respect to the reduction of Hg^{II}.[33] In previous studies, we showed that both abiotic hydroxysulfate GR[34] and biogenic hydroxycarbonate GR[35] can rapidly remove U^{VI} from solution via reduction to U^{IV} in the form of uraninite nanoparticles in batch reactors containing deionized water. Moreover, Latta et al. found that U^{VI} was reduced to monomeric-type U^{IV} species by three different ChemGRs in deionized water containing TAPS buffer, and variable extents of U^{VI} reduction (34% to 100%) were observed for hydroxycarbonate GR with and without TAPS buffer.[36] The chemical speciation of U^{VI} can also have significant effects on its redox reactivity. For example, U^{VI} can form relatively stable and soluble complexes in the presence of calcium and carbonate, which are common constituents in groundwater. The formation of Ca-UO_2-CO_3 complexes is known to limit microbial reduction of U^{VI} to U^{IV};[37] however, the effect of these complexes on the abiotic reduction of U^{VI} by Fe^{II} species is largely unknown.

In this study, we examined the potential differences between BioGR and ChemGR with respect to U^{VI} reduction in synthetic groundwater, particularly the speciation, transformation, and stability of the resulting

U^{IV} species using x-ray absorption fine structure (XAFS) spectroscopy and carbonate extraction. We hypothesized that BioGR and ChemGR affect differently the speciation, transformation, and stability of U^{VI} reduction products based on the presence of organic ligands and presumed differences in surface properties.[32]

MATERIALS AND METHODS

Synthesis of GRs

Experiments were conducted using biogenic and abiotic hydroxycarbonate GR, because hydroxycarbonate GR is the most prevalent form in natural systems;[9, 10, 38] moreover, preliminary experiments demonstrated that hydroxycarbonate GR is more stable than hydroxychloride GR or hydroxysulfate GR in our synthetic groundwater (data not shown), consistent with previous studies of GR stability.[39, 40] The ChemGR was synthesized using the coprecipitation method described by Etique et al.[23] Briefly, 9.341 g of ferrous sulfate heptahydrate and 4.789 g of ferric sulfate hydrate were dissolved in 100 mL of deoxygenated deionized water in an anoxic glovebox (N_2/H_2, 95%/5%), resulting in a ferric molar fraction ($x = [Fe^{III}]/([Fe^{II}] + [Fe^{III}])$) of 0.33. Then 100 mL of a basic solution of 1008 mM NaOH and 588 mM Na_2CO_3 was added to the Fe^{II}–Fe^{III} solution, corresponding to a $[OH^-]/([Fe^{II}] + [Fe^{III}])$ ratio of 2 and $[CO_3^{2-}]/([Fe^{II}] + [Fe^{III}])$ ratio of 7/6. A bluish-green precipitate appeared immediately. The solids were collected by centrifugation and washed three times with sterile, anoxic deionized (DI) water to remove any soluble reactants.

The BioGR was obtained from the bioreduction of lepidocrocite by Shewanella putrefaciens CN32 as described by O′Loughlin et al.[35] BioGR was pasteurized (65 °C for 1 h) to eliminate the potential for microbial reduction of U^{VI} (a control reactor with unpasteurized BioGR was also examined). The BioGR solids were collected by centrifugation and were repeatedly washed with sterile, anoxic water to promote removal of cells, cell debris, and any soluble reductants. Characterization of the ChemGR and BioGR by powder x-ray diffraction (pXRD) both before and after the washing procedure showed no indication of changes in their crystallographic features (Figure S1). Moreover, control experiments comparing unwashed BioGR and washed BioGR did not show differences in U^{VI} removal or U extraction (Figure S2), indicating the washing procedure didn't affect the reactivity of the BioGR. After the final washing, GRs were re-suspended in sterile deoxygenated CO_2-free deionized water.

Experimental Design

Unless indicated otherwise, experimental setup, execution, and sample preparation were conducted under anoxic conditions—typically in sealed containers in a glovebox with 3–5% H_2 in N_2 (O_2 < 1 ppm in the gas atmosphere). The synthetic groundwater (SGW) used in our experiments was formulated to mimic the composition of uranium-contaminated groundwater at the US DOE Hanford site.[41] The SGW was prepared by mixing three stock solutions (14.4 mM $NaHCO_3$ and 1.6 mM $KHCO_3$; 5.1 mM $MgSO_4$ and 1.2 mM $CaSO_4$; and 8.8 mM $CaCl_2$) in DI-water to obtain the following composition: 1.44 mM $NaHCO_3$, 0.16 mM $KHCO_3$, 0.51 mM $MgSO_4$, 0.12 mM $CaSO_4$, and 0.88 mM $CaCl_2$. No precipitates were observed in the SGW and the pH was 7.9. The experimental system consisted of 50-mL polypropylene centrifuge tubes with screw caps containing 40 mL of SGW, U^{VI}, and GR. SGW and U^{VI} were premixed overnight to reach equilibrium before adding the GR slurry. The DI-control system contained 40 mL of anoxic DI-water, U^{VI}, and GR. Reactions were initiated by spiking with the GR slurry to provide final Fe^{II} and U^{VI} concentrations of 60 mM and 1 mM, respectively. Then the slurry was mixed thoroughly with a rotator at 50 rpm. All the reactions and samples were prepared in duplicate. At selected times, an aliquot of the suspension was centrifuged, and the U^{VI} concentration in the supernatant was measured to determine the kinetics of U^{VI} removal from solution. The extractability of U^{IV} was examined using a carbonate extraction approach via the addition of 0.1 mL of suspension to 0.9 mL of anoxic 2 M Na_2CO_3. After 24 h, the mixture was centrifuged, and the supernatant was retained for measurement of extracted U. Our preliminary assessment of carbonate extraction efficiency indicated that 1.8 M carbonate was sufficient to extract the labile U associated with GR solids under our experimental conditions and the extraction efficiency did not change after 24 h of extraction (Figure S3). The solid samples used for XAFS analysis were collected by filtration on 0.22-μm nylon filters, and then the filter membrane with the hydrated solids was sealed with 8.4-μm-thick Kapton film and tape under anoxic conditions.

Analytical procedures

The pXRD analysis was performed with a Rigaku MiniFlex x-ray diffractometer with Ni-filtered Cu Kα radiation. Samples for pXRD analysis were collected by filtration on 25-mm, 0.22-μm nylon filters and covered with 8.4-μm-thick Kapton film under anoxic conditions. The samples were scanned between 5° and 80° 2θ at a speed of 2.5° 2θ min^{-1}. The pXRD patterns were analyzed with the JADE 6 software package (MDI, Livermore, California). The Fe(II) concentrations in the reactors and GR stock suspensions were determined using the ferrozine method[42] after digestion with anoxic 2 M HCl in the anoxic glovebox. Samples for measurement of aqueous U in GR suspensions were prepared via centrifugation at 13,000 g for 2 min inside an anoxic glovebox with 3–5% H_2 in N_2 (O_2 < 1 ppm in the gas atmosphere). Preliminary experiments didn't show any difference in aqueous U concentrations between samples centrifuged then filtered through 0.22 μm membrane filters and samples only centrifuged, therefore subsequent samples were only centrifuged. The aqueous and extracted U^{VI} concentrations in the reactors were measured using a Chemchek kinetic phosphorescence analyzer (KPA-11) following the procedure developed by Sowder et al. and Dong et al.[43, 44] Selected samples were also analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The data obtained by these two methods were consistent, with a difference always less than 6%. The speciation of U in the solid phases of the reactors was analyzed by x-ray absorption spectroscopy at sectors 10-ID and 10-BM of the Advanced Photon Source, using a setup described in more detail in the Supporting Information (SI).[34-36] Briefly, x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS) scans at the U L_{III} edge (17,166 eV) were collected in quick scanning mode (3 min each). The final spectrum was produced by averaging 30–50 quick EXAFS scans. The data were processed using ATHENA, and the contributions of distinct U^{IV} species in the EXAFS spectra were quantified using linear combination (LC) fitting.[45] Previously measured spectra from a nanoparticulate uraninite standard and U^{IV}-carbonate complexes were used as end members.[6] Additional details of the XAFS data collection and analysis are provided in the SI.

RESULTS AND DISCUSSION

U^{VI} removal by GR

U^{VI} was rapidly removed from solution in both the ChemGR and BioGR systems (Figure 1). Since the total U concentration in the systems were supersaturated with respect to schoepite, it is possible that the loss of U^{VI} from solution could be due in part to precipitation of a U^{VI} phase such as schoepite. However the aqueous U^{VI} concentrations remained stable at ~1000 µM in the control systems without GR (Figure 1) and there was no visual indication of precipitate formation over the period of observation; thus the rapid initial removal of U^{VI} can be attributed to uptake by GR. In the DI-water control system, over 99% of U^{VI} was removed within 5 min by ChemGR and BioGR, which is comparable to the results reported by O'Loughlin et al.[35] In the SGW system, U^{VI} was also rapidly removed from solutions by ChemGR and BioGR, indicating both GRs are likely to be effective for removal of U^{VI} from groundwater even in the presence of calcium and carbonate. There was no significant difference in the kinetics of U^{VI} removal from solution between ChemGR and BioGR. This is similar to the result in Remy et al., which showed no significant difference between ChemGR and BioGR with respect to Hg^{II} reduction.[33]

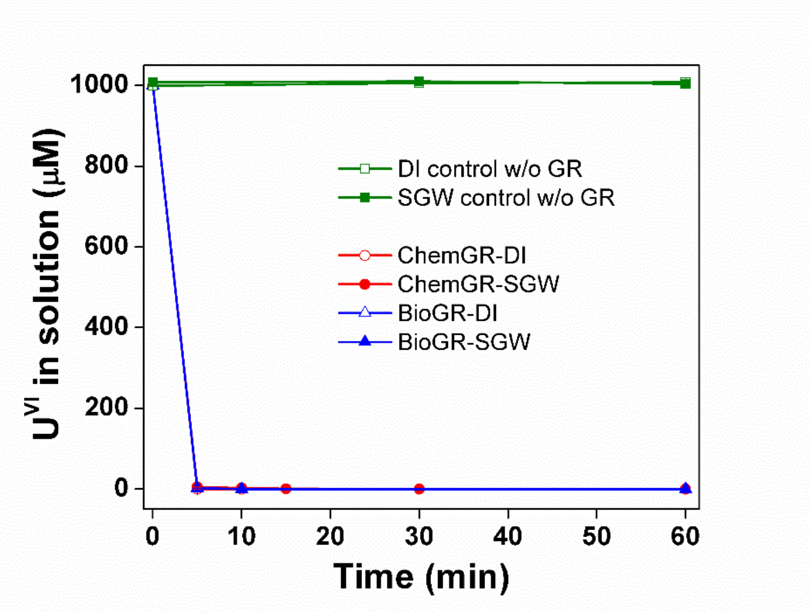

Figure 1. Removal of U^{VI} from solution by ChemGR and BioGR in deionized water (DI) and synthetic groundwater (SGW) systems.

U^{VI} Is Reduced to U^{IV} by GR

U L_{III} edge XANES spectra (Figure 2) show that under all experimental conditions the U associated with the solids is predominantly U^{IV}. The edge energy position and the spectral shape of all XANES spectra are similar to the U^{IV} standard, indicating that over 95% of the U in the solid phase is U^{IV}. Small amounts of U^{VI} were observed only in the 1 h BioGR samples from the DI-water and SGW systems (small shoulder near 17,180 eV in Figure 2), which were quantified as ~17% of solid-phase U based on LC fits of the XANES data with U^{IV} and U^{VI} standards (analysis not shown). Together with the similar and rapid uptake kinetics in all systems (Figure 1), the XANES results suggest that an adsorption step occurring on the timescale of minutes is followed by a fast (<1 h) reduction of U^{VI} to U^{IV}. Similar uptake profiles (i.e., rapid uptake followed by reduction) have been observed in previous studies with GR, as well as with other Fe^{II} phases.[35, 36, 46-48]

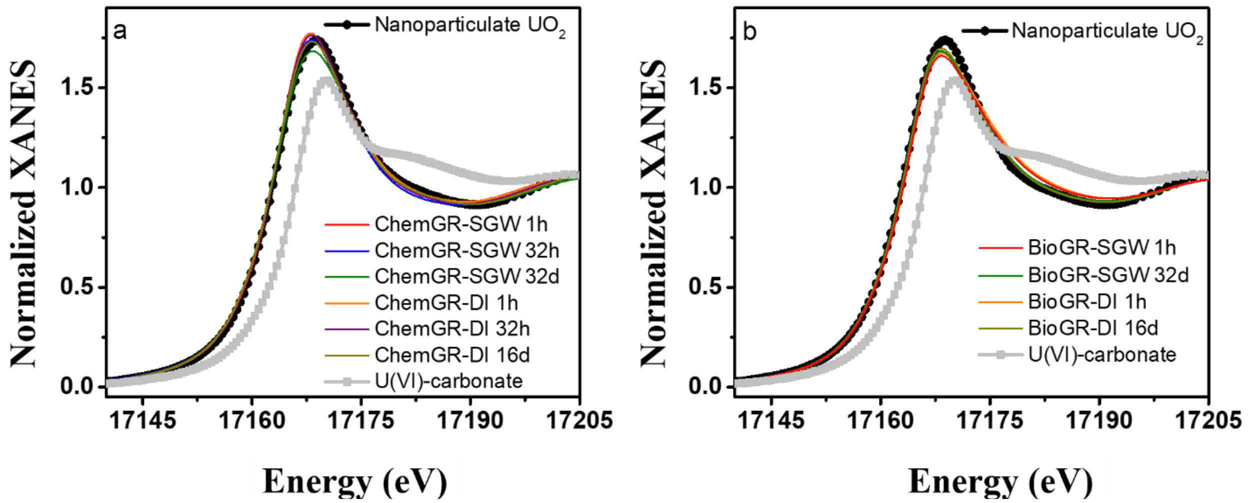

Figure 2. U L_{III} edge XANES spectra for (a) ChemGR and (b) BioGR at various times in deionized water (DI) or synthetic groundwater (SGW) systems compared with U^{IV} and U^{VI} standards.

Extraction of U by Carbonate in the ChemGR and BioGR Systems

Carbonate has been shown to extract U associated with mineral and biological solids, in both the U^{VI} [49-51] and the U^{IV} valence states.[5, 51] The latter studies also showed that U^{IV} is less extractable when present as uraninite relative to the more labile monomeric species (e.g., adsorbed or ligand-complexed U^{IV}). The XANES results indicate that U^{VI} was reduced to U^{IV} in both the ChemGR and BioGR reactors and we used a 1.8 M carbonate extraction method to evaluate the relative stability of U^{IV} in these two systems. As shown in Figure 3, the pool of labile (i.e., carbonate-extractable) U is significantly larger in the BioGR system than in the ChemGR system. The pools of extractable U in both systems gradually decreased over time until they reached steady state, suggesting that the U^{IV} species aged to a more stable form over a period of days. For instance, in SGW, about 85% of the U in the solids could be extracted in the BioGR system after 24 h, but after 4 d of reaction the carbonate-extractable U decreased to 70% and remained unchanged over the following 28 d. Similarly, in the ChemGR system about 50% of U in the solids could be extracted after 24 h, only 30% after 4 d, and only 10% after the system reached steady state at 16 d. In the reactors with BioGR, more U was extractable in SGW than in the DI-water control, which suggests that the presence of calcium and carbonate during U^{VI} reduction by BioGR increased the extractability of U in the system. In contrast, the ChemGR systems showed no significant difference in U extractability between the DI-water and SGW solution conditions.

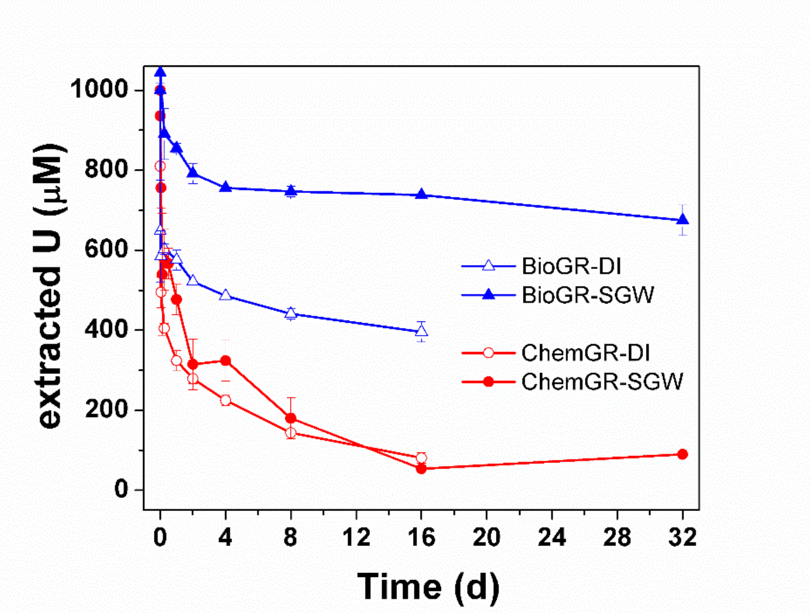

Figure 3. Changes in carbonate-extractable U over time in ChemGR and BioGR systems with deionized water (DI) or synthetic groundwater (SGW). The error bars denote the standard error of measurements made on duplicate bottles.

When interpreting the lability of solid-phase U^{IV} to carbonate extraction we need to consider the valence state of U released in solution. Stoliker et al.[5] concluded that anoxic carbonate extractions of U^{IV} resulted in dissolved U^{VI} and suggested that the change in thermodynamic conditions promoted back-transfer of electrons from U^{IV} to Fe^{III} in the same sediment matrix that originally reduced U^{VI}. It is possible that U^{IV} reoxidized to U^{VI} here as well, since the 1.8 M Na_2CO_3 added during extraction significantly increased the pH values in the SGW ChemGR and BioGR systems from 8.4 to 11.9 and from 8.0 to 11.8, respectively, and the Eh increased from -674 mV to -471 mV, and from -706 mV to -507 mV, respectively. Figure S4 presents the XANES data from the carbonate extraction supernatants, showing that predominantly U^{VI} was released in solution. We observed the same U concentrations by kinetic phosphorescence analysis before and after oxidation of the extraction supernatants in air (data not shown), also showing that predominantly U^{VI} was present in the extracts. Both of the above suggest that the change in solution conditions caused by the addition of carbonate resulted in the reoxidation of solids-associated U^{IV} leading to the release of U^{VI}. However, the possibility that U^{IV} was first removed from the solids as U^{IV}-carbonate complexes and then reoxidized as a soluble species by contact with Fe^{III} cannot be excluded by the current data. Thus, the data in Figure 3 may indicate either susceptibility of the reduced U^{IV} phases to oxidation under the conditions of the extractions or susceptibility of U^{IV} to complexation by carbonate, if the latter is the rate determining step in the observed oxidative release. Regardless of the actual oxidation mechanism during extraction, the different extractability of U^{IV} in the ChemGR and BioGR systems suggest differences in the initial U^{IV} speciation of U^{IV} produced in these two systems, as confirmed by the EXAFS results below.

U Speciation in the ChemGR and BioGR Systems

The observed differences in U^{IV} extractability suggest differences in U^{IV} speciation between the ChemGR and BioGR systems. We used EXAFS spectroscopy to examine the molecular structure around the U^{IV} atoms in both systems. In the ChemGR system, the EXAFS spectra show systematic trends as a function of reaction time, in both the SGW (Figure 4) and the DI-water control (Figure S5) systems. Specifically, the Fourier transform (FT) of the EXAFS data for the 1-h reaction time samples lacks significant amplitude around $R + \Delta = 3.7$ Å, where the U coordination shell contributes in the uraninite standard. The experimental spectra from the 1 h samples closely resemble that of a previously characterized U^{IV}-carbonate complex produced by bacteria,[6] both in the phase and amplitude of the $\chi(k)$ data, as well as in the features of the FT (Figures 4 and S5). The spectral resemblance suggests that U^{IV} in the ChemGR system has the same local structure as this previously characterized U^{IV}-carbonate complex,[6] but is possibly associated here with the minerals in our system as a ternary or an outer-sphere surface complex. There is a consistent increase in the amplitude of the U peak with reaction time, and the samples at 16 d and 32 d approach the nanoparticulate uraninite standard. The real part of the FT EXAFS also approaches the uraninite standard over the duration of the reaction, showing an increase in the U signal and a slight decrease in the bond distance of O in the first shell (Figures S6 and S7). These spectral trends suggest that initially the entire budget of U associated with the solid phase of ChemGR is predominantly in a U^{IV}-carbonate complex, which then gradually transforms to a predominant nanoparticulate uraninite phase over the 32-d reaction period.

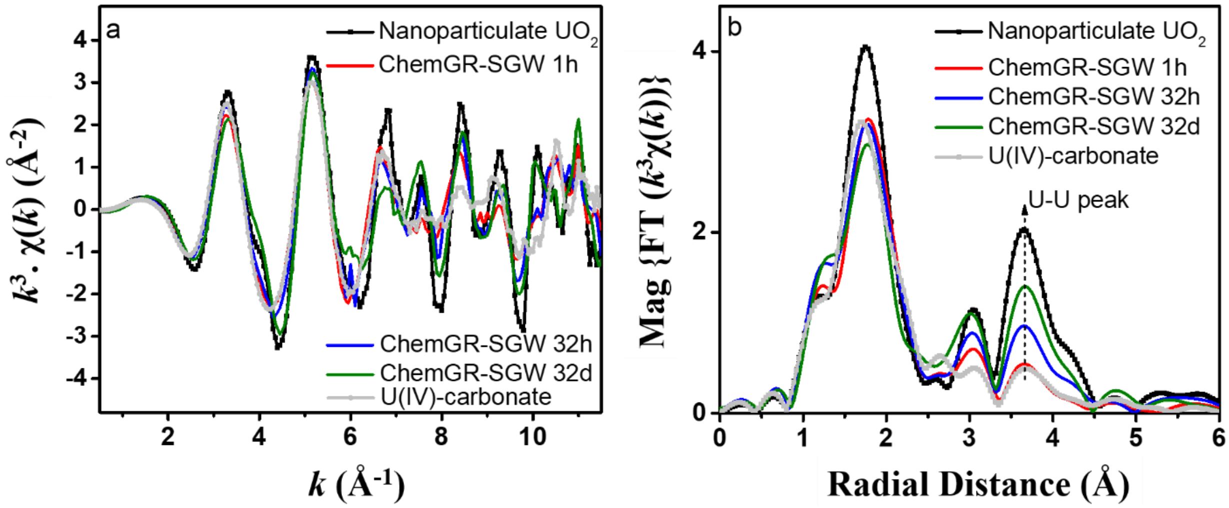

Figure 4. U L_{III} edge (a) k^3-weighed EXAFS data and (b) Fourier transformed (FT) EXAFS spectra for ChemGR in the synthetic groundwater (SGW) system after 1 h, 32 h, and 32 d, compared with nanoparticulate uraninite and U^{IV}-carbonate standards. The vertical dashed line indicates the peak in the FT EXAFS resulting from the contribution of the U shell in uraninite. The FT is within the data range k = 2.2–10.4 Å^{-1} using 1.0-Å^{-1}-wide Hanning windowsills. Significant spectral similarity is evident between the 1 h sample (red line) and a previously characterized U^{IV}-carbonate complex[6] (grey symbols).

The proportions of solid-phase U species suggested by the qualitative analysis were quantified by LC fitting of the EXAFS spectra. We used previously characterized spectra of nanoparticulate uraninite and a U^{IV}-carbonate complex as end members.[6] The data from the ChemGR systems after 1 h, 32 h and 32 d indicate an increasing contribution of the uraninite phase from 8% to 25% to 77% in SGW and from 24% to 33% to 75% in DI-water (Table S1) and a general trend of a higher proportion of uraninite in the DI-water system compared to the SGW system. However, the difference between the two solution conditions is within the uncertainty associated with the LC analysis (~10%), so uraninite formation in the SGW system is inhibited only within the first hour of reaction time. Similar proportions of adsorbed U^{IV} species and nanoparticulate uraninite were observed in the previous study by Latta et al.,[36] in which chemogenic carbonate-GR was reacted with U^{VI} in DI water for 3–4 days (58% uraninite, LC analysis shown in Figure S8). Taken together, the carbonate extraction data (Figure 3) and the LC analysis support a reaction sequence whereby an initial labile U^{IV}-carbonate species is formed following the electron transfer between ChemGR and adsorbed U^{VI}, which then transforms over time to a more stable (i.e., less extractable) nanoparticulate uraninite form.

The behavior of U^{IV} in the BioGR system is significantly different compared to its behavior in the ChemGR system. The U EXAFS data in the BioGR system are the same for the 16-d and 32-d samples in DI water and SGW (Figure S9), which indicates lack of evolution of the U^{IV} species over the reaction period and lack of dependence of the U^{IV} product on solution conditions. The 32-d BioGR-SGW spectra were highly reproducible for the pasteurized sample and the unpasteurized control, which suggests that biological processes did not play a role in the final U^{IV} speciation. The spectrum with the best signal-to-noise ratio (BioGR-SGW, 32 d) was used for comparison to U^{IV} standards and for structural analysis. The spectra of the standards were collected previously at the same beamline and include nanoparticulate uraninite,[6] aqueous U^{IV} obtained by dissolving UO_2 in 0.5 M sulfuric acid,[52] monomeric U^{IV} complexed to magnetite,[52] U^{IV} complexed to phosphate, and U^{IV} complexed to biomass without phosphate.[6, 53] Data comparisons (not shown) between the BioGR sample and the aqueous U^{IV} standard or U^{IV} complexed to magnetite indicated significant differences, allowing exclusion of an outer-sphere surface complexation mechanism or the inner-sphere complexation mechanism with increased U^{IV}-O coordination (9–10 O atoms) such as that observed previously for magnetite.[52] The position and amplitude of the main O peak in the FT EXAFS of the BioGR sample (Figure 5) is similar to that in the standards with 8-coordinated U^{IV}. The lack of a U-U backscattering signal near R + Δ = 3.8 Å in the BioGR data (Figure 5) excludes nanoparticulate uraninite as the predominant U^{IV} phase (in other words, <10% of total U may be present as uraninite). When compared to the spectra of U^{IV} associated with biomass in the presence and absence of phosphate,[6] the BioGR spectrum lacks the features assigned previously to complexation of U^{IV} by a phosphate or a R-COO group (indicated by P and C in Figure 5). The BioGR spectrum is nearly identical to that of U^{IV} produced in a previous study by reacting U^{VI} in TAPS buffer with chemically synthesized GR.[36]

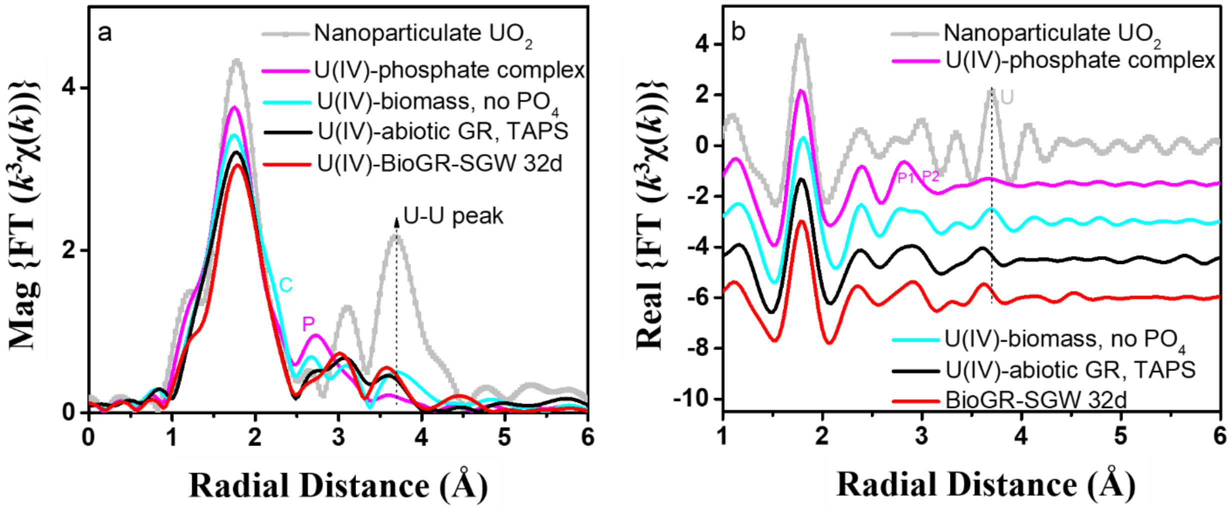

Figure 5. Comparison of the EXAFS data from the BioGR system to U^{IV} standards. (a) Magnitude of the Fourier transformed k^3-weighed EXAFS data; (b) real part of the Fourier transformed k^3-weighed EXAFS data. The shoulder in the first shell of the FT magnitude spectrum of the U^{IV}-biomass standard, representing the contribution of C, and the peak where P atoms contribute in the spectrum of the U^{IV}-phosphate standard are indicated, as determined from previous analyses.[6] The vertical dashed line indicates the signal from the U backscattering atom in uraninite. P1 and P2 indicate the approximate positions of the signals from the bi- and mono-dentate bound phosphate groups. The spectrum of U^{IV} in the abiotic GR TAPS buffer system is taken from Latta et al.[36] The Fourier transform is within the data range k = 2.2–10.4 $Å^{-1}$ using 1.0-$Å^{-1}$-wide Hanning windowsills.

In light of the similarity between the U+BioGR data and the data from U+chemical GR in the TAPS buffer from Latta et al.,[36] the EXAFS model from that work was applied to fit the U+BioGR data. The model included a near-neighbor O shell, an Fe shell, and an outer O shell, and produced the best simultaneous fit of the data at k-weights of k^1, k^2, and k^3 in the Fourier transform (Figure S10 and Table S2). The refined parameters show that the average U-O distance in the BioGR system is 2.35 ± 0.01 Å, which is similar to the U-O distance in 8-coordinated U^{IV} species such as nanoparticulate uraninite (2.32 ± 0.01 Å) and phosphate-complexed U^{IV} (2.33 ± 0.01 Å), but significantly shorter than that of 9–10 coordinated U^{IV} species such as aqueous U^{IV} or U^{IV} adsorbed to the =FeO sites in magnetite (2.42 ± 0.02 Å).[52] The lower amplitude of the O-shell peak in the BioGR data relative to nanoparticulate uraninite or phosphate-complexed U^{IV} results from a slight decrease in average coordination number and a slight increase in the disorder (Debye-Waller factor) relative to the standards. Attempts to model the BioGR data with the second shell U paths used to fit the nanoparticulate uraninite data indicated that the signal between $R + \Delta = 3.0$–4.0 Å is inconsistent with U. Similarly, EXAFS modeling efforts based on the ningyoite $CaU^{IV}(PO_4)_2$ structure representing U^{IV}-phosphate complexation were also unsuccessful.[6, 54]

The refined structural model with an O, Fe, and O coordination shells is consistent with adsorption of U^{IV} to the brucite layer in the GR structure or possibly to other Fe transformation products in the system, rather than complexation to the carbonate anions in the interlayer or to residual biological components in the BioGR system. Association of U^{IV} with Fe redox products has been observed before in laboratory and natural systems.[3, 55] The nearly identical U EXAFS data in the BioGR system here and in chemical GR systems studied previously[36] (Figure 5) also suggest U^{IV} association with the iron oxides rather than with a biological component. However, it should be noted that the adsorbed U^{IV} species in the carbonate GR reactors of Latta et al.[36] were observed only in the presence of TAPS buffer, whereas significant nanoparticulate uraninite formation occurred in DI water (LC fit shown in Figure S8). Thus, although carbonate GRs adsorb U^{IV} atoms at the ≡FeO sites, the stability of adsorbed U^{IV} with respect to desorption and uraninite formation appears dependent on the presence of residual organic components or buffers. Recent studies have also identified U^{IV}-organic matter complexation in field samples.[56] This indirect effect of organic molecules on the stability of reduced U is important in an environmental context and needs to be elucidated in further studies with controlled addition of organic matter. Stabilization of non-uraninite U^{IV} in biogenic GR reactors was also observed in the previous study by O'Loughlin et al.[35] Although the EXAFS data were interpreted at the time as a highly disordered uraninite phase, a comparison between the BioGR data here and in the previous study[35] reveals that the data are the same within measurement uncertainty (Figure S11). Thus, the analysis and conclusions presented above can be directly applied to the data in O'Loughlin et al.[35] An EXAFS model with O, Fe, and O shells that is conceptually similar to the U^{IV} adsorption mechanism determined in our study was also fit to the data from monomeric U^{IV} in magnetite solids at low U:magnetite ratios.[52] However, the U-O and U-Fe distances refined for the BioGR samples are significantly shorter than in the U^{IV}-magnetite complexes (2.35 Å vs. 2.42 Å, and 3.49 Å vs. 3.59 Å, respectively). This indicates a different binding mechanism of U^{IV} to BioGR relative to that in magnetite and suggests that the arrangement of the ≡FeO sites plays a significant role in the complexation of U^{IV} to iron oxide surfaces.

Based on the speciation for the BioGR and ChemGR systems, the persistence of adsorbed U^{IV} species in the BioGR system over the 32-d reaction period can explain their consistently high extractability with carbonate (Figure 3), whereas the transformation of adsorbed U^{IV} to uraninite in the ChemGR system can explain the significant decrease in U^{IV} extractability over time. Figure 3 also reveals a relatively higher extractability of U^{IV} in SGW compared to the DI-water samples within the BioGR system. However, the EXAFS data show no significant differences in the U spectra between the BioGR reactors (Figure S9). This suggests that the molecular structure of U alone cannot explain the observed differences in U extractability. It is possible that components of the SGW solution affect U speciation in the BioGR system in a way that is not apparent in the EXAFS spectra (e.g., outer-sphere complexation) or that the different solution compositions affect particle size or aggregation and thus the ability of carbonate to reach and extract the

U^{IV} complexes. It is also possible that interaction between the biological components and DI water versus SGW affects the efficiency of the carbonate extraction of the same U^{IV} species.

Environmental implications

The reduction of soluble uranyl to less soluble U^{IV} species is a key process in the biogeochemistry of U in both natural and engineered environments under suboxic to anoxic conditions. However, U is not typically present at high enough concentrations to control the redox state of a given environment, therefore the reduction of U^{VI} is often coupled to that of a more abundant redox active element such as Fe. As previously mentioned, GRs have been identified in Fe^{III}/Fe^{II} transitions zones in a variety of natural environments[9, 11-17] and engineered systems such as Fe^0 permeable reactive barriers[57, 58] where due to their effectiveness as reductants for U^{VI}, they may play a role in U speciation thereby impacting U fate and transport in these environments. Our results showing differences in the speciation of the U^{IV} products resulting from the reduction of U^{VI} by biogenic GR compared to chemogenic GR as well as previous studies demonstrating differential reactivity between biogenic and chemogenic Fe^{II} phases,[32, 33, 47 59] highlight the importance of identifying the processes leading to the in situ formation of these reactive species in understanding their potential role in contaminant fate and transport. However, contaminant speciation also plays a critical role. Calcium and carbonate are ubiquitous components in U-contaminated groundwater. According to equilibrium thermodynamic calculations, U^{VI} can form stable ternary calcium-uranyl-carbonate complexes in groundwater that contains calcium and carbonate.[44] Theoretically, the stable ternary complex of U^{VI} is a less thermodynamically favorable electron acceptor than the uranyl hydroxyl complex, which leads to a decrease in the rate and extent of U^{VI} reduction.[44, 50] Previous studies demonstrated that the presence of calcium and carbonate at millimolar concentrations can cause a significant decrease in the rate and extent of bacterial U^{VI} reduction.[37,60] However, our results show that the potential for formation of ternary calcium-uranyl-carbonate complexes did not have an observable effect on the rate or extent of reduction of U^{VI} by ChemGR and BioGR in synthetic groundwater containing calcium and carbonate. Thus, GRs (whether synthetic or the product of microbial Fe redox transformations) could provide a more effective means of reducing the concentration of uranium in contaminated groundwater than anaerobic U^{VI}-reducing bacteria.

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SUPPORTING INFORMATION AVAILABLE

The Supporting Information includes pXRD patterns of ChemGR and BioGR, a comparison of the reactivity of washed and unwashed BioGR, assessments of carbonate extraction efficiency, details of XAFS data collection and analysis, and supplemental XAFS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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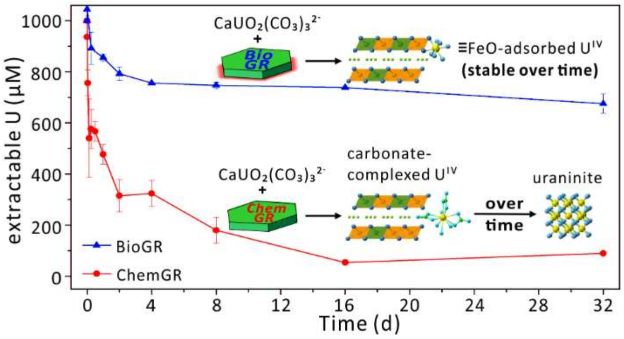

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