Characterization of U(VI)-carbonato ternary complexes on hematite: EXAFS and electrophoretic mobility measurements

JOHN R. BARGAR,1,2* REBECCA REITMEYER,2 JOHN J. LENHART,2 and JAMES A. DAVIS2

1Stanford Synchrotron Radiation Laboratory, PO Box 4349, Stanford, CA 94309, USA
2US Geological Survey, Water Resources Division, 345 Middlefield Rd., MS 465, Menlo Park, CA 94025, USA

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Abstract—We have measured U(VI) adsorption on hematite using EXAFS spectroscopy and electrophoresis under conditions relevant to surface waters and aquifers (0.01 to 10 µM dissolved uranium concentrations, in equilibrium with air, pH 4.5 to 8.5). Both techniques suggest the existence of anionic U(VI)-carbonato ternary complexes. Fits to EXAFS spectra indicate that U(VI) is simultaneously coordinated to surface FeO6 octahedra and carbonate (or bicarbonate) ligands in bidentate fashions, leading to the conclusion that the ternary complexes have an inner-sphere metal bridging (hematite-U(VI)-carbonato) structure. Greater than or equal to 50% of adsorbed U(VI) was comprised of monomeric hematite-U(VI)-carbonato ternary complexes, even at pH 4.5. Multimeric U(VI) species were observed at pH 6.5 and aqueous U(VI) concentrations approximately an order of magnitude more dilute than the solubility of crystalline β-UO2(OH)2. Based on structural constraints, these complexes were interpreted as dimeric hematite-U(VI)-carbonato ternary complexes. These results suggest that Fe-oxide-U(VI)-carbonato complexes are likely to be important transport-limiting species in oxic aquifers throughout a wide range of pH values.

1. INTRODUCTION

Uranium is a common soil and aquifer contaminant of concern at nuclear waste management facilities, uranium mining and milling sites, and heavy industry sites in the US and numerous other locations around the world. The most significant pathway for human exposure to uranium is via groundwater transported away from such sites, and evaluation of societal risks posed by such contamination rests upon assumptions about uranium transport in groundwater. Uranium mobility in oxic groundwater is believed to be controlled by adsorption of U(VI) on mineral surfaces (Hsi and Langmuir, 1985; Langmuir, 1978). Fe oxides are believed to be of particular importance due to their high sorptive capacities for uranium, high surface areas, and common occurrence as grain coatings (Waite et al., 1994; Waite et al., 1992). Fe oxide grain coatings, often formed by weathering processes, have been shown to be important metal-ion-adsorbing phases even in Fe-poor aquifers (Coston et al., 1995). Dissolved carbonate also plays a major role in U(VI) subsurface transport because of its great affinity to form aqueous complexes with U(VI) (Grenthe et al., 1992) and its ubiquity in groundwaters. Carbonate often occurs at concentrations 100 to 1000 times greater than that expected from equilibrium with air (Hem, 1989). Several groups (Hsi and Langmuir, 1985; Ho and Miller, 1986; Waite et al., 1994; Duff and Amrhein, 1996; Lenhart and Honeyman, 1999) have speculated that U(VI)-carbonato complexes adsorb on Fe oxides (i.e., forming Fe oxide-U(VI)-carbonato ternary complexes), greatly retarding U(VI) transport.

Much work is needed to develop accurate estimates of distribution coefficients for U(VI) transport in groundwater. Aqueous carbonate concentrations typically vary temporally and spatially along hydrologic gradients in aquifers. Linear distribution coefficients that traditionally have been used to quantify adsorption are inadequate under such conditions, and coupled chemical and transport modeling is necessary (Davis and Kent, 1990; Kohler et al., 1996). These approaches require knowledge of the compositions and reaction stoichiometries of adsorbate species. However, the existence of Fe oxide-U(VI)-carbonato ternary complexes under environmentally relevant conditions has only recently been demonstrated (Bargar et al., 1999). Very little is known about their compositions and reaction stoichiometries. Waite et al. (1994) postulated that such complexes would be important mostly at pH values > 7. Duff and Amrhein (1996) suggested that U(VI)-carbonato ternary complexes should adsorb weakly on goethite (α-FeOOH). In the absence of direct observations of adsorbed U(VI) species, these hypotheses cannot be tested. Spectroscopic measurements of adsorbed U(VI) species, performed in parallel with macroscopic chemical measurements, are necessary to define the pH dependence and adsorption reactions of ternary surface-U(VI)-carbonato complexes.

In this paper, we present results of U LIII-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and electrophoretic mobility measurements of U(VI)-carbonato complexes adsorbed on hematite. EXAFS measurements provide element-specific short-range structural and chemical information for U(VI) coordination environments, including identities of, coordination numbers of, and bond distances to neighboring atoms. Electrophoretic mobility measurements provide information regarding the net charges on hematite surfaces, constraining interpretation of the EXAFS results. The objectives throughout these experiments were to define the compositions and reaction stoichiometries of U(VI)-carbonato complexes on hematite throughout the pH range of uranyl uptake under conditions relevant to aquifers.

Previously, Hsi and Langmuir (1985) described U(VI) ad-

*Author to whom correspondence should be addressed (bargar@slac.stanford.edu).
sorption on amorphous and crystalline Fe-(oxyhydr-)oxides in carbonate-bearing solutions with a site-binding surface complexation model that included ternary U(VI)-carbonato complexes. Ho and Miller (1986) observed that hematite particles, which were positively charged in near- and sub-neutral pH carbonate-bearing solutions (i.e., at pH < 7.5), acquired net negative charges following adsorption of U(VI). They attributed this charge reversal to the presence of negatively charged U(VI)-carbonato-hematite complexes. Waite et al. (1992) and Waite et al. (1994) postulated the existence of ternary complexes to model U(VI) adsorption on ferrhydrite. They found that models not having this species underpredicted U(VI) uptake between pH 7 and 9. Furthermore, the degree of underprediction of U(VI) adsorption in this pH range increased with P<sub>CO2</sub>. Manceau et al. (1992), and Waite et al. (1994) used EXAFS to study U(VI) adsorption on ferrhydrite (amorphous Fe<sub>2</sub>O<sub>3</sub>xH<sub>2</sub>O), but did not report any findings regarding carbonate ligands. Dent et al. (1992) reported evidence for carbonate neighbors for U(VI) adsorbed on montmorillonite (aluminosilicate) clays at ca. pH 4 under conditions of high initial dissolved uranium (5 mM) and without control of P<sub>CO2</sub>. Bargar et al. (1999) reported evidence for the existence of adsorbed U(VI)-carbonato complexes on hematite. The results presented in the current paper (including electro- phoretic mobility measurements and systematic constant-pH constant-<i>[U(VI)]</i><sub>T</sub> studies) forcibly argue that adsorbed U(VI)-carbonato species are ternary complexes (i.e., bonded directly to hematite surfaces) having metal-bridging structures. Synthesis of this information leads to proposed compositions for hematite-U(VI)-carbonato ternary complexes. In addition, evidence is presented for the existence of multimeric U(VI) complexes.

2. MATERIALS AND METHODS

2.1. Materials

Hematite powders used in these experiments were synthesized from Fe(CIO<sub>3</sub>)<sub>3</sub>, following the method of Matijevic and Scheiner (1978) as described in Bargar et al. (1997b). This procedure was reported to produce clean hematite surfaces, having only Fe, O, and adventitious carbon, as measured by XPS, N<sub>2</sub>-BET surface areas of the dried powders were 32.8 m<sup>2</sup>/g (uptake kinetics measurements) to 46.1 m<sup>2</sup>/g (EXAFS, electrophoretic mobility samples). Powder XRD showed it to be crystalline α-Fe<sub>2</sub>O<sub>3</sub>, with no evidence for goethite. Diffuse re- flectance FTIR (DR-FTIR) spectra of the hematite showed no evidence of goethite-specific peaks.

2.2. Sample Preparation

Within this paper U<sub>T</sub> is defined as the total concentration (molarity) of all U(VI) species, dissolved and adsorbed, in the system, and U<sub>eq</sub> is defined as the sum of all aqueous U(VI) species (molarity) at the final pH of the sample equilibration and excludes adsorbed U(VI) species. All solutions were prepared from 18 megaohm Milli-Q water. A 0.01 M U(VI) stock solution was prepared from isotopically depleted UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O reagent (Johnson-Matthey). Adsorption experiments were designed so that, whenever possible, [U<sub>T</sub>] would be less than the solubility of crystalline β-UO<sub>2</sub>(OH)<sub>2</sub> (about 2 μM at pH 6.2 and in equilibrium with air), which should be the most insoluble U(VI) solid phase in this system at the experimental conditions described herein (Grenthe et al., 1992; Silva et al., 1995).

<i>Uptake Kinetics Measurements:</i> Hematite was transferred to two 500 mL Erlenmeyer flasks with enough Milli-Q water to achieve 0.2 g/L, and ultrasound was used for a few minutes to disperse the hematite. Flasks were adjusted to the desired pH using HCl or NaOH. When the pH had stabilized, 0.01 M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> stock solution (at pH 3) was added to each flask to achieve 1 μM [U<sub>T</sub>]. No ionic strength control was used. Samples were stirred vigorously with Teflon-coated magnetic stir bars at all times, and water-saturated air was bubbled through samples in order to maintain equilibrium with atmospheric CO<sub>2</sub>. Samples were transferred to 35 mL polycarbonate centrifuge tubes and placed on an end-over-end rotator for specified lengths of time (Fig. 1), after which the final pH was measured, and the samples were centri- fuged at 19,000 RPM (43,140 g RCF) for 15 min. Final pH values were 4.01 ± 0.01 and 8.89 ± 0.04. Aliquots were taken and acidified using 0.1 N HNO<sub>3</sub>, and analyzed for [U<sub>eq</sub>] using kinetic phosphorescence analysis (KPA, Chemchek Instruments). KPA calibration curves were linear over the range measured. The detection limit was 60 ppt uranium.

<i>EXAFS Measurements:</i> [U<sub>T</sub>] was set at about 12 μM for most EXAFS in order to achieve adsorption densities of 0.25 to 0.5 μmol/m<sup>2</sup> necessary to obtain usable spectra at Stanford Synchrotron Radiation Laboratory (SSRL) beamline 4 using sample volumes ≤ 2 L. Dried hematite powder and NaNO<sub>3</sub> were weighed into either 500 mL or 1 L HDPE bottles and milli-Q water was added to achieve 0.2 g/L and 0.1 M ionic strength. U(VI) uptake was achieved by the following procedures designed to avoid precipitation of U(VI) solids: Samples were initially adjusted to pH 4 or 9 (where U(VI) solubility is greater than 10<sup>-4</sup> M) using HNO<sub>3</sub> or NaHCO<sub>3</sub> and were allowed to equilibrate with humidified air, as judged by the pH stability of the suspensions. CO<sub>2</sub>-free samples were prepared in water boiled to remove CO<sub>2</sub>, and bubbled with humidified Ar during pH adjustment and measurement to prevent reintroduction of CO<sub>2</sub>. Sample bottles were then wrapped with Al foil to prevent photolytically catalyzed redox reactions. U(VI) was added dropwise as aliquots of an acidic 10 mM UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution while the samples were vigorously stirred. Samples were adjusted to their final pH values and thus maintained by dropwise addition of 20–50 μL aliquots of 0.1–0.01 N HCl and/or 0.1 M NaHCO<sub>3</sub>. Samples were then gently agitated on a shaker for 24–48 h. No significant drifts in pH occurred during this step. Prior to analysis, samples were centrifuged at approximately 40,000 × g centrifugal force for 20 min. to concentrate the solid. Supernatants were decanted.
and saved for KPA measurement of \([U]_{Ox}\). Typically, &gt;99.5% of the supernatant was removed (determined by change in mass). Since adsorption was generally &gt;27% of \([U]_{Ox}\) (Table 1), the amount (total number of moles) of surface-bound U(VI) was in excess of dissolved U(VI) in the remnant interparticle solution in the corresponding centrifuged-and-decanted samples by factors &gt;50.

The solubility of U(VI) under conditions similar to those of the adsorption samples (including equilibration time) was measured to ascertain if homogeneous precipitation of U(VI) solids could have trifuged-and-decanted samples by factors number of moles) of surface-bound U(VI) was in excess of dissolved U(VI). Estimated standard deviation of \([U]_{Ox}\) was 3.1%. \([Fe-OH]_{Ox}\) is the molarity of proton-active surface sites on hematite (based on 19 sites/nm² (Hsi and Langmuir, 1985) \([CO_3]_{Ox}\) is calculated from the sum of all aqueous carbonate species at the final pH of the sample, assuming equilibrium with air. * Units are \(\mu\)mol/mL.

<table>
<thead>
<tr>
<th>pH</th>
<th>Density*</th>
<th>([U]_{Ox}) (mM)</th>
<th>([U]_{eq})</th>
<th>([Fe-OH]_{Ox})</th>
<th>([CO_3]_{Ox})</th>
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</thead>
<tbody>
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<td>10.09</td>
<td>0.042</td>
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<td>9.23</td>
<td>0.036</td>
<td>1.015</td>
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<td>7.43</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.16</td>
<td>0.036</td>
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<td>0.124</td>
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</tr>
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<td>12.0</td>
<td>3.89</td>
<td>0.041</td>
<td>0.024</td>
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<td>8.25</td>
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<td>10.4</td>
<td>5.45</td>
<td>0.036</td>
<td>0.012</td>
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<tr>
<td>8.49</td>
<td>0.36</td>
<td>12.3</td>
<td>8.97</td>
<td>0.042</td>
<td>0.008</td>
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</table>

**Table 1. EXAFS Sample conditions (0.2 g/L).** \([U]_{T}\) is the molarity of all U(VI) added to the system. \([U]_{Ox}\) (molarity) is the sum of all aqueous U(VI) species remaining in solution after equilibration at the final pH. Estimated standard deviation of \([U]_{Ox}\) is 3.1%. \([Fe-OH]_{Ox}\) is the molarity of proton-active surface sites on hematite (based on 19 sites/nm² (Hsi and Langmuir, 1985)). \([CO_3]_{Ox}\) is calculated from the sum of all aqueous carbonate species at the final pH of the sample, assuming equilibrium with air. * Units are \(\mu\)mol/mL.

2.3. EXAFS Data Collection, Analysis, and Theoretical Calculations

Centrifuged wet hematite pastes were loaded into Teflon sample holders with Mylar windows for EXAFS analysis, and the loaded samples were wrapped with moistened tissues until analysis to prevent their desiccation. Room-temperature U LIII-edge fluorescence spectra were collected within 3 days of sample preparation at SSRL beamlines 4-1 and 4-3 using a Lytle-type ion chamber detector and/or a Canberra 13-element Ge array detector. Silicon (220) double-crystal monochromators were used to tune the incident X-ray beam to the desired energies. Energy resolution was approximately 5.5 eV (HWMM). Teflon slits were used to define 2 mm vertical &times; 20 mm horizontal beam profiles. A Sr 6 μx filter was used to reject elastic scattering off the samples, and four to five thicknesses of Nal foils were used to reject Fe-K fluorescence from the samples.

EXAFS spectra from samples were background subtracted, spline-fit, and quantitatively analyzed using the EXAFSPAK software (George, 1993). In no case did the number of parameters that were varied during fitting exceed the Nyquist limit, \(N_{xy} = 2\Delta k \Delta R / \pi\), where \(N_{xy}\) is the number of degrees of freedom, \(\Delta k\) is the range of k-space being fit, and \(\Delta R\) is the width of the characteristic frequency in the FT (Teo, 1986). Backscattering phase and amplitude functions required for fitting of spectra were obtained from FEFF 6 calculations (Rehr et al., 1992), \(\rho_s\) values for equatorial oxygenal O's were found to converge to 0.1 ± 0.01 Å² when allowed to float. To facilitate comparisons between samples, \(\rho_s\) was thereby fixed to be 0.01 Å² for O₈h shells. For similar reasons \(\rho_s\) was fixed to be 0.1 Å² for Fe shells. For C shells, \(\rho_s\) was fixed to be 0.004 Å². An average of 2-5 spectra were fit, and compared to their XRD structures. The latter two spectra were taken from the SSRL XAFS library and were originally published in Thompson et al. (1997). Accuracies of bond distances and CNs, are estimated to be ±0.03 Å and ±30%, respectively, when compared to these crystal structures. However, when comparing fit results from samples to one-another, significance of change is best estimated using the fit-derived estimated standard deviations because they do not include systematic errors arising from model assumptions used to fit all sample spectra. FEFF 6.5 calculations were performed on 18 Å-diameter fragments of the structures of andersonite (Na₂Ca[UO₂(CO₃)₃]* × H₂O and salecite (Mg₆[UO₂PO₄]₀.1H₂O). FEFF 6.5 parameters used were: exchange = 1 (based on its superior fits of EXAFS from model compounds), ipot = 1 (no overlap of muffin tins) based on the findings of Hudson et al. (1996), and ionization = 0 for all calculations of multiple scattering (MS) in the transdioxo unit were initially performed on all three of the primary MS paths. Only the four-legged path, \(U = O₈h = U = O₈h\) was used, to fit the trans-dioxo MS peak in model compounds. The same conclusion was obtained by Hudson et al. (1996). Henceforth, only the four-legged path, \(U = O₈h = U = O₈h\) was used to model trans-dioxo MS, with CN, \(\rho_s\), R, and Eo set at values of 2 atoms, 2R₁, R₁, 2R₁ and E₀-1, respectively (Hudson et al., 1996). This MS shell was added to all fits for samples containing U(VI) precipitates.

3. RESULTS

3.1. Adsorption Kinetics and Solubility of U(VI)

The kinetics of U(VI) adsorption over a 120 h. duration are shown in Figure 1. Approximately 67% of the total observed uptake occurred within the first 30 min. of reaction. Reaction times of 24 to 48 hr. were chosen for EXAFS samples to facilitate sample preparation during data collection and on the presumption that mineral surfaces would have approached metastable adsorptive equilibrium within this time scale in aquifers.
of the experiments. A series of samples was examined at pH ~ 6.5 (i.e., near the solubility minimum) and elevated total U(VI) concentrations (36, 72, and 131 µM [U]T). The [U]eq values for the 72 and 131 µM samples were found to cluster near the solubility predicted for β-UO₂(OH)₂. Spectra of the 72 and 131 µM samples (Fig. 3) bear a strong resemblance to that of U(VI)-oxide precipitates prepared at pH 7 by Allen et al. (1996). This result is consistent with the presence of backscattering from U neighbors at 3.86 Å observed in the EXAFS from the 72 and 131 µM samples (Table 2), which indicates multimeric and/or crystalline structures. These observations suggest that U(VI)-oxide solids were the solubility-limiting phase in our system, precipitating when [U]T > 36 µM (at pH 6.5). Multimeric complexes cannot be completely ruled out as the explanation for the U neighbors in the spectra from the elevated-[U]T adsorption samples. The spectra of the present samples differ from the precipitates of Allen et al. in that they contain backscattering from C/N atoms at 2.9 Å, which could be structural (most likely nitrate, due to its aqueous concentration) and/or from adsorbed U(VI)-carbonato complexes. There was no evidence for such precipitates in any of the EXAFS spectra from low-[U]T samples.

3.2. EXAFS Spectra of U(VI) Adsorbed on Hematite

3.2.1. Oxygen and carbon neighbors

Throughout this section (and the rest of the paper), FT peak distances are reported in units of Å, uncorrected for phase shift (i.e., R + ΔR). In contrast, when referring to neighboring atoms, we report actual distances. EXAFS spectra for U(VI) adsorbed on hematite between pH 4.55 and 8.49 for the low-[U]T (i.e., 10⁻⁵ M U(VI)) conditions are shown in Figure 4. Quantitative fit results, given in Table 2, indicate that adsorbed U(VI) has the common linear trans-dioxo structure: two axial oxygens at about 1.80 Å, and an equatorial shell of about 6 oxygens at 2.31–2.49 Å. The corresponding Fourier Transform (FT) peaks occur at about 1.3 and 1.8 Å. All FTs contain a peak at about 2.3 Å, which corresponds to a shell of neighboring atoms at about 2.9 Å (as indicated by fits to EXAFS). This distance is typical of carbonate groups coordinated to U(VI) in a bidentate fashion (e.g., Coda et al., 1981), and carbon atoms at 2.87 to 2.94 Å provide a good fit to the 2.9 Å shell. The 2.9 Å distance is too long to be consistent with an oxygen shell and too short to be attributed to multiple scattering in uncomplexed UO₂⁺ bonded to hematite. The 2.3 Å FT peak increases in height between pH 5.0 and 8.5. This behavior is not consistent with nitrate ligands, which should be increasingly repelled from hematite surfaces as pH and negative surface charge increase. FTIR measurements of carbonate stretching frequencies in this system (Bargar et al. 1999; Bargar et al., 2000) indicate that carbonate bonds directly to U(VI) adsorbed on hematite between pH 4.5 and 8.5. For these reasons, the 2.3 Å FT peak is interpreted as arising from carbonate (or bicarbonate) ligands for the remainder of this paper (the protonation state of carbonate cannot be ascertained by EXAFS).

FEFF 6 calculations predict that triangular U-C-O_eq multiple scattering (MS) (R_eff ~ 3.25 Å) paths can also produce an FT peak at ca. 2.3 Å, but that the EXAFS oscillations for these MS...
paths are about $\pi$ radians out of phase with the C single scattering (SS) EXAFS and hence do not fit the residual EXAFS (i.e., other shells fit and subtracted from the spectra). Furthermore, the amplitudes of the triangular paths should be much smaller than (about 1/5th) those of U-C SS paths. For these reasons, triangular U-C-O$_{eq}$ MS is hereafter omitted from discussions.

3.2.2. Fe second-neighbors and trans-dioxo multiple scattering

All spectra contain a strong frequency component giving rise to a FT peak at about 2.9 Å. Fe neighbors at about 3.43 Å provide good fits to the residual EXAFS corresponding to these FT features (cf., Fig. 5). However, it has been previously
Table 2. EXAFS fit results. C, Fe, and U shells are from fits to residual spectra. Estimated standard deviations are given in parentheses.

<table>
<thead>
<tr>
<th>pH</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>CN</th>
<th>Oeq₁</th>
<th>Oeq₂</th>
<th>C</th>
<th>Fe</th>
<th>U</th>
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<td>2.34 (.02)</td>
<td>2.49 (.02)</td>
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<td>3.45 (.005), 3.68 (.009)</td>
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<tr>
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<td>2.1 (.16)</td>
<td>5.9 (.15)</td>
<td>—</td>
<td>0.9 (.2)</td>
<td>0.9 (.1)</td>
<td>—</td>
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<td>4.68</td>
<td>1.80 (.004)</td>
<td>2.42 (.01)</td>
<td>—</td>
<td>2.87 (.016)</td>
<td>3.42 (.009)</td>
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<tr>
<td>0.13 10 µM</td>
<td>0.0036 (.0004)</td>
<td>1.9 (.10)</td>
<td>3.2 (.3)</td>
<td>3.3 (.3)</td>
<td>0.8 (.1)</td>
<td>1.0 (.1)</td>
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<tr>
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<td>2.48 (.01)</td>
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<td>3.43 (.006)</td>
<td>—</td>
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<td>2.1 (.11)</td>
<td>2.5 (.13)</td>
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<td>2.9 (.4)</td>
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<td>1.9 (.5)</td>
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<td>2.48 (.026)</td>
<td>2.87 (.007)</td>
<td>3.42 (.006)</td>
<td>3.90 (.007)</td>
<td></td>
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<tr>
<td>0.36 12 µM</td>
<td>0.0019 (.0003)</td>
<td>1.8 (.11)</td>
<td>2.0 (.3)</td>
<td>2.6 (.4)</td>
<td>—</td>
<td>0.7 (.1)</td>
<td>—</td>
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<tr>
<td>5.40</td>
<td>1.80 (.005)</td>
<td>2.31 (.03)</td>
<td>2.45 (.02)</td>
<td>—</td>
<td>3.45 (.012)</td>
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<tr>
<td>0.85 12 µM</td>
<td>0.0033 (.0003)</td>
<td>1.8 (.07)</td>
<td>3.1 (.2)</td>
<td>2.2 (.2)</td>
<td>—</td>
<td>0.8 (.1)</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>No CO₂</td>
<td>1.80 (.002)</td>
<td>2.32 (.01)</td>
<td>2.49 (.02)</td>
<td>—</td>
<td>3.45 (.01)</td>
<td>—</td>
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<tr>
<td>6.15</td>
<td>0.0028 (.0002)</td>
<td>1.8 (.04)</td>
<td>2.4 (.1)</td>
<td>3.2 (.1)</td>
<td>0.9 (.1)</td>
<td>0.7 (.1)</td>
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<tr>
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<td>0.0025 (.0001)</td>
<td>1.8 (.04)</td>
<td>2.4 (.1)</td>
<td>2.8 (.1)</td>
<td>0.9 (.1)NH⁴</td>
<td>0.6 (.07)</td>
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<tr>
<td>6.42</td>
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<td>2.46 (.004)</td>
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<td>—</td>
<td>3.86 (.002)</td>
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<tr>
<td>0.70 72 µM</td>
<td>0.0036 (.0001)</td>
<td>1.7 (.04)</td>
<td>2.6 (.1)</td>
<td>2.8 (.1)</td>
<td>0.8 (.1)NH⁴</td>
<td>—</td>
<td>0.7 (.08)</td>
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<td>6.71</td>
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<td>2.47 (.004)</td>
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<td>14.14 133 µM</td>
<td>0.0036 (.0001)</td>
<td>1.6 (.05)</td>
<td>2.7 (.1)</td>
<td>2.8 (.1)</td>
<td>1.2 (.1)NH⁴</td>
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<td>0.3 (.04)</td>
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<td>Homogenous Precipitate</td>
<td>0.0026 (.0002)</td>
<td>2.31 (.006)</td>
<td>2.51 (.007)</td>
<td>2.91 (.006)</td>
<td>3.89 (.007)</td>
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<td>CN</td>
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<td>8.7 (.3)</td>
<td>—</td>
<td>3.0</td>
<td>—</td>
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<tr>
<td>UO₃(CO₃)₂[²⁻] (aq)</td>
<td>1.80 (.003)</td>
<td>2.43 (.009)</td>
<td>—</td>
<td>2.88 (.006)</td>
<td>—</td>
<td>—</td>
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</tr>
</tbody>
</table>

a = adsorption density (µmol/m²).  
b = Some amplitude in this shell may arise from multiple scattering.  
c = Coordination number (±20%).  
d = Interatomic distance (±0.3 Å).  
e = σ² was allowed to float for this shell, obtaining 0.0173 Å².  
f = Sample was prepared to define onset of precipitation in presence of hematite.  
g = Prepared in the absence of hematite.  
h = This shell can be interpreted as C or N (c.f., section 3.1).

Table 2 demonstrates that multiple scattering in the O = U = O trans-dioxo unit, particularly from the four-legged path U = Oeq₁ = U = Oeq₂ = U (Allen et al., 1995; Hudson et al., 1996) can also give rise to FT features at about 2.9 Å. Proper interpretation of the EXAFS results requires distinction between these two scattering mechanisms. The amplitude variations of the EXAFS oscillations corresponding to the 2.9 Å FT peak provides a basis for this distinction. This principle is illustrated in Figure 6, which shows the results of FEFF 6 calculations of U = Oeq₁ = U = Oeq₂ = U MS amplitude (as measured by relative CN). The predominant O = U = O bond angle for U(VI) with 6 Oeq is 180°, and angles less than 175° should not occur (Burns et al., 1997). A change in angle between these values should produce ≤ 6% change in the amplitude of the MS EXAFS (Fig. 6A). The effect of bond length (R(U=O)) should be ≤1% (Fig. 6B). Breaking the symmetry of U = O bond lengths, from 2 Oeq at 1.82 Å, to one each at 1.82 and 1.77 Å (as occurs in andersonite), is predicted to have <2% effect on the MS peak amplitude (not plotted). Fits to residual EXAFS from adsorption samples, performed using FEFF-generated parameters for U = Oeq₁ = U = Oeq₂ = U MS (instead of Fe atoms), are shown in Figure 6C. The relative CN thus derived for MS varies by about 45%, approximately 8× more than the predicted maximum variation of 6%, suggesting that MS comprises only a small fraction of the amplitude of the 2.9 Å FT peak in this sample series. To test this conclusion, fits were
attempted using admixtures of U-Fe SS and MS contributions. The pure U-Fe SS fits provided the best match to the EXAFS because of the poor match of the O = U = O MS EXAFS amplitudes to data, particularly at \( k > 7 \text{ Å}^{-1} \) (cf., Fig. 5). Consequently, final fits (Table 2) were performed using U-Fe SS for the 2.9 Å FT EXAFS components in the low-[U] sample series.

The EXAFS-determined ca. 3.45 Å U-Fe distance suggests that U(VI) predominantly was bonded to edges of FeO₆ octahedra on hematite surfaces in bidentate or tridentate fashions, assuming that O₆ do not form covalent bonds to surface Fe atoms (covalent O₆-metal bonding typically does not occur in U(VI) coordination compounds or in aqueous complexes at near-neutral pH (Weigel, 1986)). Similar conclusions were reported by Waite et al. (1994) and Manceau et al. (1992). In contrast, monodentate bonding of U(VI) to hematite surface

Fig. 4. EXAFS spectra (A) and their Fourier transforms (B) for U(VI) adsorbed on hematite in air-equilibrated water at ca. 10 μM [U]ₜ. Dashed lines are fits. Sample conditions are described in Table 1.
Fig. 5. Residual EXAFS (produced by subtraction of U = O$_{ax}$, U-O$_{eq}$, U-C, and U-U shells) and its Fourier Transform (solid lines) corresponding to the 2.9 Å FT peak from the pH 6.39, 3.87 μmol/m$^2$ U(VI)/hematite sample. Dotted lines in top panels show the fits with U-Fe single scattering. Dashed lines in bottom panels show fits with trans-dioxo multiple scattering.
groups should produce U-Fe distances $\geq 3.85$ Å (assuming $\angle\text{Fe-O}_{eq}\text{-U} \geq 120^\circ$).

The pH 4.55 sample contains an additional shell of backscatters at about 3.3 Å in the FT, which can be well fit by Fe neighbors at 3.68 Å. No MS paths are expected to contribute to peaks at this distance, based on the structures of uranyl and carbonate groups. The 3.68 Å U-Fe distance implies bonding of U(VI) to corners of FeO$_6$ octahedra, either in bi-/tridentate geometries (most likely) or monodentate geometries with highly bent Fe-O$_{eq}$-U angles (ca. 112°). The trend to increasing corner-sharing adsorption as pH decreases (i.e., from pH 4.68 to 4.55) has been observed for other metal ions (Bargar et al., 1998; Ostergren et al., 1999). This trend is likely related to adsorption of protons at FeO sites, effectively decreasing the overall concentration of preferred bidentate binding sites. The CN for the 3.68 Å Fe shell (0.5 ± 30%) suggests that about 20% of adsorbed U(VI) occupies these corner-sharing sites (assuming bridging bidentate corner-sharing, and taking into account the 0.7 atom CN for the 3.45 Å Fe shell).

3.2.3. $U$ second-neighbors

At pH $\geq 6.5$, the adsorption sample spectra contained substantial components having FT peaks at about 3.7 Å (cf., Fig 4). U neighbors at ca. 3.9 Å provided excellent fits to the EXAFS spectra. Multiple- and single-scattering from distal oxygens (O$_{distal}$) of bidentate carbonate ligands have also been reported to produce FT features at about 3.7 Å (Allen et al., 1995; Clark et al., 1998). No FT peaks were observed at 3.7 Å in the pH 4.55, 4.68, 5.04, and 6.48 ($12 \mu M \text{[U]}_{T}$) spectra, even though U(VI) had about one bidentate carbonate ligand. This observation indicates that carbonate/bicarbonate U-O$_{distal}$ SS/MS is weak in these samples. In addition, the height of the 3.7 Å FT peak does not correlate with C CN (c.f., Table 2, Fig. 4), as should occur if the peak originated from U-O$_{distal}$ SS/M. Fits using U-O$_{distal}$ SS and MS instead of U were attempted, but did not fit the EXAFS oscillations in any way that could be described as a match. Based on these observations, we interpret the 3.7 Å FT peak as arising from U neighbors.

The equilibrium U(VI) concentrations of the low-[U]$_T$ adsorption samples were about an order of magnitude below the predicted solubility of crystalline $\beta$-UO$_2$(OH)$_2$ and the solubility of precipitates observed in the 72 and 131 $\mu M$ [U]$_T$ samples (c.f., Fig. 2A). Furthermore, the low-[U]$_T$ sample spectra are dissimilar to the U(VI) precipitate spectra collected in this study (Fig. 3) and to spectra of schoepite-like precipitates described as a match. Based on these observations, we interpret the 3.7 Å FT peak as arising from U neighbors.

3.3. Electrophoretic Mobility of Hematite in the System U(VI) + CO$_3$

The effect of U(VI) on the electrophoretic mobility of hematite in air-equilibrated solutions is shown in Figure 7. In the absence of U(VI), hematite was positively charged below pH 8, due to protonation of surface functional groups. Addition of U(VI) to the system induced a surface charge reversal between pH 6.5 and 8. This result is consistent with the findings of Ho and Miller (1986) and Lenhart and Honeyman (1999). The magnitude of charge reversal increased with increasing [U]$_T$. The deflection of surface charge to negative values indicates adsorption of anionic complexes onto hematite. The accumulation of negative charge (anions) on negatively charged hematite surfaces, which is necessary to generate the charge reversal,
requires anion-surface bonding forces strong enough to overcome electrostatic repulsion. Hence, the charge reversal suggests that the anionic species adsorbed in the presence of U(VI) were bonded to hematite via significant non-electrostatic mechanisms such as covalent inner-sphere bonding and/or hydrogen bonding.

4. DISCUSSION

The experimental conditions of the present study were chosen to be representative of those in saturated aquifers for several key parameters (pH, U(VI) concentration, dissolved carbonate). A primary objective of such studies is to develop predictive models of U(VI) adsorption and hence transport and fate in the environment. Approaches to describing U(VI) adsorption range from simplified partition coefficients (K_{d}s), which often neglect important aspects of groundwater chemistry such as pH and metal ion concentration, to surface complexation models (SCMs) that require knowledge of molecular-scale adsorbate and surface structures. Spectroscopically-derived information provides constraints on the total number (and types) of transport-limiting species, fundamental to any modeling approach. Stoichiometries of adsorption reactions can be formulated once the compositions of the species in question are known. Furthermore, structural details of surface complexes, such as the linkage of adsorbates to oxide surfaces (monodentate, bidentate, etc.) and their distances above the surfaces, can be used to predict the proton stoichiometries of adsorption reactions (Hiemstra and van Riemsdijk, 1999; Rietra et al., 1999). As described below, such constraints can be obtained from the present study.

4.1. Evidence for Metal-Bridging Ternary Hematite-U(VI)-Carbonato Complexes

Several lines of evidence suggest that U(VI) adsorbed on hematite was simultaneously bonded in an inner-sphere fashion to surface =Fe-O groups and to carbonate (or bicarbonate) ligands, i.e., comprising metal-bridging ternary hematite-U(VI)-carbonato complexes. This is a key point to demonstrate, since the appearance of C neighbors in spectra could, in principle, arise from outer-sphere or diffuse-layer adsorption of complexes such as UO_{2}(CO_{3})_{3}^{+} (aq), and hence doesn’t singularly indicate the existence of ternary species. Constraints that address this issue (as well as the issue of metal vs. ligand-bridging structures) are as follows:

1. The electrophoretic mobility measurements suggest that adsorbed U(VI) complexes are anionic in character and strongly bonded to hematite, suggesting the presence of inner-sphere ternary complexes.
2. Adsorption of ligand-bridging and/or outer-sphere U(VI)-carbonato complexes should lead to decreases in the measured number of second-neighbor Fe atoms relative to a carbonate-free system in which U(VI) is complexed directly by hematite. However, such a trend is not observed. The number of second-neighbor Fe atoms is the same or larger in the presence of carbonate than in CO_{2}-free samples (Table 2).
3. The observed U-Fe distances are sufficiently short to rule out the interposition of carbonate between U(VI) and hematite.
4. The high electrolyte concentration (0.1 M ionic strength) should hinder adsorption of outer-sphere anionic U(VI) species, including (UO_{2})_{2}(OH)_{2}CO_{3}^{-} (the predominant aqueous U(VI)-carbonato anion under the pH values reported herein, c.f., Fig 1B). Points 3 and 4 indicate that adsorbed UO_{2}(CO_{3})_{3}^{+} (aq) was a minor species or was not present at the hematite-water interfaces.

EXAFS-derived CNs for C neighbors were ≥1 (±30%) in the low-[U]_{T} sample series, suggesting that ternary hematite-U(VI)-carbonato complexes were dominant species from pH 4.5 to 8.5. This conclusion is consistent with the current electrophoretic mobility results and with previous ATR-FTIR measurements in this system (Bargar et al., 1999). The inferred anionic character of the ternary complexes is consistent with exchange of OH\textsuperscript{-} for water molecules in the U(VI) equatorial shell and/or displacement of surface-bound protons as a result of adsorption, e.g., Fe(OCO\textsubscript{2})\textsuperscript{2+} + CO\textsubscript{3}\textsuperscript{2-} = FeO\textsubscript{2} CO\textsubscript{3}\textsuperscript{2-} + 2H\textsuperscript{+}. Preliminary surface complexation modeling in the present system indicates that U(VI) uptake and proton release can be modeled using hematite-U(VI)-carbonate surface complexes (Reitmeyer et al., 1999; Reitmeyer et al., 2000).

4.2. Structures and Compositions of Monomeric Hematite-U(VI)-Carbonato Ternary Complexes

At pH ≤ 6.5 and [U]_{T} ≤ 12 μM (71 ± 1.1 μmol/m\textsuperscript{2}), there was no evidence for U neighbors in the EXAFS spectra, suggesting that adsorbed U(VI) complexes were predominantly monomeric (i.e., one U(VI) per complex). The EXAFS-derived CNs for C neighbors were about 1 under the conditions where the proposed monomeric U(VI) ternary complexes predomi-
above the putative surface plane. Since simultaneous bonding of U(VI) to carbonate and hematite requires bonding of this distal oxygen to surface Fe atoms, such arrangements should be restricted to step edges and/or defect sites.

### 4.3. Evidence for Multimeric Hematite-U(VI)-Carbonato Complexes

The EXAFS-determined ca. 3.90 Å U-U distances are characteristic of equatorial edge-sharing, hydroxyl-bridged U(VI) coordination complexes (i.e., neighboring UO$_2$ cations are linked by two common equatorial oxygens) (Åberg, 1970; Allen et al., 1996). The 3.90 Å U-U distance is significantly shorter than U-U separations in aqueous (UO$_2$)$_3$(CO$_3$)$_6$$^{2-}$ complexes (cf. Coda et al., 1981), suggesting that these species were not present. The EXAFS-derived U CN was 0.5 neighbors at pH 8.49, implying that ca 50% of adsorbed U(VI) was accounted for by dimeric complexes (i.e., with respect to U(VI)), or that smaller amounts of tri- or tetrameric complexes occurred at this pH. The number of second-neighbor Fe atoms at pH ≤ 8 was equal to or greater than observed at pH ≥ 5, where no U neighbors occurred. This observation suggests that all U(VI) atoms in multimeric complexes were bonded to hematite surfaces, i.e., the complexes were oriented parallel to hematite surfaces.

The low-[$U$]$_T$ sample series shows that C CNs increased from 0.8 to 1.7 atoms as U CN increased from 0 to 0.5 (Table 2). This trend suggests that U(VI) multimeric complexes contained about the same number of carbonate ligands per adsorbed U(VI) as did U(VI) in monomeric hematite-U(VI)-carbonato ternary complexes. As a starting point for modeling, we suggest the composition =Fe$_2$O$_3$$^{2-}$(UO$_2$)$_2$($\text{OH}_2$$^2r$CO$_3$$^2t$)(OH$_2$)$^t_0$(CO$_3$$^t_0$)$_s$ for the multimeric complexes, where $t$ has values ≤ 3. This complex (with $s = 0$, $t = 3$) is illustrated in Figure 8C. The complexes are written as dimeric species because integral multiples of the EXAFS-derived 3.9 Å U-U distances do not match any obvious structural repeat units in hematite. Hematite Fe-Fe separations, which control the spacing of surface FeO$_6$ edge sites, are 2.90, 2.97 (edge-sharing octahedral) 3.36, and 3.71 Å (corner-sharing octahedral). The bulk lattice parameters (5.04 and 13.77 Å) are non-integral products of 3.9 Å, and none of the surface unit cell dimensions of the common hematite (0001) and (1101) parting planes (Nesse, 1991) match the 3.9 Å U-U distance. We emphasize that the proposed composition should be viewed as a starting point for further refinement because of the assumptions involved.

(UO$_2$)$_3$(OH)$_5$ complexes, which previously have been proposed to adsorb on oxide surfaces (Hsi and Langmuir, 1985; Turner et al., 1996), are not consistent with the present EXAFS results. The three U(VI) in aqueous (UO$_2$)$_3$(OH)$_5$$^-$ define a triangle and are hydroxo-bridge linked to one-another via shared equatorial oxygens, all of which lie in the same plane as the U(VI) (Åberg, 1970). U(VI) axial oxygens protrude from this plane at normal angles. This trigonal planar structure would preclude simultaneous inner-sphere bonding of 1 to 2 of the U(VI) atoms in (UO$_2$)$_3$(OH)$_5$$^-$ to hematite surface sites. Thus, adsorption of (UO$_2$)$_3$(OH)$_5$$^-$ would have led to decreasing Fe CNs (as pH, [U]$_T$ increased in the sample series), which was not observed.

Complexes in which carbonate ligands simultaneously bond to U(VI) and hematite cannot be ruled out. However, if carbonate ligands are positioned normal to the surface as expected (Fig. 8), then the distal carbonate oxygen should be ca 3.9 Å...
4.4. Evidence for Hematite-U(VI)-Biscarbonato Complexes

The EXAFS-derived CNs for C at pH 8.00 to 8.49 were 1.3 to 1.7 atoms. An average CN > 1 indicates the presence of hematite-U(VI)-bicarbonato complexes (i.e., \( \text{Fe}^3\text{OH}^- \text{UO}_2(\text{CO}_3)_{2-} \)) at these pH values, since no combination of U(VI)-monocarbonato and carbonate-free U(VI) complexes can produce an average number of carbonate neighbors per adsorbed U(VI) greater than unity. The C CNs increase with pH, indicating an increase in the relative concentration of bicarbonato complexes.

If half of adsorbed U(VI) were in dimeric complexes at pH 8.49, as imputed in the preceding section, and half were monomeric bicarbonato complexes, then the maximum predicted carbonate CN would be 1.75. This conclusion agrees with the observed result at pH 8.49 (1.7 carbon neighbors), suggesting carbonate-free U(VI) complexes were minor species at this pH.

In the absence of U(VI), hematite has net positive surface charge when pH < 8. This positive charge may be a key force stabilizing the putative anionic U(VI)-bicarbonato surface complexes. Examples of low-pH stabilization of anionic surface complexes have been noted previously. For example, Bargar et al. (1997a,b) showed that anionic Pb(OH)\(_3\) surface complexes are stabilized on hematite, goethite, and alumina surfaces at pH < 7, even though hydrolyzed Pb(II) complexes were minor species in aqueous solution. Similarly, Rietra et al. (1999) proposed that positive surface charge on goethite (\( \alpha\)-FeOOH) below pH 7 should stabilize the deprotonated forms of otherwise protonated oxyanions.

5. SUMMARY AND CONCLUSIONS

EXAFS measurements of U(VI) adsorbed on hematite suggest that U(VI)-carbonato-hematite ternary complexes occur and are important species between pH 4.5 and 8.5. The EXAFS-derived U-C distances of ca. 2.9 Å indicate bidentate bonding of carbonate to U(VI). The average number of C neighbors was observed to range from 0.8 to 1.7, increasing with pH, suggesting the presence of anionic U(VI)-bicarbonato complexes that increase in relative concentration with pH. This conclusion is consistent with electrophoretic mobility measurements, which indicate the presence of anionic species on hematite adsorbed via significant non-electrostatic bonds such as covalent inner-sphere and/or hydrogen bonding. EXAFS components from neighbors at ca. 3.5 Å were also observed. Multiple scattering in the trans-dioxo \( \text{UO}_2^{2+} \) unit was found to be inadequate to account for the variable heights of these features, whereas single scattering from Fe neighbors at about 3.45 Å provide good fits to the raw and residual EXAFS. This result suggests that U(VI) bonds to hematite predominantly in a bidentate fashion (tridentate adsorption may also occur) to edges of FeO\(_x\) octahedra on the oxide surface (i.e., inner-sphere adsorption), implying reaction stoichiometries in which two surface oxygens are involved in adsorption of each U(VI). We propose the composition \( \text{Fe}^3\text{OH}_3\text{OS}(\text{OH}_2\text{H}_2\text{O})_{4-6}(\text{CO}_3)_{2-} \) for these species. Based on the ubiquity of Fe-oxide coatings and dissolved CO\(_2\) in aquifers, we speculate that Fe-oxide-U(VI)-bicarbonato complexes may be key transport-limiting species for U(VI) in oxic groundwaters.

At pH \( \leq 6.5 \), no evidence was observed for second-neighbor U(VI), indicating that adsorbrates were monomeric with respect to U(VI). At pH \( \geq 8.0 \), EXAFS spectra suggest the existence of multimicreric U(VI) complexes, even at the lowest adsorption densities measured. None of the aqueous complexes \( \text{UO}_2(\text{CO}_3)_{2-}^- , (\text{UO}_2)_{2}(\text{CO}_3)_{6-}^2- , \) or \( (\text{UO}_2)_{3}(\text{OH})_{2}^+ \) are consistent with the EXAFS results for the adsorbed species.

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Characterization of U(VI)-carbonato ternary complexes on hematite


