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Spectroscopic Confirmation of Uranium (VI)-Carbonato Adsorption Complexes on Hematite

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Abstract

Evaluating societal risks posed by uranium contamination from waste management facilities, mining sites, and heavy industry requires knowledge about uranium transport in groundwater, often the most significant pathway of exposure to humans. It has been proposed that uranium mobility in aquifers may be controlled by adsorption of U(VI)-carbonato complexes on oxide minerals. The existence of such complexes has not been demonstrated, and little is known about their compositions and reaction stoichiometries. We have used Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopies to probe the existence, structures, and compositions of $\equiv FeO_{surface}$-U(VI)-carbonato complexes on hematite throughout the pH range of uranyl uptake under conditions relevant to aquifers. U(VI)-carbonato complexes were found to be the predominant adsorbed U(VI) species at all pH values examined, a much wider pH range than previously postulated based on analogy to aqueous U(VI)-carbonato complexes, which are trace constituents at pH < 6. This result indicates the inadequacy of the common modeling assumption that the compositions and predominance of adsorbed species can be inferred from aqueous species. By extension, adsorbed carbonato complexes may be of major importance to the groundwater transport of similar actinide contaminants such as neptunium and plutonium.

Introduction

Accurate prediction of U(VI) fate and transport in aquifers, design of cost-effective remediation technologies for uranium-contaminated soils, and development of materials suitable for encapsulation and disposal of nuclear waste require fundamental knowledge of U(VI)-carbonate-mineral interactions. Fe-oxides are common in the environment and strongly adsorb both U(VI) and carbonate. Fe-oxide grain coatings, formed by weathering processes, have been shown to be important metal-ion-adsorbing phases even in Fe-poor aquifers[1]. Dissolved carbonate is ubiquitous in aquifers, often in equilibrium with CO_2 at partial pressures 100 to 1,000 times greater than ambient atmosphere[2], and has a great affinity to complex U(VI)[3] (the dominant oxidation

state in oxic groundwaters). As a rule, subsurface carbonate concentrations vary spatially and temporally 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[4, 5]. Several groups have speculated[6-9] that uranium mobility in aquifers may be controlled by adsorption of U(VI)-carbonato complexes on Fe-oxide minerals and grain coatings, particularly at pH > 7. To our knowledge, however, no studies have been reported in which spectroscopic measurements were performed to directly characterize U(VI)-carbonato-oxide adsorbate complexes, particularly under aquifer conditions (*i.e.*, dilute U(VI) concentrations, presence of CO_2, range of pH values). The objectives of the current study were to probe the existence of U(VI)-carbonato complexes on Fe-oxides and measure their pH distributions under conditions relevant to aquifers. Samples were prepared in air-equilibrated solutions between pH 4.73 - 8.25 in equilibrium with U(VI) concentrations ranging from 0.1 to 47.2 μM.

Experimental Section

Hematite synthesis and characterization are described elsewhere[10]. Hematite suspensions (0.4 g/L, ATR; 0.2 g/L, EXAFS) were preequilibrated with humidified, filtered air at pH 4 or 9. $NaNO_3$ (0.1M) was added to EXAFS samples. After addition of $UO_2(NO_3)_2$, suspensions were adjusted to desired pHs, equilibrated with air, agitated for 24 to 48 hrs, and centrifuged to concentrate the solid, thus minimizing spectral interference from aqueous species. ATR-FTIR spectra were measured from centrifuged samples covered with several mL of their supernatants. Supernatant signals and the spectrometer baseline were subtracted out of spectra. EXAFS spectra were measured from wet samples at room temperature at Stanford Synchrotron Radiation Laboratory beamline 4-1 and were processed using EXAFSPAK software. Phase and amplitude functions were obtained from FEFF 6 calculations[11]. Calculations on multiple scattering (MS) in the uranyl cation were performed primarily using the four-legged path, $U{=}O_{ax}{=}U{=}O_{ax}'{=}U$, based on its ability to fit model compound data and on previous work[12]. For fits to EXAFS, σ^2 values

were fixed at 0.01 $Å^2$ for O_{eq} and Fe shells, based on convergence of most fits to this value. σ^2 for carbon was fixed at 0.0041 $Å^2$, based on comparison to $UO_2(CO_3)_3^{4-}$(aq). Accuracies of bond distances and coordination numbers (CNs) were estimated to be ±0.03 Å and ± 30%, respectively, based on comparison to fit results of EXAFS from model compounds ($[UO_2(CO_3)_3]^{4-}$(aq), schoepite, rutherfordine[13], and uranyl nitrate[13], the latter two obtained from the SSRL EXAFS library.

Equilibrium U(VI) concentrations in most samples were an order of magnitude lower than the solubility of schoepite ($UO_2(OH_2)•H_2O$)[3] and about two orders of magnitude lower than U(VI) solids found to occur over a two-day time scale in precipitation experiments. Spectra of the solid phases were dissimilar to those of adsorption samples, indicating that adsorption samples were not contaminated with precipitates.

Results and Discussion

ATR-FTIR spectra of carbonate adsorbed on hematite in the absence and presence of U(VI) are displayed over the C-O stretching region in Figure 1. The region from about 1400 to 1600 cm^{-1} is assigned to the asymmetric (asym) C-O ν_3 stretching frequency in CO_3, whereas that between about 1300 and 1400 cm^{-1} is assigned to the symmetric (sym) ν_3 frequency[14]. As shown in Figure 1, the presence of U(VI) coincides with a shift of the undifferentiated asym ν_3 peak centroid to higher frequencies and an increase in the height ratio (asym:sym) of the (undifferentiated) ν_3 peaks. Fits to the spectra indicate these changes arise from the appearance of a pair of C-O stretching frequencies at about 1530 (asym ν_3) and 1345 cm^{-1} (sym ν_3), shown in Figure 1. U(VI) does not have peaks in this region[14]. Since this new set of ν_3 peaks occurs only in the presence of adsorbed U(VI), while pH and ionic strength remain unchanged, it can be taken as evidence for adsorbed U(VI)-carbonato complexes. The positions and relative intensities of the U(VI)-associated ν_3 peaks are consistent with bidentate coordination of carbonate anions to U(VI)[15-17], further implying the presence of adsorbed U(VI)-carbonate complexes. Monodentate

coordination of CO_3-groups to U(VI) should give rise to asym - sym ν_3 frequency differences smaller than for bidentate coordination[14] (*i.e.*, < 140 cm^{-1}), but is relatively uncommon[18]. In comparison, the asym and sym ν_3 frequencies for U(VI)-associated peaks in the sorption sample spectra (Figure 1) are separated by 177 to 188 cm^{-1}.

EXAFS spectra and their Fourier transforms (FTs) for samples are displayed in Figure 2. A key feature of all FTs is a peak at about 2.3 Å, arising from carbon neighbors at 2.88 to 2.95 Å (FT peaks typically appear at distances shorter than true interatomic distances because the ejected photoelectron experiences a phase shift when backscattered from neighboring atoms). This U-C distance is characteristic of bidentate coordination of carbonate to U(VI)[19], in agreement with the ATR-FTIR results. This U-C distance is too long to be consistent with oxygen neighbors and too short to be attributed to multiple scattering (MS) in the trans-dioxo UO_2^{2+} cation. In addition, all FTs contain peaks at about 2.9 Å, which in principle can be attributed to MS[12] and/or Fe neighbors. The amplitude of this shell does not vary in proportion to that for axial oxygens. Fits to EXAFS indicate that the CN for trans-dioxo MS varies by about 40% as a function of pH (the same variation occurs for Fe, *cf.* Table 1). However, the maximum variation in the trans-dioxo MS peak height should be ≤ 7% for samples similar to one-another having reasonable changes in O=U=O bond angles and distances. Hence, the 2.9 Å peak should not be attributed solely to trans-dioxo MS. Fe neighbors at about 3.43 Å provide excellent fits to this shell, suggesting that U(VI) bonds in a bidentate fashion to hematite via equatorial oxygens[8, 20]. This conclusion is consistent with the metal-like uptake of U(VI) in this system[8].

Fits to EXAFS indicate U(VI) has 5 to 6 equatorial oxygens (O_{eq}). Since two of these O_{eq} positions should be occupied by surface sites, it follows that adsorbed U(VI) should have at most 2 carbonate ligands. Hence, the ternary complexes should have compositions similar to $\equiv FeO_2UO_2(CO_3)_x$, where $0 \leq x \leq 2$, which includes the complex used by Waite et al.[8] to model U(VI) uptake on ferrihydrite. Overall, the CN for C (carbonate ligands) increases (from about 1 to

1.5 atoms) with increasing pH, as is expected from the increasing activities of aqueous bicarbonate and carbonate. The absolute CNs for C in the samples imply that on average ≥ 50% of adsorbed U(VI) was complexed by carbonate, even at pH 4.75. At pH 8.5, U(VI)-biscarbonato complexes occurred. The 3.7 Å FT peaks (pH > 6.5) can be attributed either to U neighbors in multimeric complexes or to MS from distal oxygens of carbonate ligands[21, 22].

Our findings contradict predictions that U(VI)-carbonato ternary complexes should predominate only above pH 6[8]. Such complexes may occur on minerals having surface charging behaviors similar to hematite (*e.g.*, Al-oxides). The coordination chemistry of aqueous Np(V), Pu(IV) and Pu(V) carbonato complexes are similar to that of U(VI)[18, 21], and the uptake of these cations on Fe-oxides is similar to that of U(VI)[23-25]. Considering the abundance of carbonate in aquifers, these conclusions suggest that adsorbed actinyl-carbonato complexes may be primary controls on actinide transport in many subsurface environments.

Acknowledgments

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Table 1. EXAFS fit results.

	U-Oax			U-Oeq		U-C		U-Fe[f]	
Sample[d]	CN[a]	R[b](Å)	σ^{2}[c] (Å^2)	CN[a]	R[b](Å)	CN[a]	R[b](Å)	CN[a]	R[b](Å)
pH 4.73 Γ 0.13	2.1	1.80	.0036	5.9[e]	2.42	1.1	2.88	1.1	3.42
pH 5.04 Γ 0.53	1.9	1.80	.0028	3.2	2.31	1.0	2.89	1.0	3.43
				3.3	2.48				
pH 6.48 Γ 1.11	2.1	1.80	.0045	2.5	2.35	0.8	2.95	0.7	3.45
				2.1	2.44				
pH 8.00 Γ 0.88	1.8	1.81	.0029	2.4	2.34	1.3	2.89	1.2	3.45
				2.9	2.47				
pH 8.19 Γ 0.53	1.8	1.82	.0027	1.9	2.33	1.5	2.88	1.2	3.44
				3.9	2.47				
$UO_2(CO_3)_3^{4-}$(aq)	2.5	1.80	.003	8.7	2.43	3.0	2.88	--	--

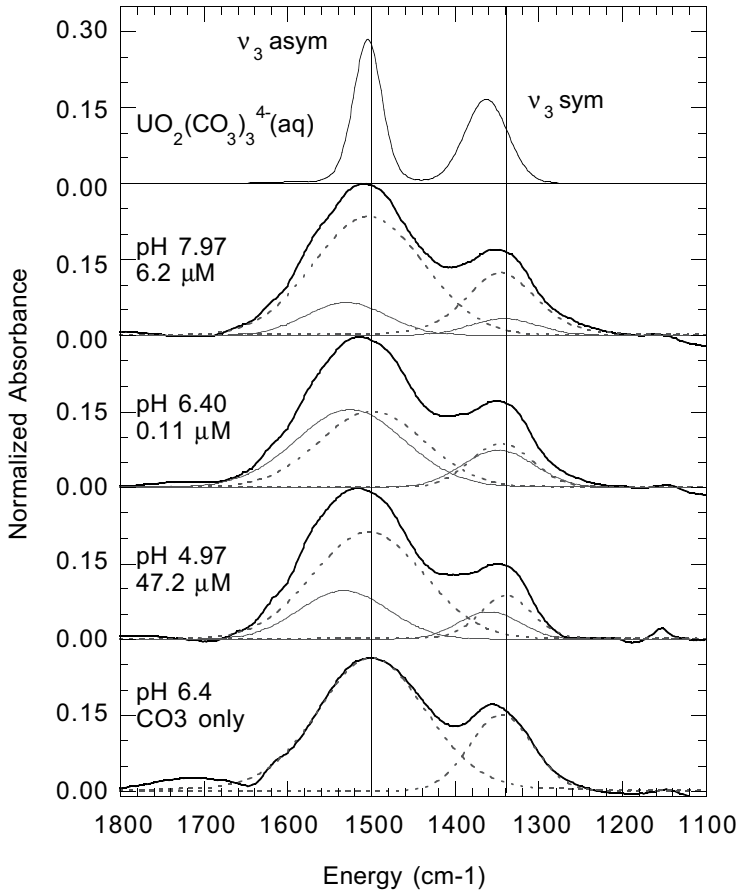
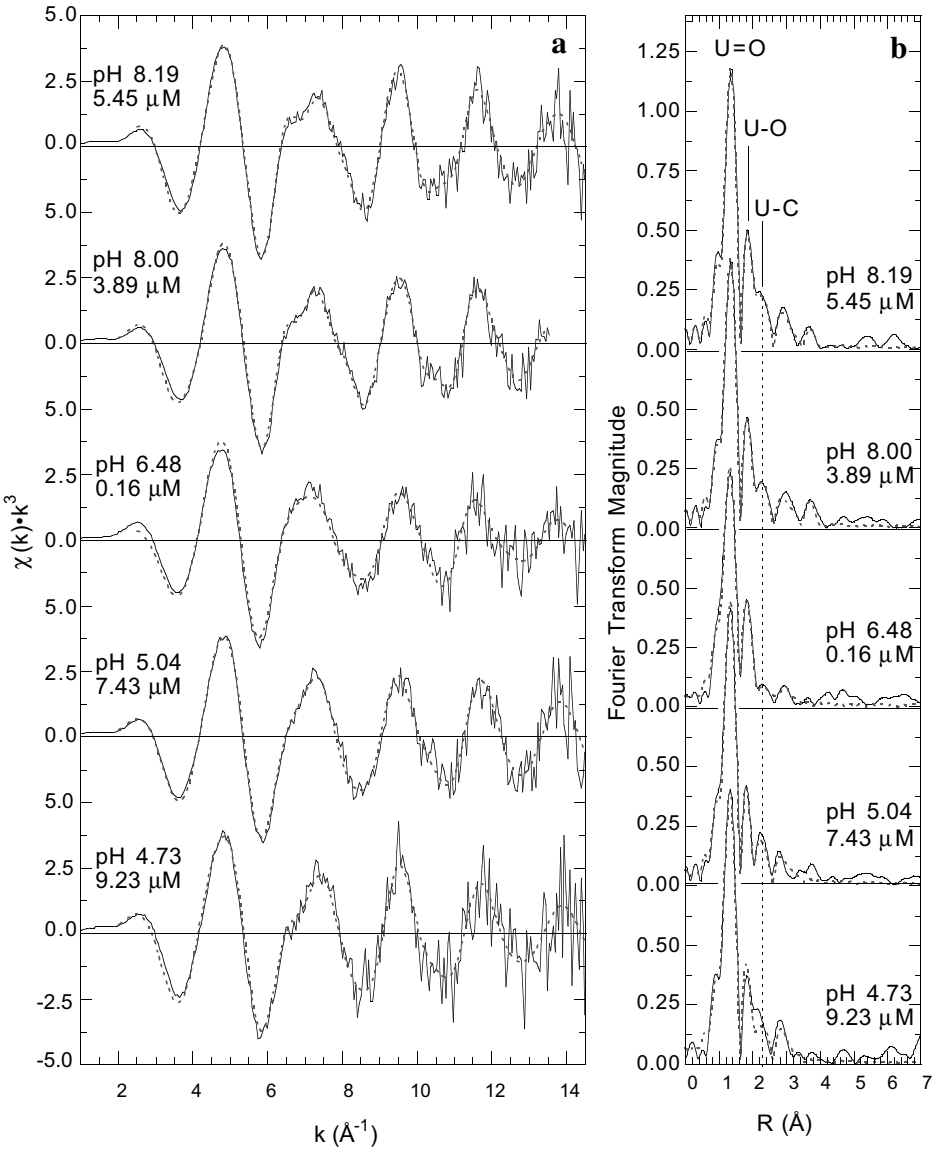
[a]Coordination number (±30%), [b]interatomic distance (±0.03 Å), [c]Debye-Waller factor, [d]Γ=adsorption density (μmol/m^2). [e]σ^2 was allowed to float for this unsplit shell, obtaining 0.0173 Å^2. [f]Part of this shell's amplitude is believed to arise from multiple scattering.

FIGURE CAPTIONS

Figure 1. ATR-FTIR spectra of U(VI)/hematite adsorption samples (bottom four spectra) and $UO_2(CO_3)_3^{4-}$ in bulk aqueous solution, for which carbonate bidentately coordinates to U(VI) (top spectrum). Solid curves are spectra and fit components for U(VI)-carbonato complexes. Dashed lines indicate species that occur in the absence of U(VI), the centroids of which are marked by vertical lines. Concentrations are final equilibrium values. Initial concentrations of U(VI) ($[U]_T$) were 75.5, 11.9, and 25.2 μM at pH 4.97, 6.4, and 7.97, respectively.

Figure 2. EXAFS spectra (a) and their Fourier transforms (b) for U(VI) adsorbed on hematite in air-equilibrated water. Dashed lines are fits. Concentrations are final equilibrium values. $[U]_T$ values were 10.4 μM at pH 4.73, 6.48, and 8.19, and 12.3 μM at pH 5.04 and 8.

Bargar et al. Figure 1.



Bargar et al. Figure 2