

EXAFS Study of U(VI) Sorption at the Calcite-Water Interface

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Introduction

Sorption of U(VI) by minerals and organic matter may be one of the dominant mechanisms that limits the mobility of this radionuclide in soil- and sediment-water systems. The effectiveness and mechanism of sorption and the stability of the sorbed species determine the retention of the contaminant and are therefore critical for predicting the long-term fate of this radionuclide. U(VI), the stable oxidation state in oxidized surface environments, exists almost exclusively as the uranyl species (UO_2^{2+}) at surface conditions and generally exhibits solubility and mobility far exceeding that of U(IV), the other common oxidation state [1].

Sorption of uranyl by minerals depends on numerous factors, including the nature and availability of surface-binding sites, solution composition and pH, and aqueous complexation. The presence of dissolved ligands may strongly influence uranyl speciation, thereby either increasing or decreasing uptake behavior. Carbonate is widely regarded as an important ligand because of its nearly ubiquitous presence in surface waters and because of the stability of uranyl carbonate complexes. In carbonate-containing waters above pH 6, carbonate complexes typically dominate the aqueous speciation of U(VI) and may significantly enhance U(VI) solubility. Precipitation of U(VI)-containing phases can provide limits for U(VI) solubility, but phases likely to form in carbonate-containing systems [e.g., rutherfordine (UO_2CO_3), liebigite ($\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$), schoepite ($\text{UO}_2(\text{OH})_2$), and $\beta\text{-UO}_2(\text{OH})_2$] exhibit moderate solubilities under a range of conditions typical for soil and sediment systems, thereby providing only modest constraints to total dissolved U(VI) concentrations.

In the present study, we investigated the interaction of U(VI) species at the calcite-water interface in an effort to determine the identity and coordination of sorbed uranyl species. Samples prepared in batch uptake experiments at pH 7.4 and 8.3 are examined *in situ* by using extended x-ray absorption fine structure (EXAFS) spectroscopy, which allow us to characterize the local coordination of sorbed species and deduce mechanisms of uptake.

Methods and Materials

Experiments used a calcite sorbent with an average particle size of 1.8 μm and a $\text{N}_2\text{-BET}$ surface area of about 10 $\text{m}^2 \text{g}^{-1}$. In all experiments, calcite-saturated solutions were used to prevent calcite dissolution or

precipitation during the sorption experiments. Uranium(VI) sorption experiments were performed at pH 8.3 and 7.4 by using U solution concentrations ($[\text{U}]$) ranging from 5 μM to 5 mM. To prevent calcite dissolution upon the addition of U(VI) as a result of uranyl-carbonate complexation in solution, we used a stock solution consisting of 0.04 M U(VI) and 0.1 M Na_2CO_3 , where U(VI) exists mainly (70%) as the triscarbonate complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$.

EXAFS samples were prepared by using calcite suspensions of 0.5 g L^{-1} . The samples were spiked with $[\text{U}]$ ranging between 5 μM and 5 mM, with addition of 0.1 M HCl to readjust pH as necessary. The samples were equilibrated on a reciprocal shaker for 3 days, measured for pH, and then filtered through 0.22- μm filter paper to a consistency of wet paste in order to preserve sorption complexes. For two samples, U was added from a stock containing only UO_2^{2+} and NO_3^- (and no Na_2CO_3) to evaluate the effect of CO_3 co-addition at $[\text{U}] = 50$ and 500 μM and pH 8.3. An isotherm for U(VI) adsorption on calcite at pH 8.3 was measured to determine the overall U(VI) uptake by calcite as a function of $[\text{U}]$ by using procedures similar to those used for EXAFS sample preparation.

Wet pastes recovered from the sorption experiments were immediately mounted in Lucite[®] or Kel-F sample holders and sealed by using a thin layer of Kapton[®] or Kel-F to prevent drying of the sample. All EXAFS spectra were collected at ambient conditions at the BESSRC sector 12 bending-magnet beamline at the APS. The beam was used in a defocused mode to give a spot size on the sample of approximately 1 \times 2 mm. A pair of Si(111) crystals was used in the monochromator, with the second crystal detuned typically by 15% to 20%. Sample cells were mounted at 45° to the incident beam, and spectra were measured in fluorescence mode by using a Canberra 13-element solid-state Ge detector positioned at 90° to the beam. Between 5 and 20 scans were collected per sample.

Individual EXAFS scans were checked for energy calibration and then averaged. Background subtraction and normalization used a linear pre-edge function and a second-order post-edge polynomial. E_0 was assigned the value of 17,171 eV. The χ function was extracted by using a cubic spline with k^3 weighting. All fitting was done with the program winXAS [2], with theoretical phases and backscattering amplitudes calculated by using FEFF7 [3].

Fitting was done in R-space on the Fourier transforms of the k^3 -weighted χ spectra. The typical k and R ranges were 3 to 12.5 \AA^{-1} and 0.6 to 4.5 \AA , respectively. Most samples had EXAFS data resembling that of the uranyl triscarbonate complex (as shown in the results) and were fitted with six shells. To reduce the number of free parameters in the initial fitting procedure, we fixed the coordination number of each shell at the value consistent with the uranyl triscarbonate complex, having three bidentate CO_3 groups in the equatorial plane. The amplitude reduction factor S_0^2 was set at 1, and a global threshold energy E_0 was allowed to vary during fitting, along with the radial distances and Debye-Waller factors of each shell. Estimated errors for the radial distance R are $\pm 0.01 \text{ \AA}$ for the first and second shells and ± 0.02 to 0.04 \AA for more distant shells.

Results

The U(VI)-calcite sorption isotherm is shown in Fig. 1. The suspension pH of the samples used in this experiment were in the range of 8.3 to 8.6, and carbonate was co-added with U(VI) in all cases. Uranyl uptake increases with the U solution concentration and shows no evidence of reaching a Langmuir sorption plateau, although there is a decrease in fractional uptake with [U] at concentrations of $< 500 \mu\text{M}$. The sharp rise in U(VI) removal from solution at concentrations of $> 500 \mu\text{M}$ suggests precipitation in the high [U] range.

The raw and fitted k^3 -weighted χ spectra of the samples analyzed by EXAFS are shown in Fig. 2A, and the radial structure functions (RSFs, Fourier transform magnitudes)

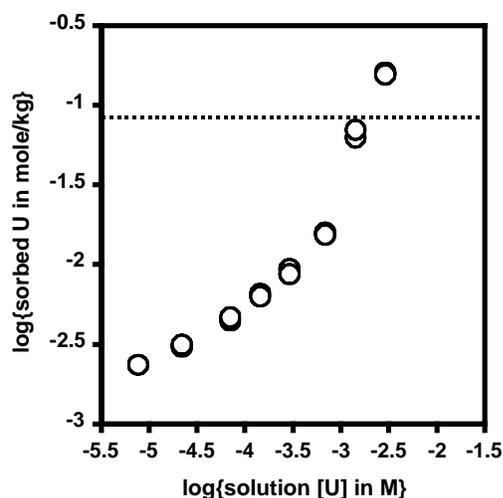


FIG. 1. Adsorption isotherm of U(VI) sorption to calcite at pH 8.3 and $P(\text{CO}_2) = 10^{-3.5}$ bar. The dashed vertical line indicates the concentration of Ca surface sites at the calcite surface.

of these spectra are shown in Fig. 2B. All the data for the samples reacted at low [U] ($< 500 \mu\text{M}$) resemble the spectrum of the aqueous triscarbonate complex, except that the contribution of the equatorial shell in the RSFs of these samples is lower in magnitude than that of the aqueous triscarbonate complex and has a shoulder on the high- R side. This indicates slight splitting in the equatorial shell of the adsorbed U(VI) complexes, or possibly the presence of a mixture of U(VI) species that have different equatorial O shell coordinations at the calcite surface. Because of the similarity in the EXAFS data for the uranyl triscarbonate complex and those for the low-loading U(VI) adsorption complexes at the calcite surface, the sorption sample fits presented in Fig. 2 were generated by using the same theoretical paths as for the triscarbonate complex. In addition to the axial ($R = 2.8 \text{ \AA}$) and equatorial O shells ($R = 2.4 \text{ \AA}$), these included scattering from a C shell at about 2.90 \AA , a multiple scattering (MS) U- $\text{O}_{\text{axial}(1)}$ -U- $\text{O}_{\text{axial}(2)}$ path with a radial distance approximately twice that of the U- O_{axial} distance, another O shell at about 4 \AA (O_{distal}), and the linear U- O_{distal} -C MS path with R of $\sim 4 \text{ \AA}$.

The sample reacted at high [U] (5 mM) shows a distinctly split equatorial O shell, with oxygens at 2.26 \AA and 2.46 \AA . Five shells were used to fit this spectrum: O_{axial} , two O_{eq} , MS at twice the distance of the U- O_{axial} path, and U-C, which resulted in a reasonable fit of the experimental spectrum (Fig. 2). Speciation calculations and the isotherm data (Fig. 1) indicated that the most likely cause for the difference in U coordination relative to the low [U] samples is the formation of uranyl (hydroxide) precipitates. No U-U scattering was identified, however, suggesting that the U that is present in the precipitates that formed does not have a single well-defined local structure but instead exhibits a range of U-U distances. This may be a result of dispersion in U-U distances within a “single” precipitate phase (as observed for Th-hydroxide [4]) and/or the formation of a multiphase precipitate (e.g., precipitate with different degrees of hydration). Speciation calculations indicated oversaturation with respect to U-hydroxides. However, it is quite likely that the precipitates that formed are not pure phases but contain Ca and CO_3 impurities, adding to the complexity of the phases that may form.

There is no discernable difference in the EXAFS spectra of samples reacted at pH 8.3 and pH 7.4 (Fig. 2), suggesting that the same mode of U(VI) uptake occurs at both pH conditions. This is consistent with speciation calculations, which indicated that the U(VI) solution speciation is essentially the same at these pH values, with the U-triscarbonate complex dominating in solution. The co-addition of CO_3 does not have a noticeable effect on U(VI) surface speciation at low ($50 \mu\text{M}$) [U]. At [U] = $500 \mu\text{M}$, however, there is an obvious effect: the sample with co-added CO_3 shows the same triscarbonate

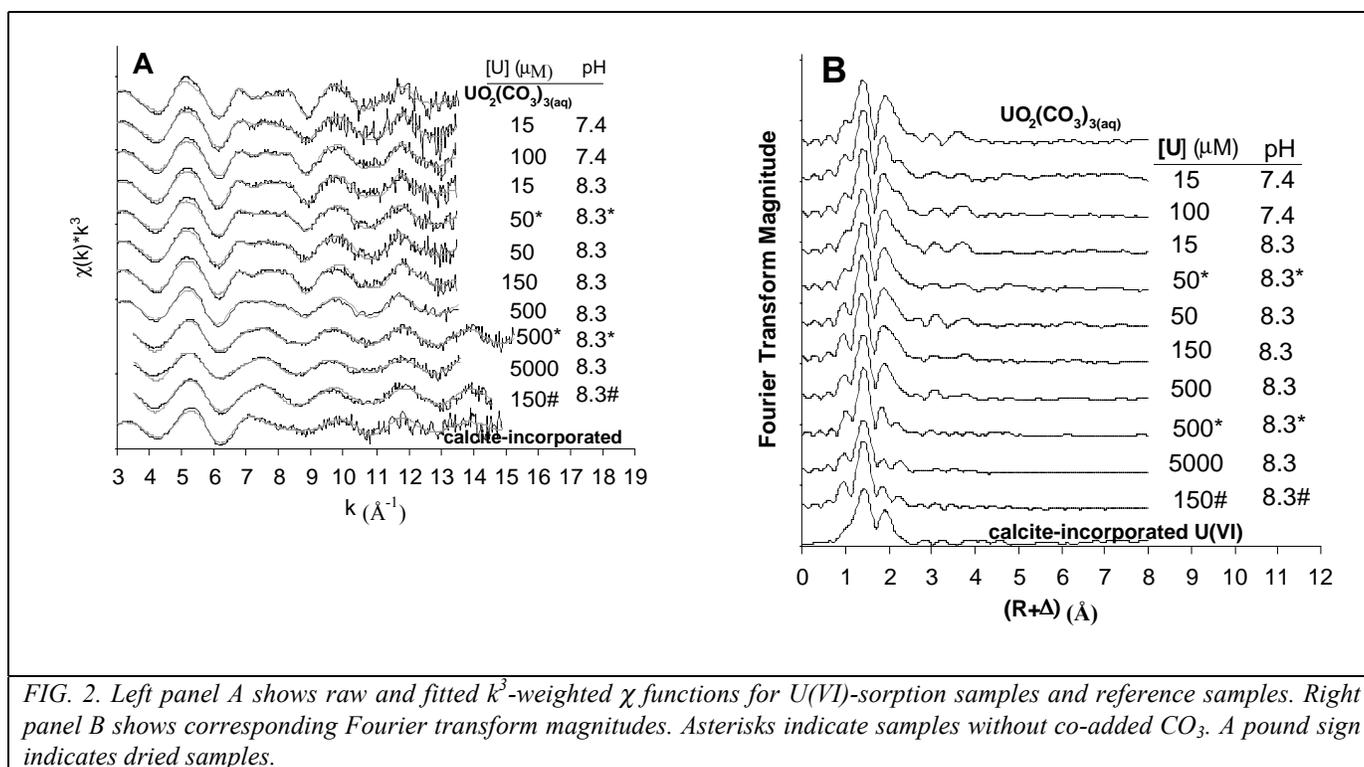


FIG. 2. Left panel A shows raw and fitted k^3 -weighted χ functions for U(VI)-sorption samples and reference samples. Right panel B shows corresponding Fourier transform magnitudes. Asterisks indicate samples without co-added CO_3 . A pound sign indicates dried samples.

surface complex that is also observed at lower [U], whereas the EXAFS data of the sample without co-added carbonate are similar to the high [U] sample, where precipitation is thought to occur. Introducing U(VI) as the triscarbonate complex to the calcite suspensions at high U(VI) concentrations is found to stabilize added U(VI) against the formation of uranyl hydroxide precipitates, which agrees with speciation calculations.

Discussion

The EXAFS data for the high U(VI) loading sample ([U] = 5 mM) indicate the formation of precipitates in this sample, which is in agreement with speciation calculations. X-ray diffraction (XRD) and luminescence data collected for this sample (not shown) indicate that the precipitates are x-ray amorphous and are likely to be multiphased but may have similarities to uranyl hydroxide or schoepitelike phases. There is also evidence in the literature for the formation of U(VI) precipitates at high U loadings in calcite-containing systems. Our findings indicate that precipitate formation is enhanced when UO_2^{2+} is introduced to a system lacking sufficient dissolved carbonate to allow for uranyl carbonate complexation, consistent with speciation calculations. Additionally, the XRD results suggest that the co-addition of CO_3 also influences the type of U(VI) precipitates that form.

For the lower U(VI) loading samples, the EXAFS data are consistent with the dominant formation of a uranyl

triscarbonate sorption complex with a slightly distorted equatorial shell. The distortion in the equatorial shell likely results from the interaction of the triscomplex with the calcite surface, although no Ca backscattering could be identified. Luminescence data collected for these samples (not shown) are consistent with the formation of U(VI) triscarbonate adsorption complexes and indicate that there is a slight change in the coordination of these complexes to the surface as the surface loading increases.

The complexity that is evident when uranyl species interact at the calcite-water interface in controlled experiments suggests the potential for equal or greater complexity in natural systems. The presence of multiple uranyl species suggests that kinetic uptake behavior could exhibit multiple trends and that the retention behavior of U(VI) sorbed by calcite may exhibit multiphase character. It must be considered, however, that the relatively short duration of the sorption experiments described here may not necessarily capture any effects associated with sample aging. For example, a local coordination of U(VI) co-precipitated with natural calcite from a speleothem sample was found that differs from the synthetic U(VI):calcite co-precipitation of our previous work [8, 9]. Presumably, factors that influence the process (including time) result in the different solid speciation. Similarly, differences in environmental parameters between laboratory and natural conditions and among different natural conditions may result in variability in the solid speciation of U(VI) sorbed with calcite.

Acknowledgments

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