XAFS Study of Calcium Complexation to Uranyl Bicarbonate

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Introduction

Current bioremediation efforts are focused on supplying indigenous metal-reducing bacteria with the appropriate metabolic requirements to induce microbiological reduction of soluble U(VI) to insoluble U(IV), forming the uranium oxide uraninite. The often complex chemistry of contaminated groundwater presents a challenge for microbiological reduction. Recent macroscopic studies of the rate and extent of U(VI) bioreduction in the presence of calcium, at calcium concentrations found in groundwater at many sites, reveal limited, slowed U(VI) reduction [1]. Fourier transform infrared studies of similar systems from acid mine drainage indicate that calcium may be forming a stable complex with the uranyl carbonate species ($Ca\text{-}UO_2\text{-}CO_3$) presumed to be most abundant [2]. This shift in the aqueous speciation of U(VI) in groundwater can have a dramatic effect on the fate and transport of uranium in groundwater and can also determine the most effective bioremediation strategies. To verify the formation of a $Ca\text{-}UO_2\text{-}CO_3$ complex, we made XAFS measurements on solutions containing 50 μM U(VI) and 30 mM bicarbonate, with various calcium concentrations from 0 mM to 5 mM.

Methods and Materials

The solution samples were prepared under anoxic conditions. Samples contained analytical grade U(VI) (50 μM), HCO_3^- (30 mM), and calcium concentrations of 0, 50, 500, or 5000 μM. The uranium concentration of 50 μM results in an edge step that is smaller by approximately two orders of magnitude than that for a standard fluorescence measurement edge step. These measurements were made possible by using a Canberra 13-element solid-state detector with X1A electronics and long integration times. Uranium L_3-edge EXAFS measurements were made at the MRCAT insertion device (10-ID) beamline [3]. The insertion device was tapered to reduce the variation in the x-ray intensity to less than 15% throughout the scanned energy range. A Si(111) double-crystal monochromator was used to select the x-ray energy. A Rh mirror was used to remove x-rays with higher harmonic energies. A nitrogen-filled ion chamber monitored the incident x-ray intensity. The integration time for each data point, approximately 12 sec, enabled the collection of one EXAFS scan per hour. Each sample was measured 3–10 times. The data were processed by using standard procedures with the UWXAFS [4] software package. The averaged $\chi(k)$ data are shown in Fig. 1. Theoretical models were constructed with the program FEFF7 [5] and the crystallographic atomic positions of andersonite [6]. Automatic overlap of the muffin tin potentials was used in the FEFF7 calculation.

Results

The U(VI) in these samples is expected to be in the form of a uranyl tricarbonate species with an unknown number of calcium atoms, presumably bound to the distant oxygen atoms (Odist) of the carbonate groups [1]. A ball-and-stick model of this uranyl tricarbonato species is shown in Fig. 2. This figure shows the equatorial oxygen atoms (Oeq) in the plane of the page, with the axial oxygen atoms (Oax) above and below the uranium atom. The model for this structure contains 4 shells of atoms. These shells contain 2 Oax, 6 Oeq, 3 C, and 3 Odist. Important U–Oax–U–Oax and U–C–Odist multiple scattering paths must also be included in the model. On the basis of other $Ca\text{–}UO_2\text{–}CO_3$ systems, the U–Ca distance is expected to be about 3.8–4.1 Å [1]. This path was added to the model for the data from samples containing calcium. All data sets were fitted simultaneously by using k-weight values of 1, 2, and 3 in the Fourier transform. The bond lengths (Δr values) are not expected to change significantly when calcium is added to the system, and thus the 4 shells were constrained to the same values for all data sets. Fig. 3 shows the Fourier transform of the data and the best-fit models.

Discussion

The best-fit value of 0.7 ± 0.5 to 1.3 ± 0.5 for the number of calcium atoms indicates the presence of a $Ca\text{–}UO_2\text{–}CO_3$ complex in these samples. All of the other parameters, including the σ^2 values and Δr values, are within the uncertainties of previously reported values. Simultaneous fitting of the data was necessary to distinguish between the contributions from the calcium atom, Odist, and the multiple scattering paths (U–C–Odist) of the carbonate groups. Direct evidence for the $Ca\text{–}UO_2\text{–}CO_3$ complex and its role in bioreduction of U(VI) in calcareous groundwaters should be considered in developing feasible bioremediation strategies.

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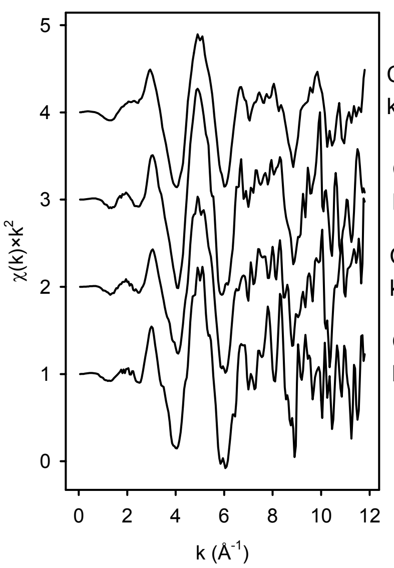

Fig. 1. Averaged $\chi(k)\cdot k^2$ data for the aqueous samples. The concentration of calcium is indicated in the identification labels (i.e., Ca5000 contains 5000 μM calcium).

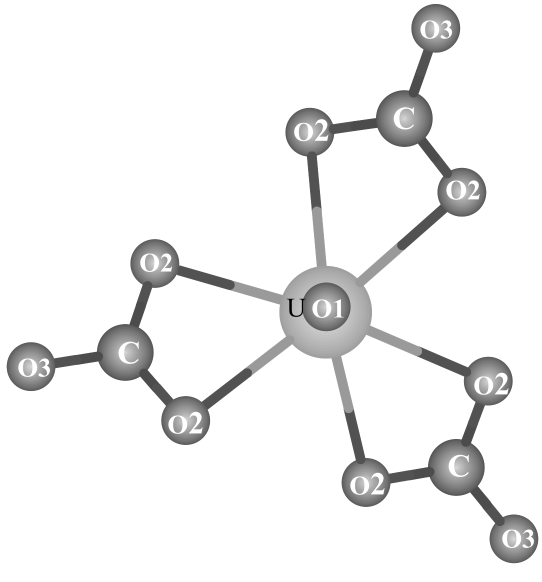

Fig. 2. Ball-and-stick figure of $(UO_2)(CO_3)_3$ species. The uranyl moiety (UO_2^{2+}) is made up of the U atom bound by 2 axial oxygen (O1 = Oax) atoms above and below the U atom and 6 equatorial oxygen atoms (O2 = Oeq) shared with the carbonate groups, which also contain 3 distant oxygen atoms (O3 = Odist).

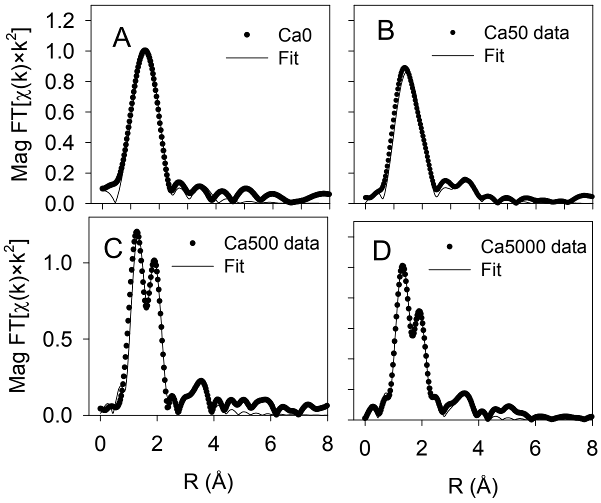

Fig. 3. The magnitude of the Fourier transform of the (A) Ca0 data, (B) Ca50 data, (C) Ca500 data, and (D) Ca5000 data (symbols) and fit (lines).

References

[1] S.C. Brooks *et al.*, Environ. Sci. & Technol. **37**, 1850-1858 (2003).

[2] G. Bernhard, G. Geipel, V. Brendler, H. Nitsche, Radiochim. Acta **74**, 87-91 (1996).

[3] C.U. Segre *et al.*, Synchrotron Radiation Instrumentation: Eleventh U.S. Conference **CP521**, 419-422 (2000).

[4] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, D. Haskel, Physica B **208 & 209**, 117-120 (1995).

[5] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, M.J. Eller, Phys. Rev. B **52**, 2995-3009 (1995).

[6] A. Coda, A. Della Giusta, V. Tazzoli, Acta Cryst. **B37**, 1496-1500 (1981).