XAFS Study of Calcium Complexation to Uranyl Bicarbonate

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Introduction

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

Methods and Materials

The solution samples were prepared under anoxic conditions. Samples contained analytical grade 50 µM U(VI), 30 mM HCO_3^-, and Ca concentrations of zero, 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. The uranium L_3-edge extended XAFS (EXAFS) measurements were made at MR-CAT insertion device beamline 10-ID at the APS [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. The measurements were made in fluorescence mode by using a 13-element solid-state detector (Canberra with X1A electronics).
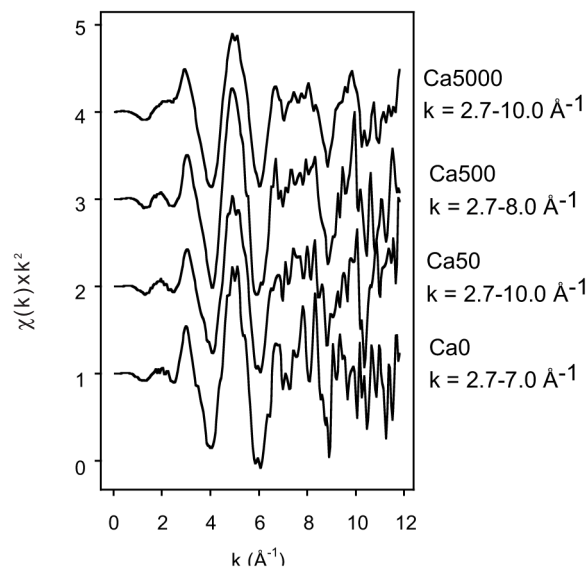

FIG. 1. Averaged $\chi(k)\cdot k^2$ data from the aqueous samples. The concentration of Ca is indicated in the identification labels (i.e., Ca5000 contains 5000 µM Ca).

A nitrogen-filled ion chamber monitored the incident x-ray intensity. The integration time for each data point, approximately 12 seconds, resulted in about approximately one EXAFS scan per hour. Each sample was measured 3 to 10 times. The data were processed by using standard procedures and 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, as reported previously [7].

Results

The U(VI) is expected to be in the form of a uranyl tricarbonate species with an unknown number of Ca atoms, presumably bound to the distant oxygen atoms (Odist) of the carbonate groups. A ball-and-stick model of this 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 four shells of atoms. These shells contain 2 Oax, 6 Oeq,
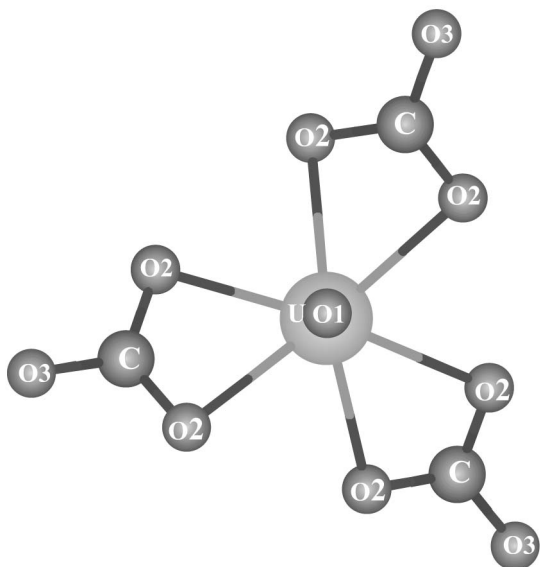
FIG. 2. Ball-and-stick figure of $(UO_2)(CO_3)^{3^-}$ species. The uranyl moiety (UO_2^{2+}) is made up of the U atom bound by two axial oxygen atoms $(O_1 = Oax)$ located above and below the U atom and six equatorial oxygen atoms $(O_2 = Oeq)$ shared with the carbonate group that also contains three distant oxygen atoms $(O_3 = Odist)$.

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 (line).

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 $Ca-UO_2-CO_3$ systems, the U-Ca distance is expected to be about 3.8-4.1 Å. This path was added to the model for the data from samples containing Ca. All data sets were fitted simultaneously by using k-weight values of 1, 2, and 3 in the Fourier transform. The Δr values for each of the four shells were constrained to the same value for all data sets, because Δr values are not expected to change significantly when Ca is added to the system. Figure 3 shows the Fourier transform of the data and the best-fit models.

Discussion

The best-fit value of 0.7 to 1.3 ±0.5 for the number of Ca atoms indicates the presence of a $Ca-UO_2-CO_3$ 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. Simultaneously fitting of the data was necessary to distinguish between the contributions from the Ca atom, the distant oxygen (Odist), and the multiple scattering paths (U-C-Odist) of the carbonate groups. Direct evidence for the $Ca-UO_2-CO_3$ complex and its role in bioreduction of U(VI) in calcareous groundwaters should be considered in developing a feasible bioremediation strategies.
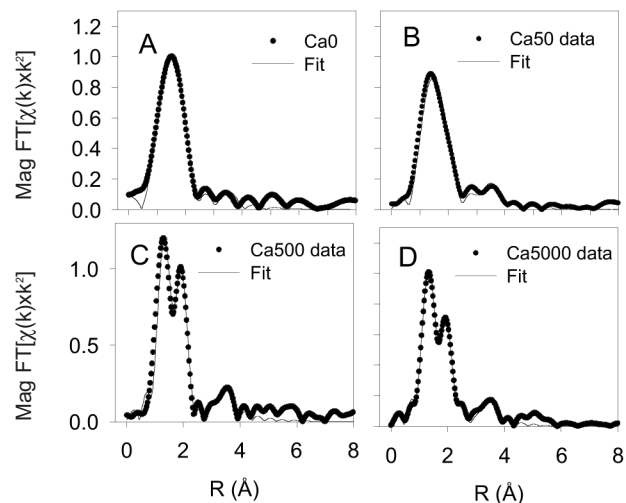
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