

XAFS Determination of a Stable Crystallographic Site for Uranyl Impurities in Natural Calcite

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Introduction

The incorporation of the uranyl (UO_2^{2+}) oxo-cation in calcite has been a long-standing problem in geochemistry because the size and shape of the linear uranyl moiety ($\text{O}=\text{U}=\text{O}$) are significantly different than those of the Ca^{2+} ion for which it may substitute in the calcite structure. Hexavalent uranium (U^{6+}) in the form of uranyl is the most common species of uranium found in surface water, oxic seawater, and oxic groundwater. Uranyl is therefore the form of uranium most likely to be incorporated in calcite precipitated from such waters. Direct structural measurement of U coordination in calcite at natural concentration levels (typically 0.1 to 10 $\mu\text{g/g}$) is difficult to obtain. New x-ray fine structure (XAFS) data were recently obtained for an anomalously U-rich (~360 ppm of U) calcite (sample LAS-20) from a 14,000-year-old speleothem deposit in the Vinschgau Valley of northernmost Italy. These data may solve the location of uranyl in typical natural calcite.

Methods and Materials

The fluorescence U L3 edge XAFS measurements were made on a piece of polished calcium carbonate (sample LAS-20) at the Materials Research Collaborative Access Team (MR-CAT) sector [1] at the APS. The energy of the incident x-rays was selected by using a double-crystal Si(111) monochromator. The undulator was tapered approximately 2 keV to reduce the variation in the incident intensity to less than 15% over the scanned energy range. Higher harmonics were rejected by using a Rh mirror. The incident x-ray intensity was sampled with a nitrogen-filled ion chamber, and the fluorescent x-ray intensity was sampled by using an argon-filled ion chamber in the Stern-Heald geometry [2] utilizing a Sr filter of three absorption lengths. Linearity tests [3] indicated less than 0.3% nonlinearity for a 50% decrease in incident x-ray intensity. Ten scans were collected at six different locations on the sample to reduce possible radiation-induced changes to the sample. The sample was exposed for approximately 2 min for each of the measurements at each location. Measuring several spectra at different sample locations enabled determination of

radiation-induced chemical effects at the 1-min timescale. No time-dependent change in the XAFS data was observed for the sample.

X-ray diffraction measurements on powdered LAS-20 samples were performed at the Basic Energy Sciences Synchrotron Radiation Center (BESSRC)-CAT 12-BM station to identify crystalline phases(s) of calcium carbonate. These measurements showed that the LAS-20 sample consisted of pure calcite with no measurable content of aragonite or other phases.

The codes contained in the UWXAFS package [4] were used to analyze the XAFS data. The program FEFF7 [5] was used to construct the theoretical model on the basis of the crystallographic atomic position of andersonite [6]. The error analysis and the goodness-of-fit parameters were calculated by the fitting routine FEFFIT [7]. The structural parameters determined in a fit to the XAFS data include N_{degen} and R , which are the number of and distance to the neighboring atoms for a single scattering path, respectively, and σ^2 , which is the relative mean square displacement of the absorbing U atom and the neighboring atoms for a single scattering path.

Results

The best-fit values for the U-calcite XAFS data are listed in Table 1, and the data and fit are shown in Fig 1. The O_{eq} shell coordination number (3.8 ± 0.4) and distance ($2.41 \pm 0.01 \text{ \AA}$) are unique to this study. Usually the distance to a fourfold coordinated O_{eq} shell is shorter ($2.05\text{-}2.35 \text{ \AA}$) [8]. The local structure of the uranyl as an impurity in the calcite structure could be different than it is in aqueous solutions or solid uranyl structures where U is a major component, which are the basis for the previously reported values ($2.05\text{-}2.35 \text{ \AA}$). Therefore, while we believe the longer distance of 0.06 \AA is significant, it is not an unrealistic increase in the bond length for our system. Figure 2A shows the local structure about a Ca atom in calcite. Figure 2B shows UO_2^{2+} substituted for Ca and two carbonate groups. This type of substitution is consistent with the extended XAFS (EXAFS) results for the coordination number of O_{eq} atoms (3.8 ± 0.4).

Table 1. Best-fit values for the calcite sample. S_0^2 was held at 1.0 ± 0.2 , as determined from the hydrated uranyl standard. ΔE_0 was determined to be 6.1 ± 1.5 eV for the U-Oax paths and 7.8 ± 1.0 eV for all other paths. The fit had 17 independent points in the data and 14 variables. Values without uncertainties were constrained to the listed value.

Path	N _{deg}	R (Å)	$\sigma^2 (10^{-3} \text{Å}^2)$
U-Oax	2	1.80 ± 0.01	2 ± 1
U-Oeq	3.8 ± 0.4	2.41 ± 0.01	6 ± 2
U-C	4.3 ± 2.7	3.51 ± 0.04	7 ± 11
U-Oax ₁ -Oax ₂	2	3.61 ± 0.02	5 ± 1
U-Oax ₁ -U-Oax ₁	2	3.61 ± 0.02	5 ± 1
U-Oax ₁ -U-Oax ₂	2	3.61 ± 0.02	5 ± 1
U-Ca ₁	2.3 ± 0.4	3.78 ± 0.03	7 ± 4
U-Ca ₂	3.7 ± 0.4	4.01 ± 0.02	7 ± 4

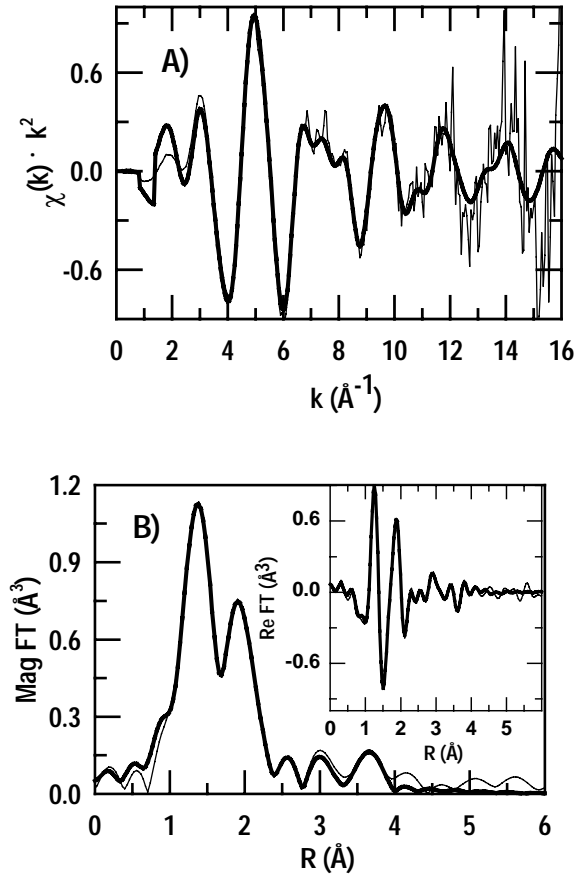


FIG. 1. The XAFS data (thin line) and best-fit model (thick line) for calcite sample LAS-20. A: Average $\chi(k) \cdot k^2$. B: Magnitude and real part (inset) of the Fourier transform of $\chi(k) \cdot k^2$. The data were processed by using $\Delta k = 2.0\text{-}10.5 \text{Å}^{-1}$ and $\Delta R = 1.1\text{-}3.9 \text{Å}$. A Hanning window was used in the Fourier transform with a full sill width of 1.0Å^{-1} .

The U-C ($3.51 \pm 0.04 \text{Å}$) distance is $\sim 0.3 \text{Å}$ longer than the Ca-C distance (3.2Å) and is consistent with a tilting of the carbonate groups toward the equatorial plane of the uranyl. The mean-square displacement for the U-C path ($0.007 \pm 0.012 \text{Å}^2$) is reasonable for this structure and similar to previously reported values for a shorter bidentate C shell ($0.002\text{-}0.007 \text{Å}^2$). The coordination number for the C shell (4.3 ± 2.7) is consistent with the expected value (4) for the configuration as shown in Fig. 2B.

The EXAFS results for the split Ca shell with distances of 3.78 ± 0.03 and $4.01 \pm 0.02 \text{Å}$ are also consistent with the model shown in Fig 2B and similar to previously reported values ($3.82\text{-}4.75 \text{Å}$). The Ca-Ca distance in calcite is 4.05Å and is also similar to our results. The mean-square displacement value for these shells ($0.007 \pm 0.004 \text{Å}^2$) is reasonable for this system and also within the range of previously reported values ($0.003\text{-}0.008 \text{Å}^2$), indicating that our constraint requiring the total coordination number for both Ca shells to six was reasonable. If this constraint is lifted, the best-fit values for the split Ca shell become nonphysical, indicating that our data range is not sufficient to determine the absolute values. The split in the coordination number determined from the fit of 2.3 and 3.7 ± 0.4 is consistent with 2 and 4, which are the expected values from the model shown in Figure 2B, where two of the Ca atoms are slightly closer to the uranyl ion because of the void from the displaced carbonate groups.

Discussion

Our results for the incorporation of U(VI) into calcite are different than previously reported for U(VI) into synthetic calcite [9]. The structure about the uranyl in synthetic calcite is similar to the initial aqueous uranyl structure with ~ 6 Oeq atoms and ~ 3 bidentate carbonate groups. Conversely, in natural calcite, monodentate carbonate (4.2 ± 2.7) groups dominate. In addition, the coordination of the U in natural calcite is sixfold, which is the same as Ca in calcite, rather than sevenfold, as previously determined for U(VI) in synthetic calcite. Also, in the synthetic calcite sample, no Ca backscatter signal was detected, which indicates a nonstable uranyl environment. This is not the case for our natural sample, where we found a signal from ~ 6 Ca atoms at $\sim 3.8\text{-}4.0 \text{Å}$, which is similar to that for the Ca atom in calcite. Our results indicate that the U(VI) incorporation into natural calcite may be more stable than previously suspected on the basis of studies of experimental systems.

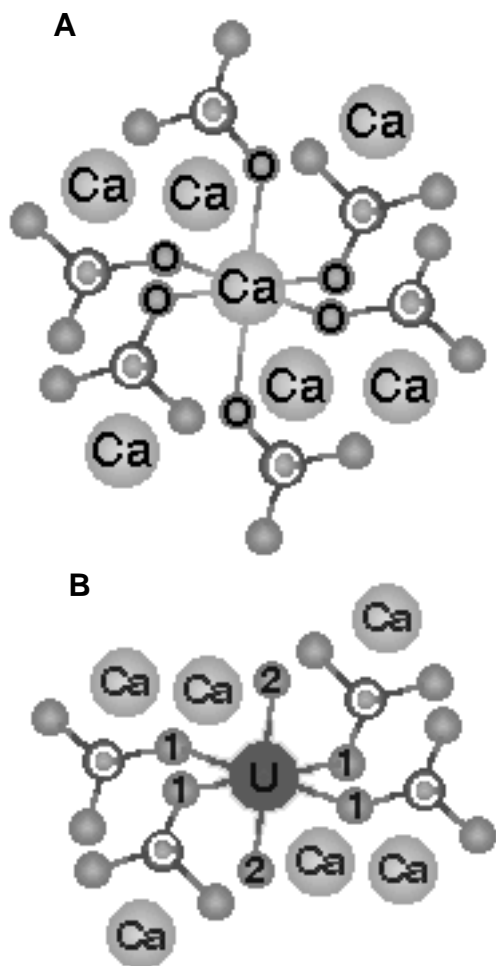


FIG. 2. A: Diagram showing calcite structure about a Ca^{2+} ion. B: Diagram showing best-fit model of local calcite structure around incorporated uranyl ion with four equatorial oxygens attached in monodentate fashion to carbonate ions and two axial oxygens. The numerals 1 and 2 indicate O_{ax} and O_{eq} atoms, respectively.

Acknowledgments

Special appreciation is extended to E. J. O'Loughlin for assistance with U XAFS data collection. J. H. Terry is acknowledged for his assistance with U XAFS data collection at the MR-CAT sector. Support for S. D. Kelly and K. M. Kemner was provided by the U.S. Department of Energy (DOE), Office of Biological and Environmental Research, Natural and Accelerated Bioremediation Research (NABIR) Program. Support for L. Cheng, P. Fenter, and N. C. Sturchio was provided by the DOE Office of Science, Office of Basic Energy Sciences (BES), Geosciences Research Program. Use of the APS was supported by DOE BES under contract W-31-109-ENG-38.

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