Uranyl Incorporation in Natural Calcite

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The occurrence of trace amounts of uranyl in natural calcite has posed a long-standing problem in crystal chemistry because of speculation that the size and shape of the uranyl ion may preclude its incorporation in a stable lattice position in calcite. This also defines an important environmental problem because of its bearing on the transport and sequestration of uranyl released from nuclear facilities and uranium mining operations. Calcite is a nearly ubiquitous mineral in soils and groundwater aquifers. X-ray absorption spectroscopy and X-ray fluorescence microprobe studies of uranium in relatively U-rich (~13 700-year-old calcite from a speleothem in northern Italy indicate substitution of uranyl for a calcium and two adjacent carbonate ions in calcite. These new data imply that uranyl has a stable lattice position in natural calcite, indicating that it may be reliably sequestered in calcite over long time scales.

Introduction

Uranium (U) is the most common radionuclide contaminant in soils and groundwaters; therefore, uranyl is the form of uranium most likely to be incorporated in calcite precipitated in such waters. The incorporation of the uranyl (UO22+) ion in calcite has posed a long-standing problem in crystal chemistry, however, because the size and shape of the uranyl ion (O=U=O) are significantly different than those of the Ca2+ ion for which it may substitute in the calcite structure. Recent XAFS and X-ray microprobe data were obtained recently for another relatively U-rich (~360 μg/g) calcite from a 13 700-year-old speleothem deposit in the Vinschgau Valley of northernmost Italy. These data, presented here, may be representative of the location of uranyl in typical natural calcites having lower U concentrations.

Experimental Methods

Experimental Setup. The relatively U-rich calcite examined for this study (sample LAS-20) is from a 13 700-year-old speleothem deposit in the Vinschgau Valley of northern Italy. The sample was prepared in three ways for X-ray measurements at the Advanced Photon Source (APS): as a powder for X-ray diffraction measurements, as a 100-μm-thick doubly polished thin-section for X-ray microprobe measurements, and as a 0.5 × 2 × 3 cm block for XAFS measurements. A bulk U concentration of 362 ± 6 μg/g was measured by isotope dilution α-spectrometry of the powdered sample.

X-ray Diffraction. Powder diffraction measurements performed at APS beamline 12-BM in transmission geometry with monochromatic X-rays (wavelength = 0.6357 Å) indicated that the sample is >99.8% pure calcite.

X-ray Fluorescence Mapping. X-ray microprobe scans were performed at APS beamline 13-ID using a doubly focused, monochromatic X-ray beam from APS undulator A. The X-ray energy was set to 17.3 keV (well above the U L3 edge) with a double-crystal Si(111) monochromator, adjusting the undulator gap to give maximum intensity at that energy. The X-ray beam was focused to 5 μm × 5 μm using Kirkpatrick-Baez mirrors, which also provided harmonic rejection. The sample was rastered across this beam in 20-μm steps. At each position, fluorescence intensities for Ca Kα, U Lα, and Sr Kα were collected using a 16-element Ge solid-state detector.

X-ray Absorption Spectroscopy. Fluorescence XAFS measurements at the U L3 absorption edge (17166 eV) were performed at the Materials Research Collaborative Access Team (MR-CAT) (13) beamline 10-ID at the APS at Argonne National Laboratory. Incident X-ray energy was selected by using a double-crystal Si(111) monochromator. The undu-
There is no evidence for U-rich inclusions at the scale of the occurrence of U in a dilute solid calcite.

Results from the X-ray fluorescence mapping indicate that the U concentration in a portion of the calcite varies from about 80 to 500 ppm. These XRF data are consistent with the occurrence of U in a dilute solid—solution within the calcite.

Results and Discussion

X-ray Fluorescence Mapping. Results from the X-ray fluorescence (XRF) mapping indicate that the U concentration in a portion of the calcite varies from about 80 to 500 ppm and is fairly homogeneous at the 100-μm scale (Figure 1). There is no evidence for U-rich inclusions at the scale of the beam spot size (5 μm). These XRF data are consistent with the occurrence of U in a dilute solid—solution within the calcite.

X-ray Absorption Spectroscopy. The X-ray absorption spectra of the calcite sample and the uranyl nitrate hexahydrate [UO₂(NO₃)₂·6H₂O] reference compound have indistinguishable peak edge energies at 17167 eV (Figure 2), indicating that U in the sample is dominantly hexavalent.

The presence of peaks between 1 and 4 Å in the magnitude of the Fourier transform (FT) of the XAFS data (Figure 2) correspond to the two axial oxygen (Oax) and approximately four (3.8 ± 0.4) equatorial oxygen (Oeq) atoms of the uranyl, with a U–Oax distance of 1.80 ± 0.01 Å and a U–Oeq distance of 2.41 ± 0.02 Å, respectively. Beyond these two shells, there is a signal from a shell (appearing at 2.2–3.2 Å in the FT) containing approximately four (4.3 ± 2.7) C atoms with a U–C distance of 3.51 ± 0.04 Å. The XRF data and best-fit model are shown in Figure 3. The individual contributions to the model for each scattering path are shown. Under the data and best-fit model, the contributions to the model for each scattering path are shown. The error analysis and the goodness-of-fit parameters were calculated by the fitting routine FEFFIT (19). The theoretical models are built from the theoretical model on the basis of the crystallographic atomic positions of andersonite (18). The goodness-of-fit parameters determined in a fit to the data include the number of atoms in a shell (Nshell) about the absorbing atom and the mean-square displacement (σ²) of the distance between the absorbing atom and the neighboring atom for a single scattering path of the photoelectron.

FIGURE 1. X-ray fluorescence map of calcite sample LAS-20 (12), showing U concentration as a function of position. The U concentration is normalized to that of Ca to account for changes in thickness of the sample.

FIGURE 2. Normalized X-ray absorbance for U L₃ edge showing XAFS for U in calcite sample LAS-20 (solid) and for uranyl nitrate hexahydrate reference compound (dashed). The similarities in energy and intensity of features A (white line at 17167 eV), B (shoulder at 17178 eV), and C (at 17202 eV) indicate that U is present as UO₂⁺ in calcite.

FIGURE 3. XAFS χ(k)² data (open circles) and best-fit model (thick line) for calcite LAS-20.

FIGURE 4. XAFS data (open circles) and best-fit model (thick line) for U in calcite sample LAS-20 (solid) and for uranyl nitrate hexahydrate reference compound (dashed). The similarities in energy and intensity of features A (white line at 17167 eV), B (shoulder at 17178 eV), and C (at 17202 eV) indicate that U is present as UO₂⁺ in calcite.

FIGURE 2. Normalized X-ray absorbance for U L₃ edge showing XAFS for U in calcite sample LAS-20 (solid) and for uranyl nitrate hexahydrate reference compound (dashed). The similarities in energy and intensity of features A (white line at 17167 eV), B (shoulder at 17178 eV), and C (at 17202 eV) indicate that U is present as UO₂⁺ in calcite.
**TABLE 1. EXAFS Model Parameters for the Calcite Sample LAS-20 (12)**

<table>
<thead>
<tr>
<th>path</th>
<th>R'</th>
<th>N_{depen}</th>
<th>ΔR (Å)</th>
<th>σ² (Å²)</th>
<th>ΔEₚ (eV)</th>
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</thead>
<tbody>
<tr>
<td>U–Oax</td>
<td>1.78</td>
<td>2⁰</td>
<td>ΔR₁</td>
<td>σ²₁</td>
<td>ΔE₁</td>
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<tr>
<td>U–Oeq</td>
<td>2.41</td>
<td>N₁</td>
<td>ΔR₂</td>
<td>σ²₂</td>
<td>ΔE₂</td>
</tr>
<tr>
<td>U–C</td>
<td>3.69</td>
<td>N₃</td>
<td>ΔR₃</td>
<td>σ²₃</td>
<td>ΔE₃</td>
</tr>
<tr>
<td>U–Oax–Oax₂</td>
<td>3.55</td>
<td>2⁰</td>
<td>2ΔR₁</td>
<td>2σ²₁</td>
<td>ΔE₁</td>
</tr>
<tr>
<td>U–Oax–Oax₃</td>
<td>3.58</td>
<td>2⁰</td>
<td>2ΔR₁</td>
<td>2σ²₁</td>
<td>ΔE₁</td>
</tr>
<tr>
<td>U–Oax–Oax₄</td>
<td>3.58</td>
<td>2⁰</td>
<td>2ΔR₁</td>
<td>2σ²₁</td>
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<tr>
<td>U–Cₐ₁</td>
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<td>N₄</td>
<td>ΔR₅</td>
<td>σ²₄</td>
<td>ΔE₄</td>
</tr>
<tr>
<td>U–Cₐ₂</td>
<td>3.96</td>
<td>6–N₄</td>
<td>ΔR₆</td>
<td>σ²₆</td>
<td>ΔE₆</td>
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* The initial path length. ⁶ These values were not varied in the fit. ⁷ Energy shift of the photoelectron.

**FIGURE 5.** (A) Diagram showing calcite structure about a Ca²⁺ ion. (B) Diagram showing the local structure of uranyl incorporated into calcite that is consistent with the XAFS data. The numerals 1 and 2 indicate Oeq and Oax atoms, respectively.

The model described above (Table 1) and shown in Figures 3 and 4 is in good agreement with the XAFS data and is consistent with the uranyl ion substituting for one Ca and two carbonate ions in the calcite structure. Calcium in calcite (Figure 5A) is coordinated by six O atoms at 2.36 Å. Each of these O atoms is a part of a carbonate group with a C atom at 3.21 Å, and there are six neighboring Ca atoms at 4.05 Å. According to our model (Figure 5B), uranium in calcite is also coordinated by six O atoms, two of which are the Oax atoms of the uranyl leaving four (3.8 ± 0.4) Oeq atoms that are each a part of a carbonate group with four (4.3 ± 2.7) C atoms at 3.51 ± 0.04 Å and there are a total of six Ca atoms at 3.78–4.01 Å from the U atom.

The distances to the neighboring shells and their mean-square displacement values of atoms determined for U in calcite (Table 2) are similar to those found for Ca in calcite and also to those found in other uranyl coordination environments. The best-fit values for the U–Oax shell distance (1.80 ± 0.01 Å) and mean-square displacement (0.002 ± 0.001 Å²) in the calcite sample are consistent with other reported values for the U–Oax distance (1.80 ± 1.81 Å) and σ² (0.001–0.004 Å²) (8, 9, 20–22). The best-fit value for the U–Oeq shell mean-square displacement (0.006 ± 0.002 Å²) is also consistent with other reported values (0.003–0.010 Å²) (8, 9, 20–22). The best-fit value U–Oeq distance in the sample (2.41 Å) is comparable to that for uranyl having 6 equatorial oxygens (2.43 Å) (23), such as for the uranyl triscarbonato aqueous complex, which has three carbonate ions bonded in bidentate fashion symmetrically about the uranyl equatorial plane. Despite this similarity in U–Oeq bond length, the best-fit value for the number of equatorial oxygens about uranyl in the sample is 3.8 ± 0.4, which is consistent with bonding of four carbonates in monodentate fashion about the uranyl equatorial plane. Furthermore, the best-fit value for the U–C distance in the sample (3.51 ± 0.04 Å) is much larger than the typical U–C distance for carbonates with bidentate bonding to uranyl (2.9 Å) (23) but more similar to the Ca–C distance in calcite (3.21 Å) in which all carbonates have monodentate bonding to Ca. Attempts to model our U XAFS data of bidentate bonding of carbonates to U resulted in significantly poorer quality fits, leading us to prefer the model in which uranyl substitutes for Ca with local relaxation of carbonates.

The proposed substitution results in net charge excess around the uranyl site of +4 because of the two missing carbonate ions. This charge excess could be compensated by a coupled, nonlocal substitution such as 5Ca²⁺ → UO₂²⁻ + 4Na⁺, which is consistent with our XAFS data and the elevated concentration of sodium (337 μg/g) in this calcite (12). The absence of the carbonate ions must create a significant defect in the local calcite structure; however, it is not clear how this might be accommodated. Substitution of water or hydroxyl for the missing carbonate may be possible. The U XAFS data do not allow determination of the exact substitution formula. The split U–Ca shell (approximately two Caₐ atoms at a shorter distance of 3.78 Å and approximately four Caₐ atoms at 4.01 Å) is not surprising. The two Caₐ atoms are most likely those nearest in the adjacent (104) planes that relax toward the uranyl position (Figure 5B) because of the displaced carbonate groups. The remaining four Caₐ atoms are at about the same distance from U (4.01 Å) as the Ca–Ca distance in calcite (4.05 Å).

**TABLE 2. Best-Fit Values for XAFS Model of Calcite Sample LAS-20 (12)**

<table>
<thead>
<tr>
<th>path</th>
<th>$N_{depen}$</th>
<th>R (Å)</th>
<th>σ² (10⁻³ Å²)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U–Oax</td>
<td>2</td>
<td>1.80 ± 0.01</td>
<td>2 ± 1</td>
<td>6.1 ± 1.5</td>
</tr>
<tr>
<td>U–Oeq</td>
<td>3.8 ± 0.4</td>
<td>2.41 ± 0.01</td>
<td>6 ± 2</td>
<td>7.8 ± 1.0</td>
</tr>
<tr>
<td>U–C</td>
<td>4.3 ± 2.7</td>
<td>3.51 ± 0.04</td>
<td>7 ± 11</td>
<td>7.8 ± 1.0</td>
</tr>
<tr>
<td>U–Oax–Oax₂</td>
<td>2</td>
<td>3.61 ± 0.02</td>
<td>5 ± 1</td>
<td>6.1 ± 1.5</td>
</tr>
<tr>
<td>U–Oax–Oax₃</td>
<td>2</td>
<td>3.61 ± 0.02</td>
<td>5 ± 1</td>
<td>6.1 ± 1.5</td>
</tr>
<tr>
<td>U–Oax–Oax₄</td>
<td>2</td>
<td>3.61 ± 0.02</td>
<td>5 ± 1</td>
<td>6.1 ± 1.5</td>
</tr>
<tr>
<td>U–Cₐ₁</td>
<td>2.3 ± 0.4</td>
<td>3.78 ± 0.03</td>
<td>7 ± 4</td>
<td>7.8 ± 1.0</td>
</tr>
<tr>
<td>U–Cₐ₂</td>
<td>3.7 ± 0.4</td>
<td>4.01 ± 0.02</td>
<td>7 ± 4</td>
<td>7.8 ± 1.0</td>
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</tbody>
</table>

* Values without uncertainties were constrained to the value listed.

**Summary**

Our XAFS results for the incorporation of uranyl into natural calcite differ significantly from those reported recently for uranyl-rich synthetic calcite (8, 9). The synthetic calcite has an Oeq coordination number of five, suggesting two bidentate linkages and one monodentate linkage with carbonate ions in the equatorial plane (8, 9). However, our best-fit results for the natural calcite indicate four monodentate linkages with carbonate ions in the equatorial plane, which is essentially the same coordination as Ca in calcite (Figure 5A, B). The total first-shell O coordination of the U⁶⁺ in our natural calcite sample is 6-fold, the same as Ca in calcite, rather than 7-fold as reported for U⁶⁺ in synthetic calcite (8, 9). No U–Ca backscatter was detected in the synthetic calcite, indicating either multiple or disordered sites for uranyl (8, 9).
9). This is not the case for the natural sample that we examined, however, where six Ca atoms occur in a split shell having an average U–Ca distance (3.93 Å) similar to that of the Ca–Ca distance in calcite (4.05 Å). The splitting of the O and Ca shells and the 4-fold coordination of the U–C shell are consistent with our model of substitution of uranyl for Ca in calcite, with $\text{U}^{6+}$ substituting for Ca and $\text{O}_{ax}$ substituting for the nearest carbonate ions in the adjacent (104) layers (see Figure 5).

The excellent agreement between the best-fit model and the XAFS data indicates that uranyl occupies a relatively stable position in this calcite. Uranyl in rapidly grown, synthetic, uranyl-rich calcite (8, 9) is apparently more likely to reside in defects or other, more disordered sites than that identified here. Our results for this 13 700-year-old natural calcite indicate either that natural calcite grows slowly enough to allow for ordering of incorporated uranyl during growth or that structural transformation of initially disordered uranyl in calcite may occur over a long time (8). Petrographic evidence indicates that this calcite formed by recrystallization of uranium-rich aragonite (12), for which our XAFS measurements also showed $\text{U}^{6+}$. This mechanism of formation (in a closed system) could explain the relatively high uranyl concentration by inheritance from the aragonite. The relatively high uranyl concentration of the precursor aragonite reflects its precipitation from uranium-rich groundwater circulating through crystalline basement rocks (12).

The stable position of uranyl in relatively uranyl-rich natural calcite, identified by analysis of our XAFS data, may provide a resolution to the problem of the location of trace uranyl in calcite. Further XAFS studies of uranyl-bearing natural calcite from a variety of contrasting geochemical environments are recommended to test the general applicability of this result. If the position of uranyl in natural calcite is generally as described above, calcite may provide a stable host for dispersed $\text{U}^{6+}$ over geological time scales, which is a result that has important bearing on the environmental fate and transport of aqueous uranyl.

Acknowledgments

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