

Influence of Growth Conditions on Uranyl Incorporation into Calcite

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Beamline(s): X11A

Introduction: The uptake of U(VI) during the crystallization of calcite represents a potentially important process affecting the mobility and sequestration of this radionuclide in the near surface environment. Coprecipitation and formation of a solid solution are likely to be the dominant mechanisms of metal uptake by carbonates over time scales relevant for environmental contaminants. Evaluating the effectiveness of this process for sequestration and the potential for remobilization depends on an understanding of how the metal species is bound within the calcite. U(VI) occurs principally as the linear uranyl moiety ($O=U=O$), which may be highly soluble and mobile in conditions characteristic of many surface waters. The formation of stable complexes with CO_3^{2-} enhances U(VI) solubility in carbonate-containing solutions and is the basis for some remediation techniques. Earlier studies compared the local structure of uranyl incorporated into calcium carbonate polymorphs calcite and aragonite¹. XAFS results clearly demonstrated a difference in equatorial coordination of the uranyl, with implications for the stability of the solid. In aragonite, the local structure resembled that of the dominant aqueous uranyl species; in calcite a change in coordination was evident, suggesting an intermediate reaction step during incorporation. Present work examines possible influences of growth solution chemistry on local structure of uranyl incorporated into calcite.

Methods and Materials: Uranyl-containing calcite ($CaCO_3$) was synthesized from room-temperature aqueous solutions using two methods. Uranyl (UO_2^{2+}) was added as aqueous uranyl nitrate. Method I used a constant-addition rate of nutrients at pH 8.2 and resulted in a fine-grained calcite precipitate. Method II relied on decomposition of solid ammonium carbonate to provide a nearly constant source of dissolved carbonate (pH 7.6), producing calcite single crystals. Final U concentrations in the solids ranged from 200 to 750 ppm.

Uranium L_3 -edge XAFS data were collected on the uranyl-doped calcite samples using Si(111) monochromator crystals and a 13-element Ge detector at beamline X11A. Samples were held at near liquid nitrogen temperature. Multiple scans were averaged, and data were analyzed with standard methods using the programs WinXAS and FEFF7.

Results and Conclusions: XAFS spectra for both samples exhibited edge positions and features characteristic of U(VI) in the linear $O=U=O$ moiety. Fourier transform magnitudes (**Figure 1**) for both samples are dominated by a low-R peak corresponding to the two axial oxygens at 1.8 Å and a partly overlapped, weaker peak of the equatorial oxygen shell. The only other significant feature is attributed to multiple scattering within the uranyl unit. Fits using a single equatorial oxygen shell yielded a distance of 2.33 Å for method I calcite and 2.36 Å for method II calcite. However, alternate fits for the latter suggested the possibility of a split equatorial oxygen shell, or more likely multiple environments. In both samples, average U-O(eq) distances suggest coordination numbers less than six.

The growth solutions differed not only in pH but also in predominance of aqueous uranyl species. Present efforts focus on correlation of aqueous speciation with differences in equatorial coordination in the solid. One preliminary conclusion is that changes in equatorial coordination may be required for uranyl incorporation into calcite, which contrasts with the behavior observed for aragonite. It also appears that incorporation could result in multiple species in calcite, and their local structure may be controlled by details of the solution chemistry. Steric constraints must require significant disruption of the local structure beyond the equatorial shell, which should be reflected in the solubility of the uranyl-containing calcite.

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References: ¹ R.J. Reeder, M. Nugent, G.M. Lamble, C.D. Tait, and D.E. Morris, "Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies," *Environmental Science and Technology*, **34**, 638, 2000.

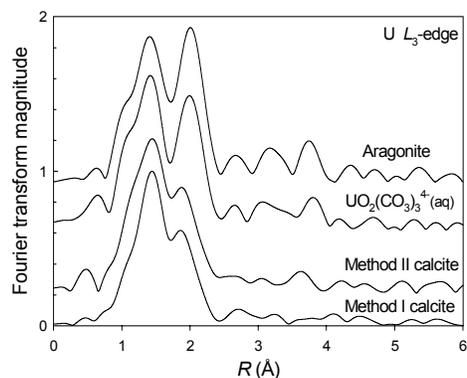


Figure 1. Fourier transform magnitudes of the two uranyl-containing calcites (method I and II) compared to uranyl-containing aragonite and the dominant aqueous species in growth solutions at pH 8.2.