X-ray Microprobe Studies of Natural High-Uranium Carbonates

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Introduction

Trace amounts of uranium (U) are found in natural carbonate minerals. These occurrences are the basis for the U-series age determinations of ancient calcites, are used as marine paleoenvironmental and diagenetic indicators, and may influence the transport behavior of U in soils and groundwater aquifers. Recently, x-ray absorption fine structure (XAFS) measurements showed that U in some high-U natural calcite (from a Tennessee ore deposit) is tetravalent and substitutes for Ca.[1] XAFS measurements on synthetic high-U calcite grown in uranyl-rich solutions (containing most uranyl as the triscarbonato complex) showed that uranyl incorporation was disordered and involved a change in the equatorial oxygen coordination about the U atom.[2] In contrast, uranyl in synthetic aragonite appears to maintain the same oxygen coordination found in the aqueous triscarbonato complex.[2] A remaining question is whether the local atomic order around uranyl in natural calcite and aragonite may differ from that in rapidly grown synthetic crystals. To address this question, we obtained natural calcite and aragonite samples having anomalously high U concentrations for investigating U oxidation state and coordination.

Methods and Materials

The investigated samples were from layered flowstone from a cave in Austria, where a layer of coarse calcite (cm-size crystals) was deposited on top of laminated (0.1-1.0 mm) aragonite. The flowstone is about 300,000 years old. A sample (2 x 4 cm) was cut into a thin (100 micrometer) section perpendicular to the depositional layering and mounted on a sheet of Kapton® film using adhesive tape at the edges. Microbeam x-ray fluorescence and XAFS measurements (U L_3 edge at 17166 eV) were made at the 13-ID beamline (Si<111> monochromator with an energy resolution of 1.3×10^{-4}); Kirkpatrick-Baez focusing mirrors were used to focus the beam to a 10 x 10 micrometer spot size. Reference XAFS spectra were obtained for uranyl nitrate hexahydrate.

Results

Uranium concentrations were mapped across a 1 mm x 10 mm strip perpendicular to the calcite/aragonite contact (Fig. 1). The U concentration in the calcite is 80-150 ppm and that in the aragonite is 400-500 ppm; these concentrations are 2-3 orders of magnitude higher than those of typical natural carbonate minerals. Distribution of U is relatively homogeneous (Fig. 2), indicating U is present as a dilute impurity and not as a discrete U mineral phase. X-ray absorption spectral features for the calcite and aragonite layers are identical to each other within statistical uncertainties, and the edge-peak energy is identical within error to that of the uranyl nitrate hexahydrate reference spectrum (Fig. 3).

FIG. 1. Strip (1 mm x 10 mm wide) across contact between aragonite (left) and calcite (right) layers in natural high-U flowstone deposit from a cave in Austria showing U concentration image scaled in concentration from 80 ppm (black) to 500 ppm (white). Note mm-scale fluctuation in U concentration within aragonite parallel to contact. Contact was subhorizontal in field.

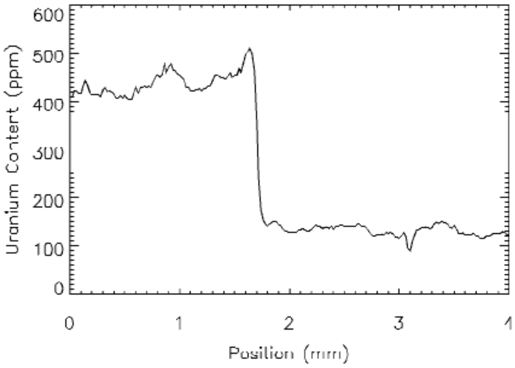

FIG. 2. Uranium concentration profile of a single row in the map (Fig. 1). The U content varies from 400 to 500 ppm in the aragonite (left) and 80 to 150 ppm in the calcite (right). The uranium is generally homogeneous in the two phases but some minor zonation is apparent, particularly in the aragonite.

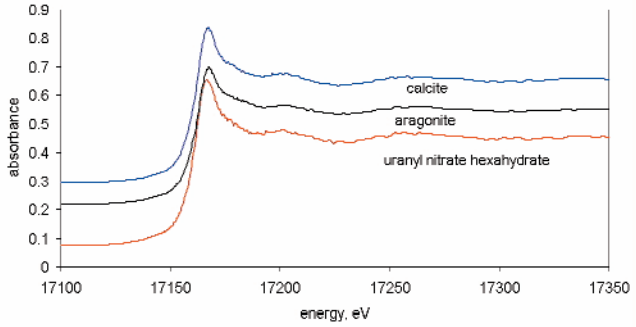

FIG. 3. Normalized x-ray absorbance vs. photon energy (keV) showing raw XAFS data for calcite (blue line) and aragonite (black line) samples, and uranyl nitrate hexahydrate reference (red line).

Discussion

The results of our measurements indicate that U in these natural high-U calcite and aragonite crystals is present as U(VI). The coordination of U in both phases is apparently similar based on inspection of the raw EXAFS data. Modeling of the corresponding local structures is in progress. Further studies of U in natural carbonates, as well as experimental adsorption and coprecipitation studies under a range of chemical and physical conditions, are required to fully understand the mechanism of U incorporation in carbonate minerals.

Acknowledgments

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