

# Micro-XRF/XAS study of uranyl incorporation on calcite 1014 growth surfaces

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## Introduction

The structure and availability of surface sites have been shown to be primary factors controlling the uptake and incorporation of metal impurities into minerals during growth. On a crystal face, growth steps associated with layer growth mechanisms may reduce surface symmetry and allow for the presence of multiple structurally distinct incorporation sites. For the spiral mechanism, in particular, the presence of polygonized symmetrically nonequivalent growth steps introduces a heterogeneous distribution of different sites over the growth surface [1, 2]. If the structurally distinct sites have different incorporation preferences, the differential incorporation of metal impurities during growth is recorded in the crystal as spatially separated regions on the surface with distinct impurity concentrations. This heterogeneous differential incorporation pattern is most easily recognized on polygonized spiral growth hillocks, where “vicinal” faces are composed of growth steps having a given orientation and structure. Such step-selective incorporation patterns have been studied extensively in carbonate and phosphate minerals in view of their role as tracers of geochemical processes and also to evaluate their potential in the sequestration of metal contaminants in environmentally impacted settings.

Our present work has focused on incorporation systematics for the highly mobile uranyl carbonate complexes [e.g.,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ]. Independent x-ray absorption fine structure (XAFS) and luminescence studies of uranyl ion coprecipitated with calcite have shown multiple coordination environments [3]. These have been attributed to changes in the equatorial coordination of the  $\text{UO}_2(\text{CO}_3)_3^{4-}$  species during incorporation. Because of size and coordination geometry, such aqueous species are not expected to substitute into the calcite structure without significant disruption. A possible explanation for the observation of multiple structural environments may be found in differential incorporation preferences at the growth surface. As a first effort to evaluate this interpretation, we have used the micro x-ray fluorescence and x-ray absorption capabilities at beamline 20-ID-B of the Advanced Photon Source (APS) at Argonne National Laboratory to assess the differential incorporation of uranyl species on the 1014 face of calcite grown by the spiral mechanism.

## Methods and Materials

Calcite single crystals were grown from room-temperature  $\text{Ca-NH}_3\text{-HCO}_3\text{-Cl}$  aqueous solutions doped with uranyl nitrate standard aqueous solutions. The calcite crystals, up to approximately 500  $\mu\text{m}$ , displayed the common {1014} growth form. Total (bulk) uranium concentrations were 19 and 243 ppm, respectively, in the two crystals analyzed. Each growth surface contained one or more polygonized

growth spirals, composed of four distinct vicinal faces, two of which were symmetrically nonequivalent. Previous studies for individual divalent metals coprecipitated with calcite (e.g., Mn, Sr, Co, and Zn), as well as complex oxyanions [e.g.,  $\text{SeO}_4$ ,  $\text{SO}_4$ , and  $\text{B}(\text{OH})_4$ ], indicate that differential incorporation between nonequivalent growth steps can be detected by elemental mapping of an area on the growth surface encompassing the nonequivalent vicinal faces. Calcite crystals were mounted on high-purity silica glass support discs, after being polished to a thickness of approximately 30  $\mu\text{m}$  with the as-grown (1014) face exposed to the incident beam. The sample was oriented at either 45 or 60 degrees with respect to the incident x-ray beam.

Scans were collected at beamline 20-ID-B operated by the PNC-CAT. The monochromator was adjusted to an energy just above the  $\text{U } L_3$  edge (17166 eV), and a K-B mirror assembly focused the beam to give an incident beam size of approximately 5  $\mu\text{m}$  x 6  $\mu\text{m}$ . A 13-element solid-state Ge detector was used for fluorescence detection. Preliminary x-ray absorption near-edge spectroscopy (XANES) spectra were also collected from the regions underlying the nonequivalent vicinal faces.

## Results

All two-dimensional scans of the calcite (1014) face showed a step-function-like change in uranium concentration coinciding with the boundary separating adjacent nonequivalent vicinals. A representative map of raw uranium counts is shown in Figure 1. For both crystals studied, a systematic trend of preferential incorporation was observed. Vicinal faces denoted a' and b' in earlier studies [1, 2] were enriched in uranium relative to those denoted a and b. In this preliminary study, no attempt was made to quantify the concentration differences. However, observed differences in count rate suggest an incorporation anisotropy as great as a factor of ten.

XANES scans were collected with the beam positioned within nonequivalent vicinal faces (Figure 2). No obvious difference was observed for the different locations. Future work will consider possible polarization differences, which may provide insight to the orientation of the uranyl moiety in the calcite.

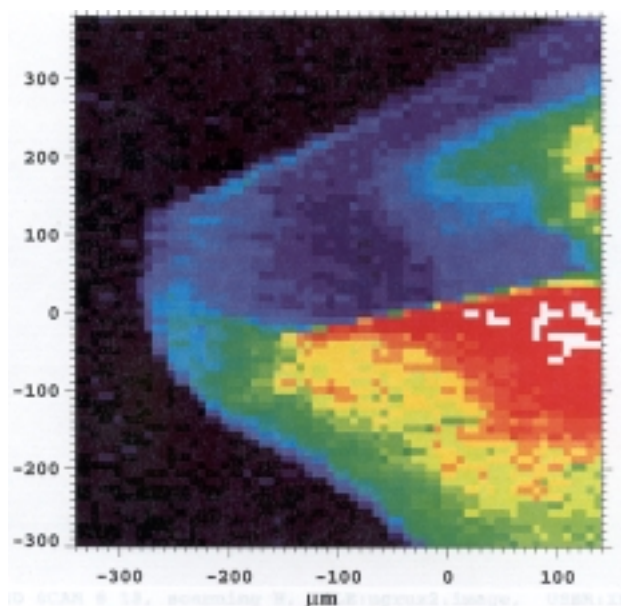


Figure 1: Element map over a portion of a calcite 1014 growth face showing total U counts. Highest counts shown in red.

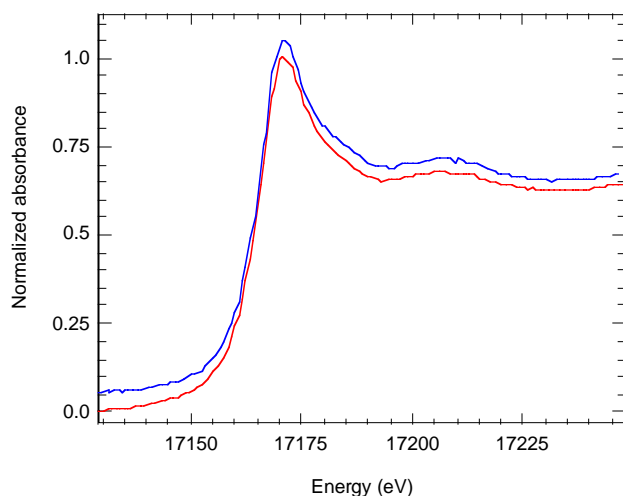


Figure 2: Normalized XANES spectra of the U  $L_3$ -edge (17166 eV) taken with a  $5\ \mu\text{m} \times 6\ \mu\text{m}$  beam in the low (top, blue) and high (bottom, red) concentration regions shown in Figure 1.

## Discussion

The finding of pronounced growth-step-specific incorporation of the uranyl ion on the calcite (1014) face is consistent with previous studies of transition metal and alkaline earth impurities and oxyanions. The observed preference of uranyl incorporation is the same as previously found for  $\text{B}(\text{OH})_4$ , but opposite to that for  $\text{SeO}_4$  and  $\text{SO}_4$ . Although a general explanation for the differential uptake is still debated, it must lie with structural differences between incorporation sites. Presumably the coordination geometry of exposed kink sites in advancing steps influences incorporation differently for different species. For aquo ions, the distinction depends on factors such as size and charge. However, for complex species such as the uranyl carbonate complexes, it remains unclear how surface sites exert a control on the incorporation preference.

The observation of similar XANES spectra for the nonequivalent regions of the calcite growth surface may reflect that the local coordination of the incorporated uranyl species is the same throughout. However, additional studies are needed to substantiate that, including examination of polarized XANES spectra for different orientations of the crystal with respect to the polarization vector of the beam.

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## References

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