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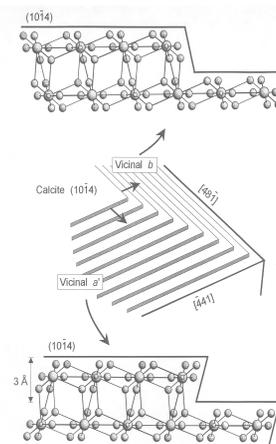
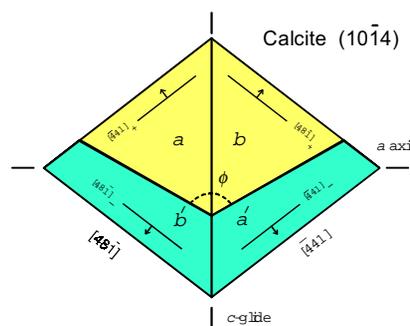
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Introduction and Overview

Uptake of dissolved metals by CaCO_3 is a potentially important mechanism influencing the mobility and sequestration of contaminants in soils and sediments. Calcite is a common mineral constituent of vadose zone materials at the Hanford Site, where it occurs as coatings, disseminated particles, and as massive calcretes. Previous studies of metal uptake by calcite have suggested that coprecipitation is the dominant sorption mechanism. Earlier experimental work on coprecipitation of divalent metals at the calcite (1014) growth surface showed that the effectiveness of uptake is strongly controlled by the distribution and availability of multiple, structurally distinct surface sites. Coprecipitation behaviors of different metals have been linked to metal ion size and the relative geometry of surface sites. Our present studies have addressed the question of whether coprecipitation of metal oxyanion complexes with calcite is also influenced by these surface site properties. CrO_4^{2-} , an important contaminant at the Hanford Site, is generally considered to be highly mobile and weakly particle reactive. Its coprecipitation behavior with calcite is unknown. Our preliminary findings for surface influences on CrO_4^{2-} coprecipitation are presented here. We compare these results with the coprecipitation behavior for another important complex metal species, $\text{UO}_2(\text{CO}_3)_3^{4-}$. The striking similarity of the results suggests that the effectiveness of metal coprecipitation with calcite is strongly dependent on the characteristics of the calcite surfaces. This suggests that metal uptake by surfaces of calcite components in soils and sediments may be highly heterogeneous.

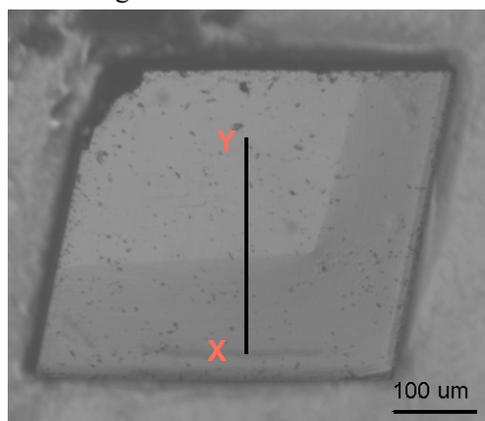
The Calcite (1014) Growth Surface

The (1014) face of calcite is the dominant growth form and is most stable in aqueous solutions. DIC and AFM studies have demonstrated that the spiral mechanism (BCF model) is the dominant growth mechanism over a wide range of supersaturations. On the (1014) calcite surface this results in the simultaneous advance of symmetrically nonequivalent growth steps containing structurally distinct incorporation sites. The schematic at the right shows the orientation and distribution of growth steps in vicinal faces composing the flanks of the polygonized growth "spirals." The structure of growth steps and their incorporation sites differ between the nonequivalent vicinal faces. This can be seen schematically in the diagram on the far right, showing cross sections through two adjacent, but nonequivalent growth steps. Additional detail is given on the next page.

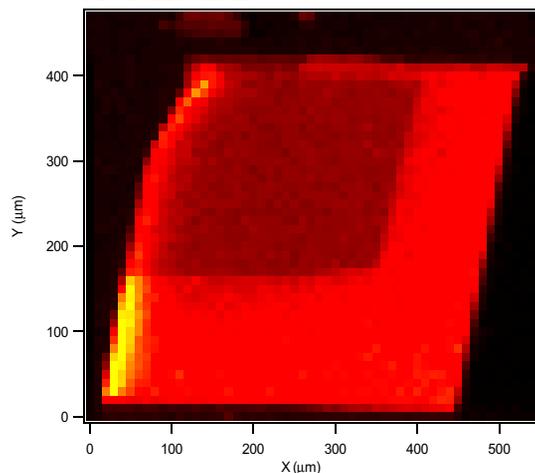


CrO_4^{2-} coprecipitation at the Calcite (1014) Growth Surface

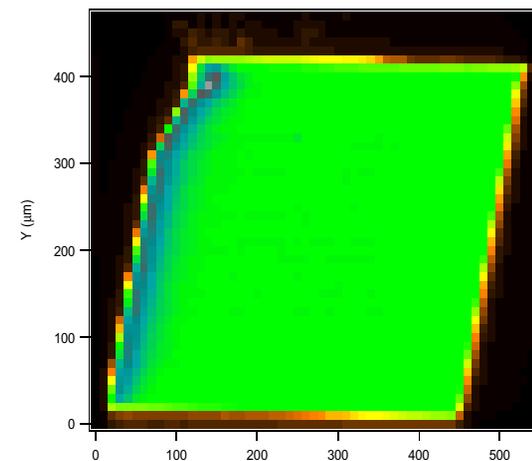
DIC image



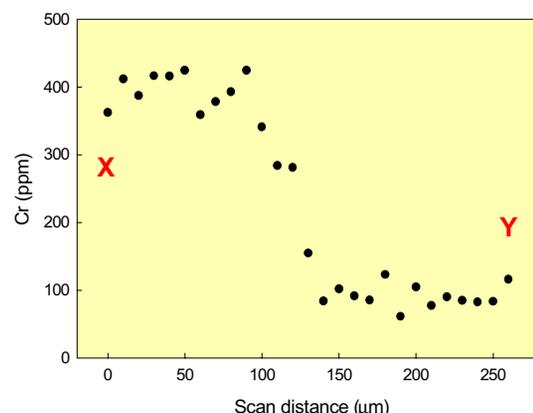
Cr distribution



Ca distribution

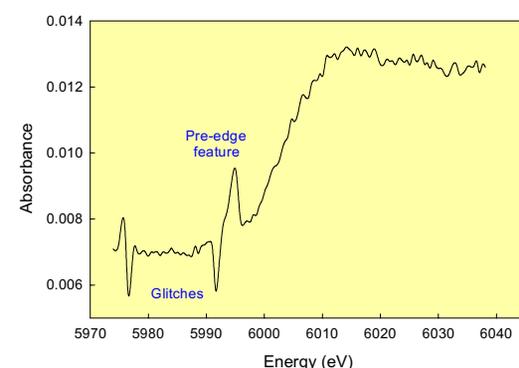


Micro-XRF Scan of CrO_4^{2-} incorporated at Calcite Surface



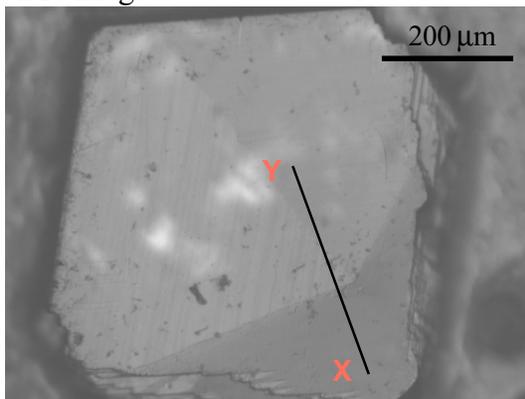
Differential interference contrast (DIC) image (upper left) of a (1014) growth surface on a calcite single crystal grown in CrO_4^{2-} solution. Shading differences show the two pairs of nonequivalent vicinal faces described above. The two color maps above show the Cr (left) and Ca (right) distributions using a $4 \mu\text{m}$ synchrotron X-ray beam at the PNC-CAT beamline of the Advanced Photon Source. The Ca distribution is uniform as expected, showing anomalies at the edges because of thickness. The Cr is strongly enriched in the lower and right vicinal faces. A line traverse X-Y (X-26A, National Synchrotron Light Source) is shown to the left. The factor of four change in Cr concentration coincides with the boundary separating nonequivalent incorporation sites. XANES spectrum (at right) obtained at the APS shows a pre-edge feature characteristic of Cr(VI). However, the feature is weaker than expected, and may be affected by a glitch.

Cr K-edge XANES Spectrum of CrO_4^{2-} in Calcite

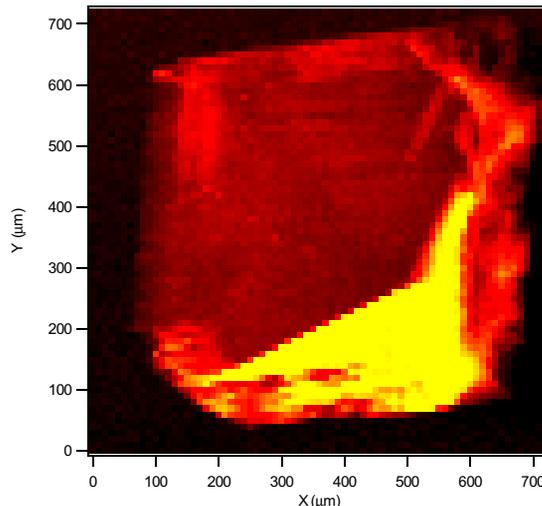


UO₂²⁺ coprecipitation at the Calcite (1014) Growth Surface

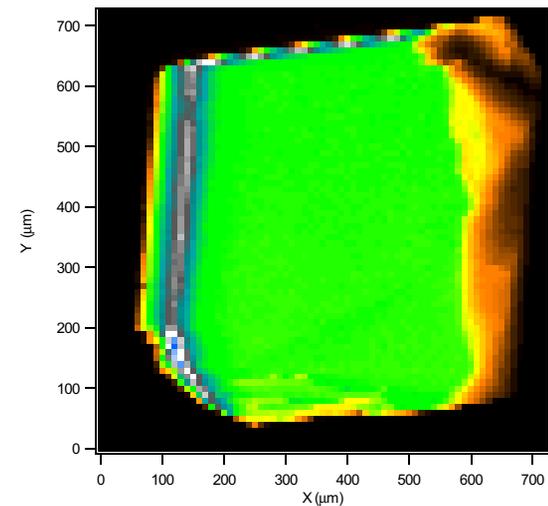
DIC image



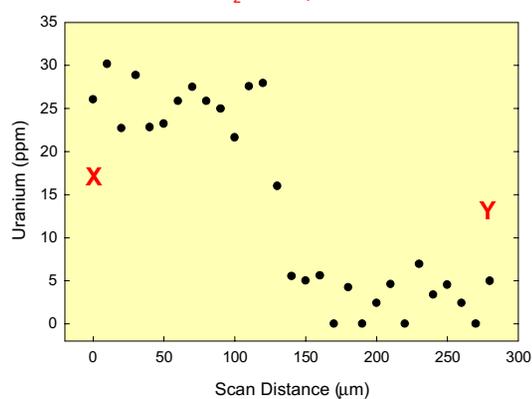
U distribution



Ca distribution

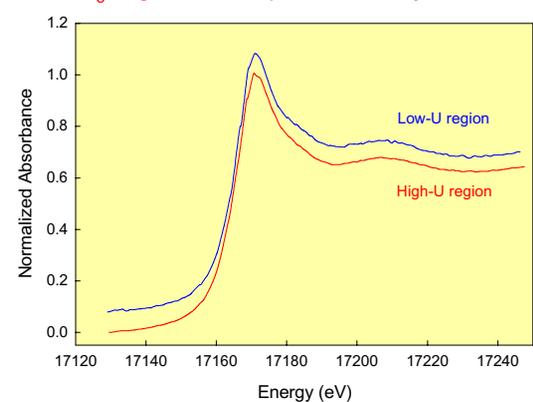


Micro-XRF Scan of UO₂²⁺ Incorporated at Calcite Surface

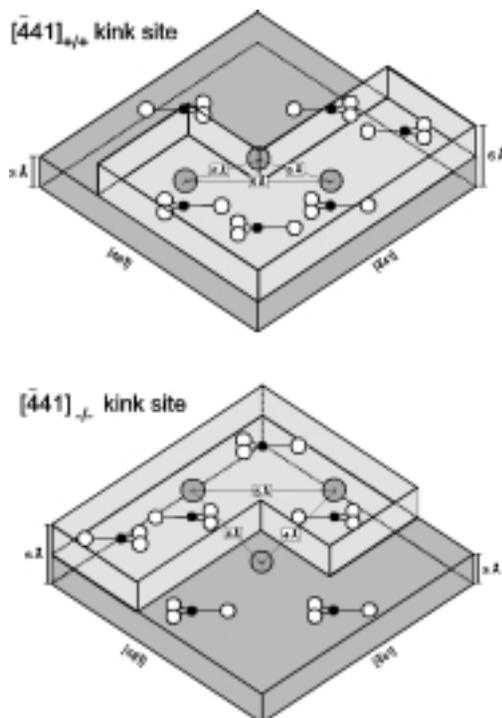


DIC image (upper left) shown two pairs of nonequivalent vicinal faces containing nonequivalent surface sites. Faint traces of macrosteps are visible in vicinals with lighter shading. Uranium fluorescence map (above) obtained using a 6 μm beam at the PNC-CAT beamline (Advanced Photon Source) shows preferential incorporation of U in the less developed vicinals at bottom and lower right of face. Ca map (upper right) shows the expected uniform distribution except for edge effects. A traverse between endpoints X-Y taken at beamline X-26A of the National Synchrotron Light Source is shown to the left. The factor of six change in U concentration coincides with the boundary separating nonequivalent incorporation sites. XANES spectra (at right) obtained at the APS from the high- and low-concentration regions are similar.

U L₃-edge XANES Spectra of Uranyl in Calcite



Surface Structural Controls on Incorporation



Previous studies have suggested that the cause of surface controls on metal coprecipitation in calcite lies in the detailed geometry and configuration of incorporation sites within growth steps. The schematic diagrams at left represent idealized geometries of structurally distinct anion incorporation sites on the calcite surface. Although these do not correctly represent hydrated surfaces, the underlying structural differences are evident. It is likely that such differences in near-neighbor coordination are primary factors that control incorporation trends for many contaminant species incorporated into calcite.

Implications of Initial Results

The spatial pattern for CrO₄²⁻ incorporation at the calcite surface is similar to that found for UO₂(CO₃)₃⁴⁺ species. These heterogeneous distribution patterns at the calcite surface indicate that uptake and incorporation of complex metal anions depend strongly on the configuration of surface sites. Previous studies have found similar effects for coprecipitation of metal cations and have attributed the differential incorporation behavior to structural differences among nonequivalent surface sites such as those shown at left. The finding that surface structure plays an important role in uptake of complex metal anion species has potentially important implications for the mobility and fate of toxic metals in the soil and vadose zone. We expect that incorporation of such species at natural calcite surfaces will be highly heterogeneous, favoring specific sites. The factors that control the availability of favored sites remain largely unexplored.

Because the *K_d*s for CrO₄²⁻ and UO₂(CO₃)₃⁴⁺ coprecipitation with calcite are less than unity, significant uptake of these species by calcite would necessarily be expected. However, the strong surface site control, coupled with a rate effect (not addressed here), may make coprecipitation with calcite a potentially important means of binding these metals in soils and vadose zone materials.