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A Macroscopic and Spectroscopic Study on Arsenate Uptake by Calcite

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Combined use of EXAFS and μ -XRF provide insight to surface-site selective uptake of arsenate (AsO_4^{3-}) by calcite. Results show strong sorption interactions between As(V) and the calcite surface. For calcite single crystals grown in the presence of As(V), μ -XRF-documented preferential incorporation of arsenate at one set of growth steps relative to the other during growth. As K-edge EXAFS results on As(V) sorbed to calcite confirm formation of a tetrahedral inner-sphere complex with two Ca shells, consistent with a strongly bound species and providing constraints to modes of surface coordination.

Uptake mechanisms on mineral surfaces, including adsorption, coprecipitation and precipitation, influence the mobility and bioavailability of chemical species in natural systems. Arsenic (As) is a toxic metalloid that can be introduced into the environment through natural sources (e.g. mineral weathering, geothermal processes) and/or through anthropogenic activities (e.g. industry, mining, agriculture). In oxidized environments As is mainly present in the 5+ oxidation state as arsenate (AsO_4^{3-}). Much research has focused on the uptake of As species by various common minerals, and specifically for As(V) it has been shown that formation of a strongly bound surface adsorption complex is a dominant mechanism over a range of environmentally relevant conditions (e.g. pH, ionic strength, reaction time). Calcite, an abundant and reactive mineral component of soil and aquifer systems, has been shown

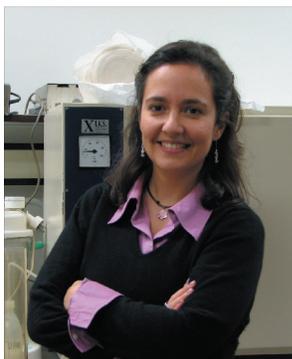
to be an effective sorbent of metals and oxyanions. Prior studies have shown that metal uptake is subject to strong surface site preferences that may control the partitioning of dissolved species between the aqueous and solid phase.

In combination with batch uptake experiments on calcite we investigated AsO_4^{3-} uptake mechanisms, including adsorption and coprecipitation, using As K-edge x-ray absorption spectroscopy and micro-x-ray fluorescence mapping (μ -XRF). Specifically, we used μ -XRF to determine selective partitioning of As(V) to different sites that were spatially segregated on the (10 $\bar{1}$ 4) surface of calcite single

crystals grown from an As(V)-containing solution. Extended x-ray absorption fine structure (EXAFS) spectroscopy was then used to gain insight to the local coordination of As(V) sorbed on the calcite surface.

The critical factor that makes it possible to identify surface site preferences for As(V) uptake is that spiral growth on the calcite (10 $\bar{1}$ 4) surface results in the formation of two characteristic non-equivalent pairs of vicinal surfaces, denoted as "+" and "-", that differ in the structure of surface sites in their growth steps (**Figure 1c**). The μ -XRF elemental mapping of these surfaces from crystals grown in

As(V)-containing solutions shows significant enrichment of As in the "-" vicinal surfaces relative to "+" vicinals (**Figure 1a**), indicating that incorpora-



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tion of As(V) is influenced by the structural characteristics of advancing growth steps. We hypothesize that the site-selective incorporation results from differences in As(V) binding at the surface steps. This is supported by differential interference contrast microscopy (**Figure 1b**), which reveals microtopographic differences as a result of differential incorporation.

To gain insight to As(V) sorption mechanisms at the calcite surface,

we collected As K-edge EXAFS data on As(V)-sorbed calcite in wet paste samples. Fitting results confirm formation of a tetrahedral inner-sphere surface complex with two separate Ca shells at distances of 3.4 and 3.6 Å. Although it is not possible to distinguish differences in sorption geometry between different sites in the batch sorption samples used for EXAFS, we can constrain aspects of the dominant binding mode. The presence of the two Ca shells indicates either

the co-existence of more than one As(V) surface complex or a dominant coordination as a bidentate complex in steps or a tridentate complex in kink sites (**Figure 2 a-d**). These conclusions are consistent with the strong binding that has been observed in batch studies, and provides information for further modeling of surface interactions of As species with calcite surfaces.

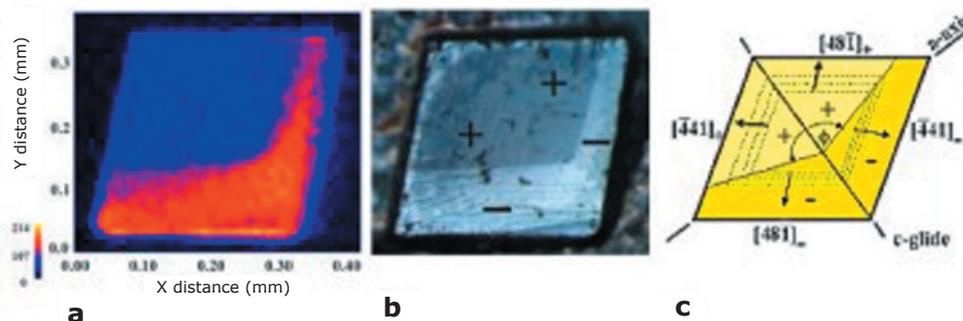


Figure 1. (a) Micro-XRF element map showing As $K\alpha$ counts on the $(10\bar{1}4)$ growth surface of a calcite single crystal. Highest As $K\alpha$ counts are shown in yellow and red; lowest counts in blue and black. (b) Corresponding DIC image of the growth surface showing the two pairs of vicinal surfaces denoted as + and -. (c) Schematic illustration showing the orientation of growth steps.

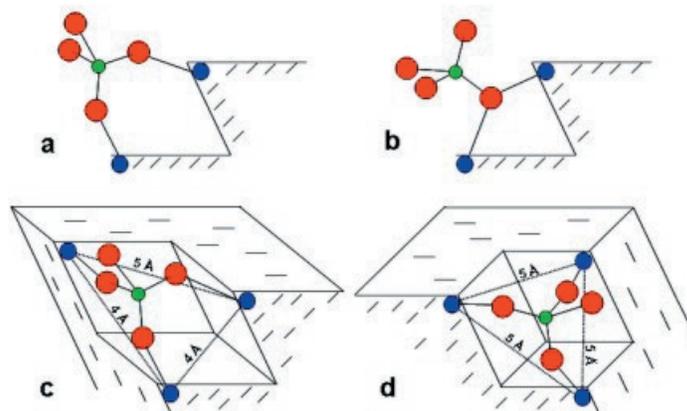


Figure 2. Schematic illustrations showing possible surface complexes for As(V) adsorption at step and kink sites on the calcite $(10\bar{1}4)$ surface: (a) bidentate corner-sharing, (b) monodentate (bridging) corner-sharing, (c) tridentate corner-sharing at kink site in "-" step, (d) tridentate corner-sharing at kink site within "+" step.