Real-Time Observations of Calcite Reactivity with X-ray Reflectivity and Microscopy*

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The structure and reactivity of the calcite-water interface has been extensively studied. Nevertheless, we have recently found some surprising results during real-time observations of the calcite-water interface with X-ray reflectivity (XR) and X-ray reflection interface microscopy (XRIM).

In the first set of measurements, we used specular XR to probe the temporal response of the calcite (104) surface morphology to changing solution conditions as a complement to more widely used AFM studies. Morphological information is encoded in the *shape* of the reflected X-ray beam (e.g., the average surface domain size can be estimated from the reflection width). We found, not surprisingly, that the average surface domain size decreased substantially after the surface was exposed to de-ionized water and recovered after "healing" in calcite-saturated solutions. This behavior was presumably due to the reversible increase in the surface step density associated with surface roughening. We also found, however, that the healing process exhibited interesting, apparently hysteretic, behavior that depended on both the solution composition as well as the solution flow rate. We will describe our initial results of these measurements and discuss possible explanations.

In the second set of measurements, we imaged the calcite-water interface morphology directly using the recently developed XRIM apparatus [1,2], a full field X-ray interfacial microscope. We observed dramatic changes to the calcite surface morphology in real-time, which were driven by the high radiation field of the focused XRIM beam. These changes are associated with the radiolysis products of water (e.g., hydroxyl radicals and hydrated electrons) that react with the calcite surface to modify the calcite solubility/stability. The results provide novel insights into the role of radiation fields in modifying mineral-water reactivity.

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