Probing the reactivity of the dolomite-water interface using high resolution X-ray reflectivity

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The interaction of cations with mineral-water interfaces is fundamental to our understanding of geochemical transport. A particularly rich range of phenomena has been observed in the interaction of metal cations with carbonate surfaces, including adsorption/incorporation of isolated ions, and growth of islands, and mono- and multi-layer films.

The interaction of dolomite surfaces with dolomite-supersatured solutions is an area that is particularly difficult to understand. Previous AFM measurements have shown that dolomite surfaces in contact with supersaturated solutions grow thin (~1 or 2 layer) films that are largely inert with respect to further growth and whose thicknesess depend upon whether the solutions are rich in Ca or Mg [1]. Lateral force images suggest that the compositions of these layers depends upon the solution compositions, but the layer compositions cannot be determined by traditional measurements due to spectral interference from the substrate.

We have applied high resolution surface X-ray reflectivity to provide new insights about the structure and composition of the dolomite-water interface. Measurements in dolomite saturated solution (saturation index, SI=0) show that the dolomite surface is ideally terminated and has characteristics similar to those found previously for the calcite-water interface [2], including a slightly relaxed surface and a distinct surface hydration layer. Additional measurements in supersaturated solutions (SI = 2.3) rich in either Ca or Mg reveal the formation of continuous surface films whose thickness and electron density are controlled by the solution compositions. These data provide new, direct insight into the composition and reactivity of dolomite-water interfaces.

References

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Investigating the effect of calcium on barite (001) and (210) surfaces using *in situ* atomic force microscopy

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Barite ($BaSO_4$) is a major component of the inorganic scale that forms in well bores and oilfield pipework due to its very low solubility. Currently, scaling is controlled by chemical inhibitors that work by inhibition of nucleation and growth retardation. However, for reasons that are poorly understood, these processes are affected by the presence of cations such as Ca^{2+}, resulting in changes in barite crystal morphology. We seek to understand why these changes occur, and thus the mechanism and efficiency of growth inhibition.

Observations of barite crystals made in air using atomic force microscopy (AFM), show surfaces to be characterized by steps commensurate with the corresponding plane spacing (d_{001} = 7 Å and d_{210} = 3.5 Å). Many of these steps are straight and parallel, while others meet at acute angles specific to that surface, suggesting some crystallographic control.

In situ AFM experiments have been used to study surface growth and dissolution processes in the presence of supersaturated solutions of $BaSO_4$. Recorded images show differences in growth on the (001) and (210) surfaces: growth island development and lateral nanoscale step edge advancement is seen on the (001) surface, and restricted linear step edge advancement on the (210) surface. In the presence of Ca^{2+}, growth islands have a less uniform shape, and step edge advancement is less ordered. Some dissolution is observed on the (210) surface. In all experiments, increased rates of growth are observed with increasing ionic strength of solution.

Comparisons of experimental investigations with computer simulation models of barite surfaces, are being used to identify mechanisms of Ca^{2+} incorporation within the barite crystal structure, and to aid prediction of resulting crystal morphologies.