Surface speciation of calcite observed *in situ* by x-ray scattering

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Introduction

The reactivity of the mineral-fluid interface (e.g., dissolution, growth, and sorption of contaminants) and its dependence on variables such as pH, fluid composition, and temperature have been studied extensively in recent decades [1]. However, the basic compositional and structural features of many geochemically important mineral-fluid interface systems remain poorly understood. Here, we demonstrate the potential of specular x-ray reflectivity for direct *in situ* measurement of mineral surface structure and the strong constraints that such measurements provide for elucidating chemical speciation at the mineral-fluid interface [2].

Methods and Materials

Calcite surfaces were prepared by cleaving optical-quality calcite in air, then quickly (<1 min) immersing the cleavage surface in water and mounting it in an x-ray reflectivity cell.

X-ray scattering techniques are ideal as probes of mineral-fluid interface structure because x-rays penetrate macroscopic quantities of fluids (such as water) with limited attenuation. The x-ray reflectivity (i.e., the ratio of the reflected to incident x-ray flux) is related to the laterally averaged electron density, $\rho(z)$, near a reflecting interface through the relation $R = (4\pi r_e/Q)^2 |\int \rho(z)\exp(iQz)dz|^2$ (where Q is related to the angle of incidence, and $r_e = 2.818 \times 10^{-5}$ Å is the classical electron radius). This simple and direct relationship between the reflectivity and $\rho(z)$ makes it possible to quantitatively test and optimize models of the interface structure to yield the atomic-scale structure.

Results and Discussion

The measured x-ray reflectivity of the calcite-water interface at pH = 8.3 is shown in Fig. 1. These data follow the expected form of a crystal truncation rod (CTR) in which R is ~ 1 near the bulk Bragg peak conditions [denoted as (104) and (208) in Fig. 1], but is much smaller, $R < 10^{-7}$, between the Bragg peaks.

The data are compared against the best-fit calculations for a series of models. The data cannot be explained by a simple bulk-terminated calcite structure, even with the inclusion of symmetry-allowed surface relaxations of the Ca and CO_3 groups in the top two layers and the presence of atomic steps at the calcite surface. However, the addition of an adsorbed monolayer at the calcite surface allows us to quantitatively explain the x-ray reflectivity over the entire range of data. A diagram of the derived electron density profile and interface structure according to this best-fit reflectivity model is shown in Fig. 2. Assuming that the
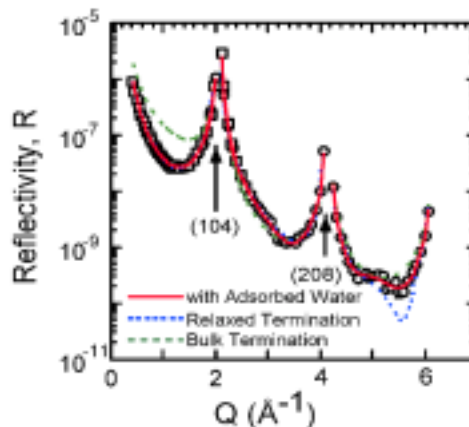

Figure 1: Measured x-ray reflectivity of the calcite-water interface at pH = 8.3.
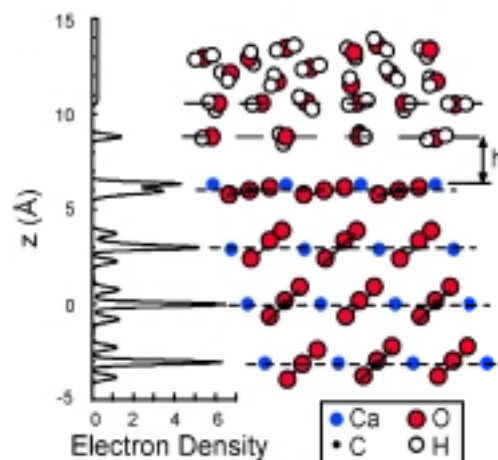

Figure 2: Diagram of the derived electron density profile and interface structure according to the best-fit reflectivity model.

adsorbed monolayer in our best-fit reflectivity model consists of a water species, we derive a coverage of 1.0 ± 0.4 ML at a height with respect to the surface Ca sites of h = 2.50 ± 0.12 Å. (A monolayer is defined as the density of surface Ca sites; 1 ML = $4.95 \times 10^{14}/cm^2$). This result is in agreement with previous predictions of surface speciation at near-neutral pH [3].

We have also probed the variation of the calcite surface termination as a function of pH. Previous studies predicted that the calcite surface termination exhibits distinct terminations for pH << pH_{pcz} and pH >> pH_{pcz}. In contrast, we observe no significant changes in the measured x-ray

reflectivity results in these pH ranges with respect to that measured near pH 8.3.

Conclusions

On the basis of these results, we suggest a simpler model of the pH-dependent surface speciation of calcite over the range $6.8 \leq pH \leq 12.1$ that invokes only protonation reactions in the surface speciation of terrace areas. This model is consistent with results of scanning force microscopy studies of calcite growth and dissolution near equilibrium, which show that attachment and detachment of Ca and CO_3 ions occur primarily at step-edge kink sites. These results demonstrate how high-resolution x-ray reflectivity can be used for direct, *in situ* measurements of mineral surface structure to provide strong constraints on chemical speciation and reactivity at the mineral-fluid interface.

Acknowledgments

References

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