

## *In-situ* X-Ray scattering study of the calcite-water interface

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The mineral-fluid interface is the principal site of low-temperature geochemical processes near Earth's surface, and exerts a powerful influence upon the natural conditions in our environment such as the composition of ground waters and surface waters. Yet at present there is relatively little that is directly known about the microscopic structure at the mineral-fluid interface, such as the precise substrate atom locations at the mineral surface (1), the location of adsorbed ions (2), or its influence upon the structure of water at the interface (3). Consequently, developing an *in-situ* atomic-scale description of well-defined mineral-fluid interface systems is a crucial step towards advancing our fundamental understanding of the dynamical processes which take place there (e.g. dissolution, growth, adsorption, and oxidation-reduction). Here, we describe our recent work using X-ray specular reflectivity to probe the *in-situ* structure of the calcite-water interface.

### Experimental

Although widely recognized as a technique to probe the structure of three-dimensional crystals, X-ray

scattering is also a powerful and direct probe of two-dimensional structures such as surfaces and buried interfaces (4). While X-ray scattering from three-dimensional crystals results in sharp 'Bragg peaks', the scattering from the surface of a crystal results in 'crystal truncation rods (CTRs)' which are sharp in directions parallel to the surface plane but diffuse in the direction perpendicular to the surface. This is shown schematically in Fig. 1, in which the observed reflectivity is the result of the interference between the reflectivity of the individual atomic planes in the near-surface region, which in turn depends upon the incident angle,  $\theta$ . The resultant CTR exhibits both the sharp (104) and (208) Bragg peaks as well as the relatively weak reflectivity throughout the Brillouin zone. It is the intensity variation along a CTR that provides a direct and quantitative measure of the mineral-fluid interface structure, such as the substrate and adsorbate atom locations, the surface topography, and the near-surface fluid structure.

A crucial characteristic of X-ray scattering techniques for these studies is the weakly interacting nature of X-rays. Since X-rays can readily penetrate a macroscopic thickness (i.e. several mm) of fluids such as water, it is straightforward to probe directly

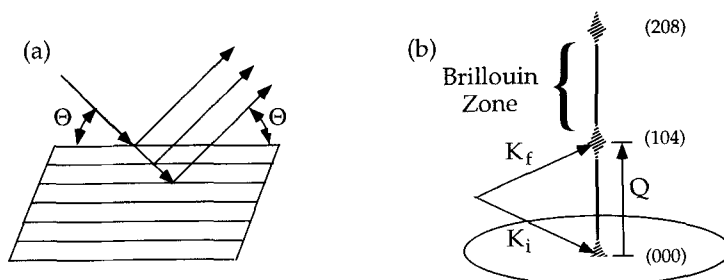


FIG. 1. Schematic of the scattering geometry in (a) real and (b) reciprocal space.

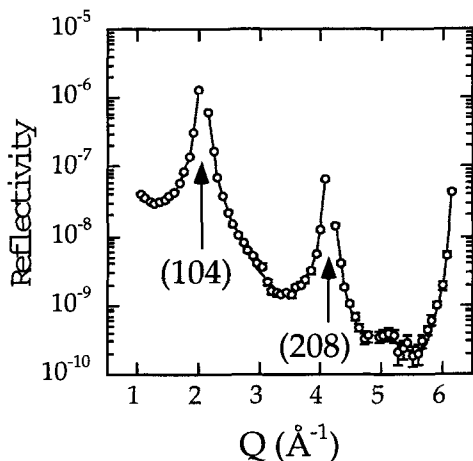


FIG. 2. X-ray specular from the calcite-water interface reflectivity.

the structure of a mineral surface in an aqueous environment. Furthermore, the recent advent of third generation X-ray synchrotron sources provides new opportunities to study both static atomic-scale structural features in greater detail as well as dynamical processes such as growth, dissolution, and leaching in real-time.

A well-defined (104) surface is obtained by cleaving an optical quality spar calcite crystal (1). These data are taken in a reflection geometry, with a thin ( $\sim 50 \mu$ ) layer of water confined at the calcite (104) surface using a kapton film.

## Results

The X-ray specular reflectivity of the calcite/water interface is shown in Fig. 2. The data are plotted as a function of the momentum transfer,  $Q$ , which is related to the incident angle,  $\theta$ , by the relation  $Q=(4\pi/\lambda)\sin(\theta)$ . The data reveal the general features expected for a CTR of a crystalline surface, in which the specular reflectivity varies by many orders of magnitude between the strong substrate Bragg peaks of calcite (where the reflectivity approaches unity) and the rather weak (but readily measurable) reflectivity between the Bragg peaks where the reflectivity approaches  $\sim 10^{-10}$ . It is primarily the weak mid-zone reflectivity which provides information concerning the surface structure. By making use of the large dynamic range available at X-ray synchrotron sources, we have been able to measure the specular reflectivity to momentum transfers as high as  $6 \text{ \AA}^{-1}$ , which provides the most detailed

measurement of the calcite-water interface structure to date.

To understand the detailed nature of the calcite-water interface structure, we make use of the simple and direct relationship between the atomic-scale structure and the observed X-ray reflectivity. Consequently, by calculating the observed specular reflectivity for different models of the calcite surface, we can determine the precise atomic coordinates at the calcite surface by comparing the observed and calculated reflectivities through a  $\chi^2$  minimization procedure.

The best fit calculation is shown as a solid line in Fig. 2. The best-fit model includes a number of features which have not previously been measured at the calcite-water interface. These include a relaxation of the calcium and carbonate positions away from the projected bulk lattice positions. Interestingly, while the calcium and carbonate ions both relax perpendicular to the surface plane, they are found to move in opposite directions. Furthermore, we find that the orientation of the carbonate ion exhibits a significant rotation at the calcite surface. We also have explored the sensitivity of the data to the presence of adsorbed OH groups (which are expected at this pH condition) as well as to the water structure at the calcite-water interface. The resulting atomic-scale model will be discussed in a later publication.

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