

Interfacial Structure of the Fluorapatite (100)-Water Interface by Using High-resolution X-ray Reflectivity

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Introduction

Apatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{Cl},\text{F})_2$, is known as a prototype of bone- and teeth-forming minerals of vertebrate animals (including humans). The adsorption on and dissolution of this mineral have been extensively studied in dentistry, the medical sciences, and related areas. Recently, the use of this mineral for the remediation of radionuclides and toxic elements in geochemical environments has been explored. A long-standing issue to be addressed in order to understand the dissolution kinetics of apatite is the mechanism of *self-inhibition* [1] at the atomic and molecular scale. A related issue concerns the *surface speciation* of apatite in conjunction with the adsorption of radionuclides [2].

Here we discuss direct observations of the interfacial structure of fluorapatite (100) surfaces in water from using high-resolution x-ray reflectivity (XRR) [3]. These results lead toward a better understanding of the structure of apatite-water interfaces.

Methods and Materials

The structure of the apatite-water interface was measured by using high-resolution XRR. Structural models were obtained by directly comparing the reflectivity data to atomistic structure factor calculations of the apatite-water interface. The 1-D structure factor for the specular reflectivity was composed of three distinctive parts, $F_{\text{bulk}}F_{\text{CTR}} + F_{\text{surface}} + F_{\text{water}}$, corresponding to the substrate, interfacial, and water structure factors. These structure factor expressions were parameterized to allow for structural modifications of the near-surface region, thermal disorders, and fractional variation of atomic occupations. Additional parameters allowed for extrinsic features, such as surface roughness (in the form of steps), the linear absorption of the x-rays by a water film, and an overall scale factor.

The material used in this study was natural gem-quality fluorapatite (FAp) from Durango, Mexico. The sample was taken from a rock specimen that included 2- to ~3-mm-wide and 5- to ~6-mm-long individual crystals grown in the matrix, which showed the hexagonal prismatic $\{10\bar{1}0\}$ and hexagonal dipyramidal $\{10\bar{1}1\}$ faces. In this study, measurements were made on the $\{10\bar{1}0\}$ natural growth surfaces, hereinafter referred to as the (100) surface. The surfaces were minimally treated by

ultrasonic cleaning in deionized water and in acetone for a few minutes after the sample was removed from the rock specimen.

Results

Initial trial-and-error comparisons of the reflectivity data (Fig. 1) to models with a stoichiometrically truncated fluorapatite lattice and featureless water profiles revealed substantial discrepancies, suggesting that the interfacial structure is distinct from a simple stoichiometric termination. The comparisons suggested that the fluorapatite surface is terminated at the unit cell boundary in the apatite lattice, consisting of the Ca_2 layer (at $z = 0 \text{ \AA}$ in Fig. 2). An alternative termination of the lattice at the unit cell center (at $z = \sim -4 \text{ \AA}$ in Fig. 2) resulted in poorer agreement with the reflectivity profiles. Substantially improved agreement was found by including in the surface structure factor F_{surface} an extra adsorbed layer at the interface. We initially assigned this layer to be Ca ions on the basis of the best-fit height and number density at the surface. Hydration of the adsorbed calcium layer was subsequently included, which overlaps with the featureless bulk water profile.

The solid lines in Fig. 1 represent the best-fit results. The open circles and error bars are for the measured data. The quality of fit $\chi^2 = (1/n)\Sigma[(R - R_{\text{calc}})/\sigma_{\text{exp}}]^2$ for the best-fit model is ~ 10 , which is somewhat larger than expected for well-defined cleavage surfaces (e.g. calcite, barite). This level of agreement, however, is satisfying, especially since these measurements were performed on natural growth surfaces, which are not as well-controlled in terms of composition, structure, or surface order. The source of the larger-than-expected quality of fit is a small but significant inconsistency between the data and the calculation, primarily at large Q (e.g., see Fig. 1b at $Q = >2.5 \text{ \AA}^{-1}$). This discrepancy could result from two sources of error. First, the exact chemical composition for these specimens may differ from the bulk structure that was used in our calculations, since fluorapatite is known to have a widely variable composition. Second, we were careful to limit the number of structural parameters in our analysis, and it is possible that all relevant details of the interfacial structure were not included in our models.

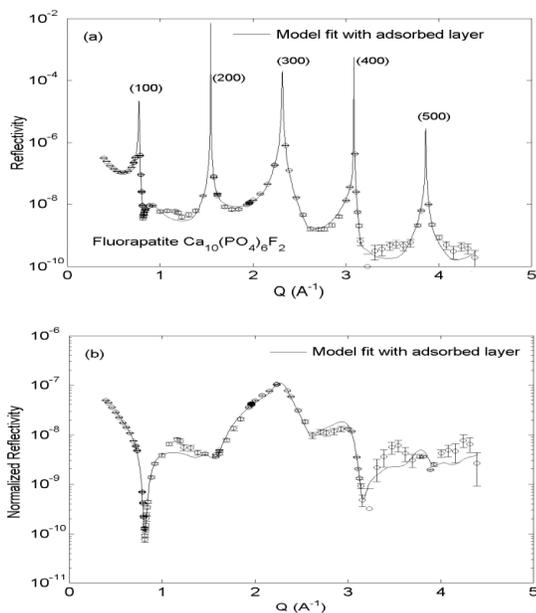


FIG. 1. (a) XRR data for fluorapatite (100)-water interface at neutral pH, shown as a function of the momentum transfer Q . (b) Normalized reflectivity $RQ^2 \sin^2(Qd_{100}/2)$ used in a least square parameters estimation. The solid lines represent the best-fit result based on the structural model with an adsorbed layer.

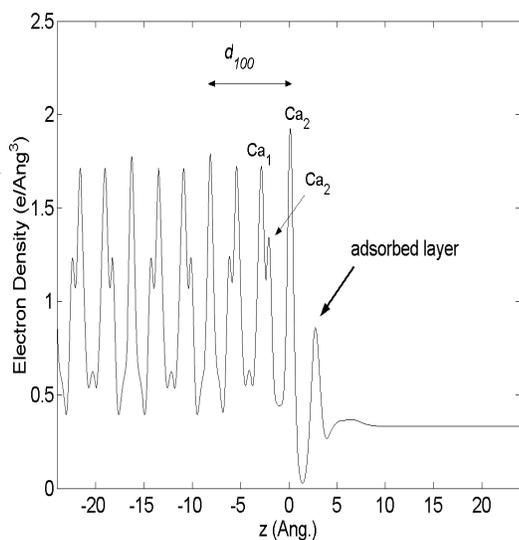


FIG. 2. Electron density profile based on the best fit model for the fluorapatite (100)-water interface.

In spite of the possible errors in the estimation of the present parameters, we conclude that the adsorbed layer is a necessary feature to explain the reflectivity data. Figure 2 shows the electron density profile based on the best-fit model structure along the surface normal direction.

Discussion

The structure of FAp along the surface normal direction consists of two distinct layers, (Ca1 + Ca2) and Ca2 layers (Fig. 2), where Ca1 and Ca2 represent the symmetrically distinct Ca ions in the FAp unit cell that create the FAp framework. By relaxing the structure near the FAp-water interface, we find that the distances between these planes maintain the framework structure with only small deviations from the original lattice locations. The adsorbed layer is found at the extension of this FAp structure above the surface by a distance $\sim d_{100}/3$. An additional feature of our model is the complexation of the surface Ca ions by adsorbed water. These two facts indicate many interesting possibilities in suggesting the surface speciation of FAp during the interfacial processes in aqueous solutions. We have yet to determine if this termination is intrinsic to the natural FAp growth surface or if it may be observed on other FAp.

Acknowledgments

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Geosciences Research Program. The XRR measurements were performed at beamlines 11-ID-D, 12-ID-D, and 1-BM at the APS. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.

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