

Crystal Truncation Rod Diffraction Study of the Hydrated α -Fe₂O₃ (1-102) Surface

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Introduction

Adsorption reactions at mineral surfaces, in particular at Fe-(oxy)hydroxide surfaces, play an important role in controlling the transport and bioavailability of contaminants in aquatic systems. The extent of a sorption reaction and the stability of the sorbed species depend strongly on the types of functional groups at the mineral surface, which are a function of the structure and composition of the bulk material and the crystallographic orientation and chemical history of the exposed surface. The impact of the surface structure and the molecular scale modes of adsorbate association on metal-oxide surfaces are reflected in the overall macroscopic surface reactivity. However, there is only a limited molecular-scale understanding of interfacial reactions. Thus, experimental results on the structure of mineral surfaces and how they are modified under geochemically relevant conditions are critical for developing a fundamental understanding of the chemical reactions that control the fate of contaminants in aquatic systems.

The systematic investigation of well-characterized model mineral-fluid interface systems requires experimental probes that can be used to determine the structure of mineral surfaces under *in situ* conditions (i.e., under bulk solution or controlled atmosphere), as well as the structure and nature of surface complexes at the mineral-water interface [1, 2]. X-ray scattering and x-ray absorption techniques are ideally suited to the *in situ* study of the structure of the solid-aqueous interface because of the high penetrating power of x-rays, the element specificity of absorption and fluorescent energies, and the molecular-scale information that may be derived from these techniques.

In this report, we present some recent crystal truncation rod (CTR) diffraction data from our investigation of the structure of the hydrated α -Fe₂O₃(1-102) surface. This surface is a common growth face of hematite and, along with the (0001) surface, is likely one of the dominant hematite surfaces exposed on natural hematite minerals under environmental conditions [3].

Methods and Materials

The α -Fe₂O₃ sample is a natural single crystal cut to approximately 1 cm² and polished along the (1-102) direction. The sample was washed in 10⁻² M nitric acid followed by multiple rinses with water. This wash procedure should have ensured that the surface was fully hydroxylated [4]. Measurements were performed at beamline 13-ID at the APS. Data were collected at 10 keV by using a double-crystal Si(111) monochromator. Diffraction data were collected at room temperature under a water-saturated He atmosphere by using a kappa-geometry diffractometer in trajectory scanning mode. Each individual structure factor was determined by rocking scans through the CTR and corrected for active area, polarization, and Lorentz factor after background subtraction.

Results

Figure 1 shows the CTR measurements for the hydrated α -Fe₂O₃(1-102) surface. The dashed line is a model calculation for the ideal stoichiometric (1-102) termination shown in Fig. 2. There are obvious large misfits in this model, leading to the conclusion that the surface is either highly relaxed or has a different chemical termination than the expected stoichiometric surface. A similar result was found in our study of the bulk isostructural hydroxylated α -Al₂O₃(1-102) surface [5]. In this study, the best fit model was determined to have a surface termination consistent with removing the topmost Al atom from the surface unit cell (Fig. 2, bottom panel). A model calculation that uses a similar termination for the α -Fe₂O₃(1-102) surface is shown as the solid line in Fig. 1. The substantial improvement in comparison between calculated CTRs and data suggests that the hydrated α -Fe₂O₃(1-102) surface is well described by this "missing Fe-termination." While this surface is not stoichiometric, excess charge is likely compensated for by binding of protons at the exposed surface oxygens. This model also suggests that the α -Fe₂O₃(1-102) has hydroxyl groups exposed at the surface that are singly, doubly, and triply coordinated with Fe.

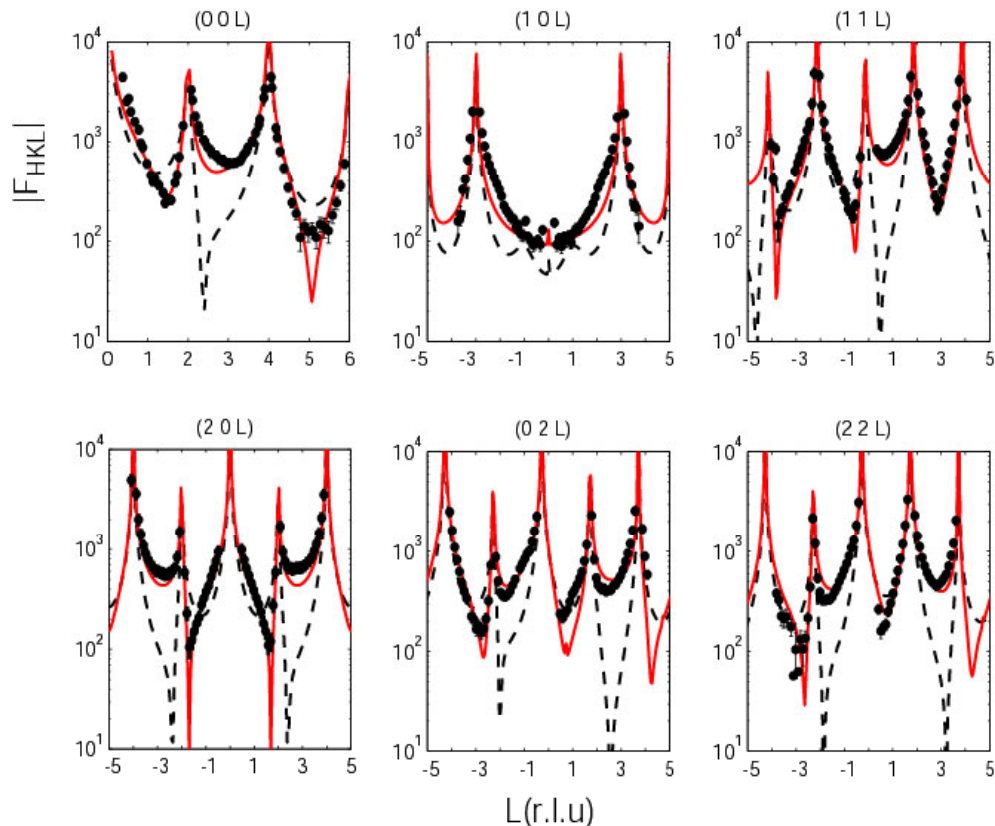


FIG. 1. CTRs measured on the hydrated $\alpha\text{-Fe}_2\text{O}_3(1\text{-}102)$ surface. Plotted is the magnitude of the experimental CTR structure factor versus perpendicular momentum transfer (L). The dashed line is the calculation for the ideal termination in Fig. 2, and the solid red line is the calculation for the missing-Fe termination in Fig. 2.

Discussion

Further analysis is ongoing to fully characterize the structure of the hydrated $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface (principally a detailed analysis of the surface relaxations). However, the preliminary results lead us to propose that the surface is best described with the missing-Fe model, similar to our previous findings on the $\alpha\text{-Al}_2\text{O}_3(1\text{-}102)$ surface [5]. The similarity of these surface models is in contrast to our previous comparison of the $\alpha\text{-Al}_2\text{O}_3(0001)$ and $\alpha\text{-Fe}_2\text{O}_3(0001)$ surfaces, which were found to have substantially different surface terminations [6]. The termination differences explained the dramatic differences in surface reactivity that had been previously observed with respect to aqueous Pb(II) adsorption [7-9]. However, recent glancing incidence x-ray absorption fine structure (GI/XAFS) studies [10] have shown that the mode of Pb(II) binding on the $\alpha\text{-Fe}_2\text{O}_3(1\text{-}102)$ surface is similar to that found on the $\alpha\text{-Al}_2\text{O}_3(1\text{-}102)$ surface, consistent with our findings of similar surface terminations.

Acknowledgments

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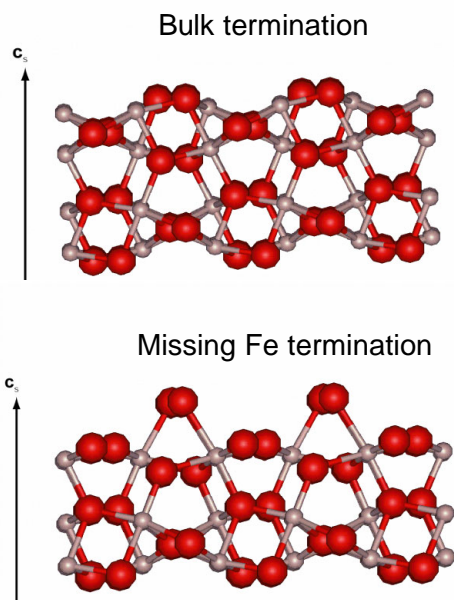


FIG. 2. α - $\text{Fe}_2\text{O}_3(1-102)$ surface models. Red and grey spheres indicate O and Fe atoms, respectively. Top panel shows the atomic layer sequence for the ideal stoichiometric termination and the bottom panel shows it for the proposed missing-Fe termination model.

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