

# Crystal Truncation Rod Diffraction Study of the Hydrated $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) Surface

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## Introduction

Chemical interactions between mineral surfaces and aqueous solutions play a major role in many geochemical and environmental processes, such as chemical weathering, crystal growth, and the partitioning and sequestration of trace elements in aquatic systems. The reactivity of a mineral surface (the potential for sorption of solutes, dissolution, etc.) depends on the composition and structure of the exposed surface. Further, the extent of solute partitioning and the stability of sorbed species depend on the molecular-level structure of the reaction products and their mode(s) of association with the surface. Systematic studies of well-characterized model systems under environmentally relevant conditions are needed to develop a fundamental understanding of the chemical interactions that occur at the mineral-solution interface. Therefore, there is a need for experimental probes that can be used to determine the structure of mineral surfaces under *in situ* (i.e., bulk solution or controlled atmosphere) conditions and to determine 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.

This report presents some recent crystal truncation rod (CTR) diffraction data from our investigation of the structure of the hydrated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface. Previous studies have shown that there is a substantial difference in the reactivity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surfaces with respect to the adsorption of aqueous Pb(II) [3]. It has been proposed that Pb(II) binds in an outer-sphere manner on the (0001) surface of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, while there is evidence that it binds in an inner-sphere manner on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface [4, 5]. In a previous study, we found that the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface is

terminated by a hydroxyl layer in which each surface oxygen is in twofold coordination with Al(III) [6]. This results in a stable surface configuration that is predicted to have a low affinity toward the binding of aqueous Pb(II). Therefore, our present work focuses on the characterization of the hydrated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface as well as the characterization of the Pb(II) sorption mode on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface (not discussed here) to provide a structural interpretation of the observed differences in reactivity.

## Methods and Materials

The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample is a natural single crystal from Bahia, Brazil. The sample was cut to approximately 1-cm square and polished along the (0001) direction (miss-cut of <0.16°). It was washed in 10<sup>-2</sup> M nitric acid followed by multiple rinses with water. This wash procedure was done to ensure that the surface was fully hydroxylated [7].

Measurements were performed at the APS on beamline 13-ID. X-rays from the first harmonic of an APS undulator "A" were monochromatized to 10 keV by using a double-crystal Si(111) monochromator. Diffraction data were collected under ambient conditions by using the 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  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>(0001) surface. The preliminary model fits suggest that the surface is oxygen terminated and that there is a substantial relaxation of the surface atoms from their bulk positions. The relaxation is primarily associated with a contraction of the spacing in the double iron layer, as shown in Fig. 2. A similar relaxation was observed in our study of the hydrated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface. However, there also appears to be a small fraction of

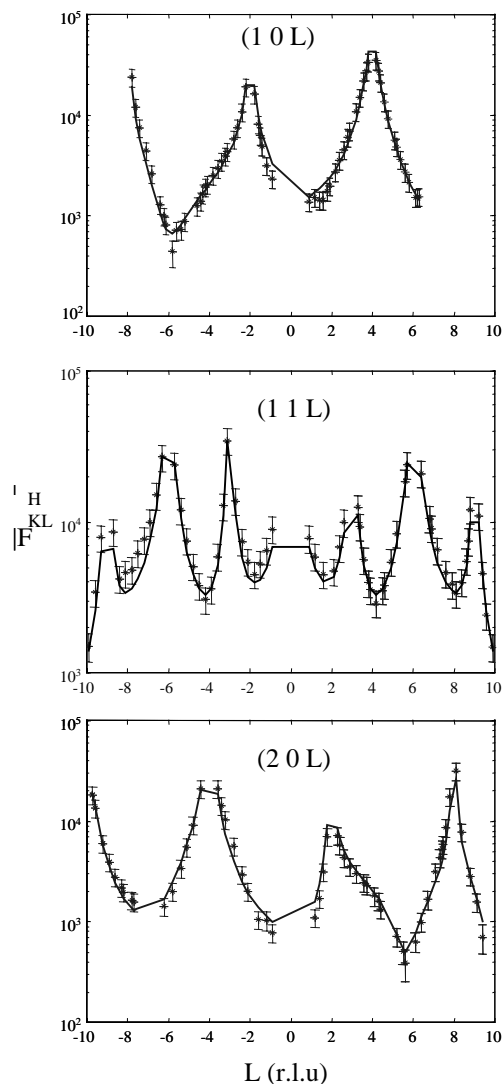


FIG. 1. CTRs measured on the hydrated  $\alpha\text{-Fe}_2\text{O}_3(0001)$  surface. Plotted is the magnitude of the experimental CTR structure factor vs. perpendicular momentum transfer ( $L$ ). Solid line represents the initial fits, which resulted in the model shown in Fig. 2.

“single-layer” Fe on the surface (occupancy of  $\sim 0.33$ ). We note that our best-fit model suggests that the single-layer Fe is not contracted toward the terminating oxygen plane. A contraction of these terminating Fe atoms toward the surface would be expected on the basis of electrostatic arguments (to reduce the surface dipole) and has been observed for the “ultrahigh vacuum (UHV) clean” single-Al terminated surface of  $\alpha\text{-Al}_2\text{O}_3(0001)$  [8]. However, the  $\alpha\text{-Fe}_2\text{O}_3(0001)$  sample was prepared under heavily hydrating conditions; therefore, the presence of the water on the surface likely results in hydroxyl binding at these

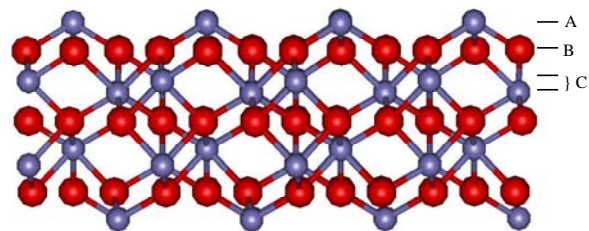


FIG. 2. Side view of a section of the  $\alpha\text{-Fe}_2\text{O}_3$  unit cell showing the atomic layering sequence along the  $[0001]$  direction for the best fit surface model. Red and purple spheres indicate O and Fe atoms, respectively. Layer A is the single-layer Fe and has an occupancy of approximately 0.33. Layer B is the terminating oxygen plane, and C shows the contraction ( $\sim 22\%$ ) of the Fe double layer.

“undercoordinated” Fe sites. The binding of the (hydr)oxy ligands at these sites should result in an expansion of the terminating Fe away from the surface (compare with Ref. 9).

## Discussion

Further data collection and analysis are ongoing to fully characterize the structure of the hydrated  $\alpha\text{-Fe}_2\text{O}_3(0001)$  surface. However, preliminary results suggest that the surface is oxygen (or hydroxyl) terminated, with a small fraction of single-layer Fe on the surface. These results provide a good starting point for interpreting the reactivity on the basis of differences in surface structure and composition, and it should lead to a broader understanding of aqueous-solid interactions in the natural environment.

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