

## Structure and reactivity of hydroxylated hematite surfaces: Application of surface x-ray diffraction and spectroscopy

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Chemical reactions at the mineral-water interface play a critical role dictating the environmental fate of aqueous compounds. In order to develop a detailed molecular scale understanding of the structure-reactivity relationship of environmental interfaces it is necessary to obtain structural information localized to mineral-fluid interfaces under realistic chemical and physical conditions. We will discuss the application of synchrotron based x-ray scattering and spectroscopic techniques to the analysis of mineral surface structure and reactivity. Specifically, we will focus on recent results of the structure of the hydroxylated hematite (0001) and (1-102) surfaces, and the crystal face specific reactivity with respect to aqueous Pb(II). These results will be compared with previous work on iso-structural  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> surfaces and *ab initio* computational studies of surface structure and reactivity.

## Hematite (012) surfaces and interaction with water by molecular modeling

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Interaction between water and solid surfaces can substantially affect the properties of both phases, including structure and dynamics of the near surface water and reactivity and functionality of the substrate surface. This interaction is largely controlled by the surface structures, compositions, and surface charge distributions and surface redox environment, that vary widely among minerals and aqueous conditions. Hematite, the most stable oxide of iron under Earth's surface environment, is abundant in natural environment. Two oxidation states of hematite (012) surfaces, (1×1) – oxidized state and (2×1) – reduced state, are an ideal model systems to elucidate mineral surface redox reaction, and the fundamental understanding of their interaction with water will provide insight on the such processes as surface induced / mediated redox reaction and the control of multi-valence ion minerals on redox condition of natural aqueous system, which has significant impacts on human being's living environment.

The present work concerns the characterizations of the structures of hematite (012) surfaces and the effect of the surface structure and oxidation state on water adsorption, e.g., surface Fe<sup>2+</sup> and Fe<sup>3+</sup> distributions and surface relaxation/reconstruction on the nature, structure and energetics of water adsorption. Energy minimizations, molecular dynamics simulations and *ab initio* calculation were performed on the (1×1) and (2×1) surfaces of hematite (012). Our results suggest that at oxidized state, the bulk terminated surface experiences significant surface relaxation but no reconstruction, consistent with the previous studies. However, at reduced state, more stable configuration was found that half of the reduced Fe<sup>2+</sup> ions stay in the octahedrons in the surface octahedral layer and the other reduced Fe<sup>2+</sup> ions are in the second layer from the surface, indicating electron transfer from the surface layer into deeper layer from the surface. The resulting structure is incomparable to the structure of neither hematite nor magnetite. Both chemically and physically adsorbed water are observed in the water adsorption simulations. The adsorption behavior on both surfaces is qualitatively consistent with experimental observations.