Hydroxyl Group Reactivity at Mineral Surfaces

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Mineral surfaces are important reaction centers for gases and solutes of central importance in geochemistry. These surfaces are populated by hydroxyl functional groups that can undergo proton and ligand exchange, as well as form extensive networks of hydrogen bonds (Figure 1). Knowledge of the types, distributions and orientations of these groups is essential for molecular-scale resolution of these reactions.

This presentation summarizes recent advancements in tracking the populations of hydroxyl groups on a suite of iron (oxyhydro)oxide nanoparticles (ferrihydrite, α, β, γ-FeOOH, α-Fe_2O_3). Our approach tracks the vibration spectroscopic response of OH groups to identify reactive binding sites, and in many cases even the crystallographic faces on which reactions occur. This approach offers new ideas for understanding a host of reactions including, proton binding, ligand exchange, organic complexation, water condensation, mineralogical transformations, as well as thermal decomposition. [*e.g.* 1-4]

Similarities and differences in O-H bond strengths of singly (–OH), doubly (μ–OH), and triply (μ3–OH) groups on iron (oxyhydro)oxide surfaces of contrasting structures and crystal habits will be used to provide insight on reactions of geochemical importance. Some to be highlighted include silica polymerization, water film formation, and photoelectrochemical water oxidation. This body of work forms the basis for a molecular-scale understanding of geochemical reactions involving these minerals, and especially in water-unsaturated environments where OH groups can be readily identified by vibration spectroscopy.

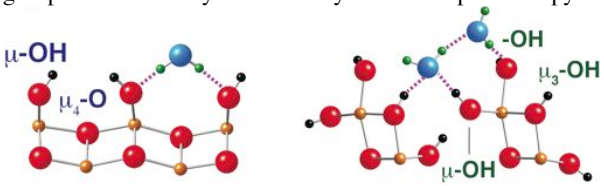

Figure 1. Schematic molecular representation of hydroxyl groups and adsorbed water on two distinct crystallographic faces of lepidocrocite (γ-FeOOH) .

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