

Sorption and structural properties of aqueous-mineral surfaces interfaces: surface x-ray techniques

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Experimental results on the structure and reactivity of the aqueous-mineral surface interface is needed to develop a fundamental understanding of controls on environmental interface reactivity. Modifications to the surface structure, composition, roughness and morphology may substantially alter overall surface reactivity. In this work we will discuss the application of a number of synchrotron based surface analysis methods, including crystal truncation rod (CTR) diffraction, grazing incidence x-ray absorption spectroscopy (GI-XAS) and grazing incidence x-ray diffraction (GI-XRD) to investigate the structure and composition of mineral surfaces. We will review the usefulness of different surface probe techniques in understanding the complex crystal structure and chemistry of the mineral surfaces under a wide range of environmental conditions. In particular we will discuss how complementary information from these techniques can be used to characterize surface associated reaction products (sorbrates and surface precipitates) and modifications of surface structure following reaction.

Modeling Zn²⁺ adsorption at the rutile-water interface to hydrothermal conditions

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We are investigating the adsorption of Zn²⁺ (and other cations) at the rutile-water interface into the hydrothermal regime with a variety of in-situ and computational techniques including macroscopic pH titration and x-ray standing wave (XSW) methods as well as ab initio, MD, and surface complexation modeling (SCM) approaches. This multifaceted approach is being pursued in iterative and complementary fashion with in-situ data helping to constrain modeling efforts, which in turn provide information on interfacial properties which are difficult to unambiguously characterize with in-situ data alone including the hydration state of adsorbed ions, and interfacial water properties.

pH titration experiments were carried out on a well-characterized rutile powder in sodium trifluoromethanesulfonate solutions (0.03 and 0.3 *m*) using both conventional glass electrodes (25 and 50°C) and stirred hydrogen electrode concentration cells (50 to 250°C). Zn²⁺ adsorption increased strongly with temperature, which is consistent with our results for other multivalent cations. Surface complexation modeling utilized the MUSIC model of surface protonation, coupled with a Stern-based three-layer description of the electric double layer. This model was able to adequately fit all pH titration data as constrained by the precise bonding geometry provided by the XSW results which indicated inner-sphere binding in predominately monodentate fashion to bridged (i.e., Ti₂-O⁻) surface groups. Moreover, observed Zn²⁺ bonding heights (3.00 ± 0.10 Å above the Ti-O surface plane) are best rationalized within the context of our SCM if a significant fraction of the adsorbed Zn²⁺ is allowed to hydrolyze (e.g., ZnOH⁺) as pH increases. Hydrolysis is confirmed by our ab initio results provided adsorbed Zn²⁺ is in overall 4-fold coordination at the rutile-water interface.