

FWP ERKCC41
Nanoscale Complexity at the Oxide/Water Interface

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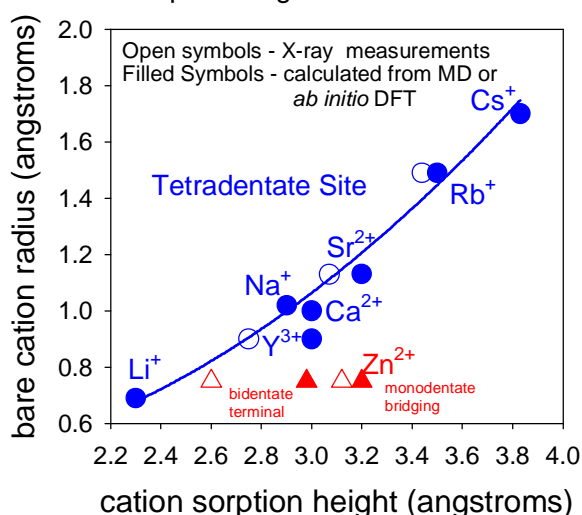
Inner-sphere cation sorption geometries on TiO₂ surfaces from X-ray standing wave triangulation, bulk powder titrations and computational models

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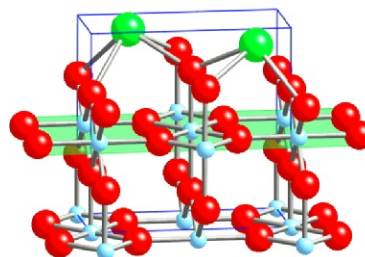
Technical Version

In this multi-disciplinary, multi-institutional study, the molecular-level details of the sorption of ions on charged metal-oxide surfaces in contact with aqueous solutions are being elucidated by integrating the results of macroscopic titration experiments, molecular-level imaging of the surface using synchrotron and neutron reflection approaches, and computational models ranging from macroscopic surface site complexation models to classical molecular dynamics simulations to *ab initio* calculations. Rutile (α -TiO₂) is one of the most widely investigated oxides, due to its wide applications in ceramic processing, photocatalysis, pigments and its similarity to more common oxides, such as SiO₂ (quartz) abundant in natural environments. The rutile (110) surface in contact with water consists of alternating rows of terminal oxygen atoms bound to a single titanium atom and bridging oxygens bound to two titanium atoms in the surface plane. These protruding oxygen atoms undergo protonation reactions which impart a pH-dependent charge to the surface, and these charged sites attract dissolve ions to form the electrical double layer. Our studies for the first time reveal the full details of the interaction of ions having a wide range of charges and ionic radii with this surface. As indicated in the Figure, many cations are shown to form tetradentate complexes in direct contact with two terminal and two bridging oxygens, while small transition metal ions like Zn²⁺ bind to a single bridging oxygen or form bidentate complexes with two terminal oxygens. The three-dimensional positions of surface atoms, sorbed ions and water and dissolved ions in the interfacial region are revealed with subangstrom resolution by the synchrotron X-ray standing wave technique, and the sorption sites agree extremely well with our *ab initio*-optimized MD simulations. *Ab initio* DFT calculations as well as X-ray standing wave studies indicate a radically different mode of adsorption of small transition metal ions like Zn²⁺. The latter calculations predict that, while Zn²⁺ in water is in six-fold octahedral coordination with hydrating water molecules, the sorbed zinc exhibits four-fold coordination, including one or two surface oxygens as well as water molecules. In each surface configuration, one of the water molecules is deprotonated. This surface-enhanced hydrolysis of the cation helps explain the large proton release associated with surface adsorption indicated from our macroscopic powder titrations.

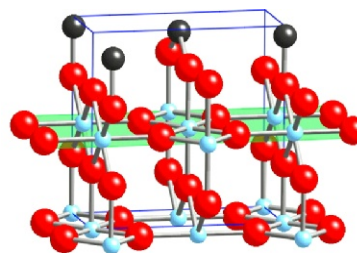
Cation adsorption heights above Ti-O surface plane



Tetradentate site



Mono- and Bi-dentate sites



Non-technical Version

The charge developed on metal oxide surfaces in contact with water depends directly on the fluid pH and the mineral surface chemistry and structure. The adsorption of dissolved ions, which changes with this change in surface charge, exerts a major influence on toxic and radioactive element migration in natural environments, the mobility of colloidal particle suspensions in both natural and industrial environments, and a number of important catalytic processes. Very simplistic models have been used to explain the observed effects of water/mineral interactions, with no clear relationship to the crystalline structure of the mineral surfaces. Our combined experimental, analytical and computational studies reveal that the molecular level processes of surface charge development and ion adsorption are entirely dictated by the structure of the truncated array of metal and oxygen atoms exposed at the mineral surfaces. We have also been able to develop computational models that predict the molecular level structure and dynamic properties of the mineral/water interface accurately at sub-atomic length scales, and which are fully consistent with synchrotron X-ray studies of the interface at similar levels of resolution. These models will help improve our understanding of waste remediation, water purification, and economically-important surface-enhanced reactions.