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Ion adsorption at the rutile-water interface to hydrothermal conditions

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Our group is investigating the adsorption of a variety of ions (Rb^+, Na^+, Cl^-, Br^-, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Y^{3+}, Nd^{3+}) at the rutile-water interface into the hydrothermal regime with a variety of in-situ techniques including macroscopic pH titration[1,2] and electrophoretic mobility measurements[3], and x-ray standing wave[4] and crystal truncation rod methods. These data are being coupled with ab-initio, molecular dynamics, and surface complexation modeling approaches with the ultimate goal being an unambiguous description of ion adsorption structure and distribution within the interfacial region. 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[5]. A primary consensus conclusion is that all cations (including Rb^+ and Na^+) show some degree of inner-sphere binding on the 110 surface of rutile. Moreover, the extent of this binding increases with temperature, at least to 250°C.

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Interpretation of surface species from spectroscopy and CD modelling

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In-situ characterisation of surface species can be done with various spectroscopic techniques. The spectra need to be interpreted to arrive at a conclusion about the type of surface species being present. Interpretation of spectroscopic data leads sometimes to different interpretations by various authors with respect to the surface species being present. Structural information can be used in the CD-MUSIC model [1,2] to arrive at an estimate of the CD (Charge Distribution) value needed in the model. The CD parameter is critical for the correct description of the pH dependence of the binding and should ideally not be treated as a fitting parameter, because the link with the surface speciation as determined from spectroscopy will then be lost [3]. IR data for adsorption of (bi)carbonate on goethite has been interpreted as being due to a monodentate unprotonated surface species [4]. This interpretation is in our opinion in conflict with the CD value that is required to describe (bi)carbonate adsorption on goethite. This discepancy could be due to the weakness of the CD model or due to an incorrect interpretation of the IR results. We will discus both possibilities. A critical evaluation also shows that a similar discrepancy exists for the surface speciation of phosphate at low pH on goethite. An advantage of in-situ IR spectroscopy is that one can also interpret the surface species with respect to the degree of protonation of the adsorbed species. This information is also required for the ion adsorption modelling. The validity of adsorption models can further be tested using competitive adsorption data over a range of pH values. We will show and discuss data of the competition between phosphate and (bi)carbonate for a rather wide range of conditions. Such competition data are not only sensitive to the surface species used in the modelling but also to the structure of the double layer near the interface. Critical evaluation of both spectroscopic data [3,5] and the CD modelling can in certain situations lead to more insight in the speciation of ions at the surface.

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