

Surface complexation and surface speciation

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Surface complexation models (SCM) are powerful tools to describe and rationalize the macroscopic adsorption behavior as a function of environmental conditions and these models are essential for practical applications. However, SCM models are based on thermodynamic principles that do not require an exclusive molecular picture. Therefore, they can be fitted to macroscopic data using virtual species and site densities. Surface characterization by various spectroscopic techniques in combination with quantum chemical modeling and molecular dynamic studies has increased our understanding of the mineral-water interface at the molecular level considerably. The relevant information at the microscopic level has been included in the evolution of the CD and MUSIC modeling framework. An overview will be given of the approach with emphasis on recent developments.

Spectroscopy and MD simulations have shown for rutile innersphere complexation of monovalent electrolyte ions. This process can also be revealed by detailed modeling of the proton adsorption in various electrolytes using the CD and MUSIC framework, and the predicted surface speciation agrees *qualitatively and quantitatively* with microscopic data [1]. In this and other examples, it will be shown how the interfacial charge distribution (CD value) can be used to link macroscopic adsorption data to the information collected at the microscopic level with EXAFS and/or MO-DFT computations.

In practical systems, the competitive and cooperative effect of natural organic matter (NOM) on the ion binding to mineral surfaces can be very large. Therefore, modeling of the mineral-NOM interaction is crucial for application of SCM to natural systems. Great progress has been made in the development of a Ligand and Charge Distribution model (LCD) combining the NICA and CD-MUSIC approach that is able to describe these processes [2].

Reactive particles in nature are often nano-sized and information of the reactive surface area is essential for applying SCM. Work is in progress to estimate the effective reactive surface area of the metal oxide fraction in natural samples and its effective interaction with NOM.

[1] Ridley, *et al* (2009). *Geochim. Cosmochim. Acta*. [2] Weng *et al.*(2008) *Environ. Sci. Technol.* **42**: 8747-8752

Titanium complexation in subduction zone fluids: Insights from *ab initio* molecular dynamics

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The governing mechanisms that control element mobility in subduction zones besides pressure (p) and temperature (T) are the presence and concentrations of (1) major elements in solution, (2) accessory minerals and their preferential incorporation of trace elements and (3) complexing ligands. Rutile (TiO_2) is an accessory mineral frequently used to constrain subduction zone processes. Its preferential incorporation of high field strength elements (HFSE) for instance, make rutile an ideal candidate to explain the low HFSE concentrations in subduction-derived magmas. Rutile's solubility behaviour is key to these arguments. At present, experimental and field-based evidence provides contradicting results of very low rutile solubility in aqueous fluids versus enhanced Ti mobility in metasomatic high-pressure terranes.

The atomic-scale behaviour of Ti in subduction zone fluids has not been studied to date. Here, we use *ab initio* molecular dynamics (AIMD) to investigate Ti complexation in water at elevated p and T . While static simulations indicate 6-fold coordination of titanium at 0 K, our AIMD results at high p and T reveal that 5-fold coordinated complexes $\text{Ti}(\text{H}_2\text{O})_5$ are stable (up to 1.0 GPa and 800 K) in (supercritical) aqueous fluids. The complexes undergo relatively fast Berry pseudo-rotations from a trigonal bipyramidal to a square prismatic geometry as previously found for Cu(II) under ambient conditions. At 1000 K and 1.5 GPa, Ti coordination increases to 6-fold. A typical feature of supercritical water is the reduction of structure caused by the breakdown of the hydrogen bond network. This is confirmed by the current simulations. The change in solvation geometry however appears to be related to (p,T) induced vibrational destabilisation of the Berry pseudo-rotation. On the timescale of the current simulations (2 ps), we do not observe any titanium-hydroxyl complexation. Preliminary results indicate that fluoride preferentially associates with H^+ at 400 K, forming a HF complex with Ti via linking of two hydration shells.

These results show that AIMD simulations have considerable potential to access details of element behaviour in aqueous fluids at geologically relevant conditions that are difficult to probe otherwise.