

## **Multi-scale atomistic simulations of pH dependent ion sorption by minerals: Case study disordered tobermorite surface.**

S. V. CHURAKOV<sup>1</sup>, CH. LABBEZ<sup>2</sup> AND L. PEGADO<sup>12</sup>

<sup>1</sup>Paul Scherrer Institute, Switzerland

<sup>2</sup>CNRS, Université de Bourgogne, France

The stability of mineral surfaces depends strongly on the composition of the wetting fluid. Typically, the oxide and silicate surfaces are oxygen terminated. In presence of water, the surface oxygen atoms participate in protonation reactions. The extent of surface protonation can significantly modify electrostatic properties of the mineral surfaces leading to pH dependent sorption of cations and anions. Exemplary in this context, is a strong pH dependent sorption of ions by clay minerals and Calcium-Silicate-Hydrates (C-S-H). Understanding the ion sorption mechanism in such systems and a mechanistic description of the sorption process require a combination of multi-scale simulations and experimental studies. Such an approach has been developed and applied to simulate the ion uptake by disordered surface of tobermorite [1]. The disordered surface of tobermorite is also widely accepted as a model for wide range semi-amorphous C-S-H phases formed in hardened cement paste.

Recent advances in computational methods make possible to determine the free energy of ion exchange reactions by direct ab initio simulations in realistic systems taking into account effects of molecular solvent explicitly. Protolysis of OH groups associated with the bridging and pairing silica tetrahedra on disordered tobermorite surface by far controls the pH dependent uptake of ions. We calculate pKa values of these sites using the thermodynamic integration technique based on molecular dynamics simulations at the density functional level of theory [2]. Incorporating ab initio pKa values and a more realistic site distribution in GCMC simulations [3] we estimate their effects on ion uptake by the surface of tobermorite. We further apply ab initio thermodynamic integration technique to calculate the free energy of Al incorporation into Si-tetrahedra from aqueous solution. Consistent with recent ab initio studies of Al-Si exchange in C-S-H [4], Al preferentially substitutes for Si in bridging tetrahedra.

[1] Churakov et al. (2014) JPC C, 118, 11752-11762. [2] Sulpizi & Sprik (2008) PCCP, 10, 5238-5249. [3] Labbez et al. (2006) JPC B, 110, 9219-9230. [4] Pegado et al. (2014) JMC A 2, 3477-3483.