

Simulation of mineral-fluid interfaces and their influence on surface binding

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The mineral-fluid interface plays a critical role in a wide range of geochemical processes from crystal growth and dissolution through to incorporation of impurities. Both experimental studies, using techniques such as atomic force microscopy [1] and X-ray reflectivity [2], and computer simulations [3] have shown that water can form structured layers at the interface with mineral surfaces, such as those found for the calcite basal plane. This creates the potential to not only modify the adsorption thermodynamics of ions and molecules at the surface, but also to significantly alter the kinetics of reactions [4].

In this work, the use of molecular dynamics simulation based on both force field [5] and quantum mechanical methods will be examined to compute the properties of mineral-water interfaces. Examples will include both the basal surface of calcite (CaCO₃), with and without acute and obtuse steps, and the brushite-{010}-water interface (CaHPO₄·2H₂O) where comparisons can be made against measurements from surface X-ray diffraction [6]. The consequences of the ordered interfacial water for the free energies of adsorption of ions will be presented [7], along with a discussion of the challenges of obtaining reliable thermodynamics for surface features with slow water exchange.

[1] Marutschke *et al.* (2014) *Nanotech.* **25**, 335703. [2] Fenter (2002) *Rev. Miner. Geochem.* **49**, 149–220. [3] Fenter *et al.* (2013) *J. Phys. Chem. C* **117**, 5028–5042. [4] De La Pierre *et al.* (2016) *Cryst. Growth Des.* **16**, 5907–5914. [5] Raiteri *et al.* (2015) *J. Phys. Chem. C* **119**, 24447–24458. [6] Arsic *et al.* (2004) *Phys. Rev. B* **69**, 245406. [7] De La Pierre *et al.* (2017) *Angew. Chem. Int. Ed.* **56**, 8464–8467.