Ion adsorption at heterogeneous mineral-electrolyte interfaces probed by high-resolution Atomic Force Microscopy

IGOR SIRETANU, DANIEL EBELING, CUNLU ZHAO, DIRK VAN DEN ENDE AND FRIEDER MUGELE

[1]University of Twente, Physics of Complex Fluids, PO Box 217, 7500AE Enschede, (The Netherlands)

The distribution of ions and charge at solid-water interfaces plays an essential role in a wide range of processes in biology, geology and technology. While theoretical models of the solid-electrolyte interface date back to the early 20th century, experimental techniques largely rely on macroscopic averaging and therefore lack the spatial resolution to test key predictions. Using recent advances in high-resolution Atomic Force Microscopy (AFM) we reveal, with atomic level precision, the ordered adsorption of common cations in natural environments to heterogeneous gibbsite:silica-electrolyte interfaces. Complemented by density functional theory, our experiments produce a detailed picture of the formation of surface phases by templated adsorption of cations, anions and water, stabilized by hydrogen bonding. In particular, we demonstrate the sequential build-up of the Stern layer by consecutive adsorption of hydrated Ca^{2+} and Cl^{-} ions upon increasing the bulk concentration of $CaCl_2$ [1]. Complementary measurements on natural kaolinite and montmorillonite nanoparticles display strong charge heterogeneity on the basal planes suggesting that common assumptions regarding the chemical homogeneity may not be appropriate.

[1] Siretanu et al. (2014) *Scientific Reports*, **4**, 4956.