

An *in situ* look at water, ions and forces at mineral surfaces and in confinement

J.J. DE YOREO,^{1,2,*} S.N. KERISIT,¹ A. TALADHAR,¹ X. ZHANG,¹ M.L. SUSHKO,¹ S. ZHANG,¹ D. LI,¹ J. CHUN,¹ Z. WANG¹, E. NAKOUZI¹ AND K.M. ROSSO¹

¹Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, USA
[sebastien.kerisit@pnnl.gov, aasish.taladhar@pnnl.gov, xin.zhang@pnnl.gov, maria.sushko@pnnl.gov, shuai.zhang@pnnl.gov, dongsheng.li2@pnnl.gov, jaehun.chun@pnnl.gov, zheming.wang@pnnl.gov, elias.nakouzi@pnnl.gov, kevin.rosso@pnnl.gov, *correspondence: james.deyoreo@pnnl.gov]

²Department of Materials Science and Engineering, University of Washington, Seattle WA, USA

The structure of water and ions in confined regions between mineral surfaces is a major factor in the forces that drive both the individual and collective behavior of nanoparticles. To understand water structure, ion distributions, and the impact of both on interparticle forces in confinement, we are applying a suite of *in situ* techniques, theory and simulations to mineral surfaces in electrolyte solutions. Sum frequency generation spectroscopy of electrolytes on mica reveal a strong anisotropic distribution of highly-ordered water, which disorders as monovalent cation concentrations increase from 10 to 100 mM, which is the range over which X-ray reflectivity shows development of complete coverage. In contrast, *in situ* AFM finds full coverage already at 10 mM and reveals ion positions differing from those seen in X-ray data, implying the close approach of mineral surfaces strongly alters ion distributions. Dynamic force spectroscopy applied to a number of mineral systems demonstrates that adhesion forces between particles depend on relative crystallographic orientation, but reveal a wide variation in strength and orientation dependence. Introduction of salts causes a strong non-monotonic dependence of these forces on concentration in an ion-specific and temperature dependent fashion. The electrolyte effects are explained by theoretical analyses that consider the impact of molecular details from surface and water structure on the competition between electrostatic and dispersion forces. MD and cDFT simulations give an understanding of orientation dependence and insights into the source of mineral specificity. However, the magnitude of repulsive hydration barriers greatly exceeds kT , implying fluctuations in water structure are required for particles to achieve contact. The findings provide a physical picture of water, ions and forces between mineral surfaces.