

Mass Transport and Mineral Transformations in Nanoscale Interfacial Water Films Triggered by Critical Water Coverages

Quin R.S. Miller ^{1*}, Sebastien N. Kerisit ¹, John P. Kaszuba ², H. Todd Schaefer ¹, Mark E. Bowden ¹, B. Pete McGrail ¹ and Kevin M. Rosso ¹

¹Pacific Northwest National Laboratory

²University of Wyoming Department of Geology and Geophysics and School of Energy Resources

*correspondance: quin.miller@pnnl.gov

Chemical transformations in nanoscale water films have poorly-understood constraints and are difficult to quantitatively examine, yet remain relevant across many natural and engineered environments. In most such cases, the roles of water as both a reactant and a solvent can diverge dramatically from bulk liquid due to the highly structured nature of nanoconfined H₂O. Forsterite (Mg₂SiO₄) carbonation kinetics in ~1 nm interfacial water films from 35-90 °C and 90 atm were monitored with high-pressure in situ X-ray diffraction, conditions with direct relevance for geologic carbon storage and utilization¹. We report how monolayer (ML)-scale changes in water film coverage influence the rates, pathways, and apparent activation energies of Mg-carbonate precipitation. Specifically, the apparent activation energy of magnesite (MgCO₃) precipitation (50-90 °C) was determined to be anomalously-low, at only ~35 kJ/mol. This experimentally-derived result indicates nanoconfined Mg²⁺ adopts a hydration configuration that mimics that of aqueous Ca²⁺, in energetics, if not necessarily in structure². Further experiments demonstrated that decreasing the water film thickness by ~1.5 ML revealed a previously unrecognized reactivity regime dominated by competing kinetic and thermodynamic effects of ion diffusion and dehydration. Complementary molecular dynamics simulations were used to describe the free energy landscape of Mg²⁺ adsorption and diffusion on forsterite surfaces covered in water films 3-10 monolayers thick. The transport simulations suggest that four monolayers are required to enable sufficiently facile Mg²⁺ diffusion and subsequent mineral dissolution-precipitation, helping explain previously observed water film thickness-dependent reactivity thresholds. Our study adds to existing knowledge by pointing to the importance of mass transfer kinetics determining rates and reactivity thresholds at complex hydrated interfaces in rocks, soil, and other porous media.

1. Miller et al. *Environ. Sci. & Technol. Lett.* **2019**, *6*, 431-442.

2. Miller et al. *Chem. Commun.* **2019**, *55*, 6835-6837.