

Role of Mass Transport in Mineral Carbonation in Confined H₂O Films

J.S. LORING^{1*}, R. E. PLACENCIA-GOMEZ², S.N. KERISIT¹,
E.S. ILTON, O. QAFOKU, Q. R. S. MILLER¹, K.M. ROSSO¹

¹Pacific Northwest National Laboratory (PNNL), Richland,
WA 99352 (*correspondence: john.loring@pnnl.gov)

²Urban and Environmental Engineering, University of Liege,
Belgium

Minerals in low-H₂O, humidified fluids are covered in H₂O films that are only monolayers thick. They react under conditions that are dramatically different than in bulk solutions, such as 2D nanoconfinement, low mobility, and low dielectric constant. Hydrophilic surface interactions restrict the ability of H₂O to solvate ions and facilitate diffusive mass transport for processes such as dissolution or precipitation and growth. This surface imposed structuring is relaxed as the H₂O film thickens, but bulk-like behavior may never be obtained because of an inadequate driving force for the formation of a liquid phase in H₂O-undersaturated conditions. Despite numerous examples of H₂O-limited domains in nature, we lack a fundamental understanding of coupled mineral dissolution and nucleation/growth reactions of minerals in confined adsorbed H₂O films.

Here, we present results from *in situ* infrared (IR) spectroscopy combined with electrical impedance (EI) experiments on the carbonation of forsterite (Mg₂SiO₄) in supercritical carbon dioxide (scCO₂, 50 °C, 90 bar) as a function of fluid relative humidity. Comparisons are made to similar results for both forsterite and fumed silica (SiO₂) in an unreactive supercritical nitrogen (scN₂) environment. Molecular dynamics (MD) simulations were performed to help with interpretation. IR measurements detailed adsorbed H₂O concentrations, surface speciation, and carbonation reaction rates. EI results were fit to an equivalent circuit representing the electrically charged Stern and diffuse layers of the thin H₂O films. A diffuse layer was absent at monolayer coverages of H₂O where IR spectroscopy only detected (bi)carbonate surface complexes. Detection of the diffuse layer coincided with the H₂O coverage where IR first evidenced dissolution and carbonate precipitation. The MD simulations showed that a threshold amount of water is required to allow for diffusion of [Mg(H₂O)₆]²⁺ across the surface as an outer-sphere complex

This study clearly demonstrates that mass transport facilitated by H₂O films of a threshold thickness is a key process in controlling mineral reactivity in thin H₂O films and specifically mineral carbonation in low-water environments. This research advances a predictive understanding of complex fluid systems involving interfaces and confinement and is important for CO₂ utilization and storage operations, including enhanced gas recovery (EGR), geologic carbon sequestration (GCS), and enhanced geothermal systems (EGS).