

Effects of pore size, mineral type, and solution composition on water film thickness in rock pores

NAOKI NISHIYAMA^{1*}, TADASHI YOKOYAMA²

¹National Institute for Materials Science, Japan

(*correspondence:

NISHIYAMA.Naoki@nims.go.jp)

²Osaka University, Japan (tadashi@ess.sci.osaka-u.ac.jp)

Rock pores above the water table are characterized by the coexistence of water and air, which potentially causes heterogeneity in pore-scale dissolution rate. Previous studies [1,2] showed that even if a pore is filled with air, water film covers the surfaces of the pore and induces the dissolution of the surfaces and the transport of dissolved solutes. The thickness of water film is an important factor because it determines whether the dissolution of the surface wetted by film is transport-limited or reaction-limited [2]. We constructed a model for estimating the film thickness in rock pores and investigated how the differences in mineral type and pore solution composition affect the film thickness.

In our model, a water film wetting the surface of the air-containing pore in unsaturated rock is considered. DLVO theory has been widely used to predict the van der Waals force and electric double layer (EDL) force between colloids (i.e., mineral/water/mineral system). By applying the DLVO theory to the case of water film (i.e., mineral/water/air system), we calculated the relationship between the thickness and pressure in water film (disjoining pressure). In the calculation, the EDL force was estimated using electric potentials at mineral/water and air/water interface predicted by a surface complexation model. The disjoining pressure in the film is related to relative humidity in the pore air. The relative humidity is controlled by the curvature of meniscus at water/air interface (~pore diameter) according to the Kelvin equation. Combining these relationships, we obtained an expression describing the film thickness-pore diameter relation for various minerals, pH, and ion concentration.

The calculation showed that water film is generally thicker for minerals having higher wettability (higher hydrophilicity): smectite > quartz > calcite > ferrihydrite. If pore solution is dilute (<0.1 mM) and the mineral has high electric potential (e.g., quartz), pore diameter is the most important factor controlling the film thickness. Our model would be useful for considering various reactive-transport processes including the chemical weathering in vadose zone and the geological storage of carbon dioxide.

[1] Stipp et al. (1996), *Am. Mineral* **81**, 1–8. [2] Nishiyama & Yokoyama (2013), *Geochim. Cosmochim. Acta* **122**, 153–169.