

Effect of water saturation on mineral-water reactive surface area: role of water film

NISHIYAMA, Naoki^{1*}, YOKOYAMA, Tadashi¹

¹Dept. Earth & Space Sci., Osaka Univ.

Accurate estimation of mineral-water reactive surface area is essential for quantifying water-rock interaction. Rocks above water tables are usually water-unsaturated, where water and air coexist in pores. There is a possibility that the reactive surface area under unsaturated condition is smaller than that under saturated condition and as the result total amount of reaction becomes smaller. This study aims to investigate the relationship between water saturation and mineral-water reactive surface area.

Fontainebleau sandstone from France, total porosity 7.4%, quartz ~100%, was used. A core was cut from the rock and water-saturation was adjusted to 0, 50, and 100%. Water was run into the sample by applying a constant water pressure. Under an unsaturated condition, only quartz surfaces in contact with water dissolve and the dissolved Si is transported to the outside of the sample by flow of water in pores. At a water saturation S , the relationship between volume flow rate $Q(S)$ ($\text{cm}^3 \text{sec}^{-1}$), Si concentration in effluent $C_{Si}(S)$ (mol cm^{-3}), reactive surface area $A(S)$ (cm^2), quartz dissolution rate at far from equilibrium k_{Qz} ($\text{mol cm}^{-2} \text{sec}^{-1}$) (independent of water saturation) is given by $Q(S) \times C_{Si}(S) = k_{Qz} \times A(S)$. Therefore, by measuring the flow rate and Si concentration at various water saturations and comparing them with those at saturated condition, variation of reactive surface area with changing water saturation can be evaluated.

Result of experiments showed that the reactive surface area was almost unchanged by the decrease of water saturation. This result indicates that mineral surfaces exposed to air-containing pores were wetted with thick water film, by which dissolution occurred. Furthermore, it suggests that the rate of flushing of dissolved Si to outside of film water was fast enough to keep concentration in film water far lower than equilibrium concentration of quartz. If the flushing rate was small dissolution rate of quartz would have decreased because of the concentration dependence of dissolution rate, but this was not the case. To theoretically evaluate whether or not sufficiently low concentration is maintained by diffusional transport of dissolved element, we derived a theoretical reactive transport model that describes the interplay between dissolution and diffusion through water film. In this model, water film wetting mineral surfaces was assumed to be in equilibrium with relative humidity in pores. It was confirmed that flushing in the film was fast enough to keep sufficiently low Si concentration in the case of our sample. The model shows that the concentration in film water is a function of water film thickness, diffusion length, and mineral properties (dissolution rate, equilibrium concentration, and roughness factor). Thus, effects of water saturation on reactive surface area and dissolution rate differ depending on the type of rock. The model can be applied to predict the relationship of "water saturation"- "reactive surface area"- "dissolution rate" for rocks having various mineral compositions and pore structures.

Keywords: mineral-water reactive surface area, mass transport, water film, rock weathering