The effect of slow diffusion of ions in interstitial water on the dissolution rate of rocks

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It is important to elucidate the mechanism and rate of weathering/dissolution of rocks and minerals for quantitative modeling of the element cycle on the earth's surface. In weathering of rocks, the reaction between interstitial water and mineral or glass plays a significant role. If the interstitial water is relatively immobile, dissolved ions are transported to a main flow pathway mainly by diffusion, and then removed from the system. The diffusion coefficient in intricate interstitial water is known to be fairly small compared with bulk free water. We can therefore predict that the slow diffusion in the interstitial water lowers the efficiency of flushing, keeps the ion concentrations and saturation state of the interstitial water high, and lowers the dissolution rates of rocks.

In dissolution experiments, whether it is open or closed system, the solution is vigorously agitated or the amount of samples is adjusted to avoid thick sedimentation in a vessel so that local saturation will not arise. This type of experiment may be appropriate to investigate the mechanism of dissolution. However, a difference in dissolution rate between field and laboratory by up to five orders of magnitude has been reported. Thus, it is quite difficult to quantitatively predict the kinetics of element cycle by extrapolating the results of the above laboratory experiment.

For the present study, the experiment devices were designed to simulate the field condition, where samples reacted mainly with interstitial water (Fig.1). In the type A system, interstitial water is relatively immobile because the solution is injected above the surface of the sediments. The rate of outflow of ions from the sediments (mainly by diffusion) can be measured by analyzing the output solution. In this system, it is possible to collect the interstitial water by pushing down the piston of the syringe. In the type B system, the interstitial water flows constantly because the solution is inserted from the bottom of the sediments. This system is essentially equal to the ordinal dissolution experiment in the open system.

The experiments were conducted using 5.5 g of powdered Kozushima rhyolite samples (50-100 um) at 40 degC, deionized water (pH 6-7), and a flow rate of 30 (ml/day). The result is shown in Fig.2. The dissolution rate in type A was clearly slower than that in type B. In type A, the concentrations of ions in the interstitial water were 10-100 times higher than that of the output solution, while in type B the concentrations of ions in the interstitial water were lower than that of the output solution.

In type A, the dissolution rate of the sample is fast at the beginning of the reaction. As the reaction proceeds, the concentrations of ions in the interstitial water increase rapidly due to the slow outflow of dissolved ions from the interstitial water. As the concentrations of ions in the interstitial water increase, the dissolution rate decreases due to the effect of chemical affinity, whereas the rate of outflow increases because the concentration gradient between the interstitial water and bulk water increases. The dissolution rate and outflow rate become equal at some concentration and after then the condition will be maintained. In the present experiment, the water content was 35 (vol.%). In the field, there are many cases that the water content is considerably lower. In such cases the dissolution rate of rocks may be much further decreased.
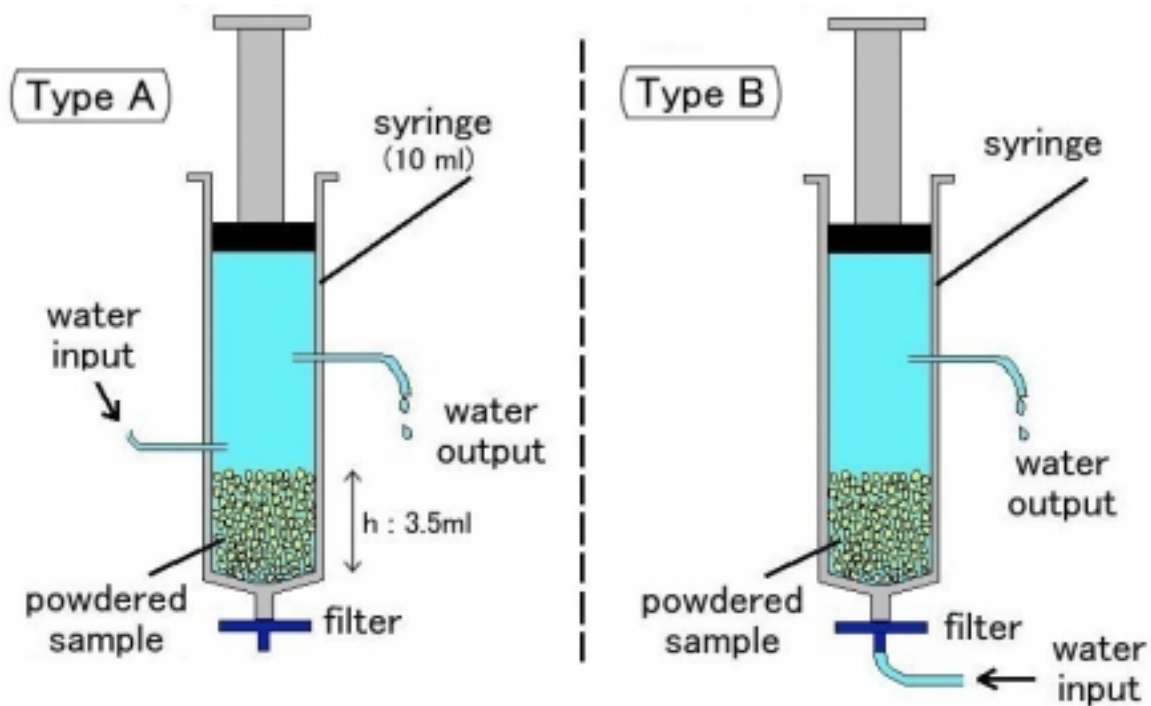
Fig.1

Type A

syringe (10 ml)

water input

water output

powdered sample

h : 3.5ml

filter

Type B

syringe

water output

powdered sample

filter

water input

Fig.2