

Water Rock Interaction [WRI 14]

Role of water film in weathering of porous rhyolite under water unsaturated condition

T. Yokoyama*, N. Nishiyama

Department of Earth and Space Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan.

Abstract

To study weathering behavior under water-unsaturated conditions, flow-through dissolution experiments using a porous rhyolite were performed under both saturated and unsaturated conditions. When water was passed into a dried rock core, water saturation rapidly increased to 0.3 in 2 hours, and then reached 0.4 in 6 days. The proportion of the reactive surface area under the unsaturated condition to that under the saturated condition, $A_{\text{uns}}/A_{\text{s}}$, was 0.46 after 1 day and increased to 0.90 in 6 days. Because $A_{\text{uns}}/A_{\text{s}}$ was always greater than water saturation, the surfaces of air-filled pores seemed to be wetted with a water film and dissolved. The water film thickness was estimated to be 2–3 nm. The reason for $A_{\text{uns}}/A_{\text{s}} < 1$ may be that the flushing efficiency of dissolved elements in the water film was not enough to keep the concentration far from equilibrium, and thereby the dissolution rate in the water film was decreased.

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1. Introduction

The pores of rocks near the ground surface often become unsaturated, as the result of intermittent rainfall, evaporation, and drainage. Under unsaturated conditions, some pores are not filled with water but may be wetted with water film. Although reactive surface area and dissolution rate are presumed to be affected by the presence of water film, the extent at which they are affected by water film is less well understood (e.g., [1]). Such information is important for the understanding of the weathering of rock near the ground surface. The aim of this study is to evaluate how water film influences the reactive surface area and dissolution rate of rock under unsaturated conditions.

* Corresponding author. Tel.: +81-6-6850-5499; fax: +81-6-6850-5480.

E-mail address: tadashi@ess.sci.osaka-u.ac.jp

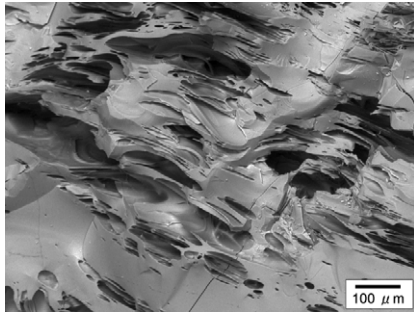


Fig. 1. SEM image of the rhyolite, showing highly porous texture

2. Sample

A porous rhyolite from Kozushima, a volcanic island in Japan, was used for the experiment. Details of rock properties including composition, age (1.2 ka), pore size, and dissolution rate have been previously characterized [2], [3]. Fig. 1 shows a scanning electron microscope image of the rhyolite. The porosity of open pores of the rock is 18%, and the pore radii range from 8 nm to 25 μm, with a peak around 5–7 μm, as measured by the mercury intrusion method [3]. The specific surface area of the rock determined by the N₂ adsorption BET method is 0.22 m² g⁻¹. The mineral composition of the rock is 87% glass, 8.9% plagioclase, 3.8% quartz, and 0.5 % biotite by volume [4].

3. Experiment

3.1. Flow-through dissolution experiments under water saturated and unsaturated conditions

The experimental setup for measuring the dissolution rate under water-saturated and unsaturated conditions is shown in Fig. 2a. Water was passed into a rock core (diameter 3.5 cm, height 1.7 cm) under a constant water head difference of 52 cm. The temperature of the experiment was at 20°C. Output solution was collected at intervals, and the volumetric flow rate and the concentration of dissolved Si were determined. For the saturated condition, the rock pores were first saturated with pure water under vacuum and the core was installed on the sample holder. For the unsaturated condition, the same core was dried in an oven at 70°C and installed on the sample holder. After onset of the experiment, water infiltrated into the sample, dissolution occurred in pore water, and the solution including dissolved elements was discharged from the bottom of the sample. To evaluate the temporal change in water saturation, the sample was taken out from the sample holder at intervals and weighed, and the volume of water absorbed was determined. Water saturation was calculated by dividing the volume of water absorbed by total volume of open pores. The relationships between flow rate, solute concentration, reactive surface area, and dissolution rate under saturated and unsaturated conditions are given by

$$q_s c_s = A_s r_s \quad (1)$$

$$q_{uns} c_{uns} = A_{uns} r_{uns} \quad (2)$$

where q_s and q_{uns} are the flow rate (cm³ s⁻¹), c_s and c_{uns} are the concentration of Si in output solution (mol cm⁻³), A_s and A_{uns} are the reactive surface area (cm²), and r_s and r_{uns} are the dissolution rate (mol cm⁻² s⁻¹) under the saturated and the unsaturated conditions at each elapsed time, respectively. From these, we have

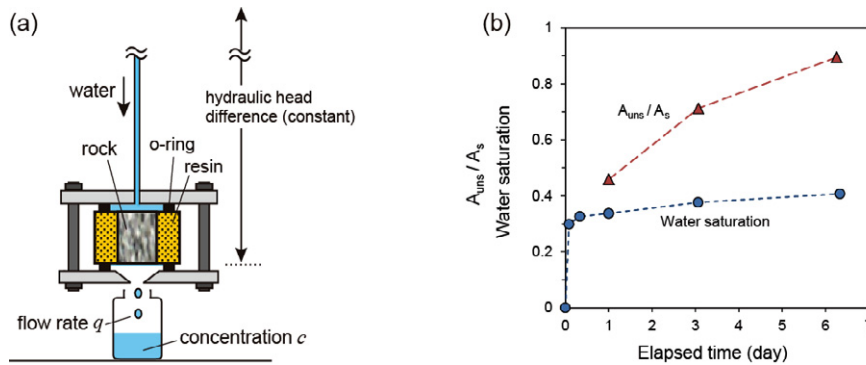


Fig. 2. (a) Setup of flow-through dissolution experiments under water-saturated and unsaturated conditions; (b) Results of the experiments. A_{uns}/A_s denotes the proportion of the reactive surface area under the unsaturated condition to that under the saturated condition

$$A_{\text{uns}}/A_s = (q_{\text{uns}} c_{\text{uns}} / q_s c_s) (r_s / r_{\text{uns}}). \quad (3)$$

If r_s and r_{uns} can be regarded as equal ($r_s = r_{\text{uns}} = \text{rate constant } r_0$, at far from equilibrium condition), A_{uns}/A_s is obtained by measured values of q_s , c_s , q_{uns} , and c_{uns} . However, in fact, r_s seemed to be larger than r_{uns} because the concentrations of Si under the unsaturated condition (17–42 μM) were higher than those under the saturated condition (4–14 μM). The values of A_{uns}/A_s shown in this study are calculated by assuming $r_s = r_{\text{uns}}$; thus they are regarded as minimum estimations.

3.2. Adsorption experiment

The increase of water saturation during the flow-through dissolution experiment under the unsaturated condition is induced by several effects, including infiltration due to gravity and capillary action, and adsorption of water on pore wall (e.g., [5]). To evaluate the amount of water adsorbed during the dissolution experiment, a rhyolite core was placed in a bottle containing aqueous solution (pure water or saturated KCl solution) as the core does not contact the solution, and relative humidity RH was kept 100% (pure water) or 86% (KCl) at 20°C (accuracy of RH $\pm 3\%$). The experiments were conducted at two RH, because the RH in the pores during the dissolution experiment is estimated to be slightly less than 100% (RH=98–100% for most of pores) due to the effect of capillary action [3]. The sample was taken out at intervals, weighed, and the thickness of water film was determined by dividing the amount of water adsorbed by total surface area determined by the BET method.

4. Results and Discussion

Fig. 2b shows the results of the flow-through dissolution experiments under water-saturated and unsaturated conditions. Water saturation rapidly increased to 0.30 within 2 hours and after this its increase became slow. The water saturation at the end of the experiment (6.3 days) was 0.41. It is known that water saturation does not become 1.0 because air is entrapped in pores when water infiltrates into a dried rock [6]. Fig. 3 is the model illustration of how water, entrapped air, and water film were distributed during the experiment under the unsaturated condition. The result of the adsorption experiment showed that water films of thicknesses of ~ 1 nm (RH=86%) to 2–3 nm (RH=100%) were formed within 1 day

and after that the thicknesses became constant. The increase of water saturation during 1–6 days (Fig. 2b) indicates that the volume of entrapped air decreased with time, probably because of the outflow of air to the exterior of the rock as bubble or dissolved air. In Fig. 2b, relative reactive surface area (A_{uns}/A_s) was 0.46 after 1 day and increased to 0.90 in 6 days. Thus, A_{uns}/A_s was always greater than water saturation.

Occurrence of dissolution requires that the solid surface contacts water. Because A_{uns}/A_s was always greater than water saturation, it is likely that dissolution occurred not only at water-filled pores but also at the surfaces of pores occupied by entrapped air. However, A_{uns}/A_s was expected to become 1 if all solid surfaces were coated with water film and dissolution occurred, but the experimental result showed that A_{uns}/A_s was smaller than 1 especially at the early stage of reaction. For dissolution to progress, the concentration in water film needs to be lower than equilibrium concentration. Even if all pore surfaces were coated with water film, the flushing efficiency of dissolved elements from water films toward main flow paths was unlikely to be enough to keep the concentration in water film far from equilibrium, because the thickness of water film was thin. This seems to be the reason that A_{uns}/A_s was smaller than 1. The increase of A_{uns}/A_s with increasing time (Fig. 2b) might be attributed to the decrease of the distance from water films toward main flow paths due to the decrease in the volume of entrapped air.

These results show that the dissolution under unsaturated condition is fairly influenced by the dissolution and the transport in water film. Thus, considering the role of water film is important for understanding the weathering of rock near the ground surface.

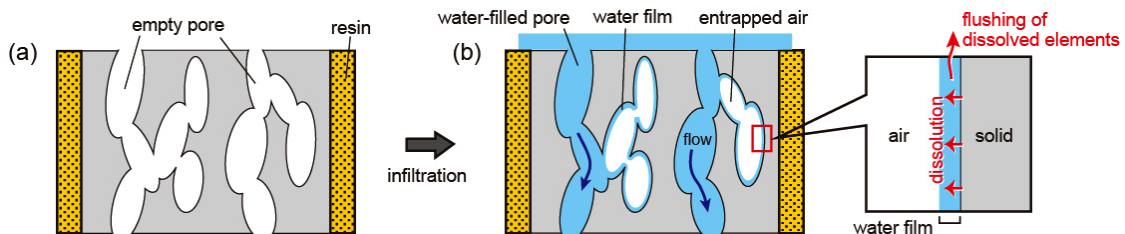


Fig. 3. Model illustrations of the rock sample before infiltration (a) and during flow (b) in the flow-through dissolution experiment under unsaturated condition.

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