

Dissolution rates of limestone tablets in a flow-through system: A laboratory experiment

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Abstract

To examine dissolution rate of limestone as a function of saturation index (SI) for calcite of solution, a flow-through laboratory experiment was carried out using eight solutions with different concentration of Ca. A limestone tablet with a diameter of 3.5 cm and a thickness of 1 cm was set in a reaction bottle where solution flows at a low rate (~63 mL/day) under the conditions of constant temperature at 20°C and constant CO₂ concentration of room atmosphere (0.04–0.1 %). Concentrations of Ca and other primary elements, alkalinity, and pH for the output solutions were monitored to calculate SI of output solutions and amount of Ca dissolved from the limestone tablets. Dissolution rate of calcite was calculated from increments of Ca concentration between the input and the output solutions after the system achieved a steady state condition. The results show that dissolution rates of calcite (0.113–0.448 mg/day) increase with decreasing SI. The relationship between SI and dissolution rate of calcite was well explained with an empirical model.

Key words: limestone; calcite; dissolution experiment; saturation index; flow-through system

1. Introduction

Chemical weathering of limestone and other carbonate rocks, which cover 12% of terrestrial surface of the earth, is an essential factor for landscape evolution of karst terrains as well as global circulation of carbon. Dissolution rates of limestone and calcite have been investigated by many researchers in various fields including geochemistry, marine geology, hydrology, speleology, and geomorphology. From early 1970's, geochemists investigated dissolution rate of calcite powders using a closed-system apparatus called 'pH-stat' system, which monitors pH of a solution and automatically adds HCl to keep the pH constant (Berner and Morse, 1974; Plummer *et al.*, 1978; Rickard and Sjöberg, 1983). The geomorphology research group in University of Tsukuba focuses dissolution processes of limestone and other rocks

using closed batch systems (Hirose *et al.*, 1995; Takaya *et al.*, 1996; Suzuki *et al.*, 2000; Hashimoto *et al.*, 2003; Takaya *et al.*, 2006) or field experiments (Matsukura and Hirose, 1999; Matsukura *et al.*, 2007). HattANJI and Matsukura (2007) implied that water chemistry, especially degree of saturation for calcite, is a major controlling factor for 'in situ' weathering rate of limestone tablets in stream water.

Few studies, however, link the results of laboratory and field experiments. Most laboratory experiments concentrate dissolution rates and processes in closed-system apparatus, while most field experiments lack detailed geochemical analysis. Recently, Yokoyama and Matsukura (2006) confirmed how chemical weathering affects weight loss of granodiorite tablets, using a flow-through apparatus. Various types of flow-through apparatus have also been used to explore dissolution process of calcite in deep aquifers (Pokrovsky *et al.*, 2005) or on exposed surface (Kaufmann and Dreybrodt, 2007). Laboratory experiment using flow-through apparatus as well as field experiment must improve our understanding of denudation process of limestone around karst terrains. The present paper reports methods and the preliminary results of a dissolution experiment of limestone tablets using a flow-through apparatus.

2. Methods

Limestone blocks taken near the Abukuma Cave, Fukushima Prefecture, were cored and the cores were sliced into standard-sized tablets (3.45 cm in diameter, 1.08±0.02 cm thick). Weight of the tablets was measured to an accuracy of ±0.001g after drying at 110°C for 24 hours and cleaning with acetone. Average initial weight of the tablets is 26.73±0.44 g (Table 1). Bulk density of the tablets is 2.67±0.02 g/cm³. The X-ray fluorescence analysis by Suzuki *et al.* (2000) showed that the same limestone contains 55.5% of CaO, 0.22% of MgO, 0.19% of Al₂O₃, 0.10% of FeO+Fe₂O₃, and ~44% of CO₂, i.e., the limestone is composed of calcite (CaCO₃) and slightly contains dolomite (CaMg(CO₃)₂, < 1%).

The remained limestone blocks were ground and put in distilled water over one month. The distilled water approaches chemical equilibrium (i.e., saturation) to calcite due to dissolution of the limestone powders. Then the near-saturated solution was filtered to 0.20 μm to

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Table 1 Results of chemical analysis of solutions and weight measurement of tablets.

		Run A	Run B	Run C	Run D	Run E	Run F	Run G	Run H
Input solution	Average Ca ²⁺ concentration (ppm)	18.5	9.12	4.48	0.22	2.55	1.56	0.92	0.60
	Average SI	-0.38	-1.23	-1.97	-5.63	-3.03	-3.58	-4.15	-4.70
Output solution	Average SI at steady state condition	-0.20	-1.01	-1.64	-2.83	-2.12	-2.18	-2.56	-2.66
	Dissolution rate of calcite (mg/day)	0.113	0.231	0.261	0.316	0.280	0.448	0.376	0.421
	Total loss of calcite (mg)	2.4	5.5	7.0	8.8	6.9	10.6	10.0	10.3
Weight of tablet	Before experiment (g)	26.729	26.946	26.519	26.402	27.167	26.596	27.170	26.296
	After experiment (g)	26.721	26.936	26.508	26.389	27.153	26.577	27.152	26.276
	Weight loss (mg)	8	10	11	13	14	19	18	20

remove the remained limestone powders. Finally, eight solutions with different Ca concentrations were prepared for the experiment by mixing fresh distilled water and the near-saturated solution. Run A uses the undiluted near-saturated solution, and run D uses fresh distilled water as the input solution.

We composed a flow-through apparatus for the experiment (Fig. 1). A limestone tablet was inserted into a 60mL plastic bottle (reaction bottle) settled in an incubator to keep the temperature at 20°C. Input solution in a 2L plastic bottle was infused into the reaction bottle with a peristaltic pump at a flow rate of 63±2 mL/day, and the solution in the reaction bottle was drained at the same rate simultaneously. Partial pressure of CO₂ calculated from alkalinity and pH of the input solution using the PHREEQC software (version 2.12, Parkhurst and Appelo, 1999) was same as air in the laboratory, i.e. 0.04–0.10 %. Following is the procedure for setting tablets into the apparatus: (1) turn on the pump and fill the connection tube with an input solution, (2) set a tablet in an empty reaction bottle with tweezers, (3) infuse the same input solution into the reaction bottle with a syringe, and (4) cap the reaction bottle. Finally, the reaction bottle was settled into the incubator.

We conducted two sets of four runs (A–D and E–H) for 23 days each. The first set (runs A–D) started on

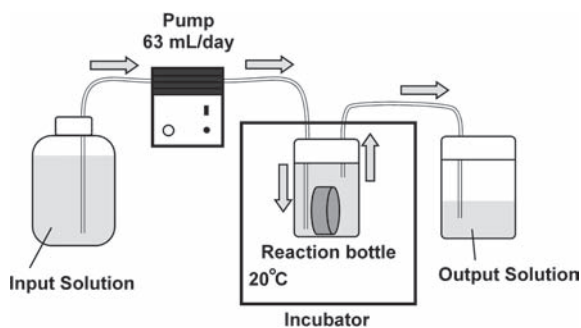


Fig. 1 A flow-through system used for the experiment.

October 22, 2008, and the second set (runs E–H) started on November 28, 2008. On the final day, the tablets were taken out with tweezers to measure their dry weight (110°C for 24 h). The output solution drained from the reaction bottle was collected for chemical analysis. A drop-type pH meter (Shindengen KS723) was used for pH measurement. Alkalinity was determined by titration to pH 4.8 using 0.01N H₂SO₄ and BCG-MR indicator. Remained solution was filtered to 0.20 μm to measure concentrations of dissolved Ca, Mg, Si, K, and Na with ICP-AES (Nippon Jarrell-Ash ICAP-757) at Research Facility Center for Science and Technology, University of Tsukuba. During measurements of the output solutions for runs E–H, we have repeated measurements of standard solutions of Ca (0, 5, 10, 20, and 50 ppm) every 10 samples to minimize errors derived from the ICP analysis.

In the case of pH < 8.4, the standard equation of saturation ratio for calcite, Ω , is (White, 1988):

$$\Omega = \frac{\gamma_{\text{Ca}^{2+}} \cdot m_{\text{Ca}^{2+}} \cdot \gamma_{\text{HCO}_3^-} \cdot m_{\text{HCO}_3^-} \cdot K_2}{a_{\text{H}^+} \cdot K_c} \quad (1)$$

where m is molality, γ is activity coefficient, K_2 is equilibrium constant for $\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$, K_c is equilibrium constant for calcite dissolution ($\text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$), and a_{H^+} is activity of proton, i.e., $\text{pH} = -\log a_{\text{H}^+}$. The equilibrium constants are function of temperature, and the activity coefficients are function of ionic strength. Since Ω usually becomes very small except for karst streams, common logarithm of saturation ratio, i.e., saturation index ($\text{SI} = \log \Omega$), is frequently used instead of Ω . We used the PHREEQC software with a database of essential geochemical constants for calculation of SI.

3. Results and discussion

Figure 2 shows the results of chemical analysis for the output solutions. The Ca concentration of day 0 is that

of the input solution. The output solutions had higher Ca concentration than the input solutions, although run A showed little difference between the input and output solutions. For all the runs, alkalinity and Ca concentration became steady after the 5th day. Saturation indices and pH for the output solutions fluctuated at the earlier stage but became almost stable after the 11th day. These results imply that a physical equilibrium between dissolution and transport of solution has been achieved within 11 days. We therefore assumed the solution in the reaction bottles after the 11th day to be steady state condition. The average SI for the steady state conditions decreased in the following order: $A \gg B > C > E > F > G > H > D$ (Table 1).

For all the runs, the output solution has higher Ca concentration than its input solution. Dissolution of the limestone tablets contributes this increment of Ca concentration. Therefore, loss of Ca from the tablets can be estimated from the increments. Cumulative loss of Ca from a tablet by the n th day, W_n (mg), is:

$$W_n = \sum_{i=1}^n ([Ca^{2+}]_i - [Ca^{2+}]_0) \cdot \rho v_i \quad (2)$$

where $[Ca^{2+}]_i$ is concentration of calcium ion in the output solution on the i th day in ppm (mg/kg solution), $[Ca^{2+}]_0$ is concentration of calcium ion in the input solution in ppm (mg/kg solution), v_i is volume of the output solution on the i th day in liter, and ρ is density of solution ($= 1 \text{ kg/L}$).

Figure 3 shows increase of W_n with time. The fluctuation of Ca concentration (0.02 – 0.52 ppm) in the input solutions gives errors in Ca loss of the tablets. We estimated dissolution rate of Ca using the slope of regression line for the data points under the steady state condition (after the 11th day). Assuming that all the increments of Ca ions are originated from dissolution of calcite ($CaCO_3$) on the limestone tablet, we converted

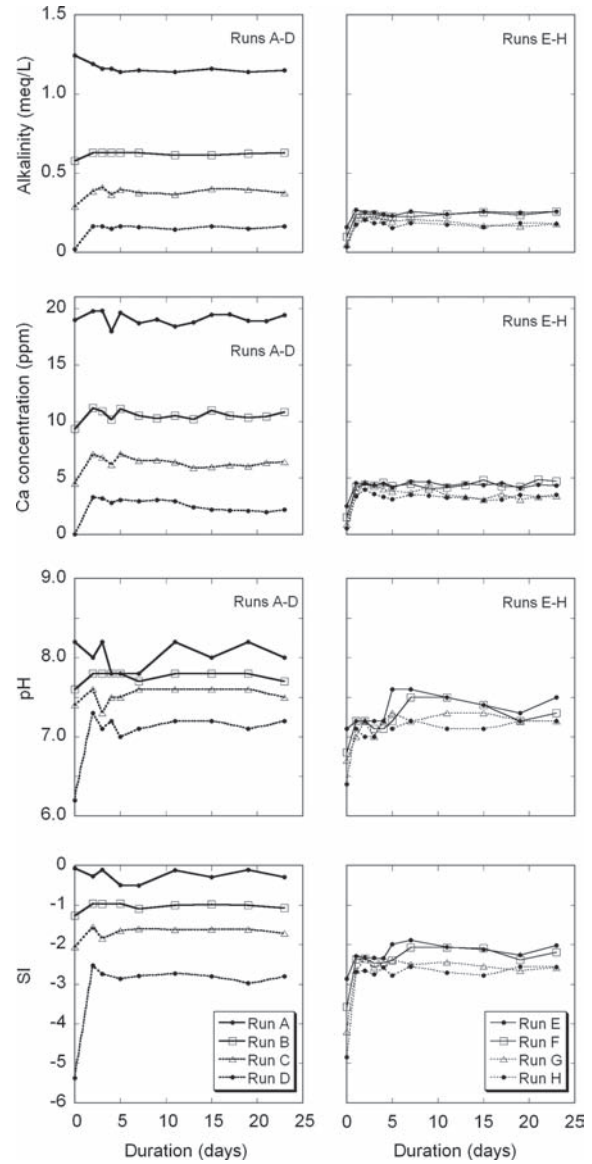


Fig. 2 Temporal change in Ca concentration, alkalinity, pH, and SI for output solutions.

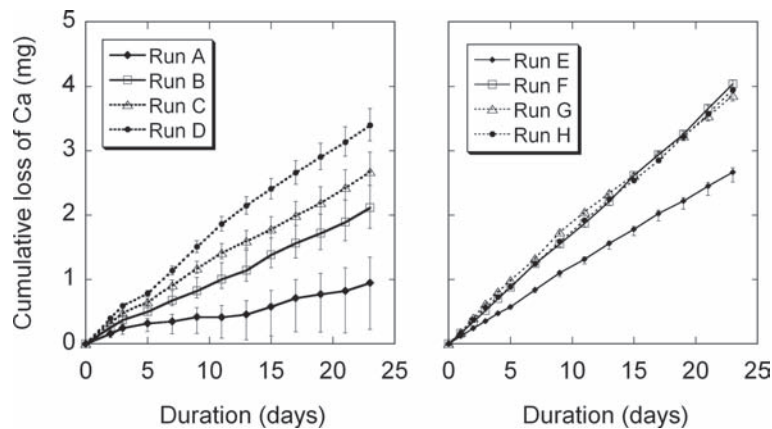


Fig. 3 Cumulative loss of Ca calculated from Ca concentration of input and output solutions. Errors are derived from the temporal fluctuation of the Ca concentration in the input solutions during the experiment.

dissolution rate of Ca into dissolution rate of calcite using weight ratio of calcite to Ca (100/40). The calculated dissolution rate of calcite ranges from 0.113 to 0.448 mg/day (Table 1).

Total loss of Ca for 23 days is the sum of W_{23} and amount of tablet-derived Ca remained in the reaction bottle. Assuming that Ca concentration in the reaction bottle on the 23rd day is same as that of the output solution of the 23rd day, we estimated total loss of calcite again using weight ratio of calcite to Ca (100/40). Total loss of calcite ranges from 2.4 to 10.6 mg (Table 1). We also directly measured weight of tablets before and after the experiment (Table 1). The weight loss ranges from 8 mg to 20 mg, which was 4–10 mg greater than the total loss of calcite calculated from chemical analysis. Dissolution of $MgCO_3$ slightly contained in the tablets was negligible (0–0.6 mg) compared to the difference (4–10 mg). Possible causes of the difference would be: (1) physical detachment during the experiment or oven drying, and (2) higher Ca concentration in the boundary layer between tablet and solutions.

Dissolution rate of calcite was plotted against average SI at steady state conditions (Fig. 4). Run F shows about 4-times higher dissolution rate than run A. Dissolution rate of calcite decreases with increasing SI, though runs F, G, and H show relatively high dissolution rate than run D. The cause is unknown.

The result agrees with previous laboratory studies, showing that dissolution rate decreases with increasing SI. The reduction of dissolution rate for near-saturated solution would be explained by back reaction, i.e., precipitation of calcite (Plummer *et al.* 1978; Chou *et al.* 1989). Rickard and Sjöberg (1983) proposed an empirical model for dissolution rate of calcite, r , as a function of saturation ratio, Ω :

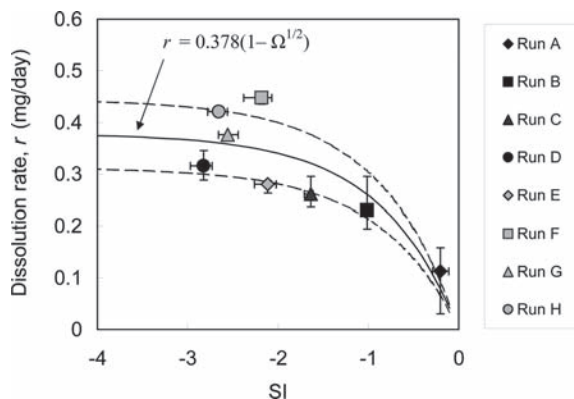


Fig. 4 Dissolution rate of calcite on limestone tablets plotted against average SI of output solutions. The solid line shows an empirical model for dissolution rate of calcite, r , as a function of saturation ratio of calcite, Ω , where $SI = \log \Omega$. Errors of dissolution rates (y-axis) are originated from the errors shown in Fig. 3.

$$r = kA(1 - \Omega^{1/2}) \quad (3)$$

where A is surface area of solid, k is constant, and $SI = \log \Omega$. An empirical equation for the present study was obtained by fitting the data to Eq. (3):

$$r = 0.378 (1 - \Omega^{1/2}) \quad (4)$$

The unit of r in Eq. (4) is mg/day. The empirical model well explains the dissolution rate of the limestone tablets although the plots are scattered to some extent. The dashed lines in Fig. 4 mean the standard error (± 0.066) for the coefficient (0.378). This coefficient is valid only for the following conditions: (1) temperature of 20°C, (2) CO_2 concentration of 0.04–0.10 %, and (3) low flow rate (63 ± 2 mL/day). Future studies should confirm how these environmental factors affect dissolution rate of limestone tablets.

4. Concluding remarks

Dissolution rate of limestone tablets under different saturation indices ($-3 < SI < 0$) was measured using a flow-through apparatus. Dissolution rate of calcite from limestone tablets clearly increased with decreasing SI, and the relationship between them fit into an empirical model proposed by Rickard and Sjöberg (1983).

Flowing water in mountain stream usually has low SI (< -2) for watersheds underlain by plutonic or sedimentary rocks except for limestone. Considering hydrogeomorphic conditions around karst terrains, the result of this experiment implies that stream or groundwater flow from non-limestone basins has a potential to dissolve limestone at least 4 times faster than karst water ($SI \sim -0.2$). Further researches should focus on following problems: (1) effects of temperature, flow rate and CO_2 concentration on dissolution rate of tablet in flowing water, and (2) comparison to the results of field experiment.

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