

NOTE

Elemental dissolution of basalts with ultra-pure water at 340°C and 40 MPa in a newly developed flow-type hydrothermal apparatus

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To simulate the discharge zone of hydrothermal systems in the laboratory, we developed a flow-type hydrothermal apparatus that can reproduce water–rock reactions at elevated temperatures and pressures under flow-through conditions and also the mixing of hydrothermal fluids with seawater. Using this apparatus, basaltic rocks were reacted with ultra-pure water at 340°C and 40 MPa for 1271 h under flow-through conditions. An increase in Al, Fe, K, Na, P and Si in the reacted water was observed during the experiment, reproducing the process of dissolution from the basaltic rocks. An increase in pH to 9 during the experiment can be attributed to the dissolution of silicate minerals in the basaltic rocks. That the pH in the experiment is higher than the pH observed in natural hydrothermal fluids at mid-ocean ridges is a result of higher Si concentrations observed in the experiment than those of natural hydrothermal fluids.

Keywords: hydrothermal system, water–basalt reaction, elemental dissolution, flow-type experiment, sub-terrestrial microbial ecosystem

INTRODUCTION

In natural hydrothermal systems, fluid chemistry is mainly controlled by hydrothermal reactions between water and rocks. Numerous field studies have predicted that physicochemical conditions (e.g., temperature, pH and rock compositions) influence the compositions of the generated hydrothermal fluids (Tivey, 2007). However, it is practically impossible to observe the *in-situ* hydrothermal reactions in deep subsurface environments due to the inaccessibility and the elevated temperature and pressure conditions of these environments. Therefore, laboratory hydrothermal experiments have long been conducted to understand the reactions between rock and

(sea)water that occur in these extreme environments (e.g., Yoshizaki *et al.*, 2009).

To date, hydrothermal experiments have been mainly performed using batch-type apparatuses that simulate a closed system (Seyfried, Jr. and Mottl, 1982; Ghiara *et al.*, 1993; Gislason and Arnórsson, 1993). In particular, batch experiments of basalt–seawater reactions have been performed under high temperature (300°C or higher) and high pressure (50 MPa or higher) conditions (e.g., Seyfried, Jr. and Mottl, 1982). In contrast, flowing conditions can occur in open systems (i.e., flow-through systems), where kinetic water–rock reactions and flow rates strongly affect fluid compositions. Here, we developed a new flow-type hydrothermal apparatus to perform experiments in an open system under flowing conditions. This apparatus can reproduce water–rock reactions at elevated temperatures and pressures (up to 500°C, 50 MPa) under flow-through conditions, corresponding to a water–rock reaction zone in the sub-seafloor hydrothermal systems. Furthermore, the apparatus can also reproduce the mixing of hydrothermal fluids with cool seawater. A flow-

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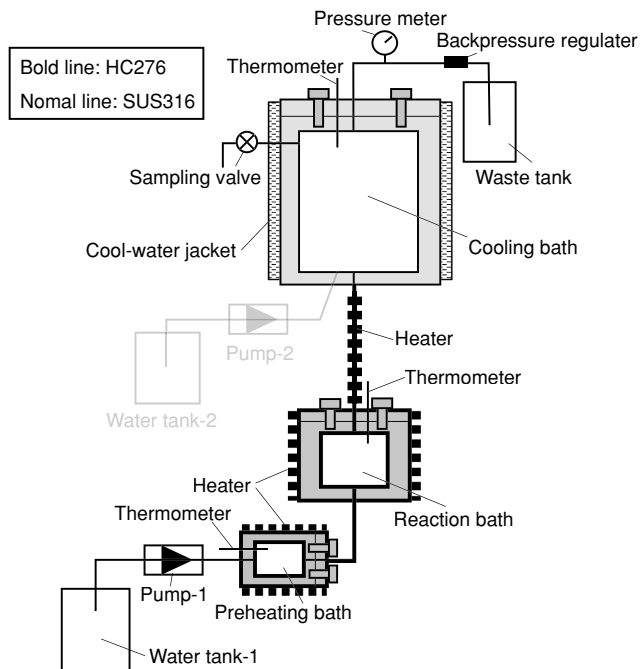


Fig. 1. Illustration of the flow-type hydrothermal apparatus developed in this study.

type hydrothermal apparatus has been reported previously; however, the apparatus could reproduce only water–rock reactions (Normand *et al.*, 2002). The newly developed hydrothermal apparatus will help us to elucidate the mechanism of the generation of hydrothermal fluids in deep-subsurface hydrothermal systems.

MATERIAL AND METHODS

The flow-type hydrothermal apparatus was assembled in Tokyo University of Pharmacy and Life Science. This apparatus consists of two high-pressure liquid chromatography (HPLC) pumps (flow rates ranging between 6–600 ml/h), a preheating bath (SUS316, 100 ml), a water–rock reaction bath (Hastelloy C276, 390 ml) and a cooling bath (SUS316, 5 L) (Fig. 1). The flow lines are made of SUS316 or Hastelloy C276 (Fig. 1). The preheating and reaction baths are equipped with heaters and can be subjected to temperatures up to 300°C and 500°C, respectively. The cooling bath is maintained at 5°C by a cooling water jacket. Fluid pressure inside the apparatus can be increased to 50 MPa, which is kept stable by a backpressure regulator at the end of the flow path. The ultimate goal of the experiments conducted with this apparatus is to simulate deep-sea hydrothermal systems including the mixing processes of hydrothermal fluids with cool seawater. For this purpose, the apparatus is equipped with a cooling bath and the line from pump-2, although

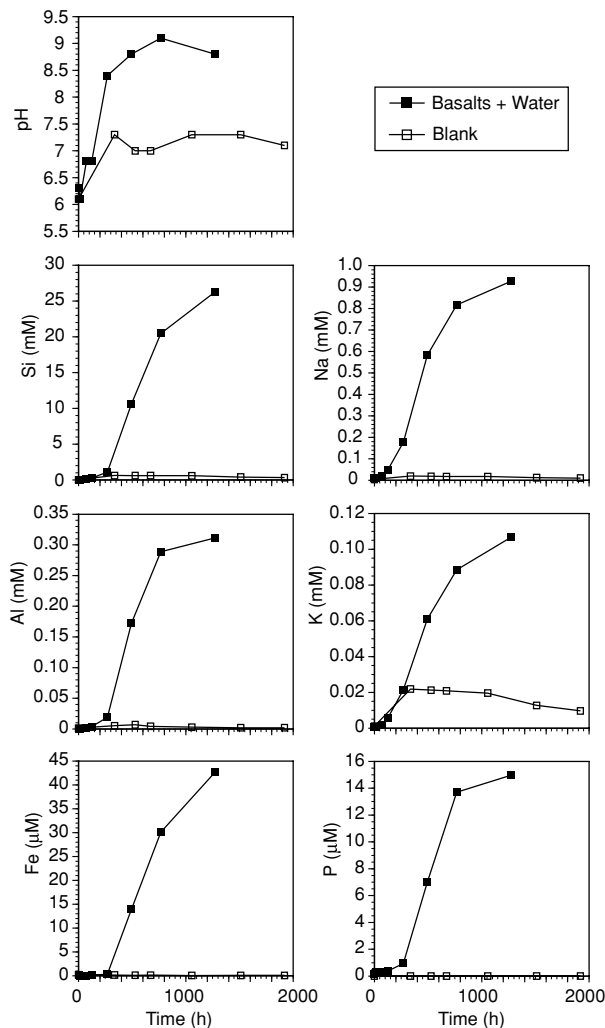


Fig. 2. Temporal change of pH and concentrations of Si, Na, Al, K, Fe, and P in the reacted water in the cooling bath.

pump-2 was not used in the present study. Instead, only pump-1 was used; hence a single path from the water tank-1 to the waste tank-1 was available (Fig. 1).

A basaltic rock collected from Izu-Oshima Volcano, located about 110 km SSW of Tokyo, Japan, and ultra-pure water were used for the hydrothermal experiments. The basaltic rock was crushed and sifted into 5 mm size grains. The grains were cleaned with ethanol and acetone and then dried at 60°C. The reaction bath was filled with the cleaned basaltic rock grains (300 g). Before heating, the apparatus were filled with ultra-pure water and the pressure was adjusted to 40 MPa using the pump-1 and backpressure regulator. A blank test without basalts was also performed using ultra-pure water. The chemical composition of the basaltic rock used in the experiment was determined using a portion of powder of the original basaltic rock by X-ray fluorescence (XRF) spectroscopy

(Supplementary Table S1).

The hydrothermal experiments discussed here used a flow rate of 6 ml/h, preheating bath temperature of 250°C, reaction bath temperature of 400°C, and pressure of 40 MPa. The measured temperature of the water in the reaction bath was 340°C during the experiments, possibly because the residence time of the water was insufficient to maintain a temperature of 400°C. We operated the apparatus for 1271 h for the reaction of basalt grains with ultra-pure water, and for 1920 h without basalt grains (blank test). The reacted water samples were collected from the cooling bath intermittently, and then pH and concentration of elements of these samples were determined by a TWIN pH meter (HORIBA, Kyoto, Japan) and a multi-channel inductively coupled plasma-atomic emission spectrometry (ICP-AES) (SPS5500; SII NanoTechnology, Chiba, Japan). We started the sample collections at the time when the heaters were switched on (time = 0).

It was assumed that the concentration ($C_{i,\text{original}}$) of each element (i) in the original 340°C fluids in the reaction bath was stable and the fluids discharging from the reaction bath were completely mixed with water in the cooling bath. The ideal increase curve of $C_{i,\text{measured}}$ was calculated by optimization analysis using a Solver program (ver. 12.1.1) based on the final point of $C_{i,\text{measured}}$ (i.e., at the sampling time, 1271 h), which resulted in the derivation of $C_{i,\text{original}}$ value.

RESULTS AND DISCUSSION

The pH in the experiment with ultra-pure water only (blank test) was stable between 7.0 and 7.3 (Fig. 2). The pH in the experiment with basalts and ultra-pure water was stable between 8.7 and 9.1 (Fig. 2). Such high pH has been also reported in other experiments of water–basalt reactions in a batch-type hydrothermal system (Ghiara *et al.*, 1993; Berger *et al.*, 1994) and in natural freshwater (Gislason and Arnórsson, 1993). The pH increased over time, which is consistent with the previous reports. The high pH is interpreted to be due to the dissolution reaction of silicate minerals: protons + silicate minerals → cations + silicic acids.

In the experiment with ultra-pure water and basalts, concentrations of Si, Na, Al, K, Fe, and P in the reacted water in the cooling bath increased with time (Fig. 2). These concentrations were clearly higher than those in the experiment with ultra-pure water only (Fig. 2). The concentration of K in the experiment with basalts and ultra-pure water was relatively low, but still clearly higher than that in the blank test (Fig. 2).

The measured concentration of Si in the cooled water ($10 \pm 1^\circ\text{C}$) was 26.3 mM and the calculated concentration of Si in original hydrothermal fluids ($340 \pm 1^\circ\text{C}$) was

33.6 mM (Supplementary Table S2). This high concentration of Si is comparable to or higher than those for high-temperature hydrothermal fluids in natural basalt-hosted hydrothermal systems at mid-ocean ridges, where end member concentrations range between 14.3–22.0 mM (Elderfield and Schultz, 1996). The dissolution of Si is unlikely to be significantly influenced by the difference between ultra-pure water and seawater in reaction, i.e., the presence/absence of Cl^- anions, because Si is also likely to be represented mainly as $\text{SiO}_{2(\text{aq})}$ and HSiO_3^- in fluids. We interpret that the behavior of Si observed in the present experiment could reproduce the Si behavior in basalt-hosted hydrothermal systems. One possibility is that the relatively higher concentration of Si in the present experiment compared to that in natural hydrothermal fluids at similar temperatures (around 340°C) is caused by the difference in pH. The pH was ~9 in the present experiment, in contrast to the pH values of 2.8–4.5 in natural hydrothermal fluids at mid-ocean ridges (Tivey, 2007). High pH leads to the increase in dissolved Si concentration; concentration of Si at pH 4 is about 15 mM (mainly $\text{SiO}_{2(\text{aq})}$) assuming equilibrium with quartz, which increases to 57 mM at pH = 10 ($\text{HSiO}_3^-/\text{SiO}_{2(\text{aq})} = 2.9$). Thus, the relatively high Si concentration observed in the present study may be a result of the high pH. Overall, the results regarding Si indicate that the water–rock reactions occurring in natural hydrothermal system can be simulated in the laboratory using our apparatus.

Similar to Si, P also dissolves as an anion (e.g., HPO_4^{2-}) in fluids. The calculated P concentration in the 340°C fluids was 18.9 μM (Table S2). The result indicates that considerable amounts of P are dissolved from basaltic rocks at the elevated temperature and pressure in flow-through systems. Generally, the end-member concentrations of P for sediment-starved ridge-axis vent fluids range between 0.09–2.0 μM (Wheat *et al.*, 1996). The higher concentration of P in our results as compared to the natural vent fluids may also be caused by the difference in the pH, as with Si.

The major elements of the basaltic rocks, i.e., Na, K, Al and Fe, were also clearly dissolved from the basaltic rocks (Fig. 2). The calculated concentrations of these elements in the 340°C fluids were 1.18 mM, 136 μM , 398 μM , and 54.4 μM , respectively (Table S2). The measured and calculated concentrations of these elements in the 340°C fluids are in good agreement (Table S2). Basaltic rocks contain these elements within glass and silicate minerals. Previous experimental studies have indicated that these elements are dissolved from the basaltic glasses in ultra-pure water due to the dissolution reactions of silicate minerals (Gislason and Eugster, 1987; Ghiara *et al.*, 1993; Berger *et al.*, 1994) as described above. Our results are consistent with the previous studies.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/47/MS240.pdf>)
Tables S1 to S2