

Dissolution rates of crystalline basalt at pH 4 and 10 and 25–75°C

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ABSTRACT

Far-from-equilibrium dissolution rates of crystalline basalt were measured in a mixed-flow reactor at pH 4 and 10, and at temperatures from 25 to 75°C. The material used was obtained from a dyke on Stapafell Mountain on Reykjanes peninsula in Iceland because of its similarity with previous experiments on dissolution rates on basaltic glass by Oelkers and Gislason (2001) and Gislason and Oelkers (2003). Comparison of dissolution rates of basaltic glass and of crystalline basalt of similar chemical composition (from Gislason and Oelkers, 2003) indicates lower rates for crystalline material.

Introduction

REDUCING CO₂ emission into the atmosphere is one of the most important environmental challenges of the 21st century. The search for a permanent solution for large-scale CO₂ storage, with low risk of leakage, has become an important geochemical issue. Injecting CO₂-charged waters into basaltic rock formations may be a viable solution given the large amount of Ca, Mg and Fe in basalt and the relatively fast dissolution of the host rock compared to silicic rocks (e.g. Wolff-Boenisch *et al.*, 2004). In the process, the dissolved CO₂ will react with the basalt to form Ca-, Mg-, and Fe-carbonates. The dissolution rate of basaltic glass has been extensively studied under controlled conditions in the laboratory (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003). These rates can be used in reactive transport modelling of the reaction of dissolved CO₂ with basaltic glass at various temperatures and solution compositions. No such general dissolution rate is available for crystalline basalt dissolution. The overall purpose of this study is to fill this gap. Here we present the dissolution rates of crystalline basalt at varying pH and temperatures.

Methods and materials

Crystalline basalt was collected from a basaltic dyke on Stapafell Mountain, SW-Iceland. Stapafell is the first mountain on the Reykjanes peninsula where the Mid-Atlantic Ridge appears onshore in Iceland. The composition of the rocks in Stapafell is similar to that of mid-ocean ridge basalts (MORB; e.g. Oelkers and Gislason, 2001). This location was also chosen because the dissolution rates for basaltic glass were determined with material from the same location (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003). Stapafell is a hyaloclastite (broken glass) formation, consisting mostly of basaltic glass, crystalline rock fragments and pillow lavas. The hyaloclastite formation at Stapafell is crossed by various dykes. The sampled dyke had no visible alteration features on the surface.

The material was dried at room temperature for several days before it was crushed with a jaw crusher. The fine-grained material was dry sieved to yield the 45–125 µm size fraction. This size fraction was cleaned ultrasonically five times in de-ionized water and then in acetone. Subsequently, the sample was dried at ~50°C for several days. The chemical composition of the dyke was analysed by XRF and is shown in Table 1. Its composition is comparable to basaltic glass used to determine glass-dissolution rates.

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TABLE 1. Chemical analyses of the basaltic rocks of this comparative study.

Major elements Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃ ^c	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	Total
Stapafell dyke	47.9	13.4	12.3	10.0	12.2	1.5	0.3	1.6	0.2	0.2	-0.5	99.1
Stapafell glass ^a	48.1	14.6	10.9	9.1	11.8	2.0	0.3	1.6	0.2	0.2		98.8
Krafla glass ^b	49.8	13.4	14.6	5.7	10.2	2.4	0.3	2.0	0.2	0.2	-0.9	98.9

^a Oelkers and Gíslason (2001)

^b Wolff-Boenisch *et al.* (2004)

^c most Fe is in the form Fe²⁺ (Oelkers and Gíslason, 2001)

These glasses will serve as points of reference in the discussion section and therefore their chemical composition was added to Table 1.

Based on CIPW norm calculations, the crystalline basalt is composed of the following minerals (mol. %): hypersthene 28%, diopside 22%, anorthite 21%, olivine 13%, albite 9%, ilmenite 4%, orthoclase 1% and apatite 0.2%. The specific surface area of the cleaned and dried 45–125 µm size fraction was determined via 11 point krypton adsorption using a Quantachrome Gas Sorption system. The measured BET surface of the crystalline basalt was 7030 cm²/g. The dissolution experiments were performed in a ParrTM mixed-flow reactor shown in Fig. 1, consisting of a 300 mL titanium container with temperature and stirring controller (e.g. Wolff-Boenisch *et al.*, 2004).

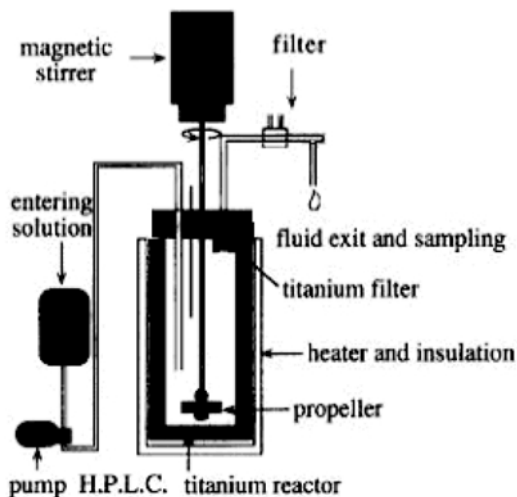


FIG. 1. Mixed-flow reactor for dissolution experiments.

The solution was delivered using an HPLC pump at a constant flow rate between 1 and 4.5 ml/min. The reactor was vigorously and continuously stirred at ~400 rpm and the outlet solution was filtered with 0.2 µm cellulose acetate filter, acidified with HNO₃ and subsequently analysed by means of ICP-OES.

These experiments were performed at pH 4 and 10 with an ionic strength of 10 mM. The acid inlet solution was made of de-ionized water and Merck analytical grade NH₄Cl and HCl, whereas ammonia replaced HCl at pH 10. The compositions of the solutions were pre-defined using *PHREQC* 2.14 (Parkhurst and Appelo, 1990) to yield the desired ionic strength and pH. The inlet solution with alkaline pH was purged with N₂ during the experiment to prevent dissolved carbonate precipitation due to CO₂ entering the reactor. At the beginning of each experiment the reactor was cleaned thoroughly, assembled and run for at least 24 h with de-ionized water and another 24 hour with solution to rinse the tubing and clean the reactor.

Results and discussion

For experiments conducted far-from-equilibrium, the dissolution rate ($r_{+,bet}$) is calculated using the formula:

$$r_{+,BET} = \frac{C_{Si} \cdot fr}{A_{BET} \times m}$$

where C_{Si} is the silica content in the outlet solution, fr is the flow rate, A_{BET} is the specific surface area and m is the mass of sample in the solution.

Figure 2 shows the pH-dependent dissolution of basaltic glass, reported by Gíslason and

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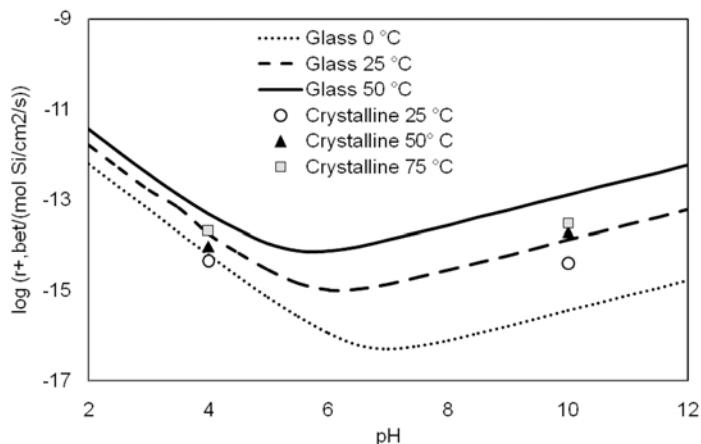


FIG. 2. Dissolution rates of crystalline basalt (symbols) are compared to modelled dissolution rates (curves) of basaltic glass from the same location (Gislason and Oelkers, 2003).

Oelkers (2003). Our own data have been added to these modelled curves to illustrate that the dissolution rate of crystalline basalt is considerably slower than its glassy counterpart, in acid and alkaline conditions. For example, the dissolution rate for crystalline basalt at pH 4 and 75°C falls on the 25°C isothermal line for basaltic glass dissolution. From the experimental results we can obtain apparent activation energies (E_a):

$$E_a = \frac{\delta \ln r_{+,BET}}{\delta(1/T)} \times R$$

where R is the gas constant, T is the temperature in Kelvin and $r_{+,BET}$ is the forward rate. At pH 4 we find an E_a of 26 kJ/mol, in very good agreement with the $E_a = 27$ kJ/mol that Wolff-Boenisch *et al.* (2004) reported for a basaltic glass of similar composition (Krafla, cf. Table 1). At pH 10, the calculated E_a is 35 kJ/mol compared to 41 kJ/mol for Krafla at pH 10.6 (Wolff-Boenisch *et al.*, 2004). Overall, the temperature dependence of the dissolution mechanisms seems slightly greater at pH 10 than at pH 4. This observation is consistent with the curves in Fig. 1 which lie more closely together at acidic pH and start to spread when the conditions become more alkaline.

Summary

We have started to map the dissolution rates of crystalline basalt as a function of pH, solution composition and temperature. These rates can

eventually be used in reactive-transport modelling of the reaction of dissolved CO_2 with crystalline MORB basaltic at various temperatures and solution compositions. Dissolution rates have been obtained by similar methods for basaltic glass from the same volcanic formation. The preliminary results indicate lower rates for crystalline basalt than for basaltic glass of comparable chemical composition under same experimental conditions. This is in concert with previous studies on the effect of crystallinity on dissolution rates (Gislason and Eugster, 1987; Wolff-Boenisch *et al.*, 2006). Further investigations are required to probe the reasons for this phenomenon.

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