

The effect of aqueous sulphate on basaltic glass dissolution rates

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ABSTRACT

Steady-state dissolution rates of basaltic glass were measured in mixed-flow reactors at 50°C at pH 3 and 4 as a function of aqueous sulphate concentration. Dissolution rates in the presence of 0.1 moles/kg SO_4^{2-} were found to be ~3 times greater than those in corresponding SO_4^{2-} free solutions. This rate increase is found to be approximately consistent with that calculated using a rate equation previously proposed by Gislason and Oelkers (2003). These results suggest that the addition of sulphate to injected CO_2 may facilitate CO_2 sequestration in basalts by accelerating basaltic glass dissolution rates thus more rapidly releasing aqueous Ca and Mg to solution.

KEYWORDS: basaltic glass, dissolution rates, CO_2 sequestration, kinetics, aqueous sulphate.

Introduction

INCREASED CO_2 concentration in the atmosphere is thought to provoke climate change. To reduce the emission of this greenhouse gas to the atmosphere, the possibility of sequestering CO_2 in basaltic rocks is being investigated (McGrail *et al.*, 2006; Gislason *et al.*, 2007; Matter *et al.*, 2007). This process involves dissolution of the basaltic rock and release of divalent metallic cations such as Ca^{2+} . The Ca^{2+} ions then react with dissolved CO_2 and precipitate as carbonate minerals. One way to enhance the amount of CO_2 that can be sequestered in this process is to increase the amount of Ca^{2+} ions available for carbonate precipitation. The dissolution rate of basaltic glass decreases with increased activity of Al^{3+} (Oelkers and Gislason, 2001; Gislason and Oelkers, 2001). By adding an aqueous species that leads to Al-complex formation, the dissolution rate of basaltic glass will increase (Wolff-Boenisch *et al.*, 2004).

One other implication of this work is that power plants emitting CO_2 often produce sulphuric gases as a bi-product. The high

reactivity and oxidation capacity of sulphuric species make them difficult to store on land. By adding sulphate to the injected CO_2 solution, it may be possible to store the sulphate safely underground. The purpose of this study was to investigate how much sulphate enhances the dissolution rate of basaltic glass.

Materials and methods

The dissolution-rate experiments were performed with Stapafell basaltic glass in titanium and polypropylene mixed-flow reactor systems at different pH and with solutions containing different amounts of sulphate (Oelkers and Gislason, 2001). The grain size was 125–250 μm and the BET surface area was measured at 1.524 m^2/g . The geometric surface area was estimated to be 120 cm^2/g assuming that the glass powder used consisted of identical 187.5 μm cubes. This method of estimating the geometric surface area was used in the work of Gislason and Oelkers (2003). The experiments were all performed at $50 \pm 2^\circ\text{C}$. Information about flow rates and the composition of the various inlet solutions used in this study is given in Table 1.

The dissolution rate of basaltic glass was described by Gislason and Oelkers (2003) and can be written:

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TABLE 1. The composition of the solutions and flow rates used in the experiments.

Experiment	pH (25°C) input	HCl (moles/kg)	NaCl (moles/kg)	Na ₂ SO ₄ (moles/kg)	Ionic strength (moles/kg)	Flow rate (g/min)
BG6 D	3.05	0.00110	0.009	–	0.010	0.424
BG7 A	3.02	0.00132	0.008	0.001	0.012	0.401
BG7 B	3.02	0.00142	–	0.010	0.030	0.343
BG7 C	3.01	0.00245	–	0.050	0.136	0.371
BG7 D	3.03	0.00332	–	0.100	0.261	0.384
BG6 A	3.97	0.00009	0.010	–	0.010	0.382
BG6 B	3.96	0.00010	0.008	0.001	0.011	0.406
BG6 C	3.99	0.00014	–	0.010	0.029	0.402
BG6 E	4.01	0.00024	–	0.050	0.135	0.356
BG6 F	3.96	0.00042	–	0.100	0.259	0.408

$$r_{+geo} = A_A \exp^{-E_A/RT} \left(\frac{a_{H^+}^3}{a_{Al^{3+}}} \right)^{1/3} \quad (1)$$

where r_{+geo} signifies the geometric surface area normalized steady-state basaltic glass dissolution rate at far-from-equilibrium conditions, A_A refers to a constant equal to $10^{-5.6}$ (mol of Si) cm^2/s , E_A , designates a pH independent activation energy equal to 25.5 kJ/mol, R stands for the gas constant, T signifies temperature in K and a_i represents the activity of the subscripted aqueous species. By decreasing the activity of Al^{3+} , the dissolution rate increases. A study performed by Wolff-Boenisch *et al.* (2004) showed that by complexing Al^{3+} ions with fluorine, they could increase the dissolution rate of the basaltic glass by an order of magnitude or more.

Results

Surface-reaction controlled, far-from-equilibrium basaltic glass dissolution rates as a function of aqueous solution composition at 50°C can be predicted using equation 1. Figure 1 shows the dissolution rates of basaltic glass with different amounts of sulphate. The curves in the figure were generated using aqueous activities computed with PHREEQC 2.12.5 (Parkhurst and Appelo, 1999) at a total Al concentration of 10^{-6} moles/kg. The basaltic glass dissolution rate increases by increased concentration of aqueous sulphate at acid to neutral conditions. Basaltic glass is calculated to dissolve 5.5 times faster in a 0.1 moles/kg SO_4 solution than in a SO_4 -free solution at pH = 4. In contrast, there is no predicted effect of sulphate on basaltic glass

dissolution rates at pH >7.5. The lack of effect at basic conditions can be explained by the lack of $Al-SO_4$ complexation at these pH values.

To further investigate the effect of sulphate on the dissolution rate of basaltic glass at far-from-equilibrium conditions, experiments using mixed-flow reactors were performed at pH 3 and 4. As shown in Fig. 2, a solution with 0.001 moles/kg sulphate almost doubles the dissolution rate while 0.1 moles/kg of sulphate triples the dissolution rate of basaltic glass. Calculations generated using equation 1 (Fig. 1) suggests that basaltic glass dissolution rates increase by a factor of 1.5 and 5.5 in 0.001 moles/kg and 0.1 moles/kg aqueous sulphate solutions, respectively, compared to that in sulphate-free solutions.

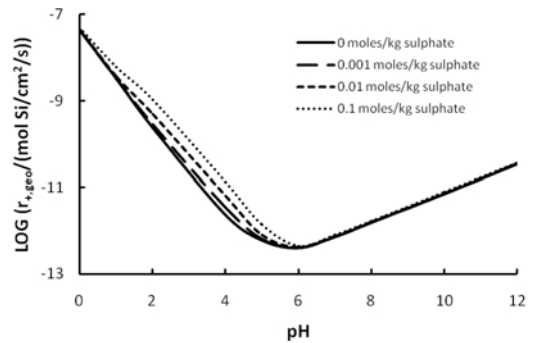


FIG. 1. The logarithm of the dissolution rate vs. pH for basaltic glass at 50°C. The aqueous activities were computed using PHREEQC 2.12.5 and equation 1. The total Al concentration was 10^{-6} moles/kg and the sulphate concentration is given in the legend.

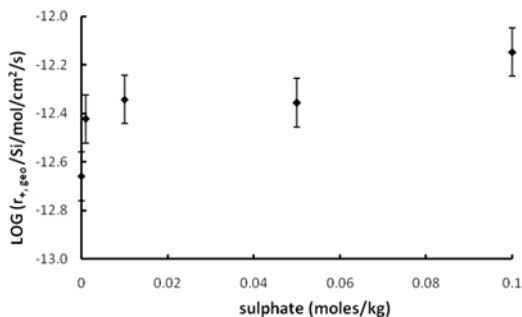


FIG. 2. Variation of measured steady-state basaltic glass dissolution rates obtained from Al- and Si-free inlet solutions at pH 4 with aqueous SO_4^{2-} concentration at 50°C. The error bars correspond to a 0.1 log unit uncertainty, which is consistent with the 20% uncertainty estimated for these data.

Discussion and conclusions

(1) Preliminary results show that the effect of aqueous sulphate on basaltic glass dissolution rates calculated using equation 1 is approximately consistent with their experimentally measured counterparts. This approximate coherence provides support for using this equation for the prediction of the reactive behaviour of basaltic glass in complex natural systems.

(2) Aqueous sulphate is found to increase basaltic glass dissolution rates. As such, the addition of sulphate to injected CO_2 may enhance carbonate mineral sequestration during carbon sequestration in basaltic rocks. Such co-injection may prove to be an effective method for the safe storage of sulphur emissions from power plants.

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