

Dissolution of diopside and basaltic glass: the effect of carbonate coating

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ABSTRACT

Far-from-equilibrium dissolution experiments with diopside and basaltic glass in mixed-flow reactors at 70°C and pH 8.2 show that solute concentrations do not reach steady state over the experimental duration of 45–60 days. Chemical modelling indicates that during the dissolution experiments, solutions have become supersaturated with respect to carbonates in the case of diopside, and carbonates, clay minerals and zeolites in the case of the basaltic glass. Decreasing dissolution is therefore interpreted as a result of secondary surface precipitates blocking the reactive surface area. Calcite formation was supported in both experiments by a significant increase in Ca (and Sr) concentrations as pH was abruptly lowered from 8.2 to 7 because this change increased carbonate solubility and caused all potential carbonate precipitates to re-dissolve. The reduction in pH also led to an increase in Si concentration for diopside and a decrease in Si concentration for basaltic glass. This observation is in accordance with previous experiments on the pH-dependent dissolution rates of pyroxenes and basaltic glass.

KEYWORDS: dissolution, diopside, basaltic glass, carbonate coating, carbon dioxide sequestration, mixed-flow reactor.

Introduction

INCREASING emission of industrial carbon dioxide (CO₂) into the atmosphere has been identified as one of the biggest challenges of this century because of its effect on the global climate (Hoffert *et al.*, 2002; Broecker, 2005). One solution to solve this problem is to inject CO₂ into a geological stable environment, where it can be stored safely. The Hellisheidi geothermal power plant in Iceland and its vicinity has been suggested as a good testing ground for trapping CO₂ directly from the power plant and storing it in the underlying basaltic rocks. Basalt is known for its high reactivity and easy weathering (e.g. Gíslason and Oelkers, 2003; Gíslason *et al.*, 2006). There are several examples in nature and

laboratory experiments of carbonates being formed by chemical weathering of basalts (e.g. McGrail *et al.*, 2006).

Prior to the CO₂ injection a series of laboratory experiments and modelling are required to optimize the injection conditions at the Hellisheidi site. The main components of basaltic rocks are pyroxenes, plagioclase and basaltic glass rich in Ca, Mg and Fe, and chemical modelling predicts that these minerals will dissolve in contact with CO₂-saturated water and form carbonates, clays and zeolites (Gysi and Stefánsson, 2008). The dissolution rates of basaltic glass and pyroxenes are known at far-from-equilibrium conditions (Oelkers and Gíslason, 2001; Gíslason and Oelkers, 2003; Wolff-Boenisch *et al.*, 2004; Knauss *et al.*, 1993; Golubev *et al.*, 2005), but it is unknown how dissolution of these components will evolve in a solution saturated with carbonates, clays and zeolites. A decrease in dissolution of basaltic

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rocks caused by precipitation will have implications for the amount and rate of CO₂ being sequestered. In this paper we report on an experiment conducted to study the changes in dissolution kinetics of basaltic glass and diopside in a solution saturated with calcite (CaCO₃).

Method and materials

Natural crystals of diopside from the Transbaikal region in Russia and basaltic glass from Stapafell in SW Iceland were used in this experiment. Previous electron microprobe analysis showed the diopside composition to be Ca_{0.99}Mg_{0.98}Fe_{0.02}Cr_{0.01}Si₂O₆ (Golubev *et al.*, 2005). Acid and deionized water-washed crystals of diopside were ground with an agate mortar and pestle and sieved, whereas the basaltic glass was crushed in plastic bags with a soft plastic hammer and then sieved. For both mineral and glass, the 45 to 125 µm size fraction was ultrasonically cleaned in cycles of deionized water and acetone, separating

and discarding the ultra fine suspension at the end of each cleaning cycle, and finally dried overnight at 60°C.

10 g of each material were transferred into a 300 ml polyethylene mixed-flow reactor. Both reactors were placed in a 70°C water bath heated by a thermo heater (Thermo-Haake C10) and kept at constant temperature during the 60 days of the experiment. Teflon[™]-coated floating stir bars from Nalgene[™] were placed on the bottom of the reactors and propelled by a multi-position magnetic stirrer located underneath the water bath. A constant pumping rate of 0.6 ml/min was maintained using a Masterflex[™] cartridge pump. Inlet solutions comprised Millipore[™] water and Merck analytical grade NaHCO₃ and HCl. The ionic strength of the inlet solution was 0.035. The outlet solution was filtered through a 0.2 µm cellulose acetate membrane filter, acidified with concentrated supra-pure HNO₃ and analysed for Si, Ca and Mg content by ICP-OES spectrometry (Spectro Ciros Vision).

TABLE 1. Summary of diopside dissolution experiments performed at 70°C.

Sample no.	Duration (days)	pH ^a	[Si] (µM)	[Ca ²⁺] (µM)	[Mg ²⁺] (µM)	[Sr ²⁺] (µM)
D-1	1	8.2	65.2	22.2	27.5	0.15
D-3	3	8.2	28.3	12.7	10.6	0.09
D-5	5	8.2	21.7	9.0	7.7	0.06
D-7	7	8.2	19.4	8.1	7.1	0.05
D-9	8	8.2	19.6	7.8	7.0	0.04
D-11	10	8.2	19.1	6.3	6.6	0.04
D-13	18	8.2	17.3	5.9	6.0	0.03
D-15	20	8.2	20.3	8.2	6.6	0.05
D-17	23	8.2	18.7	7.7	7.2	0.04
D-19	25	8.2	18.8	7.8	7.3	0.04
D-21	27	8.2	16.4	6.1	6.1	0.03
D-23	31	8.2	17.3	5.5	5.6	0.03
D-25	33	8.2	15.2	4.7	5.1	0.03
D-27	35	8.2	14.7	4.4	4.7	0.03
D-29	39	8.2	14.1	4.6	4.9	0.03
D-31	41	8.2	14.1	5.3	5.3	0.03
D-33	45	8.2	11.1	3.7	3.9	0.02
D-35	47	8.2	11.3	3.8	4.1	0.02
D-37	52	8.2	8.3	4.0	4.0	0.02
D-38	53	8.2	7.1	3.6	4.0	0.02
D-39	56	7.0	44.6	30.9	27.7	0.15
D-40	57	7.0	33.7	20.5	20.1	0.10
D-41	58	7.0	28.3	15.5	16.1	0.08
D-42	59	7.0	23.4	11.8	13.3	0.06
Change in conc. D-39/D-38			6.3	8.6	7.0	8.6

^a Background electrolyte was a NaHCO₃/HCl buffer.

In this study, dissolution experiments of diopside and basaltic glass ran for 60 and 45 days, respectively. The pH of the inlet solution was kept constant at pH 8.2 during the main part of the experiments. One final batch of pH 7 inlet solution over four days ended both experiments.

Results and discussion

The results of the diopside dissolution experiment are listed in Table 1. The values show a continuous decrease in Si, Ca and Mg concentrations with time and did not reach a steady state (Fig. 1). In contrast, Knauss *et al.* (1993) reported a steady state for diopside dissolution under similar experimental conditions (but in the absence of bicarbonate) within 10–15 days. Dissolution rates are known to slow down in near-equilibrium solutions; however, our experiments were carried out in far-from-equilibrium conditions with respect to diopside. Rather, we interpret this discrepancy as a result of calcite precipitation in our experiments, covering the diopside surface and impeding the dissolution process and the achievement of a steady state. A similar tendency has been reported by Cubillas *et al.* (2005) who observed decreasing dissolution rates of calcite by overgrowth of otavite (CdCO_3).

Not only calcite would hamper dissolution, but probably any kind of precipitate (e.g. Hodson, 2002). The reason we favour calcite as the dominating precipitate is because chemical modelling with *PHREEQC* (Parkhurst and Appelo, 1999) shows calcite (and dolomite) to be the only saturated phases in the initial solution. Ca release rates from diopside were estimated using the formula given in Golubev *et al.* (2005). A temperature of 70°C was chosen because *PHREEQC* calculations indicated that from this

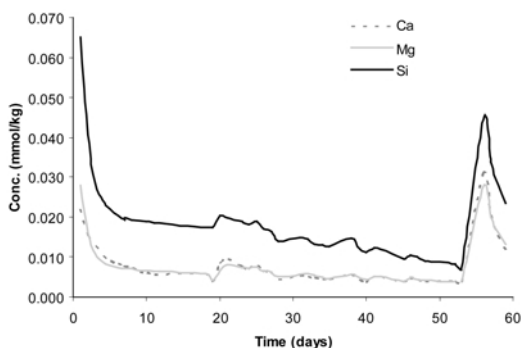


FIG. 1. Dissolution of diopside at 70°C.

temperature on, sufficient material would dissolve and provide the required amount of Ca ions to assure calcite saturation in combination with a 35 mM NaHCO_3 inlet solution. As for dolomite, it rarely forms in laboratory experiments and has therefore been tentatively ruled out in this study.

At the end of the experiment a 4-day pulse of pH 7 solution was injected into the reactors by adding HCl to the NaHCO_3 inlet solution. The purpose was to dissolve potential carbonates that might have precipitated on the surface. This pulse led to a consistent increase in solute concentrations of Si, Ca and Mg by a factor of 6–9 (cf. Table 1 and Fig. 1). The change in Sr concentration is also listed in Table 1 as Sr is known to substitute for Ca in calcite. Both ions increased by a factor 8.6, suggestive of calcite precipitation. The observed increase in Si concentration by lowering pH is in accordance with results from Knauss *et al.* (1993) who showed that dissolution rates of diopside based on the Si concentration follow a linear trend where dissolution rates (and by extension the Si solute concentrations) increase with lowering pH (see Fig. 2).

Table 2 reports a summary of the results from dissolution of basaltic glass at 70°C. The trend was similar to the experiment with diopside; i.e., decreasing Si, Ca, Mg and Sr concentrations over time and no attainment of a steady state. Again, we attribute this to precipitates on the surface of basaltic glass crystals that limited the dissolution. *PHREEQC* modelling of the 31 samples indicated

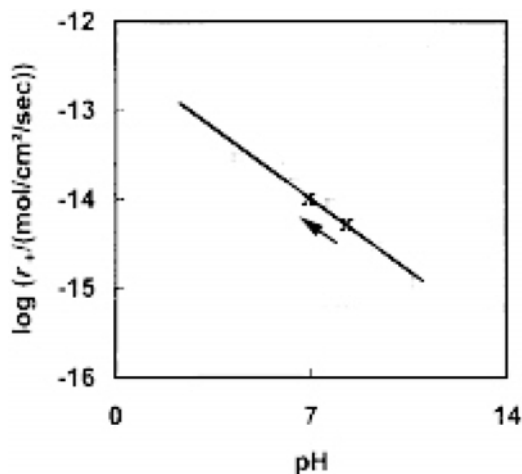


FIG. 2. Dissolution rates of diopside at 70°C as a function of pH. The arrow marks the route from pH 8 to 7 in the experiment in this study. Modified from Knauss *et al.* (1993) and Oelkers and Schott (2001).

TABLE 2. Summary of basaltic glass dissolution experiments performed at 70°C.

Sample no.	Duration Days	pH ^a	[Si] μM	[Ca ²⁺] μM	[Mg ²⁺] μM	[Sr ²⁺] μM
B-1	6	8.2	317.6	16.7	69.3	0.02
B-3	8	8.2	308.9	23.6	81.1	0.03
B-5	11	8.2	298.2	21.0	73.1	0.03
B-7	13	8.2	291.7	21.2	73.4	0.03
B-9	15	8.2	280.9	19.5	69.1	0.02
B-11	19	8.2	258.0	21.7	70.0	0.03
B-13	21	8.2	250.2	20.8	64.0	0.03
B-15	23	8.2	256.9	18.9	66.9	0.03
B-17	27	8.2	237.2	19.6	60.7	0.03
B-19	29	8.2	228.3	22.2	64.1	0.03
B-21	33	8.2	229.7	18.5	61.1	0.03
B-23	35	8.2	208.9	20.6	55.8	0.03
B-25	37	8.2	221.5	17.9	54.2	0.03
B-27	41	8.2	207.4	18.0	50.8	0.03
B-28	42	7.0	198.1	758.2	66.8	1.33
B-29	43	7.0	168.3	450.7	58.0	0.68
B-30	44	7.0	147.3	228.5	42.8	0.36
B-31	45	7.0	110.8	108.2	25.8	0.17
Change in conc. B-28/B-27			1.0	42	1.3	46

^a Background electrolyte was NaHCO₃/HCl.

supersaturation not only with respect to calcite and dolomite but also clay minerals and zeolites. However, of these minerals calcite and dolomite were the only phases containing Ca.

Analogously to the diopside experiments, lowering the pH to 7 resulted in a major increase in Ca and Sr concentrations. The magnitude of this rise was very similar, indicating again the close link between stoichiometric Sr and Ca substitution. As to Si, its concentration kept on decreasing (Fig. 3), which was again consistent with findings in the literature (Gislason and Oelkers, 2003). In contrast to diopside and other

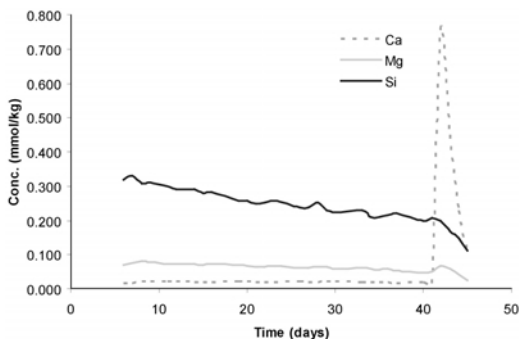


FIG. 3. Dissolution of basaltic glass at 70°C.

pyroxenes, basaltic glass dissolution rates were expected to decrease when going from pH 8.2 to 7 (Fig. 4) and this behaviour was observed in our experiments.

In the future, a characterization of the precipitates present on the silicate surface will be performed in order to unequivocally confirm and quantify the amount of carbonates. In these preliminary experiments, interpretations have been based on a combination of chemical

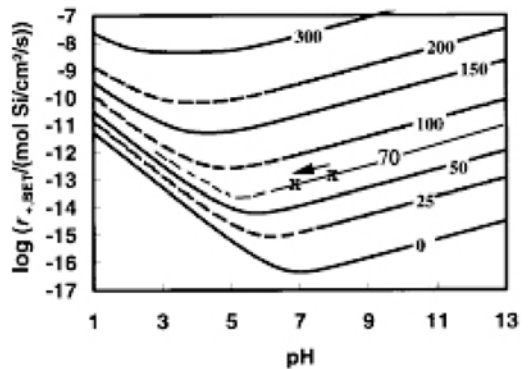


FIG. 4. Dissolution rate of Si in basaltic glass at 0–300°C. The 70°C curve has been added and the arrow marks the route from pH 8 to 7 (modified from Gislason and Oelkers, 2003).

modelling and consistent observations of solute concentrations as a function of small pH changes.

Conclusion

The preliminary results displayed a decrease in dissolution concentrations for Si, Ca and Mg over time for diopside and basaltic glass in a solution saturated with calcite at a constant temperature of 70°C and pH 8.2, thus indicating that carbonate coatings will slow down the dissolution rates of diopside and basaltic glass.

The implication for the CO₂ sequestration project at Hellisheidi is that, if coatings reduce the dissolution rates of basaltic minerals, this could affect the amount of Ca, Mg and Fe being released by CO₂-supersaturated water and thereby limit the amount of CO₂ being trapped as carbonate minerals.

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