

Experimental Determination of Low-temperature Dissolution Kinetics of Silicate Glasses

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The determination of chemical fluxes at the ocean floor - seawater interface is essential for understanding the chemical evolution of the oceans. Pore water profiles, which significantly distinguish from seawater chemistry, are controlled by submarine chemical weathering processes of the oceanic crust. One widespread component of marine sediments is volcanic glass, which is thermodynamically unstable and thus highly reactive. Sediments, which mainly consist of basaltic volcanoclastic debris, are often characterized by highly saline pore waters with unusual chemical composition (Egeberg et al., 1990). The dissolution mechanisms of silicate glasses in aquatic environments are still unclear and only few data exist on trace element mobility during low-temperature alteration of volcanic glass. Most of the studies focus on the dissolution rates of basaltic glass at high temperatures (e.g. Berger et al., 1994; Daux et al., 1997) or take only fluxes of the major constituents into account (Eick et al., 1996). We will present data on the dissolution rates of volcanic glasses of different chemical composition at low temperature depending on different physico-chemical parameters (pH, ionic strength, organic acid concentration) and data on the leaching behavior of selected trace metals (V, Mn, Cu, Rb, Sr, Y, Mo, Ba, REE).

Samples of the international geostandards JB-3 (basalt), QLO-1 (quartz latite), STM-1 (syenite), and RGM-1 (rhyolite) were prepared for the dissolution experiments. These rocks provide a wide range of SiO₂ (49.1 - 70.1 wt-%) and total alkali contents (3.5-12.7 wt-%). The powdered rocks were spiked with trace metals, homogenized and melted at 1300 °C in Pt-crucibles after addition of 2 wt% Li₂B₄O₇ for obtaining complete melting. In addition to the experiments with synthetic glasses, dissolution experiments of natural volcanic glasses were performed (basalt glass and obsidian). The dissolution rates were determined by continuous-flow experiments in stirred 65 ml polypropylene reactors at 22 °C with H₂O and 0.7 M NaCl solution (particle size: 70-125 µm). The pH of the solutions were buffered with TRIS to pH 7, 8, 9, and 10 (±0.1). Low pH was achieved by addition of HCl. Steady state conditions were reached within 20 days at flow rates of 2 to 4 ml/h (±0.1 ml). The Si-concentrations were measured photometrically by the molybdate blue method, Al by Zeeman-GFAAS and the trace metals by ICP-MS.

The experimentally determined dissolution rate of 6.8 10⁻¹¹ [mole m⁻² s⁻¹] for the basalt glass JB-3 at pH 8 and 22 C matches with previously published rates (e.g. Berger et al., 1994). The dissolution rate decreases with increasing Si-concentration of the input solution and reaches a minimum of ~7 10⁻¹³ [mole m⁻² s⁻¹] at Si_{input} = 400 µM. Further increase of Si_{input} does not diminish the dissolution rate. The dissolution rates of the glasses with higher SiO₂-contents are approximately half of the rates of the basalt glass. The dissolution rates of the natural glasses are similar to the rates of the synthetic glasses. The H⁺-concentration is, among with temperature, the major control factor of the dissolution rate. The minimum of the dissolution rates versus pH is at pH 7 with one order of magnitude lower rates than the dissolution rates at pH 9 and 10. The dissolution rate of the basalt increases with increasing H⁺-conc. (~ 10² at pH 3), however the rate of the obsidian shows no significant change from pH 7 to pH 3. Organic acids enhance the dissolution of silicates by forming complexes with the network builders Si and Al. The addition of oxalic acid to the reactor solution in a pH-buffered system induces a linear increase of the dissolution rate of Al. The above listed trace metals are preferably leached from the glasses compared with the dissolution rates of Si. The REE are relatively immobile with rates threefold lower than the alkali and alkaline earth metals. Trace metals with typical very low mobility (e.g. Ti) could not be detected in the solutions.

The results of this study reveal significant differences of the dissolution mechanisms between silicate glasses of different chemical composition. At constant T the pH controls the kinetic of the glass dissolution. The presence of organic acids plays an important role in enhancing the dissolution rates. The ionic strength of the solution has a relatively small effect on the dissolution rates.

Berger G, Claparols C, Guy C & Daux V, *Geochim. Cosmochim. A.*, **58**, 4875-4886, (1994).

Daux V, Guy C, Advocat T, Crovisier J-L & Stille P, *Chem. Geol.*, **142**, 109-126, (1997).

Egeberg PK & the Leg 126 Shipboard Scientific Party, *Nature*, **344**, 215-218, (1990).

Eick MJ, Grossl PR, Golden DC, Sparks DL & Ming DW, *Geochim. Cosmochim. A.*, **60**, 157-170, (1996).