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Enhanced dissolution of basaltic glass in brackish waters: Impact on biogeochemical cycles

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ABSTRACT

In order to better constrain the geochemical budget of Si in the ocean, and potentially other elements released by the dissolution of silicates, the alteration of riverine particulate material in estuaries and seawater needs to be estimated. For this, a series of alteration experiments of basaltic glass were performed at various degrees of salinity (from 0 to 3.5 $\mathrm{g\,L^{-1}}$) in far-from-equilibrium conditions. The solution used is a filtered natural seawater standard from the Atlantic Ocean. The forward dissolution rates increase from $2.1 \cdot 10^{-7}\ \mathrm{mol\,Si\,m^{-2}\,s^{-1}}$ ($S = 0\ \mathrm{g\,L^{-1}}$) to $7.7 \cdot 10^{-7}\ \mathrm{mol\,Si\,m^{-2}\,s^{-1}}$ ($S = 3.5\ \mathrm{g\,L^{-1}}$) at 90 °C and were extrapolated at 16 °C (from $2.9 \cdot 10^{-10}\ \mathrm{mol\,Si\,m^{-2}\,s^{-1}}$ at $S = 0\ \mathrm{g\,L^{-1}}$ to $1.1 \cdot 10^{-9}\ \mathrm{mol\,Si\,m^{-2}\,s^{-1}}$ at $S = 3.5\ \mathrm{g\,L^{-1}}$). This positive relationship between glass dissolution rate and salinity degree is consistent with published investigations concerning the role of specific cations and ligands present in seawater, which can promote dissolution at the glass surface. These results illustrate the potential of river basaltic glass particles to dissolve quickly in the water column after entering into the brackish waters of estuaries, and before sinking on continental margins. Based on these dissolution rates and on assumptions on the particulate solid flux of fresh basaltic glass exported by rivers towards the ocean, the corresponding flux of dissolved Si is estimated to range between 2 and $8 \cdot 10^{12}\ \mathrm{mol\,Si\,yr^{-1}}$. This is of the same order of magnitude as the estimated river dissolved Si flux, which represents therefore a significant input of Si into the ocean. Additionally, if the glass dissolution process remains congruent during the residence time of suspended particles into the water column, the K flux to the ocean could also be significantly affected.

1. Introduction

The ocean chemistry results mainly from riverine and atmospheric inputs, hydrothermal exchange with oceanic crust, sedimentation processes and biological cycles. However, present-day disequilibrium for a majority of dissolved elements has been highlighted (e.g. Vance et al., 2009 and references therein). This was shown for example for Ca (Gislason et al., 2006), Mg (Holland, 2005; Tipper et al., 2006), Sr (Hodell et al., 1989; Davis et al., 2003; Jones et al., 2014), Os (Oxburgh et al., 2007; Paul et al., 2010), U and Mo (Dunk et al., 2002; Rahaman et al., 2010).

These imbalances in marine geochemical budgets are thought to stem from uncertainties on input fluxes, especially on the riverine particulate material. Several authors (Lacan and Jeandel, 2005; Gislason et al., 2006; Arsouze et al., 2009; Oelkers et al., 2011; Jones et al., 2012a, 2012b, 2014; Pearce et al., 2013) have shown an underestimation of elemental fluxes from continents, due to the dissolution of river suspended material in estuaries and seawater. Jones et al. (2014) recently highlighted a strong impact of riverine particulate dissolution on the Sr ocean budget as they estimated the range of Sr flux derived by volcanic particulate dissolution in an Icelandic estuary to be 1.1 to 7.5 times greater than river dissolved Sr. These results show that changes of conditions (salinity, biological activity), that are indeed drastic when river particulate matter passes from river freshwaters to estuarine waters, trigger a series of rapid reactions difficult to monitor but of a first order importance.

The dissolution of riverine particulate material in estuaries may also impact the concentration and fluxes of major nutrients (Si, P, and N) playing a key role for the primary productivity (Falkowski, 1997; Falkowski et al., 1998; Cloern et al., 2014). In particular, Si

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as a limiting and major nutrient in marine ecosystems (Nelson et al., 1995; Tréguer et al., 1995; Tréguer and De la Rocha, 2013) and in estuaries where the phytoplankton is principally composed of diatoms (Roubeix et al., 2008). This element can be responsible for environmental catastrophes such as harmful algal blooms (Anderson et al., 2002; Berner and Berner, 2012). Tréguer et al. (1995) estimated that around 80% of dissolved Si in the ocean is delivered by rivers.

The major source of dissolved Si is the weathering of continental rocks (Berner et al., 1983), and especially of basalts (either from volcanic islands or large basaltic provinces) as they are easily weathered (e.g. Louvat and Allègre, 1997, 1998; Gaillardet et al., 1999; Dessert et al., 2001, 2003; Rad et al., 2006; Gislason et al., 2009; Allègre et al., 2010). The alteration kinetics of basaltic glass was determined in various controlled conditions (e.g. Crovisier et al., 1987; 2003; Guy and Schott, 1989; Daux et al., 1997; Techer et al., 2000; Oelkers and Gislason, 2001; Gordon and Brady, 2002; Gislason and Oelkers, 2003; Flaathen et al., 2010; Verney-Carron et al., 2011). However, little is known about the influence of salinity on the dissolution rate of basalts and basaltic glass over short timescales, while this parameter may play a key role in the case of a direct input of volcanic material into the ocean (during an intensive volcanic activity), or when river particles enter estuaries. Previous alteration experiments of basaltic glass have been performed using seawater or NaCl solutions (Gislason and Eugster, 1987; Guy and Schott, 1989; Crovisier et al., 1987, 2003; Gislason and Oelkers, 2003), but the impact of increasing salinity on the forward dissolution rate was not investigated. Some studies explored the role of specific element concentrations: NaCl (Gislason and Eugster, 1987), sulphate (Flaathen et al., 2010), carbonate (Stockmann et al., 2011) on dissolution rate. Increasing NaCl concentrations has been shown to enhance amorphous silica dissolution (~ 20 times in 0.05 M NaCl compared to deionized water, Icenhower and Dove, 2000). This “salt effect” was also seen for quartz with a dependency to the nature of the cation. The dissolution rate increases in the order: $Mg^{2+} < Ca^{2+} \approx Li^{+} \approx Na^{+} \approx K^{+} \approx Ba^{+}$ (Dove, 1994, 1999; Dove and Nix, 1997). The correlation between the dissolution rate and the exchange rate of the solvent around the aqueous cations suggests that the cations present at the silica–water interface are attracted to the negatively charged surface of silica, thus changing the interfacial environment (Dove and Nix, 1997). Dove (1999) has shown that in presence of only 2 salts the dissolution rate is limited by the cation with the lowest rate-enhancing effect, which highlights a competition between cations at the solid–water interface. These studies allowed the dissolution mechanism to be better understood, but the results are difficult to extrapolate to the natural waters that are complex mixtures of cations. Moreover, there is no study focusing on the effect of several seawater dilutions over very short reaction timescales. The principal difficulty in obtaining these very short timescale rates relies on very low amounts of cations released by leaching in comparison to the ones already present in the initial seawater solutions, as well as the difficulty in analyzing chlorine-rich solutions by conventional methods.

The objective of this study is thus to determine the role of increasing salinity on the dissolution rates of small particles of basaltic glass during very short times of reaction. For this, we performed dissolution experiments of a basaltic glass powder with solutions of various salinities in far-from-equilibrium conditions. We then evaluate the potential of brackish waters present in mixing zones to affect the global input to the ocean of dissolved silicon and other elements.

2. Experimental methods

2.1. Characteristics of the basaltic glass powder

The glass used in the experiments is a synthetic basaltic glass (SBG) (Techer et al., 2000, 2001). It was constituted by melting a mixture of powdered oxides, carbonates, nitrates and phosphates in an alumina crucible for 3 h at 1500 °C in a Saint-Gobain furnace. The melt was poured into a graphite crucible preheated at 700 °C, annealed for 1 h at 670 °C, and quenched by pouring onto a plate at room temperature. The chemical composition of SBG is close to a typical basaltic glass from mid-ocean ridges (MORB), except that it was doped with 1 wt.% Li_2O (Techer et al., 2001). Its chemical composition is (in wt.%) 49.1% SiO_2, 14.8% Al_2O_3, 10.8% Fe_2O_3, 8.2% MgO, 10.7% CaO, 2.7% Na_2O and 1.7% TiO_2.

The glass was ground in an agate mortar and was sieved to isolate the 40–100 µm size fraction. This powder was then washed several times in acetone and the finest particles (<40 µm) were removed according to Stokes' law (settling time used). The absence of remaining finest particles was confirmed by optical microscope observations.

Specific surface area (S_s) was determined using three different methods. First, the geometric specific surface area $S_{geo}(calc)$ was calculated from the radius of particles considered as spheres:

$$S_{geo}(calc) = \frac{n \times S_{grain}}{m} = \frac{n \times 4\pi \times r^2}{n \times 4/3\pi \times r^3 \times \rho} = \frac{3}{r \times \rho} \tag{1}$$

with n the number of particles, S the particle surface, r the particle average radius (here, 70 µm), ρ the density of SBG measured by picnometry ($\rho = 2.7 \pm 0.1\ \mathrm{g\,cm^{-3}}$, Verney-Carron et al., 2011). Particle-size measurements were also performed using a Laser–Granulometer (Symantec's HELOS/BF with a classic wet disperser SUCELL at LIEC, Nancy, France). Detailed grain-size distribution spectra (on 5 replicates) for each grain-size class gives a $S_{geo}(opt)$ expressed as:

$$S_{geo}(opt) = \sum_{0}^{1}\left(X_r \times \frac{3}{r \times \rho}\right) \tag{2}$$

with X_r, the optical fraction of a given radius r.

This value was also compared to the specific surface area (S_{BET}) measured by gas (Kr) adsorption according to Brunauer, Emmett and Teller method (BET) (GET, Toulouse, France).

2.2. Experimental conditions

The seawater standard used for the leaching experiments is a filtered natural Atlantic Ocean water provided by OSIL, with a guaranteed salinity of $35.0 \pm 0.2\%$. The solutions SW 1‰, SW 1% and SW 10% used in the experiments were prepared by diluting the seawater standard by a factor 1000, 100 and 10, respectively, with Millipore® deionized water (pure water) (see Table 1 for their initial chemical compositions). One leaching experiment was performed using pure water (PW, Table 2). All diluted solutions were stored in the dark at 4 °C and were heat conditioned at 90 °C in 240 mL Savillex® PTFE reactors a few hours before the onset of the experiments.

Glass leaching experiments were carried out in Savillex® PTFE reactors in static conditions, in an oven at 90 °C to accelerate alteration. Solid/fluid (S/V) ratio were set to low value ($S/V < 0.027\ \mathrm{cm^{-1}}$), which are high Water/Rock ratios (W/R) between 6200 and 6400 g/g, and the experiments were run for short durations (<8 days) in order to maintain far-from-equilibrium conditions during the duration of experiments and to simulate a diluted medium. A maximum of 3 solution aliquots were removed from