



Alteration of synthetic basaltic glass in silica saturated conditions: Analogy with nuclear glass

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ABSTRACT

This study investigates the analogy between basaltic and borosilicate glasses of nuclear interest, by focusing on mechanisms controlling glass dissolution under silica saturation conditions. These conditions are representative of a non- or slowly renewed contacting solution, favouring the formation of a potentially passivating silica rich gel layer and secondary phases. Laboratory batch experiments were performed with synthetic basaltic glass altered at 90 °C, at pH 7 in a saturated ²⁹Si-doped aqueous solution for more than 600 days. Using elemental and isotopic solution analysis and solid characterizations by SEM, TEM and ToF-SIMS, we show that basaltic glass corrodes at an unexpectedly high and constant dissolution rate of $4 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ associated with the absence of passivating gel. Our results highlight the fact that the dissolution rate is controlled by the hydrolysis of the glassy network, sustained by the precipitation of clay-type minerals and amorphous silica. When tested in similar conditions, the International Simple Glass (ISG), a six oxide borosilicate glasses of nuclear interest displays a much lower rate limited by water diffusion through a passivating layer. The different behavior of the two glasses is explained by their ability to form secondary crystalline phases at the expense of an amorphous passivating film.

1. Introduction

Understanding the processes responsible for the alteration of basaltic glass is of great interest in many research fields. Because of its widespread presence on the ocean floor and in volcanic rock, basaltic glass partly controls the chemical mass balance of the ocean (Benzerara et al., 2007; Morin et al., 2015) and the stability of volcanic terrain (Barone et al., 2016). The geological storage of CO₂ in mafic formations such as basalt bedrock also requires good knowledge of the interactions between water and silicate rock (Gislason et al., 2013; Guyot et al., 2011; Wolff-Boenisch et al., 2011). Studying the alteration of basaltic glass is also important for its use as a natural analogue of nuclear glass to assess the safety of deep geological nuclear waste storage (Crovisier et al., 2003; Ewing, 1979; Libourel et al., 2011; Poinssot and Gin, 2012). The basic idea is that the long-term behavior of nuclear glass can be predicted by a kinetic model provided that this model captures the main processes governing both the short- and long-term behavior of natural glasses.

Considerable experimental work has already been carried out on the

first stages of the alteration of basaltic glass (Berger et al., 1987; Crovisier, 1989; Crovisier et al., 1987; Gislason and Eugster, 1987; Gislason and Oelkers, 2003; Techer et al., 2001; Verney-Carron et al., 2011; Wolff-Boenisch et al., 2004) and the nature of the products formed (Jercinovic et al., 1990; Le Gal, 1999; Stockmann et al., 2011). However, the dissolution rate of both borosilicate and aluminosilicate glasses in confined media is known to achieve low values of typically several orders of magnitude lower than the initial dissolution rate (Gin et al., 2012; Parruzot et al., 2015). In these conditions, the silica concentration reaches apparent saturation and the glass dissolves in a steady-state regime also called the residual rate regime (Parruzot et al., 2015; Vienna et al., 2013). Unfortunately, there are too few kinetic measurements and comparisons between in-lab and in-field data to give credit to long-term predictions from existing kinetic models (Daux et al., 1997; Frugier et al., 2008; Grambow and Muller, 2001; Oelkers, 2001).

Parruzot et al. (2015) provided new insights into the long-term alteration in confined media of basaltic glass. These authors measured the residual rates of synthetic basaltic glass in batch experiments at 30 °C

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and 90 °C and the diffusion coefficient of water and alkali metals from the pristine glass to the solution through the alteration layer. After extrapolating these rates to environmental conditions, Parruzot et al. (2015) showed that the constant residual rates derived from laboratory measurements were in reasonable agreement with the mean apparent rates calculated for natural samples of various ages (Parruzot, 2014). Unfortunately, this approach did not rely on the understanding of the rate-limiting processes assumed to govern the long-term alteration rate of basaltic glasses in nature.

The resistance of glass to aqueous corrosion is not an intrinsic property of the glass but a response to a range of environmental factors. The reactions between silicate glass and water include: (1) the hydration of the glass and ion-exchange between ionic species in water (particularly H^+) and ionic components in the glass (primarily alkali) (2) the hydrolysis of network forming species (e.g., Si, B, Al); and (3) the transport of hydrolyzed species into the solution. As these three primary reactions proceed, glass components are released into the solution and/or are incorporated into alteration products (amorphous and crystalline phases) on the surface of the reacting glass. The reaction rates are controlled by many factors, chief among which are the glass composition, the temperature and pH of the solution and the concentration of the species dissolved in the solution (e.g., H_4SiO_4 and $Al(OH)_4^-$). These processes have been summarized in many reviews (Bunker, 1994; Fournier et al., 2014; Gin, 2014; Gin et al., 2013a; Inagaki et al., 1998; Jantzen et al., 2010; Van Iseghem et al., 2006, 2009; Vienna et al., 2013).

The amorphous phase formed on the surface of the glass by the hydrolysis and condensation of glass forming species can be transport-limiting in some situations (Cailleteau et al., 2008, 2011; Gin et al., 2015a; Jollivet et al., 2008; Rebiscoul et al., 2004, 2005). The mechanism responsible for the formation of this so called “passivating layer” is currently the subject of debate. Observations of sharp interfacial gradients have led some authors to propose that the glass dissolves congruently within a thin interfacial film of water. The alteration products then form by precipitation from species released in this film (Geisler et al., 2010, 2015; Hellmann et al., 2015; Putnis, 2015). This interpretation has been supported by isotope studies: the altered layer of a silicate sample was shown to be enriched in isotopes such as ^{18}O and ^{26}Mg artificially introduced into the contacted solution, with no observable sigmoid diffusion profile (Geisler et al., 2015).

More recently, Gin et al. (2016) replicated a key experiment of Hellmann et al. (2015) and concluded that processes by which the passivating gel forms is dependent on both the glass composition and the leaching conditions. An alternative model has been proposed on the basis of experiments conducted with International Simple Glass (ISG), a six-oxide borosilicate glass. In near-neutral and slightly alkaline pH conditions, the passivating film in this model forms a low diffusive structure by in-situ reorganization of the silicate network after the release of the most soluble species (Na, B, Ca). The reorganization of the silicate network would explain the lower water diffusion coefficients in this layer than in the pristine glass (Gin et al., 2015a, 2017, 2018).

The present study aims at determining whether the processes described for nuclear glasses also occur during the alteration of basaltic glass. Using a multi-scale approach including the characterization of both liquids and solids, we investigate the processes governing alteration of basaltic glass in steady-state conditions. In this article we report the results of experiments conducted using the same protocol as the one used for ISG (Gin et al., 2015a): a long-term static test was performed over 600 days with glass powder and coupons placed in contact with water initially saturated with respect to $SiO_2(am)$ at 90 °C and $pH_{90°C}$ 7. Our results show that there are major differences between the two glasses and highlight that the precipitation of secondary crystalline or amorphous phases dominates over the formation of a passivating film.

2. Material and methods

2.1. Reagents and samples

All the solution aliquots were diluted with 0.5 M nitric acid obtained from distilled 15 M ($mol\ L^{-1}$) nitric acid (EVAPOCLEAN system, Analab, France) and 18 MΩ cm de-ionized water (Milli Q system, Millipore, Milford, MA, USA).

2.2. Glass preparation

A model basaltic glass (BG_B) was prepared and doped with the equivalent of 1 wt% B_2O_3 as a potential alteration tracer. Since boron is not present in natural basaltic glasses, a small amount of B_2O_3 has been chosen to remain as representative of natural materials as possible. The composition of BG_B is similar to that of the glass synthesized by Techer and coworkers (Techer et al., 2000). The precursors were oxide, carbonate, oxalate and nitrate powders. After weighing, the powders were poured into a Pt-Rh crucible. Two melts were prepared at 1500 °C in an electric furnace with 3 h of refining. Part of the glass was quenched; the remainder was cast into a graphite mold and annealed at 700 °C for 3 h in an electric oven and cooled to room temperature.

From the resulting glass bars, eight monoliths of $1 \times 1 \times 0.1\ cm^3$ each were prepared. The two large faces were polished up to grade 4000 using SiC paper. The density measured for these samples from the glass bar on a hydrostatic balance was $2.793 \pm 0.0005\ g\ cm^{-3}$ (Parruzot et al., 2015).

Quenched BG_B glass samples were ground and milled to obtain a mean particle diameter between 125 and 200 μm. Fine particles were removed by washing the glass powder in absolute ethanol several times and allowing the powder to settle at appropriate times calculated using Stokes' law. The specific surface area of the powder was measured at $0.0295 \pm 0.0015\ m^2\ g^{-1}$ by krypton absorption using the Brunauer, Emmett and Teller (BET) method (Brunauer et al., 1938). Laser diffraction (Malvern Mastersizer 3000) was used to calculate the particle size distribution and geometric surface area from the measured angular variation in the scattered light intensity produced by a laser beam passing through a dispersed particulate sample. As glass grains are not spherical but rather ellipsoidal, we used the technique described by (Fournier et al., 2016) to determine the size fraction. The angular scattering intensity data were analyzed to calculate the size of the particles responsible for the scattering pattern, using Mie theory and a volume equivalent sphere model. The refractive indices were taken to be 1.54 for the glass and 1.33 for the dispersant (water). The results were divided into 100 size fractions logarithmically distributed between 10^{-2} and $3 \cdot 10^3\ \mu m$. The BG_B 125–200 μm powder had a particle size distribution centered on 160 μm and a geometric surface area of $0.0125\ m^2\ g^{-1}$, leading to a ratio between the BET and the geometric surface area of 2.36, which is common for glass particles (Fournier et al., 2016; Icenhower and Steefel, 2015).

Elemental concentrations in the glass were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after dissolution of the glass by alkaline fusion followed by neutralization with HNO_3 (Table 1). A similar protocol was used to dissolve $^{29}SiO_2$ (see below and (Gin et al., 2015b)). The concentration uncertainties were estimated to be $\pm 5\%$ for elements with more than 1 wt % in the glass, and $\pm 10\%$ for less concentrated elements. An uncertainty of $\pm 25\%$ was considered for B concentrations which were close to the detection limit.

2.3. Leaching experiments

2.3.1. Main leaching experiment

The main leaching experiment involved studying the alteration of both 8 coupons ($\sim 19\ cm^2$ based on geometric considerations) and 0.38 g of 125–200 μm BG_B glass powder ($\sim 112\ cm^2$ based on BET

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