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Long-term alteration of basaltic glass: Mechanisms and rates

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Abstract

The long-term behavior study of archaeological artifacts and natural minerals and glasses revealed discrepancies between laboratory and field data. For a better understanding of the cause of these discrepancies and to reinforce the use of basaltic glass as an analog for nuclear waste glasses, this study focuses on the determination of alteration rates and processes of synthetic basaltic glass in residual rate regime. Laboratory batch experiments were performed at high surface-to-volume ratios at 90 and 30 °C for more than 1000 days. In all the experiments, the residual rate regime was reached after about 6 months. The residual alteration rates at 30 and 90 °C were $4.0 \pm 1.0 \times 10^{-6}$ and $9.5 \pm 3.2 \times 10^{-6}$ $g \cdot m^{-2} \cdot d^{-1}$, respectively. At 90 °C, this residual alteration rate is five orders of magnitude lower than the forward alteration rate ($0.8\ g \cdot m^{-2} \cdot d^{-1}$). Altered powders and monoliths were characterized by Transmission Electron Microscopy and Time-of-Flight Secondary Ion Mass Spectrometry. From glass core to solution, the altered materials are structured as follows: pristine glass, gel (corresponding to the palagonitic layer of natural glasses) and intergranular clays. To assess the passivating properties of this alteration film, we used solid characterization, an isotopically-tagged post-leaching experiment and the measurement of mobile species diffusion coefficients through the alteration film at different stages of reaction using various techniques (solution analysis and X-ray Reflectometry). These characterizations showed that the alteration film formed during residual rate alteration is passivating even without clogged porosity within the gel. Diffusion coefficients of water and alkali metals – respectively diffusing to and from the pristine glass – through the alteration film dropped from 10^{-20} to 10^{-19} $m^2 \cdot s^{-1}$ during the first alteration stages to 10^{-25} $m^2 \cdot s^{-1}$ in residual rate regime.

1. INTRODUCTION

Basaltic glasses are volcanic glasses found in different settings such as hyaloclastites and pillow-lavas, and in various contexts such as submarine, subglacial or lacustrine environments. Understanding their alteration mechanisms and rates is a preliminary step toward the comprehension of different natural phenomena such as volcano slope stability (Schiffman et al., 2006), the chemical mass balance of the oceans (Walton et al., 2005), and the geological history of the planet Mars (Minitti et al., 2007). This knowledge may also lead to industrial applications such as geological storage of CO_2 (Stockmann et al., 2011; Gysi and Stefansson, 2012) and their use as a natural analog of nuclear glasses (Ewing, 1979; Crovisier et al., 2003; Libourel et al., 2011). In this last case, the long-term behavior of nuclear waste glasses will be predicted by building mechanistic models of their alteration (Grambow and Muller, 2001; Frugier et al., 2008) which cannot be directly validated over the long term. In order to ensure the reliability of these models, basaltic glass may be used as a natural analog whose long-term alteration mechanisms, rates and alteration conditions must be deeply investigated (Poinssot and Gin, 2012).

For nuclear glasses as well as for basaltic glasses, the first alteration step when pristine glass is immersed in

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deionized water is interdiffusion where glass modifiers cation (alkalis and, to a lesser extent, alkaline earths) diffuse outside the glass as positively charged water species diffuse inward (Boksay et al., 1967; Petit et al., 1990a; Verney-Carron et al., 2011). When dominating, this process leads to the formation of a microporous and hydrated layer called hydrated glass. In parallel to interdiffusion, hydrolysis reactions of the covalent bonds Si–O–M (M = Si, Al, Fe, Zr, etc.) takes place, eventually leading to the congruent release of all the elements from the glass at a maximum rate (forward alteration rate) (Techer et al., 2001; Frugier et al., 2008). As the reaction progresses, an alteration layer then forms by precipitation or condensation on the surface of the glass of elements accumulated in solution, while the alteration rate diminishes due to the decreasing affinity of the glass network hydrolysis reaction (Lasaga, 1981; Grambow, 1984; Berger et al., 1994; Daux et al., 1997; Techer et al., 2001; Oelkers and Gislason, 2001; Frugier et al., 2008) and limitation of the transport of elements through the alteration layer (Techer et al., 2001).

For nuclear glasses, the alteration rate does not drop to zero: a slowly-decreasing or constant residual alteration rate remains over time (Petit et al., 1990b; Frugier et al., 2008). This characterizes the residual rate regime which is expected to be the main regime over the long-term in sufficiently confined media and in the absence of massive precipitation of secondary minerals (Gin et al., 2013b). However, this regime has never been studied for basaltic glass. For nuclear glasses, the currently identified processes responsible for the residual rate (Frugier et al., 2008; Gin et al., 2013b) include: (1) precipitation of silicate minerals, e.g. phyllosilicates, sustaining glass network hydrolysis (Abrajano et al., 1990; Curti et al., 2006; Frugier et al., 2006; Valle et al., 2010); (2) continuation of the interdiffusion process (McGrail et al., 2001; Rebiscoul et al., 2004; Chave et al., 2007; Gin et al., 2011, 2013c) potentially slowed down by a dense layer, generally called passivating layer, displaying lower apparent diffusion coefficient than at the beginning of the corrosion process (Gin et al., 2013c). In this view, the passivating layer is expected to rapidly form during the interdiffusion process, therefore the limiting process is interdiffusion. The passivating layer dissolves at a similar rate as it forms, leading to a near constant apparent rate (Frugier et al., 2008; Gin et al., 2013c). It can be claimed that the transformation of the passivating layer into more stable compounds (porous gel and crystalline phases) is driven by thermodynamics, but the dynamics of this transformation, involving transport of reactive species and chemical reaction at nanometer and micrometer scales, remains insufficiently understood (Gin et al., 2013a). The porous gel could play a major role in the glass alteration behavior. Its restructuring over time leads to a densification (Rebiscoul et al., 2004), and even to a porosity closure in particular cases (Casey and Bunker, 1990; Cailleteau et al., 2008; Jollivet et al., 2008); crystalline phases may also precipitate in its porosities (Gin et al., 2011). The evolution of the surface species and pore size can locally affect the water mobility and reactivity (Fenter and Sturchio, 2004; Wang et al., 2006; Kerisit and Liu, 2009; Briman et al., 2012, 2013). Experimentally, the slow residual rate has been shown to result from competing mechanisms aforementioned can last up to 15 years (Gin et al., 2012). However, under specific conditions, the high precipitation rate of particular silicate minerals such as zeolites and calcium silicate hydrates may lead to a resumption of alteration: the alteration rate increases again (Van Iseghem et al., 1984; Van Iseghem and Grambow, 1987; Ebert and Bates, 1990; Gin and Mestre, 2001; Ribet and Gin, 2004; Fournier et al., 2014).

Studies of the long-term alteration of basaltic glasses are based mainly on the examination of natural samples. The occurrence of an alteration layer generally called palagonite has been attested under various alteration conditions. This layer may be more or less crystalline and is generally associated with the presence of intergranular clays (e.g. Crovisier et al., 1992; Le Gal et al., 1999; Stroncik and Schmincke, 2001, 2002; Crovisier et al., 2003). Zeolites are observed only at advanced stages of alteration at low temperatures, e.g. after 10^5 years for Icelandic samples studied by Crovisier et al. (2003), or under hydrothermal conditions (Berger et al., 1988).

The presence of a passivating layer within the alteration layer of basaltic glass has never been directly evidenced, although it has been hypothesized. For Techer et al., during alteration of synthetic basaltic glasses at high reaction progress, correct modeling of the experimental results is only possible when considering that the alteration layer slows down the release of element from the glass toward the bulk solution (Techer et al., 2001). On natural glasses, Jeong et al. considered diffusive phenomena to explain the formation of specific patterns in alteration layers on Jeju Island samples (Jeong and Sohn, 2011). Crovisier et al. consider that intergranular porosity-filling zeolites may reduce element transport from and to the glass, modifying the alteration rate and mechanisms (Le Gal et al., 1999; Crovisier et al., 2003).

Both laboratory-altered synthetic basaltic glasses and naturally-altered basaltic glasses provide data concerning long-term alteration mechanisms. However, discrepancies between laboratory and field data are observed for basaltic glass as well as for other archaeological or natural materials (Techer et al., 2001). These discrepancies must be resolved in order to better understand the long-term processes (Verney-Carron et al., 2010; Hellmann et al., 2012; Yokoyama, 2013). This study aims to determine whether or not basaltic glass undergoes a residual rate beyond saturation of the solution with respect to amorphous silica (or another polymorph controlling the equilibrium between the hydrated glass surface and the bulk solution) and if any, what could be the rate limiting mechanisms? Here are reported laboratory experiments conducted using the same protocol as for nuclear glasses (Gin et al., 2013b): they consist in long duration static test with glass powder initially placed in contact with deionized water. Between six months – the time required to reach the residual regime – and four years, concentrations of mobile species are accurately monitored and solids are characterized at the end of the tests after a short contacting time with a solution doped with exogenous tracers. Part of altered glass underwent a second short duration leaching experiment in