



The mechanism of borosilicate glass corrosion revisited

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Abstract

Currently accepted mechanistic models describing aqueous corrosion of borosilicate glasses are based on diffusion-controlled hydrolysis, hydration, ion exchange reactions, and subsequent re-condensation of the hydrolyzed glass network, leaving behind a residual hydrated glass or gel layer. Here, we report results of novel oxygen and silicon isotope tracer experiments with ternary Na borosilicate glasses that can be better explained by a process that involves the congruent dissolution of the glass, which is spatially and temporally coupled to the precipitation and growth of an amorphous silica layer at an inwardly moving reaction interface. Such a process is thermodynamically driven by the solubility difference between the glass and amorphous silica, and kinetically controlled by glass dissolution reactions at the reaction front, which, in turn, are controlled by the transport of water and solute elements through the growing corrosion zone. Understanding the coupling of these reactions is the key to understand the formation of laminar or more complex structural and chemical patterns observed in natural corrosion zones of ancient glasses. We suggest that these coupled processes also have to be considered to realistically model the long-term performance of silicate glasses in aqueous environments.

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1. INTRODUCTION

One of the most challenging modern problems facing the scientific community, politicians, and the public throughout the world is the disposal of 19,900 tonnes of high-level nuclear waste, containing $\sim 200 \times 10^{18}$ Bq of activity stored in impermanent surface facilities (Gin et al., 2013a). Borosilicate glass is the leading candidate for a disposal

matrix in permanent geologic repositories (Grambow, 2006; Gin et al., 2013a). Since corrosion of nuclear waste-containing borosilicate glass by groundwater or meteoric water cannot be ruled out for long-term storage over geological time scales (up to 10^6 years), scientists have conducted numerous experiments in an effort to identify the key mechanism that leads to glass breakdown when contacted with aqueous solution (Grambow, 2006; Gin et al., 2013a). In most of these studies it has been appreciated that a nano- to micro-porous corrosion layer (or “leach layer”, “gel”, or “hydrated residual glass”) develops on the glass surface that has the potential to govern the long-term reactivity of glass. However, there is

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still no consensus how this layer forms and how it influences the long-term corrosion behavior.

At least three glass corrosion models have gained widespread acceptance and, although these models are not necessarily mutually exclusive, each regard the role played by the corrosion layer differently. The chemical affinity model is based on the notions of “deviation from equilibrium”, defined by the degree of silica saturation in solution (Grambow, 1985; Abraitis et al., 2000; Grambow and Müller, 2001). This model is based on the rate law developed by Aagaard-Helgeson (Aagaard and Helgeson, 1982) and neglects the importance of the corrosion layer (Gin et al., 2008) until discrete secondary phases begin to precipitate that affect the long-term solution saturation state and thus the dissolution kinetics. However, a recent study acknowledges the effect of a growing silica rim on the dissolution kinetics in addition to the affinity effect (Neeway et al., 2011). In the alkali-proton exchange model, the corrosion layer is regarded as the product of rate-limiting ion exchange reactions between protons and network modifiers such as Na, producing silanol (Si-OH) groups (Doremus, 1975; Bunker et al., 1984; Bunker, 1994; McGrail et al., 2001). The silanol groups are believed to re-polymerize in the solid state, forming the residual, hydrated glass layer (“leach layer”). The third model postulates that the corrosion layer constitutes a protective “gel” layer (Jégou et al., 2000; Rebiscol et al., 2004; Cailleteau et al., 2008; Frugier et al., 2008; Gin et al., 2011, 2013b). The most comprehensively developed variant of this model is the GRAAL (Glass Reactivity with Allowance for the Alteration Layer) model (Frugier et al., 2008). It proposes that the release of elements to solution, i.e., the corrosion rate, is governed by the transport properties of the “leach layer”. Similar to the alkali-proton exchange model, the corrosion layer is regarded as a dynamically restructured, residual, hydrated glass that with increasing reaction time becomes so dense and the pore spaces so constricted that a relatively impermeable “Passivating Reactive Interface” (PRI) develops that slows down the corrosion process. Analyses by secondary ion mass spectrometry (SIMS) and related techniques showed that element profiles from pristine glass through the “leach layer” commonly possess a characteristic sigmoidal shape, basically consonant with element diffusion (e.g., Petit et al., 1990; Shutthanandan et al., 2002; Valle et al., 2010; Gin et al., 2011). However, the reaction layer is sometimes comprised of components that can come only from solution (Valle et al., 2010) and the shape of the element profiles across the pristine glass and into the alteration (“leach”) rim has recently been demonstrated to be dependent upon the analytical technique used to make the measurement (Gin et al., 2013b), casting the original interpretation of the observed elemental profiles as diffusion profiles into question.

A recent set of studies illustrates this apparent dichotomy (Gin et al., 2011, 2013b). A monolith of boroaluminosilicate (SON68) glass was lately removed from a reactor in which the glass was reacted for nearly 26 years at 90 °C. The interface between pristine and altered glass was first analyzed by NanoSIMS (Gin et al., 2011) and more recently by the Atom Probe Tomography (APT)

technique (Gin et al., 2013b), which yielded significantly different observations. Whereas a 350 ± 150 and 170 ± 30 nm-wide boron concentration profile was obtained by NanoSIMS (O^- and Cs^+ ion sources, respectively), subsequent analyses by the APT technique (3.4 ± 1 nm resolution) revealed only ~ 3 – 15 nm wide profiles at the reaction interface. The authors concluded that the sharp profile revealed by APT more accurately describes the distribution of elements across the reaction interface. Such a sharp, step-like profile, however, is not consistent with a diffusion model, but calls for an interface-controlled reaction.

In this paper, we report the results of novel oxygen and silicon isotope tracer corrosion experiments that yield evidence for an alternate mechanistic model for the formation of glass corrosion zones. We note here that we did not attempt to experimentally quantify the glass dissolution kinetics, although we are aware, of course, that measuring the glass dissolution kinetics is an essential part of any program assessing the corrosion resistance of vitreous waste forms, and the numerous experiments that purport to do so are testimony to this priority. However, mechanistic information, particularly on the molecular scale, cannot be determined through knowledge of a rate equation alone that is obtained from analyzing the solution composition after different reaction times. The rate equation is a mathematical description of the rate of the slowest or rate controlling reaction in the process. In many reactions where this step is transport controlled, this may have little relationship to the chemical reaction process. It follows that kinetic data alone are usually inadequate to describe the reaction mechanism. We consider in our isotope tracer study that a missing component of many glass corrosion studies is the detailed investigation of the textural, chemical, and isotopic evolution of the corrosion layer in order to identify the mesoscopic mechanisms of its formation.

The isotope tracer experiments were performed with ternary Na borosilicate glasses in “batch” Teflon reactors at 90 °C for 672 h with solutions having had an initial, unbuffered pH (25 °C) of 4.1, ~ 7.0 , and 9.7 (Table 1). A low solid-to-solution mass ratio of 0.02 was chosen to replicate the likely conditions if a waste glass-containing metal canister is breached by solution. Only a small amount of glass surface area would be exposed and the interaction of small volumes of solution will cause a rise in solution pH (as in our experiments) if not buffered by the near field materials. Ternary Na borosilicate glasses were used in this investigation, which differ significantly in its silicon isotope composition from the natural value (Table 1). ^{30}Si -enriched glass spheroids ($^{28}\text{Si}/^{30}\text{Si} = 5$ – 8), designated as glass “S”, were reacted in solution along with powder of a second glass with a target chemical composition similar to that of glass “S, designated as glass “M”, which however possessed a natural Si isotopic composition (i.e., $^{28}\text{Si}/^{30}\text{Si} = 29.752$). Thus, during the reaction with aqueous solution, the powder of glass “M” served as a dynamic source of ^{28}Si , which allowed us to determine both the relative timing of dissolution and precipitation processes and the extent to which ^{28}Si derived from solution is incorporated into the corrosion layer (high $^{28}\text{Si}/^{30}\text{Si}$). Initially, two experiments

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