



The controversial role of inter-diffusion in glass alteration

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ABSTRACT

Current kinetic models for nuclear waste glasses (e.g. GM2001, GRAAL) are based on a set of mechanisms that have been generally agreed upon within the international waste glass community. These mechanisms are: hydration and ion exchange reactions (the two processes are referred as inter-diffusion), hydrolysis of the silicate network, and condensation/precipitation of partly or completely hydrolyzed species that produces a porous and amorphous layer and crystalline phases on surface of the altered glass. Recently, a new idea with origins in the mineral dissolution community has been proposed that excludes inter-diffusion processes as a potential rate-limiting mechanism. To understand how the newly proposed interfacial dissolution/precipitation model can change the current understanding of glass corrosion, a key experiment used to account for this model was replicated to further revisit the interpretation. This experiment was performed far from saturation, at 50 °C, with SON68 glass, in static mode, deionized water, and a S/V ratio of 10 m⁻¹ for 6 months. Results were repeatable and showed that glass dissolution rate progressively dropped by ~1 order of magnitude compared to the forward rate, suggesting that a dense surface layer was under construction. According to previous and new solids characterizations, it is concluded that neither a simple inter-diffusion model nor the interfacial dissolution/precipitation model can account for the observed elemental profiles within the alteration layer. More generally, far-from- and close-to-saturation conditions must be distinguished. This argument is bolstered by literature where evidence shows that inter-diffusion takes place in acidic conditions and far from saturation. However, closer to saturation, when a sufficiently dense layer is formed, a new approach is proposed requiring a full description of chemical reactions taking place within the alteration layer and an accurate budget of hydrous species along the profile as it is thought that the access of a sufficient amount of water to the pristine glass is the rate-limiting process in these conditions.

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1. Introduction

The question of stability of silicate glasses over times is of importance in many sectors including earth sciences and the nuclear industry. For example, understanding the alteration of basaltic glasses provides insight into global elemental geochemical cycles, potential storage of CO₂, and geological transformation on Mars (Galeczka et al., 2014; Knowles et al., 2012; Miniti et al., 2007; Seyfried et al., 1984). One important step to determine silicate glass behavior in a variety of systems, whether biological or environmental, is to understand interactions with water (Conradt, 2008; Filgueras et al., 1993; Morin et al., 2015). Additionally, glass is being considered as a containment matrix for high, intermediate, and low-level radioactive waste arising from the reprocessing of

spent nuclear fuel by many countries (Chaou et al., 2015; Ojovan and Lee, 2011; Pierce et al., 2008). The geological storage of nuclear waste in general, and glass in particular, is under consideration worldwide and it is agreed upon that the fate of radionuclides and their impact on the biosphere is strongly tied to waste form alteration by ground waters. One major challenge in this field is to reliably demonstrate the safety of the disposal site over the next hundreds of thousands of years (Gin et al., 2013a; Grambow, 2006; Vernaz and Dussossoy, 1992).

One approach to develop predictive mechanistic models has been designed by the scientific community (ASTM International, 2008; Campbell and Cranwell, 1988; Poinssot and Gin, 2012). This approach involves, initially, designing mechanistic and parametric studies to understand basic processes. From this point, various conditions are coupled and progressively represent realistic conditions. Experiments and in-depth characterization of altered glass samples allow the determination of the key processes that must be captured by a model.

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Mechanistic kinetic models are then developed to interpret experimental data with increasing complexity and eventually extrapolate long-term behavior under repository conditions. One additional method to validate models is to study natural or archeological glasses that have been subjected to a variety of conditions for periods exceeding the human timeframe (Dillmann et al., 2016; Libourel et al., 2011; Michelin et al., 2013; Parruzot et al., 2015; Techer et al., 2000; Verney-Carron et al., 2008).

Several mechanistic models are currently being used to assess the long-term stability of glass waste forms, such as GM2001 (Grambow and Müller, 2001), GRAAL (Frugier et al., 2008), and simpler rate laws derived from the general transition state theory equation given by Lasaga (1995). GM2001 (Grambow and Müller, 2001) couples an affinity-based rate law between the glass and dissolved silica and allows the diffusion of Si and H₂O through the gel (Ferrand et al., 2006). The affinity term is based on the activity of H₄SiO₄ in solution and a corresponding saturation constant, K_{SiO_2} , at the dissolving glass surface. In this model, the formation of the gel is due to the precipitation of silica following its dissolution from the glass network. Another advanced model, GRAAL, couples inter-diffusion and dissolution-precipitation reactions, and assumes that the glass dissolution rate is dependent on the diffusion properties of a dense altered layer designated as passivating reactive interphase (PRI) (Frugier et al., 2008). The PRI forms by water diffusion into the glass, ion exchange, and self-reorganization, although the detailed processes are not explicitly described. From a modeling point of view, the PRI is seen as a precipitate that limits mass transfer between the glass and the solution. The PRI transforms by dissolution/precipitation into a porous, non-passivating gel and secondary phases. The PRI and the gel are modelled by a set of 6 end-members whose composition and solubility have been empirically determined (Rajmohan et al., 2010). A unique diffusion coefficient is considered for all species passing through the PRI. This coefficient is pH- and temperature-dependent (Chave et al., 2007). Insofar, GRAAL has been the only model able to calculate residual rate without the use of additional parameters (Frugier et al., 2009; Gin et al., 2013b) although the range of conditions in which the model is applicable is still relatively narrow (SON68 type glass, 50 °C or 90 °C, pH 6–10).

Recently, a new theory initially built for silicate minerals (Hellmann et al. (2012) and references therein) was extended to silicate glasses based on specific observations (Geisler et al., 2015; Hellmann et al., 2015). This theory suggests that both silicate minerals and glasses dissolve congruently within a thin interfacial film of water and alteration products then form by precipitation from species released into this film. This idea is supported by many observations of cross sections of alteration rims formed on silicate minerals, which show sharp chemical gradients of species that were once assumed to diffuse (Hellmann et al., 2012). In the attempt to generalize the theory to glass, Hellmann et al. (2015) characterized samples altered at 50 °C in dilute conditions with Atom Probe Tomography (APT), Transmission Electron Microscopy (TEM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The glass that was used was SON68 (composition given in Table 1) – the inactive surrogate of the French R7T7 glass fabricated at the La Hague facility for high-level waste arising from spent nuclear fuel reprocessing. The observation of sharp gradients for highly mobile species, such as Na and B, led to the assumption by the authors that, at least in the tested conditions, the sole mechanism responsible for glass corrosion was dissolution/precipitation and no inter-diffusion (resulting from water diffusion in the glass and ion exchange reaction) was present.

This present paper attempts to understand how this interfacial dissolution/precipitation idea fits in with the observations and with the currently accepted waste glass corrosion models. The experiment described by Hellmann et al. (2015) – and referred as “Hellmann et al.’s experiment” in the following – has been replicated to re-examine their results.

Table 1
Composition of SON68 glass.

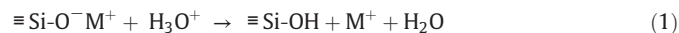
Oxide	mol%
SiO ₂	52.72
Al ₂ O ₃	3.39
B ₂ O ₃	14.03
Na ₂ O	11.39
CaO	5.02
Li ₂ O	4.6
ZnO	2.15
ZrO ₂	1.54
Fe ₂ O ₃	1.31
MoO ₃	0.85
Cs ₂ O	0.28
NiO	0.4
P ₂ O ₅	0.14
SrO	0.23
Cr ₂ O ₃	0.24
Y ₂ O ₃	0.06
MnO ₃	0.31
Ag ₂ O	0.01
CdO	0.02
SnO ₂	0.01
TeO ₂	0.1
BaO	0.28
La ₂ O ₃	0.2
Ce ₂ O ₃	0.2
Pr ₂ O ₃	0.1
La ₂ O ₃	0.42

2. Fundamentals in glass alteration

2.1. Mechanisms and kinetics of glass alteration

2.1.1. Mechanisms of glass alteration

A general set of mechanisms and kinetic regimes have been agreed upon in the international community to describe the interaction between borosilicate glasses and an initially dilute aqueous medium (Conradt, 2008; Vienna et al., 2013). The initial stage of glass dissolution in deionized water is represented by several coupled processes (Bunker, 1994): hydration by water diffusion in the glass structure (Doremus, 1975; Rébiscoul et al., 2007; Rébiscoul et al., 2004; Smets and Lommen, 1983) and the ion-exchange of the alkali ions of the glass surface with hydronium ions in solution (Angeli et al., 2001; Boksay et al., 1967; Doremus, 1983; McGrail et al., 2001; Ojovan et al., 2006; Rebiscoul et al., 2003). This is shown in Eq. (1) where M⁺ is an alkali ion.



It has previously been demonstrated that water diffuses into the glass as an intact molecular species only through large rings made of at least six silica tetrahedrons (Bunker, 1994). As glasses of nuclear interest are dense and highly polymerized, they do not contain many large rings, thus ion-exchange, and not hydration, dominates the first stage of nuclear glass alteration. McGrail et al. (2001) suggest that water dissociation could be the rate-limiting step controlling ion exchange. Moreover, it is often seen that B is released along with alkali. Although B is a glass former, the fast hydrolysis, associated with a low energy barrier for breaking B—O—Si bond, can explain why B is often seen to be released congruently with the alkali. In the present paper, the term inter-diffusion refers only to counter-directional diffusion of positively charged water species and positively charged glass modifier elements (alkali and alkaline earth) that results from the ion exchange process that occurs at the pristine glass/altered glass interface.

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