Glass-Water Interaction: Effect of High-Valence Cations on Glass Structure and Chemical Durability

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ABSTRACT:

Borosilicate glass is a durable solid, but it dissolves when in contact with aqueous fluids. The dissolution mechanism, which involves a variety of sequential reactions that occur at the solid-fluid interface, has important implications for the corrosion resistance of industrial and nuclear waste glasses. In this study, spectroscopic measurements, dissolution experiments, and Monte Carlo simulations were performed to investigate the effect of high-valence cations (HVC) on the mechanisms of glass dissolution under dilute and near-saturated conditions. Raman and NMR spectroscopy were used to determine the structural changes that occur in glass, specifically network formers (e.g., Al, Si, and B), with the addition of the HVC element hafnium in the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-HfO}_2\text{-SiO}_2$ system (e.g., $\text{Na}/[\text{Al}+\text{B}] = 1.0$ and $\text{HfO}_2/\text{SiO}_2$ from 0.0 to 0.42). Spectroscopic measurements revealed that increasing hafnium content decreases N_4 (tetrahedral boron/total boron) and increases the amount of Si—O—Hf moieties in the glass. Results from flow-through experiments conducted under dilute and near-saturated conditions show a decrease of approximately 100× or more in the dissolution rate over the series from 0 to 20 mol% HfO_2 . Comparing the average steady-state rates obtained under dilute conditions to the rates obtained for near-saturated conditions reveals a divergence in the magnitude between the average steady state rates measured in these different conditions. The reason for this divergence was investigated more thoroughly using Monte Carlo simulations. Simulations indicate that the divergence in glass dissolution behavior under dilute and near-saturated conditions result from the stronger binding of Si sites that deposit on the surface from the influent when Hf is present in the glass. As a result, the residence time at the glass surface of these newly-formed Si sites is longer in the presence of Hf, which increases the density of anchor sites from which altered layers with higher Si densities can form. These results illustrate the importance of understanding solid-water/solid-fluid interactions by linking macroscopic reaction kinetics to nanometer scale interfacial processes.

Key Words: solid-water reactions, borosilicate glass, high valence cations, Monte Carlo simulations, glass corrosion, glass durability, solid state NMR

1 INTRODUCTION

Reactions that occur at the solid-fluid interface have relevance to a range of areas with energy and industrial applications (e.g., natural gas recovery, material fabrication and durability, battery research, and various industrial chemical separation processes utilizing heterogeneous catalytic reactions). In a global context, the importance of solid-water interfacial reactions is difficult to overstate. These interactions control the composition of the world's fresh water (e.g., lakes, streams, rivers, etc.), soil development and nutrient distribution, formation of certain ore and hydrocarbon deposits, and the geochemical cycling of elements in the Earth's Critical Zone (e.g., near surface environment that determine the availability of life-sustaining resources) (Brown and Calas, 2012; Herndon and Brantley, 2011; Herndon et al., 2011; Hochella and White, 1990; Oelkers and Schott, 2009). Moreover, solid-water interfacial reactions also impact the sequestration, release, transport, and transformation of pollutants and contaminants (Davis and Kent, 1990; Liu et al., 2006; Zachara et al., 2004). Recently, multi-scale or hybrid models, which capitalize on advancements in the understanding of solid-water interfacial reactions, have been used in an attempt to better predict the geochemical evolution of natural and engineered systems (Steefel et al., 2005; Steefel and Maher, 2009). However, knowledge gaps in the fundamental understanding of solid-water reactions impede our ability to link macroscopic reaction kinetics to nanometer scale interfacial processes. These knowledge gaps result in the inability to adequately and accurately describe a variety of microscopic processes (e.g., absorption, ion diffusion, growth, dissolution, precipitation, and interfacial redox reactions) that represent the underlying phenomena controlling element cycles and transport in natural systems.

Interest in the immobilization and disposal of vitrified nuclear waste (nuclear waste glass) has resulted in the application of multi-scale or hybrid models to forecast radionuclide release originating from possible glass-water reactions (Bacon and Pierce, 2011; Bourcier, 1994; Bunker et al., 1986; Cailleteau et al., 2008; Chick and Pederson, 1984; Frugier et al., 2005; Gin et al., 2013; Gin et al., 2001; Grambow, 1985; Grambow and Müller, 2001; Icenhower et al., 2008; Jegou et al., 2000; Jollivet et al.,

2008; McGrail et al., 1997; McGrail et al., 2001; Pierce and Bacon, 2009, 2011; Pierce et al., 2014; Pierce et al., 2010; Pierce et al., 2008). Because of the critical role glass-water reactions play in the estimates of radionuclide release, an increase in the fundamental understanding of these processes is required to improve confidence in the long-term storage of vitrified nuclear waste in geologic systems (Gin, 2014; Gin et al., 2015; Grambow, 2006; Hellman et al., 2015; Putnis, 2015).

An important step in improving our ability to accurately forecast radionuclide release from corroding nuclear waste glass is to establish a link between the glass atomic-level structure and macroscopic dissolution behavior. In recent years, studies have placed emphasis on exploring this linkage in greater detail (Angeli et al., 2008; Arab et al., 2008; Bergeron et al., 2010; Cailleteau et al., 2008; Hopf and Pierce, 2014; Icenhower et al., 2008; Kerisit and Pierce, 2011, 2012; Pierce et al., 2010). For example, the study by Pierce et al. (2010), focused on determining the effects of varying the boron to aluminum ratio (B/Al) on the dissolution rate of aluminoborosilicate glasses along the nepheline to malinkoite join - referred to as the NeB glass series. The experimental study by Pierce et al. (2010) concluded that the rupture of either Al—O or Si—O bonds was the rate-limiting step controlling the dissolution. This conclusion was refined using the Monte Carlo simulations conducted by Kerisit and Pierce (2011) which indicated that at low B/Al ratios the rupture of both Al—O—Si and Si—O—Si linkages contributed to the dissolution rate, whereas, at high B/Al ratios, the dissolution rate was independent of the rupture of Al—O—Si linkages and was controlled by the dissolution of surface silicon sites with one bond to the glass and by dissolution via detachment of clusters. Furthermore high-valence cations (HVC) (e.g., hafnium and zirconium), which can be inserted into a Si network in the presence of charge compensators, can have a significant impact on the atomic-level structure and macroscopic dissolution behavior of aluminoborosilicate glasses (Cormier et al., 2000; Galois et al., 1999; McKeown et al., 2000; McKeown et al., 1999).

The present work seeks to extend the previous results by evaluating the influence HVCs—such as hafnium and zirconium—have on the structure and dissolution rate of sodium aluminoborosilicate

glasses. The HVC element hafnium is extremely effective in minimizing the risk of criticality during glass storage and/or disposal in a geologic repository because of its high thermal neutron capture cross section (~115 barn). Additionally, hafnium is also used as a chemical surrogate for tetravalent actinides, such as plutonium. Lastly, the effect of HVCs, such as zirconium, on the chemical durability of aluminoborosilicate glasses has been well documented (Bergeron et al., 2010; Cailleteau et al., 2008; Cailleteau et al., 2011; Lobanova et al., 2002). Because of the structural and chemical similarities between hafnium and zirconium, hafnium is expected to also exert a similar effect on the rate of Si—O hydrolysis when added to the glass composition. These structural and chemical similarities include similar octahedral coordination moieties ($[\text{ZrO}_6]^{2-}$ and $[\text{HfO}_6]^{2-}$) in borosilicate glass, with alkali or alkaline earth elements serving as charge-compensators. In addition to similar coordination moieties, the average bond distance for Hf—O (2.08 Å) is approximately 0.01 Å smaller than Zr—O (2.09 Å) in borosilicate glasses (Connelly et al., 2011b; Farges et al., 1991; Jollivet et al., 2013; Lopez et al., 2005); which is consistent with the 0.01 Å difference observed in the crystalline minerals hafnon (Hf—O = 2.188 Å) and zircon (Zr—O = 2.198 Å) (Hazen and Finger, 1979; Speer and Cooper, 1982). The reason for the structural similarities between hafnium and zirconium is thought to be related to the similarities in ionic radii for Hf(IV) = 0.85 Å and Zr(IV) = 0.86 Å (Shannon, 1976). The present study adds to the knowledge obtained for zirconium-bearing borosilicate glasses by studying the effect of hafnium in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{HfO}_2-\text{SiO}_2$ system.

The main objective of this work is to quantify the effect HfO_2 substitution has on glass durability under dilute and near-saturated conditions with respect to amorphous silica. Additionally, we provide insight into the structural changes that occur to the glass network as HfO_2 content increases from 0 to 20 mol%.

2 EXPERIMENTAL DETAILS

2.1 Glass Chemistry, Material Preparation, Surface Area, and RMS roughness

The glasses evaluated in this investigation were prepared according to the formula:

$$(1-n)Na_2O \cdot \frac{1}{4}(1-n)Al_2O_3 \cdot \frac{3}{4}(1-n)B_2O_3 \cdot 5nHfO_2 \cdot 3(1-n)SiO_2 \quad (1)$$

where $0 \leq n \leq 0.2$.

A series of Hf-bearing glasses were batched in 100 gram quantities and prepared by mixing reagent grade chemicals (Al_2O_3 , Na_2CO_3 , H_3BO_3 , HfO_2 , and SiO_2) together in a ceramic ball mill. The mixtures were melted at $1500^\circ C$ for 1 hour using a 10% platinum-90% rhodium ($Pt_{10}Rh_{90}$) crucible and then quenched on a steel plate. The resulting glass was then ground and re-melted in a covered $Pt_{10}Rh_{90}$ crucible. After an additional hour at melt temperature, the melt was poured into a mold to yield bars with approximate dimensions of $1.5 \text{ cm} \times 1.5 \text{ cm} \times 3.8 \text{ cm}$. The bars were then annealed for 2 hours in a box furnace at $570^\circ C$. After the 2 hour anneal, the furnace was turned off and the bars were allowed to cool to ambient temperature overnight. Each glass was readily pourable and yielded a clear visibly homogenous glass. The target composition in weight percent and mole percent is provided in Table 1 and 2, respectively. Electron microprobe data for Al, Hf, Na, and Si with O obtained by stoichiometry and B obtained by difference of select samples confirmed that the target glass compositions are within 0.6 mol% of the measured compositions (Davis et al., 2003; Zhao et al., 2000). The glass samples used were designed to have a $Na/(Al+B) = 1.0$ and a HfO_2/SiO_2 molar ratio that ranges from 0.0 to 0.42. A brief discussion of how these glasses compare to the HfO_2 glasses evaluated by Davis et al. (2003) is provided in supplemental information (Fig. SI1).

Prior to conducting experiments, the melted glass bars were then used to cut $20 \text{ mm} \times 20 \text{ mm} \times 1 \text{ mm}$ coupons. The coupon samples were then polished initially using 200 grit sandpaper samples and then with CeO_2 ($<1 \mu m$) paste. The surface area (S) of each sample was estimated by measuring the coupon dimensions using an electronic caliper and ranged from 0.98 to $1.22 \times 10^{-3} \text{ m}^2$. The apparent glass density was also estimated by obtaining the mass of the specimen (ranged between 0.33 and 0.45 grams) and

calculating the volume from the coupon dimensions. The density ranged from $\sim 2.8 \text{ g/cm}^3$ for HF-1 to 3.0 g/cm^3 for HF-5. After preparation, each sample was stored in a sealed container containing a CaSO_4 desiccant.

The atomic force microscopy (AFM) surface profile images were collected on polished coupons using a Bruker Multimode 8 AFM in tapping mode to evaluate the surface topography of each sample. The HF-2 data discussed in the supplemental information are representative of all the glass coupons tested (Fig. SI2). For the topography and roughness, multiple scans were taken at $10 \mu\text{m} \times 10 \mu\text{m}$. Roughness calculations were performed with the Nanoscope Analysis software and the parameters RMS (root mean square roughness, Sq) was determined after conducting a simple plane fit. No additional image processing was performed on the results.

2.2 Raman Spectroscopy

Raman spectra were collected on glass powder and polished coupons, respectively. The Raman spectra were collected using a Horiba JY LabRAM HR (Edison, NJ, high resolution) Raman (confocal) microscope system. With a focal length of 0.8 m and dual gratings with groove density of 2400 grooves/mm the instrument can achieve a nominal spectral resolution of about 1 cm^{-1} . Excitation was provided by the 244 nm line of a Lexel 85-SHG frequency-doubled Ar ion laser (Fremont, CA) equipped with a non-linear BBO (beta barium borate) crystal. Laser power was 25 mW at the source and approximately 2 mW at the sample. A $40\times$ UV-compatible microscope objective ($\text{NA} = 0.75$) was used. The spectrometer pinhole was kept fairly large, at $400 \mu\text{m}$, resulting in less-than-optimal depth and lateral resolution. However, laser throughput was improved with the larger pinhole, giving exceptionally high Raman intensities, in some cases tens-of-thousands of counts when collected with a relatively short exposure time (200 s). The spectra range was restricted to Raman shift above 450 cm^{-1} . Measurements at lower frequencies were not possible because of the presence of a factory-installed edge filter for eliminating the exciting line. As a consequence, Raman bands associated with deformation modes, commonly observed below 500 cm^{-1} , were not observable in this study. Windisch et al. (2011) provides a

detailed discussion on the poor signal-to-noise observed when using different configurations to collect conventional and deep-UV Raman spectra on a range of glass compositions. The poor signal-to-noise in conventional Raman spectroscopy with visible light (457.9 nm and 514.5 nm) was the result of weak Raman signals and excessive Rayleigh scattering and fluorescence arising from surface features. The decision to select deep-UV to minimize the impact background noise resulted in a trade-off because of the restricted spectral range. Therefore, the spectral analyses focus on the stretching modes, both network and those involving non-bridging oxygen (NBO) atoms, which occur at higher frequencies.

A more detailed description of the curve fitting procedure is provided in Windisch et al. (2011). Briefly, spectral analysis including curve fitting was performed using Thermo Scientific (Waltham, MA) Grams/32 AI software. Grams/32 AI uses the Levenburg-Marquardt non-linear peak fitting method. It was applied here using Gaussian peak functions and restricted to the 800-1200 cm^{-1} region of the spectrum. Prior to curve fitting, a weak exponential baseline correction was used to remove the small amount of background that persists in this region even with deep-UV excitation.

2.3 Magic Angle Spinning-Nuclear Magnetic Resonance spectroscopy

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy was conducted on unreacted glass powder samples, $<75\ \mu\text{m}$ (e.g., <200 mesh), to obtain information on glass structure and relate the effect structure exerts on glass dissolution. The local coordination geometry around the Al, B, Na, and Si atoms on four of the five glasses was investigated at room temperature by ^{27}Al , ^{29}Si , ^{23}Na , and ^{11}B MAS-NMR.

The ^{11}B , ^{23}Na , and ^{27}Al MAS-NMR spectra were collected on a Bruker Avance II Spectrometer at a magnetic field of 11.72 T (500 MHz) using a 4 mm (o.d.) Bruker CPMAS probe (spinning frequency 14 kHz). All spectra were acquired using a single pulse excitation (SPE) with a short pulse length (1 μs , tip angle 15°) to obtain a quantitative measurement (homogeneous excitation of all sites with respect to their quadrupolar coupling constant strength) and a recycle delay of 1 s for ^{23}Na and ^{27}Al , and 2 s for ^{11}B . Approximately, 4096 scans were collected for each sample. For ^{11}B , multiple-quantum magic-angle

spinning (MQMAS) spectra optimized for BO_3 and BO_4 observation (2 spectra for each sample) were acquired as described in Angeli et al., (2010). A correction was applied for the contribution of the satellite transition (ST) spinning sidebands to the BO_4 centerband in the ^{11}B SPE MAS NMR spectra. We performed this correction by subtracting the ST spinning sideband (second order) from the spectrum centerband. As discussed in the Supplemental Information, this method is supported by the fact that all spinning sidebands near the centerband have the same lineshape (Fig. SI3) and their variation in intensity from second order to centerband can be neglected (Fig. SI4). This correction is displayed in Fig. SI5 and typically amounts to a reduction of $\sim 2\%$ of the BO_4 population. Further analysis of the BO_4 peak was obtained by the TOP method (Massiot et al., 2006). Briefly, this approach consists of folding back all the spinning sidebands into the centerband frequency range, but introducing their order in a second dimension. By extracting columns at a given chemical shift the shape of its spinning sideband manifold is revealed, which mostly reflects the quadrupolar NMR parameters. Angeli et al. (2010) demonstrated that this type of analysis is critical in identifying the existence of at least two BO_4 species and in the applicability of the Gaussian Isotropic Model (GIM) (thus the existence of a finite quadrupolar interaction with a non-zero asymmetry parameter). Those two sites are also evidence in the MQMAS spectra (as discussed below). The ^{11}B chemical shifts are referenced to an external sample of 1 M boric acid solution (19.6 ppm). A 1 M AlCl_3 solution was used as external reference for ^{27}Al NMR spectra and ^{23}Na chemical shifts were referenced to a 1 M NaCl solution. The ^{29}Si MAS-NMR spectra were acquired on a Bruker Avance I spectrometer at a magnetic field of 7.02 T using a Bruker 4 mm (o.d.) Bruker CPMAS probe (spinning frequency 12.5 kHz). A Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (Larsen and Farnan, 2002) was used with a recycle delay of 20 s (no change in lineshape was observed for longer recycle delay of 200 s, 800 s, Fig. SI6 and Fig. SI7). The spectra are referenced to an external *tetrakis(trimethyl)silane* (TKS) sample for which the highest intensity peak is situated at -9.9 ppm from that of *tetramethylsilane* (TMS).

All data were processed and fitted using in-house written software. Methods for fitting the spectra have been detailed in (Angeli et al., 2010; Angeli et al., 2012). Briefly, the ^{27}Al , ^{23}Na , and ^{11}B lineshapes were fit considering a distribution of the NMR parameters and corresponding fit parameters (i.e., isotropic chemical shift $[\delta_{\text{iso}}]$, quadrupolar coupling constant $[C_Q]$, and quadrupolar asymmetry parameter $[\eta_Q]$) represent the mean of those distributions (Angeli et al., 2010; Angeli et al., 2007; Angeli et al., 2012; Quintas et al., 2007). For ^{27}Al , ^{23}Na , and ^{11}B (BO_4 units only), this distribution was chosen as the product between a Gaussian distribution for the isotropic chemical shift and the GIM for the quadrupolar parameters (namely the C_Q and η_Q). It is important to note that the GIM distribution yields a constant mean value of 0.6 for η_Q . For BO_3 units, the product of three Gaussian distributions was chosen, as detailed in Angeli et al. (2010). All 1D spectra are displayed normalized to the same maximum height.

2.4 Buffer Solutions

The influent solutions used to control the pH during the dissolution experiments were prepared with 0.05 M *tris hydroxymethyl aminomethane* (THAM) buffer in 18 M Ω ·cm deionized water (DIW). The silicon concentration in the influent solution was varied from dilute to saturated for these experiments by adding the appropriate amount of analytical grade silicic acid powder ($\text{SiO}_2 \cdot \text{H}_2\text{O}$) to the THAM buffer and heating the solution in a 40°C oven for no less than three days to facilitate complete dissolution of $\text{SiO}_2 \cdot \text{H}_2\text{O}$. Upon complete dissolution each solution was removed from the oven, allowed to cool, and pH adjusted [target pH(23°C) = 9.0] with aliquots of 15.8M HNO_3 or 1M LiOH . Prior to pH-adjusting the influent solutions, the pH probe was calibrated with National Bureau of Standards (NBS) buffers (pH = 7.00, 10.00, and 12.00 at 23°C). The precision of the pH measurement was ± 0.1 pH units. Based on the results from calculations with the geochemical code EQ3NR [version 7.2b (Helgeson et al., 1978; Johnson et al., 1992; Wolery, 1992)] the amount of Si added was altered from dilute to near-saturated with respect to amorphous silica [$\text{SiO}_2(\text{am})$]. It is important to note that the solubility behavior of $\text{SiO}_2(\text{am})$ changes with experimental conditions, therefore, the target amount of Si added to the buffer solution was calculated for the experimental temperature of 23°C, resulting in a Si solution concentration

of 60 ppm. Although a 60 ppm Si solution is saturated at room temperature, we did not observe precipitation of silica in the influent or effluent solutions during the course of the experiments. Additionally, for Si saturated experiments conducted as a function of pH, the solution pH was adjusted to the target values, $\text{pH}(23^\circ\text{C}) = 8.0$ and 9.0 , using aliquots of 15.8M HNO_3 or 1M LiOH .

The pH of the influent and a select number of effluent solutions were monitored over the duration of the experiments. Concentrations of Al, B, Na, and Si in the influent and effluent solution samples were determined with inductively coupled plasma-optical emission spectroscopy (ICP-OES). The average background concentration, based on analysis of the influent solution and three blank solutions, ranged from 10 to $30\text{ }\mu\text{g/L}$ for Al, from 10 to $50\text{ }\mu\text{g/L}$ for B, and from 100 to $500\text{ }\mu\text{g/L}$ for Na in experiments conducted under diluted and near-saturated conditions. The average silica background concentration varies from 1 mg/L for experiments conducted under dilute conditions to 88 mg/L for experiments conducted under near-saturated conditions. Typically, background concentrations of elements are below the sample estimated quantification limit (EQL). The sample EQL is determined by multiplying the sample dilution factor by the lowest calibration standard that can be determined reproducibly during an analytical run within 10% . Before analysis, aliquots of the influent and effluent solutions were acidified with ultra-high-purity concentrated HNO_3 .

2.5 Single-Pass Flow-Through (SPFT) System and Effluent Solution Analysis

For dilute solutions, the dissolution experiments were conducted at the forward or maximum dissolution rate with the single-pass flow-through (SPFT) apparatus (Fig. 1). For consistency, the solutions containing dissolved Si were carried out under the same forward rate conditions (i.e., similar ratio of the flow rate to surface area $[q/S]$ conditions) as the dilute solutions. The SPFT system and the techniques used to calculate the dissolution rate has been extensively described by others (Icenhower et al., 2008; Icenhower et al., 2006; McGrail et al., 1997; Pierce et al., 2005; Pierce et al., 2008; Wellman et al., 2006). To limit duplication, the reader should refer to the aforementioned references, as well as the references contained therein for more details on the SPFT system.

All SPFT experiments were conducted in a constant temperature oven ($\pm 2^\circ\text{C}$) at 23°C and at flow rates ranging from 2 to 20 mL d^{-1} (~ 0.03 to 0.25 reactor volumes per day). The solution temperature inside of a blank reactor was measured with an in-situ thermocouple. The flow rate was determined by weighing the volume of solution collected at each sampling time (i.e., gravimetrically) and variations were typically less than 5%. Once constant conditions (i.e., buffers, flow rates, temperature, etc.) were established, the pre-weighed glass coupons were placed into a test vessel. Experiments were run until steady-state effluent solution chemistries prevailed, which typically occurred after 3 to 8 reactor volumes. The abbreviations selected to describe all of the glass samples and dissolution experiments are: HF-1 to HF-5 corresponds to the 5 glass samples used with increasing hafnium concentration (untreated), D and S are used for the dissolution experiments conducted under diluted conditions and near-saturated conditions, respectively (e.g. HF-4D and HF-4S refers to experiments conducted with 15% hafnium glass sample under diluted and saturated conditions, respectively).

2.6 Quantification of Dissolution Rates

Dissolution rates, based on steady-state concentrations of elements in the effluent, are normalized to the mass fraction of the element present in the sample by the following formula:

$$r_i = \frac{(C_i - \bar{C}_{i,b})q}{f_i S}, \quad (2)$$

where r_i is the normalized glass dissolution rate based on the release of a particular element, i , [$\text{g}/(\text{m}^2 \cdot \text{d})$], C_i is the concentration of the element, i , in the effluent (g/m^3), $\bar{C}_{i,b}$ is the average background concentration of the element of interest (g/m^3), q is the flow rate (m^3/s), f_i is the mass fraction of the element in glass (dimensionless), and S is the surface area of the sample (m^2). The value of f_i is also calculated from the chemical composition of the sample. Flow rates are determined by gravimetric analysis of the fluid collected in each tared effluent collection vessel upon sampling. The background concentration of the element of interest is determined, as previously discussed, by analyses of the starting input solution and the three blank solutions. Typically, background concentrations of elements are below

their respective detection threshold. In cases where the analyte is below the detection threshold, the background concentration of the element is set at the value of the detection threshold.

Determining the experimental uncertainty of the dissolution rate takes into account uncertainties of each parameter in Eqn. (2). For uncorrelated random errors, the standard deviation of a function $f(x_1, x_2, \dots, x_n)$ is given by:

$$\sigma_f = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2}, \quad (3)$$

where σ_f is the standard deviation of the function f , x_i is the parameter i , and σ_i is the standard deviation of parameter i . Substituting Eqn. (2) into Eqn. (3) and converting to relative error, $\hat{\sigma} = \sigma / r_i$, yields:

$$\hat{\sigma}_{r_i} = \sqrt{\frac{(\hat{\sigma}_{C_i} C_i)^2 + (\hat{\sigma}_{\bar{C}_{i,b}} \bar{C}_{i,b})^2}{(C_i - \bar{C}_{i,b})^2} + \hat{\sigma}_q^2 + \hat{\sigma}_{f_i}^2 + \hat{\sigma}_S^2}, \quad (4)$$

Relative errors of $\hat{\sigma}_{C_i}$, $\hat{\sigma}_{\bar{C}_{i,b}}$, $\hat{\sigma}_q$, $\hat{\sigma}_{f_i}$, and $\hat{\sigma}_{S_{geo}}$ are 10%, 10%, 5%, 3%, and 15%, respectively. The errors assigned to the parameters in Eqn. (4), in addition to the practice of substituting detection threshold values for situations where the sample results were below the background concentrations because of instrument limitations, results in typical 2σ uncertainties of approximately $\pm 30\%$ for SPFT-measured dissolution rates (or ± 0.2 log units when reported as $\log_{10}$ rates). To ensure the SPFT system yielded reproducible results replicates of select experiments were conducted and a comparison of these results indicated a deviation between replicates to be $< 30\%$.

2.7 Computational Methods

All the calculations reported in this work were carried out with a parallel Monte Carlo computer program developed and implemented for the purposes of this work. The Monte Carlo model is based on the glass dissolution model of Devreux, Barboux, and co-workers (Devreux et al., 2001; Devreux et al., 2004; Ledieu et al., 2006; Lobanova et al., 2001). The Monte Carlo model is only briefly described here

and the reader is referred to our previous publications (Kerisit and Pierce, 2011, 2012; Kerisit et al., 2015; Kerisit et al., 2013) for more details.

In the MC model, the glass framework is mapped onto a cubic lattice wherein each lattice site represents a network-former cation (e.g. Si or B) and its first oxygen coordination shell and network-modifier cations (e.g. Na) are placed in interstitial positions. Two connections are removed at each lattice site to represent the fourfold connectivity of the network-former cations. Four elements were considered in the simulations carried out in this work: boron, silicon, sodium, and hafnium. Boron sites dissolve instantaneously once in contact with the aqueous solution and are considered fully soluble. Silicon sites with one, two, or three connections to silicon nearest neighbors dissolve with probabilities w_1 , w_2 , and w_3 , respectively. In addition, silicon can deposit back at surface sites with probability $w_r = w_{c-Si}c_{Si}$ where w_{c-Si} is the silicon condensation probability and c_{Si} is the silicon concentration in the aqueous solution. Hafnium was added in octahedral sites, following the implementation of Arab et al. (2008) for octahedral cations. Hafnium sites are considered insoluble, which means that all the network formers in its coordination shell need to have dissolved for it to dissolve into the aqueous solution. To represent the strengthening effect of Hf nearest neighbors on the Si dissolution probabilities, w_d , we employed the formulation of Ledieu et al. (2006):

$$w_d(n, m) = \frac{w_n}{r_{Hf}^m} \quad (5)$$

where n is the number of Si and Hf nearest neighbors, m is the number of Hf nearest neighbors, and r_{Hf} is the relative strength between Si—O—Hf and Si—O—Si linkages.

In all the simulations, the initial configuration of the glass was that of a slab with a perfectly smooth surface with a surface area of 32×32 sites and a thickness of 4096 lattice sites. The aqueous solution volume was set to be equivalent to 3.411335×10^{12} sites. Using a side length of 0.3 nm for a lattice site (Devreux et al., 2004), this number of aqueous sites corresponds to a S/V ratio of 1 m⁻¹. The parameters $w_1 = 0.01$, $w_2 = 0.001$, $w_3 = 0.0001$, and $w_{c-Si} = 10$ were used in this work as was used in our previous

work (Kerisit and Pierce, 2012) and in the work of Devreux and co-workers (Devreux et al., 2004; Ledieu et al., 2006). To represent the strong hardening effect of Hf, the parameter r_{Hf} was set to an arbitrary large value ($r_{\text{Hf}} = 100$).

The experimental chemical compositions given in Table 2 were used as a basis for the MC simulations. However, to simplify the glass compositions and isolate the effects of hafnium, aluminum was considered to behave similarly to silicon and thus the SiO_2 mole percent was set to be equal to the $\text{SiO}_2 + \text{Al}_2\text{O}_3 \times 2$ mole percents shown in the experimental compositions. This leads to a Si/B ratio of 2.33 in all five HF glasses, and this value was thus also used in all the MC simulations. 0 to 13 mol% HfO_2 were added to the glasses. The Na_2O content was set to exactly charge compensate $[\text{BO}_4]^-$ and $[\text{HfO}_6]^{2-}$ groups. To mimic the single-pass flow-through experiments, a flow probability of 0.01 was used in the MC simulations. More details on the approach used in the simulations for simulating the effect of flow can be found in our previous publication (Kerisit and Pierce, 2012). In that study, the flow probability value used here was found to yield dissolution rates equal to the forward/initial dissolution rate of sodium borosilicate glasses. Here we define flow probability as the probability for removal of dissolved glass components from aqueous solution. This parameters is used to simulate the effect of flow on glass dissolution. In addition, to simulate the presence of silicon in the influent of the near-saturated dissolution experiments, a constant silicon background concentration was added in the MC simulations. To investigate the effects of the influent Si concentration, the silicon background concentration was varied from 0 to 90% of the Si saturation concentration obtained with the model parameters given above.

3 EXPERIMENTAL RESULTS

3.1 ^{27}Al , ^{23}Na , ^{29}Si , and ^{11}B MAS-NMR

The ^{27}Al MAS-NMR spectra (Fig. 2) collected for the HF-series glasses confirm that Al is in a tetrahedral coordination, as indicated by a ^{27}Al peak maxima centered near 60 ppm. Furthermore less than a ± 0.5 ppm shift in the ^{27}Al spectra is observed suggesting that Al local environment is not being significantly altered with the addition of hafnium. ^{27}Al MAS-NMR spectra were fitted using the methods

described in (Angeli et al., 2007). It was also found that using Lorentzian broadening improved the fit (Fig. SI8, 0.5 – 0.7 ppm). NMR parameters are reported in Table 3 (i.e., isotropic chemical shift [δ_{iso}] and quadrupolar coupling constant [C_Q]). As previously mentioned this fit procedure yields a constant value of 0.6 for the quadrupolar asymmetry parameter [η_Q] and therefore it is omitted from Table 3.

The ^{23}Na MAS-NMR spectra are reported in Fig. 3. ^{23}Na MAS-NMR spectra have been fitted accounting for the distribution of the NMR parameters (Angeli et al., 2007). It was found that a small Lorentzian broadening (same for all samples 4.3 ppm, this might be reflective of small amount of paramagnetic impurities such as Fe) improve the fit (Fig. SI9). NMR parameters are given in Table 4. A small decrease of the mean value of the δ_{iso} with Hf content increasing is observed.

The ^{29}Si MAS-NMR spectra shown in Fig. 4 confirms the dominant local coordination for Si-atoms within the HF-series glasses are tetrahedral (^{4}Si) with corresponding resonances centered near -95 ppm. As the hafnium content in the glass increases the peaks near -95 ppm slightly shifts from a peak maximum of -96 ppm for HF-1 to a peak maximum of -94 ppm for HF-5, with a lower broadening.

Fig. 5 shows the ^{11}B MAS-NMR spectra for the hafnium formulation (HF) glass series (HF-1, HF-3, HF-4, and HF-5). Signals from trigonal (^{3}B) and tetrahedral (^{4}B) groups are both present. The broader band centered around 13 ppm corresponds to ^{3}B , whereas the sharper peak centered around -2 ppm corresponds to ^{4}B . An increase of the ^{3}B fraction with the Hf content increasing is clearly observed, along with only a slight modification of the ^{3}B lineshape (see Fig. 5 inset) and a shift of the ^{4}B line to higher chemical shifts. In the case of the broad peak for the ^{3}B results from the presence of two sites: boron surrounded by bridging bonds in boroxyl rings ($\text{BO}_3(\text{B})$) or other borate units involving B—O—B bonds and boron distributed in silicate units ($\text{BO}_3(\text{Si})$) (Angeli et al., 2010; Du and Stebbins, 2003a, b, 2005; Pierce et al., 2010). These results are consistent with previous results collected on other borosilicate glasses that contain high-field strength cations, such as hafnium, titanium, and zirconium (Angeli et al., 2010; Bergeron et al., 2010). This is also consistent with the Raman band observed between 1400 and 1480 cm^{-1} , which is directly associated with changes in B local structure. Additional analysis of the

spectra was required to quantify the percentage of $\text{BO}_3(\text{B})$ and $\text{BO}_3(\text{Si})$ and is discussed in the sections to follow. Although the ^{11}B MAS-NMR collected at 11.7 T are discussed in detail, similar ^{11}B MAS-NMR measurements were also performed at higher field [i.e., 17.6 T (750 MHz) and 20 T (850 MHz)] illustrated that the N_4 fraction ($N_4 = [^{11}\text{B}]/([^{11}\text{B}] + [^{13}\text{B}])$) measured at each field was within 1 to 2% of each other (see Fig. SI10).

3.2 Dissolution Experiments on HF Series Glasses

All SPFT experiments were monitored for Al, B, Na, and Si concentration in effluent solutions. The experiments were conducted until element concentrations were invariant with respect to time, i.e., steady-state conditions were achieved (see Fig. SI11). Average steady-state normalized dissolution rates in dilute and silica saturated experiments are listed in Table 5 along with the experimental conditions, including average steady-state element concentrations, flow-through rates, and coupon surface areas. In all experiments the Al and Hf concentrations were below the detection limit and the B and Na concentrations for HF-5S glass sample tested under near-saturated conditions was below the detection limit; therefore the value for this experiment represents a maximum rate. All experimental uncertainties reported in Table 5 are 2σ errors.

Dissolution rates under dilute conditions and $\text{pH}(23^\circ\text{C}) = 9.0$ decreased with increasing Hf-content of the glass (Fig. 6). For the HF-1 glass composition, the average dissolution rate, based on B, is $3.20(\pm 0.47) \times 10^{-1} \text{ g}/(\text{m}^2 \text{ d})$ for HF-1D; whereas, the average dissolution rate, based on B, for the HF-5 glass composition under dilute conditions is $2.87(\pm 0.54) \times 10^{-3} \text{ g}/(\text{m}^2 \text{ d})$ for HF-5D. This corresponds to a 112× decrease in the dissolution rate over the glass series from 0 to 20 mol% HfO_2 . Similarly under near-saturated conditions and $\text{pH}(23^\circ\text{C}) = 8.0$ dissolution rates decrease from $9.58(\pm 1.68) \times 10^{-2} \text{ g}/(\text{m}^2 \text{ d})$ for HF-1S to $1.29(\pm 0.30) \times 10^{-4} \text{ g}/(\text{m}^2 \text{ d})$ for HF-4S, which corresponds to a 74× decrease in the dissolution rate over the glass series from 0 to 15 mol% HfO_2 . As previously mentioned, B and Na concentrations for the HF-5S sample (20 mol% HfO_2 glass under saturated conditions) was at or below the detection limit. Using the detection limit to estimate the dissolution rate would result in $<2.62 \times 10^{-4} \text{ g}/(\text{m}^2 \text{ d})$ and

$<3.78 \times 10^{-4} \text{ g/(m}^2 \text{ d)}$ for HF-5S, based on B and Na release respectively. Saturated experiments were conducted at $\text{pH}(23^\circ\text{C}) = 8.0$ to control the speciation of dissolved Si which is 100% and ~90% $\text{H}_4\text{SiO}_4 \text{ (aq)}$ at $\text{pH}(23^\circ\text{C}) = 8.0$ and 9.0, respectively. The effect Si saturation state has on the dissolution rate of borosilicate glass dissolution has been well document and is directly related to the presence of $\text{H}_4\text{SiO}_4 \text{ (aq)}$ (Grambow, 1985; Grambow and Müller, 2001).

In addition to the aforementioned tests, a select number of experiments were conducted on HF-1 glass at $\text{pH}(23^\circ\text{C}) = 8.0$ and 9.0 to evaluate the impact pH has on the dissolution rate under near-saturated conditions. Results suggest that increasing pH causes the dissolution rate, based on B release, to increase from $9.58(\pm 1.68) \times 10^{-2} \text{ g/(m}^2 \text{ d)}$ at $\text{pH}(23^\circ\text{C}) = 8.0$ to an average rate at $\text{pH}(23^\circ\text{C}) = 9.0$ of $3.07(\pm 0.32) \times 10^{-1} \text{ g/(m}^2 \text{ d)}$ for the two replicates. Similarly, the dissolution rates based on Na release increased from $1.19(\pm 0.21) \times 10^{-1} \text{ g/(m}^2 \text{ d)}$ to an average rate of $4.04(\pm 0.39) \times 10^{-1} \text{ g/(m}^2 \text{ d)}$ at $\text{pH}(23^\circ\text{C}) = 8.0$ and 9.0, respectively. These results illustrate roughly a 3.2 $\times$ and 3.4 $\times$ difference between the rates measured at $\text{pH}(23^\circ\text{C}) = 8.0$ and 9.0 for B and Na, respectively.

4 DISCUSSION

4.1 Effect of Hf on ^{29}Si and ^{11}B coordination

Although the presence of tetrahedral Al and B in glasses are known to have an effect on the Si peak position (Hålenius et al., 2010; Lippmaa et al., 1980; Lippmaa et al., 1981; Nanba et al., 2009; Soleilhavoup et al., 2010), an effect related to the shielding of the Si framework by the addition of Al or B, the shift to more positive values observed for these glasses are almost certainly due to the addition of hafnium. The fraction of Al and $^{[4]}\text{B}$ contained in these samples decreases by 0.75 mol% and 3.2 mol%, respectively, from HF-1 to HF-4; but instead of the peak positioning shifting to more negative values or remaining the same, it moves in the direction of more positive values (Fig. 4). This is somewhat counter intuitive because a decrease in the $^{[4]}\text{Al}$ and $^{[4]}\text{B}$ content should result in the Si spectra shifting to more negative values or staying the same which would be consistent with the formation of Q^n species equal to or greater than 3 or the similar distribution of these species. This behavior is consistent with X-ray

absorption fine-structure (XAFS) spectroscopy measurements of select glass samples which revealed that hafnium is octahedral coordinated $[\text{HfO}_6]^{2-}$ and resembles a hafnium metallasiloxane compound (Caulder et al., 2000; Motevalli et al., 1993; Strachan et al., 2001; Zhao et al., 2000) [see Fig. SI12]. The hafnium metallasiloxane moieties in these glasses consist of octahedral coordinated hafnium that is connected to siloxane ring units (Caulder et al., 2000; Motevalli et al., 1993). Although the current assessment is qualitative, these results suggests an increase in the number of Si—O—Hf bonds mainly at the expense of $^{[4]}\text{B}$ —O—Si bonds and is consistent with the Raman results (see supplemental information Fig. SI13-SI15). Note the decrease in $^{[4]}\text{B}$ —O—Si bonds is associated with the availability of Na_2O and is discussed in greater detail next.

For $^{[4]}\text{B}$ coordination sites, the spectrum is also consistent with the presence of multiple sites—specifically tetrahedral borate groups surrounded by either four Si ($^{[4]}\text{B}(0\text{B}, 4\text{Si})$) or three Si and one B ($^{[4]}\text{B}(1\text{B}, 3\text{Si})$). This deconvolution into (at least) two components was previously discussed in Angeli et al. (2010) and stems from the analysis of the Spinning Sidebands manifold using the TOP method (Massiot et al., 2006), as shown in Fig. 7 (see Fig. SI16 for TOP method results for other samples). Indeed, at least two sites can be distinguished for the $^{[4]}\text{B}$ line, one characterized by a larger (~ 1.2 ppm) and narrower (~ 1.8 ppm) Spinning Sidebands manifold (see Fig. SI4 and Fig. SI5). This suggests two sites with different quadrupolar interactions. Similar features appear in the MQMAS spectrum, as shown in Fig. 8, where a continuous increase of the line width (reflective of the quadrupolar interaction strength) is observed for an increase of the isotropic chemical shifts (see Fig. SI17 for MQMAS results for other samples).

For $^{[3]}\text{B}$, two components were used as constrained from the MQMAS lineshape of the $^{[3]}\text{B}$, as shown in Fig. 9 where the asymmetrical lineshape of the isotropic projection require the use of (at least) two components. Using all these constraints from the MQMAS data, the MAS-NMR spectra could be fitted simultaneously using four components as described in Table 6 (see Fig. SI18 and Fig. SI19). The quantification of the boron sites is reported in Table 7. The variation of the N_4 fraction (ratio of $^{[4]}\text{B}$ to

total B), as extracted from the analysis of the ^{11}B MAS NMR spectra, as shown in Fig. 10 shows a decrease with increasing HfO_2 content. This is the result of Na_2O being used to charge compensate for the addition of hafnium in the glass. The N_4 fraction for HF-2 was estimated using Eqn. (6):

$$N_4 = -0.752 \text{HfO}_2 + 0.7616 \quad (6)$$

Eqn. (6) was obtained plotting the N_4 fraction as a function of mol% HfO_2 for HF-1, HF-3, HF-4, and HF-5 and conducting a linear regression. These results suggest that Na_2O preferentially charge compensates with Al_2O_3 and HfO_2 and only the residual Na_2O is available to charge compensate for B_2O_3 to form $^{[4]}\text{B}$. Previous studies have reported a similar behavior for other alkali aluminoborosilicate glasses (El-Damrawi et al., 1993; Pierce et al., 2010), but this is the first time this has been observed in HfO_2 bearing alkali alumino-borosilicate glasses. The results shown in Fig. 10 illustrate that as the HfO_2 content increases from 0 mol% for HF-1 to 20 mol% for HF-5 the N_4 fraction decreases from 75.5% to 60.2%, respectively.

Although the mechanism that governs the preferred order that Na_2O charge compensates for specific structural units in glass is not fully understood, studies have used the Pauling bond valence theory as a plausible model to structurally and chemically explain the observed behavior (Pauling, 1929). The bond valence theory is based on Pauling's second rule and has been used to provide insight to the structure of crystals (Brown, 1981), glasses (Cormier et al., 2000; Rossano et al., 2002), and silicate melts (Calas et al., 2014; Ellison and Hess, 1994). Pauling's second rule requires the sum of bond valences (defined as the formal charge of an ion divided by its coordination number) to all ions to equal the absolute value of their formal charges to within ± 0.05 valence units (νu). Recently, Connelly et al. (2011a) used a modified bond valence concept (i.e., coordination stabilization index [CSI]) to qualitatively predict a hierarchy for sodium to preferentially charge compensate for specific structural units in complex oxide glasses. The CSI is defined as:

$$\text{CSI} = S_{nc} - S_{cc} \quad (7)$$

where S_{nc} is the stability of a species stable in glass without alkali charge compensation in vu and S_{cc} is the stability of a species stable in glass with alkali charge compensation in vu . The simplified CSI model does not account for changes in bond length which will almost certainly vary with glass composition. Both S_{nc} and S_{cc} are calculated using the ratio of the species valence to the coordination number. For example, aluminum occurs in both 6-fold ($^{VI}Al^{3+}$) and 4-fold ($^{IV}Al^{3+}$) coordination in glass; therefore S_{nc} for $^{VI}Al = 0.5 vu$ and S_{cc} for $^{IV}Al = 0.75 vu$ which corresponds to a CSI = -0.25 vu . In glass, hafnium predominantly occurs in both 8-fold ($^{VIII}Hf^{4+}$) and 6-fold ($^{VI}Hf^{4+}$) coordination and boron predominantly occurs in 3-fold ($^{III}B^{3+}$) and 4-fold ($^{IV}B^{3+}$) coordination. Based on these calculations the CSI is -0.25 vu for Al, -0.17 vu for Hf, and +0.25 vu for B suggesting sodium charge compensation occurs in the following order: $^{IV}Al > ^{VI}Hf > ^{IV}B$ for this glass series, a result consistent with the NMR results discussed in this section.

Lastly, also shown in Fig. 10 are the results collected by Angeli and colleagues (Angeli et al., 2008; Bergeron et al., 2010) for Hf-bearing and Zr-bearing soda-lime borosilicate glass formulations. Both zirconium and hafnium form octahedral structures in the borosilicate glasses; therefore the data collected on soda-lime borosilicate glass formulations by Angeli and colleagues were included and used to provide insight into the behavior of hafnium in the glasses evaluated in this study. Although the trend is similar the magnitude of the decrease in the N_4 fraction is different for the glasses examine in this study compared to soda-lime borosilicate glasses and arise because of differences in composition. The borosilicate glasses studied by Angeli and colleagues contained calcium, but did not contain aluminum; both elements are known to have an impact on the N_4 fraction (Angeli et al., 2010; Pierce et al., 2010).

4.2 Comparison of rates measured under dilute and near-saturated conditions

To compare the rates measured under dilute and near saturated conditions, the rates measured in experiments conducted at $pH(23^\circ C) = 8.0$ in saturated solutions were adjusted using Eqn. (8).

$$\log_{10}(r_2) = \log_{10}(r_1) + (\gamma - 1) \quad (8)$$

In Eqn. (8) the r_2 is the pH-corrected rate [$g/(m^2 d)$]; r_1 is the uncorrected rate [$g/(m^2 d)$]; γ is the pH power law coefficient (dimensionless); and pH_1 is the pH of the test solution. The power law coefficient

($\gamma = 0.25$) was derived by performing is linear regression on the results collected for HF-1 at pH(23°C) = 8.0 and 9.0 under near saturated conditions.

A comparison of the rates collected under dilute and saturated conditions shows that the decrease in element release rates with increasing HfO₂ mol% in the glass is not as strong as in silica saturated solutions (Fig. 11). For example, a comparison between the HF-1D and HF-1S rates (collected under dilute and saturated conditions) show a 1.8× difference in rate, whereas a comparison of the same data for HF-4D and HF-4S shows a 7× difference in the rates. These results illustrate that the addition of high-field strength cations have a significant impact on the dissolution rate of aluminoborosilicate glass. Changes in the structure through the distribution of Si—O—Hf bonds, which makes the glass network increasingly resistant to hydrolysis, with increasing hafnium content explains a portion of the observed decrease.

Comparing these results to dissolution rates measured by Bergeron et al. (2010) on Hf-bearing soda-lime borosilicate glasses (Fig. 11). These experiments were conducted under dilute conditions at T = 90°C, pH(23°C) = 7.0, and krypton adsorption Brunauer-Emmett-Teller (Kr-BET) (Brunauer et al., 1938). Due to the differences in experimental conditions between the two studies, the results from Bergeron et al. (2010) were normalized to the experimental conditions conducted in this study (see Supplemental Information). A comparison of these results suggests the rates measured by Bergeron et al. (2010) are comparable, but slightly faster than the rates measured in this study. The slightly higher rates are probably the result of aluminum being absent from the Hf-bearing and Zr-bearing soda-lime borosilicate glasses tested by Bergeron et al. (2010).

4.3 Effect of Hf on dissolved Si at glass-fluid interface

Monte Carlo simulations of the HF glass-water reaction were conducted to determine why the glass dissolution rate is affected by the concentration of Si in the influent solution. The main objective was to determine the reason for the deviation in dissolution rates measured under dilute and near saturated conditions. Fig. 12(a) shows the B release rates as a function of HfO₂ mole percent relative to that

calculated at 0 HfO₂ mol% and Fig. 12(b) shows the same data but presented as a function of the percentage of Si saturation concentration and relative to the B release rate obtained in dilute conditions. Each data point represents the average of five different simulations. All the simulations were run for 80,000 steps or until the glass slab dissolved entirely, whichever came first.

It should be noted that some of the simulations predicted the formation of a blocking layer at the glass-water interface through which water does not percolate, as is observed during simulations of the dissolution of sodium borosilicate glasses in static conditions (Aertsens, 1999; Devreux et al., 2001; Devreux et al., 2004; Kerisit and Pierce, 2012). In static conditions, as the Si concentration in solution increases due to the glass dissolution through hydrolysis, Si condensation at the glass surface becomes increasingly prominent and the combined effects of hydrolysis and condensation reactions lead to a decrease in the proportion of Si sites with a low number of connections to nearest-neighbor Si sites in favor of Si sites with a high number of such connections, which will be referred to as low-connectivity and high-connectivity sites, respectively. As this process is more advanced in the upper part of the altered layer, which has been in contact with the aqueous solution the longest, a dense Si layer can form eventually and thus prevents water from corroding the glass further.

In the conditions simulated here, the overall process is similar except that the source of silicon that deposits on the surface comes predominantly from the influent rather than from the dissolving glass due to the high flow and the presence of Si in the influent. Consequently, the likelihood for forming a blocking layer increases with increasing Si concentration in the influent. Additionally, as discussed in more detail below, the presence of Hf strengthens the altered layer and provides strong binding sites for silicon atoms that deposit on the surface. Therefore, the likelihood for forming a blocking layer also increases with increasing Hf content. As a result, a blocking layer formed within the time scale of the simulations for all glasses containing Hf when the Si concentration in the influent was 80% or 90% of the Si saturation concentration as well as for HfO₂ contents of at least 4.5%, 8.3%, and 11.5% when the Si influent concentrations were 70, 50, and 25% of the Si saturation concentration, respectively. In instances

where a blocking layer formed, the B release rate was calculated from the period of time preceding its formation. As the blocking layer forms more rapidly with increasing Si concentration in the influent and HfO₂ content, the B release rates determined in high Si influent concentrations and HfO₂ mole percents were extracted from fewer data points and thus carried higher uncertainties. Therefore, linear regressions that yielded R² values of less than 0.99 are not shown in Fig. 12.

The main finding, illustrated in Fig. 12(a), is that the extent of the decrease in the B release rate, relative to that determined for glasses without Hf, is dependent on the influent Si concentration, with steeper drops for larger amounts of Si in the influent. This trend is in qualitative agreement with the experimental results shown in Fig. 10 and 11. To explain this phenomenon, we first note that, in dilute conditions, there is essentially no condensation of Si at the surface and the decrease in rate with increasing Hf content is solely due to the strengthening effect of Hf, which makes the glass more difficult to dissolve. As the Si influent concentration increases, the rate of Si condensation at the glass surface also increases. For glasses that do not contain Hf, the hydrolysis and condensation reactions take place as described above, where low-connectivity sites are easily detached and the proportion of high-connectivity site increases. As the Hf content is increased, Hf atoms exposed at the surface provide sites where silicon atoms that deposit from the influent onto the surface can bind strongly. Because of this effect, newly-formed low-connectivity sites that would otherwise be dissolved easily now have a much longer residence time at the glass surface. This process, in effect, provides a greater density of anchor points from which altered layers can form with greater Si densities than in the absence of Hf. As a result and as illustrated in Fig. 13, water penetrates the glass at an even slower rate when the influent contains Si than in dilute conditions and thus the B release rate decreases to a greater extent. Fig. 12(b) offers a different way to visualize this effect. Indeed, it shows that, although the B release rates do decrease with increasing Si influent concentration in the absence of Hf, as is seen experimentally, the extent of decrease becomes more significant as the HfO₂ content is raised. Therefore, the experimental observation that the effect of Hf is greater in near-saturated conditions is explained by the Monte Carlo simulations to be due to an

increased probability for formation of a blocking layer and to an increased driving force for condensation of silicon at the glass surface in the presence of Hf.

To conclude this section, there are two effects of the presence of Hf on glass dissolution: (1) strengthening of the glass network and (2) stronger binding at the surface of Si condensing from aqueous solution. The first effect can be isolated in the simulations in dilute conditions and the role of the second effect increases as the Si concentration in the influent is increased. The two parts of Fig. 12 allow for a quantitative determination of these two effects. For example, Fig. 12(a) shows that strengthening of the glass network leads to a ~50% reduction in dissolution rate when 10 mol% HfO₂ is added to the glass and Fig. 12(b) shows that stronger surface binding in the presence of Hf results in a ~55% reduction in dissolution rate of the glass with 10 mol% HfO₂ when the influent concentration is 70% of the Si saturation concentration.

5 CONCLUDING REMARKS

The addition of high-field strength cations into the structure of borosilicate glass has a significant impact on its dissolution rate. Changes in the structure of network former elements, specifically boron, and the distribution of Si—O—Hf bonds with increasing hafnium content explains a portion of the observed decrease in the dissolution rate. The divergence in magnitude between the average steady-state release rates measured under dilute and near-saturated conditions are the result of silicon atoms in the influent binding to Hf atoms exposed at the surface forming a low connectivity site. Because of the longer residence time of low connectivity sites at the glass surface, the density of anchor sites from which altered layers can form with higher silicon densities are greater in the presence than in the absence of Hf. These results highlight the importance of improving our understanding of solid-water reactions with the goal of linking macroscopic reaction kinetics to nanometer scale interfacial processes. Overcoming this knowledge gap is key to the advancement of multi-scale or hybrid models used to forecast contaminant release from nuclear waste glass, and in a more global sense, the geochemical cycling of elements in the Earth's Critical Zone.

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8 FIGURES

Fig. 1 Schematic of the single-pass flow-through (SPFT) apparatus. 35

Fig. 2 ^{27}Al MAS spectra of the Hf glass series. 35

Fig. 3 ^{23}Na MAS spectra of the Hf glass series. 36

Fig. 4 ^{29}Si MAS NMR of the Hf glass series. 36

Fig. 5 ^{11}B MAS-NMR spectra of the Hf glass series. Inset shows the BO_3 line. 37

Fig. 6 Dissolution Rate, in $\text{g}/(\text{m}^2 \text{ d})$, for B as a function of mol% HfO_2 in glass for experiments conducted under diluted conditions and $\text{pH}(23^\circ\text{C}) = 9.0$ (top) and near-saturated conditions at $\text{pH}(23^\circ\text{C}) = 8.0$ (bottom). The rate measured for the HF-5 sample (20 mol% HfO_2) under near saturated conditions represents a maximum value. 38

Fig. 7 ^{11}B MAS-NMR spectrum analysis by the TOP method. Left panel shows the TOP spectrum and right panel shows two columns extracted at two chemical shifts (spectra are normalized to the same spinning sideband manifold maximum height). 39

Fig. 8 ^{11}B MQMAS-NMR spectrum (^{41}B region) of the Hf 10% glass. Right panel shows slices extracted at isotropic shifts (isotropic dimension) -4, 0 and 3 ppm. 39

Fig. 9 ^{11}B MQMAS spectrum (^{31}B region) and its projection (of the regions between dashed line) on the isotropic dimension. 40

Fig. 10 Comparison of the N_4 fraction (ratio of ^{41}B to total B) as a function of mol% MO_2 (where M = Hf or Zr) for the HF series glasses used in this study and the Hf-bearing glasses tested by Bergeron et al. (2010). Also shown for comparison are the results collected on Zr-bearing glasses by Bergeron et al. (2010) and Angeli et al. (2008). Note: For the HF-2 glass, the N_4 fraction was estimated by conducting a linear regression using the results collected for HF-1 through HF-5. 40

Fig. 11 Log_{10} (Dissolution Rate), in $\text{g}/(\text{m}^2 \text{ d})$, for B and Na as a function of mol% HfO_2 in glass for experiments conducted under diluted and near-saturated conditions. The B and Na values for 20 mol% HfO_2 represents a maximum value, the actual rates are much lower. 41

Fig. 12 Results of the Monte Carlo simulation showing (a) B release rates as a function of HfO_2 content relative to that at 0 HfO_2 mole percent for a range of Si concentrations in the influent expressed as percentages of the Si saturation concentration; and (b) B release rates as a function of the Si influent concentration relative to that obtained in dilute conditions for a range of HfO_2 contents. 41

Fig. 13 Results of the Monte Carlo simulation showing the deepest glass layers reached by the aqueous solution (where zero depth corresponds to the initial glass surface) as a function of computer steps for two HfO_2 contents in dilute conditions and at 70% of the Si saturation concentration. 42

Fig. 1 Schematic of the single-pass flow-through (SPFT) apparatus.

Fig. 2 ²⁷Al MAS spectra of the Hf glass series.

— Hf 0%
 — Hf 10%
 — Hf 15%
 — Hf 20%

Fig. 3 ^{23}Na MAS spectra of the Hf glass series.

— Hf 0%
 — Hf 10%
 — Hf 15%
 — Hf 20%

Fig. 4 ^{29}Si MAS NMR of the Hf glass series.

Fig. 5 ^{11}B MAS-NMR spectra of the Hf glass series. Inset shows the BO_3 line.

Fig. 6 Dissolution Rate, in g/(m² d), for B as a function of mol% HfO₂ in glass for experiments conducted under diluted conditions and pH(23°C) = 9.0 (top) and near-saturated conditions at pH(23°C) = 8.0 (bottom). The rate measured for the HF-5 sample (20 mol% HfO₂) under near saturated conditions represents a maximum value.

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Fig. 9 ^{11}B MQMAS spectrum (^{13}B region) and its projection (of the regions between dashed line) on the isotropic dimension.

Fig. 10 Comparison of the N_4 fraction (ratio of ^{14}B to total B) as a function of mol% MO_2 (where M = Hf or Zr) for the HF series glasses used in this study and the Hf-bearing glasses tested by Bergeron et al. (2010). Also shown for comparison are the results collected on Zr-bearing glasses by Bergeron et al. (2010) and Angeli et al. (2008). Note: For the HF-2 glass, the N_4 fraction was estimated by conducting a linear regression using the results collected for HF-1 through HF-5.

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9 TABLES

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Table 1. Target chemical compositions (weight %) of hafnium formulation (HF) glass series specimens.

Oxide	Sample ID				
	HF-1	HF-2	HF-3	HF-4	HF-5
Al_2O_3	8.0	6.8	5.8	5.0	4.4
B_2O_3	16.3	13.9	12.0	10.3	9.0
HfO_2	-	14.8	26.8	36.7	45.1
Na_2O	19.4	16.5	14.2	12.3	10.6
SiO_2	56.3	48.0	41.2	35.7	30.9
Total	100.0%	100.0%	100.0%	100.0%	100.0%

Table 2. Chemical compositions (mol%), Hf/Si, Si/Al, B/Al, B/Si, and select ΔH_f values for the hafnium formulation (HF) glass series specimens.

Oxide/Ratio	Sample ID				
	HF-1	HF-2	HF-3	HF-4	HF-5
Al_2O_3	5.02	4.76	4.50	4.25	4.00
B_2O_3	14.98	14.24	13.50	12.75	12.00
HfO_2	0.00	5.02	10.00	15.00	20.00
Na_2O	20.03	18.99	18.00	17.00	16.00
SiO_2	59.97	56.99	54.00	51.00	48.00
Total	1.00	1.00	1.00	1.00	1.00
Hf/Si	0.0	0.09	0.19	0.29	0.42
Si/Al	5.97	5.99	6.00	6.00	6.00
B/Al	2.98	2.99	3.00	3.0	3.00
B/Si	0.50	0.50	0.50	0.50	0.50
* ΔH_f	-	-42.4 ± 0.7	-44.5 ± 0.7	-	-

* ΔH_f values are in kJ/mol, were reported in Zhang et al. (2001), and were only measured for HF-2 and HF-3 glass compositions.

987 **Table 3. ^{27}Al MAS-NMR parameters of the Hf glass series.**

Glass	δ_{iso} (ppm)		C_Q (MHz)	
	mean	Std. Dev.	mean	Std. Dev.
HF-1	61.2	4.4	4.0	1.3
HF-3	62.0	4.3	4.3	1.4
HF-3 ^(a)	61.3	4.4	4.3	1.4
HF-4	62.1	4.4	4.1	1.4
HF-5	62.2	4.4	4.2	1.2
δ_{iso} – isotropic chemical shift C_Q – quadrupolar coupling constant η_Q – quadrupolar asymmetry parameter (constant value of 0.6) ^(a) from MQMAS, Lorentzian broadening $\lambda = 0.5 - 0.7$ ppm for all glasses.				

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990 **Table 4. ^{23}Na NMR parameters of the Hf glass series.**

Glass	δ_{iso} (ppm)		C_Q (MHz)	
	mean	Std. Dev.	mean	Std. Dev.
HF-1	-3.4	7.8	2.9	0.9
HF-3	-4.6	7.8	2.7	0.9
HF-4	-5.3	7.5	2.6	0.9
HF-5	-6.0	7.5	2.5	0.8
δ_{iso} – isotropic chemical shift C_Q – quadrupolar coupling constant η_Q – quadrupolar asymmetry parameter (constant value of 0.6)				

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Table 5. Single-pass flow-through experimental conditions and dissolution rates for HF-glass series and Bergeron et al. (2010).

Sample	T (°C)	pH (23°C)	Flow rate (mL/d)	^a SA (m ²)	^b q/S (m/s)	C _B (mg/L)	C _{Na} (mg/L)	C _{Si} (mg/L)	Rate B [g/(m ² d)]	Rate Na [g/(m ² d)]
near-saturated conditions										
HF-1S	23	8	2.0	1.21×10^{-3}	$1.92 (\pm 0.27) \times 10^{-8}$	2.67	9.33	88.59	$9.58 (\pm 1.68) \times 10^{-2}$	$1.19 (\pm 0.21) \times 10^{-1}$
HF-2S	23	8	2.0	1.34×10^{-3}	$1.73 (\pm 0.24) \times 10^{-8}$	0.19	0.75	89.49	$8.67 (\pm 1.62) \times 10^{-3}$	$1.33 (\pm 0.25) \times 10^{-2}$
HF-3S	23	8	2.0	1.25×10^{-3}	$1.86 (\pm 0.26) \times 10^{-8}$	0.05	0.25	90.32	$2.93 (\pm 0.58) \times 10^{-3}$	$4.52 (\pm 0.91) \times 10^{-3}$
HF-4S	23	8	2.0	1.39×10^{-3}	$1.67 (\pm 0.24) \times 10^{-8}$	0.02	0.08	88.19	$1.29 (\pm 0.30) \times 10^{-3}$	$2.30 (\pm 0.52) \times 10^{-3}$
HF-5S	23	8	2.0	1.21×10^{-3}	$1.79 (\pm 0.24) \times 10^{-8}$	0.0045	0.0206	90.09	$< 2.62 \times 10^{-4}$	$< 3.78 \times 10^{-4}$
HF-1S	23	9	19.25	2.58×10^{-4}	$8.66 (\pm 1.16) \times 10^{-7}$	0.22	0.79	88.37	$3.07 (\pm 0.32) \times 10^{-1}$	$4.11 (\pm 0.56) \times 10^{-1}$
HF-1S	23	9	19.22	2.36×10^{-4}	$9.45 (\pm 1.16) \times 10^{-7}$	0.18	0.70	87.54	$2.92 (\pm 0.44) \times 10^{-1}$	$3.97 (\pm 0.55) \times 10^{-1}$
pH corrected (near-saturated conditions)										
HF-1S	23	9	-	-	-	-	-	-	$1.70 (\pm 0.30) \times 10^{-1}$	$2.10 (\pm 0.37) \times 10^{-1}$
HF-2S	23	9	-	-	-	-	-	-	$1.54 (\pm 0.29) \times 10^{-2}$	$2.36 (\pm 0.44) \times 10^{-2}$
HF-3S	23	9	-	-	-	-	-	-	$5.18 (\pm 1.03) \times 10^{-3}$	$8.01 (\pm 1.60) \times 10^{-3}$
HF-4S	23	9	-	-	-	-	-	-	$2.29 (\pm 0.54) \times 10^{-3}$	$4.08 (\pm 0.92) \times 10^{-3}$
HF-5S	23	9	-	-	-	-	-	-	$< 4.64 \times 10^{-4}$	$< 6.70 \times 10^{-4}$
diluted conditions										
HF-1D	23	9	18.3	2.59×10^{-4}	$8.21 (\pm 1.16) \times 10^{-7}$	0.23	0.76	<1	$3.20 (\pm 0.47) \times 10^{-1}$	$3.72 (\pm 0.51) \times 10^{-1}$
HF-1D	23	9	19.1	2.34×10^{-4}	$9.44 (\pm 1.34) \times 10^{-7}$	0.21	0.68	<1	$3.34 (\pm 0.49) \times 10^{-1}$	$3.82 (\pm 0.53) \times 10^{-1}$
HF-2D	23	9	18.8	2.76×10^{-4}	$7.88 (\pm 1.11) \times 10^{-7}$	0.10	0.35	<1	$1.59 (\pm 0.28) \times 10^{-1}$	$1.96 (\pm 0.30) \times 10^{-1}$
HF-2D	23	9	1.9	1.22×10^{-3}	$1.82 (\pm 0.26) \times 10^{-8}$	2.43	7.01	<1	$8.82 (\pm 1.12) \times 10^{-2}$	$8.96 (\pm 1.15) \times 10^{-2}$
HF-3D	23	9	1.9	1.18×10^{-3}	$1.90 (\pm 0.27) \times 10^{-8}$	1.38	4.14	<1	$6.09 (\pm 0.78) \times 10^{-2}$	$6.42 (\pm 0.82) \times 10^{-2}$
HF-4D	23	9	1.9	1.27×10^{-3}	$1.72 (\pm 0.24) \times 10^{-8}$	0.35	1.06	<1	$1.63 (\pm 0.22) \times 10^{-2}$	$1.72 (\pm 0.23) \times 10^{-2}$
HF-5D	23	9	1.9	9.75×10^{-4}	$2.20 (\pm 0.31) \times 10^{-8}$	0.04	0.13	<1	$2.87 (\pm 0.54) \times 10^{-3}$	$3.08 (\pm 0.64) \times 10^{-3}$
Bergeron et al. (2010) – pH corrected, T corrected, surface area corrected										
H4C4	23	9	-	7.14×10^{-2}	-	-	-	<1	$3.68 (\pm 0.37) \times 10^{-1}$	-
H8C4	23	9	-	7.14×10^{-2}	-	-	-	<1	$2.32 (\pm 0.23) \times 10^{-1}$	-
H8C8	23	9	-	7.14×10^{-2}	-	-	-	<1	$9.07 (\pm 0.91) \times 10^{-2}$	-
^a SA – Surface Area ^b q/S – ratio of flow-rate (q) to sample surface area (S)										

Table 6. ^{11}B NMR parameters used to decompose the MAS-NMR spectra.

Site	δ_{iso} (ppm)		C_Q (MHz)	
	mean	Std. Dev.	mean	Std. Dev.
$\text{BO}_4(3\text{Si},1\text{B})$	0.1	1.1	0.6	0.2
$\text{BO}_4(4\text{Si},0\text{B})$	-1.5	1.0	0.2	0.1
$\text{BO}_3(\text{B})$	17.5	1.4	2.5	0.1
$\text{BO}_3(\text{Si})$	13.7	2.4	2.7	0.1
δ_{iso} – isotropic chemical shift C_Q – quadrupolar coupling constant η_Q – quadrupolar asymmetry parameter (constant value of 0.6).				

Table 7. Quantification of the boron sites as obtained from the fit of the ^{11}B MAS-NMR spectra

Glass	$\text{BO}_4(3\text{Si},\text{B})$	$\text{BO}_4(4\text{Si},0\text{B})$	$\text{BO}_3(\text{B})$	$\text{BO}_3(\text{Si})$	N_4
HF-1	48.9	26.6	16.9	7.6	75.5
HF-2*	-	-	-	-	72.4
HF-3	47.8	21.9	21.0	9.3	69.7
HF-4	47.5	17.9	24.4	10.3	65.4
HF-5	44.0	16.2	28.1	11.8	60.2
*Value estimated by performing a linear regression of N_4 fraction versus molar fraction HfO_2 content for HF-1 through HF-5. Equation of the line – $\text{N}_4 = -0.752 \times \text{molar HfO}_2 + 0.7616$.					