**Dissolution Rate of Borosilicate Glass SON68: A Method of Quantification
Based upon Interferometry and Implications for Experimental and Natural
Weathering Rates of Glass**

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Re-submitted to *Geochimica et Cosmochimica Acta* on February 20, 2015.

Abstract

Rates of glass dissolution from laboratory and field studies are often considered to be irreconcilable, although potential causes for the difference, such as solution saturation state and increasing surface area from progressive weathering, have not been explored in depth. The dissolution rate of SON68 glass, the non-radioactive analog of the French R7T7 composition, was determined in a single-pass flow-through (SPFT) system at 90 °C and pH 9 over a silica-saturation interval. Dissolution rates were determined on both powdered and monolithic specimens by assaying the concentration of elements released from glass to effluent solution. In addition, rates of twelve monolithic specimens were quantified using a Vertical Scanning Interferometry (VSI) method. The method entails measuring the difference in height between a reference and reaction surface. The height difference is proportional to the dissolution rate. By adjusting the relative position of the reacted surface to average surface roughness, the effects of surface area on the dissolution rate can be minimized. Values of the dissolution rate, based upon chemical assay of the effluent solution on the one hand, and VSI methods on the other, were compared. In general, rates determined by the two methods are within a factor of 2×. The difference in rates may be due to the presence of a reaction layer that develops on the glass surface, resulting in an underestimation of the height difference measurement. The dissolution rates of SON68 glass in silica-saturated solutions were then compared to rates previously determined on basalt glass in natural weathering environments [Gordon and Brady, 2002, *Chem. Geol.* **190**, 113-122]. When adjusted for differences in temperature and pH, the ranges of borosilicate and basalt glass dissolution rates overlap, indicating that laboratory and field rates can be reconciled and that the principal control on glass dissolution is solution saturation with respect to amorphous silica.

1. INTRODUCTION

An internationally supported strategy for the safe disposal of high level nuclear waste is to immobilize radioactive materials within a chemically durable borosilicate matrix (e.g., Gin et al. 2013a; Jantzen et al., 2010). The viability of this strategy hinges on maintaining exclusion of groundwater from a geologic repository and a demonstrated slow rate of release of radioactive elements from the glass should groundwater contact the waste package. Accordingly, a great deal of attention has been focused on quantifying dissolution kinetics of borosilicate glass through laboratory experiments. Many of the experimental investigations have centered on determining dissolution rates as a function of temperature, pH and glass composition (e.g., Abraitis et al., 2000a; Arab et al., 2008; Bergeron et al., 2010; Icenhower et al., 2008; Inagaki et al., 2012; McGrail et al., 1997; Pierce et al., 2008; Utton et al., 2013), and these experiments have been conducted in dilute (i.e., non-silica saturated) solutions. Experiments carried out under dilute solutions serve two main purposes: They can be used to parameterize the rate equation, and they quantify the forward rate of reaction, the maximum velocity of the rate at a given set of experimental conditions. The latter is useful in setting the upper bound for the safety case applied to repository performance.

Rates determined on natural glasses obtained from weathering environments indicate that rates measured in the laboratory are orders of magnitude faster (Gordon and Brady, 2002). The discrepancy in dissolution rates was attributed to differences in solution saturation state, although the difference was large enough (4 to 7 orders of magnitude) to suggest that factors other than solution saturation state contribute to the difference. A similar critique of laboratory silicate mineral dissolution rates was published by White and Brantley (2003). They also found orders of magnitude differences between field and laboratory rates and imputed these differences to both “intrinsic” (surface area changes over time) and “extrinsic” (solution saturation state and

diminished contact between solids and solution due to low degrees of hydraulic saturation)
factors. The two studies cited above precipitated an epistemological dilemma for glass chemists:
How can we assure the public that radionuclide release rates from the source term are accurately
determined? If dissolution rate data from the laboratory yield inherently wrong data, then why
should laboratory experiments be conducted in the first place?

As an example of a response to this question for silicate mineral dissolution, a combined field
and modeling investigation indicated that once solution saturation state and clay precipitation
rates are accounted for, silicate mineral dissolution rates approach expected values (Maher et al.,
2009). A similar exercise has not been carried out for glass. Experiments carried out in both
static and flow-through systems have shown that increasing concentrations of silicic acid
correlate with slower glass dissolution rates. However, far fewer experiments have been
undertaken to quantify the dissolution rates of glass at or near saturation with respect to silica
saturation. Comparing dissolution rates in dilute and silica saturated solutions, the available data
indicate that rates decrease by four to five orders of magnitude (see Rebiscoul et al., 2007; Curti
et al., 2006; Frugier et al., 2005; 2008; Jégou et al., 2000; Neeway et al., 2011). The question
remains as to whether or not the saturation state of the solution controls glass dissolution or, as
suggested by White and Brantley (2003), changes in reactive surface area over time impose a
major influence on the rate of reaction.

The objectives of this paper are to evaluate whether or not laboratory rates can be compared
favorably to field rates and if uncertainties related to the evolution of surface area with time
affect glass rate measurements. Experiments were carried out on the borosilicate glass SON68,
the non-radioactive analog to the French R7T7 composition. A number of investigators have
argued that basalt is a natural analog to borosilicate glass (e.g., Techer et al. 2000; Wolff-

Boenisch et al., 2004), so results on the one can be compared to those on the other. Experiments were conducted over a solution saturation state interval at a fixed pH (9) and temperature (90 °C). Both powders and monoliths (1.5 cm × 1.5 cm × 4 mm “coupons”) of glass were used. Dissolution rates were calculated based on release of elements from glass to solution in a single-pass flow-through (SPFT) system. In addition, rates were calculated on glass monoliths using Vertical Scanning Interferometry (VSI). In this method, the height difference between a reference surface, not exposed to solution, and a surface that has undergone dissolution with attendant surface retreat, was measured. The difference in height between these two surfaces is proportional to the rate, and this value can then be compared to that obtained from element release rates determined on the same monolithic sample. We first show that rates obtained by VSI are comparable to those obtained on powders and monoliths by traditional methods, a finding consonant with results reported earlier by Icenhower et al. (2003). Together, these independent and complementary determinations of the rates can show how close or how far the rates are from one another and can be used to evaluate the efficacy of the VSI method for rapid, accurate determination of rates. More importantly, the VSI method minimizes surface area uncertainties and allows us to evaluate the proposition that changes to sample surface area contributes to major differences between field and laboratory rates. Other investigators have reported results of techniques aimed at quantifying surface roughness of glass as dissolution reactions proceed (Donzel et al., 2003; Hopf and Pierce, 2014; Mellott and Pantano, 2013) and it is clear that glass surfaces exposed to solution roughen substantially over time. Because the rate of dissolution measured by VSI is proportional to the height difference described above, the position of the reaction surface can be averaged over large areas to account for an increase in surface roughness as dissolution proceeds. The uncertainty in this method can therefore be

included into the rate uncertainty, providing for a more reproducible rate measurement. The experimentally-determined dissolution rates can then be adjusted for differences in temperature and pH to the field-based rates. We then compare the rates obtained in this study, in addition to those reported in the literature, to field rates and identify the control over glass dissolution.

2. MATERIALS AND METHODS

2.1. Glass composition and preparation of run materials

The glass used in this study was batched at Pacific Northwest National Laboratory (PNNL) using reagent grade materials. The glass components were blended in large (>100 g) quantities and melted in a Pt crucible at 1500°C in a resistance-heated furnace. Molten glass was poured onto a metal plate, cooled, then crushed and melted again to obtain chemical homogeneity. The glass was then poured into molds to produce rectangular bars approximately $1.5 \times 1.5 \times 20$ cm long. The resulting glass bars appeared to be homogeneous with few bubbles or inclusions and showed no signs of devitrification. The chemical composition of the SON68 glass, both on a weight and mole percent basis, is listed in Table 1.

Glass coupons (monoliths) with dimensions of $\sim 1.5 \text{ cm} \times 1.5 \text{ cm} \times 4 \text{ mm}$ thick were cut from the glass bars described above. The angles between edges and adjacent faces on these rectangular objects were 90° and thicknesses were uniform across each monolith. The faces of the coupons were polished in ethanol using decreasing grit size and a final polish using a diamond suspension was utilized. One of the two principal faces of the coupons was polished using a Chemical-Mechanical Polishing (CMP) technique. An alkaline solution ($\text{pH} \sim 10$) containing colloidal silica was applied to a lapping wheel and the coupons were temporarily attached to a metal plate using CrystalbondTM. The metal plate with the attached monoliths was placed on the rotating lapping wheel for several minutes. The coupons were then removed from the metal plate and

gently rinsed in ethanol. The surface areas of the coupons were determined by measuring the dimensions of the coupons with a digital caliper. Masses of the coupons were determined using a four place digital balance and the accompanying density could be compared with the value determined independently using the Archimedes method. In every case, the density determined by the measured dimensions and the mass of the coupons match the value determined by the Archimedes method within 5% relative (average 3% relative). These data assured us that the surface area measured by digital caliper are correct and can be used in determining dissolution rates accurately.

Powdered samples for dissolution experiments were prepared by crushing glass into gravel-size fragments and then reducing the size of the fragments using a ceramic ball mill apparatus. The resulting fine powders were then dry sieved and size fractions segregated using standard sieves to obtain a variety of size fractions. Most of the powdered experiments utilized the -100 to +200 mesh fraction (149 to 75 μm diameter), and select experiments made use of -60 to +100 and -200 to +325 (74 to 45 μm and 250 to 150 μm diameter size fractions, respectively) mesh size fractions. The powders were ultrasonically cleaned in methanol to remove fine fragments that adhered to the powders of the desired size range. This step required several iterations and ceased once the decanted liquid was clear. The powders were dried and kept in a desiccator until use.

The geometric surface area of the glass powder was estimated using the formula:

$$SA = (3 \cdot m) / (\rho \cdot r) \quad (1)$$

where m is the mass in grams, ρ is the density in grams per cubic meter and r is the average radius of a grain of glass powder in meters. The density of the glass was measured independently

by the Archimedes method, which yielded a value of $2.78 \times 10^6 \text{ g/m}^3$. The geometric surface areas of the various powder size fractions, based on Eq. (2), are listed in Table 2.

The surface areas of the powders were also determined using the B.E.T. method (Brunauer et al., 1938) with Kr as the adsorbing gas. The B.E.T. method yielded surface area values that are $\sim 3\times$ larger than that of the corresponding geometric surface area measurements. The B.E.T. determined surface areas of the powders are listed in Table 2. For reasons outlined in Icenhower and Steefel (2013), the geometric surface area is preferred over that measured by B.E.T.

2.2. Initial solution compositions

The solutions used in these experiments were made by mixing small amounts of the organic THAM or TRIS (*tris hydroxymethyl aminomethane*) buffer (0.015 M) with deionized water (DIW) and then adding minor volumes of reagent grade HNO_3 to bring the solution to the pH value of 9. Tournié et al. (2013) reported data demonstrating that complexation of boron with TRIS molecules, resulting in spuriously faster dissolution rate values compared to solutions lacking the TRIS buffer. They noted that this effect occurs with relatively concentrated buffers ($>0.04 \text{ M}$) and when HCl is used to adjust the final pH of the solution. The concentration of TRIS in our solutions is far lower (0.015 M) and we used HNO_3 , not HCl, so the effect of our buffer choice on dissolution rates is likely to be small. For solutions containing 15, 60 and 150 ppm Si, we added an appropriate amount of analytical grade Si (1,000 ppm SPEX[®]) standard. The SPEX Si standard contains trace amounts of HF, but evidence for enhanced rates was not detected. The solutions were then titrated with KOH to achieve a pH of 9. The *in-situ* pH values of the solutions at 90 °C were calculated using EQ3/6 and are listed in Table 3. For all solutions the pH values at the temperature of interest are lower than those at ambient temperature. Therefore, the fraction of Si manifested as silicic acid (H_4SiO_4) is $>95\%$.

2.3. Single-pass flow-through method

All experiments were performed in a single-pass flow-through (SPFT) system in which a solution continuously flows into a Teflon[®] reactor, reacts with the glass sample, and then exits to collection vials, as illustrated schematically in Figure 1. Solution transfer from the input reservoir to the reactor was actuated by an automated programmable syringe pump (Kloehn; model 7400) through 1/8 inch (O.D.) Teflon lines. Each pump had four valves that distribute input solution to four separate reactors set to individual flow rates (200 to 6 mL/day). The reaction vessels consisted of *polytetrafluoroethane* (PTFE) lids and jars that screwed together to form a 60 mL reactor. Lines carrying input and effluent solutions to and from the reactors were accommodated by twin ports in the lid. Input solutions and reactors were kept at 90 °C by residing in a constant temperature oven. It was necessary to keep input solutions at the temperature of interest (90 °C) so that dissolved silica would remain in solution. Because the input solution was drawn into the syringe on the pump outside the oven, there was a risk that precipitation of silica could occur as the solution sat at room temperature. The residence time of the solution in the syringe was, however, short (<1 hour), and we never observed precipitation of silica in the syringe.

Aliquots of effluent solution were routinely checked to ensure that pH control was maintained during the experiments. Over the course of the experiments, the measured effluent pH was 8.9 ± 0.1 . A second aliquot of the effluent solution was acidified by spectroscopic grade nitric acid and the chemical composition of the solution was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) methods. Typically, three blank solutions were drawn before glass was added to the reactor. The blank solutions were analyzed for background

concentrations of elements of interest and, together with analyses of starting solution aliquots, assured us that contamination was not a factor.

Because dissolution rates of glass are sensitive to solution saturation state, we conducted our experiments on powdered and monolithic specimens at the same flow-rate (q) to sample surface area (S). On a plot of dissolution rate versus the log (q/S), the combination of slow flow rate coupled with high surface area results in solutions that are concentrated in silicic acid, and the corresponding rates are relatively slow. On the other hand, when flow-rates are fast and sample surface area is low, the solution becomes dilute and rates increase. At some value of log (q/S), the dissolution rate becomes independent of solution saturation state and the value of the rate reaches a constant “dissolution plateau,” or the forward rate of reaction, which is the maximum rate for the conditions of the experiment. As part of our investigation, we wished to determine if the dissolution rates of powdered and monolithic specimens were the same for identical log (q/S) values, and if the rates determined by VSI methods could replicate the “dissolution plateau” behavior.

Experiments were terminated when the concentrations of elements in the effluent solution became invariant with respect to time (steady-state conditions). Typically, this would take from three to ten weeks, depending on the flow-rate and the concentration of dissolved silica in solution. Extended experiments (up to fifteen weeks) were performed to document the long-term dissolution rates.

2.4. Interferometry

Chernov et al. (1986) and investigators from Tohoku University (Maiwa et al., 1990; Onuma et al., 1990; 1994) pioneered the technique of interferometry to the study of crystal growth and dissolution. Lüttge and co-workers applied the technique systematically to the study of Earth

235 materials, reporting the dissolution rates of dolomite (Lüttge et al., 2003), plagioclase feldspar
236 (Arvidson et al., 2004), calcite (Arvidson et al., 2003), and muscovite (Kurganskaya and Lüttge,
237 2013). Other investigators have exploited the technique to determine dissolution anisotropy
238 (Daval et al., 2013). Interferometry is a technique that makes use of reflected white light from a
239 polished sample surface to measure minute vertical height differences. The Vertical Scanning
240 Interferometer (VSI) is similar to a conventional microscope, but is equipped with a Mirau
241 objective that splits a beam of light into two paths, one that serves as a reference beam and the
242 other that impinges upon the sample surface. In VSI, the sample height with respect to the light
243 source moves over several micrometers through the focal plane using a calibrated piezoelectric
244 transducer (PZT). The scan height is a function of the instrument and objectives used, but the
245 vertical height difference between objects on a rough surface are typically only several μm or
246 mm maximum, easily within the range of most VSI instruments. Each scan takes only a few
247 seconds and many thousands of measurements on the surface are made. Minute height
248 differences on the sample surface are detected through the phase difference between the sample
249 and reference beam and this is expressed as interferometric fringes. The fringes represent areas
250 of constructive and destructive interference between the reference and impinging beam of light.
251 Height differences detected in this interferogram are computed using a high-resolution CCD
252 camera that measures differences in contrast in sets of fringes. The data are then presented as a 3-
253 D map over several hundred μm in lateral extent and the height difference between a reference
254 and a reacted surface can be measured. Because relatively large areas of the sample surface can
255 be measured and processed, representative features can be determined, such as surface
256 roughness. For more details on the interferometric technique, the interested reader is referred to
257 Lüttge and Arvidson (2010) and Lüttge et al. (2003).

Figure 2 illustrates the experimental strategy. A masking agent is applied to a polished glass coupon (monolith) cut with nearly parallel top and bottom sides. The mask prevents solution from coming into contact with a portion of the glass surface. In our experiments, the masking agent is an RTV silicon-based sealant that is stable in water at the experimental conditions. The coupon with mask is placed into a flow-through reactor system (described below) for a prescribed amount of time. The portion of the glass exposed to solution dissolves, and the surface height retreats over the duration of the experiment. The coupon is then removed from the reactor, carefully dried and the mask removed. The area covered by the mask preserves a reference surface to which a height difference with respect to the reacted surface can be measured. The height difference can be converted to a dissolution rate by:

$$rate = (\rho \cdot \Delta h) / \Delta t \quad (2)$$

where the rate [$\text{g}/(\text{m}^2 \cdot \text{d})$] is equal to the product of the density, ρ (g/m^3), times the height difference, Δh (m), divided by elapsed time, Δt (days). Because even a small preserved area of a millimeter or so in diameter yields a large circumference at the microscopic scale, numerous height difference measurements can be made on a single sample. Depending upon the quality of the images and the size of the reference surface, numerous height measurements can be made and multiple rate determinations can be averaged and uncertainties based upon these rates computed. Multiple areas can be masked on a monolithic sample and the analysis procedure can be repeated over a longer period of time to yield dissolution rate values over time. In this way, we can establish the constancy of the rate over time.

If dissolution is simple, the method is an accurate way to determine rates, but the accuracy of the VSI method may be limited by the presence of a secondary layer. Numerous investigators have reported that the glass surface exposed to solution is converted into a hydrated secondary

layer, either as a result of re-condensation of bonds after more labile elements, such as boron and sodium, are removed (e.g., Valle et al., 2010) or as the result of coupled dissolution-precipitation processes (e.g., Geisler et al., 2010). It is not within the scope of this investigation to differentiate between these two competing models, but simply to point out that the presence of a secondary layer may affect the calculated dissolution rate obtained by VSI by underestimating the height difference. This potential effect is illustrated in Figure 3, which is a representation of the measured height difference, Δh , the secondary layer thickness, and the total dissolution depth. The total dissolution depth represents the depth to which boron, the element that is used as an index of the dissolution process, has been removed. In studies of the reaction layer, investigators have emphasized that boron is nearly absent in the secondary layer (e.g., Gin et al., 2011; 2013b; Valle et al., 2010). Accordingly, if the secondary layer is relatively thick compared to the height difference measured between the reference surface and the top of the reaction layer, the dissolution rate would be underestimated. The data presented in this investigation provides us with the opportunity to evaluate the effects of a reaction layer on rates determined by VSI.

The VSI instrument is a 7300 NewView manufactured by Zygo and is equipped with a 10 $\times$ and 50 $\times$ objective and a 2 $\times$ magnifying insert. The lateral and vertical resolution was calibrated by a NIST-traceable precision calibration standard. The standard consists of a Si wafer in which a set of furrows were machined to a precise depth and distance from each other. Lateral resolution can be calibrated to determine the actual dimensions of the pixel-to-pixel spacing of the camera. The uncertainty on the vertical resolution is ~ 7 nm and lateral resolution is on the order of 200 nanometers.

2.5. Scanning Electron Microscopy

Glass coupons were examined by Scanning Electron Microscopy (SEM) at Lawrence Berkeley National Laboratory (Zeiss LS10) both before and after reaction with solution. A small piece of a monolith corner was cut, mounted in epoxy, and polished. The polished mounts were held in place on an aluminum stub by double-sided sticky carbon-tape and coated with gold. The SEM used for the analysis of the solid samples is equipped with an energy-dispersive spectrometer and a backscattered electron detector. Images of the glass fragments were acquired in back-scattered electron mode. Mapping of the distribution of elements within the image field ($K\alpha$ x-ray mapping) and Energy Dispersive Spectrometry (EDS) was performed using Aztec software. Accelerating potentials of 15 – 20 keV and currents of 20 nA were used to image these specimens.

2.5. Dissolution rates and error calculations

The error analysis employed for the dissolution rate depended upon the method used to determine dissolution rates. For the VSI-based rates, a simple error analysis based upon rules for product and quotient terms was used:

$$relative\ rate\ error = rate \cdot \sqrt{\left[\left(\frac{x}{X}\right)^2 + \left(\frac{y}{Y}\right)^2 + \left(\frac{z}{Z}\right)^2\right]} \quad (3)$$

where x , y and z are the uncertainties on the parameters in equation (1) (namely, ρ , Δh and Δt).

The uncertainties on density, Δh and Δt are 5%, 20 nanometers and 60 seconds, respectively. The value of ± 20 nanometers was selected based on measurements of average surface roughness on the surfaces of reacted glass monoliths. In every case, the variation in Δh was larger than the error in (3), which led us to list the standard deviation of the resulting rates as the uncertainty. For the most part, the uncertainties on the rate based on interferometry are ~ 10 to 20% (2σ) in dilute solutions, but became larger in silica-bearing solution (up to 40% 2σ) as the height difference between the reference and reaction surface diminished.

In the case of rates determined on monoliths or powders based on release of elements from glass to solution, a more sophisticated error analysis was needed. Dissolution rates were calculated based on the steady-state concentration of the element of interest in the effluent, the flow-rate of solution, the chemical composition of the glass, and the specific surface area of the glass. Normalized rates were calculated using the following formula:

$$r_{i,j} = \frac{(C_{i,j} - \bar{C}_{i,b})q_j}{f_i S_j} \quad (4)$$

where $r_{i,j}$ is the normalized release rate [g/(m²·d)] based on element i at the j^{th} sampling, $C_{i,j}$ is the concentration (g/L) of the element, i , in the effluent at the j^{th} sampling, $\bar{C}_{i,b}$ is the average background concentration (g/L) of the element of interest, q_j is the flow-through rate (L/d) at the j^{th} sampling, f_i is the mass fraction of the element in glass (dimensionless), and S_j is the average surface area (m²) of the glass. The average flow-rate was determined gravimetrically on collected effluent samples.

Determining the experimental uncertainty of the dissolution rate takes into account all the uncertainties of each parameter in Eq. (4). For uncorrelated random errors the standard deviation of a function $f(x_1, x_2, \dots, x_n)$ is given by:

$$\sigma_f = \sqrt{\sum_{i=1}^n \left(\frac{\partial f}{\partial x_i} \right)^2 \sigma_i^2} \quad (5)$$

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 .

In the case of the dissolution of a solid, the function of interest is Eq. (4). Substituting (4) into (5) and converting to relative standard deviations, σ_r/r , gives:

$$\hat{\sigma}_r = \sqrt{\frac{(\hat{\sigma}_c c_i^{out})^2 + (\hat{\sigma}_b c_i^{in})^2}{(c_i^{out} + c_i^{in})^2} + \hat{\sigma}_{f_i}^2 + \hat{\sigma}_S^2 + \hat{\sigma}_q^2} \quad (6)$$

Errors for $\hat{\sigma}_c$, $\hat{\sigma}_b$, $\hat{\sigma}_{f_i}$, and $\hat{\sigma}_q$ are 10%, 10%, 3% and 5%, respectively, and for $\hat{\sigma}_s$ are 15% for powders and 5% for monoliths. Typical uncertainties for SPFT dissolution rates are approximately 35% for powders and 25% (both 2σ) for monoliths.

In some cases the concentrations of elements in the effluent solution were very low. We regard the concentration of an element in solution to be quantitatively valid only if the measured concentration is greater than a factor of $3\times$ above the established background. Thus, the lower limit of quantification is different for each element and depends on the background concentration of the element in the initial solution and the machine detection limit. Dissolution rates based upon Si release were only computed for experiments in which no Si was added to the initial solution.

3. RESULTS

3.1 Dissolution rates based upon chemical assay

Tables 4 lists the experimental parameters used in this study and Table 5 the steady-state concentrations of the elements, along with measured uncertainties, in the effluent solution. A wide range in flow-through rates (~ 10 to 200 mL/d) coupled with adjustments to sample surface area (either by changing the mass of powder, the powder size fraction or the number of monoliths in the reactor) were used to produce a range of q/S values (a factor of $130\times$). A wide range of q/S values is needed to define the forward rate of reaction and, in this case, to make comparisons between powdered and monolith rates and rates based on VSI measurements.

Dissolution rates of powdered and monolithic specimens, based on steady-state release of elements to solution, are listed, along with their associated $2\text{-}\sigma$ uncertainties, in Table 6. The data indicate that there is an inverse correlation between the concentration of dissolved Si in solution and glass dissolution rates. In general, the dissolution rates were congruent for experiments in

which Si concentrations were low with differences in rates based on release of different elements less than a factor of 2×. For the experiments carried out at the highest concentrations of added Si (Experiments 27 and 29), concentrations of Al, Ca and Na were near or below their respective lower limit of quantification, indicating that these elements were retained in the secondary phases. Examination of the post-run materials by SEM indicated the presence of Na-Ca-Al zeolites, which were identified on the basis of morphology and EDS data (data not shown).

3.2 Dissolution rates based upon interferometry

Figure 4 is a representative VSI image obtained using the 50× objective of a $55 \times 73 \mu\text{m}$ area of a polished glass surface that was *not* exposed to solution. The surface of the glass is flat, smooth and featureless (with the exception of two small pits) with a maximum height difference across the profile of ~9 nm. Figure 5 is a VSI image (10× objective) of a glass surface reacted for 100 days in a solution that contained 58 ppm Si. A ~250 μm long height profile revealed a maximum height difference of ~60 nanometers, the largest height difference we measured in our reacted samples. More typically, the maximum height difference on a reacted surface is on the order of 20 nanometers. Height profiles on reacted glass monoliths indicate that surface roughness, and hence, surface area increases during reaction. Because the dissolution rate based on the VSI technique is proportional to the measured difference between reference and reacted surface, it is important to define the height of the dissolution roughened surface. For the situation depicted in Figure 5, an average surface can be drawn that splits the difference between the highest peak and the lowest valley. Thus, in the worst case, the height difference between the reference and reacted surface is ± 30 nanometers. As shown below, the uncertainty in the height difference between reference and reacted surfaces, based upon multiple measurements, is always the same or slightly larger than the height difference measured on the reacted surface. Therefore,

the uncertainty based on multiple height difference measurements between reference and reacted surfaces is the more conservative indicator of dissolution rate uncertainty.

Figure 6 is a VSI image obtained using a 10× objective of a $105 \times 140 \mu\text{m}$ area of a reacted glass surface. The left-hand side depicts the 3-D image while the right-hand side shows the camera (reflected light) image. Upon removing some glass coupons from the reactor, the hydrous secondary layer dehydrates and shrinks, causing the cracks seen in the images. For experiments run in solutions without added Si (Experiments 21 and 33), we found a correlation with dehydrated and cracked gel layers developing on the glass surface. For these experiments, it was easy to partially remove the gel layer with a cotton swab and measure the thickness of the gel. Figure 7a is a VSI image of the reacted surface in which a portion of the gel layer has been removed. Figure 7b is a reflected light image of the same area and it is easy to identify the areas where the gel layer was removed. The two profiles (Figures 7c and d) indicate that the gel layer for this glass at these particular experimental conditions is 300 – 600 nm thick. Where it was possible to do so (coupons 38, 39, 41 and 43 from Experiments 21 and 33), we removed the gel layer from around the reference surface to make a height difference measurement that reflects the total depth of reaction. It was not possible to do this completely, so the measured height difference has a relatively high uncertainty associated with it, but this uncertainty does not undercut the conclusions of this study. In other cases where we could not accurately determine the gel layer thickness, the rates based on interferometry and from chemical assays of effluent solution were compared. If the two rates were similar in value, we could conclude that the presence of a secondary layer does not substantially compromise the VSI rate.

Figure 8 displays representative VSI images of two areas on a glass monolith (coupon 41) exposed to solution with the masks removed and the corresponding height difference profiles.

Figures 8a and c are the 3-D images in which the relatively high elevation regions, or “plateaus,” are the reference surface preserved by the chemical mask. The surrounding areas are the exposed surfaces that have retreated $\sim 3\mu\text{m}$, as indicated by the corresponding profiles on the right-hand side of the figure (Figures 8b and d). Note the sharp change of relative height and the lack of large height differences on the reacted glass surface, at least on the scale of the figures.

Because of the surface roughness observed on some reacted glass surfaces (see Figure 5), there is some question concerning whether or not we can accurately and reproducibly measure small height differences between reference and reaction surfaces. Figure 9 indicates that we can. In this figure, the height difference between the reference and reacted surfaces is only 27 nanometers, but the difference in height with respect to surface roughness for this sample is distinct enough to lend confidence to the measurement.

Table 7 lists the experimental parameters, the depth of surface retreat, and the calculated average dissolution rates of the monolithic specimens used in this study. The surface retreat measurements are listed alongside the uncertainty of the measurement, based upon repeated height measurements. For monoliths in which we were able to partially remove the gel layer, for example, coupon 41, the measurement made on Day 18 lists the uncertainty as 300 nm, which is the same magnitude as the thickness of the gel layer measured on the same sample (Figure 7).

Table 7 also lists the average dissolution rate of the monoliths based on chemical assay of the effluent solution from the same experiment. For nearly every conjugate VSI and assay dissolution rate value, the difference between the two rates is less than a factor of $2\times$. The exceptions to this are Experiments 27 and 29, in which the difference in VSI and assay rates varies between a factor of 2.1 and $3.5\times$. These experiments were conducted in relatively Si-rich

solutions and we discuss the discrepancy between rates based on chemical assay and surface retreat depth measurements below.

The close correspondence between rate values determined by VSI and by chemical assay of effluent solutions is illustrated in Figure 10. On this figure, the average rates of dissolution are plotted versus q/S . Rates determined on powdered and monolithic specimens are the same within uncertainty, provided that powder surface areas are normalized on a geometric, rather than B.E.T. basis (see Icenhower and Steefel, 2013). In addition, the rates determined by VSI and chemical assay on the same monolithic samples, are also identical within experimental uncertainty. Note also that rate behavior of all glass specimens is the same; i.e., the rates show a dependence on solution saturation state at low values of q/S , but become independent of q/S , defining the forward rate of reaction for the temperature and pH of the experiment. The forward rate of reaction determined by these data is $0.30 \text{ g}/(\text{m}^2 \cdot \text{d})$, which is the same value obtained with an overlapping and larger data set reported by Icenhower and Steefel (2013), and is also within experimental uncertainty of the rate reported in Jollivet et al. (2012).

Figure 11 illustrates the surface retreat measured on the coupons versus time. The lines, drawn as a guide to the eye, extend from the origin and through the points to form a linear array that indicate that the rates of surface retreat are relatively constant over time. The data indicate that for fast flow-through rates and dilute solutions reproducible measurements can be obtained in the first ~20 days. The average rates of surface retreat differ by a factor of $320\times$ between the fastest and slowest rates. The data also indicate that the rate of surface retreat, and therefore dissolution rate, partially depends on the concentration of dissolved Si; i.e., higher concentrations of dissolved Si correlate with slower dissolution rates. In apparent contradiction to this simple idea, the two fastest flowing experiments both had measured Si concentrations of 4 ppm, yet the

surface retreat rates were different (-24 vs. -148 nm/day). These two different surface retreat rates indicate that something other than only dissolved Si is controlling the dissolution rate. One potentially important difference in solution chemistry is aluminum, which was a factor of 10× higher in concentration in the slower of the two dissolution rates (Table 5; compare Experiments 21 and 33). We argued in a previous contribution that dissolved Al plays an important role in suppressing the dissolution rate of borosilicate glass (Icenhower and Steefel, 2013), consonant with results reported by other investigators (e.g., Abraitis et al., 2000b).

The depth at which boron is removed from the glass can be calculated from knowledge of the dissolution rate and glass density:

$$depth (m) = \frac{r_B \cdot t}{\rho} \quad (7)$$

where r_B is the dissolution rate [$\text{g}/(\text{m}^2 \cdot \text{d})$] of the glass based on chemical assay of the release of boron to solution, t is time (days), and ρ is the density of glass (g/m^3). The calculated depth of boron removal can then be compared with the height change measured by VSI. The usefulness of this comparison is that a depth of boron removal value that is larger than the measured height change may indicate that a secondary layer, characterized by a lack of boron, may be present. Calculated depths of boron removal, based on Equation (7), are listed in Table 7 and are plotted against measured height change depths in Figure 12. Figure 12a shows the full range of data, most of which lies near the line with a slope of one, indicating that calculated depths of boron removal and measured height differences closely correspond. The fastest surface retreat shows the greatest apparent discrepancy from the calculated depths, but the actual difference in rates is only 1.5× [0.300 vs. 0.458 ($\text{g}/\text{m}^2 \cdot \text{d}$); c.f., Table 7]. Figure 12b is a close-up of the data near the origin showing that as the concentration of Si in solution increased, many of the data points plot above the one-to-one line, indicating the presence of a secondary layer. In nearly every case

where we could compare VSI- and chemical assay-based dissolution rates, the difference in rate values are generally less than 2 $\times$, and a maximum difference of 3.5 $\times$ (Table 7 and Figure 12). On the other hand, the calculated depths of boron removal become relatively large with respect to the measured height difference. For example, in the experiments with the highest concentrations of added Si (Experiments 26 and 27), the measured height differences are as small as ~30% of the calculated boron removal depth, which may indicate that the secondary layer is significantly thicker than that which was dissolved. In order to determine if such a layer exists, and how this might affect the VSI measurements, we conducted an SEM investigation of the reacted glass monoliths.

3.3 SEM results

The mounted and polished glass fragments were imaged in back-scattered electron (BSE) mode and representative images are displayed in Figure 13. In the BSE images, the medium grey regions correspond to glass whereas the dark grey to epoxy. A fragment of glass that was *not* exposed to dissolution was imaged to determine if the CMP technique produced a reaction layer; the images did not reveal a secondary layer, at least on the scale investigated. On the other hand, the glass exposed to solution indicated the presence of a secondary layer. Figures 13a and b show evidence for a thin, relatively bright colored strip at the glass—epoxy interface. Figure 13a is an image of a fragment of the glass exposed to solution in which no Si was added initially (Solution 1, Table 3). Figure 13b looks similar to that of 13a, but in this case, the glass was *not* exposed to solution. We conclude from these two images that the thin light colored strip at the interface is likely an artifact of the polishing of the glass fragments. In contrast to these images, Figures 13c and d show evidence for a slightly wider relatively light colored band at the glass—epoxy interface. The bands appear to be approximately 1 μm wide and, because lighter colors

correspond to areas of relatively higher average atomic number, the band in this case may represent an area of secondary layer formation. In order to determine the reason for the apparently higher atomic number in this region we obtained x-ray maps of representative areas that displayed higher BSE values.

Figure 14a is a BSE image of a portion of the glass fragment retrieved from Experiment 27, in which Si was added to the contacting solution up to 40% of the saturation value. A series of $K\alpha$ x-ray maps were obtained from this region, and several of these are displayed along with the BSE image (Figures 14b, c and d). Figures 14b and c show that both O and Si are concentrated in a zone several μm wide at the interface compared with the rest of the (unaltered) glass. Figure 14d is a K $K\alpha$ x-ray map, and shows relatively high concentrations of K in the interface compared to the rest of the glass. Note that the sizes of the pixels are exaggerated, making it appear that K is more widely distributed than it actually is. The point here is that potassium is present in a region at the glass-water interface. Because the SON68 glass is practically devoid of K, the source of potassium is the KOH we used to adjust the solution pH. It is clear that K penetrated into the reaction layer and the relatively high concentration of K in the secondary layer may explain the higher BSE signal. The presence of a secondary layer is conclusively demonstrated, although the resolution of the images prevents us from determining its thickness.

4. DISCUSSION

4.1 Comparison of experimental rates to natural weathering rates of basaltic glass

In order to assess if laboratory determined rates are similar in value to those obtained on natural glasses in the field, we collected rates determined in experiments in which the solution was saturated with respect to amorphous silica and compared these rates with those determined on basalt glass (Gordon and Brady, 2002). We assumed that silica-saturated or near saturated

conditions prevail in natural weathering environments that contain volcanic rocks, including basalt, as borne out by numerous field studies (e.g., Kamei et al., 2000; Cruz et al. 1999; Kristmannsdóttir and Ármannsson, 2004; Gambardella et al., 2005; Locsey et al., 2012). Rates of dissolution of the borosilicate SON68 glass at silica saturation, from this investigation and from Frugier et al. (2008), Curti et al. (2006) and Chave et al. (2007) are listed in Table 8. These rates are in units of g/(m²·d), whereas those in Gordon and Brady (2002) are listed in mol/(cm²·s). After converting the units into mol/(cm²·s), the rates were projected down to a temperature of 10 °C, the average temperature in the weathering environment reported by Gordon and Brady (2002). We used an Arrhenius expression:

$$\log\left(\frac{k_1}{k_2}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (8)$$

where E_a is the activation energy (76 kJ/mol; a value recommended by Frugier et al., 2008), R is the gas constant [8.314×10⁻³ kJ/(mol·K)], k_1 and k_2 are the rates [mol/(m²·s)] at T_1 and T_2 (K), respectively, for the temperature correction. The pH correction was made using the expression:

$$\log_{10}r_c = \log_{10}r_u + \eta(9 - pH_T) \quad (9)$$

where r_c and r_u are the corrected and uncorrected rates, η is the pH power law coefficient (dimensionless), and pH_T is the pH of the test solution. The power law coefficient was assigned a typical literature value of 0.40 (e.g., Pierce et al., 2008). We also adjusted the borosilicate glass dissolution rates to a geometric surface area normalization.

Table 8 lists the dissolution rates of borosilicate glass projected to 10 °C and with the adjustments discussed above alongside the rates of the basalt glass determined by Gordon and Brady (2002). It is evident that the rates of the borosilicate glass SON68 overlap with those of the basaltic glass, but the rates reported in this investigation are faster by a factor of ~5×.

However, even in this case, our main point is that large differences between field and laboratory rates do not exist when solution saturation state is taken into account. Although Gordon and Brady (2002) cited experimental work on natural (including basalt) and anthropogenic glass that indicated a large discrepancy between field and laboratory rates, all of the experiments referred to in their study were conducted under dilute solution conditions. At the time this paper (Gordon and Brady, 2002) was written, there were only very limited data on borosilicate glass dissolving in silica-saturated solutions. Note also that the choice of reasonable dissolution parameters (experimental activation energy, the pH power law coefficient, etc.) do not substantially affect these conclusions: Dissolution rates are not many orders of magnitude faster than rates determined on natural glasses.

4.2 Comparison of surface retreat and element removal depth in borosilicate glass

Surface retreat during dissolution correlates with the calculated depths of boron removal (Eq. 7) and the results reported by other investigators on SON68 glass can potentially be used to indicate if our results are consistent. Donzel et al. (2003), Gin et al. (2013b), Guittonneau et al. (2011) and Valle et al. (2010) reported rates of boron removal depth (in nm/d) are 67, 2.16, 2.09, and 70, in the order in which these studies are cited above. In all cases, experiments were performed at 90 °C and pH values near 9. In the experiments of Gin et al. (2013b) and Guittonneau et al. (2011), the rate of the depth of glass reacted was calculated based on the dissolution rate divided by the glass density, whereas for Donzel et al. (2003) the depth rate was calculated by AFM, and Valle et al. (2010) by a combination of SEM, SIMS depth profiles, and dissolution rate divided by glass density. These rates of depth of reaction overlap in value with the rates of surface retreat reported herein (Table 7).

Our investigation indicates that the rate of surface retreat depends on the concentration of dissolved Si in solution, so it is not always possible to make valid comparisons to other work. The data reported in Gin et al. (2013b), however, provided us with the opportunity to compare their value of alteration rate with ours. Gin et al. (2013b) reported results of a test performed on a SON68 glass monolith at 90 °C and a pH value of 9 that took place over a 25.75 year interval. The concentration of Si in solution was 50 to 60 ppm, which is nearly identical to the concentration of Si in Experiment 27 (Table 5). Assuming that the rate of alteration is relatively constant, as Figure 11 indicates, we can then compare the depth of alteration for the three sample times for Experiment 27 (62.96, 76.83 and 100 days) based on the rate of alteration reported by Gin et al. (2013b) (2.16 nm/d). The calculated depths, using this rate, are 136, 166 and 216 nm and compare reasonably well with the surface retreat measured by VSI for this experiment: 98, 186 and 347 nm (Table 7).

The dissolution rates reported in Gin et al. (2013b) were not conducted at silica saturation, so there is some question if calculated boron removal depths accord with our results in silica-bearing solutions. The experiments carried out by Chave et al. (2007) at 90 °C, pH = 9 and silica-saturated conditions provides us with the opportunity to compare results. In two experiments, the calculated boron removal depth rates are 0.39 and 0.78 nm/d, which are comparable to surface retreat rates determined on coupons 46 and 48 in the silica-saturated Experiment 29 (0.42 and 0.50 nm/d; Table 7). These data indicate that techniques for determining the dissolution rate by measuring surface retreat (interferometry, profilometry, atomic force microscopy) on glass can supply useful data.

Although the extent of agreement with other investigators is encouraging, there is one important area of potential disagreement that we wish to highlight. In many previous papers, the

depth of reaction is implied to be the depth of boron removal only, with no wholesale dissolution of the glass. In other words, the reaction is “isovolumetric”, in that labile cations, such as Na and B are plucked out of the glass, and the residuum re-condenses without a change in volume. The data presented in this study indicates that the reactions are not “isovolumetric”; at least some dissolution accompanies glass reactivity over the wide range of experimental conditions examined herein.

5. CONCLUSIONS

The kinetics of silicate dissolution are subject to a variety of parameters (T , pH, identity and concentrations of rate-affecting elements, fraction of surface area in contact with solution, e.g.) and identifying the dominant control over dissolution at various stages of reaction is still a major point of contention. An increase in surface area over time has been advanced as a reason why silicate mineral dissolution rates determined in the laboratory do not match those obtained in the field. We investigated the dissolution rate of SON68 glass at constant temperature and pH over a dissolved silica concentration interval using both the chemical assay of effluent solution and a method based upon measuring surface retreat of a monolithic sample using interferometry. Rates determined from the two methods agreed within experimental uncertainty. In addition, the method based on interferometry showed that the evolution of surface roughness added uncertainty to the relative height measurement, but could be folded into the calculated error on the rate measurement. The contribution of surface roughness to the rate uncertainty is relatively minor. Comparing the rates of glass dissolution at silica saturation with field rates determined for natural silicate glass in the field showed that, when differences in temperature and pH are accounted for, there is no significant (orders of magnitude) difference between rates. Therefore, although the reactive surface area of borosilicate glass undoubtedly increases with reaction

progress, the data presented herein indicate that this control is minimal and that the concentration of silica in solution exerts a major governing influence on rates.

ACKNOWLEDGEMENTS

The comments of three anonymous reviewers improved the manuscript and their efforts are gratefully acknowledged. We thank Joern Larsen and April Van Hise for providing ICP-MS analyses and Li Yang and Giuseppe Saldi for B.E.T. analyses. We thank Joe Ryan for supplying the glass and David Singer for help with Chemical Mechanical Polishing (CMP). We thank Burnham Petrographics for SEM sample preparation. Funding for this work was provided by the Separations and Waste Form Campaign, Office of Nuclear Energy of the U.S. Department of Energy under Contract Number DE-AC02-05Ch11231 with Berkeley Lab.

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774

775

776 **Figure Captions**

777 **Fig. 1.** Schematic of the single-pass flow-through system.

778 **Fig. 2.** Cartoon illustrating the VSI sample dissolution strategy.

779 **Fig. 3.** A cartoon illustrating the possible relationships amongst the measured height difference
780 between the reference surface and the top of the reaction layer surface, the depth of the reaction
781 layer, and the depth of boron removal. If the reaction layer depth is large with respect to the Δh
782 measured by interferometry, then the apparent dissolution rate based on VSI will be much slower
783 than realized.

784 **Fig. 4.** Interferometry image of a $55 \times 73 \mu\text{m}$ area of a polished glass monolith before exposure
785 to solution. Analysis by interferometry shows that the height difference along the profile is 9 nm.

786 **Fig. 5.** Interferometry image ($690 \times 520 \mu\text{m}$) of a reacted glass surface (coupon 50) that was
787 reacted for 100 days (A). The profile (B) indicates an unusually large degree of surface
788 roughness ($\sim 60 \text{ nm}$). The average surface height is shown by the white dashed line.

789 **Fig. 6.** Interferometer (left) and reflected light (right) images of a $105 \times 140 \mu\text{m}$ portion of a
790 glass coupon (#38) that has undergone post-run cracking as a result of cooling and contraction of
791 a hydrated secondary layer. This cracking occurred most frequently in glasses exposed to
792 solutions lacking added aqueous Si.

793 **Fig. 7.** VSI (A) and reflected light (B) image of a reacted glass surface (coupon 41) that has
794 undergone cracking due to dehydration after the coupon was removed from the reactor and dried.
795 Relatively high elevations are shown in red, medium elevations in yellow and low elevations in
796 green and blue. The lowest elevations correspond to areas where the gel layer has been removed,
797 revealing the underlying glass. Height profiles across the surface show that the glass run for 100
798 days developed a gel layer 300 – 600 nanometers thick. The total surface retreat for this sample
799 is 3,050 nanometers.

800 **Fig. 8.** Three-dimensional interferometer images (A and C) and corresponding height profiles (B
801 and D) of two $360 \times 270 \mu\text{m}$ areas on a glass monolith surface. Red and blue areas are regions of
802 relative high and low elevation, respectively. The profiles indicate 3.6 and 3.4 μm height
803 differences between the reacted and preserved (masked) areas, respectively.

804 **Fig. 9.** VSI image (A) showing masked area (red and orange) and reacted surface (green and
805 yellow) for an experiment conducted in silica-saturated solution (coupon 51). The position of the
806 height profile is shown in purple. The height profile (B) indicates at least 27 nm of height
807 difference between the reference and reacted surface.

Fig. 10. Plot of the $\log_{10}$ of the rate of glass dissolution versus the ratio of flow rate to surface area. Dissolution rates were determined by two different methods: chemical assay of elements released from glass to solution (powdered and monolithic glass), and by interferometry on monoliths. Rates determined on monoliths by interferometry (grey diamonds) overlap with rates determined by chemical assay within experimental error.

Fig. 11. Plot of surface retreat (nm) of dissolving glass coupon versus time for the SON68 glass at 90 °C and pH 9. Rates of retreat are relatively constant over time and depend, in part, on the amount of dissolved Si in solution.

Fig. 12. (A) Plot of measured height difference (by VSI) versus calculated depth of boron removal (both in nm) for glass monoliths. The data indicate good correspondence between measured and calculated rates, except for the fastest VSI rate, which may overestimate the rate. The line has a slope of one. (B) Close up of (A) showing that with increasing Si in the contacting solution, the calculated depth of boron removal is deeper than the measured value, indicating that a boron-deficient secondary layer may be present.

Fig. 13. Back-scattered electron images of glass (medium grey) mounted in epoxy (dark grey). (A) Glass from Experiment #21, in which no silicon was added to the contacting solution. (B) Glass that was *not* contacted with solution. The thin lighter grey color at the interface between glass and epoxy may be an artifact of polishing. (C) Glass from Experiment #29, in which silicon was added up to saturation with respect to amorphous silica. (D) Glass from Experiment #27, in which silicon was added up to 40% of the saturation value. In both (C) and (D), the lighter grey color at the interface may be due to the presence of elements whose average atomic number is greater than that of pristine glass.

Fig. 14. (A) Back-scattered electron image of glass (medium grey) set in epoxy (dark grey). The glass is from Experiment #27, in which the Si was added to the contacting solution to 40% of the saturation value. (B) and (C) An O $K\alpha$ and Si $K\alpha$ map showing higher concentrations of O and Si in the secondary reaction layer relative to pristine glass. (D) A K $K\alpha$ map displaying the distribution of K in the secondary reaction layer. The source of the K is the KOH added to solution to modify the solution pH.

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Table 1. Nominal chemical composition (in weight and mole %) of the SON68 glass.

oxide	wt%	mol%
SiO ₂	45.85	52.73
B ₂ O ₃	14.14	14.03
Al ₂ O ₃	5.00	3.39
Na ₂ O	10.22	11.39
Li ₂ O	1.99	4.60
Cs ₂ O	1.12	0.27
CaO	4.07	5.01
SrO	0.35	0.23
BaO	0.62	0.28
Fe ₂ O ₃	3.03	1.31
NiO	0.43	0.40
ZnO	2.53	2.15
CdO	0.03	0.02
MnO ₂	0.39	0.32
SnO ₂	0.02	0.01
Ag ₂ O	0.03	0.01
Cr ₂ O ₃	0.53	0.24
ZrO ₂	2.75	1.54
MoO ₃	1.78	0.85
Y ₂ O ₃	0.20	0.06
La ₂ O ₃	0.93	0.20
Ce ₂ O ₃	0.97	0.20
Pr ₂ O ₃	0.46	0.10
Nd ₂ O ₃	2.04	0.42
TeO ₂	0.23	0.10
P ₂ O ₅	0.29	0.14
Total	100.00	100.00

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Table 2: Size fractions of powders used in this investigation and their corresponding calculated geometric surface areas.

Size fraction I.D. #	1	2	3
Mesh size	60 to 100	100 to 200	200 to 325
Corresponding diameter (µm)	250 to 150	150 to 75	75 to 45
Mean radius (µm)	100	56.3	30.0
Calculated geometric SA (m ² /g) × 10 ²	1.09	1.94	3.64
B.E.T. SA (m ² /g) × 10 ²	2.80	4.90	9.60

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Table 3: Starting solution compositions used in SPFT experiments. The values of pH at 90 °C were calculated using EQ3/6.

Solution #	Added Si (ppm)	pH at 90 °C
1	0	7.57
2	15	7.58
3	60	7.63
4	150	7.73

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Table 4: Experimental parameters, including the geometric surface area, flow rate and the ratio of flow (q) to surface area (S) with associated uncertainties (in parentheses).

Expt. #	Solution #*	Solid [M] or [P]**	Time (hours)	Powder Mass (g)	Size Fraction†	SA (geo) (m ²)	Flow (mL/d)	q/S (m/s)
1	1	M	504	NA	NA	2.56x10 ⁻³ (1.28x10 ⁻⁴)	205 (6.16)	9.00x10 ⁻⁷ (5.25x10 ⁻⁸)
2	1	P	504	0.156	2	3.01x10 ⁻³ (4.52x10 ⁻⁴)	205 (6.15)	7.88x10 ⁻⁷ (1.42x10 ⁻⁷)
3	1	P	504	0.498	2	9.61x10 ⁻³ (1.44x10 ⁻³)	66.1 (1.98)	8.23x10 ⁻⁸ (1.48x10 ⁻⁸)
21	1	M	1,721	NA	NA	1.65x10 ⁻³ (8.26x10 ⁻⁵)	13.6 (0.108)	9.51x10 ⁻⁸ (5.54x10 ⁻⁹)
22	1	M	1,507	NA	NA	1.65x10 ⁻³ (8.26x10 ⁻⁵)	13.3 (0.400)	9.29x10 ⁻⁸ (5.42x10 ⁻⁹)
23	1	P	905	0.050	1	5.45x10 ⁻⁴ (8.18x10 ⁻⁵)	200 (5.99)	4.24x10 ⁻⁶ (6.48x10 ⁻⁷)
24	1	P	1,498	1.100	2	2.12x10 ⁻² (3.18x10 ⁻³)	20.0 (0.600)	1.09x10 ⁻⁸ (1.67x10 ⁻⁹)
25	2	M	977	NA	NA	1.32x10 ⁻³ (6.60x10 ⁻⁵)	14.2 (0.426)	1.25x10 ⁻⁷ (7.27x10 ⁻⁹)
26	2	P	905	0.150	2	2.91x10 ⁻³ (4.37x10 ⁻⁴)	22.5 (0.675)	8.94x10 ⁻⁸ (1.37x10 ⁻⁸)
27	3	M	1,498	NA	NA	1.38x10 ⁻³ (6.90x10 ⁻⁵)	10.4 (0.312)	8.78x10 ⁻⁸ (5.12x10 ⁻⁹)
28	3	P	1,507	0.150	2	2.91x10 ⁻³ (4.37x10 ⁻⁴)	24.6 (0.738)	9.80x10 ⁻⁸ (1.50x10 ⁻⁸)
29	4	M	2,420	NA	NA	1.52x10 ⁻³ (7.60x10 ⁻⁵)	13.8 (0.414)	1.06x10 ⁻⁷ (6.16x10 ⁻⁹)
30	4	P	2,420	0.150	2	2.91x10 ⁻³ (4.37x10 ⁻⁴)	25.9 (0.777)	1.03x10 ⁻⁷ (1.58x10 ⁻⁸)
31	4	P	2,420	0.383	3	1.39x10 ⁻² (2.09x10 ⁻³)	15.6 (0.468)	1.30x10 ⁻⁸ (1.98x10 ⁻⁹)
32	4	P	2,420	2.013	3	7.34x10 ⁻² (1.10x10 ⁻²)	9.20 (0.276)	1.45x10 ⁻⁹ (2.22x10 ⁻¹⁰)
33	1	M	432	NA	NA	5.16x10 ⁻⁴ (2.58x10 ⁻⁵)	200 (5.99)	4.48x10 ⁻⁶ (2.61x10 ⁻⁷)
36	2	P	309	0.055	1	6.00x10 ⁻⁴ (9.00x10 ⁻⁵)	87.6 (2.63)	1.69x10 ⁻⁶ (2.59x10 ⁻⁷)
37	2	P	309	0.121	1	1.32x10 ⁻³ (1.98x10 ⁻⁴)	182 (5.46)	1.54x10 ⁻⁶ (2.36x10 ⁻⁷)

Notes: *See Table 3. **[M] and [P] refer to monolith or powder, respectively. †See Table 2.

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Table 5: Average concentrations of elements (ppb) released from glass to solution. The uncertainty of the measurement is in parentheses.

Expt. #	Al	B	Ba	Ca	Cs	Li	Na	Si
1	176 (3)	243 (4)	--	149 (2)	61 (1)	54 (1)	423 (8)	1,731 (22)
2	374 (5)	375 (7)	--	191 (3)	80 (1)	73 (1)	618 (8)	1,811 (23)
3	1,347 (17)	978 (15)	--	701 (5)	292 (3)	252 (3)	2,189 (27)	5,448 (63)
21	454 (10)	730 (11)	98 (1)	404 (3)	179 (2)	154 (2)	1,445 (24)	3,860 (69)
22	499 (10)	593 (7)	176 (2)	376 (3)	170 (2)	122 (1)	1,018 (90)	4,218 (39)
23	60 (2)	68 (1)	8 (0.1)	d.l.	15 (0.1)	14 (0.2)	132 (26)	4,144 (60)
24	1,440 (137)	1,601 (15)	199 (3)	1,015 (4)	502 (6)	325 (2)	3,570 (51)	8,575 (56)
25	261 (5)	427 (5)	53 (0.4)	216 (2)	104 (1)	89 (1)	722 (14)	19,325 (115)
26	388 (7)	448 (4)	54 (0.5)	216 (2)	107 (1)	90 (1)	754 (13)	19,471 (116)
27	29 (1)	161 (3)	17 (0.3)	91 (2)	47 (0.4)	35 (0.2)	135 (9)	63,575 (1,718)
28	44 (2)	139 (3)	16 (0.2)	80 (2)	45 (0.3)	32 (0.2)	377 (10)	58,356 (2,059)
29	21 (1)	32 (2)	15 (0.3)	105 (3)	30 (0.4)	8 (1)	237 (3)	168,000 (5,000)
30	d.l.	50 (2)	11 (0.3)	111 (3)	35 (1)	12 (1)	237 (6)	179,000 (7,000)
31	17 (1)	418 (17)	63 (0.9)	113 (3)	132 (2)	98 (4)	741 (19)	165,000 (7,000)
32	d.l.	3,271 (118)	152 (2)	104 (3)	2,305 (39)	810 (6)	7,953 (190)	210,000 (12,000)
33	46 (1)	63 (1)	8 (0.1)	d.l.	15 (0.1)	14 (0.3)	112 (25)	3,933 (48)
36	114 (4)	139 (7)	27 (0.8)	911 (31)	30 (1)	29 (2)	222 (5)	16,100 (300)
37	110 (4)	118 (6)	22 (0.2)	1,060 (23)	27 (0.7)	25 (2)	194 (6)	15,800 (600)

Notes: d.l. = detection limit. -- = not determined.

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Table 6: Normalized average dissolution rates [g/(m²·d)] of glass based on element release. 2-σ uncertainties are in parentheses.

Expt. #	Al	B	Ba	Ca
1	2.80x10 ⁻¹ (3.80x10 ⁻²)	2.41x10 ⁻¹ (5.77x10 ⁻²)	--	1.89x10 ⁻¹ (3.05x10 ⁻²)
2	5.22x10 ⁻¹ (1.63x10 ⁻¹)	2.74x10 ⁻¹ (8.62x10 ⁻²)	--	2.24x10 ⁻¹ (7.03x10 ⁻²)
3	6.44x10 ⁻² (2.02x10 ⁻²)	8.33x10 ⁻² (2.61x10 ⁻²)	--	2.99x10 ⁻² (9.32x10 ⁻³)
21	7.33x10 ⁻² (1.02x10 ⁻²)	7.41x10 ⁻² (1.00x10 ⁻²)	7.79x10 ⁻² (1.04x10 ⁻²)	6.00x10 ⁻² (8.29x10 ⁻³)
22	7.83x10 ⁻² (1.08x10 ⁻²)	5.90x10 ⁻² (7.87x10 ⁻³)	1.40x10 ⁻¹ (1.86x10 ⁻²)	5.70x10 ⁻² (7.53x10 ⁻³)
23	3.47x10 ⁻¹ (1.13x10 ⁻¹)	2.93x10 ⁻¹ (9.18x10 ⁻²)	2.94x10 ⁻¹ (9.20x10 ⁻²)	d.l.
24	2.76x10 ⁻² (1.01x10 ⁻²)	1.87x10 ⁻² (5.84x10 ⁻³)	1.84x10 ⁻² (5.74x10 ⁻³)	1.79x10 ⁻² (5.58x10 ⁻³)
25	5.35x10 ⁻² (7.43x10 ⁻³)	5.67x10 ⁻² (7.55x10 ⁻³)	5.53x10 ⁻² (7.31x10 ⁻³)	4.29x10 ⁻² (6.29x10 ⁻³)
26	5.91x10 ⁻² (1.86x10 ⁻²)	4.28x10 ⁻² (1.34x10 ⁻²)	4.11x10 ⁻² (1.28x10 ⁻²)	3.11x10 ⁻² (9.51x10 ⁻³)
27	--	1.52x10 ⁻² (2.04x10 ⁻³)	1.28x10 ⁻² (1.73x10 ⁻³)	1.29x10 ⁻² (1.80x10 ⁻³)
28	--	1.46x10 ⁻² (4.60x10 ⁻³)	1.33x10 ⁻² (4.17x10 ⁻³)	1.26x10 ⁻² (3.96x10 ⁻³)
29	--	3.55x10 ⁻³ (5.91x10 ⁻⁴)	1.28x10 ⁻² (1.78x10 ⁻³)	--
30	d.l.	5.52x10 ⁻³ (1.79x10 ⁻³)	9.19x10 ⁻³ (2.94x10 ⁻³)	--
31	--	5.79x10 ⁻³ (1.87x10 ⁻³)	6.09x10 ⁻³ (2.16x10 ⁻³)	--
32	d.l.	5.10x10 ⁻³ (1.63x10 ⁻³)	2.47x10 ⁻³ (7.77x10 ⁻⁴)	--
33	3.09x10 ⁻¹ (4.74x10 ⁻²)	3.00x10 ⁻¹ (4.12x10 ⁻²)	2.98x10 ⁻¹ (3.97x10 ⁻²)	d.l.
36	3.22x10 ⁻¹ (1.03x10 ⁻¹)	2.56x10 ⁻¹ (8.20x10 ⁻²)	3.85x10 ⁻¹ (1.22x10 ⁻¹)	2.22 (7.13x10 ⁻¹)
37	2.82x10 ⁻¹ (9.10x10 ⁻²)	2.15x10 ⁻¹ (6.36x10 ⁻²)	2.82x10 ⁻¹ (8.80x10 ⁻²)	2.39 (7.56x10 ⁻¹)

Table 6: Continued

Expt. #	Cs	Li	Na	Si
1	2.46×10^{-1} (3.27×10^{-2})	2.48×10^{-1} (3.44×10^{-2})	1.86×10^{-1} (2.87×10^{-2})	3.03×10^{-1} (4.18×10^{-2})
2	2.81×10^{-1} (8.77×10^{-2})	2.91×10^{-1} (9.12×10^{-2})	2.53×10^{-1} (8.00×10^{-2})	2.74×10^{-1} (8.63×10^{-2})
3	3.42×10^{-2} (1.07×10^{-2})	3.44×10^{-2} (1.08×10^{-2})	3.49×10^{-2} (1.09×10^{-2})	3.22×10^{-2} (1.01×10^{-2})
21	7.53×10^{-2} (1.01×10^{-2})	7.44×10^{-2} (1.01×10^{-2})	8.07×10^{-2} (1.10×10^{-2})	7.62×10^{-2} (1.06×10^{-2})
22	7.15×10^{-2} (9.49×10^{-3})	5.77×10^{-2} (7.63×10^{-3})	5.74×10^{-2} (1.30×10^{-2})	8.09×10^{-2} (1.08×10^{-2})
23	2.92×10^{-1} (9.13×10^{-2})	2.99×10^{-1} (9.37×10^{-2})	2.97×10^{-1} (1.66×10^{-1})	3.42 (1.07)
24	2.44×10^{-2} (7.62×10^{-3})	1.80×10^{-2} (5.62×10^{-3})	2.39×10^{-2} (7.49×10^{-3})	2.05×10^{-2} (6.41×10^{-3})
25	5.61×10^{-2} (7.44×10^{-3})	5.63×10^{-2} (7.46×10^{-3})	5.22×10^{-2} (7.21×10^{-3})	--
26	4.18×10^{-2} (1.31×10^{-2})	4.10×10^{-2} (1.28×10^{-2})	3.97×10^{-2} (1.25×10^{-2})	--
27	1.51×10^{-2} (2.12×10^{-3})	1.55×10^{-2} (2.04×10^{-3})	7.04×10^{-3} (2.51×10^{-3})	--
28	1.51×10^{-2} (4.80×10^{-3})	1.62×10^{-2} (5.05×10^{-3})	1.75×10^{-2} (5.69×10^{-3})	--
29	4.44×10^{-3} (2.10×10^{-3})	4.43×10^{-3} (8.83×10^{-4})	--	--
30	5.37×10^{-3} (2.87×10^{-3})	6.34×10^{-3} (2.21×10^{-3})	--	--
31	6.40×10^{-3} (2.03×10^{-3})	6.45×10^{-3} (2.07×10^{-3})	3.03×10^{-3} (1.15×10^{-3})	--
32	2.02×10^{-2} (6.34×10^{-3})	7.99×10^{-3} (2.50×10^{-3})	6.89×10^{-3} (2.18×10^{-3})	--
33	2.95×10^{-1} (3.92×10^{-2})	2.97×10^{-1} (4.18×10^{-2})	2.87×10^{-1} (1.44×10^{-1})	3.37 (4.64×10^{-1})
36	2.24×10^{-1} (7.15×10^{-2})	2.49×10^{-1} (8.25×10^{-2})	2.25×10^{-1} (7.08×10^{-2})	--
37	1.83×10^{-1} (5.80×10^{-2})	1.94×10^{-1} (4.67×10^{-2})	1.78×10^{-1} (5.66×10^{-2})	--

Notes: d.l. = detection limit. -- = rates cannot be determined due to high background concentration.

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Table 7. Experimental parameters, surface retreat, retreat rate, VSI dissolution rate and comparison to rates obtained by chemical assay of effluent solutions in single-pass flow-through system. The numbers in parentheses are the uncertainties. The uncertainties associated with the dissolution rates are the 2-σ errors.

Expt. #	Solution #	Time (days)	No. of Meas. ¹	Coupon #	Surface retreat (nm)	Retreat rate (nm/day)	VSI Dissolution rate [g/(m ² ·d)]	Assay Dissolution rate [g/(m ² ·d)]	Calculated Depth (nm)
33	1	11.35	52	41	1,480 (220)	130	3.61x10 ⁻¹ (1.15x10 ⁻¹)	3.00x10 ⁻¹ (4.12x10 ⁻²)	1,225 (89)
33	1	18.35	64	41	3,030 (300)	165	4.58x10 ⁻¹ (9.13x10 ⁻²)		1,980 (145)
21	1	16.79	21	43	424 (54)	25	7.00x10 ⁻² (1.80x10 ⁻²)	7.41x10 ⁻² (1.00x10 ⁻²)	448 (60)
21	1	30.79	43	39	758 (55)	25	6.83x10 ⁻² (9.97x10 ⁻³)		821 (110)
21	1	41.90	63	38	926 (88)	22	6.13x10 ⁻² (1.16x10 ⁻²)		1,117 (150)
25	2	30.96	25	45	451 (42)	15	4.04x10 ⁻² (7.48x10 ⁻³)	5.67x10 ⁻² (7.55x10 ⁻³)	631 (47)
25	2	42.02	36	52	536 (76)	13	3.42x10 ⁻² (1.01x10 ⁻²)		857 (64)
27	3	62.93	27	44	98 (17)	1.6	4.31x10 ⁻³ (1.49x10 ⁻³)	1.52x10 ⁻² (2.04x10 ⁻³)	344 (26)
27	3	76.83	21	51	186 (25)	2.4	6.71x10 ⁻³ (1.80x10 ⁻³)		420 (31)
27	3	100.00	15	50	347 (31)	3.5	9.62x10 ⁻³ (1.73x10 ⁻³)		547 (41)
29	4	71.79	32	48	30 (14)	0.42	1.71x10 ⁻³ (1.27x10 ⁻³)	3.55x10 ⁻³ (5.91x10 ⁻⁴)	92 (6)
29	4	100.81	17	46	50 (9)	0.50	1.38x10 ⁻³ (5.06x10 ⁻⁴)		129 (8)

Notes: ¹Number of measurements.

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Table 8. Dissolution rates of borosilicate glass at 90 °C, pH = 9 in silica-saturated solutions, projected to 10 °C, pH = 7 with a geometric surface area normalization compared to basalt glass dissolution determined by Gordon and Brady (2002)

Dissolution rate [g/(m ² ·d)] T = 90 °C, pH = 9	Dissolution rate [mol/(cm ² ·s)] T = 10 °C, pH = 7	Reference
1.7 × 10 ⁻⁴	3.60 × 10 ⁻¹⁹	Frugier et al. (2008)
1.3 × 10 ⁻⁴	2.75 × 10 ⁻¹⁹	Curti et al. (2006)
2.75 × 10 ⁻⁴	5.82 × 10 ⁻¹⁹	Chave et al. (2007)
1.35 × 10 ⁻³	2.80 × 10 ⁻¹⁸	This work
--	2 – 5 × 10 ⁻¹⁹	Gordon and Brady (2002)

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Figure 1.

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Figure 2.

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Figure 3.

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Figure 4.

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Figure 5.

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Figure 6.

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Figure 7.

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Figure 8.

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Figure 9.

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Figure 10.

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Figure 11.

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Figure 12.

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Figure 13.

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Figure 14.