Characterization of corrosion of simulated ancient glasses following variable temperature product consistency tests

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ABSTRACT

Lamella formation in altered glasses remains an understudied and poorly understood aspect of glass corrosion. Ancient glass, recovered from a Roman cargo ship sunk in the Gulf of Trieste, is coated with lamellae that are suspected to be the product of the complex conditions in which the glass was altered. Here seasonal temperature variation is examined as a possible mechanism to account for this phenomenon. To accomplish this, glass with compositions mimicking ancient glass was exposed to either fixed or alternating temperatures in fixed aqueous alteration environments. SEM and EDS analysis of corroded specimens shows the formation of a single alteration layer without lamellar patterning. These results suggest that variations in temperature do not provide a satisfactory explanation for lamellae formation. Investigations of simulated ancient glass chemical durability and proposed future work are also discussed.

Keywords: Ancient glass analogues; corrosion; glass durability; materials science
INTRODUCTION

Methods of storing high-level nuclear waste (HLW) are currently being studied in order to meet cleanup and remediation standards laid out for the Hanford nuclear production complex in the Tri-Party agreement between the DOE, EPA and State of Washington Department of Ecology. Of the storage methods being developed, vitrification of HLW has been determined to be an effective storage method, as HLW glass appears to have a greater chemical durability than currently used nuclear waste storage materials and requires a smaller volume of nuclear waste to be produced in order to store a similar amount of HLW (Ojovan and Lee, 2010). However, models of HLW glass durability in geologic repositories are not comprehensive, as several mechanisms of aqueous glass corrosion remain poorly understood, limiting the modeling of long term storage.

Traditionally, models for aqueous glass dissolution have conceived the phenomenon as a single alteration layer that consists of a surficial authigenic precipitate region, a partially-leeched, porous amorphous zone that extends beneath the surface of the glass, and a hydrated region that demarcates the alteration layer from the pristine glass (Gin et al., 2016) (Fig. 1). The external alteration rim is marked by the significant leeching of soluble elements (e.g. Na, B, Li, etc.). Similarly, the partially-leeched altered region shows a loss of soluble elements. However, the mobility of water to and from the alteration layer-pristine glass interface is constrained within this region. This interfacial solution may then become saturated in solutes derived from the glass, limiting the diffusion of hydrolyzed solutes out of the glass (Gin et al., 2016; Miller et al., 2011). Clays commonly precipitate between the surficial precipitate and heavily leached regions
(Miller et al., 2011). Finally, a thin, slightly-hydrolyzed band of glass has been observed between the heavily leached region and the pristine glass, though glass components are retained as ion-exchange and hydrolysis reactions not significant in this region (Gin et al., 2016).

Performance assessment models of silicate glass corrosion in aqueous solution are commonly divided into three distinct alteration periods: Stage I, Stage II, and Stage III (Fig. 2) (IAEA, 2005; Vienna et al. 2013). Stage I is marked by the rapid initial dissolution of glass in a dilute solution (Vienna et al. 2013). During this stage, corrosion has been demonstrated to be controlled by ion-exchange and is congruent, with dissolution entirely dissolving the existing glass framework (Ojovan and Lee, 2007).

Stage II is characterized by the onset of a significantly slower residual dissolution rate as concentrations of rate-limiting species in the alteration solution increase, reducing the kinetic driving force for glass dissolution. Additionally, the formation of a repolymerized, transport-limiting layer between the alteration solution and the reacting glass surface, termed the passivating layer, can contribute to the onset of this residual rate (Vienna et al. 2013; Gin et al. 2016). Growth of the passivating layer, in conjunction with a saturation of the solution with silicic acid and other glass components, appear to be the primary processes limiting the residual rate (Ebert, 1995; Gin et al., 2013); other corrosion system factors, such as diffusion rate of solution into the glass, transformation of the amorphous material of the passivating layer into stable, crystalline phases, the dominance of hydrolysis over ion-exchange in corrosion processes, and the tortuosity and effective porosity of the passivating layer, appear to play a critical role in the initiation of the residual rate (Gin et al., 2013; Ojovan and Lee, 2010).
The acceleration of the dissolution rate, similar in magnitude to but not exceeding the dissolution rate characteristic of Stage I, indicates that the glass corrosion has entered Stage III (Ojovan and Lee, 2010). Clearly, Stage III dissolution of the glass significantly reduces the chemical durability of the affected glass. The transition from Stage II corrosion to Stage III corrosion remains poorly understood. This transition has been associated with the precipitation of secondary silicate phases, such as zeolites, within the altered layer and progression of the interfacial solution from a neutral to highly alkaline state. The nucleation and growth of zeolite secondary phases during silicate glass degradation is believed to couple with dissolution kinetics; however, a definitive mechanism has yet to be determined (Fournier et al., 2013; Trivelpiece et al., 2017).

Zeolite precipitation has been found to be dependent upon the composition of alteration solutions and glasses (favored by higher aluminum content) in addition to alteration conditions (pH and temperature). The precipitation of these aluminosilicate minerals and subsequent Stage III initiation presents a great uncertainty for performance assessment models of silicate glass corrosion; this acceleration of alteration may be the factor that decides whether a glass fails to meet durability standards once a corrosion model is applied to the glass. The drastic consequence of Stage III corrosion for long term durability of silicate glasses then creates an impetus for a holistic mechanistic model of glass corrosion to be constructed that accounts for a wide range of complex glass corrosion behaviors. In particular, the cause of the formation of alteration lamellae on the surface of silicate glasses in aqueous solution is not properly accounted for in existing glass corrosion models and has been debated amongst members of the international nuclear glass community. This project was designed to contribute to this dialogue by
investigating temperature variation in alteration conditions as a proposed mechanism of alteration lamella formation.

**BACKGROUND**

**Previous Work**

In 1986, the remains of the Roman cargo ship *Iulia Felix* was discovered submerged off the coast of present-day Grado, Italy (Fig. 3). In the shipwreck, marine salvagers found barrels containing bluish-green and colorless shards of ancient glass cullets (glasses intended for remelting) cemented by calcite and weighing about 140 kg in total (Strachan et al., 2013). These 1800-year-old glasses have served as the focus for several archaeological investigations concerning the logistics of Roman glass production and distribution.

Of scientific interest here is an iridescent alteration rind evident on the colored *Iulia Felix* glass shards (Silvestri et al., 2011). This alteration layer consists of numerous micron-scale lamellae, with individual lamella possessing distinct chemical and structural properties (Fig. 4). These lamellae have been reported in other archeological glass studies, suggesting that this is not an alteration phenomenon unique to the glasses of the *Iulia Felix* (Silvestri et al., 2011, Dohnen et al., 2013; Newton, 1971). Indeed, these lamellar patterns have been observed in the alteration layers of both naturally and experimentally corroded silicate glasses. The production of alteration lamellae in laboratory settings without fluctuations in hydrologic conditions has led some workers to point to self-organizational processes as the mechanism responsible for lamella formation; Dohnen et al. (2013) propose that an interfacial solution-coupled dissolution
and precipitation process would allow for the development of silica lamellae (à la Liesegang bands), with the differing chemical and structural properties of the lamellae reflecting the pH and salinity of the interfacial solution at time of genesis (Oswald, 1897). In this conceptual model, lamellae are silica structures that precipitate following periods of supersaturation in the interfacial solution. As some glass-forming ions in solution are consumed to form these precipitates, further dissolution of the glass can occur, because it is now more kinetically favorable for dissolution reactions to resume. Saturation and depletion of the interfacial solution with glass-forming ions has significant effects on the pH of the solution, which in turn affects the dissolution rate of the glass as well as the precipitation rate of silica (Dohnen et al., 2013). This cyclic dissolution of the glass network and precipitation of silicate (incorporating former network modifying ions now in solution) would also influence local ionic strength in solution. According to the model of Dohnen et al. and others, this solution feedback then provides a mechanism that explains the origin of chemical fluctuations in the interfacial solution and the resulting lamellar patterning left behind by the advancing reaction front of the solution-glass interface (Wang et al., 2016).

**Experiment Rationale**

While other proposed mechanisms exist for lamella formation, such as variations in silica particle density allowing for sorting of distinct lamellae, oscillatory dissolution behavior associated with fluctuations in pH underpin most mechanistic models put forward by workers examining laminated alteration layers in silicate glasses (Dohnen et al., 2013; Geisler et al., 2010; Lenting et al., 2015; Schalm and Anaf, 2016; Wang et al., 2016). However, alternative or additional mechanisms for lamella formation may exist.
Early investigations by Brill and Hood (1961) concluded that seasonal changes in temperature provide the most likely explanation for lamella formation in altered ancient glass. By counting the number of alteration lamellae on the surface of weathered ancient glasses, Brill and Hood were able to approximately determine the ages of the glasses (in a process similar to dendrochronology). Recent work conducted at Pacific Northwest National Labs (PNNL) has correlated the number of lamellae in *Iulia Felix* glass samples to an annual alteration cycle (Ryan, personal communication). Additionally, in the northern Adriatic Sea, both changes in pH and temperature have been demonstrated to occur as a result of benthic flux and seasonal climate change, respectively (Artegiani et al., 1997; Cantoni et al., 2012; Cermelj et al., 1997; Degobbis et al., 2000; Justić, 1987; Petrović, et al., 2004; Puddu et al., 1998). Though lamellae have formed in silicate glass corrosion experiments where physiochemical changes were not externally imposed over the course of the experiment duration, the alternating physiochemical conditions in which the *Iulia Felix* glass was altered necessitates that temperature variations be examined as a possible mechanism for lamella formation.

The evaluation of this current mechanistic model of lamella formation is supported by a theoretical framework: variations in temperature of a solution influence the ionic strength of the solution. Similarly to the pH fluctuation model, alternating interfacial solution-coupled dissolution and precipitation processes would then also result from variations in temperature, as changes in ionic strength would impact the chemical equilibria of glass dissolution and silicate precipitation reactions.
The ionic strength ($I$) of a solution is related to the solution temperature through the Debye-Hückel equation:

$$\log \gamma_\pm = -\frac{1.824 \times 10^6}{(\varepsilon T)^{\frac{3}{2}}} |Z_+ Z_-| \sqrt{I}$$  \hspace{1cm} (1)

Where $\varepsilon$ = dielectric constant  \hspace{0.5cm} $Z_+$ = charge of cation  \hspace{0.5cm} $Z_-$ = charge of anion

$\gamma$ = activity coefficient \hspace{1cm} $T$ = temperature

To calculate ionic strength, the following equation is used:

$$I = \frac{1}{2} \sum_{i=1}^{n} m_i z_i^2$$  \hspace{1cm} (2)

Where $m_i$ = molality of $i$th ion in electrolyte \hspace{1cm} $z_i$ = charge of $i$th ion in electrolyte

Ionic strength is related to the chemical equilibria through $\gamma$, the activity coefficient, determined in equation (1):

$$A + B \leftrightarrow C + D$$

$$K_{eq} = \frac{[C] \gamma_C [D] \gamma_D}{[A] \gamma_A [B] \gamma_B}$$

For the solubility products ($K_{sp}$):

$$K_{sp[AB]} = [A] \gamma_A [B] \gamma_B$$

This relationship demonstrates that the solubility of ions increases with ionic strength, which is inversely related to temperature. Fluctuations in temperature of an alteration solution could then cause associated changes in solution ionic strength and solubility, consequently affecting the structural formation of an alteration layer on glass immersed in solution. Work conducted by Brinker and Scherer (1990) on sol-gels indicates that
large changes on ionic strength can have drastic implications for the structure of gels that resemble the hydrated passivating layer characteristic of Stage II corrosion. Periodic, coupled changes in temperature and ionic strength may then be manifested on glass surfaces as lamella alteration formations. This study seeks to test this temperature variation model and further constrain the possible mechanisms by which of alteration lamellae form.

METHODS

Several methods were employed in order to characterize the alteration of simulated ancient glass due to variable alteration environment temperatures. First, a quantity of simulated ancient glass, titled IF-B45, was produced. Monolithic specimens and powder specimens of this glass were then prepared for experimentation using polishing and sieving techniques, respectively. The ASTM Product Consistency Type B test method was then conducted on both of these IF-B45 sample types. Following termination of experiments, altered monolithic specimens and powder specimens were analyzed using digital microscopy, x-ray diffraction (XRD), scanning electron and field emission scanning electron microscopy (SEM and FE-SEM), and energy-dispersive x-ray spectroscopy (EDS) to determine alteration behavior and chemical durability of IF-B45. Resulting solutions were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the elements released during alteration, and to supplement the aforementioned techniques. Utilizing these ICP-OES data, aqueous geochemical modeling was performed with the Geochemist’s Workbench (GWB) software. All experimentation and analysis took place at PNNL.
Vitrification of simulated ancient glass

A 220 g mass of IF-B45 was prepared by mixing the required raw materials (Table 1). Na was used as the corrosion tracer in this experiment. These materials were then melted in a platinum crucible at 1450° C in a Thermolyne 47900 furnace, allowed to cool until solid, and annealed to remove internal stress inconsistencies (Tool, 1945).

Sample preparation

Specimens with dimensions of approximately 8 x 13.5 and 1.5 mm were cut from the original IF-B45 block. These specimens then underwent a polishing sequence of 240 grit, 320 grit, 400 grit, 600 grit, 1200 grit, and 3 μm. A Buehler SS-200 polisher was used to polish the samples to this degree. This polishing sequence also reduced the dimensions of each specimen to approximately 7.5 x 13.25 x 0.9 mm. The remaining portion of the original IF-B45 block was then milled to produce glass powder. In order to produce glass particles of the desired particle-size distribution of 150-75 μm, the IF-B45 powder was sieved using 100 and 200 mesh ASTM sieves. The retained 150-75 μm IF-B45 powder was then ultrasonically washed to remove fines.

Product Consistency Tests

For the ASTM product consistency tests (PCT), two IF-B45 specimens and 3 g of IF-B45 powder were placed in sealed stainless steel vessels along with 20 ml of deionized water (Ω = 21.8) in order to achieve a desired surface-area-to-volume ratio between the glass surface and volume of water (2000 m⁻¹) (Fig. 5). Tightening structures were then placed on the stainless steel vessels and the tightening structures were torqued to 18 ft-lb.
Eight experiments were conducted in total, with four vessels placed into a Cole-Parmer StableTemp 90° C oven and four vessels placed into a Cole-Parmer StableTemp 70° C oven. Two vessels per initial temperature condition were swapped between the 90° C and 70° C ovens every three weeks while two vessels per initial temperature condition were not swapped from their initial temperature condition. A solution sample was taken from each experiment approximately 24 hours after initiation. In order to compensate for solution loss due to evaporation, vessels were weighed every two weeks to ensure that the desired water content was maintained throughout the duration of the experiments. Vessels found to have suffered evaporation loss were refilled with deionized water. Experiments were allowed to run for a total duration of 21 weeks. After 21 weeks, the vessels were removed from their respective ovens. Following a slight cooling period, a final solution sample was taken from each vessel and IF-B45 specimens and powder were extracted. The altered IF-B45 specimens and powder were then critically dried to avoid damaging any delicate surficial alteration structures (Scherer, 1990).

**Altered sample preparation**

IF-B45 specimens were halved using a diamond scriber. IF-B45 specimen halves were then mounted in puck-shaped epoxy molds with the cut face of each specimen half exposed on the bottom of the epoxy puck. The IF-B45 powders were similarly mounted on the bottom of puck-shaped epoxy molds. The bottom face of each epoxy puck then underwent a polishing sequence of 15 μm, 9 μm, 3 μm, 1 μm, and submicron using diamond glycol-based polishing suspension. A Buehler EcoMet 250 was used to polish
the epoxy pucks to 3 μm polishing level while a Buehler VibroMet was used to polish the epoxy pucks to the submicron polishing level.

**Digital microscopy**

Initial images of IF-B45 specimen surface cross-sections were taken using a Keyence VHX-2000 microscope. Images taken at the highest magnification achievable by the Keyence VHX-2000 (1000x magnification) were found to be inadequate for identification of alteration structures and the IF-B45 specimens were subsequently analyzed with SEM instrumentation.

**Scanning electron microscopy**

A JOEL JSM-5900 SEM and a JOEL JSM-7001 FE-SEM were used to identify and characterize alteration of IF-B45 specimens and powders. A 5 to 25 kv acceleration voltage and a 5 to 10 mm working distance were used for all SEM and FE-SEM imaging and analyses.

**Energy dispersive x-ray spectroscopy**

EDAX energy-dispersive x-ray spectrometers equipped to both the JOEL JSM-5900 SEM and a JOEL JSM-7001 FE-SEM were used to determine oxide distributions within IF-B45 samples. This compositional analysis consisted of constructing element profiles and maps.
**Inductively coupled plasma-optical emission spectroscopy**

Major glass-forming cations leached into solution were analyzed using external standards with a PerkinElmer Optima 8300 DV ICP-OES and quantified. Sample solutions were diluted with 3% weight/volume nitric acid to a sample volume of 5 ml. ICP-OES tests were performed approximately a week following sampling.

**X-ray diffraction**

Analysis of IF-B45 specimen and powder surficial surface alteration products consisted of X-ray diffraction using a Bruker D8 Advance powder X-ray diffractometer.

**Aqueous geochemical modeling**

Mineral equilibrium analysis was accomplished using the Geochemist’s Workbench software. ICP data and solution conditions (pH, temperature, resistivity, etc.) were input into React, the GWB mineral dissolution and precipitation modeling program. Minerals considered possible to precipitate out of each solution were species that had saturation index values that indicated that the species was equilibrated with the solution in question or was supersaturated with respect to the solution ($\log_{\frac{Q}{K}} > -3$).

**Alteration layer measurements**

All SEM and FE-SEM images of IF-B45 specimens were measured using ImageJ, an imaging processing program. Alteration layer thicknesses were determined by averaging the 30 measurements per specimen. Surface alteration sites where significant pitting or
other localized features were evident were not measured as these sites were not considered representative of any IF-B45 specimen alteration layers.

RESULTS

Scanning electron microscopy

Backscattered SEM images reveal the presence of alteration layers on each of the IF-B45 specimens analyzed (one for each set of experiment conditions) (Fig. 6). As heavier (higher atomic number) elements produce more backscatter events when they are struck by an electron beam than do lighter elements, on average, backscatter imaging provides a means of identifying compositional contrast in IF-B45 specimens and thereby allows for alteration layers and lamellae to be detected. As shown in Figure, an alteration layer is evident in samples C01, C03, C04, and C05. However, individual lamellae are not distinguishable in any of the samples.

Measurements of alteration layer extent show the thickness of the C05 (90° C initial temperature condition; not switched between 70° C and 90° C) alteration layer to be the greatest (0.707 μm) (Table 2). The alteration layers of C01 (70° C initial temperature condition; switched between 70° C and 90° C) and C04 (90° C initial temperature condition; switched between 70° C and 90° C) are comparable in thickness (0.615 and 0.608 μm, respectively). Finally, C03 (70° C initial temperature condition; not switched between 70° C and 90° C) experienced the least alteration of the examined specimens (0.374 μm).

Lower-magnification SEM images show a precipitate phase on the surface of IF-B45 grains (Fig. 7; Fig. 8). This precipitate, though not apparent in cross-sectional, higher
magnification SEM images of IF-B45 specimens, almost entirely covers the surfaces of the examined grains and in some cases serves to cement grains together. Additionally, pitting is prominent along the edges of IF-B45 grains (Fig. 8)

**Energy dispersive x-ray spectroscopy**

Energy dispersive x-ray spectroscopy element weight percent profiles of C01, C03, C04, and C05 reveal Na profiles to resemble a sharp, sigmoidal shape (Fig. 9, Fig. 10, Fig. 11, Fig. 12), with the highest Na concentrations recorded in the pristine IF-B45 glass, high Na concentrations recorded in the perceived alteration layer near the pristine glass transitioning to low Na concentrations in the perceived alteration layer near the epoxy, and the lowest Na concentrations recorded in the epoxy. These profiles demonstrate that Na has leached significantly and confirm the presence of an alteration layer in all specimens. There were no apparent trends in the Si, O, and Al profiles taken of the IF-B45 specimens.

Elemental phase maps taken of C01 show Na to have slightly leached from the surface of the IF-B45 specimen (Fig. 13). Other elements of interest, including Mg and K, appear to be evenly distributed. The elemental phase maps taken of C01 are representative of those collected from the other IF-B45 specimens.
Inductively coupled plasma-optical emission spectroscopy

Alteration layer thicknesses calculated using Na concentrations from vial solutions at time of experimental run termination corroborate the alteration thicknesses measured using SEM imaging (Table 2) Rising Na concentrations, measured periodically during experiments, further indicate that IF-B45 specimens experienced a rapid initial alteration rate that eventually plateaued (Fig. 14). Vial solutions appear to have become and remained alkaline, with vial solutions at time of experimental run termination having measured pH values between 10.5 and 11 (Table 2).

X-ray diffraction

X-ray diffraction spectra reveal the alteration products on all IF-B45 powder surfaces to be amorphous (Fig. 15). The XRD diffraction peaks that were obtained are not distinct, which is indicative of a non-crystalline material.

Aqueous geochemical modeling

Mineral dissolution and precipitation modeling results are listed in Table 3. All vial solution compositions are shown to allow for the precipitation of brucite, goethite, and hematite.

DISCUSSION AND CONCLUSIONS

Assessment of the temperature variation model

The reported results indicate that variation in temperature of alteration conditions does not account for lamella formation in corroded silicate glasses. Were lamellar patterning to have formed in the alteration layers of the IF-B45 specimens exposed to
varied temperature conditions during alteration, oscillatory compositional zones should be apparent in the SEM imaging of the specimens (Strachan et al., 2014). Likewise, these lamellar patterns would cause the alteration layer to appear as a stepwise trend in the Na profiles taken of the specimens, rather than a rough sigmoidal trend (Geisler et al., 2015). Neither of these phenomena are observed (Fig. 6; Fig. 9; Fig. 10; Fig. 11; Fig. 12). SEM and EDS analysis then show the formation of a single alteration layer on all IF-B45 specimens, regardless of alteration condition, with no indication that these single alteration layers are composed of finer lamellae. The combination of this lack of alteration lamellae formation due to temperature variation, and the relatively stable pH measurements of the PCT vial solutions, tentatively lends credence to the alternate model of pH fluctuation for alteration lamellae formation.

**Investigations of IF-B45 chemical durability**

*Alteration extent*

As temperature greatly influences glass dissolution kinetics and is directly correlated to the glass corrosion rate (Frugier et al., 2008), it is unsurprising that the IF-B45 specimen (C05) exposed to the higher temperature condition (90° C) for the longest time experienced the greatest alteration extent, while the specimen (C03) exposed to the lower temperature condition (70° C) for the longest time experienced the least alteration extent (Table 2). In this sense, the IF-B45 glass behaved in a comparable manner to most other silicate glasses altered in environments with stable temperatures.
**Precipitate analysis**

Though a non-crystalline material was the only identified precipitate on IF-B45 specimen and grain surfaces, it should be noted that certain phases, such as magnesium silicates, are difficult to identify using XRD when they are located in close proximity to amorphous materials (Strachan et al., 2013). Consequentially, the presence of any clay phases may have been obscured by the abundance of amorphous alteration products. However, the absence of Mg and K enriched areas in obtained EDS elemental phase maps indicate that these phases did not form (Fig. 13).

The absence of a magnesium silicate phase on the surfaces of altered IF-B45 glass is of interest because Silvestri et al. (2008) and Strachen et al. (2013) note the dominance of this precipitate on the surface of the corroded, original Iulia Felix glass. This difference then suggests that the experimental design constructed for this project may not account for an external factor relevant to glass corrosion processes, such as the composition of local seawater or of neighboring sediments.

While the potential for any mineral species to precipitate out of each alteration solution is of interest for determining the chemical durability of IF-B45, the relatively high saturation indexes of brucite across all alteration solutions is the most critical (Table 3). Brucite, or another octahedral sheet-forming component, is an essential building block of phyllosilicates because it serves as a bridging layer between tetrahedral silicate sheets. Because brucite saturation is indicated by our chemical models for solutions present at run termination, it is expected that aluminosilicate products would eventually form (Pokrovsky and Schott, 2004). Aluminum comprises a significant portion of the IF-B45 composition (1.3 wt%), providing a potentially sufficient source of the element for
further aluminosilicate formation were the aluminum to be mobilized. This mobilization of aluminum from the glass network may result from a thermodynamic driving force engendered by the precipitation of aluminosilicates from solution, forming a positive feedback system controlled by Al behavior: the consumption of aluminum in solution through precipitation processes could drive the dissolution of more aluminum out of the glass and initiate a coupled resumption of rapid glass dissolution, marking the transition of corrosion from Stage II to Stage III (Trivelpiece et al., 2017). Stage III behavior has the potential to strongly impact the long-term performance of the glass. As a result, the lifetime of IF-B45 glass in a geologic repository may be assumed to be relatively short with respect to other glasses that have been experimentally demonstrated to be less susceptible to aluminosilicate precipitation (Gin, 2014).

**Concerns regarding successful vitrification of IF-B45**

The pitting observed along the edges of IF-B45 powder grains likely represents areas of structural weakness. Such weakness is typically caused by stress lines, phase separation, and surface roughening (Harker and Flintoff, 1987). Pits are formed by dissolution rather than repolymerization of the glass network. Hence, the edges of the IF-B45 powder grain surfaces likely advanced to a Stage III state, where the increased glass surface-area-to-volume ratio of these sites served as an accelerating factor for alteration and allowed for advanced corrosion stages to be achieved (Ebert, 1995).

These localized differences in alteration, in addition to anomalous imperfections observed in the IF-B45 specimens, indicate that the original IF-B45 melt may have separated into two or more distinct phases during cooling. The high temperature (1450
°C) required to melt the IF-B45 components could have contributed to this occurrence, as the quench rate necessary to avoid phase separation was difficult to achieve without imparting significant transient stresses to the glass during cooling (Narayanaswamy, 1977; Uhlmann, 1976).

**Future work**

The results of the PCTs conducted for this study indicate that varying temperatures do not account for alteration lamellae formation in the glass of the *Iulia Felix*. These experiments may have suffered from a problem of scale; the PCTs did not produce extensive alteration of sample IF-B45 specimens, which may have impeded observation of lamellae even if they had formed. In order to address this concern with the original variable temperature PCT experiments conducted for this study, future investigations should test glass specimens utilizing greater surface-area-to-solution-volume ratios. Additionally, an examination of the pH fluctuation model for alteration lamellae formation would complement investigations of the temperature variation model. *In situ* monitoring of both proposed experiments would further elucidate the effects that these intensive parameters have on glass alteration processes and would contribute to an improved understanding of alteration lamellae formation and silicate material corrosion.

**ACKNOWLEDGEMENTS**

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Tables and Figures
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<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.15</td>
<td>S</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>SiO₂</td>
<td>70.05</td>
<td>Si</td>
<td>32.60</td>
<td>24.21</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.08</td>
<td>Ti</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O</td>
<td>45.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>59.58</td>
</tr>
<tr>
<td>∑</td>
<td>100.00</td>
<td>∑</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 1. IF-B45 glass reference expressed in oxide and element weight percent. Composition modeled after Silvestri, et al. (2008).
<table>
<thead>
<tr>
<th>Specimen (Vial)</th>
<th>Initial Temp. (°C)</th>
<th>Variable Temp.</th>
<th>Na Equivalent Thickness (μm)</th>
<th>Top Alteration Layer Thickness (μm)</th>
<th>Bottom Alteration Layer Thickness (μm)</th>
<th>Final Solution pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01 (1-A3)</td>
<td>70</td>
<td>Yes</td>
<td>0.602</td>
<td>0.615</td>
<td>0.651</td>
<td>10.63</td>
</tr>
<tr>
<td>C02 (99A20)</td>
<td>70</td>
<td>Yes</td>
<td>0.549</td>
<td></td>
<td></td>
<td>10.50</td>
</tr>
<tr>
<td>C03 (C2)</td>
<td>70</td>
<td>No</td>
<td>0.382</td>
<td>0.374</td>
<td>NA</td>
<td>10.62</td>
</tr>
<tr>
<td>C04 (1A40)</td>
<td>90</td>
<td>Yes</td>
<td>0.582</td>
<td>0.608</td>
<td>NA</td>
<td>10.85</td>
</tr>
<tr>
<td>C05 (A1)</td>
<td>90</td>
<td>No</td>
<td>0.716</td>
<td>0.707</td>
<td>NA</td>
<td>10.64</td>
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</table>

Table 2. Equivalent and measured alteration layer thickness of IF-B45 specimens analyzed with SEM. One specimen from each of the four experimental conditions and a duplicate of the 70 °C variable temperature test are included. All alteration layer thickness measurements were taken using ImageJ.
<table>
<thead>
<tr>
<th>Vial Solution</th>
<th>Initial Temp. (°C)</th>
<th>Variable Temp. (°C)</th>
<th>Mineral Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-A3</td>
<td>70</td>
<td>Yes</td>
<td>Brucite, Chrysotile, Enstatite, Ferrite-Ca, Ferrite-Mg, Forsterite, Goethite, Hematite, Saponite-Ca, Saponite-Mg, Saponite-Na, Talc</td>
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<tr>
<td>99A20</td>
<td>70</td>
<td>Yes</td>
<td>Brucite, Fe(OH3), Ferrite-Ca, Ferrite-Mg, Goethite, Hematite</td>
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<tr>
<td>C2</td>
<td>70</td>
<td>No</td>
<td>Andradite, Brucite, Chrysotile, Clinochl-7A, Enstatite, Ferrite-Ca, Ferrite-Mg, Forsterite, Goethite, Hematite, Montillecite, Saponite-Ca, Saponite-Mg, Saponite-Na, Talc</td>
</tr>
<tr>
<td>1A40</td>
<td>90</td>
<td>Yes</td>
<td>Brucite, Ferrite-Ca, Goethite, Hematite</td>
</tr>
<tr>
<td>A1</td>
<td>90</td>
<td>No</td>
<td>Brucite, Fe(OH3), Ferrite-Ca, Ferrite-Mg, Goethite, Hematite</td>
</tr>
</tbody>
</table>

Table 3. Modeled mineral species equilibrated with or supersaturated with respect to vial solutions modeled (Saturation Index > -3). Note the prevalence of brucite as a precipitation product across all solutions.
Figure 1. Diagram showing commonly observed layers and interfaces prior to (T=1) and following corrosion of silicate glass (T=2). Figure adapted from Gin et al. (2016).
Figure 2. Mechanisms and stages of glass dissolution. Stage I is characterized by removal of univalent cations from glass framework through ion exchange and initial, fast alteration. Stage II is marked by less rapid liberation of Si from the glass framework. Removal of Al from the glass framework and precipitation of secondary silicate minerals signals the onset of Stage III. Underlying graph shows glass alteration versus reaction time of glass with Stage I (green), a transition stage (blue), Stage II (yellow), and Stage III (red) color-coded.
Figure 3. Map of Italy. The red box indicates the location of the Gulf of Trieste and a portion of the northern Adriatic Sea. The green box indicates approximate location of the *Iulia Felix* shipwreck.
Figure 4. TEM photomicrograph of the alteration lamellae on the surface of a glass specimen from the glass cullet on the *Iulia Felix*. Figure adapted from Strachan et al. (2013).
Figure 5. Experiment assemblage prior to experiment initiation. The assemblage is composed of (A) a stainless steel vessel, (B) 20 ml of deionized water, (C) two IF-B45 specimens, and (D) 3 g of IF-B45 powder.
Figure 6. FE-SEM images (backscattered) of cross-sectional views of C01, C03, C04, and C05 specimen surfaces. Note the alteration layers evident below the epoxy-glass interface in each of the SEM images. All images taken at 25,000x magnification.
Figure 7. SEM images of the IF-B45 powder. (A) IF-B45 powder prior to variable temperature PCTs. (B) Altered IF-B45 powder following variable temperature PCTs. Precipitates are evident on grain surfaces.
Figure 8. SEM image of IF-B45 grains. (A) Altered IF-B45 grain following variable temperature PCTs. Surface precipitates are widespread and pitting is prominent along grain edges (marked with red rectangles). (B) Corner of altered IF-B45 grain following variable temperature PCTs. Surface precipitates are pervasive and pitting is extensive.
Figure 9. A) FE-SEM image (backscattered) of cross-section of C01 surface with an element weight percent profile marked with red line extending from a to a’. B) Graph of Na weight percent (%) versus position (μm) for associated a to a’ weight percent profile.
Figure 10. A) FE-SEM image (backscattered) of cross-section of C03 surface with an element weight percent profile marked with red line extending from a to a’. B) Graph of Na weight percent (%) versus position (μm) for associated a to a’ weight percent profile.
Figure 11. A) FE-SEM image (backscattered) of cross-section of C04 surface with an element weight percent profile marked with red line extending from a to a’. B) Graph of Na weight percent (%) versus position (μm) for associated a to a’ weight percent profile.
Figure 12. A) FE-SEM image (backscattered) of cross-section of C05 surface with an element weight percent profile marked with red line extending from a to a’. B) Graph of Na weight percent (%) versus position (μm) for associated a to a’ weight percent profile.
same portion of the Na elemental phase map, there is a corresponding slight depression of Na.

Figure 13. SEM image (backscattered) of cross-section of C11 surface with EDS elemental phase maps for Na, Ca, and K. Epoxy-glass interface marked with dashed yellow line. Note that an alteration layer is evident in the SEM image below the epoxy-glass interface in the lower right corner of the image.
Figure 14. Graph of Na content (µg) versus time (d) for C03 vial solution samples. As Na serves as the tracer element for this glass corrosion study, the amount of Na released from the glass mirrors the amount of glass altered. The graph indicates that the C03 specimen and powder experienced rapid initial dissolution followed by a slower dissolution rate, indicating the transition from the Stage I kinetic regime to the Stage II kinetic regime. The shape of this graph showing C03 alteration is representative of those constructed for the other IF-B45 specimens.
Figure 15. XRD spectrum of the precipitates on Co2 specimen surface. The diffraction peaks are not distinct, which is indicative of a non-crystalline material. This XRD spectrum is representative of XRD spectra obtained for precipitates on other Ni-B+5 specimen surfaces.