The fate of silicon during glass corrosion under alkaline conditions: a mechanistic and kinetic study with the International Simple Glass

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Abstract

International Simple Glass – a six oxide borosilicate glass selected by the international nuclear glass community to improve the understanding of glass corrosion mechanisms and kinetics – was altered at 90°C in a solution initially saturated with respect to amorphous ²⁹SiO₂. The pH_{90°C} was fixed at 9 at the start of the experiment and raised to 11.5 after 209 d by the addition of KOH. Isotope sensitive analytical techniques were used to analyze the solution and altered glass samples, helping to understand the driving forces and rate limiting processes controlling long-term glass alteration. At pH 9, the corrosion rate continuously drops and the glass slowly transforms into a uniform, homogeneous amorphous alteration layer. The mechanisms responsible for this transformation are water penetration through the growing alteration layer and ion exchange. We demonstrate that this amorphous alteration layer is not a precipitate resulting from the hydrolysis of the silicate network; it is mostly inherited from the glass structure from which the most weakly bonded cations (Na, Ca and B) have been released. At pH 11.5, the alteration process is very different: the high solubility of glass network formers (Si, Al, Zr) triggers the rapid and complete dissolution of the glass (dissolution becomes congruent) and precipitation of amorphous and crystalline phases. Unlike at pH 9 where glass corrosion rate decreased by 3 orders of magnitude likely due to the retroaction of the alteration layer on water dynamics/reactivity at the reaction front, the rate at pH 11.5 is maintained at a value close to the forward rate due to both the hydrolysis of the silicate network promoted by OH⁻ and the precipitation of CSH and zeolites. This study provides key information for a unified model for glass dissolution.

Keywords: ISG glass, borosilicate, corrosion, kinetics, zeolite, CSH

1. INTRODUCTION

1.1 Context

For decades, borosilicate glass has been produced in several countries to confine fission products and minor actinides remaining after the reprocessing of spent nuclear fuels (Ojovan and Lee, 2011). Such high-level radioactive wastes are intended to be stored in deep geological repositories. The question of how fast the radionuclides (RN) confined in the glass are released to the geosphere has mobilized a broad scientific community since the beginning of the 1980s and continues to be challenging because of the high complexity of the system (Gin, 2014; Gin et al., 2013a; Grambow, 2006; Jantzen et al., 2010; Van Iseghem et al., 2009). Glass undergoes both dissolution and the irreversible transformation into more stable phases but the rate of this transformation strongly depends on the geochemical boundary conditions (T, pH, solution composition, flow rate, etc). Moreover, from a safety standpoint, the glass and RN behavior must be calculated to be below regulatory limits for geological timescales (typically a million years in certain countries). Only a robust methodology can meet such an objective. This methodology must be a science-based understanding of the chemical and physical processes associated with the dissolution of the glass and the transport of the RN to the near- and far-field environment. This understanding forms the basis for a multi-scale modeling effort (ASTM, 1997; Poinssot and Gin, 2012). Historic, archeological and natural glasses are used to test the model for a wide range of environmental conditions and long time periods (Ewing, 1979; Libourel et al., 2011; Lutze et al., 1985).

1.2. State of the art

Knowledge about nuclear glass durability and the remaining open questions have been discussed in recent papers (Fournier et al., 2014b; Gin, 2014; Pierce et al., 2014; Van Iseghem et al., 2009; Vienna et al., 2013). Briefly, when placed in static or slightly renewed solution, nuclear glass corrosion generally follows 3 behavioral stages:

- I. The *initial* or *forward rate*, denoted as r_0 , that is characterized by hydration (diffusion of water molecules into the glass), ion exchange (interdiffusion) (Eq. 1) and the hydrolysis of the silicate network (Eq. 2) in relatively dilute conditions that do not hinder the forward hydrolysis reactions and preclude the formation of effective barrier layers.

- II. As the concentration of silica in solution increases, the corrosion rate decreases as it begins to be affected by the diminishing of the affinity for reaction (2) accompanied by the formation of a passivating layer. This eventually leads to the *residual rate*, denoted as r_r , a relatively constant or slowly decreasing rate much slower than the forward rate. It is suggested that the residual rate could correspond to a steady-state between the formation and the dissolution of the passivating layer (Frugier et al., 2008). However there is not yet a broad consensus on the mechanisms that control this particular regime (Van Iseghem et al., 2009; Vienna et al., 2013).
- III. The potential sudden *resumption of alteration* that is coincident with the rapid precipitation of certain silica-bearing alteration products. This increase in dissolution rate for some glasses

appears to occur only under specific conditions, typically high temperature and/or high pH (Fournier et al., 2014b).

In geological disposal, glass packages only have the potential to last hundreds of thousands years to few million years if glass reaches and stays in the residual rate regime (Gin et al., 2004). Thus, it is of primary importance to better understand and model the mechanism(s) responsible for the residual rate and understand when and why glass alteration can suddenly resume. The pH is a first order parameter in this regard. The presence of B in nuclear glasses contributes to buffer the pH of most leaching solutions at around 9, but in some cases (e.g. cement-type waters) hyperalkaline pH values are expected.

There is a strong consensus on the fact that dissolved Si ($\text{SiO}_2(\text{aq})$ or H_4SiO_4 (Icenhower and Steefel, 2013) and the ionized forms) plays a major role in the different processes involved in the regimes listed above. Aqueous Si affects the ΔG (i.e. the affinity) of reaction (2) (Abratis et al., 2000; Advocat et al., 1998; Neeway et al., 2011; Pierce et al., 2008), the passivating layer is mainly composed of Si (Frugier et al., 2008; Grambow and Muller, 2001; Rajmohan et al., 2010), and secondary phases acknowledged to affect the rate are mostly silicates (Abrajano et al., 1990; Caurel et al., 1990; Debure et al., 2012; Ebert and Bates, 1991; Gin et al., 2013b; Gong et al., 1998; Michelin et al., 2013; Pierce et al., 2007; Pierce et al., 2006; Valle et al., 2010).

1.3. Objectives

In this paper, we focus on the fate of Si during glass corrosion in the residual rate (II above) and alteration resumption (III above) stages. The two regimes are investigated in a single experiment carried out on the International Simple Glass (ISG), a six-component glass selected by the international community to build a consensus on the understanding of glass corrosion processes because it has the same cation ratios as the major components in the SON68 glass, a more representative material of actual nuclear glasses (Gin et al., 2013a). Moreover it has been shown that both ISG and SON68 glass have similar initial and residual release rates (Gin et al., 2012). The experiment discussed in this paper was started with a solution initially saturated with respect to $^{29}\text{SiO}_2(\text{am})$ at 90 °C and a $\text{pH}_{90^\circ\text{C}}$ value of 9. The monitoring of Si isotopes with isotope-sensitive analytical techniques provides information about the dynamics of exchanges between aqueous species and solid species during glass corrosion and therefore about the solubility of the silicate network. Since $\text{SiO}_2(\text{am})$ is the silica polymorph with the highest solubility, glass alteration occurred in the presence of the highest possible concentration of H_4SiO_4 at pH 9 (Iler, 1979). Moreover, these starting conditions enabled us to dramatically reduce the time associated with regime I above (initial dissolution rate) and rate drop and thus focus on the residual rate.

After 209 days at $\text{pH}_{90^\circ\text{C}}$ 9, the solution pH was raised to 11.5 by the addition of KOH and maintained at this value. The results of this second stage of the experiment improve the understanding of how the slow residual rate observed at pH 9 can suddenly increase.

1.4. Terminology

As a result of the complex suite of corrosion processes listed above (hydration, interdiffusion, hydrolysis, condensation, precipitation), the dissolution of glass is rarely congruent. This means that, in addition to soluble species directly released into the solution, solid products are also formed. The

latter are hydrated phases that can be amorphous or crystalline. Unlike crystalline phases that can be identified, generally with X-ray or electron diffraction, the identification of amorphous phases is more complicated because of the number of phases of variable composition that can form. Attempts have been made to model the amorphous phases as solid solutions (Bourcier et al., 1990; Munier et al., 2004). Moreover, their structure and porosity can vary significantly for a given composition, further complicating the attempts to model them. Various labels have been used in the literature for these phases: gel layer, hydrated glass, hydrated layer, amorphous layer, leach layer, etc. In this article, we refer to the whole suite of alteration products as the *alteration layer* and the amorphous part of it as the *amorphous alteration layer*, irrespective of homogeneity, composition, porosity and properties.

2. EXPERIMENTAL AND ANALYTICAL TECHNIQUES

2.1. Glass specimen preparation

The ISG glass was produced in 2012 by MoSci Corporation (Rolla, Mo, USA). Three individual batches yielding approximately 25 kg of glass cullet each were produced by blending powdered raw materials in a V-blender. Each batch was melted in high purity fused silica crucibles in an electric furnace at 1300 °C and water quenched to produce glass frit. After drying in an electric oven the three batches of frit were blended together to create a master lot. This frit was then re-melted in platinum-rhodium crucibles in an electric furnace at 1300 °C for approximately four hours, stirred once with a quartz rod, and cast into a graphite mold. The ingots were annealed at 569 °C for 6 hours in an electric oven and cooled to room temperature at a rate of 50 °C per hour. The nominal composition of ISG is recalled in Table 1. A detailed analysis showed that the composition was within the stated synthesis specifications.

From the ingots, 16 coupons of $2 (\pm 0.1) \times 2 (\pm 0.1) \times 0.11 (\pm 0.005)$ cm were cut with a diamond saw and the upper face of each coupon was polished first with SiC papers and finally with diamond paste (7, 3 and 1 μm). The resulting geometric surface area of one glass coupon was $8.8 (\pm 0.4) \text{ cm}^2$. Because 5 of the 6 faces of each coupon were kept unpolished, the reactive surface area – at least at the beginning of the leaching experiment – was larger than the geometric surface area. This initial reactive surface area was determined knowing the initial dissolution rate of this glass at pH 9 ($3.7 \text{ g.m}^{-2}.\text{d}^{-1}$, (Inagaki et al., 2013)). A leaching experiment was performed with one glass coupon similar to the 16 ones above-mentioned. The glass coupon was altered 8 hours in 125 mL of deionized water whose pH was fixed at 9 by addition of KOH (Suprapur). The glass dissolution was congruent for Si, B and Na (the 3 elements regularly monitored) and linear during the first 6 hours (R^2 of 0.969 for Si). The corresponding rate was 5.6 g.d^{-1} . The congruency and linearity show that the glass coupon was altered at the maximum dissolution rate. The unknown reactive surface area of the glass coupons was then deduced by dividing the obtained rate expressed in g.d^{-1} by the initial dissolution rate given by Inagaki et al. The resulting reactive surface area was 15.2 cm^2 , i.e. 1.7 times greater than the geometric surface area. Therefore, for the calculations presented below, a surface of $15 (\pm 1) \text{ cm}^2$ per glass coupon was considered. It is shown further that this estimation of the reactive surface area is reasonable at pH 9 whereas it certainly underestimates glass alteration at pH 11.5.

2.2. Leaching experiment

The experiment consisted of studying the alteration of 16 ISG glass coupons placed in contact with 380 mL of solution initially enriched in ^{29}Si until the equilibrium with respect to amorphous silica. The corresponding S/V ratio at the beginning of the experiment was 60 m^{-1} . The experiment was run at 90°C in static mode. Initially, the pH of the experiment was adjusted at $9.0 (\pm 0.1)$ for 209 days. At 209 days the pH was then raised to $11.5 (\pm 0.2)$ by addition of $\text{KOH } 10 \text{ mol.L}^{-1}$ and maintained at this value until the end of the experiment. During this second stage, six additions of few mL of $\text{KOH } 10 \text{ mol.L}^{-1}$ were performed in order to maintain the pH at 11.5. At regular intervals, the solution was sampled and a coupon was withdrawn for characterization. Therefore two timescales are defined: t represents the duration since the beginning of the experiment and t^* the duration after the pH disturbance. It results that $t = t^* + 209 \text{ d}$.

The leaching solution was prepared as follows. $^{29}\text{SiO}_2$ (Eurisotop®, $^{29}\text{Si} > 95\%$) was mixed with KOH (Suprapur) and melted at 600°C . The resulting potassium silicate was dissolved in deionized water at 90°C in order to obtain a concentration of Si of 260 mg.L^{-1} at pH 9 (Table 2). The corresponding solution $^{29}\text{Si}/^{28}\text{Si}$ ratio was 41.5 to be compared to 0.0507 in the glass (natural abundance). Note that the analysis of solution sampled during the test required a high dilution because of the concentration of K: the onset solution contained about 3 g.L^{-1} of K, the pH rise increased the concentration up to 5 g.L^{-1} and the stabilization of the pH at 11.5 required six KOH additions leading to maximum concentration of K of about 22 g.L^{-1} (Table 2). It was verified that the high concentration of K hasn't a great effect on the glass corrosion behavior.

Glass coupons were placed onto two polytetrafluoroethylene (PTFE) holders as depicted in Fig. 1.

At the following durations one glass coupon was withdrawn, rinsed with deionized water, dried for 1 night at 90°C , and placed in a desiccator to await further characterization: 209, 210, 223, 262, 307, 363 and 374 days.

In parallel, 29 liquid samples of 1 mL each were taken from the reactor during the experiment, then filtered at $0.45 \mu\text{m}$, and acidified with concentrated HNO_3 (Suprapur) prior to analyses. At each sampling duration, the pH was recorded at 90°C (in the following, all pH values are given at 90°C). At the last duration, the sample was split and part of it was ultrafiltered at 10000 D in order to examine the potential presence of colloids.

2.3. Analytical methods

2.3.1. Solution analyses

Solutions were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (Thermo Scientific® ICAP 6300 DUO) after dilution and acidification with HNO_3 . For the first stage of the experiment, because of the low concentrations and a dilution factor of 10, uncertainties for B and Na are of 10 % and 20 %, respectively. In other cases, uncertainties for Si, B, Al, K and Na are of 3 %.

Silicon isotopic analyses were performed by Multicollector Inductively Coupled Plasma – Mass Spectroscopy (MC-ICP-MS) (Nu Instruments® Nu Plasma HR). This kind of isotopic analyses usually represent a significant challenge, because of strong molecular interferences: N_2^+ for $^{28}Si^+$, N_2H^+ for $^{29}Si^+$, NO^+ for $^{30}Si^+$. An Aridus® II desolvating nebulizer was used in order to increase sensitivity and to reduce molecular interferences. Pseudo high resolution with 0.05 mm source entrance slit provided sufficient separation of silicon isotope peaks from the molecular interferences. This analytical method provides precision in the range 0.1-0.2% and the accuracy of about 1 % for both measured ratios: $^{29}Si/^{28}Si$ and $^{30}Si/^{28}Si$ and about 15% for the concentration of each of the 3 silicon isotopes (mainly due to matrix effects). Selected samples were also analyzed for Ca, Al and Zr. Normally, when the total concentrations of elements with natural isotopic ratios are to be analyzed, the isotopes that are more abundant and less affected by the interferences are measured and the total concentration is calculated based on the assumption of a natural isotopic distribution. Nevertheless, in our analyses we have also monitored all other isotopes and isotopic ratios, which is useful to do in order to confirm the natural isotopic ratios and to evaluate the possible influence of interferences. The lower the concentration of certain isotope is, the more likely it is to be affected by the interferences. For Ca, the total concentration was based on the measurement of ^{44}Ca and its natural abundance. The most abundant isotope ^{40}Ca cannot be measured by the ICP-MS method, because of a strong ^{40}Ar interference. For the samples with higher concentrations, the natural ratios $^{42}Ca/^{44}Ca$ and $^{43}Ca/^{44}Ca$ were confirmed, whereas for lower concentration samples the interferences for ^{42}Ca and ^{43}Ca were more significant and the ratios were different from natural. The Al analyses were straightforward as Al has only one isotope, ^{27}Al . Finally, the total concentration of Zr in the samples was quite low. There are strong interferences for all 4 isotopes of Zr, beside ^{90}Zr , therefore none of the isotopic ratios for Zr were equal to the natural values. For the calculation of total Zr, only the concentration of ^{90}Zr was used.

As B is known to be a tracer for glass dissolution (i.e. it does not precipitate and it is not retained in the alteration products), altered glass fraction at the duration t , AGF_t , was calculated:

$$AGF_t = AGF_{t-1} + \frac{(C(B)_t - C(B)_{t-1}) \times V_t}{\sum m_t \times x_B} \quad (3)$$

where $C(B)_t$ is the concentration of B at the duration t , V_t the volume of the solution at the duration t , $\sum m_t$ the mass of the coupons still present in the solution at the duration t and x_B the mass fraction of B in the glass.

Normalized mass loss of element i , present at the concentration $C(i)$ at the duration t , was calculated following:

$$NL(i)_t = NL(i)_{t-1} + \frac{(C(i)_t - C(i)_{t-1}) \times V_t}{N_t S_0 \times x_i} \quad (4)$$

where N_t is the number of glass coupons still present in the reactor at the duration t and S_0 the reactive surface area of one glass coupon (15 cm^2).

The equivalent thickness of altered glass can be obtained by dividing $NL(B)$ by the glass density (2.50 g.cm^{-3}).

The glass dissolution rate was derived from $NL(B)$:

$$r = \frac{d(NL(B))}{dt} \quad (5)$$

As a first approximation, the glass dissolution rate at time t was calculated by a linear regression on three points ranging between durations $t-1$ and $t+1$. Rates were estimated with a relative uncertainty of $\pm 25\%$ at pH 9 and $[-0\%; +50\%]$ at pH 11.5. The later uncertainty arises from the error on the reactive surface area.

2.3.2. Liquid-state NMR analyses

^{29}Si liquid NMR analyses were performed lately, on solutions sampled after 503 days of experiment, and thus after the last data point presented in the paper. The solution at pH 9 was sampled in a similar experiment as that presented here but in which the pH was maintained at 9 until 503 days. It is assumed that the results obtained for this solution will be applicable to our experiment until 209 days. The solution at pH 11.5 was collected in the experiment presented in this paper. Hence the corresponding t^* was 294 days.

Spectra were recorded on a 400 MHz Agilent DD2 spectrometer equipped with the OneNMR 5mm probe and without sample spinning. The ^{29}Si chemical shift reference scale was set up with a deuterated trimethylsilyl propanoic acid (TMSP-d4) solution in D_2O prior sample analysis. A standard pulse sequence was used and optimized using the Ernst function after ^{29}Si 90° pulse and relaxation checking on the TMSP-D4 sample (pw90=6 μs @ 61dB). For both analyses, 500 μL of solution were combined with 200 μL of 99.9 ^2H -enriched water at 90°C . Spectra were recorded at 90°C in order to avoid polymerization of Si species during the cooling stage of the solution. 46300 and 96400 scans were collected on sample at pH 9 and at pH 11.5 representing acquisition times of 42 and 89 hours, respectively. A baseline correction was performed in the processing to remove the broad ^{29}Si signal arising from the NMR tubes.

2.3.3. Solid characterization

Morphological analyses were carried out on a JEOL® 6330 Field Emission Scanning Electron Microscope equipped with an Energy-Dispersive Spectrometer system.

A Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS) (TOF.SIMS5, IONTOF GmbH®, Münster, Germany) was used to perform the elemental and isotopic mapping. The lateral resolution was 200 nm. A 1.0-keV O_2^+ beam was used as a sputter beam, which was scanned on a $200 \times 200 \mu\text{m}^2$ area for glass coupons altered 262 days and $350 \times 350 \mu\text{m}^2$ for glass coupon altered 307 days. A 25.0-keV Bi beam was used as an analysis beam which was scanned on a $120 \times 120 \mu\text{m}^2$ area at the center of the O_2 crater for glass coupon altered 262 days and $200 \times 200 \mu\text{m}^2$ for glass coupon altered 307 days. Quantitative information about the chemical composition of minerals was derived from the ToF-SIMS analyses. For that, ionization efficiencies IE related to the ratio of elements i/j were calculated from the composition of the pristine glass PG :

$$(IE_{i/j})_{PG} = \frac{\left(\frac{n_i}{n_j}\right)_{PG}}{\left(\frac{x_i}{x_j}\right)_{PG}} \quad (6)$$

where n_i , n_j , x_i and x_j are the counts of i and j and the molar fraction of elements i and j in the pristine glass, respectively. Then the ratio x_i/x_j within a mineral Min is given by:

$$\left(\frac{x_i}{x_j}\right)_{Min} = \frac{\left(\frac{n_i}{n_j}\right)_{Min}}{(IE_{i/j})_{PG}} \quad (7)$$

A similar method was used in sputtering mode to determine the elemental and isotopic depth profiles on the glass coupon altered 209 days at pH 9. In this case, each of the analyzed areas was $60 \times 60 \mu\text{m}^2$. A first analysis was performed with a 2-keV, 520-nA sputter beam of O_2^+ to detect Si, B, Na, Ca, Zr and Al. A second analysis was performed close to the first crater with a 2-keV, 240-nA sputter beam of Cs^+ to detect H. The depth of the craters was measured after the analyses and profiles were calculated assuming that the sputtering rate was constant. The amounts of Si, B, Na, Al and Ca were normalized to that of Zr because this element can be considered as immobile during glass corrosion at pH 9 (Cailleteau et al., 2008; Cailleteau et al., 2011; Lobanova et al., 2002). The $^{29}\text{Si}/^{28}\text{Si}$ ratio was not normalized because ionization efficiencies of the two isotopes are similar (this can be verified by comparing measured $^{29}\text{Si}/^{28}\text{Si}$ in the pristine glass to the nominal value, 0.05).

2.4. Geochemical calculations

The speciation of the solution was calculated by the Chess geochemical code (van der Lee et al., 2003) using the CTDTP thermodynamic database (CTDP). Silica species taken into account are mainly H_4SiO_4 , H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$ and NaHSiO_3 . The saturation index ($\text{SI} = \log Q/K$) of the fluid with respect to some minerals were also calculated.

3. RESULTS

3.1. Solution analysis

Data related to the chemical composition of the solution are given in Table 2. In general, considering uncertainties and interference issues, results from ICP-OES for Si are in agreement with those from MC-ICP-MS. For minor elements (Ca, Al), discrepancies between the two techniques are noticed: for Ca, the main reason for the difference is that Ca concentrations are close to the detection limit by ICP-OES because of the high dilution factor. For Al, the concentration changed by a factor of 2 to 3x for the last several samplings with no clear explanation. The absence of colloids was verified by comparing two filtration methods applied on the same solution (simple filtration with a $0.45 \mu\text{m}$ cutoff and ultrafiltration with a 10000 D cutoff). Despite the cooling of the solution during ultrafiltration, concentrations of major elements (Si, K, B, Na) were similar within uncertainties.

^{29}Si liquid-state NMR analysis of the pH 9 solution (Fig. 2) shows only one peak at -73 ppm corresponding to monomer species (Cho et al., 2006). At pH 11.5, in addition to the main peak at -73 ppm, a second peak is visible at -81 ppm likely due to dimer species (Cho et al., 2006). According to this analysis, dimers represent about 10% of the total silica. These data indicate that during the first stage of the experiment, even though the solution remains at equilibrium with amorphous silica, no polycondensation reactions occurred in solution that could affect glass corrosion processes. These

data also indicate that polycondensation reactions took place slowly at pH 11.5 and that no large polymers have formed.

Fig. 3 displays the evolution of the main glass elements before and after the pH change. First of all, note that the pH remained stable at 9.0 ± 0.1 during the first stage (with no addition of acid or base) and was also stable at 11.5 ± 0.2 within the second stage thanks to regular additions of small volumes (about one mL) of KOH 10 mol.L^{-1} . During the first stage, the glass dissolution was not congruent: B and Na were released at the same rate (and perhaps Ca but the concentrations of this element are scattered), whereas the other elements were almost fully retained in the alteration layer. Once the pH was raised to 11.5, all the glass elements except Ca and Zr ($NL(\text{Ca}, \text{Zr})$ are close to zero) were released to solution at a high and near-constant rate, even including glass network formers like Si and Al. This behavior lasted for a few days before Al releases slowed down. After 237 d of leaching ($t^* = 28 \text{ d}$), Al concentration achieved a maximum and then dropped dramatically. At the last duration considered in this paper, the AGF was 43.1 %.

The behavior of Si is shown in Fig. 4. During the first stage, concentrations of the three isotopes remained very constant (see also Table 2), meaning that under these conditions, dissolved silica initially available in solution was not consumed by any process like sorption or precipitation. Once the pH rose, however, approximately 40 % of the available ^{29}Si was pulled out from solution within three days (see the insert, Fig. 4). Surprisingly, despite this massive removal of dissolved silicon, the overall silicon concentration was relatively unchanged due to the sudden rapid release of ^{28}Si from the glass. Because ^{29}Si was present in the glass at the natural isotopic abundance, the fast glass dissolution eventually led to an increasing concentration of ^{29}Si in solution. However, the $^{29}\text{Si}/^{28}\text{Si}$ ratio continuously decreased with time (fit given by Eq. 8) after the pH change, with a near step decrease resulting initially from the rapid consumption of ^{29}Si initially present in solution by alteration products and then continuing due to isotopic dilution from the rapid glass dissolution.

$$\frac{^{29}\text{Si}}{^{28}\text{Si}} = 5.31 \times t^{*-0.83} \quad (R^2 = 0.934) \quad (8)$$

3.2. Solid characterization

ISG glass altered at pH 9 formed a uniform amorphous alteration layer free of secondary minerals (Fig. 5a). Just before the pH change, the thickness of this layer measured by SEM was about 300 nm, in good agreement with the equivalent thickness derived from the B release (292 nm). Half a day after the pH rise, the previously formed amorphous alteration layer displays pits and cracks consistent with a fast resumption of alteration, but there is still no sign of secondary phases (Fig. 5b). At $t^* = 14 \text{ d}$, a newly formed amorphous alteration layer covered by a thin film characteristic of calcium silicate hydrate minerals (CSH) was observed (Fig. 5c). Below the amorphous alteration layer, the glass surface was uneven. At this duration, no zeolites have yet been seen. After 53 days at pH 11.5, the amorphous alteration layer is made of several sub-layers covered by large clusters of CSH on which zeolites have grown (Fig. 5d). According to SEM observations, zeolites seem to appear between 14 and 52 days after the pH rise. At longer duration, both the amorphous alteration layers and secondary minerals (CSH and zeolites) continued to grow (Figs. 5e and 5f). At the last duration of observation, a thick film of zeolites and CSH covers the whole surface of the glass coupons. The alteration layer formed at pH 11.5 is certainly very porous, this can be deduced from cracks and voids

characteristic of dehydration during sample preparation (Figs. 5b, d, e). The morphology of minerals changed with time: zeolites show cuboids and round shapes at $t^* = 53$ d and mostly needle shapes at $t^* = 165$ d, whereas CSH form a thin layer at $t^* = 14$ d and spheres at longer durations. Interestingly, the underside of the coupons had significantly fewer amount of minerals (or even none in some cases) than were observed on the coupon side that faced up. The rest of the alteration layer, however, appeared to be very similar to those of the upper surface. It is not known if minerals precipitate at the same rate on both sides and fall down from the underside of the coupons, if minerals fall off during the sample preparation, or if the minerals only precipitate on the upper surface.

The ISG glass sample altered 209 d (just before the pH change) has been characterized by ToF-SIMS. Depth profiles of glass components and hydrogen, normalized to Zr, show that (Fig. 6a):

- Boron, sodium and calcium were released from the amorphous alteration layer, except within a gradient zone located near the pristine glass surface. Slight differences in B, Na and Ca profiles cannot be considered as meaningful based on this single analysis.
- The concentration of sparingly soluble elements (Si and Al) is near constant throughout the amorphous alteration layer. As noted below, the slight fluctuations observed on the profiles ($\pm 20\%$ compared to the nominal) cannot be considered as meaningful. They are likely due to matrix effects.
- Hydrogen displays a profile roughly anti correlated to that of the mobile elements.
- Assuming that the pristine glass surface is characterized by the drop of H concentration to near zero, the amorphous alteration layer is 280 nm thick, in agreement with SEM observations.

Fig. 6b shows that the enrichment of ^{29}Si within the amorphous alteration layer is very low. The mass balance based on ToF-SIMS analysis gives an enrichment of ^{29}Si in the amorphous alteration layer of 5×10^{-3} . This figure corresponds to one atom of ^{29}Si supplied by the solution for 200 atoms of Si issuing from the glass. Even the much larger increase of the $^{29}\text{Si}/^{28}\text{Si}$ ratio noticed in the first tens of nm of the outer part of the amorphous alteration layer only reaches a maximum of 0.1, which is extremely low compared to that of the solution (41.5). These data show that the amorphous alteration layer is not in isotopic equilibrium with the bulk solution.

Samples altered 262 d ($t^* = 53$ d) (Fig. 5d) and 307 d ($t^* = 98$ d) (Fig. 5e) have been characterized by ToF-SIMS. Since the results were qualitatively the same, only data obtained for the oldest sample are presented here (Fig. 7). The SEM image (Fig. 7a) shows 7 regions of interest (ROI) corresponding to large variations in chemical composition. B is completely released from the alteration layer, confirming that this element remains a good alteration tracer at high pH (Fig. 7b). Si, Al, Ca and Zr underwent a complete redistribution within the alteration layer, contrary to what is generally observed at lower pH for these sparingly soluble elements (e.g. (Gin et al., 2011)). The case of Zr is remarkable: whereas this element is known to be insoluble during glass corrosion at $\text{pH}_{90^\circ\text{C}} < 10.5$ (Caillateau et al., 2008; Caillateau et al., 2011; Lobanova et al., 2002), its heterogeneous distribution within the alteration layer of our sample (Zr is absent in ROI 4 and enriched in ROI 5) is a direct evidence of its mobility under these alkaline conditions. Note also that, compared to pristine glass, Si and Al are enriched in zeolites and Ca is enriched in the external part of the amorphous alteration layer and in CSH.

Using Eq. 7 and 8, we calculated the following molar ratios within zeolites: $\text{Al/Si} = 0.5 \pm 0.05$, $\text{K/Si} = 0.15 \pm 0.1$ and $\text{Na/Si} = 0.04 \pm 0.01$. Note that the uncertainty for K/Si is large because of the very low amount of K in the glass (0.008 mol%). These data do not change between 262 and 307 d. The zeolites were difficult to identify by XRD because of peak broadening and possible substitution within their framework. Nonetheless, most of the peaks correspond to hershelite and merlinoite or zeolite W (Bieniok et al., 1996). The ratio Ca/Si within CSH is 0.5 ± 0.05 at 262 d and 0.6 ± 0.05 at 307 d.

3.3. Evolution of the reactive surface area

As explained in section 2.1, the initial reactive surface area of the glass coupons was supposed to be 1.7 times greater than their geometric surface area. An analysis relying on measurements by independent techniques of the glass alteration thickness at three durations within the first stage at pH 9 showed that the reactive surface area remains constant over time. This result was confirmed by similar measurements performed on glass coupons sampled from a similar experiment conducted at pH 7.

Regarding the second stage at pH 11.5, the width of the remaining unaltered glass coupon sampled at 307 days, measured by SEM was 700 μm (to be compared to 1000 μm at the beginning of the experiment). It can be deduced that 150 μm of glass was altered on each face of the coupon at this duration. This last number is 1.32 times greater than the equivalent thickness derived from the B release (114 μm). This comparison means that the B equivalent thickness is underestimated likely because the reactive surface area of the glass coupons diminished compared to the beginning. In other words, it can be thought that the initial roughness of the unpolished surfaced progressively vanished due to the rapid dissolution of the glass at pH 11.5. For the calculations presented in the discussion, the reactive surface area was kept constant at the initial value, because a better knowledge of the time evolution of the reactive surface is required to calculate a correction factor. Last, because of the amorphous alteration layer was 100 μm thick at this duration (Fig. 5e), it is worth noting that under these hyperalkaline conditions, glass alteration is not isovolumic, the volume of the amorphous alteration layer becomes significantly smaller than the volume of altered glass.

4. DISCUSSION

4.1. Effect of pH on glass dissolution rate

The approximate glass dissolution rate, calculated from B release, is displayed in Fig. 8. Data from our experiment were compared to those from a reference experiment conducted in same conditions except that the pH was maintained at 9 during the whole duration of the experiment. Until 209 days, results of the two sets of data are similar, indicating a good repeatability of the experiment. During the first stage of the experiment, the glass dissolution rate continuously dropped. At the first sampling duration ($t = 7$ d), the rate was 43 times lower than the forward rate, r_0 , which is the maximum dissolution rate at a given pH ($r_{0(90^\circ\text{C}, \text{pH } 9)} = 3.7 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ according to Inagaki et al., 2013). Just before the pH rise, at $t = 209$ d, the rate had decreased from r_0 by a factor 2000. This rate remained higher than but close to the residual rate, r_r , obtained after one year of leaching in initially deionized water and at high S/V ratio ($r_r(1\text{y}) = 4.9 \times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (Gin et al., 2012)). This result

confirms that the residual rate is moderately susceptible to S/V (Gin et al., 2013b). The pH disturbance performed at $t = 209$ d led to a sudden increase of the dissolution rate by a factor of 3000, followed by fluctuations within the same order of magnitude between 1.0 and 2.8 $\text{g.m}^{-2}.\text{d}^{-1}$ before settling at a near constant rate of 1.5 $\text{g.m}^{-2}.\text{d}^{-1}$. This final rate is about one order of magnitude smaller than the initial dissolution rate at pH 11.5 (18 $\text{g.m}^{-2}.\text{d}^{-1}$) (Fournier et al., 2014a; Inagaki et al., 2013).

This response of the glass to a pH disturbance raises the question of rate-limiting mechanisms for the two stages of the experiment.

4.2. Driving forces and rate limiting mechanisms

In agreement with previous studies (Debure et al., 2012; Gin et al., 2012), the ISG glass altered at pH 9 in the silica saturated solution forms an amorphous alteration layer, i.e. a homogeneous, hydrated and secondary-mineral free material largely depleted in B, Na and Ca completely surrounding the pristine glass. The new and most important result from our isotopically-tagged experiment is the absence of equilibration between Si isotopes in solution and in the amorphous alteration layer during glass alteration at pH 9 (Fig. 4), because both the solution and the amorphous alteration layer keep quasi-constant the initial distribution of Si isotopes as long as the pH remains at 9. This result significantly differs from that obtained by Valle and co-workers showing that the amorphous alteration layer formed on the SON68 borosilicate glass displayed an isotopic signature ranging between that of the solution and that of the glass, with large variations along the profile (Valle et al., 2010). The main differences between the two studies lie on the glass composition and on the leaching conditions. In Valle et al., the studied glass was the SON68 and the leaching solution remained very undersaturated with respect to amorphous silica whereas in our experiment the glass was the ISG and the solution was initially saturated with respect to amorphous silica. Because of the similarity of the short- and long-term corrosion behavior of the two glasses (section 1.3), the effect of glass composition is assumed here to be minimal and the leaching conditions differences are emphasized. Unlike our experiment, the conditions used by Valle et al., favored the reactions of hydrolysis and condensation of silica. Hydrolysis reactions were favored because the inlet solution was only slightly enriched in silica. Under such conditions of high reactivity of silicon species, condensation reactions occurred within the amorphous alteration layer involving aqueous species and species only partly detached from the solids (glass and amorphous alteration layer) (Arab et al., 2008; Bunker, 1994; Cailleteau et al., 2008; Casey and Bunker, 1990; Ledieu et al., 2004). These processes explain why, in the Valle study, H_4SiO_4 initially present in solution was highly incorporated into the gel layer.

Solution data (Table 2) and ToF-SIMS analyses performed on the glass sample altered 209 days at pH 9 (Fig. 6) showed that i) the enrichment in ^{29}Si of the amorphous alteration layer is extremely low, ii) the concentrations of sparingly soluble elements (Si, Al) are constant along the depth profile, iii) the porosity of the amorphous alteration layer allows the water (and likely silica monomers) to diffuse up to the pristine glass. It can thus be concluded that the amorphous alteration layer formed at pH 9 cannot result from a dissolution/precipitation process. Indeed, such a reaction, implying the formation of species detached from the glass surface prior to their condensation to form a new silicate network, would have led to a significant increase of the ^{29}Si concentration within the

amorphous alteration layer and a decrease of the concentration of this isotope in the solution as it was shown in the Valle study. This is not observed here. As a consequence, i) the amorphous alteration layer formed at pH 9 in silica saturated conditions is a silica-alumina-zirconia-rich material whose structure is to a large extent inherited from that of the glass and ii) the complete hydrolysis of all the Si-O-X bonds ($X = \text{Si, Al, Zr}$) at the glass interface has not occurred or a portion of these bonds are hydrolyzed at a slower rate than that of the ingress of the alteration front determined by the release of Na, Ca and B. Therefore, complete hydrolysis of Si tetrahedra of the glassy structure cannot be the driving force of the glass alteration under these conditions. Following this reasoning, the most likely mechanism responsible for the release of Na, Ca and B from the glass would be direct dissolution into solution that has penetrated through the amorphous alteration layer. Ion-exchange (Eq 1) could provide a mechanism for alkali and, to a lesser extent for alkaline earth ions, but formally there is no mechanism for B to undergo ion exchange, as B in ISG glass acts as a glass network former and is shared into $[\text{BO}_3]$ and $[\text{BO}_4^- \text{Na}^+]$ entities linked to the silicate network by bridging oxygen atoms (Bunker et al., 1991; Bunker et al., 1990). However, first principles calculation showed that ion-exchange in borosilicate also affects B, especially when Na^+ acts as a charge compensator of four-fold coordinated B (Geneste et al., 2006). Once detached from the glass, these ions need to move through the growing amorphous alteration layer to the bulk solution. The driving force of such a process is the concentration gradients of Na, Ca, B between the glass and the bulk solution, with the magnitude directly depending on the pH (Bunker et al., 1983; Ojovan et al., 2006; Rebiscoul et al., 2012): the lower the pH, the faster the ion exchange process (Eq. 1). The fact that the 3 weakly bonded elements display similar profiles within the amorphous alteration layer suggests that their release from the glass is not the rate limiting step. This observation is a clue in favor of a control of the reaction by the reactive transport of water species through the amorphous alteration layer.

As soon as pH was raised to 11.5, hydrolysis of Si-O-X bonds ($X = \text{Si, Al, Zr}$) dramatically increased, as shown by the fast release of ^{28}Si into solution (Table 2). The morphological changes within the existing amorphous alteration layer (Fig. 4 and Fig. 5b) suggest that it was involved in the hydrolysis as well, despite being stable up to that point in the experiment. This reaction did not stop throughout the remainder of the experiment, with the achievement of 2.3 g.L^{-1} of Si in solution. Even this high concentration of Si could not be sufficient for making the glass and the alteration layer formed at pH 9 stable as silica is highly soluble in this pH domain (Iler, 1979), with speciation calculations performed by Chess code showing that the solution remained very undersaturated with respect to amorphous silica (Fig. 9). We do not know if hydrolysis of Si-O-X bonds would stop if solution becomes saturated with respect to amorphous silica in this very alkaline pH but for the purpose of this study, it can be stated that there is no doubt that hydrolysis was a main driving force of glass dissolution at pH 11.5.

Coupled with the increase in hydrolysis promoted by OH^- , the precipitation of alteration phases can also drive dissolution. Corrosion experiments of borosilicate glass under hyperalkaline conditions generally lead to an induction period during which the dissolution rate diminishes by several orders of magnitude compared to r_0 before the alteration suddenly resumes (Ebert et al., 1993; Gin and Mestre, 2001; Inagaki et al., 2006; Ribet and Gin, 2004; Ribet et al., 2004). Such a behavior was observed for numerous of glasses including ISG glass at pH 10.7 and 11 (Fournier et al., 2014a). However at pH 11.3, no induction period was observed for this glass (Fournier et al., 2014a). In the current understanding, the induction period is construed as the duration necessary to nucleate a

sufficient amount of CSH and zeolites, to eventually affect the budget of Si, Al and Ca. To grow, zeolites first consume dissolved Al (Ebert et al., 1991; Gin and Mestre, 2001) and then Al still present in the amorphous alteration layer along with Si, initiating the resumption of alteration (Feng et al., 1993; Ribet and Gin, 2004). Such a theory supposes that the amorphous alteration layer formed during the induction period is passivating or that the chemical composition of the fluid diminishes the affinity of the glass hydrolysis (as it was the case of the starting solution at pH 9). In our experiment, we do see precipitation and growth of CSH and zeolites (Fig. 5) but with no induction period (Fig. 3). Does this mean that secondary phases precipitate instantaneously after the pH rise? That does not seem to be the case. Equation 8 and ToF-SIMS profiles of $^{29}\text{Si}/^{28}\text{Si}$ along zeolites and CSH crystals enable us to determine when and at what rate such minerals formed. Figs. 10 and 11 show the isotope distribution of Si within minerals and, using Eq. 8, we calculated the time at which each crystal portion precipitated. Based on the characterization of several minerals observed at $t^* = 53$ d and $t^* = 98$ d, it can be said that CSH and zeolites started growing near $t^* = 15$ d and $t^* = 30$ d, respectively. This result is in agreement with SEM observations along with solution analyses (Table 2) which show that the highest concentration of Al is measured at $t^* = 28$ d. Beyond $t^* = 28$ d, dissolved Al feeds zeolite precipitation. Geochemical calculations also confirm these results (Fig. 9). For the calculation we have selected analcime to simulate the zeolite present in our experiment, because i) thermodynamic data of this mineral are well established and available at 90°C, ii) Al/Si are similar in the two phases, iii) analcime is one of the most common minerals that precipitate during nuclear glass corrosion experiments at high pH (Fournier et al., 2014b). The dissolution/precipitation reaction of analcime is given by:

and the corresponding $\log K$ at 90°C is -3.4. Once the pH was raised to 11.5, SI with respect to analcime ($\text{SI}_{\text{analcime}}$) sharply dropped by 3 units and then rose because of the dissolution of Si and Al. Fluctuations of $\text{SI}_{\text{analcime}}$ around 210 – 220 d are due to small pH fluctuations around the target. Solution then became supersaturated about 25 days after the pH change, followed by fluctuations around the equilibrium. Growth rate of zeolites can be estimated from the slopes of the variations of $^{29}\text{Si}/^{28}\text{Si}$ ratio along the main axis of the crystal (Fig. 10): the isotopic ratio decreases linearly from 0.27 ($x = 19 \mu\text{m}$) to 0.13 ($x = 26 \mu\text{m}$), corresponding to $t^* = 36.8$ d and $t^* = 83.7$ d, respectively, (according to Eq 8). The mean growth rate of zeolite along the main axis of the crystal is of $0.15 \mu\text{m} \cdot \text{d}^{-1}$. It appears that this rate is about 6 times smaller than the glass dissolution rate, once the steady state is achieved. Unfortunately this comparison cannot serve to calculate a mass balance and evaluate the impact of zeolite precipitation on glass corrosion because the growing surface of zeolites remains unknown. Regarding CSH, the calculation of precipitation rate of these minerals was not possible because of the not well defined shape of these minerals and the bumpy variations of the silicon isotopic ratio (Fig. 11).

From these findings, it can be proposed that the precipitation of CSH minerals – which consumes Ca and Si at the expense of the amorphous alteration layer – and that of zeolites – which consumes Al and Si at the expense of the amorphous alteration layer – become significant dissolution drivers after about 15 d and 30 d, respectively. Although the precipitation of these phases is likely a driving force for glass dissolution, it does not explain why no induction period is noticed prior to $t^* = 15$ d. For that, we suggest that the duration required to reach a sufficiently high concentration of Si in solution for the rate to drop is much longer than $t^* = 15$ d because of the low S/V (60 m^{-1}) of our experiment. As previously mentioned, this assumption is consistent with other experimental data obtained for

ISG glass altered at 90°C, pH 11.3 showing no induction period prior to zeolites growth despite a higher S/V and a concentration of Si close to 1 g.L⁻¹ (Fournier et al., 2014a).

Several other studies have demonstrated the role of zeolites in fast dissolution rate of silicate glasses (Fournier et al., 2014b) and references therein). The case of CSH is less documented, likely because alteration resumptions are generally triggered by zeolite precipitation only. Here we show that CSH minerals precipitate prior to zeolites and cover the surface more or less uniformly, with zeolites precipitating on the CSH when they begin to form (Fig. 5d). However ToF-SIMS mapping shows that Ca is highly depleted from the internal amorphous alteration layer and highly enriched within the external amorphous alteration layer and CSH. According to this observation and the fact that, in the absence of CSH, Ca has been shown to help polymerize the amorphous alteration layer and make it more passivating (Chave et al., 2011; Mercado-Depierre et al., 2013), it can be proposed that precipitation of CSH can also be a glass dissolution driver in our experiment.

4.3. What model to unify our experimental observations?

The ISG glass behaves differently at the two studied pH values. At pH 9, Si, Al and Zr remain immobile while soluble elements are released from the glass by reaction with pore solution and diffusion through the amorphous alteration layer. At pH 11.5, the hydrolysis of Si-O-X bonds (X = Si, Al, Zr) become the dominant process with enhancement from the precipitation of amorphous and crystalline phases. These two processes led to a complete redistribution of the Si, Al, Ca and Zr within the alteration layer. The glass dissolution rate and the rate limiting mechanism(s) are thus strongly affected by the pH.

These results suggest that the dominant mechanism controlling the formation of the amorphous alteration layer at pH 9 was ion exchange followed by potential in situ repolymerization of the silica network rather than the dissolution / precipitation mechanism being proposed by Geisler (Geisler et al., 2010) and Hellmann (Hellmann et al., 2012). The dissolution / precipitation theory hypothesizes that the glass alteration products are formed by precipitation following the congruent dissolution of the glass, with a thin film of liquid water separating the reacting glass and the newly formed precipitates. It is clear that, at pH 9, the distribution of Si isotopes cannot account for a model that requires the dissolution of the glass and the reprecipitation of the amorphous alteration layer from solution unless it is assumed that the silicon from solution is not present at that interface but that water and other soluble ions are; an unlikely proposition since it was shown only Si monomers were present in solution. In the conditions studied here, one must consider that the amorphous alteration layer is a relic structure of the glass (potentially reorganized after the release of B, Na and Ca) and that the extent of glass alteration is driven by a combination of dissolution at the reacting interface and ion exchange through the amorphous alteration layer. Another model, called GRAAL (Frugier et al., 2008), formalized, parameterized for simple glasses as well as for SON68 glass and successfully applied to various leaching conditions with a unique set of parameters (Debure et al., 2013a; Frugier et al., 2009; Godon et al., 2013; Jollivet et al., 2012), considers the formation of a passivating layer (slowing down the water ingress and the release of mobile species) within the amorphous alteration layer. The passivation layer and the rest of the amorphous layer are simulated by 6 end-members (Debure et al., 2013a; Debure et al., 2012, 2013b). Observations arising from the first stage at pH 9 are not in full agreement with GRAAL as we didn't evidenced the existence of a passivating layer

made of Si and Al only as it is considered in the model. This highlights how it is complicated to properly link kinetics and thermodynamics for glasses.

At pH 11.5, the Geisler and Hellmann models seem valid as all the glass elements are congruently dissolved and, among them, the less soluble reprecipitate. Under these hyperalkaline conditions, GRAAL could also explain our experimental results even though it is thought that both composition and solubility of the passivating layer should certainly be reconsidered to take into account the high solubility of the glass formers.

5. CONCLUDING REMARKS

This study provides new insight into driving forces and rate-limiting mechanisms controlling glass alteration under slightly and hyperalkaline conditions. Fig. 12 summarizes our main observations. It is shown that the dissolution of the silicate network at pH 9 in a silica saturated solution is either non-existent or slow enough so that a glassy structure depleted in mobile elements (likely a relic more or less reorganized) remains on the surface through a mechanism other than precipitation. This layer appears to have a large effect on the transport of ions from the reacting interface to the bulk solution. In another study performed with the SON68 glass, we claimed that this material can be passivating because the apparent diffusion coefficient derived from the chemical gradients is much smaller than that expected in the pristine glass in the absence of any alteration layer (Gin et al., 2013c). Unfortunately mechanism by which this material achieves passivation remains to be determined. For that, more characterization is needed. Until now, the limitation was the means to produce sufficient amount of this material to perform in situ analyses. Following our experimental protocol, perhaps by lowering the pH below 9 in order to accelerate ion exchange reaction, it would be possible to prepare enough material in a reasonable time.

As expected, hyperalkaline water makes the silicon and other glass formers highly soluble and leads to the congruent rapid dissolution of the glass and the precipitation of amorphous and crystalline phases. This does not mean that the glass alteration rate cannot decrease at longer duration, but the solubility of silicon is extremely high in these conditions and the alteration phases deplete the solution concentration of all glass formers. For a rate decrease, it would require another mechanism like the formation of a dense layer (i.e. non porous) within the amorphous alteration layer or a complete coating of the glass by zeolites as seen on some old basaltic glass samples (Crovisier et al., 2003).

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Table Captions

Table 1. Nominal composition of ISG glass.

Table 2. Data from solution analyses. uf: solutions ultrafiltered at 10000 D.

Figures Captions

Figure 1. Design of the leaching experiment.

Figure 2. ^{29}Si liquid-state NMR spectra of the two solutions: that at pH 9 after 503 days of glass alteration in similar conditions as those of the first stage of our experiment (left) and that at pH 11.5 at $t = 503$ days ($t^* = 294$ days) (right). Analyses have been performed at 90°C to prevent polycondensation of Si species during cooling.

Figure 3. Normalized mass loss (NL) of the main glass elements, calculated from ICP-OES data (top) and pH measured at 90°C and prior to any correction (bottom). The insert displays the variation of $NL(B)$ under linear scales during the second stage of the experiment (pH 11.5).

Figure 4. Concentrations of the isotopes of Si. Focus on ^{29}Si concentration just before and after the pH rise (insert). Concentration of ^{28}Si and ^{30}Si are close during the first stage (see Table 2).

Figure 5. SEM images (sample broken and tilted: a, b, c ; cross section: d, e ; direct observation: f) showing the alteration layer at various durations: (a) 209 d (just before the pH disruption), (b) $t = 209.5$ d ($t^* = 0.5$ d), (c) $t = 223$ d ($t^* = 14$ d), (d) $t = 262$ d ($t^* = 53$ d), (e) $t = 307$ d ($t^* = 98$ d) and (f) $t = 374$ d ($t^* = 165$ d)

Figure 6. ToF-SIMS profiles of glass components and H, normalized to that of Zr, for the altered glass sample withdrawn at 209 days (just before the pH rise).

Figure 7. SEM image (a) and ToF-SIMS elemental maps (b-i) of the alteration layer obtained at $t = 307$ d ($t^* = 98$ d). ROIs shown in (a) correspond to: pristine glass (1), internal amorphous alteration layer (2), intermediate amorphous alteration layer (3), external amorphous alteration layer (4), thin Zr-rich film (5), CSH (6, dark grey phases), Zeolites (7, light grey phases).

Figure 8. Glass dissolution rate in our experiment and in a similar experiment maintained at pH 9. Rates are calculated from B release. Uncertainties are of 25 %.

Figure 9. Simulation by Chess code of saturation index (SI) of the leaching solution with respect to analcime and amorphous silica.

Figure 10. Evolution of $^{29}\text{Si}/^{28}\text{Si}$ along a crystal of zeolite (dotted line displayed in the ToF-SIMS map of ^{28}Si) at $t = 307$ d ($t^* = 98$ d). For each dot, the time at which the corresponding part of the crystal has precipitated is calculated according to Eq (8).

Figure 11. Evolution of $^{29}\text{Si}/^{28}\text{Si}$ within CSH following the dotted line displayed in the ToF-SIMS map of ^{28}Si . Left: $t = 262$ d ($t^* = 53$ d). Right: $t = 307$ d ($t^* = 98$ d). For each dot, the time at which the corresponding part of the phase has precipitated is calculated according to Eq. (8).

Figure 12. Schematic representation of ISG glass alteration at pH 9 (top) and 11.5 (bottom).

Figure 1. Design of the leaching experiment.

Corrosion at pH 9

Corrosion at pH 11.5

Table 1

	SiO ₂	B ₂ O ₃	Na ₂ O	Al ₂ O ₃	CaO	ZrO ₂	
Wt%	56.2	17.3	12.2	6.1	5.0	3.3	
Mol%	60.1	16.0	12.7	3.8	5.7	1.7	
	Si	B	Na	Al	Ca	Zr	O
Wt%	26.3	5.4	9.0	3.2	3.6	2.4	50.1
Mol%	18.0	9.6	7.6	2.3	1.7	0.5	60.3

Table 2

t	t*	pH ₉ °C	AG F	ICP-OES						MC-ICP-MS						
				Si	B	Na	Al	Ca	K	²⁸ Si	²⁹ Si	³⁰ Si	Si total	Al	Ca	Zr
(da ys)	(da ys)		(%)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(g. L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(mg .L ⁻¹)	(μg .L ⁻¹)
0		8.9			<0.		<0.	<0.	2.					-		
		8	0	266	2	<1	1	5	8	5.6	240	5.5	251			
0.3		9.0	<0.		<0.		0.1	2.1	2.					-	-	-
		0	01	265	2	1.0	1	0	9	5.7	238	5.5	249			
7		9.0	0.0				0.1	<0.	2.					-	-	-
		1	6	267	1.3	2.7	1	5	9	5.6	238	5.5	249			
14		9.0	0.0				<0.	<0.	2.					-	-	-
		0	7	266	1.5	3.3	1	5	9	6.1	247	5.7	258			
28		8.9	0.0				<0.	0.6	2.					-	-	-
		8	7	268	1.7	3.3	1	7	9	5.5	234	5.4	245			
91		9.0	0.0				<0.	0.8	3.					-	-	-
		2	9	274	2.0	4.6	1	7	0	5.2	229	5.3	240			
209		9.0	0.1				<0.	<0.	3.					-	-	-
		4	1	271	2.5	4.1	1	5	1	6.4	251	5.7	263			
209		11.	0.1				0.5	<0.	5.					-	-	-
.3	0.3	30	2	275	2.7	4.8	3	5	0	9.2	218	5.1	232			
210		11.				18.		<0.	6.	33.				-	-	-
	1	25	0.4	325	9.4	2	4.6	5	6	4	199	5.5	238			
211		11.			22.	44.	11.	<0.	11	66.				-	-	-
	2	54	1.0	372	9	4	4	5	.5	5	168	5.9	240			
212		11.			33.	73.	17.	<0.	8.	88.				-	-	-
	3	61	1.5	414	9	4	2	5	1	6	149	6.4	244			
213		11.			46.	94.	22.	<0.	11					-	-	-
	4	58	2.3	462	2	0	8	5	.5	118	150	7.4	275			
216		11.			72.		33.	<0.	9.					-	-	-
	7	58	3.6	569	0	144	2	5	2	178	152	9.5	339			
220		11.			87.		37.	<0.	14			12.		-	-	-
	11	40	4.3	512	0	121	1	5	.6	244	163	0	420			
223		11.					42.	<0.	16			11.		-	-	-
	14	46	4.7	590	107	144	1	5	.2	250	145	9	408			
225		11.					43.	<0.	16			12.		-	-	-
	16	47	5.1	648	103	147	1	5	.2	262	144	3	419			
227		11.					43.	<0.	21					-	-	-
	18	70	5.6	682	111	165	1	5	.4	-	-	-	-			
230		11.					51.	<0.	20			19.		45.	0.8	4
	21	64	6.2	775	122	195	3	5	.7	441	190	9	651	5	4	
234		11.					57.	<0.	21			21.		-	-	-
	25	56	7.4	854	146	228	9	5	.4	482	182	1	685			
237		11.					62.	<0.	20			22.		-	-	-
	28	52	8.4	860	165	248	4	5	.9	515	183	3	721			
244		11.					59.	<0.	20					-	-	-
	35	46	9.0	983	176	261	9	5	.9	-	-	-	-			
258		11.	11.	111			26.	<0.	21			28.		-	-	-
	49	45	5	7	222	346	6	5	.9	695	166	1	889			
272		11.	18.	137			10.	<0.	22			31.		-	-	-
	63	44	8	5	351	539	0	5	.3	803	140	5	975			
286		11.	23.	158	430	699	6.6	<0.	21	116	168	44.	137	-	-	-

		55	3	8					5	.6	6		8	9			
307		11.	26.	191					<0.	21	134		50.	155	3.2	1.9	2
	98	51	9	8	495	828	3.9		5	.8	3	163	9	7	2	7	
318		11.	30.	188	552	713	3.6		<0.	18	175		66.	201	-	-	-
	109	41	4	6					5	.5	0	199	3	5			
335		11.	33.	204	609	793	2.7		<0.	18	194		73.	223	1.3	2.4	2
	126	51	9	4					5	.8	9	207	4	0	2	9	
349		11.	36.	217	652	851	2.6		<0.	18	185		69.	211	-	-	-
	140	36	5	6					5	.7	5	188	7	3			
363		11.	40.	234	721	934	2.7		0.5	19	221		83.	251	1.0	3.0	3
uf	154	46	7	8					4	.0	3	215	1	1	7	3	
377		11.	43.	244	755	988	-		1.8	18					-	-	-
	168	50	1	7					4	.3	-	-	-	-			
377		11.	43.	244	769	103	1.9		0.2	20					-	-	-
uf	168	50	1	0		8			8	.3	-	-	-	-			