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Effect of pH on the stability of passivating gel layers formed on International Simple Glass

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Abstract

20 It has been well established that borosilicate glass dissolves much more slowly in saturated silica solutions than in deionized water. The present study assesses this assertion for the specific case of International Simple Glass, which is a 6-oxide borosilicate glass of nuclear interest, and was altered between $\text{pH} = 1$ and 10.7 at $90\text{ }^\circ\text{C}$. Depending on the reaction stage, aqueous silica can promote either the formation of a passivating gel layer on the glass
25 surface or the precipitation of certain secondary phases at the expense of the passivating gel. In this study, a negligible effect of aqueous silica on glass dissolution at acidic pH is demonstrated, while a marked effect above $\text{pH}_{90\text{ }^\circ\text{C}} = 7$ is observed, ensuring better chemical durability of the glass. Conversely, at higher reaction progress and above $\text{pH}_{90\text{ }^\circ\text{C}} = 9.5$, the chemical durability of the glass decreases owing to the formation of secondary phases such
30 as hydroxides or zeolites.

Keywords

ISG, nuclear glass, amorphous silica, pH.

Graphical abstract

Effect of dissolved silica on glass durability:

Low

Increasingly positive

Detrimental



Highlights

- $\text{SiO}_2(\text{aq})$ has no effect on the ISG dissolution rate at acidic pH
- Aqueous SiO_2 slows glass dissolution at $\text{pH}_{90^\circ\text{C}} \geq 7$ and low reaction progress
- Aqueous SiO_2 increases glass dissolution at $\text{pH}_{90^\circ\text{C}} \geq 9.5$ and high reaction progress

1. Introduction

Countries such as France, Japan, Russia, India, and Great Britain have chosen to reprocess their spent nuclear fuel. The minor actinides and fission products that arise from this
50 reprocessing are vitrified in borosilicate or, to a lesser extent, phosphate glasses. In France, the vitrified waste form, usually called “nuclear glass,” is packed in carbon steel containers and will eventually be stored in a deep, stable claystone formation with low permeability. Assessment of the safety of the geological repository relies on the performance of various barriers and thus is partly dependent on the chemical durability and radiation resistance of
55 the glass. Although research on the durability of nuclear glass has been ongoing for several decades, it is still a field of intense investigation [1].

In contact with water, glass dissolves and transforms into more stable phases at a rate that is highly dependent on the geochemical conditions. The formation of a Si-rich passivating layer (also called a “gel”) under the most favorable conditions can guarantee a glass package
60 lifetime of several hundred thousand years [2]. For the same glass, the composition and structure of the gel vary depending on environmental parameters, particularly the pH and composition of the solution. A chemical element resulting from the glass dissolution may participate in the formation of the gel and/or the precipitation of secondary minerals, which are thermodynamically more stable but less protective [3-9]. Studies conducted on SON68
65 and ISG and involving solution spiked in ^{29}Si and ^{18}O have demonstrated that secondary silicate phases form by precipitation of aqueous species, whereas gel forms by in situ hydrolysis/condensation reactions preventing the complete dissolution of silica [10-12]. As an example of competition between gel formation and phases precipitation, some experiments have evidenced gel dissolution reaction at the expense of precipitation reaction of calcium
70 silicate hydrates and zeolites [13, 14]. Finally, thermodynamic data on the gel and secondary phases are of interest for the geochemical modeling of nuclear glasses alteration [15, 16].

The presence of aqueous silica [17-22] has two major effects on glass: on the one hand, it decreases the affinity of the matrix dissolution reaction ($\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4$); on the other hand, it favors the backward reaction of condensation. The latter reaction accounts for the formation of the gel layer, which can, in some circumstances, be transport-limiting [12, 23]. Aqueous silica is not the only dissolved species that can affect the glass durability. In fact, most dissolved species can have an effect, either directly on the hydrolysis reaction of the –Si–O–Si– bonds [24, 25], or indirectly through the pH or the gel formation [6, 26-31].

Because the pH of leaching solutions is generally buffered around 9–9.5 by boron released from the glass ($\text{B(OH)}_3 + \text{H}_2\text{O} \rightarrow \text{B(OH)}_4^- + \text{H}^+$, $\text{pK}_a = 9.14$ at room temperature), and because the pH of many natural groundwaters is in the range of 6–8, many studies have been conducted between pH 7 and 9.5. However, some disposal designs would lead to more alkaline pH conditions [32], raising concerns about the gel stability above pH 9.5. In addition, below pH 7, the role of aqueous silica on the reactivity of glass is unclear.

This study thus reports the dissolution behavior of an international reference glass (International Simple Glass, ISG) [33], which is a 6-oxide borosilicate glass, in solutions that are saturated or unsaturated with respect to amorphous silica at 90 °C for $\text{pH}_{90\text{ °C}}$ ranging between 1 and 10.7. Above pH 10.7, it becomes experimentally challenging to saturate the solution due to spontaneous reactions of oligomerization [34]. Two different ratios of the reactive glass surface area to the solution volume (S/V) are considered. These two ratios differ by two orders of magnitude and are complementary over the entire pH range of the study while making it possible to (i) maximize the difference in silica concentrations between a pre-saturated solution and a solution where the silica originates solely from the glass dissolution, and (ii) measure the boron concentration with sufficient analytical precision. More than twenty static tests were conducted over durations up to one year with regular solution sampling. Solid characterization was performed to identify the formation of secondary phases. No specific attention was paid to the passivating properties of the gels formed at various pHs, but previous studies have investigated this aspect, especially at pH 7 and 9 [11,

12, 35-37]. Overall, this study demonstrates that the positive effect of aqueous silica on the durability of ISG is limited to a $\text{pH}_{90\text{ }^\circ\text{C}}$ range of 7–9.5.

2. Material and Methods

2.1. Preparation of the material

The tests in this study were conducted using ISG; its composition is summarized in Table 1. ISG ingots were prepared by the MO-SCI Corporation (Rolla, MO, USA) [38] and provided by the Savannah River National Laboratory (Aiken, SC, USA). Two different sizes of glass powder were prepared from successive steps of crushing with a vario-planetary mill and sieving to isolate 125–250 μm and 20–40 μm size fractions. The powders were washed to remove fine particles by an iterative decantation process using acetone and absolute ethanol according to Stokes' law.

| ISG | SiO ₂ | B ₂ O ₃ | Na ₂ O | Al ₂ O ₃ | CaO | ZrO ₂ |
|-----------|------------------|-------------------------------|-------------------|--------------------------------|-----------|------------------|
| Oxide wt% | 56.2 ± 1.5 | 17.3 ± 0.9 | 12.2 ± 0.7 | 6.1 ± 0.8 | 5.0 ± 0.6 | 3.3 ± 0.5 |

110 **Table 1:** ISG composition expressed in oxide weight percent

2.2. Leaching tests

Static leaching tests were performed at $90 \pm 2\text{ }^\circ\text{C}$ in a perfluoroalkoxy vessel. Two series of tests were conducted: the first (S1) with an S/V ratio of 60 m^{-1} using the 125–250 μm size fraction (0.13 g of glass in 40 mL of solution), and the second (S2) with $S/V = 10\text{ 000 m}^{-1}$ using the 20–40 μm size fraction (4.25 g in 40 mL). The reactive surfaces correspond to the geometric surfaces by considering the glass grains as spheres, corrected by a factor of 1.3 to take into account the non-sphericity of the glass grains [39].

Leaching tests (Table 2) were conducted in solutions saturated with respect to amorphous silica (“Sat” test series) at various pHs, and in solutions with the same pH but no initial aqueous silica (“Blk” test series). Acid solutions were prepared by diluting nitric acid (65%, Merck Suprapur[®]) in 18 M Ω ·cm ultrapure water, and basic solutions were prepared by

dissolving KOH pellets (Merck Emsure®). The amount of silica introduced to reach saturation at 90 °C in the “Sat” test series was calculated using the Chess code [40]. For $\text{pH}_{90\text{ °C}} \geq 9.5$, silica-containing solutions were prepared by dissolving amorphous silica for about a week at 90 °C while stirring. To prepare lower pH solutions, the solution prepared with a $\text{pH}_{90\text{ °C}} = 9.5$ was split and acidified. The silica concentration of each solution was checked using a UV-visible spectrometer (Cary® 50 Scan UV-Vis) according to a method analogous to ASTM D859-10 [41]. During the tests, the pH was manually controlled at the set point through regular addition of micro-volumes of concentrated HNO_3 or KOH solutions to counterbalance variations due to glass dissolution or carbonation of solutions.

| Test name | Test series | S/V (m^{-1}) | T (°C) | $\text{pH}_{90\text{ °C}}$ | C_{Si} ($\text{mg}\cdot\text{L}^{-1}$) | Duration (d) |
|-------------|-------------|---------------------------|----------|----------------------------|---|--------------|
| S1-Sat-1 | 1 | 60 | 90 | 1 | $3.1\cdot 10^2$ | 365 |
| S1-Blk-3 | 1 | 60 | 90 | 3 | 0 | 365 |
| S1-Sat-3 | 1 | 60 | 90 | 3 | $3.0\cdot 10^2$ | 365 |
| S1-Blk-7 | 1 | 60 | 90 | 7 | 0 | 365 |
| S1-Sat-7 | 1 | 60 | 90 | 7 | $1.5\cdot 10^2$ | 365 |
| S1-Sat-8 | 1 | 60 | 90 | 8 | $1.8\cdot 10^2$ | 365 |
| S1-Sat-9 | 1 | 60 | 90 | 9 | $2.8\cdot 10^2$ | 365 |
| S1-Blk-9.5 | 1 | 60 | 90 | 9.5 | 0 | 365 |
| S1-Sat-9.5 | 1 | 60 | 90 | 9.5 | $7.4\cdot 10^2$ | 365 |
| S1-Sat-9.8 | 1 | 60 | 90 | 9.8 | $1.4\cdot 10^3$ | 365 |
| S1-Blk-10.1 | 1 | 60 | 90 | 10.1 | 0 | 365 |
| S1-Sat-10.1 | 1 | 60 | 90 | 10.1 | $3.9\cdot 10^3$ | 365 |
| S1-Sat-10.3 | 1 | 60 | 90 | 10.3 | $1.2\cdot 10^4$ | 365 |
| S2-Blk-9.5 | 2 | 10 000 | 90 | 9.5 | 0 | 379 |
| S2-Sat-9.5 | 2 | 10 000 | 90 | 9.5 | $7.4\cdot 10^2$ | 379 |
| S2-Blk-9.8 | 2 | 10 000 | 90 | 9.8 | 0 | 379 |
| S2-Sat-9.8 | 2 | 10 000 | 90 | 9.8 | $1.4\cdot 10^3$ | 379 |
| S2-Blk-10.1 | 2 | 10 000 | 90 | 10.1 | 0 | 379 |
| S2-Sat-10.1 | 2 | 10 000 | 90 | 10.1 | $3.9\cdot 10^3$ | 379 |
| S2-Blk-10.3 | 2 | 10 000 | 90 | 10.3 | 0 | 379 |
| S2-Sat-10.3 | 2 | 10 000 | 90 | 10.3 | $1.2\cdot 10^4$ | 379 |
| S2-Blk-10.7 | 2 | 10 000 | 90 | 10.7 | 0 | 379 |
| S2-Sat-10.7 | 2 | 10 000 | 90 | 10.7 | $2.7\cdot 10^4$ | 379 |

Table 2: Characteristics of the “Sat” and “Blk” test series, including the ratio of the glass surface area to the solution volume (S/V), temperature (T), target pH value maintained at 90 °C, initial silicon concentration (C_{Si}), and total duration.

2.3. Solution analyses

135 Samples of 0.5 mL of solution were removed at 1, 3, 7, 14, and 28 d, 3 months, and 1 y.
 Samples were ultrafiltered at 10 000 D, acidified with 0.5 N HNO₃, and analyzed using
 inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific
 iCAP™ 6000 Series) to determine the boron and silicon concentrations. As boron is known to
 be a glass alteration tracer, the boron concentration was used to calculate the altered glass
 140 percentage, %AG, from a mass balance taking into account the change in volume (Equation
 1).

$$\%AG = \frac{C_i(t) \times V(t) + \sum_{j=1}^{t-1} C_i(j) \times V_S(j)}{m \times x_i} \quad 1$$

where $C_i(t)$ is the mass concentration of element i at time t , x_i is the mass fraction of element
 i in the glass composition, $V(t)$ is the solution volume at time t , $V_S(j)$ is the volume of the j -th
 sampling, and m is the mass of the glass.

145 The equivalent thickness of altered glass, eTh(B), was calculated as a function of time using
 Equation 2, where r_0 is the glass particle radius at $t = 0$, and r_t is the radius at time t .

$$eTh(B) = r_0 - r_t = r_0 \times \left[1 - (1 - \%AG)^{\frac{1}{3}} \right] \quad 2$$

2.4. Solid analyses

X-ray diffraction (XRD). XRD patterns of the altered glass powders were acquired with a
 Phillips X'PERT Pro diffractometer equipped with a Cu-K α monochromatic source ($\lambda =$
 150 1.5418 Å) operating at 40 mA, 40 kV in Bragg-Brentano geometry. Scans were taken for 2 θ
 ranges from 4° to 80° with a speed of 0.11°·min⁻¹ and a step of 0.017° (2 θ) using amorphous
 silica sample holders. The XRD patterns were processed using the DIFFRAC.EVA v. 4.2
 (Bruker) software and compared to reference patterns from the International Center for
 Diffraction Data PDF-4+ 2018 RDB.

155 *Scanning electron microscopy (SEM)*. Solid samples taken at the end of the leaching experiments were rinsed, dried, coated with a carbon deposit, and observed using a Zeiss Merlin scanning electron microscope operated with an accelerating voltage of 15 kV and coupled with a lithium-doped silicon detector for energy dispersive X-ray spectrometry.

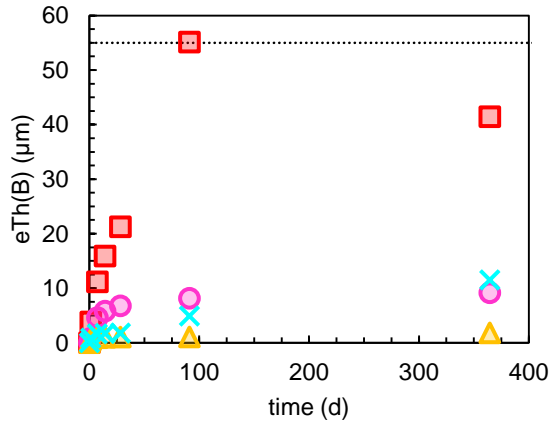
160 3. Results

3.1. S1 test series: low S/V ratio

In the S1 test series, the pH values were generally maintained at the set values within ± 0.3 pH unit, with the exception of a few cases, especially in the first 10 d of the $\text{pH}_{90^\circ\text{C}} = 7$ tests where the pH control was the most difficult (Figure A.1). The evolution of the silicon
165 concentration is summarized in Table 3, and the complete results of the solution analyses are presented in Appendix D.

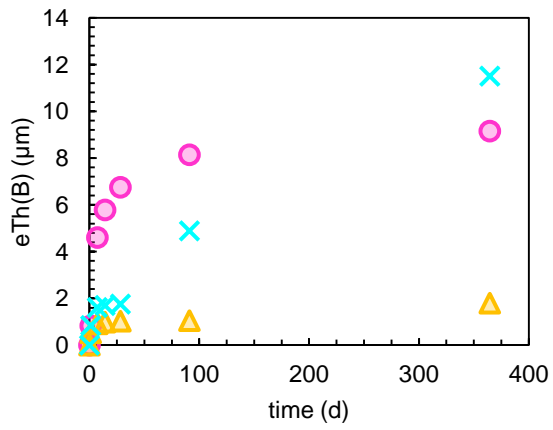
In the “S1-Blk” tests (Figure 1.a-b), the highest altered glass thicknesses are observed at $\text{pH}_{90^\circ\text{C}} = 3$ (S1-Blk-3), while the lowest are observed at $\text{pH}_{90^\circ\text{C}} = 9.5$ (S1-Blk-9.5). Between $\text{pH}_{90^\circ\text{C}} = 3$ and 9.5, the altered thicknesses gradually decrease with increasing pH. Above
170 $\text{pH}_{90^\circ\text{C}} = 9.5$, the altered glass thicknesses increase and exhibit a sharp variation in the alteration rate between 28 and 91 d. This sharp increase is associated with the precipitation of calcium silicate hydrate-like phases (CSH) [38, 42], as evidenced by the SEM results (Figure 2.a), but which cannot be identified by XRD because of the absence of diffraction peaks.

175 In the “S1-Sat” tests (Figure 1.c-d), the same evolution of the altered glass thicknesses as a function of pH is observed as in the “S1-Blk” tests: a decrease between $\text{pH}_{90^\circ\text{C}} = 3$ (S1-Sat-3) and $\text{pH}_{90^\circ\text{C}} = 9.5$ (S1-Sat-9.5) and an increase beyond that point. However, it should be noted that $e\text{Th}(\text{B})$ at $\text{pH}_{90^\circ\text{C}} = 3$ is slightly larger than at $\text{pH}_{90^\circ\text{C}} = 1$ (S1-Sat-1). For the tests at $\text{pH}_{90^\circ\text{C}} \geq 9.5$, only the boron concentration of the last sample at 1 y can be measured owing
180 to the high dilution factor necessary for the ICP-OES analyses due to the high silica content of these solutions. This result motivated a second test series conducted at a higher S/V ratio (Section 3.2). Finally, only small amounts of phyllosilicate-like secondary phases [43, 44] are observed by SEM in these tests (Figure 2.b).



(a)

■ S1-Blk-3 ● S1-Blk-7
▲ S1-Blk-9.5 × S1-Blk-10.1



(b)

● S1-Blk-7 ▲ S1-Blk-9.5 × S1-Blk-10.1

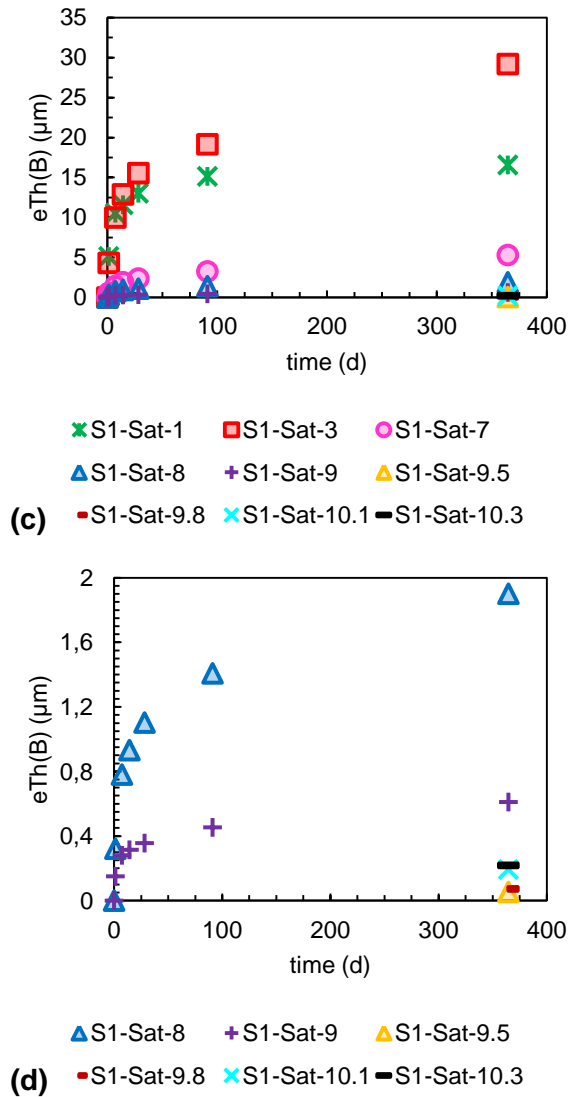


Figure 1: Evolution of the equivalent thickness of altered glass calculated from the boron concentration, $eTh(B)$, for the (a, b) S1-Blk and (c, d) S1-Sat test series with an S/V ratio of 60 m^{-1} . The dotted line represents the total alteration of the glass ($\%AG = 100$). Figures (b) and (d) are zoomed-in subfigures of (a) and (c), respectively.

190

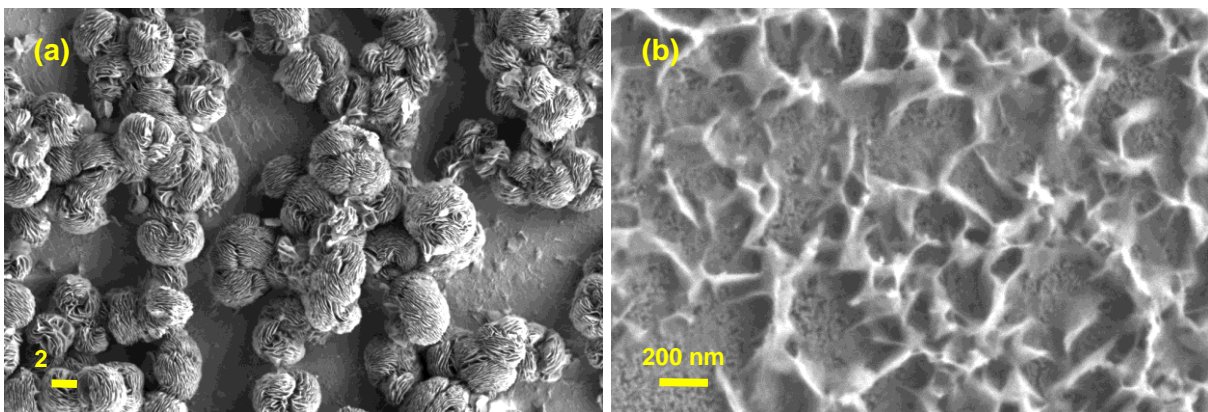


Figure 2: SEM images of ISG after 1 y in tests (a) S1-Blk-10.1, showing the precipitation of CSH-like phases, and (b) S1-Sat-10.1, showing minimal precipitation of phyllosilicates.

| Time (d) | S1-Sat-1 | S1-Blk-3 | S1-Sat-3 | S1-Blk-7 | S1-Sat-7 | S1-Sat-8 | S1-Sat-9 | S1-Blk-9.5 | S1-Sat-9.5 | S1-Sat-9.8 | S1-Blk-10.1 | S1-Sat-10.1 | S1-Sat-10.3 |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 0 | $3.1 \cdot 10^2$ | 3.3 | $3.0 \cdot 10^2$ | 2.2 | $1.5 \cdot 10^2$ | $1.8 \cdot 10^2$ | $2.8 \cdot 10^2$ | 5.7 | $7.4 \cdot 10^2$ | $1.3 \cdot 10^3$ | $2.4 \cdot 10^1$ | $3.8 \cdot 10^3$ | $1.2 \cdot 10^4$ |
| 1.2 | $2.9 \cdot 10^2$ | $8.4 \cdot 10^1$ | $3.1 \cdot 10^2$ | $1.7 \cdot 10^1$ | $1.5 \cdot 10^2$ | $1.5 \cdot 10^2$ | $2.5 \cdot 10^2$ | $2.0 \cdot 10^1$ | $6.4 \cdot 10^2$ | $1.2 \cdot 10^3$ | $3.6 \cdot 10^1$ | $3.4 \cdot 10^3$ | $9.9 \cdot 10^3$ |
| 7.2 | $3.1 \cdot 10^2$ | $3.3 \cdot 10^1$ | $3.2 \cdot 10^2$ | $5.9 \cdot 10^1$ | $1.4 \cdot 10^2$ | $1.5 \cdot 10^2$ | $2.8 \cdot 10^2$ | $3.6 \cdot 10^1$ | $6.3 \cdot 10^2$ | $1.2 \cdot 10^3$ | $6.7 \cdot 10^1$ | $3.5 \cdot 10^3$ | $1.1 \cdot 10^4$ |
| 14.2 | $3.4 \cdot 10^2$ | $4.6 \cdot 10^1$ | $3.1 \cdot 10^2$ | $6.3 \cdot 10^1$ | $1.4 \cdot 10^2$ | $1.5 \cdot 10^2$ | $2.5 \cdot 10^2$ | $4.2 \cdot 10^1$ | $5.9 \cdot 10^2$ | $1.2 \cdot 10^3$ | $6.7 \cdot 10^1$ | $3.4 \cdot 10^3$ | $9.7 \cdot 10^3$ |
| 28.2 | $4.9 \cdot 10^2$ | $5.5 \cdot 10^1$ | $3.2 \cdot 10^2$ | $6.6 \cdot 10^1$ | $1.4 \cdot 10^2$ | $1.5 \cdot 10^2$ | $2.5 \cdot 10^2$ | $4.4 \cdot 10^1$ | $5.5 \cdot 10^2$ | $1.0 \cdot 10^3$ | $7.5 \cdot 10^1$ | $2.8 \cdot 10^3$ | $1.0 \cdot 10^4$ |
| 91.1 | $5.9 \cdot 10^2$ | $9.3 \cdot 10^1$ | $3.6 \cdot 10^2$ | $7.6 \cdot 10^1$ | $1.8 \cdot 10^2$ | $1.6 \cdot 10^2$ | $2.8 \cdot 10^2$ | $6.2 \cdot 10^1$ | NA | $1.6 \cdot 10^3$ | $1.4 \cdot 10^2$ | NA | $1.8 \cdot 10^4$ |
| 364.6 | $5.6 \cdot 10^2$ | $6.0 \cdot 10^2$ | $9.5 \cdot 10^2$ | $2.5 \cdot 10^2$ | $3.3 \cdot 10^2$ | $2.6 \cdot 10^2$ | $4.7 \cdot 10^2$ | $1.4 \cdot 10^2$ | $8.4 \cdot 10^2$ | $1.3 \cdot 10^3$ | $5.1 \cdot 10^2$ | $4.0 \cdot 10^3$ | $1.2 \cdot 10^4$ |

Table 3: Silicon concentrations of the S1 test series, expressed in $\text{g} \cdot \text{m}^{-3}$ ($\text{mg} \cdot \text{L}^{-1}$) (NA: not analyzed).

| Time (d) | S2-Blk-9.5 | S2-Sat-9.5 | S2-Blk-9.8 | S2-Sat-9.8 | S2-Blk-10.1 | S2-Sat-10.1 | S2-Blk-10.3 | S2-Sat-10.3 | S2-Blk-10.7 | S2-Sat-10.7 |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 0.0 | 4.3 | $7.2 \cdot 10^2$ | 2.8 | $1.8 \cdot 10^3$ | 2.1 | $3.8 \cdot 10^3$ | 3.0 | $1.1 \cdot 10^4$ | 6.8 | $3.5 \cdot 10^4$ |
| 1.1 | $1.9 \cdot 10^1$ | $6.3 \cdot 10^2$ | $1.0 \cdot 10^2$ | $1.2 \cdot 10^3$ | $1.5 \cdot 10^2$ | $3.5 \cdot 10^3$ | $1.1 \cdot 10^2$ | $1.0 \cdot 10^4$ | $1.8 \cdot 10^2$ | $2.7 \cdot 10^4$ |
| 3.0 | $2.1 \cdot 10^1$ | $6.0 \cdot 10^2$ | $1.2 \cdot 10^2$ | $1.1 \cdot 10^3$ | $1.6 \cdot 10^2$ | $3.4 \cdot 10^3$ | $1.2 \cdot 10^2$ | $9.4 \cdot 10^3$ | $2.0 \cdot 10^2$ | $2.9 \cdot 10^4$ |
| 7.0 | $1.9 \cdot 10^1$ | $6.2 \cdot 10^2$ | $1.5 \cdot 10^2$ | $1.2 \cdot 10^3$ | $1.6 \cdot 10^2$ | $3.6 \cdot 10^3$ | $1.3 \cdot 10^2$ | $9.4 \cdot 10^3$ | $2.3 \cdot 10^2$ | $2.5 \cdot 10^4$ |
| 14.0 | $1.9 \cdot 10^1$ | $5.5 \cdot 10^2$ | $1.9 \cdot 10^2$ | $1.3 \cdot 10^3$ | $1.5 \cdot 10^2$ | $3.3 \cdot 10^3$ | $1.2 \cdot 10^2$ | $1.0 \cdot 10^4$ | $1.9 \cdot 10^2$ | $2.5 \cdot 10^4$ |
| 28.1 | $1.9 \cdot 10^1$ | $3.3 \cdot 10^2$ | $1.4 \cdot 10^2$ | $1.1 \cdot 10^3$ | $1.4 \cdot 10^2$ | $3.5 \cdot 10^2$ | $1.7 \cdot 10^2$ | $8.6 \cdot 10^3$ | $2.2 \cdot 10^2$ | $2.5 \cdot 10^4$ |
| 91.1 | $1.2 \cdot 10^1$ | $5.1 \cdot 10^2$ | $1.9 \cdot 10^2$ | $9.4 \cdot 10^2$ | $1.9 \cdot 10^2$ | $3.0 \cdot 10^3$ | $2.0 \cdot 10^2$ | $8.0 \cdot 10^3$ | $2.2 \cdot 10^2$ | $2.4 \cdot 10^4$ |
| 379.0 | $3.6 \cdot 10^1$ | $5.5 \cdot 10^2$ | $2.2 \cdot 10^2$ | $9.5 \cdot 10^2$ | $3.2 \cdot 10^2$ | $2.1 \cdot 10^3$ | $3.5 \cdot 10^2$ | $1.1 \cdot 10^4$ | $5.2 \cdot 10^2$ | $2.5 \cdot 10^4$ |

195

Table 4: Silicon concentrations of the S2 test series, expressed in $\text{g} \cdot \text{m}^{-3}$ ($\text{mg} \cdot \text{L}^{-1}$).

3.2. S2 test series: high S/V ratio

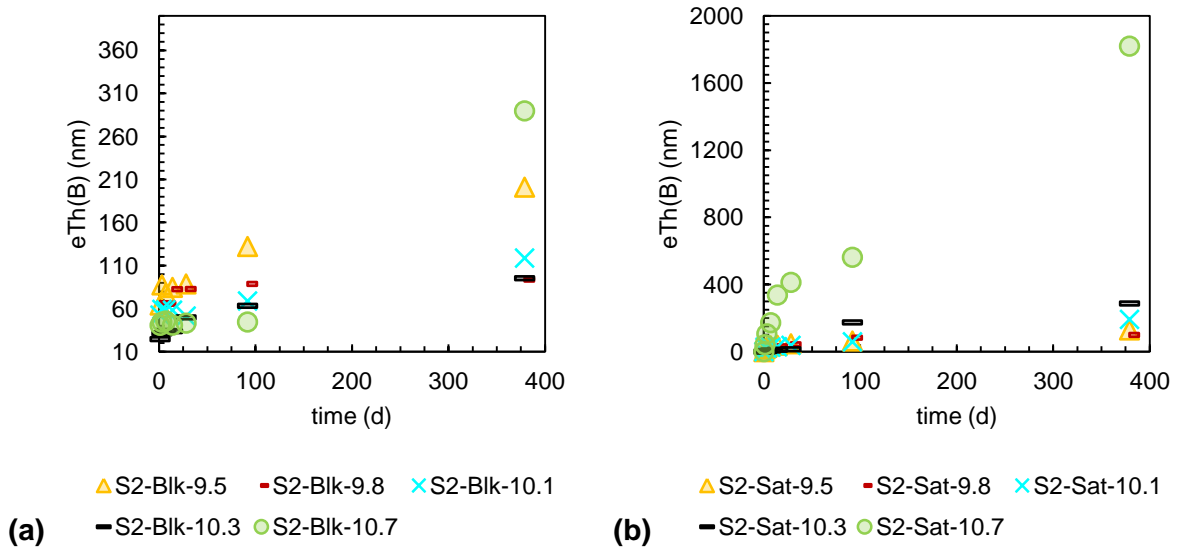
As in the S1 test series, the pHs in the S2 test series were maintained around the set values during the first 100 d (Figure A.2). However, the pH decreased significantly between 100 d and 1 y: by accident this variation was not compensated by alkaline additions. The evolution of the silicon concentration is summarized in Table 4, and the complete results of the solution analyses are presented in Appendix D. In the “S2-Blk” tests (Figure 3.a, Figure 4.a, Figure 5.a), the equivalent altered thicknesses for experiments conducted at all pHs are similar during the first 100 d, and increase slightly with decreasing pH from 10.7 (S2-Blk-10.7) and 9.5 (S2-Blk-9.5). Between 100 d and 1 y, only results from the experiment conducted at the highest pH ($\text{pH}_{90^\circ\text{C}} =$ 10.7) deviates from this trend, as the samples are altered faster. The higher altered equivalent thicknesses in this test correlate with the precipitation of secondary phases, which could be identified as calcium aluminum silicate hydrates by XRD.

In the “S2-Sat” test series (Figure 4.b, Figure 5.b), larger amounts of secondary phases can be identified: oxyhydroxides, silicates, carbonates, and zeolites. The higher the pH, the greater the amount of precipitated crystalline phases after 1 y of leaching will be. These greater amounts of secondary phases result in greater equivalent thicknesses of altered glass. In detail (Figure 5):

- no diffraction peaks are observed at $\text{pH}_{90^\circ\text{C}} < 10.1$;
- at $\text{pH}_{90^\circ\text{C}} = 10.1$ (S2-Sat-10.1): potassium calcium silicate hydrate (PDF 04-012-5493, $\text{K}_2\text{Ca}_2\text{Si}_8\text{O}_{19} \cdot (\text{H}_2\text{O}_4)$) and potassium sodium silicate (04-014-8491, $\text{K}_4\text{Na}_2\text{Si}_6\text{O}_{15}$) can be identified;
- at $\text{pH}_{90^\circ\text{C}} = 10.3$ (S2-Sat-10.3): potassium calcium silicate hydrate (04-012-5493), potassium hydrogen carbonate (04-013-5503, $\text{HK}(\text{CO}_3)$), sodium silicate (00-018-1241, $\text{Na}_2\text{Si}_2\text{O}_5$), and leucite (00-038-1423, KAlSi_2O_6) are present;
- at $\text{pH}_{90^\circ\text{C}} = 10.7$ (S2-Sat-10.7): potassium calcium silicate hydrate (04-012-5493), hydrogen potassium sodium carbonate hydrate (04-010-8201, $\text{C}_2\text{H}_5\text{K}_2\text{NaO}_8$), shlykovite (00-061-0758, $\text{KCa}(\text{Si}_4\text{O}_9(\text{OH})) \cdot 3\text{H}_2\text{O}$), phillipsite-K (00-034-0542), and leucite (00-038-

1423) are observed. In addition, the XRD patterns exhibit a broad reflection around $2\theta = 30^\circ$, which is characteristic of CSH [45, 46].

225 Figure 3.b shows that the altered thicknesses are higher in the test at $\text{pH}_{90^\circ\text{C}} = 10.7$. For the other pHs, glass dissolution decreases during the first tens of days whatever the pH, before a further increase occurs for $\text{pH}_{90^\circ\text{C}} = 10.1$ and 10.3 (Appendix B). The higher the pH, the faster and earlier is this increase.



230 **Figure 3:** Evolution of the equivalent thickness of altered glass calculated from the boron concentration, $eTh(B)$, for the (a) S2-Blk and (b) S2-Sat test series with an S/V ratio of $10\,000\text{ m}^{-1}$. Zoomed-in subfigures are presented in Appendix B.

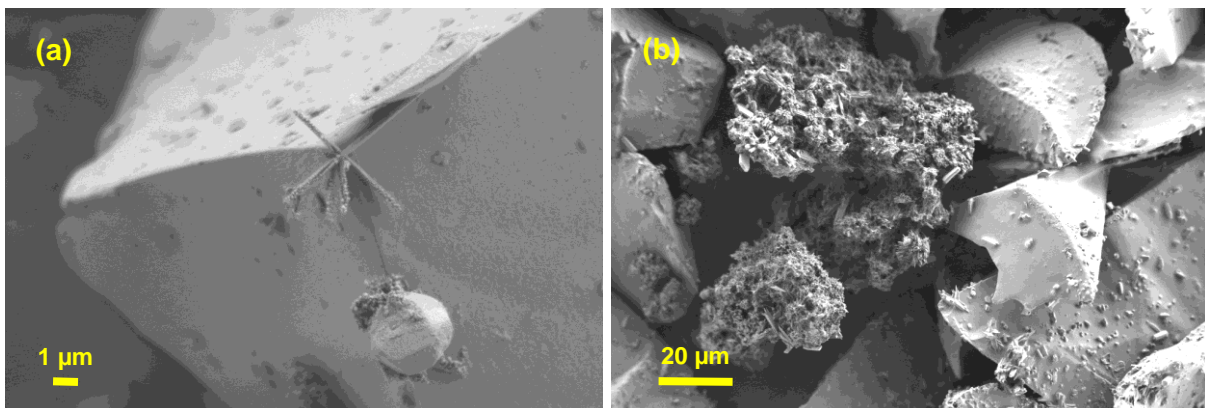
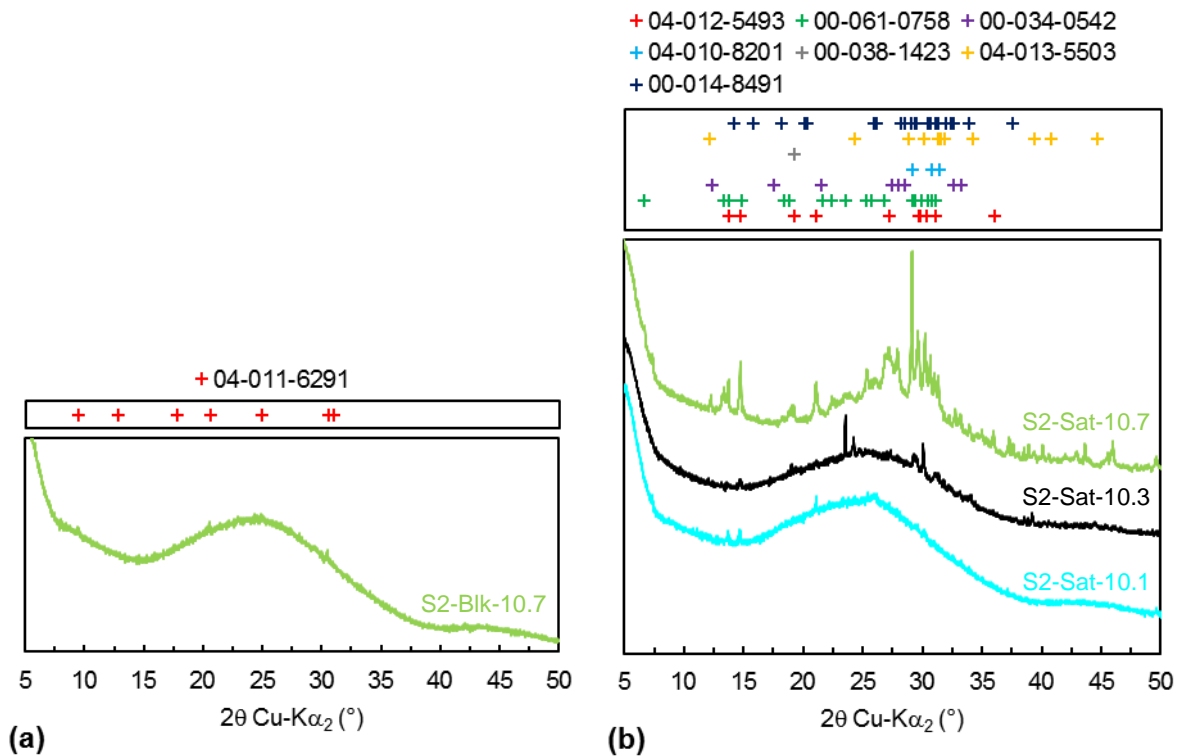


Figure 4: Secondary electron SEM images after 1 y for tests (a) S2-Blk-10.3 and (b) S2-Sat-10.3.



235 **Figure 5:** X-ray diffraction patterns for the S2 **(a)** “Blk” and **(b)** “Sat” test series. The positions of the major peaks ($I \geq 0.3 \times I_{\max}$) in reference diffractograms (PDF-4+ 2018 RDB, database 4.1801) corresponding to the identified phases are indicated: K-Ca-Si oxyhydroxide (PDF 04-012-5493), shlykovite (PDF 00-061-0758), phillipsite-K (PDF 00-034-0542), Na-K carbonate (PDF 04-010-8201), leucite (PDF 00-038-1423), K carbonate (PDF 04-013-5503), K-Na-Si oxide (PDF 04-014-8491), and Ca-Al-Si hydrate (PDF 04-011-6291).

240 **4. Discussion**

A “low” S/V ratio was selected for the S1 test series to maintain a large difference in the silica concentration between the “S1-Sat” test series (aqueous silica-containing solutions) and the “S1-Blk” test series (solutions without silica) for as long as possible. However, the results show that this experimental design did not allow for quantification of the glass alteration in strongly alkaline solutions because of the dilution of the samples (necessitated by the high silica concentrations) required for ICP-OES analysis (e.g., dilution factor > 200 at $\text{pH}_{90^\circ\text{C}} = 10.3$). To circumvent this shortcoming, the S2 test series was conducted with a higher S/V ratio and focused on alkaline pHs. However, it was more difficult to highlight the effect of the initial solution under these conditions because the solutions rapidly reached saturation owing to the greater surface area of the glass. As an example, assuming no retention of silica in the gel nor precipitation of secondary silicate phases, at $\text{pH}_{90^\circ\text{C}} = 9.8$, it is necessary to dissolve $35 \mu\text{m}$ of glass to reach

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saturation with respect to amorphous silica at $S/V = 60 \text{ cm}^{-1}$, and only $0.2 \text{ }\mu\text{m}$ at $S/V = 10\,000 \text{ cm}^{-1}$. Both the S1 and S2 test series will be considered in the following discussion.

In the S1 test series and at $\text{pH}_{90^\circ\text{C}} = 1$ (S1-Sat-1), an initial dissolution rate of $3.2 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ is
255 calculated between 0 and 7 days by linear regression from boron release (despite the beginning of inflection of the alteration rate). This value can be compared to that acquired at 90°C and $\text{pH}_{90^\circ\text{C}} = 1.5$ by Pérez, *et al.* [47] of $\approx 2.5 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. The fact that these two values are close, added to the comparison in the equivalent thickness of altered glass between the “S1-Blk” and “S1-Sat” tests (Figure 6.a and Figure C.1) shows that the effect of aqueous silica on the glass dissolution
260 is negligible at $\text{pH}_{90^\circ\text{C}} \leq 3$. However, the effect of aqueous silica becomes more significant at $\text{pH}_{90^\circ\text{C}} = 7$: the equivalent thickness of the altered glass at the end of the S1-Blk-7 test is 1.5 to 3 times greater than that for the S1-Sat-7 test (Figure C.1.b). This difference increases significantly with the pH, from a factor of ≈ 35 at $\text{pH}_{90^\circ\text{C}} = 9.5$ (S1-Blk-9.5 vs. S1-Sat-9.5) to a factor of ≈ 60 at $\text{pH}_{90^\circ\text{C}} = 10.1$ (S1-Blk-10.1 vs. S1-Sat-10.1). At $\text{pH}_{90^\circ\text{C}} = 9.5$ and 10.1 in the S1
265 test series, the gap due to the initial presence of aqueous silica should likely be even greater before 1 y. Indeed, the silicon concentrations in solution due to the glass dissolution in the S1-Blk-9.5 and S1-Blk-10.1 tests end up being significantly high after 1 y ($1.4\cdot 10^2 \text{ mg}\cdot\text{L}^{-1}$ and $5.1\cdot 10^2 \text{ mg}\cdot\text{L}^{-1}$ respectively, Table 3). Therefore, it is clear from the S1 test series that aqueous silica causes an increase in glass durability above a threshold of $\text{pH}_{90^\circ\text{C}} \approx 7$, and this effect
270 increases with pH, at least up to $\text{pH}_{90^\circ\text{C}} \approx 10.1$, with a low S/V ratio of 60 m^{-1} . This beneficial effect on the glass durability can be interpreted as the rapid formation of a passivating layer in the silica-rich solutions of the “S1-Sat” test series [11], while partial dissolution of the glass in the “S1-Blk” tests is required to reach saturation. An increase in glass durability with the addition of silica in solution was also observed for SON68 glass at 90°C and $\text{pH} = 9$ [20]. Note that by
275 focusing only on silica, it is possible that the rate drop tied to the affinity effect is lower than that expected with a solution saturated with all the glass constituents. This verification is difficult and requires the use of isotopes to monitor the glass dissolution rate.

Unexpectedly, the results of the S1 test series show that aqueous silica seems to have no direct nor indirect effect on the glass alteration at acidic pH. This could be for several reasons: (i) the rate was calculated from the release of B, and it can be hypothesized that B is preferentially leached out in acidic pH along with alkalis, the release of which from glass is known to be driven by ion-exchange [48-51]; or (ii) a passivating gel cannot form because the condensation reactions are slower in acidic pH than in basic pH [34]. At this stage, it is not possible to decide between these two hypotheses.

On the one hand, the first hypothesis is supported by the observation that in the S1-Blk-3 test B and Na are released congruently, following a square root-dependent time law until total alteration of the glass (Figure 7.a). Thus, it is plausible that ion-exchange is responsible for the release of Na and that the penetration of hydronium ions into the glass also drives the hydrolysis of B. At $\text{pH}_{90\text{ }^\circ\text{C}} = 3$ (S1-Blk-3), Si dissolves approximately 20 times slower than B and Na. This preferential release of B and Na relative to Si suggests that a thick Si-rich surface layer will remain. The observed preferential leaching of B and Na relative to Si in acidic conditions also explains why the initial Si concentration in solution is not a determinant parameter in acidic systems. In contrast, at $\text{pH}_{90\text{ }^\circ\text{C}} = 10.1$ (S1-Blk-10.1), B, Na, and Si dissolve at almost the same rate (Figure 7.b). These results suggest that in the $\text{pH}_{90\text{ }^\circ\text{C}}$ range of 7–9.5, the release of weakly bonded elements such as Na and B is controlled by hydrolysis-condensation reaction within the aluminosilicate network.

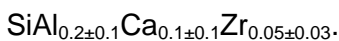
On the other hand, the second hypothesis stating that a passivating gel cannot form at acidic pH is similar to the one suggested by Daval, *et al.* [52] to account for the passivating ability of Si-rich layers developed on slow-dissolving wollastonite cleavage planes as opposed to fast-dissolving cleavage planes. More generally, the non-passivating behavior of silica layers developed in acidic solutions has previously been demonstrated by the mineralogical community for a series of Fe-free silicate minerals altered at acidic pH, including wollastonite [53], feldspars [54-57] and forsterite [58]. In particular, Wild, *et al.* [56] demonstrated that the Si-rich layers formed on labradorite switched from non-passivating at $\text{pH} \leq 2.5$ to passivating at $\text{pH} > 2.5$, indicating that

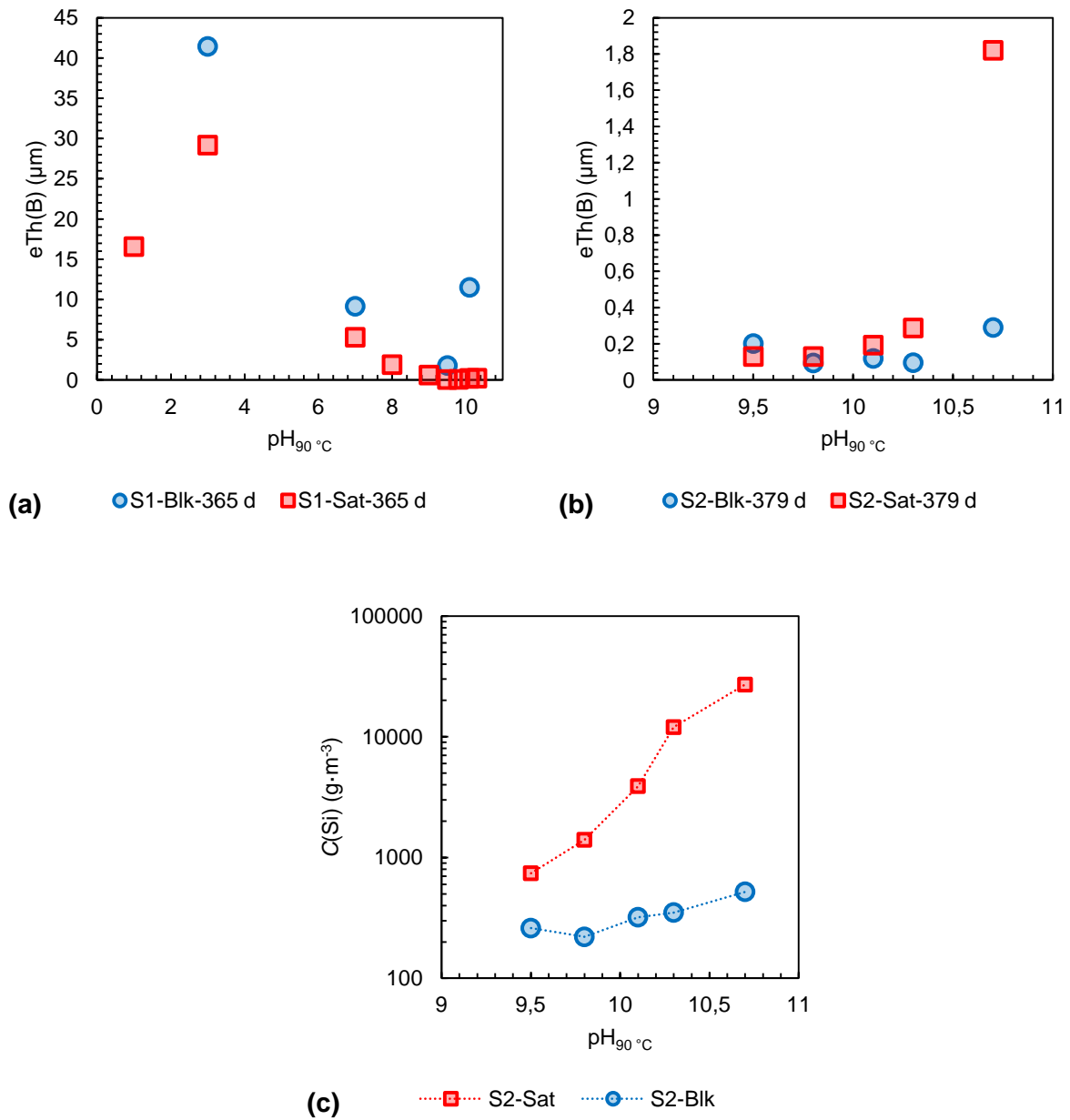
305 the pH value for passivation is lower for feldspars than for ISG. This suggests that there might be a strong coupling between the intrinsic dissolution rate of the parent phase (which increases with decreasing pH in the acidic pH range) and the rate of the silica layer condensation/polymerization (which decreases with decreasing pH in the acidic pH range).

The S2 test series with the higher S/V ratio of $10\,000\text{ m}^{-1}$ can provide valuable new insights through comparison with the first series. Indeed, at $\text{pH}_{90\text{ }^\circ\text{C}} = 9.8$ and $S/V = 10\,000\text{ m}^{-1}$, i.e., the pH at which it has been shown that the presence of aqueous silica causes a dramatic decrease in the glass alteration, the altered glass fraction is the same in the S2-Blk-9.8 and S2-Sat-9.8 tests after a year, irrespective of the initial aqueous silica concentration of the solution (Figure 6.b and Figure C2.b). This trend is different at $\text{pH}_{90\text{ }^\circ\text{C}} = 10.1, 10.3,$ and 10.7 , where the glass is significantly more altered in the “S2-Sat” silica-rich solutions. This can be interpreted as a destabilization of the passivating gel whose formation was favored by the initial presence of aqueous silica. This destabilization could be linked to the precipitation of Si-rich secondary phases: C(A)SH, zeolites, carbonates, and poorly crystallized hydrated and anhydrous silicates. Of these secondary phases, C(A)SH and zeolites are already known to be at the origin of the so-called “resumption of alteration” phenomenon that leads to an acceleration of the glass alteration rate [59]. The formation of a passivating gel before the formation of zeolites has been documented [38], and its destabilization due to their precipitation is consistent with the experimental results reported by Fournier, *et al.* [7] and the associated modeling [60]. Table 3 shows that the precipitation of these Si-bearing minerals does not necessarily go with a decrease in the silicon concentration. This can be explained by a Si/i ratio of the phases (with i the chemical element limiting their precipitation) lower than the Si/i ratio of the glass. This result is well known when zeolites precipitate during resumptions of alteration of glasses [7, 59, 61, 62].

For the three most alkaline pHs in this second test series ($\text{pH}_{90\text{ }^\circ\text{C}} = 10.1, 10.3,$ and 10.7), a significant difference is observed between the silica concentrations reached in the “S2-Blk” tests (≈ 300 to $500\text{ g}\cdot\text{m}^{-3}$) and those in the pre-saturated solution “S2-Sat” tests ($2\cdot 10^3$ to $2.5\cdot 10^4\text{ g}\cdot\text{m}^{-3}$)

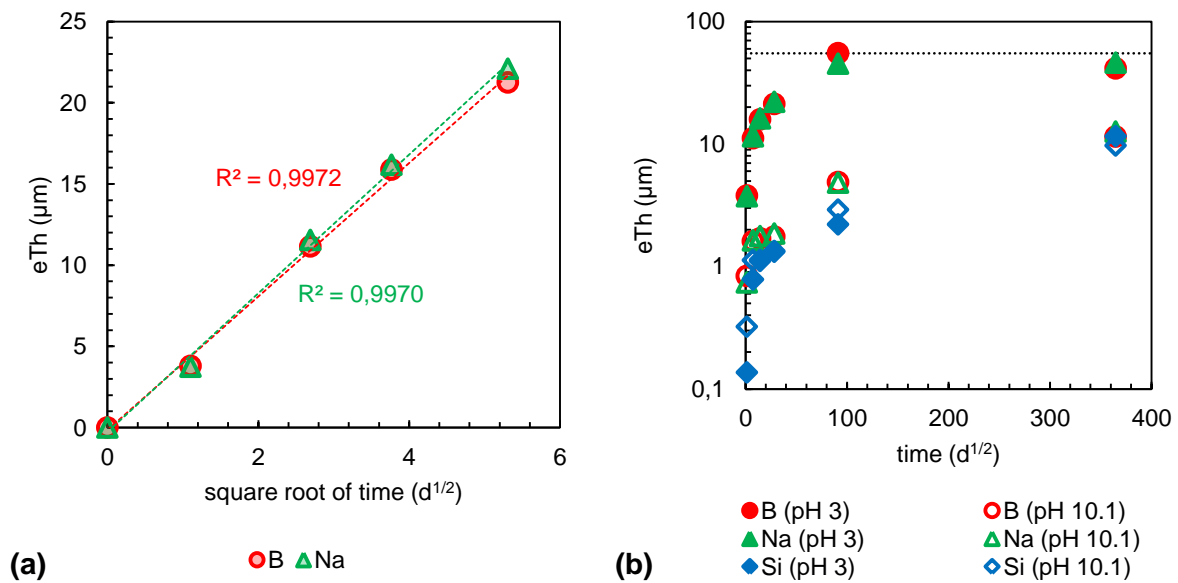
3) (Figure 6.c). This difference increases with the pH. At $\text{pH}_{90\text{ }^\circ\text{C}} = 9.5$ (S2-Blk-9.5 vs. S2-Sat-9.5), the difference in the silica concentrations is small, and it is expected that this difference would decrease further at longer times. Indeed, it was demonstrated in a 14-year-long experiment [63] that a solution at this pH will eventually achieve equilibrium with amorphous silica. This was possible because no secondary phases precipitated at this pH. Here, because silicate minerals precipitate above $\text{pH}_{90\text{ }^\circ\text{C}} = 9.5$, they partly control the solution composition. Studies conducted at high pH have shown that the precipitation of silicate minerals such as CSH and zeolites is not instantaneous; there is an induction period during which the glass dissolves slowly before alteration resumes [7, 59, 61]. During this so-called "plateau regime," the solution composition, and possibly the transport of reactive species toward the pristine glass surface, are controlled by various amorphous materials, whose composition, structure, and diffusion properties are poorly understood [16, 64, 65]. The mechanisms for the formation of these materials are pH-dependent, although the average composition of the alteration layer (gel and secondary phases) deduced from the elemental concentrations in solution varies little regardless of the pH:





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Figure 6: Comparison of the equivalent thickness of altered glass calculated from the boron concentrations, $e\text{Th}(B)$, at the last sampling time (≈ 1 y) at various pH for the **(a)** S1 test series ($S/V = 60 \text{ m}^{-1}$) and **(b)** S2 test series ($S/V = 10\,000 \text{ m}^{-1}$). **(c)** Comparison of the silicon concentrations, $C(\text{Si})$, reached at the end of the experiment (379 d) at various pH for the S2 test series.



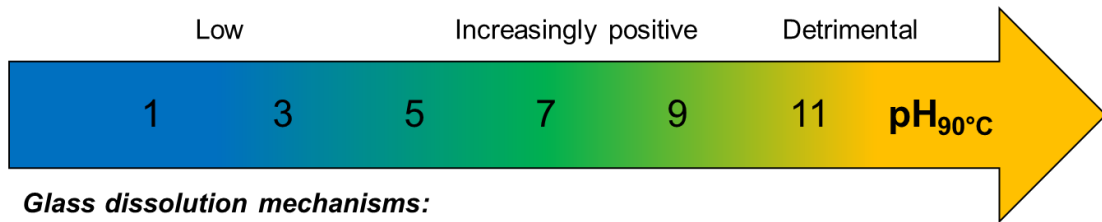
355 **Figure 7: (a)** Evolution of the equivalent thickness of altered glass, eTh, calculated from boron and sodium concentrations as a function of the square root of the time during the first month for the S1-Blk-3 test. **(b)** Comparison of the evolution of B, Na, and Si eTh for the S1-Blk-3 (plain symbols) and S1-Blk-10.1 (open symbols) tests. The dotted line represents the total alteration of the glass (%AG = 100).

5. Conclusions

For a silica concentration equal to that reached at saturation with amorphous silica, the experimental work reported in this study shows a negligible effect of aqueous silica on the glass dissolution rate (measured from B release) at acidic pH and a marked effect above $\text{pH}_{90\text{ }^\circ\text{C}} = 7$ with a low S/V ratio of 60 m^{-1} , thus ensuring better chemical durability of the glass. Thus, pH-induced changes in solution chemistry shift the equilibria. At a higher S/V ratio of $10\,000\text{ m}^{-1}$ and at $\text{pH}_{90\text{ }^\circ\text{C}} \geq 9.5$, the aqueous silica decreases the glass durability due to the formation of secondary phases (Figure 8). Most of the phases identified are hydroxides, which are likely precursors of better-crystallized phases formed by Ostwald ripening.

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Effect of dissolved silica on glass durability:



Glass dissolution mechanisms:

Ion exchange and fast hydrolysis of boron
Negligible effect of the Si-rich layer

Formation of a passivating Si-rich layer after the release of mobile glass elements (e.g. B, Na, Ca)

Precipitation of silicate minerals at the expense of a passivating layer

370 **Figure 8:** Diagram summarizing the effects of dissolved silica on the glass dissolution mechanisms as a function of pH.

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375 Data availability statement

The authors declare that the data supporting the findings of this study are available within the article and its appendixes, and from the corresponding author upon reasonable request.

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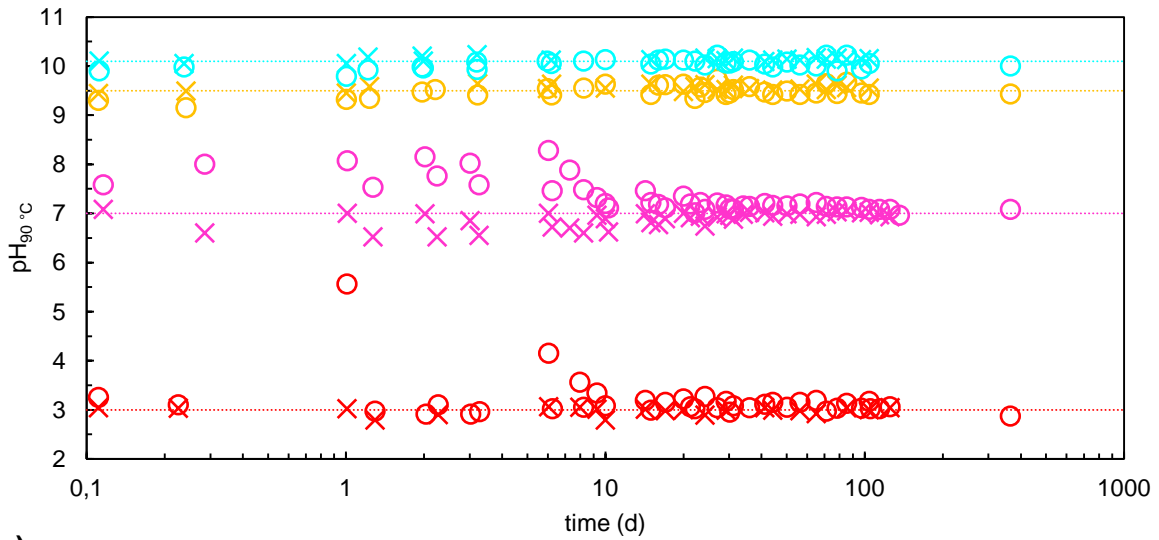
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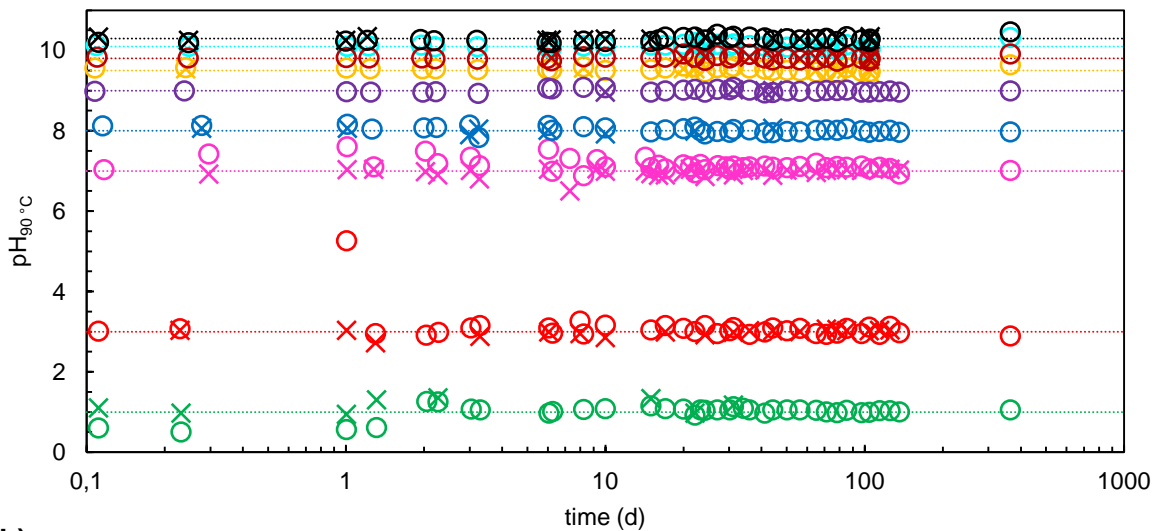
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Appendix A

In the tests conducted in this study, the pH was manually regulated around a set value. Figures 560 A.1 (for the S1 test series) and A.2 (for the S2 test series) show the different set pH values (dashed lines), measured pH values (circles), and pH values reached after addition of micro-volumes of KOH or HNO₃ solutions if necessary (crosses). Mean pH values (m) and standard deviations (σ) are given in the caption.



(a)

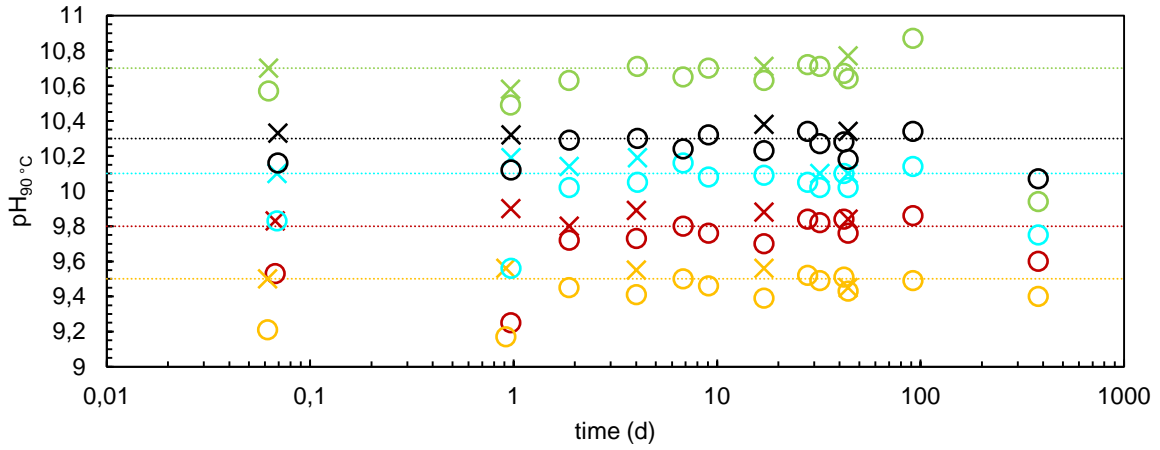


(b)

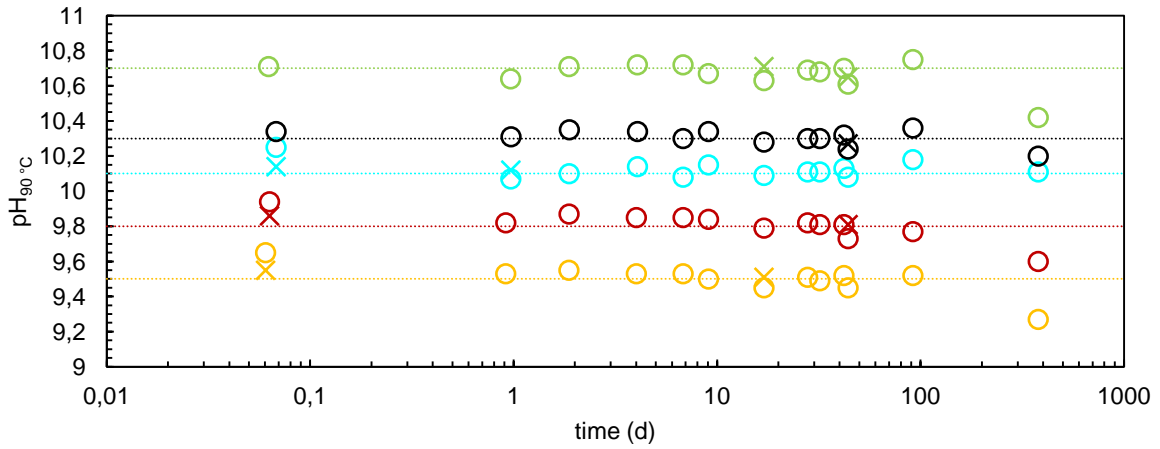
565

Figure A.1: pH measured in the S1 (a) “Blk” and (b) “Sat” test series before regulation (○) and after regulation (×) around set values (dotted lines) of pH_{90 °C} = 1 (green, $m_{\text{sat}} = 1.0$, $\sigma_{\text{sat}} = 0.2$), 3 (red, $m_{\text{Blk}} = 3.1$, $\sigma_{\text{Blk}} = 0.4$, $m_{\text{sat}} = 3.1$, $\sigma_{\text{sat}} = 0.3$), 7 (pink, $m_{\text{Blk}} = 7.1$, $\sigma_{\text{Blk}} = 0.4$, $m_{\text{sat}} = 7.1$, $\sigma_{\text{sat}} = 0.2$), 8 (blue, $m_{\text{sat}} = 8.0$, $\sigma_{\text{sat}} = 0.1$), 9 (purple, $m_{\text{sat}} = 9.0$, $\sigma_{\text{sat}} = 0.0$), 9.5 (orange, $m_{\text{Blk}} = 9.5$, $\sigma_{\text{Blk}} = 0.1$, $m_{\text{sat}} = 9.5$, $\sigma_{\text{sat}} = 0.0$), 9.8 (dark red, $m_{\text{sat}} = 9.8$, $\sigma_{\text{sat}} = 0.0$), 10.1 (light blue, $m_{\text{Blk}} = 10.1$, $\sigma_{\text{Blk}} = 0.1$, $m_{\text{sat}} = 10.1$, $\sigma_{\text{sat}} = 0.1$), and 10.3 (black, $m_{\text{sat}} = 10.3$, $\sigma_{\text{sat}} = 0.1$).

570



(a)

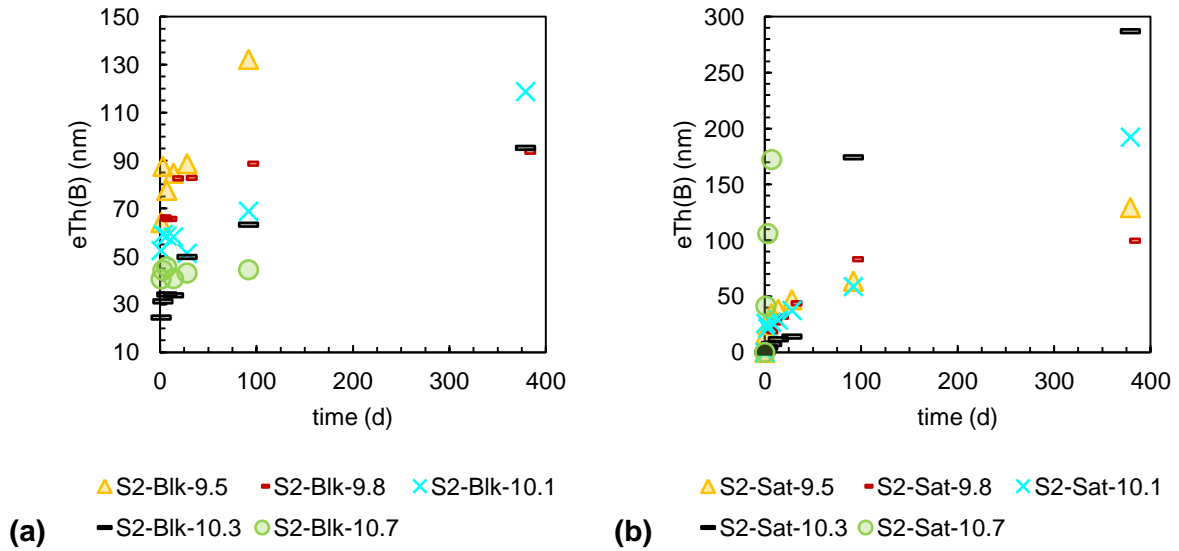


(b)

Figure A.2: pH measured in the S2 **(a)** “Blk” and **(b)** “Sat” test series before regulation (○) and after regulation (×) around set values (dotted lines) of $\text{pH}_{90\text{ }^\circ\text{C}} = 9.5$ (orange, $m_{\text{Blk}} = 9.4$, $\sigma_{\text{Blk}} = 0.1$, $m_{\text{sat}} = 9.5$, $\sigma_{\text{sat}} = 0.1$), 9.8 (dark red, $m_{\text{Blk}} = 9.8$, $\sigma_{\text{Blk}} = 0.2$, $m_{\text{sat}} = 9.8$, $\sigma_{\text{sat}} = 0.1$), 10.1 (light blue, $m_{\text{Blk}} = 10.0$, $\sigma_{\text{Blk}} = 0.2$, $m_{\text{sat}} = 10.1$, $\sigma_{\text{sat}} = 0.0$), 10.3 (black, $m_{\text{Blk}} = 10.3$, $\sigma_{\text{Blk}} = 0.1$, $m_{\text{sat}} = 10.3$, $\sigma_{\text{sat}} = 0.0$), and 10.7 (light green, $m_{\text{Blk}} = 10.6$, $\sigma_{\text{Blk}} = 0.2$, $m_{\text{sat}} = 10.7$, $\sigma_{\text{sat}} = 0.1$).

Appendix B

Zoomed-in subfigures of Figure 3 are shown in Figure B.1.



580 **Figure B.1:** Zoomed-in subfigures of (a) Figure 3.a and (b) Figure 3.b, showing the evolution of the equivalent thickness of altered glass calculated from the boron concentration, $eTh(B)$, for the (a) S2-Blk and (b) S2-Sat test series with an S/V ratio of $10\,000\text{ m}^{-1}$.

Appendix C

A direct comparison between the “Blk” and “Sat” tests at all sampling dates is shown in Figures

585 C.1 and C.2.

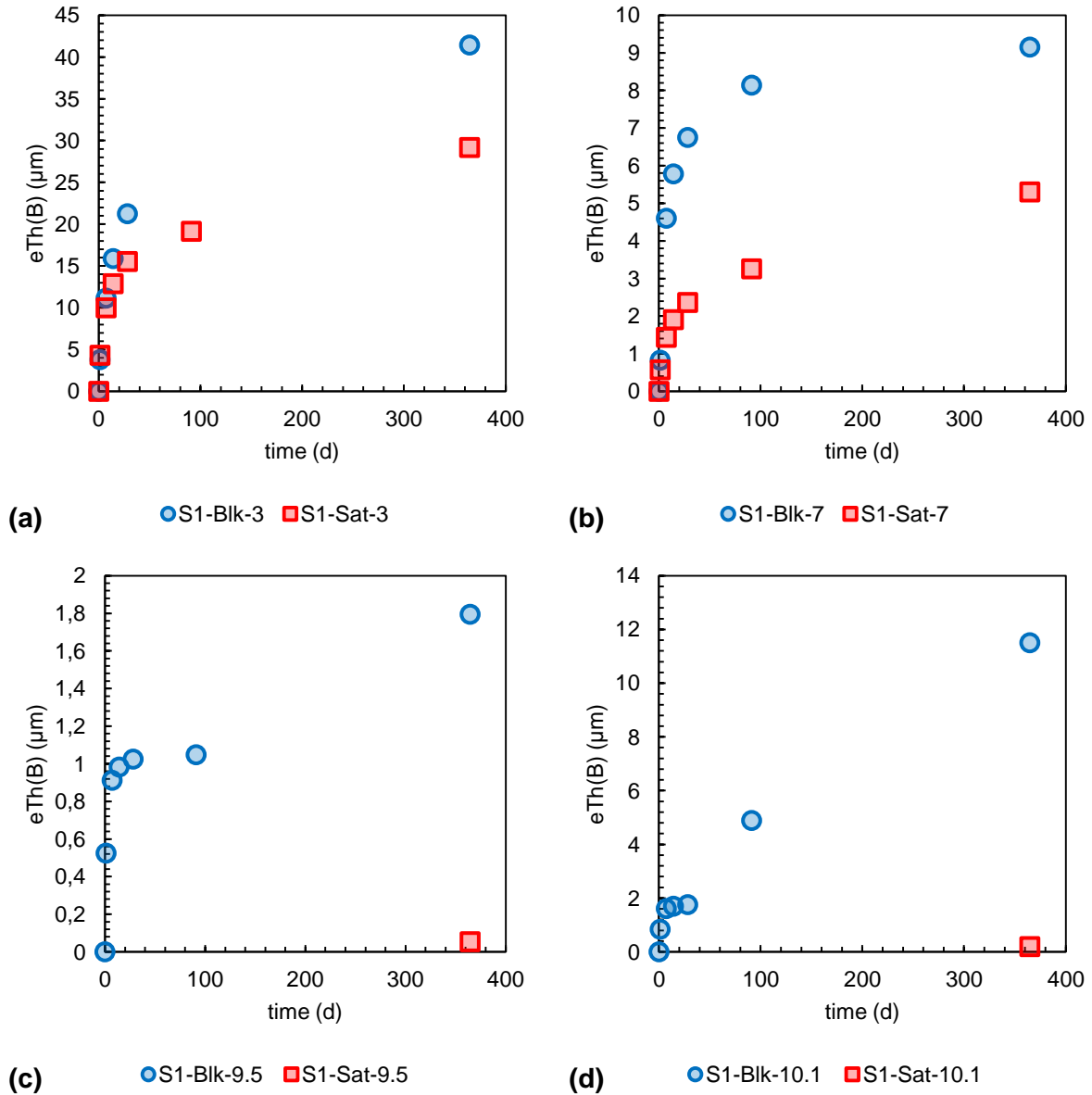


Figure C.1: Comparison of the evolution of the equivalent thickness of altered glass calculated from the boron concentration, $eTh(B)$, for the S1 test series with an S/V ratio of 60 m^{-1} at $pH_{90\text{ }^{\circ}C}$ values of (a) 3, (b) 7, (c) 9.5, and (d) 10.1.

590

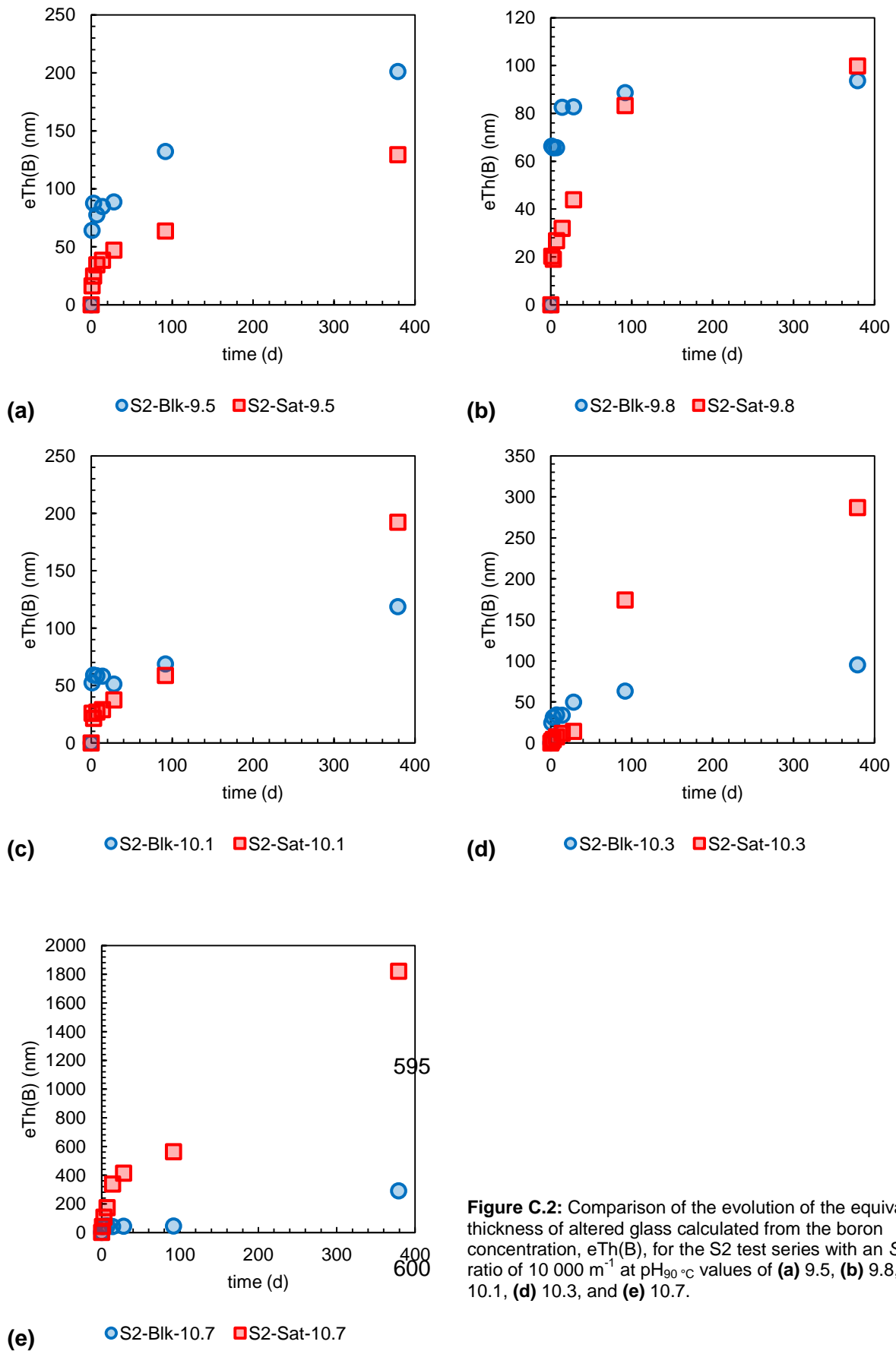


Figure C.2: Comparison of the evolution of the equivalent thickness of altered glass calculated from the boron concentration, $eTh(B)$, for the S2 test series with an S/V ratio of $10\,000\text{ m}^{-1}$ at $pH_{90^\circ\text{C}}$ values of (a) 9.5, (b) 9.8, (c) 10.1, (d) 10.3, and (e) 10.7.

Appendix D

605 The solution concentrations measured in the tests are summarized in the tables in Appendix D in the order given in Table 2 (LoQ: limit of quantification, NA: not analyzed).

D.1. S1-Sat-1

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 307.7 | < LoQ | 62.7 | < LoQ | < LoQ | < LoQ |
| 1.2 | 288.3 | 37.4 | 93.0 | 1.2 | 13.7 | < LoQ |
| 7.3 | 308.0 | 72.0 | 210.2 | 1.5 | 20.5 | < LoQ |
| 14.2 | 343.5 | 78.5 | 234.5 | 1.6 | 21.0 | < LoQ |
| 28.2 | 487.8 | 88.0 | 247.5 | 2.2 | 22.4 | < LoQ |
| 91.1 | 585.1 | 101.7 | 421.7 | 4.1 | 31.1 | < LoQ |
| 364.6 | 558.7 | 111.5 | 358.8 | 4.2 | 30.3 | < LoQ |

D.2. S1-Blk-3

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 3.3 | < LoQ | < LoQ | < LoQ | < LoQ | < LoQ |
| 1.2 | 8.4 | 27.3 | 45.3 | 0.8 | 11.4 | < LoQ |
| 7.2 | 33.0 | 74.1 | 128.5 | 2.7 | 28.3 | < LoQ |
| 14.2 | 45.9 | 99.9 | 170.5 | 4.8 | 37.8 | < LoQ |
| 28.2 | 54.5 | 125.7 | 217.5 | 5.7 | 47.0 | < LoQ |
| 91.1 | 93.1 | 201.6 | 324.2 | 6.5 | 145.9 | < LoQ |
| 364.6 | 600.1 | 180.8 | 326.9 | 8.3 | 71.8 | < LoQ |

D.3. S1-Sat-3

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 298.9 | < LoQ | 5.5 | < LoQ | 1.3 | < LoQ |
| 1.2 | 306.5 | 31.8 | 57.4 | < LoQ | 17.0 | < LoQ |
| 7.2 | 320.3 | 69.2 | 125.9 | < LoQ | 25.1 | < LoQ |
| 14.2 | 313.9 | 86.6 | 162.0 | < LoQ | 28.6 | < LoQ |
| 28.2 | 317.9 | 101.9 | 195.7 | < LoQ | 31.2 | < LoQ |
| 91.1 | 361.4 | 121.5 | 246.4 | < LoQ | 74.2 | < LoQ |
| 364.6 | 945.8 | 172.9 | 417.1 | < LoQ | 57.4 | < LoQ |

610 **D.4. S1-Blk-7**

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 2.2 | < LoQ | < LoQ | < LoQ | 0.7 | < LoQ |
| 1.2 | 17.3 | 6.0 | 10.7 | 0.9 | 3.1 | < LoQ |
| 7.2 | 58.5 | 34.3 | 57.2 | < LoQ | 11.1 | < LoQ |
| 14.2 | 62.8 | 42.8 | 71.9 | < LoQ | 15.1 | < LoQ |
| 28.2 | 65.9 | 50.0 | 86.6 | < LoQ | 19.3 | < LoQ |
| 91.1 | 76.0 | 60.2 | 100.2 | < LoQ | 50.7 | < LoQ |
| 364.6 | 249.3 | 67.6 | 117.4 | < LoQ | 27.5 | < LoQ |

D.5. S1-Sat-7

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 146.4 | < LoQ | 5.6 | < LoQ | 1.4 | < LoQ |
| 1.2 | 150.8 | 4.5 | 12.0 | < LoQ | 3.3 | < LoQ |
| 7.2 | 139.9 | 11.6 | 25.9 | < LoQ | 7.0 | < LoQ |
| 14.2 | 138.6 | 15.5 | 31.2 | < LoQ | 9.1 | < LoQ |
| 28.2 | 134.6 | 19.5 | 39.4 | < LoQ | 11.2 | < LoQ |
| 91.1 | 177.4 | 27.5 | 52.2 | < LoQ | 27.8 | < LoQ |
| 364.6 | 332.5 | 45.9 | 9.6 | < LoQ | 23.6 | < LoQ |

D.6. S1-Sat-8

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 175.9 | < LoQ | 6.1 | < LoQ | 1.9 | < LoQ |
| 1.2 | 154.5 | 2.6 | 8.9 | < LoQ | 2.1 | < LoQ |
| 7.2 | 154.4 | 6.4 | 17.9 | < LoQ | 5.0 | < LoQ |
| 14.2 | 147.6 | 7.7 | 20.8 | < LoQ | 5.1 | < LoQ |
| 28.2 | 148.5 | 9.2 | 23.3 | < LoQ | 5.9 | < LoQ |
| 91.1 | 164.1 | 12.0 | 27.9 | < LoQ | 12.2 | < LoQ |
| 364.6 | 257.3 | 16.7 | 38.6 | < LoQ | 9.5 | < LoQ |

D.7. S1-Sat-9

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 276.0 | < LoQ | 5.6 | < LoQ | 1.2 | < LoQ |
| 1.1 | 252.0 | 1.2 | 6.8 | < LoQ | 1.2 | < LoQ |
| 7.2 | 276.2 | 2.2 | 9.2 | < LoQ | 1.8 | < LoQ |
| 14.2 | 248.5 | 2.5 | 9.9 | < LoQ | 1.9 | < LoQ |
| 28.2 | 247.1 | 2.9 | 10.4 | < LoQ | 1.9 | < LoQ |
| 91.0 | 283.8 | 3.7 | 11.5 | < LoQ | 10.1 | < LoQ |
| 364.6 | 471.6 | 5.2 | 21.3 | < LoQ | 2.6 | < LoQ |

615 **D.8. S1-Blk-9.5**

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 5.7 | < LoQ | 0.5 | < LoQ | < LoQ | < LoQ |
| 1.1 | 20.0 | 4.2 | 7.8 | 2.1 | 2.4 | < LoQ |
| 7.2 | 35.9 | 7.3 | 13.4 | 2.9 | 2.9 | < LoQ |
| 14.2 | 41.8 | 7.9 | 14.8 | 2.7 | 2.6 | < LoQ |
| 28.2 | 44.0 | 8.2 | 16.0 | 2.4 | 2.6 | < LoQ |
| 91.0 | 61.7 | 8.4 | 19.8 | 2.1 | 10.9 | < LoQ |
| 364.6 | 142.1 | 15.3 | 29.6 | < LoQ | 2.3 | < LoQ |

D.9. S1-Sat-9.5

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 743.0 | < LoQ | 11.0 | < LoQ | 1.2 | < LoQ |
| 1.1 | 641.8 | < LoQ | 11.2 | < LoQ | 1.1 | < LoQ |
| 7.2 | 629.2 | < LoQ | 11.4 | < LoQ | 0.9 | < LoQ |
| 14.2 | 592.6 | < LoQ | 10.9 | < LoQ | 0.8 | < LoQ |
| 28.2 | 546.7 | < LoQ | 11.6 | < LoQ | 1.1 | < LoQ |
| 364.6 | 838.2 | 1.0 | 20.2 | < LoQ | < LoQ | < LoQ |

D.10. S1-Sat-9.8

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 1349.5 | < LoQ | 20.1 | < LoQ | 3.3 | < LoQ |
| 1.2 | 1192.2 | < LoQ | 18.7 | < LoQ | 2.0 | < LoQ |
| 7.2 | 1171.9 | < LoQ | 20.2 | < LoQ | 2.0 | < LoQ |
| 14.2 | 1161.8 | < LoQ | 19.5 | < LoQ | 1.4 | < LoQ |
| 28.2 | 1013.6 | < LoQ | 20.3 | < LoQ | < LoQ | < LoQ |
| 364.6 | 1579.0 | 1.1 | 29.8 | < LoQ | < LoQ | < LoQ |

D.11. S1-Blk-10.1

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 23.6 | < LoQ | 3.1 | < LoQ | < LoQ | < LoQ |
| 1.1 | 35.7 | 6.3 | 12.5 | 3.2 | 1.8 | < LoQ |
| 7.1 | 66.7 | 12.3 | 24.2 | 5.3 | 1.4 | < LoQ |
| 14.2 | 66.8 | 13.0 | 26.1 | 5.1 | 1.3 | < LoQ |
| 28.2 | 75.3 | 13.5 | 27.3 | 4.8 | 1.2 | < LoQ |
| 91.1 | 138.2 | 38.3 | 66.9 | 2.6 | 39.4 | < LoQ |
| 364.6 | 510.0 | 108.0 | 203.1 | 0.7 | < LoQ | < LoQ |

620 **D.12. S1-Sat-10.1**

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 3846.8 | < LoQ | 49.9 | < LoQ | 9.7 | < LoQ |
| 1.1 | 3358.4 | < LoQ | 42.1 | < LoQ | < LoQ | < LoQ |
| 7.2 | 3450.0 | < LoQ | 47.6 | < LoQ | < LoQ | < LoQ |
| 14.2 | 3406.3 | < LoQ | 45.8 | < LoQ | < LoQ | < LoQ |
| 28.2 | 2831.7 | < LoQ | 46.7 | < LoQ | 6.1 | < LoQ |
| 364.6 | 3966.4 | 2.5 | 62.7 | < LoQ | < LoQ | < LoQ |

D.13. S1-Sat-10.3

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 11844.4 | < LoQ | 132.4 | < LoQ | 17.2 | < LoQ |
| 1.0 | 9931.4 | < LoQ | 114.6 | < LoQ | < LoQ | < LoQ |
| 7.1 | 10724.6 | < LoQ | 123.7 | < LoQ | < LoQ | < LoQ |
| 14.2 | 9742.5 | < LoQ | 117.7 | < LoQ | < LoQ | < LoQ |
| 28.2 | 10311.8 | < LoQ | 128.1 | < LoQ | < LoQ | < LoQ |
| 364.6 | 18112.3 | 3.1 | 178.4 | 4.1 | < LoQ | < LoQ |
| 364.6 | 18112.3 | 3.1 | 178.4 | 4.1 | < LoQ | < LoQ |

D.14. S2-Blk-9.5

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 4.3 | NA | NA | NA | NA | NA |
| 1.1 | 106.3 | 93.9 | 167.3 | < LoQ | 7.6 | NA |
| 3.0 | 119.1 | 129.9 | 193.3 | < LoQ | 11.4 | NA |
| 7.0 | 126.7 | 114.1 | 208.5 | < LoQ | 11.2 | NA |
| 14.0 | 113.1 | 125.7 | 228.2 | < LoQ | 12.1 | NA |
| 28.1 | 111.2 | 132.4 | 254.1 | < LoQ | 16.0 | NA |
| 91.8 | 79.7 | 207.3 | 354.3 | < LoQ | 8.3 | NA |
| 379.0 | 211.4 | 322.7 | 558.0 | 0.0 | 7.7 | NA |

D.15. S2-Sat-9.5

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 7.2·10 ² | NA | NA | NA | NA | NA |
| 1.1 | 106.3 | 93.9 | 167.3 | < LoQ | 7.6 | NA |
| 3.0 | 119.1 | 129.9 | 193.3 | < LoQ | 11.4 | NA |
| 7.0 | 126.7 | 114.1 | 208.5 | < LoQ | 11.2 | NA |
| 14.0 | 113.1 | 125.7 | 228.2 | < LoQ | 12.1 | NA |
| 28.1 | 111.2 | 132.4 | 254.1 | < LoQ | 16.0 | NA |
| 91.8 | 79.7 | 207.3 | 354.3 | < LoQ | 8.3 | NA |
| 379.0 | 211.4 | 322.7 | 558.0 | < LoQ | 7.7 | NA |

625 **D.16. S2-Blk-9.8**

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 2.8 | NA | NA | NA | NA | NA |
| 1.1 | 102.6 | 94.2 | 150.8 | 0.7 | 9.1 | NA |
| 3.0 | 119.6 | 93.2 | 166.5 | 0.7 | 9.4 | NA |
| 7.0 | 146.6 | 93.3 | 173.6 | 0.7 | 26.5 | NA |
| 14.0 | 187.5 | 119.1 | 185.9 | 0.6 | 9.3 | NA |
| 28.1 | 135.9 | 119.4 | 201.8 | 0.8 | 10.8 | NA |
| 91.8 | 186.9 | 164.2 | 322.1 | 4.4 | 21.5 | NA |
| 379.0 | 217.3 | 219.1 | 359.7 | < LoQ | 4.5 | NA |

D.17. S2-Sat-9.8

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 1.8·10 ³ | NA | NA | NA | NA | NA |
| 1.1 | 1200.1 | 29.9 | 55.1 | < LoQ | 12.0 | NA |
| 3.0 | 1149.0 | 28.0 | 76.1 | < LoQ | 9.5 | NA |
| 7.0 | 1200.3 | 40.5 | 97.9 | < LoQ | 21.7 | NA |
| 14.0 | 1288.9 | 49.0 | 112.3 | < LoQ | 20.4 | NA |
| 28.1 | 1086.7 | 69.4 | 156.3 | < LoQ | 19.6 | NA |
| 91.8 | 944.9 | 259.1 | 491.1 | < LoQ | 11.5 | NA |
| 379.0 | 954.7 | 401.3 | 766.0 | < LoQ | 36.7 | NA |

D.18. S2-Blk-10.1

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 2.1 | NA | NA | NA | NA | NA |
| 1.1 | 148.2 | 79.0 | 137.5 | 1.3 | 6.6 | NA |
| 3.0 | 161.6 | 89.3 | 162.3 | 1.6 | 4.3 | NA |
| 7.0 | 157.0 | 88.3 | 169.6 | 1.5 | 6.5 | NA |
| 14.0 | 149.6 | 87.8 | 150.0 | 1.2 | 7.2 | NA |
| 28.1 | 139.9 | 76.1 | 146.3 | 1.1 | 4.2 | NA |
| 91.8 | 190.6 | 106.7 | 209.4 | 0.8 | 6.6 | NA |
| 379.0 | 323.9 | 201.4 | 363.9 | < LoQ | 3.4 | NA |

D.19. S2-Sat-10.1

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 3.8·10 ³ | NA | NA | NA | NA | NA |
| 1.1 | 3454.8 | 35.5 | 100.9 | < LoQ | 30.3 | NA |
| 3.0 | 3411.8 | 29.0 | 114.7 | < LoQ | 40.6 | NA |
| 7.0 | 3558.2 | 36.7 | 145.7 | < LoQ | 50.4 | NA |
| 14.0 | 3297.4 | 39.7 | 145.6 | < LoQ | 35.4 | NA |
| 28.1 | 345.7 | 52.0 | 167.5 | < LoQ | 35.3 | NA |
| 91.8 | 3022.5 | 83.4 | 209.1 | < LoQ | 26.2 | NA |
| 379.0 | 2072.5 | 283.6 | 549.0 | < LoQ | 4.0 | NA |

D.20. S2-Blk-10.3

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 3.0 | < LoQ | < LoQ | < LoQ | < LoQ | NA |
| 1.1 | 110.2 | 36.4 | 79.9 | 4.6 | 6.0 | NA |
| 3.0 | 122.7 | 46.6 | 94.6 | 4.3 | 6.7 | NA |
| 7.0 | 132.1 | 51.1 | 100.5 | 4.4 | 3.7 | NA |
| 14.0 | 121.6 | 50.5 | 110.4 | 3.6 | 3.6 | NA |
| 28.1 | 172.6 | 77.0 | 148.2 | 2.9 | 6.3 | NA |
| 91.8 | 199.4 | 100.0 | 187.9 | 2.1 | 5.3 | NA |
| 379.0 | 348.5 | 160.6 | 289.8 | < LoQ | 2.3 | NA |

630 **D.21. S2-Sat-10.3**

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 1.1·10 ⁴ | NA | NA | NA | NA | NA |
| 1.1 | 10143.0 | 3.1 | 255.1 | < LoQ | 14.4 | NA |
| 3.0 | 9411.5 | 6.4 | 316.2 | < LoQ | 32.9 | NA |
| 7.0 | 9389.4 | 11.1 | 507.9 | < LoQ | 35.1 | NA |
| 14.0 | 10201.7 | 17.5 | 592.7 | < LoQ | 57.2 | NA |
| 28.1 | 8601.0 | 21.2 | 405.8 | < LoQ | 20.8 | NA |
| 91.7 | 7977.4 | 268.2 | 622.4 | < LoQ | 54.3 | NA |
| 379.0 | 11372.4 | 499.9 | 1170.3 | 15.9 | 116.4 | NA |

D.22. S2-Blk-10.7

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 6.8 | NA | NA | NA | NA | NA |
| 1.1 | 182.3 | 59.2 | 124.8 | 9.6 | 7.3 | NA |
| 3.0 | 199.2 | 64.6 | 132.4 | 10.6 | 10.9 | NA |
| 7.0 | 232.3 | 66.8 | 138.8 | 9.8 | 10.1 | NA |
| 14.0 | 192.3 | 59.0 | 123.7 | 8.9 | 7.3 | NA |
| 28.1 | 219.2 | 62.9 | 128.9 | 8.3 | 8.7 | NA |
| 91.8 | 223.6 | 65.1 | 138.9 | 9.8 | 4.1 | NA |
| 379.0 | 523.4 | 494.5 | 845.0 | < LoQ | 1.9 | NA |

D.23. S2-Sat-10.7

| Time (d) | Si (g·m ⁻³) | B (g·m ⁻³) | Na (g·m ⁻³) | Al (g·m ⁻³) | Ca (g·m ⁻³) | Zr (g·m ⁻³) |
|----------|-------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 3.5·10 ⁴ | NA | NA | NA | NA | NA |
| 1.1 | 27212.2 | 58.7 | 532.6 | 17.5 | 54.8 | NA |
| 3.0 | 28906.7 | 149.8 | 752.3 | 22.4 | 57.9 | NA |
| 7.0 | 24827.6 | 243.0 | 796.5 | 23.5 | 71.1 | NA |
| 14.0 | 24505.0 | 471.5 | 1178.2 | 23.9 | 55.3 | NA |
| 28.1 | 24983.9 | 574.2 | 1357.2 | 23.7 | < LoQ | NA |
| 91.7 | 24054.0 | 772.2 | 1722.1 | 19.1 | 64.2 | NA |
| 379.0 | 25165.1 | 2502.4 | 5243.9 | 29.5 | 30.9 | NA |

