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Short communication on the Influence of the temperature between 30 and 70°C on the hydration of SON68 nuclear waste glass in a vapour phase

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Abstract

The hydration of SON68 glass (non-radioactive surrogate for R7T7 glass, the French industrial glass for high-level radioactive waste management) was studied at between 30 and 70°C at a relative humidity of 95% for a period of 6 months. The hydration thicknesses were shown to increase with temperature and did not exceed a few nanometres at 30 and 50°C, or a few tens of nanometres at 70°C. The temperature dependence of hydration rates followed Arrhenius law and enabled the determination of an activation energy. This is $62 \pm 13 \text{ kJ.mol}^{-1}$, which is compatible with a hydration mechanism involving a hydrolysis of the silicate bonds. All these results are discussed, taking into account data available in the literature.

The high-level activity radioactive waste (HLW) from the nuclear power industry is immobilized in a vitreous matrix. This matrix is very stable for thousands of years as shown by studies on archaeological glasses and natural analogues [1,2]. According to the permanent nuclear waste disposal solution envisaged by ANDRA (the French national radioactive waste management agency), the waste glass packages (glass in a stainless steel canister encased in a low-alloy steel overpack) will be disposed of in an underground repository constructed with concrete and steel reinforcements in a clay layer 490 m beneath the surface. Steel corrosion in the closed underground repository would result in hydrogen gas release. As a result, the re-saturation of the site with groundwater from the surrounding clay medium will be slowed down. Consequently, it is expected that nuclear waste glasses maybe exposed to an unsaturated medium for up to tens of thousands of years before being completely immersed in aqueous groundwater [3]. Therefore it is mandatory to investigate the consequences of glass alteration in vapour phase, the mechanisms involved, and the influence of intrinsic and extrinsic parameters. In order to evaluate the influence of temperature, hydration experiments on SON68 glass pellets (non-radioactive surrogate of R7T7 glass, the French

industrial glass for high-level radioactive waste management) were carried out at 30, 50, and 70°C over a period of 6 months.

The chemical composition of SON68 glass is identical to that studied by Bouakkaz et al., [4,5]. Six experiments were carried out (Table 1) in order to test the effect of temperature but also the influence of the experimental setup used (Stainless Steel Autoclave with saline solution or Climatic Chamber) and of the relative humidity (95% and 98% RH) on the glass hydration.

5 tests (Tests 1, 2, 3, 5 and 6) were performed in a stainless steel autoclave with a Teflon liner. Polished glass monoliths (to optical finish, with roughness less than 0.25 μm) of dimensions 2.5x2.5x0.1 cm^3 were placed vertically in a Teflon walled stainless steel autoclave above NaCl solution, which imposed the 95% RH relative humidity. The sodium chloride used is an Analar Normapur[®] product ($\geq 99.8\%$). Some impurities such as halogens, alkalis and alkaline earth metals are present. A test with a relative humidity of 98% was also carried out (Test 5). To impose the relative humidity, two saline solutions containing 32.5 $\text{g}\cdot\text{L}^{-1}$ (98% RH) and 80 $\text{g}\cdot\text{L}^{-1}$ (95% RH) of salt were used. The autoclave was placed inside an aluminium cylinder to prevent rapid heating and cooling cycles, which might induce water condensation on the glass monoliths. The setup was then placed in an oven at study temperatures during 6 months.

A WEISS WKL64 climatic chamber was also used to hydrate a monolith at 50°C and 95% RH (Test 4) over 6 months. The apparatus continuously monitored and displayed the temperature and RH in the test zone. De-mineralized water was used to produce steam, and then de-humidified to maintain the programmed RH in the test zone. The monolithic glass samples were placed horizontally in a curved grid Teflon basket that allowed the sample to be exposed to vapour on both faces.

Secondary Ion Mass Spectrometry (TOF.SIMS 5 IONTOF) was used to determine the distribution of chemical species at the solid surfaces. For secondary positive ion analysis, depth profiles of secondary positive ions were obtained by alternating analysis and abrasion cycles. 25 keV Bi_1^+ primary ions at 1.5 pA current were used for the analysis cycles. 2 keV primary O_2^+ ions at 600 nA current were used for the abrasion cycles. The eroded area was 300x300 μm^2 . The analysed area was 50x50 μm^2 for the samples altered for 6 months. The surface charge was neutralized on the monoliths by a pulsed low-energy (<20 keV) electron flux. At the end of the analysis, the depth of the crater (portion of the sample analyzed) was

measured using a mechanical profilometer, and was used for depth calibration. Thus at the end of the analyses, the intensities of different elements were obtained as a function of the depth of the sample analyzed (depth profiles).

The profiles shown here were normalized compared to pristine glass and to silicon, as it is one of the least mobile glass element during glass hydration in vapour phase. The thickness of the layer x corresponded to the interface between the pristine glass and the hydrated layer. This interface was determined in two different ways, on the basis of boron or hydrogen behaviour, to establish a comparison. It was therefore determined classically for the nil difference value:

$$R_1 = \frac{1}{2} - \left[\frac{(C/Si)}{(C/Si)_g} \right] \quad (1)$$

for the boron profile.

It was also determined from hydrogen profiles for the value:

$$R_2 = \frac{1 + \left[\frac{(C/Si)}{(C/Si)_g} \right]_{x=gel}}{2} \quad (2)$$

where $[(C/Si)/(C/Si)_g]_{x=gel}$ represents the average intensity of the hydrogen signal in the alteration layer. Furthermore, it was supposed that the abrasion rate in the altered layer would be identical to that of pristine glass, a hypothesis which we will discuss below.

Morphological analyses of the altered samples were carried out using a field emission Scanning Electron Microscope (SEM) Zeiss Gemini Supra 55, JEOL JSM 6330F with an Energy Dispersive Spectroscopy (EDS) system. The alteration layer could be visually identified through density differences between the pristine glass and the gel layer. The spatial resolution of the SEM (100 nm) does not permit easily detection of the presence of gel layers for low temperatures.

The NaCl solution was analysed for its boron concentration by UV-spectrophotometry (Cary 50 SCAN UV-visible spectrophotometer) at the end of the experiment. The borate ion forms a yellow complex with azomethine-H, which absorbs in the visible range at 410 nm. A calibration was carried out between 0.1 and 2 mg.L⁻¹ of boron corresponding to an absorbance ranging from 0.35 to 1.5. Absorbance variations of 0.005 are detectable corresponding to a change in boron concentrations of 0.01 mg.L⁻¹. Part of the boron volatilized and/or ran off during the

test, and analysis of the solution enabled the calculation of an equivalent thickness of glass alteration which could be compared to the data obtained by TOF SIMS. This equivalent thickness was calculated in nm using the following equation:

$$EE(B) = \frac{C_B}{x_B \times \frac{S}{V} \times \rho} \times 1000 \quad (3)$$

where C_B is the concentration of boron in saline solution (mg L^{-1}), x_B the mass percentage of boron in the glass, S the glass surface area (cm^2), V the volume of saline solution (cm^3), and ρ the glass density (2.75 g.cm^{-3}). The uncertainty on this thickness comes mainly from the boron analysis and is around 5%.

The TOF-SIMS profiles for the three temperatures studied and a relative humidity of 95% are given in Figure 1. Overall, the glass hydration advanced from the external surface inwards for the pristine glass, as shown by the H and Si-OH profile evolutions. These two profiles are complementary because one provides information on the penetration of water at the interface (adsorption, poral water, hydrolysis, ion exchange, etc.) and the other one relates to the interaction between water and the silicate network (mainly hydrolysis and ion exchange). A good agreement between the two kinds of profiles is observed. Surface boron depletion (i.e. retention not exceeding 3 to 4%) can also be seen systematically, but the thickness concerned remains lower than that observed for the hydrogen profiles. Table 2 summarizes all the alteration thicknesses obtained and calculated, considering both boron and hydrogen. Boron is generally used as an alteration marker in an aqueous medium (i.e. under saturated conditions), and its behaviour is therefore interesting to follow but also to compare to that of hydrogen. The thicknesses based on the hydrogen TOF-SIMS profiles are systematically greater (by a factor of 1.2 to 2.2) than those obtained with boron (Table 2). Hereafter the generic term hydration thickness will be used whatever the element under consideration, H or B. Concerning the alkalis, a surface depletion was also observed. Caesium was the element most retained in the gel, followed by sodium, and finally by lithium. The alkaline earths had fairly similar behaviours and generally a higher retention than that of boron. Nevertheless alkaline earth retention remained less than 10%, and therefore low.

Concerning result repeatability and the impact of the experimental setup on the relative humidity monitoring, Tests 2, 3, and 4 at 50°C and $\text{RH} = 95\%$ led to alteration thicknesses which were very similar (Table 2). This indicated good test reproducibility for the same experimental

conditions, but also that the choice of an experimental setup enabling the control of relative humidity (autoclave with salt or climatic chamber) had no impact on the final results. The presence or not in the system of an aqueous solution containing a salt therefore did not modify the hydrated glass thicknesses, and validates the implementation of various approaches among laboratories.

Figure 2 and Table 2 also show that the hydration thickness increased noticeably under a relative humidity between 95 and 98% for a given temperature (50°C), as the thicknesses calculated evolved from 5.5 nm to 9.1 nm for boron and from 8.5 nm to 11.4 nm for hydrogen. This increase in hydration is coherent with data found in the literature, and could come from a rise in the number of monolayers of water adsorbed onto the glass surface when the relative humidity rises [6].

Figure 3 presents the images of the altered layers obtained by SEM for the three temperatures studied, after 6 months of alteration. The surface of the SON68 glass hydrated at 30°C and 95% RH in an autoclave shows no signs of large-scale alteration. The density of precipitates remains much lower at 30°C as shown in figure 3 for the lowest magnification. In certain places, some 10 to 20 µm diameter blister shapes appeared, with a few white precipitates as well as some very fine cracks, as shown in Figure 3. EDX analyses showed that the latter were composed of sodium, potassium, chlorine, and carbon, probably indicating the presence of sodium and potassium chlorides and carbonates. The potassium was certainly contributed by the NaCl solution which was used to ensure the relative humidity within the reactor. The surface of the SON68 glass hydrated at 50°C and 95% RH had the same appearance as that of the sample hydrated at 30°C, but with a greater surface density of blisters (Figure 3). The presence of a few little white precipitates can be noted. The blisters probably come from the beginning of the glass alteration. The surface of the SON68 glass hydrated at 70°C and 95% RH had an identical appearance to that of the other samples, but with a higher surface density of little white precipitates and with more micrometric-sized altered zones (Figure 3). For this sample, there were no blisters. They had probably transformed into the altered zones whose centres showed a morphology which was fairly similar to phyllosilicates. It was not possible to clearly identify these phases by XRD, given that the weak intensities cannot be distinguished from the noisy background.

Figure 4 shows the hydration thickness evolutions depending on the temperature, as determined from both the TOF-SIMS profiles and the analyses of the saline solution. Whatever the element and the analytical technique used, the trend remained the same and the thickness increased with the temperature. For a given temperature, the thicknesses differed by a factor of between 2.5 and 4, depending on the approach used to calculate the hydration thickness (analysis of the solution or TOF-SIMS profiles). The thicknesses at the lower temperatures (30 and 50°C) did not exceed around ten nanometres, and were significantly below the data found in the literature [4,5] obtained in autoclaves, in the presence of a saline solution saline and for the same SON68 glass composition. These past results, obtained after 7 months of alteration, were between 300 and 380 nm for a temperature of 50°C with 92 and 98% RH, and around 250 nm at 35°C with a 95% relative humidity. It is important to remember that in these studies [4,5] alteration kinetics monitoring was carried out by IR following the evolution of the Si-OH line intensity over time, and that evolution was coupled with an alteration thickness evolution determined by SEM observations. Thus a conversion factor of 0.09 Absorbance Units was considered for 1µm of alteration thickness [4,5]. The same conversion factor can be found in studies performed on SON68 glass at higher temperature [7,8]. The application of such a factor to the TOF-SIMS data in our study would lead to IR absorbance evolutions of around 0.0005, incompatible with the technique's resolution level. An additional test confirmed the impossibility of using IR for such low thicknesses, as the IR spectra obtained at 6 months perfectly overlapped the initial spectra. Moreover, the observation by SEM of a polished section for test 3 did not reveal any alteration layer indicating that if the latter exists it is less than 100nm. It therefore seems that there is a notable difference between the two studies and the alteration thicknesses they obtained. The thicknesses were determined with methods which were certainly different, but apparently suitably adapted to the spatial scales involved in each study. Another hypothesis could be based on the different initial sample surface states (roughness, and stress linked to the polishing, for example) which may have led to different hydration behaviour. Indeed, the surface roughness between the two studies are not the same and are respectively less than 0.25 µm for this work and around 3 µm for the Bouakkaz's previous work [5]. Fine polishes greatly reduce the reactivity with respect to hydration, in particular by reducing the number of surface defects and the presence of reactive sites [9].

Concerning the hydration thicknesses calculated based on boron behaviour, it is interesting to note that analyses of the saline solution gave greater thicknesses than results obtained from TOF-SIMS (Table 2). As the surface showed boron depletion, it is likely that this element could have volatilized, even at low temperature, and/or dissolved, in the hypothesis of a surface run off. This preferential departure of boron at low temperature has already been observed on glasses of the AVM type and more recently on a simplified glass of the ISG type with retention factor of less than 10% [10, 11]. The hydration of metal cations associated with the tetrahedral borate species creates an unstable, protonated tetrahedral borate that converts to a more stable protonated trigonal species [12, 13]. In addition, studies on simple chemical compounds (H_3BO_3 , $Na_2B_4O_7$ and $NaBO_2 \cdot 4H_2O$) and on ISG glass have confirmed the high volatility of H_3BO_3 at low temperature [11]. The TOF-SIMS technique may well have underestimated the thicknesses, as the in-depth calibration was carried out by the measurement of a crater depth over several hundreds of nanometres using a 3D profilometer. The information received was therefore mainly related to the abrasion rate of pristine glass and not to the very thin hydrated layer. While additional tests performed on glass samples with thicker hydrated layers obtained at higher temperature did not show any difference between the abrasion rates in the two zones (hydrated layer or pristine glass), this hypothesis cannot be completely excluded for low temperatures. Finally, it is clearly important to work with all the data sets available (surface characterizations and saline solution analyses). The evolutions are confirmed as a function of the temperature, but in the absolute a factor of at least 2.5 to 4 must be considered when estimating the thicknesses of hydrated glass.

The hydration rate values are also listed in Table 2. This hydration rate R_H ($g \cdot m^{-2} \cdot d^{-1}$) is an average calculated over 6 months based on:

$$R_H = \frac{E_{6m} \times \rho}{t \times 1000} \quad (4)$$

where E_{6m} is the hydration thickness (nm), t the time (180 days) and ρ the glass density ($2.75 \text{ g} \cdot \text{cm}^{-3}$).

The natural logarithm of the glass hydration rate $\ln(R_H)$ versus the inverse of the absolute temperature is plotted in Figure 4. The apparent activation energy (E_a , $J \cdot \text{mol}^{-1}$) is calculated from these plots using the Arrhenius equation [4]:

$$k = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Where k is the rate constant (i.e. the glass hydration rate R_H ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)), A is the Arrhenius parameter ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and T is the temperature in Kelvin (K). $-E_a/R$ is the slope of the different plots.

The value obtained for the activation energy is $62 \pm 13 \text{ kJ}\cdot\text{mol}^{-1}$ based on hydrogen data. Whether the thickness data took into account H or B , the associated slope changed very little (Figure 4). This value of E_a , although lower than that determined for the initial dissolution rate of SON68 glass ($77.7 \text{ kJ}\cdot\text{mol}^{-1}$) [14] in aqueous medium (i.e. saturated), is compatible with the monitoring of SON68 glass hydration at low temperatures by hydrolysis of the glassy network. Thus water penetration into the glassy network would need hydrolysis of silicate bonds like Si-O-B, Si-O-Si, whose hydrolysis energies are around $60 - 80 \text{ kJ}\cdot\text{mol}^{-1}$ [13]. It should be noted that this E_a value determined between 30°C and 70°C is higher than that found by Bouakkaz ($34 \text{ kJ}\cdot\text{mol}^{-1}$) [4] at between 35°C and 125°C , on the basis of a similar experimental approach. The authors attributed this low activation energy to a reactive water molecule diffusion process in the glassy network.

To conclude, the differences in activation energies and in hydration thicknesses at low temperatures found by the different studies carried out to date reveal the need to deepen our understanding of the SON68 glass hydration process in vapour phase. This will require a comparison of the study methodologies applied for the initial surface state checks (roughness, glass stress state...) and for the determination of the hydrated glass thicknesses under the conditions where they are the thinnest (low temperatures). Once these approaches and methodologies have been settled, it will be possible to advance and to stabilize our understanding of complex glass hydration mechanisms at low temperatures.

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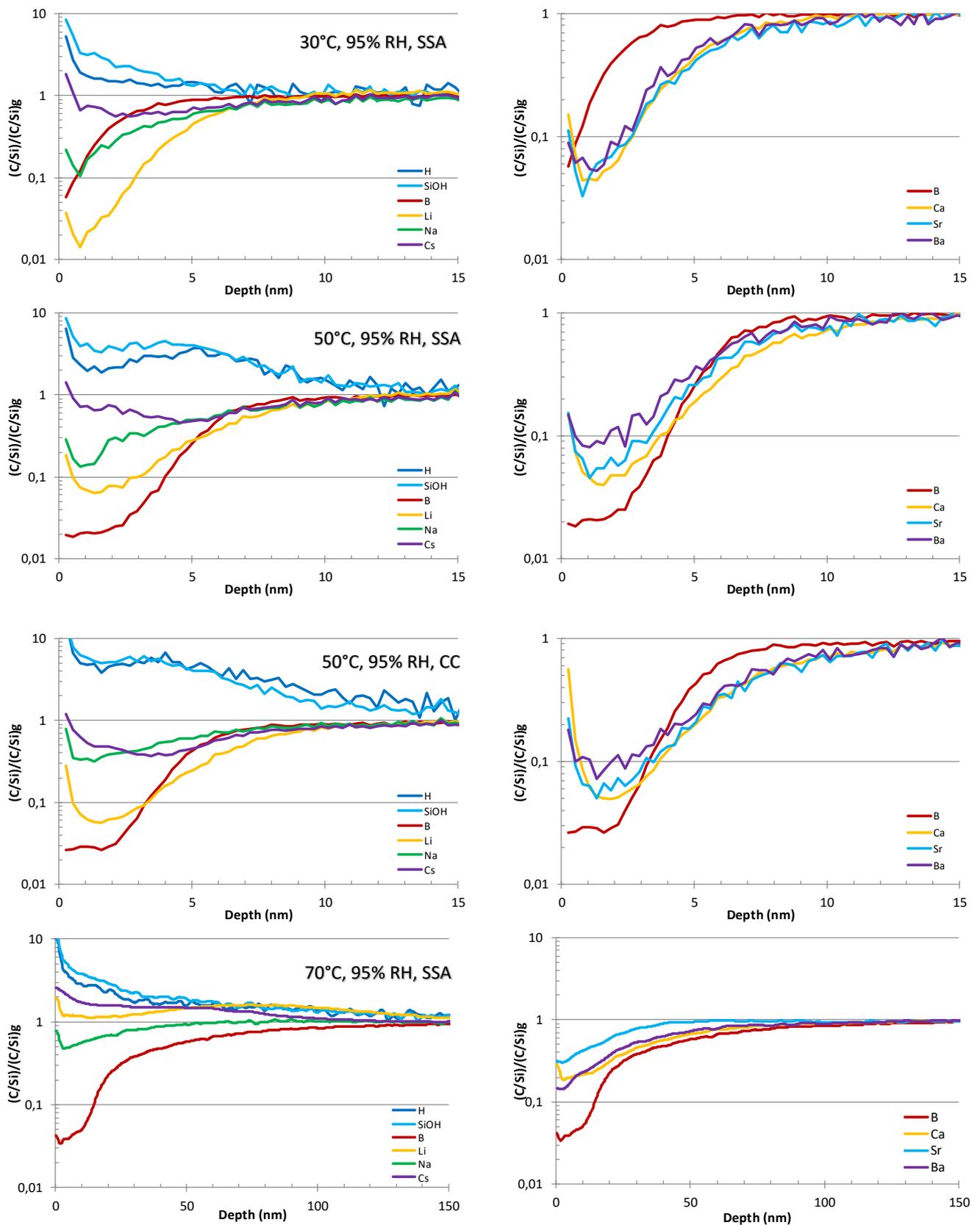


Figure 1: Elemental TOF-SIMS profiles for SON68 glass hydrated over 6 months at 30, 50, 70 °C, and 95% RH. From top to bottom: Test 1: 30°C (Stainless Steel Autoclave), Test 2: 50°C (SSA), Test 4: 50°C (Climatic Chamber), Test 6: 70°C (SSA).

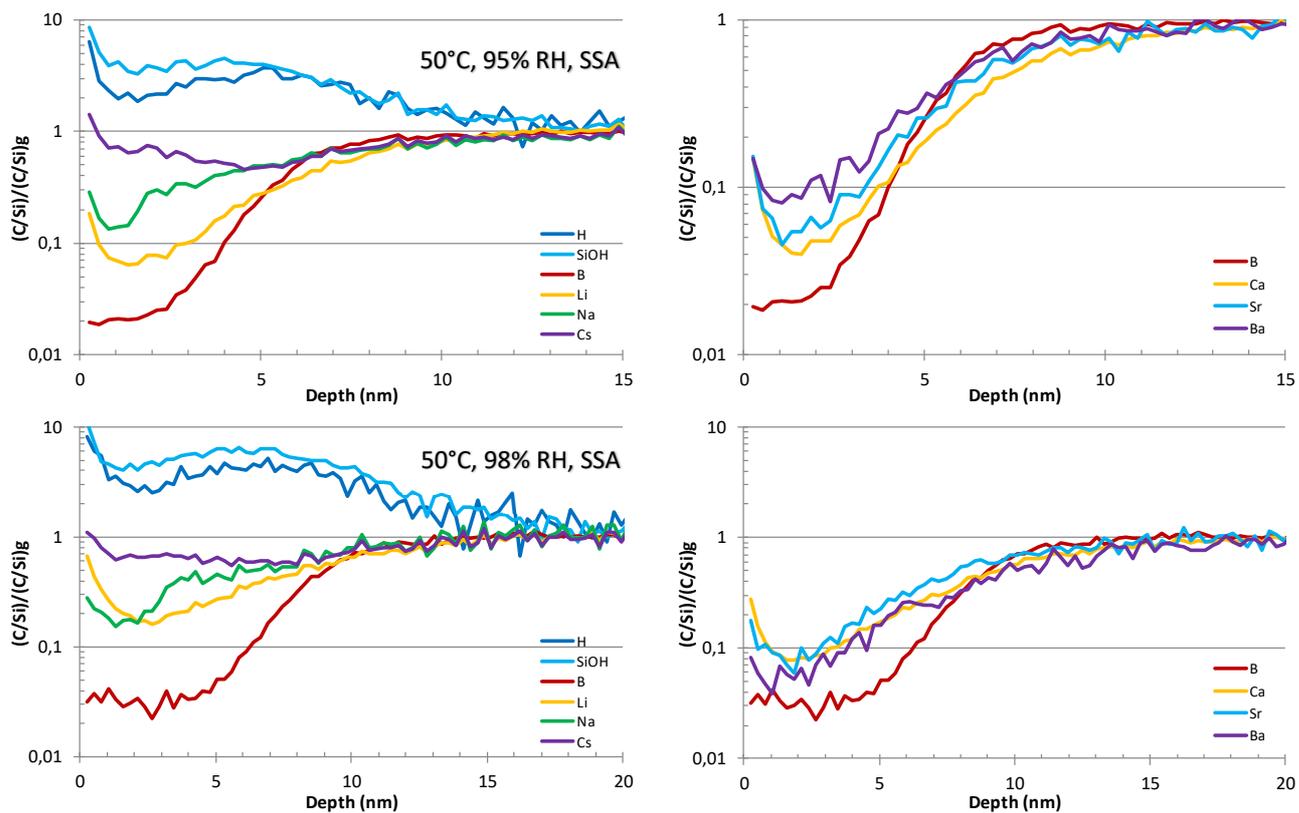


Figure 2: Elemental TOF-SIMS profiles for SON68 glass hydrated over 6 months at 50°C in a Stainless Steel Autoclave for two different Relative Humidities (top: Test 2: 95% RH, and bottom: Test 5: 98% RH).

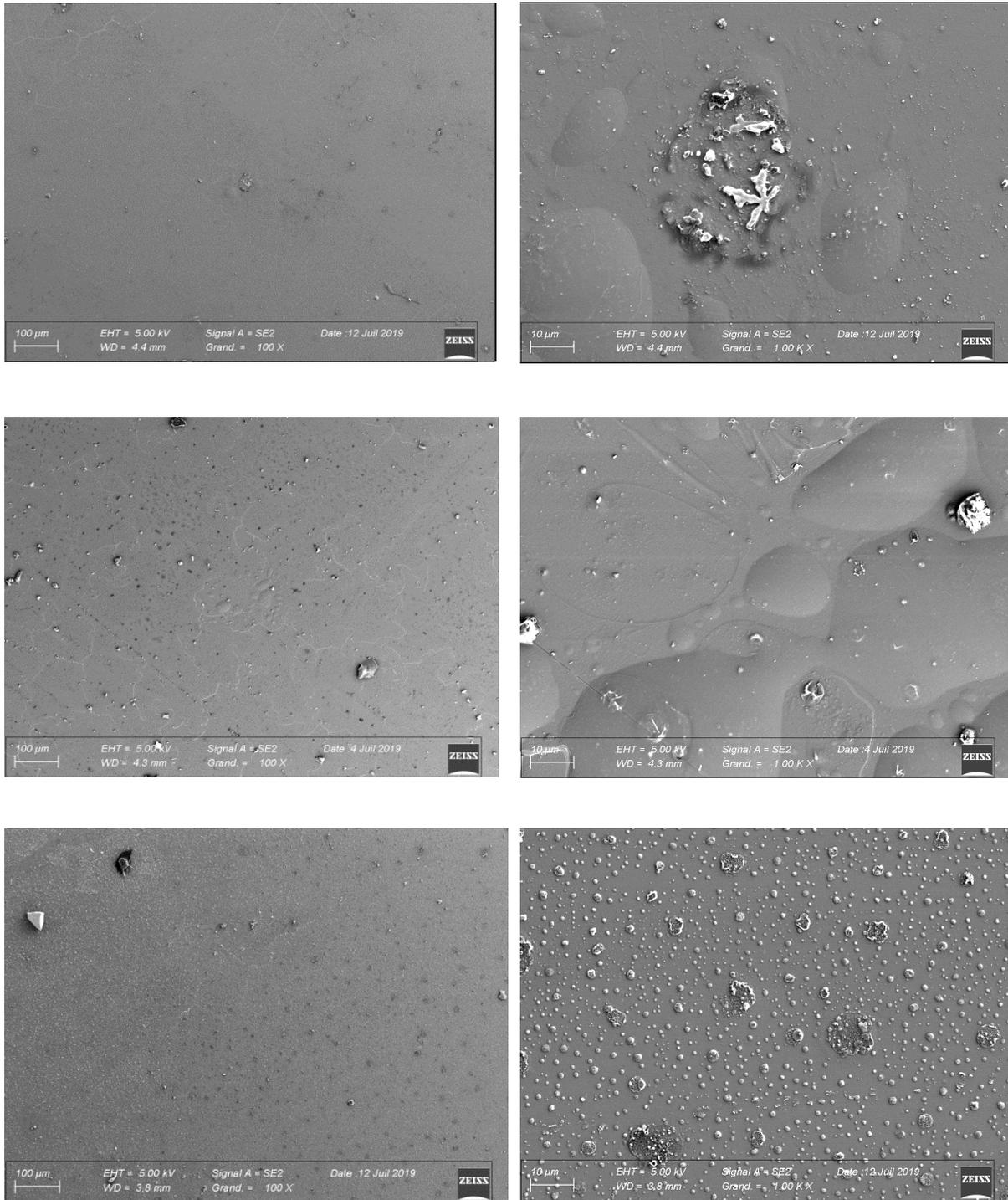


Figure 3: SEM images of the surface for SON68 glass hydrated over 6 months at 30, 50, 70 °C, and 95% RH. From top to bottom: 30°C (Stainless Steel Autoclave), 50°C (SSA), 70°C (SSA).

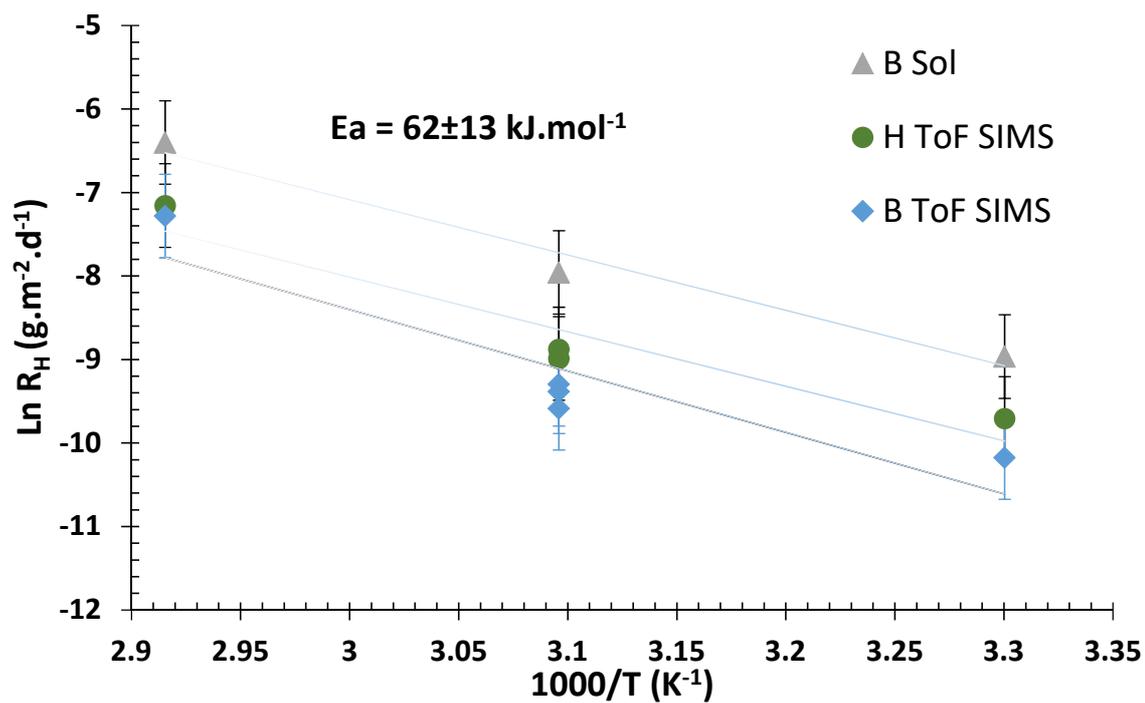
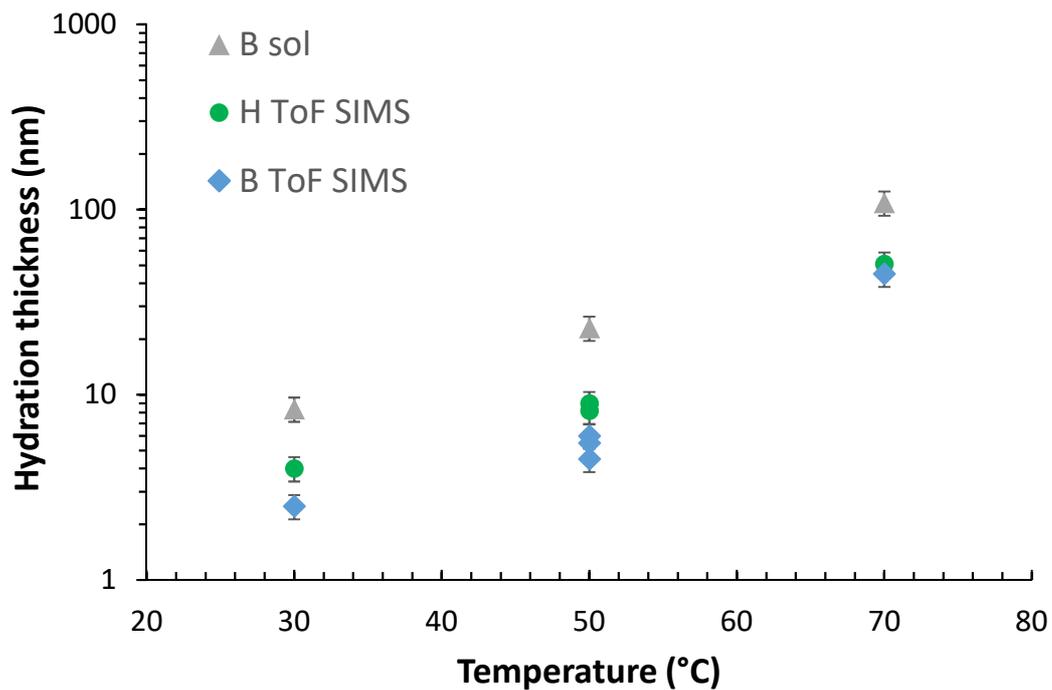


Figure 4: Evolution of the thickness (top) and the hydration rate (bottom) of the SON68 glass as a function of the temperature (6 months of hydration and RH = 95%).

Test	Temperature (°C)	RH (%)	Protocol	Duration (months)
1	30	95	SSA + saline solution	6
2	50	95	SSA + saline solution	6
3	50	95	SSA + saline solution	6
4	50	95	Climatic Chamber	6
5	50	98	SSA + saline solution	6
6	70	95	SSA + saline solution	6

Table 1: Hydration experiments carried out on the SON68 glass with the experimental conditions.

Test	Depth (B) (nm)	Hydration rate (B) ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)	EE(B) (nm)	Hydration rate (B) ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)	Depth (H) (nm)	Hydration rate (H) ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)
1	2.5	3.8×10^{-5}	8.4	1.4×10^{-4}	4	6.1×10^{-5}
2	6	9.2×10^{-5}	23	3.5×10^{-4}	9	1.4×10^{-4}
3	4.5	6.9×10^{-5}	nd	nd	10	1.5×10^{-4}
4	5.5	8.4×10^{-5}			8.2	1.25×10^{-4}
5	9.1	1.4×10^{-4}	23	3.5×10^{-4}	11.4	1.7×10^{-4}
6	45	6.9×10^{-4}	109	1.7×10^{-3}	51	7.8×10^{-4}

Table 2: Hydration rates of SON68 glass obtained at different temperatures and relative humidities. The depth of the altered layer was measured by TOF-SIMS, and EE(B) is based on the analysis of the solution at the end of the test. The uncertainties on the measurements by TOF-SIMS are at least 10% and around 5% for the solution analyzes. The rate is an average value over 6 months of hydration.