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► **To cite this version:**

Sathya Narayanasamy, Patrick Jollivet, Nicole Godon, Frédéric Angeli, S. Gin, et al.. Influence of composition of nuclear waste glasses on vapor phase hydration. *Journal of Nuclear Materials*, 2019, *Journal of Nuclear Materials*, pp.53-71. 10.1016/j.jnucmat.2019.07.015 . hal-02277978

**HAL Id: hal-02277978**

**<https://hal.univ-lille.fr/hal-02277978>**

Submitted on 27 Sep 2019

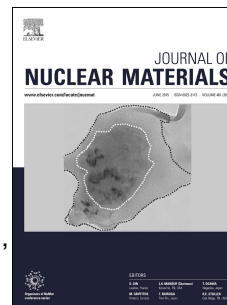
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# Accepted Manuscript

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PII: S0022-3115(19)30397-6

DOI: <https://doi.org/10.1016/j.jnucmat.2019.07.015>

Reference: NUMA 51715

To appear in: *Journal of Nuclear Materials*

Received Date: 1 April 2019

Revised Date: 12 July 2019

Accepted Date: 14 July 2019

Please cite this article as: S. Narayanasamy, P. Jollivet, N. Godon, Fr  . Angeli, St  . Gin, M. Cabi  , J. Cambedouzou, C. Le Guillou, A. Abdelouas, Influence of composition of nuclear waste glasses on vapor phase hydration, *Journal of Nuclear Materials* (2019), doi: <https://doi.org/10.1016/j.jnucmat.2019.07.015>.

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## 1 Influence of composition of nuclear waste glasses on vapor phase hydration

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## 12 Abstract

13 For the first time, the influence of glass composition on the vapor hydration kinetics of the French AVM  
14 nuclear waste glass simulants was investigated. Three complex borosilicate glasses (> 20 oxides) along  
15 with three simplified Na/(Ca, Na)/(Mg, Na)-alumino-borosilicate glasses with four or five oxides were  
16 altered at 50°C in water vapor (95% RH) for up to 557 days. The solid characterization of the altered  
17 samples (by SEM, TEM, XRD, ToF-SIMS, SAXS) revealed that the rate-controlling vapor hydration  
18 mechanism is composition dependent. The vapor hydration rate of the more durable glasses, whose  
19 molar ratio of Al<sub>2</sub>O<sub>3</sub>/(CaO or MgO) is ≥1, seems to be limited by network-hydrolysis, whereas the overall  
20 glass alteration rate of the less durable glasses, whose Al<sub>2</sub>O<sub>3</sub>/MgO ratio is <1, seems to be driven by the  
21 precipitation of Mg-rich secondary phases. All the vapor hydrated glasses show the presence of a  
22 homogeneous gel layer of a few tens of nm thickness. The more durable glasses have a smaller quantity  
23 of secondary phases precipitated on their surface. The less durable glasses have a relatively significant  
24 quantity of secondary phases precipitated above the gel layer and irregularly shaped, scattered and  
25 highly porous altered zones formed beneath the gel layer. The overall alteration rate of the less durable  
26 glasses was 10-20 times faster than the more durable glasses. For all glasses, FTIR spectroscopy indicated  
27 an inflexion in the vapor hydration rate after 120-200 days of alteration, likely due to a passivating effect  
28 of the altered layer formed under unsaturated conditions. The average pore size of the altered layer in

29 certain vapor hydrated glasses measured by SAXS is similar to the pore sizes of the gel layer formed in  
30 aqueous medium and varies very slightly with glass composition.

### 31 1. Introduction

32 The high-level activity radioactive waste (HLW), issued from the nuclear power industry, is immobilized  
33 in a vitreous matrix, since glass has been proven to be a stable solid form for thousands of years based  
34 on archeological or geological evidence [1, 2]. According to the permanent nuclear waste disposal  
35 solution envisaged by ANDRA (the French national radioactive waste management agency), the waste  
36 glass packages (glass in a stainless steel canister encased in a low-alloy steel overpack) will be stored in  
37 an underground repository constructed with steel and concrete reinforcements in clay layer 500 m  
38 beneath the earth's surface. The steel corrosion in the closed underground repository would result in  
39 hydrogen gas liberation. As a result, the re-saturation of the site with ground water from the surrounding  
40 clay medium will be slowed down. Consequently, it is expected that nuclear waste glasses maybe  
41 exposed to an unsaturated medium for up to tens of thousands of years before being completely  
42 immersed in aqueous ground water [3]. Therefore it is mandatory to investigate the consequences of  
43 glass alteration in vapor phase, the mechanisms involved and the influence of intrinsic and extrinsic  
44 parameters [4]. Glass alteration in vapor phase has been relatively less studied in comparison to  
45 alteration in aqueous medium [5-15].

46 Vapor hydration experiments on a variety of nuclear waste glasses and their non-radioactive surrogates  
47 have been conducted by different laboratories in USA [16-26], UK [27] and France [28-33]. From the  
48 experimental results so far, it can be understood that the reactions occurring between glass and water  
49 are the same for alteration in aqueous medium and unsaturated water vapor. However, the rate  
50 controlling reaction mechanism and the driving force for alteration are different in both cases. The  
51 difference arises largely due to the very small volume of water in vapor phase and almost no leaching by  
52 solution, unless water condenses and flows away from the altered surface. The precipitation of  
53 secondary phases seems to be the strongest driving force for alteration in vapor phase at high  
54 temperature. A majority of the vapor hydration studies conducted so far have been done in extreme  
55 conditions (150-200°C & 100% relative humidity (RH)) favorable for secondary phases precipitation. This  
56 temperature range is not representative of the expected scenario in the French geological disposal  
57 facility. It is expected that the temperature of the waste glass packages will be lower than or equal to  
58 50°C [34]. The vapor hydration of SON68 (French inactive reference nuclear waste glass) at high  
59 temperatures (90-200°C, activation energy ( $E_a$ )=43-47 KJ/mol) [28] and lower temperatures (35-90°C,

60  $E_a=34\pm 0.4$  KJ/mol) [31] suggests that the rate-controlling mechanisms may depend on temperature. The  
61 limited data of the studies have also confirmed the influence of relative humidity [16], glass composition  
62 [22, 27, 35-37], composition of the vapor phase [30] and radioactivity [38] on vapor hydration kinetics.  
63 Insights on glass alteration in vapor phase can also be obtained from studies on atmospheric alteration  
64 of window glasses, art crafts, stained-glass windows of historic sites etc. [39-41]. Almost all these studies  
65 have shown similar altered layer morphology on the glass surface in contact with an unsaturated  
66 medium. An altered layer, commonly referred to as 'gel layer', is formed adjacent to pristine glass. This  
67 gel layer has been suggested to be formed by mechanisms of hydration (penetration of water molecules)  
68 [37] / inter-diffusion ( $(\equiv Si - O^- M^+)_{glass} + H_{water}^+ \rightarrow (\equiv Si - OH)_{glass} + M_{water}^+$ ) [40, 42] / network  
69 hydrolysis ( $(\equiv Si - O - Si \equiv)_{glass} + H_2O \rightarrow 2 (\equiv Si - OH)_{glass}$ ) [31, 43, 44] or a combination of  
70 these mechanisms [39, 41]. Localized dissolution-precipitation or condensation mechanisms and re-  
71 organization of the gel layer have also been discussed in literature [31, 39]. On the surface of this gel  
72 layer, amorphous / crystalline secondary precipitates maybe present [23, 31, 36]. In certain cases, the  
73 secondary phases may also accelerate the vapor hydration kinetics [22].

74 In this article, the focus is on the influence of glass composition on vapor hydration. Through literature  
75 survey, it can be understood that glass composition can affect glass durability in three ways. (i) The  
76 presence of alkaline elements in the glass can promote the quantity of water adsorbed on surface,  
77 facilitate inter-diffusion mechanism and may result in increased hydration rate [22, 37, 45]. (ii) Glass  
78 composition plays an important role in the precipitation of secondary phases under given conditions and  
79 thus may accelerate glass alteration [22, 35]. (iii) Presence of elements such as Zn, which increases the  
80 resistance to network hydrolysis, may increase glass durability in vapor phase [27]. The literature study  
81 led us to understand that certain elements such as Al may have a dual role depending on whether the  
82 conditions are favorable for secondary phase precipitation (negative effect) or if they participate in  
83 increasing the resistance of glass network to hydrolysis (positive effect). Therefore, the temperature of  
84 the experiments needs to be carefully chosen, as the influence of the glass composition on its alteration  
85 could vary with temperature.

86 In this study, the influence of nuclear waste glass composition on vapor hydration has been investigated  
87 by studying the behavior of three AVM (*Atelier de Vitrification de Marcoule*) glasses in contact with water  
88 vapor. The AVM glasses are complex borosilicate glasses containing more than 20 oxides including fission  
89 products issued from the UNGG (*Uranium Naturel Graphite-Gaz*) reactor at Marcoule. The range in the  
90 AVM glasses composition is extensive due to the variation in the composition of fission products

91 solution. The long-term behavior of these HLW radioactive glasses in aqueous media was studied using  
92 many inactive surrogates [46, 47]. Based on this study, the glasses AVM6, AVM10 and AVMV4 are the  
93 three inactive surrogates selected for the current study. AVM6 is known to alter at the highest residual  
94 rate ( $r_r$ ) in deionized water at 50°C and AVM10 alters at the lowest  $r_r$ . AVMV4 is a simulant of the actual  
95 composition of the HLW glass produced at Marcoule facility.

96 The specific influence of alkaline-earth elements such as Mg and Ca was investigated, since AVM glasses  
97 contain a significant amount of Mg and very little Ca and the effects of these elements on glass alteration  
98 rate in aqueous medium are relatively well-known [48-52]. Based on literature review, it is expected that  
99 these elements would be detrimental to glass durability in unsaturated medium due to their tendency to  
100 form secondary precipitates. The study of their specific influence cannot be carried out using a complex  
101 glass with several oxides due to possible interference and synergies between other elements. Therefore,  
102 three simplified glasses (Q, QCa and QMg) were prepared based on the Si/Al stoichiometry of AVMV4.  
103 The use of simplified glass compositions helps to understand the role of specific element on glass  
104 durability [53-56].

105 The fission products loading of AVM glasses suggests that the temperature of the glass packages during  
106 the expected time of exposure to water vapor will be around 50°C. Therefore, it was decided to conduct  
107 our experiments at 50°C. It is suspected that the rate-controlling vapor hydration mechanisms may vary  
108 with conditions favorable for precipitations of certain silica-rich secondary phases at higher  
109 temperatures (>90°C). The relative humidity (RH) was chosen to be 95% since the conditions expected in  
110 the repository are close to saturation [34].

## 111 2. Materials and methods

### 112 2.1 Sample preparation

113 The synthesis of the AVM glasses has already been described by Thien [46]. The glass samples for this  
114 study were retrieved from the same batch. Q, QCa and QMg were prepared using the oxide precursors  
115 ( $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  (for QCa) and  $\text{MgO}$  (for QMg)). The mixtures were put in a Pt-Rh  
116 crucible and heated during 3 h at 1450°C. They were then annealed at 620°C during 1 h in a graphite  
117 crucible. Afterwards, the temperature of the furnace was decreased at a rate of 0.5°C/min until 300°C  
118 and then it was turned off. The compositions of the glasses after dissolution in acid solution were  
119 determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The data in mol%  
120 oxides are provided in table 1. The error percentage associated with the measured values is 3%. The

121 fraction of Non-Bridging Oxygen (NBO) atoms in the glass network was theoretically calculated based on  
 122 equation 2.1.1 and equation 2.1.2.  $^{11}\text{B}$  NMR spectra (not presented here) were collected on a Bruker  
 123 Avance II 500WB spectrometer. The calculated NBO values and the fraction of  $\text{B}^{(\text{IV})}$  for each glass are  
 124 provided in table 1. The error associated varies between 3 to 8%.

$$125 \quad NBO = \frac{2 * (\text{mol fr. of oxides of modifier cations} - \text{mol fr. of oxides of network former requiring charge compensation})}{N(O)} \quad \text{Equation 2.1.1}$$

$$126 \quad N(O) = \sum(\text{no. of oxygen atoms in 1 molecule of oxide} * \text{mol fr. of oxide}) \quad \text{Equation 2.1.2}$$

127 For all glasses, the NBO values are similar despite their differences in compositions (except Q). The  
 128 percentage of  $\text{B}^{(\text{IV})}$  in each glass shows that Mg is less efficient to compensate  $[\text{BO}_4]^-$  entities than Ca.

129  
 130 For each glass, two monoliths of dimensions ( $2.5 \times 2.5 \times 0.1 \text{ cm}^3$ ) were prepared for vapor hydration during  
 131 180 days and 557 days, respectively. These monoliths were cut from the glass bars and polished to  
 132 optical finish (surface roughness  $\ll 1 \mu\text{m}$ ) on both faces. Similarly, one polished monolith for each glass  
 133 was also prepared with dimensions ( $2.5 \times 2.5 \times 0.08 \text{ cm}^3$ ) for the purpose of studying hydration kinetics  
 134 using Fourier Transform Infrared (FTIR) spectroscopy. All the glass monoliths were washed in ultra-pure  
 135 acetone and absolute ethanol under ultrasonic agitation and dried for a few hours in an oven at  $50^\circ\text{C}$   
 136 before starting the experiment. Powder samples of each glass were prepared by crushing glass pieces  
 137 using Retsch MM400 ball-mill apparatus equipped with tungsten carbide balls. The size fraction of 2 – 5  
 138  $\mu\text{m}$  were separated using pure acetone solvent and the application of Stokes law, for Small Angle X-ray  
 139 Scattering (SAXS) measurement.

## 140 **2.2 Alteration Protocol**

141 A WEISS WKL64 climatic chamber was used to hydrate the samples at  $50^\circ\text{C}$  and 95% RH. The apparatus  
 142 continuously monitors and displays the temperature and RH in the test zone. De-mineralized water is  
 143 used to produce steam and then de-humidified to have the programmed RH in the test zone. The  
 144 monolithic glass samples are placed horizontally in a curved grid Teflon basket that allows the sample to  
 145 be exposed to vapor on both faces. The glass powders were dispersed in plastic petri dishes. Similar  
 146 protocol for vapor hydration of glasses has been used before in literature [39].

## 147        **2.3 Experiments**

### 148        **2.3.1 Hydration kinetics**

149        A glass monolith of dimensions ( $2.5 \times 2.5 \times 0.08 \text{ cm}^3$ ) was placed in the climatic chamber at  $50^\circ\text{C}$  and 95%  
150        RH. The sample was removed periodically (approximately once a month) for a short duration ( $\sim 10$   
151        minutes) and analyzed in transmission mode using a Vertex 70 FTIR spectrometer. It was then replaced  
152        in the chamber to continue hydration. Five spectra at different regions of the monolith were recorded  
153        and averaged. The diameter of the diaphragm was set to 6 mm. The spectra were recorded from 4000 to  
154         $400 \text{ cm}^{-1}$ . The deconvolution of the spectra from 4000 to  $2600 \text{ cm}^{-1}$  into five Gaussian bands was  
155        attributed to the vibration of the OH stretching mode in SiOH molecules ( $\sim 3595\text{-}3605 \text{ cm}^{-1}$ ), bound  
156        water-silanol groups ( $\sim 3515\text{-}3518 \text{ cm}^{-1}$  &  $\sim 3170\text{-}3185 \text{ cm}^{-1}$ ), symmetrical OH stretching mode in the free  
157        water molecule ( $\sim 3400\text{-}3415 \text{ cm}^{-1}$ ) and the glass matrix ( $\sim 2700 \text{ cm}^{-1}$ ). This type of deconvolution is based  
158        on the protocol used to follow vapor hydration kinetics using infrared spectroscopy in recent literature  
159        [29, 32, 57, 58]. The hydration kinetics was followed by studying the evolution of the increase in  
160        absorbance of the band attributed to the OH stretching mode in SiOH molecules over time.

161        Calculation of error in the increase in absorbance values: With every deconvolution, the standard error  
162        associated with the increase in the area of the Gaussian is calculated by Origin software. The error values  
163        for the Gaussian fit are less than 2%. However, while measuring the FTIR spectrum at 5 different places  
164        for the same sample, the sample compartment is opened and closed. Due to this the background that  
165        was earlier measured is disturbed. Therefore, several backgrounds were measured throughout the day  
166        of the FTIR analysis, and the standard deviation among the absorbance values in the range of  
167        wavenumbers  $3595\text{-}3605 \text{ cm}^{-1}$  was used to calculate the error value. After error propagation calculation,  
168        0.02 (a.u.) was calculated as the error value.

### 169        **2.3.2 Characterization of altered glasses**

170        For each composition, two glass monoliths of dimensions ( $2.5 \times 2.5 \times 0.1 \text{ cm}^3$ ) and the glass powders  
171        were placed in the climatic chamber at  $50^\circ\text{C}$  and 95% RH for a period of 180 days and 557 days  
172        respectively. Afterwards, the monoliths were removed from the chamber and cut into dimensions of  
173        ( $1 \times 1 \times 0.1 \text{ cm}^3$ ) approximately for characterization by Scanning Electron Microscope (SEM), Transmission  
174        Electron Microscope (TEM), X-Ray Diffraction (XRD) and Time-of-Flight Secondary Ion Mass Spectrometry  
175        (ToF-SIMS). The glass powders were characterized by Small Angle X-ray Scattering (SAXS) to probe the  
176        porosity and the pore-size of the gel layer.



177 For the purpose of studying the evolution of pore characteristics of the gel layer with time, the  
178 powdered samples of AVM6 were altered for 11 days, 31 days and 90 days at 50°C and 95% RH, in  
179 addition to the standard alteration time of 180 days and 557 days. These samples were characterized by  
180 SAXS.

## 181 **2.4 Characterization techniques**

### 182 **2.4.1 SEM**

183 Morphological analysis of the altered samples were carried out using a field emission Scanning Electron  
184 Microscope (SEM) Zeiss Gemini Supra 55, JEOL JSM 6330F with an Energy Dispersive Spectroscopy (EDS)  
185 system.

### 186 **2.4.2 TEM**

187 FEI TECNAI G2 Transmission Electron Microscope (TEM) was used for morphological and chemical  
188 analysis. The 80 kV to 200 kV TEM permits to do conventional imaging and analytics, disposes of bright-  
189 field and dark-field imaging, EDS and Scanning TEM (STEM) to probe chemical composition of materials.  
190 The spatial resolution is 0.27 nm. Ultra-thin samples for observation by TEM (the length of the sample is  
191 approx. 5  $\mu\text{m}$  and it is about one hundred nm thick) were prepared using Dual Beam FIB (FEI Helios 600  
192 NanoLab). The uncertainty associated with the quantitative STEM-EDX analyses was estimated to be  
193 around 12% relative error. Scanning transmission electron microscopy (STEM) and EDS mapping were  
194 performed on QMg sample altered for 180 days using a Thermofisher Titan Themis 300 microscope  
195 operated at 300 keV, located at the "Centre Commun de Microscopie – CCM" at the university of Lille.  
196 Hyperspectral EDS data were obtained using the super-X detector system equipped with four  
197 windowless silicon drift detectors. The probe current was set at 50 pA. The analysis of the hyperspectral  
198 data was performed using the Hyperspy python-based package [59]. The signal was first denoised using  
199 Principal Component Analysis (PCA). Then, the EDS spectra at each pixel were fitted by a series of  
200 Gaussian functions and a physical model for background/bremsstrahlung. Quantification was performed  
201 thanks to the Cliff-Lorimer method, using experimentally determined k-factors and absorption correction  
202 routines.

### 203 **2.4.3 XRD**

204 Crystalline secondary phases were identified using a Philips X'Pert diffractometer X-Ray Diffraction (XRD)  
205 apparatus equipped with a copper tube and a goniometer (4-80° 2 $\theta$ , step size 0.01744°). Each glass  
206 monolith was analyzed for 12 h on a multiple purpose sample stage (MPSS).

207 **2.4.4 ToF-SIMS**

208 The behavior of elements in the altered layer was characterized using ToF-SIMS (SSIMS on TOF 5  
 209 (IONTOF)). Depth profiles of secondary positive ions were obtained by alternating analysis and abrasion  
 210 cycles. 25 keV  $\text{Bi}_1^+$  primary ions at 2 pA current were used for analysis cycles. 1 keV primary  $\text{O}_2^+$  ions at  
 211 250 nA current were used for the abrasion cycles. The eroded area was  $200 \times 200 \mu\text{m}^2$ . The analyzed area  
 212 was  $60 \times 60 \mu\text{m}^2$  for the samples altered for 180 days and  $50 \times 50 \mu\text{m}^2$  for the samples altered for 557 days.  
 213 The surface charge was neutralized on the monoliths by a pulsed low-energy (<20 keV) electron flux. The  
 214 depth calibration was carried out using the abrasion rate and a mechanical profilometer to measure the  
 215 crater depth at the end of the analysis. It is to be noted that the same abrasion rate was used for  
 216 analyzing the gel layer and the pristine glass. This choice was justified by the good correspondence  
 217 between thickness of altered layer measured by SEM and ToF-SIMS in other works [31].

218 The profiles were normalized with respect to the intensity of each element ( $C$ ) in the pristine glass  
 219 (denoted as PG) and with respect to the intensity of Si ( $C_{\text{Si}}$ ) at given depth as shown in the equation  
 220 2.4.4.1 below.

$$221 \quad \text{Normalized intensity} = \frac{\frac{C}{C_{\text{Si}}}}{\left(\frac{C}{C_{\text{Si}}}\right)_{\text{PG}}} \quad \text{Equation 2.4.4.1}$$

$$222 \quad \text{Altered layer depth} = x_0 \text{ at which } \left( 0.5 - \frac{\frac{C_B}{C_{\text{Si}}}}{\left(\frac{C_B}{C_{\text{Si}}}\right)_{\text{PG}}} = 0 \right) \quad \text{Equation 2.4.4.2}$$

223 In literature, the most immobile element in the glass network is used for normalization of ToF-SIMS  
 224 profiles to avoid matrix effects, which could be either Si or Zr [60, 61]. In our experiments, Si can be  
 225 considered immobile. This is valid after verification that Si bearing phases are in relatively small quantity.  
 226 It was chosen as the element for normalization since it is present in a sufficiently large quantity in the  
 227 glass, such that the precipitation of secondary phases on the glass surface will not result in depletion of a  
 228 large fraction of this element.

229 Boron is a good tracer for glass alteration in aqueous medium since it is neither retained in the gel layer  
 230 nor forms secondary phases. In vapor phase it would be logical to expect that the retention of boron in  
 231 the gel layer is much higher since the quantity of water available to leach boron is highly limited.  
 232 However, the ToF-SIMS profiles indicate that the retention of boron in the gel layers is very limited (<  
 233 20%). Therefore, boron is used as a tracer to measure altered layer thickness in the vapor hydration

234 phenomenon as well. The thickness of the altered layer was determined based on the profile of boron as  
235 shown in equation 2.4.4.2. The thickness of the zone of interface between gel layer and pristine glass  
236 measured by ToF-SIMS could be influenced by sample artefacts such as surface roughness of the sample  
237 due to precipitates or due to the heterogeneity of the altered layer.

#### 238 **2.4.5 SAXS**

239 The apparatus used is a SAXS-Mo apparatus emitting monochromatic X-ray beam at  $\lambda$  0.709 Å and the  
240 photon flux is  $3 \times 10^6$  photons.s<sup>-1</sup> approximately. The q-range covered is 0.2 to 30 nm<sup>-1</sup>. The distance scale  
241 D is related to the scattering vector q by the formula  $D = 2\pi/q$ . The sample was filled in a glass capillary  
242 tube of 2 mm ( $e_s$ ) diameter and approximately 10 μm wall thickness. In the section of the sample  
243 analyzed, the inter-grain porosity is filled with air. The inner porosity of each grain could be filled with air  
244 or water. The data treatment for a porous or granular medium with special attention to the case of glass  
245 leaching by water was handled by Spalla et al. 2003 [62]. The data treatment was based on previous  
246 works [62-64] and is explained in detail in the supplementary data (section1).

247

### 248 **3. Results**

249 The solid characterization of the altered glass has given insights into the morphology of the altered layer,  
250 behavior of elements in the altered layer, porosity of the altered layer and the vapor hydration kinetics.  
251 In each subsection, the results of all six glasses have been presented. An overall analysis of the results  
252 showed that the behavior of the altered glasses AVM6 and AVM10 is similar and that of AVMV4 and  
253 QMg is similar. For this reason, the results of these two couples of glasses have been presented together  
254 in section 3.1 and section 3.3. The Q and QCa glasses, which do not contain Mg, are also presented  
255 following the four above mentioned Mg-containing glasses.

#### 256 **3.1 Morphology of the altered layer (SEM/TEM images)**

##### 257 **3.1.1 AVM6 and AVM10**

258 The SEM images showed that the alteration of these two glasses is similar in the following  
259 accounts:

260 (i) Irregular alteration: SEM images of cross-sections showed that both glasses had altered in a  
261 heterogeneous manner. Figure 1 shows the SEM and TEM cross-sections of AVM6 and AVM10 altered  
262 for 180 days and 557 days (denoted hereafter as AVM6-180, AVM6-557, AVM10-180 and AVM10-557).

263 The altered surface was punctuated with low density altered zones in the shape of irregular cups whose  
264 widths and depths varied from a few hundred nm to a few  $\mu\text{m}$  (figure 1 (a) and (c) and supplementary  
265 data-figure S 1). They were formed on both faces. TEM images of micro-sections showed that in both  
266 glasses, these irregular zones were highly porous. This was the case for all four samples. According to  
267 STEM-EDX analysis (supplementary data-Section 3, figures S 6, S 7 and S 8), the porous zone is depleted  
268 in Mg, Fe and enriched in Ca.

269 An attempt to calculate a statistical average thickness of the altered layer of the AVM10-180  
270 sample was made. Ten cross-section SEM images on both faces of AVM10-180 were taken. These images  
271 spanned a width of approx. 10  $\mu\text{m}$  each and were taken at a distance of approx. 500  $\mu\text{m}$  apart from one  
272 another. From these images, 334 measurements of the irregular altered zone thicknesses were  
273 calculated using GIMP image processing software. The average of these measurements for the AVM10  
274 glass is around 659 nm. The minimum thickness measured is 78 nm and the maximum thickness  
275 measured is 1.9  $\mu\text{m}$ . The same process could not be repeated for other samples due to technical  
276 difficulties.

277 (ii) Precipitation of Mg-rich phyllosilicates and other secondary precipitates: Both glass surfaces  
278 were covered by secondary precipitates. SEM images showed well-developed leafy precipitates on both  
279 AVM6-180 and AVM6-557 (figure 2(a) and figure 1(b)). Needle shaped precipitates were present  
280 sporadically on the altered surface (figure 2(a)). In AVM6-557, these needle-shaped phases were much  
281 more developed and formed clusters. As shown in figure 2(c) and 2(d), curiously, these clusters formed  
282 in straight lines. It seems as though these phases preferentially formed along surface defects created  
283 during sample preparation (polishing). TEM images also showed the presence of a layer of phyllosilicates  
284 on the surface of the micro-sections that measured approx. 70 nm in AVM6-180 (Figure 2(b)) and  
285 approx. 200-250 nm in AVM6-557 (figure 1 (b)). TEM-EDX analysis and EDS mapping of an altered zone  
286 also indicated that the phyllosilicates were enriched in Mg, Fe and Na in addition to Si and they were  
287 depleted in Al with respect to the pristine glass composition (supplementary data –section 3, figure S 6  
288 and S 7). Figure S4 in supplementary data shows the enrichment of Mg in the phyllosilicate layer.

289 The leafy precipitates in AVM10-180 seemed to be under-developed and visually different in  
290 comparison to AVM6. In AVM10-557, they were better developed than AVM10-180, as can be seen in  
291 figure 2(f) in comparison to 2(e). This can also be affirmed by the SEM & TEM images provided in the  
292 supplementary data-section 2, figure S 3. The quantity of the needle shaped crystalline phases also seem  
293 lower than that on the AVM6 samples and the AVM10-557 samples seem to contain more of them than

294 AVM10-180 samples (supplementary data- figure S 2). The TEM images show a phyllosilicate layer of  
295 approx. 300 nm thickness for AVM10-180 and approximately 70 nm thick phyllosilicate layer for AVM10-  
296 557 (figures 2(e) and 2(f)). It is to be noted here that it is not the overall layer thickness, but just the  
297 thickness of the phyllosilicate section.

298 (iii) The third similarity between AVM6 and AVM10 samples is the presence of a dense  
299 homogeneous gel layer beneath the phyllosilicate layer but above the porous irregularly altered zones.  
300 This gel layer is approximately 50 nm thick in AVM6-180 (figure 2(b)) and 70 nm thick in AVM6-557  
301 (figure 1(b)). It is approx. 30 nm thick in AVM10-180 and AVM10-557 (figures 2(e) and 2(f) respectively).  
302 This layer is enriched in Mg, Si and Ca, and sometimes slightly depleted in Al (supplementary data-  
303 figures S 5, S 6, S 7 and S 9).

304 To summarize, under the tested conditions, AVM6 and AVM10 glasses alter similarly, which is  
305 not the case for aqueous alteration of these glasses at the same temperature. The altered surface is  
306 composed of a phyllosilicate layer at the top (few tens to a few hundreds of nm thick) that is composed  
307 of Si, Al, Mg, Fe, Ca and Na. Underneath the phyllosilicates, TEM images have revealed a uniform gel  
308 layer of a few tens of nm thickness that seems enriched in Mg and Si and depleted in Al, with respect to  
309 the pristine glass. Porous irregularly altered zones are present in a heterogeneous/discontinuous manner  
310 beneath the gel layer.

311

### 312 ***Identification of secondary precipitates***

313 The compositions of the phyllosilicates were analyzed using STEM-EDX. It is to be noted that the  
314 Na concentration was not constant throughout the analysis. The Na atoms migrated under the beam  
315 towards the resin. It was verified that the concentration of other major elements were not affected due  
316 to long exposure to electron beam. The stoichiometry of elements (excluding Na) in the phyllosilicate  
317 layer, calculated from the STEM-EDX analysis, for the four samples described in section 3.1.1 are  
318 provided in table 2 (the estimated uncertainty is around 12% relative error). It can be noted that the  
319 composition of phyllosilicates is variable during the alteration of different glasses. No correlation could  
320 be identified with pristine glass compositions (Si/Al ratio for example) as was previously suggested [65].  
321 The phyllosilicates formed on AVM6-180 and AVM6-557 have a very similar composition. The  
322 stoichiometric ratio of Si/Mg suggests that the composition of the phyllosilicates formed on AVM6 glass  
323 is similar to that of a di-octahedral smectite such as montmorillonite- $((\text{Na,Ca})_{0.33}(\text{Al,Fe,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot$

324 nH<sub>2</sub>O), with slight variations in the composition based on the different transition metal substitutes  
 325 available. The quantity of Al and other elements capable of occupying octahedral sites in the smectite  
 326 (Mg, Fe) is not sufficient to envisage a tri-octahedral smectite.

327 The XRD patterns of the AVM6 samples showed an intense peak corresponding to (001)  
 328 reflection at 15 Å (supplementary data figure S 10), which can be associated with montmorillonites [66].  
 329 Other peaks, if present, were not clearly distinguishable from the background noise. Apart from the  
 330 composition given by EDX analyses, the other method to distinguish di-octahedral smectites from tri-  
 331 octahedral smectites is the appearance of the (060) reflection between 1.49 and 1.51 Å [67, 68]. It is  
 332 difficult to distinguish the peaks around 1.51Å in the XRD patterns from the background noise. The  
 333 physical magnitude represented by the (001) and (060) lines have different orientations. Therefore, it is  
 334 possible that the intensity of one of the two peaks increases preferentially than the other. Nevertheless,  
 335 these results confirm the formation of a di-octahedral smectite (montmorillonite) on the glass surface  
 336 during vapor phase hydration in this study.

337 The composition of the phyllosilicates formed on AVM10-180 and AVM10-557 seem to differ, notably in  
 338 Mg and O content. AVM10-180 sample has higher Mg and O contents. It is reasonable to suggest that  
 339 the excess Mg and O in the AVM10-180 sample may be due to the presence of brucite (Mg(OH)<sub>2</sub>), which  
 340 is a well-known precursor of Mg-rich smectites [69-71]. No peaks were distinguishable in the XRD  
 341 pattern, although the TEM images (figure 2(f) and supplementary data-figure S 3) clearly show the  
 342 presence of a sheet-type mineral. The stoichiometric ratios suggest the possibility of either a di-  
 343 octahedral smectite or a tri-octahedral smectite, depending on the incorporation of Al in tetrahedral  
 344 sites or octahedral sites, respectively.

345 At this stage the exact composition of the smectite formed on AVM10 samples in this study cannot be  
 346 affirmed with the available information. However, a possible smectite composition is proposed based on  
 347 the EDX analyses of AVM10-557 (table 2) and the generic formula for tri-octahedral smectites proposed  
 348 by Joly et al. [72]. This generic formula shown in equation 3.1.1.1 was earlier used by Arena et al. for  
 349 identification of a phyllosilicate formed on nuclear waste glass simulant ISG in the presence of Fe and Mg  
 350 (aqueous alteration, SA/V 20000 m<sup>-1</sup>, 50°C, 511 days) [49]. "X" in equation 3.1.1.1 corresponds to cations  
 351 other than Al that may occupy octahedral sites, such as Mg or Fe. The proposed composition is  
 352  $[(\text{Si}_{3.85}\text{Al}_{0.15})((\text{Mg}, \text{Fe})_{2.13}\text{Al}_{0.87})\text{O}_{10}(\text{OH})_2]^{0.72+}[\text{Na}_{0.1}\text{Ca}_{0.1}]^{0.3+}$ .

353  $[\text{Si}_{(4-a)}\text{Al}_a](\text{X}_{(3-b)}\text{Al}_b)\text{O}_{10}(\text{OH})_2]^{(a+b)-}[\text{X}_c\text{Na}_d\text{Ca}_e]^{(2c+d+2e)+}$  (Equation 3.1.1.1)

### 354 **3.1.2 AVMV4 and QMg**

355 The Si/Al ratio of the glass QMg is the same as the glass AVMV4. The SEM images of both the Mg-  
356 containing glasses showed some similarities (i) The altered surface showed the presence of thread-like  
357 carpet of precipitates along with  $\mu\text{m}$  sized cluster of fibrous precipitates in the SEM images of samples  
358 altered for 180 days (AVMV4-180 and QMg-180) (figure 3(c) and 3(a) respectively). The altered surface of  
359 the samples altered for 557 days (AVMV4-557 and QMg-557) showed the presence of holes of 400-500  
360 nm in diameter and a gnawed appearance, with pit size of a few hundred nm, respectively (figure 3(d)  
361 and 3(b) respectively) (ii) The altered layers of all four samples were not visible in SEM, indicating that  
362 their thickness must be less than 100 nm. Irregularly altered zones were also not observed in the SEM  
363 images.

364 TEM images of cross-section of AVMV4-557 show the presence of a gel layer of approximately 80 nm  
365 thickness (figure 3(e) & (f) and Supplementary data, figure S11). Above this apparently homogeneous gel  
366 layer, a mixture of amorphous and crystalline phases is distributed across the 5  $\mu\text{m}$  cross-section in  
367 varying thicknesses (200 nm to 20 nm). STEM image of QMg-180 showed an altered layer next to the  
368 pristine glass that appears homogeneous and is between 40-60 nm in thickness (figure 4(a)). On the  
369 surface of the altered layer, a layer of fibrous precipitates of 30-40 nm in thickness is present. The  
370 electron diffraction patterns obtained from TEM imaging did not show any fringes in the zone of  
371 precipitates, indicating that the precipitates are probably amorphous. The STEM-EDX analysis indicated  
372 that the amorphous precipitates and the gel layer in the surface are enriched in Mg and Na and depleted  
373 in Al, with respect to pristine glass (supplementary data-figure S 12).

### 374 **3.1.3 Q**

375 SEM images of Q altered for 180 days and 557 days (Q-180 & Q-557) do not show any recognizable  
376 secondary precipitates. TEM image of a micro-section of Q-180 shows the presence of a seemingly  
377 homogeneous altered layer of approx. 40 nm thickness (figure 4(b)). The pores that are visible on the  
378 altered layer-pristine glass interface were formed / enlarged during exposure of the sample to the  
379 electron beam.

### 380 **3.1.4 QCa**

381 SEM images of QCa altered for 180 days (QCa-180) show a few unidentified scattered precipitates on  
382 the surface. TEM image of QCa-180 shows the presence of an apparently homogeneous altered layer of  
383 approximately 80 nm (figure 5(a)). The difference in density between the pristine glass and gel layer  
384 seems to be higher than other glasses observed.

385 Figure 5(b) shows the SEM image of QCa altered for 557 days (QCa-557). The sample surface contained  
386 significantly more surface precipitates than QCa-180. There seems to be two types of secondary phases;  
387 clusters of pointed needle-like secondary phases and cuboid precipitates. Figure 5(c) shows the SEM  
388 image of sample cross-section. An altered layer of approx. 110-150 nm thickness is distinguishable due to  
389 the contrast difference between the layer and the pristine glass. Calcite was identified by XRD patterns  
390 on QCa-180 and QCa-557.

### 391 **3.2 Behavior of elements in the altered layers (ToF-SIMS profiles)**

392 Among all the characterization techniques presented in this study, ToF-SIMS and FTIR analyze the largest  
393 surface area of the sample in a uniform manner for all six samples. Therefore, it is considered to be the  
394 most suitable method for inter-comparison and the most representative in terms of element behavior in  
395 the altered layer and the average depth of altered zone. Table 3 summarizes and compares the  
396 thicknesses of the altered layers measured using ToF-SIMS and TEM images. The uncertainties of the  
397 given values could not be calculated. The percent error associated with ToF-SIMS measures is generally  
398 considered to be less than 3% [73]. Other factors contributing to the uncertainty are surface irregularity  
399 due to precipitates, constant speed of abrasion used for the entire zone of analysis and  
400 irregular/discontinuous altered zones. However, based on the coherence between the results of ToF-  
401 SIMS and other characterization techniques, it can be presumed that the uncertainty associated with the  
402 altered layer thicknesses can be overlooked.

403 Figure 6 presents the normalized ToF-SIMS profiles of the major elements present in the six glasses  
404 altered for 180 days. The normalized ToF-SIMS profiles of all the elements present in all six samples  
405 altered for 180 days and 557 days are presented in supplementary data (figures S 13 to S 19).

406 As observed in section 3.1, a similarity in the behavior of elements of the glasses AVM6 / AVM10 and  
407 AVMV4 / QMg is noticeable. The striking similarity in the behavior of H, B, Al, Na and Mg in the glasses  
408 AVMV4 and QMg are presented in supplementary data (figure S 20). Globally, for each glass, the  
409 behavior of elements in the altered layer is remarkably similar among the two different samples altered  
410 for two different durations. The four Mg-containing glasses show the presence of a layer of precipitates  
411 towards the surface of the altered layer. As in SEM images, the thickness of this precipitate layer is much  
412 higher in AVM6 (250-300 nm) and AVM10 (150-250 nm) than the AVMV4 and QMg glasses (<10 nm).  
413 This precipitate layer mainly contains Mg, Na, Li, Cs and Fe (in addition to Si).



414 The altered layer-pristine glass interface is rather sharp for the samples AVMV4, Q, QCa and QMg, unlike  
415 for the AVM6 and AVM10 samples. This apparently broad interface is due to the irregular and  
416 discontinuous altered zones observed in SEM images. Therefore the thickness estimated for these two  
417 glasses is considered as an average thickness of the analyzed zone. Based on the ToF-SIMS thickness  
418 (boron) from table 3, the glasses AVM6 and AVM10 alter 10-30 times faster than the other four glasses.  
419 Among the samples altered for 180 days, AVMV4, QCa and QMg alter 1.7 times faster than the glass Q.  
420 Among the samples altered for 557 days, QCa alters almost twice that of AVMV4, QMg and Q. In testing  
421 two samples of each glass for durations of 180 and 557 days, we considered that the rate of alteration  
422 would be similar. However, the increase in the thickness of altered layer from 180 days to 557 days  
423 suggests that the vapor hydration rate has decreased by a factor of 9.1 for AVMV4, 8.5 for QMg, 1.9 for  
424 Q and 1.6 for QCa after 180 days of alteration (considering that the vapor hydration rate is constant  
425 between 0-180 days and between 180-557 days).

426 In coherence with the STEM-EDX results, Al is depleted in the zone of surface precipitates of the Mg-  
427 containing glasses, indicating that the Si/Al ratio is higher in the phyllosilicate layer than the glass.

428 The ToF-SIMS profiles, which have been normalized to Si and to PG, might give an impression  
429 that many elements are depleted from the gel layer, even though not as extensively as boron. It seems  
430 likely that this depletion is due to a migration of the element towards the surface to form precipitates. In  
431 the zone of precipitates, the normalization with respect to Si creates an artificial depletion of elements  
432 such as Zr, rare-earths and Al, because they are almost absent in the precipitate layer, towards the  
433 surface. The elements which are really depleted (absent in gel layer and precipitate layer) are boron, Ca  
434 in QCa and Na from the surface of Q. The retention of Ca is < 3% in the gel layer of QCa (in both QCa-180  
435 and QCa-557).

### 436 **3.3 Porosity of the altered layer (SAXS)**

437 The porosity, pore-size and specific surface area values reported in this paper were calculated by  
438 considering that the pores of the gel layer are filled with water. This assumption will be discussed later in  
439 section 4. The data treatment was based on previous works [62-64] and is explained in detail in the  
440 supplementary data (section1).  $q$  is the scattering vector in  $\text{nm}^{-1}$  and  $I_{corr}$  ( $\text{cm}^{-1}$ ), calculated from  
441 equation S9 in supplementary data, separates the scattering intensity in the high  $q$  domain by the pores  
442 in the gel layer from the scattering in the low  $q$  domain by the grain envelopes.

443 AVM6 and AVM10: The plots of  $I_{corr}$  vs.  $q$  of these two glasses show a porod regime  
444 ( $I_{corr} \propto q^{-4}$ ). The SAXS spectra of these glasses are provided in figure S 21 (supplementary data). In both  
445 glasses, the high  $q$  porod regime shifts to higher  $q$  values with time. However, porod's law cannot be  
446 used to calculate the porosity and specific surface area of pores for these two glasses, since the SEM  
447 images of the monolith samples indicate that these glass surfaces are covered with phyllosilicates.  
448 Therefore, the SAXS diagram contains information regarding both the porosity of the gel layer and the  
449 inter-layer spacing of the phyllosilicates and they cannot be deconvoluted.

450 AVM6 glass powders of particle size 2-5  $\mu\text{m}$  that were prepared as described in section 2.1 were altered  
451 at 50°C and 95% RH for 11 days, 31 days and 90 days, for the purpose of characterization by SAXS and  
452 identification of possible trends in the evolution of the gel layer. These samples are referred to as AVM6-  
453 11, AVM6-31 and AVM6-90. The  $I_{corr}$  vs.  $q$  plots of these glasses are shown in figure S 22  
454 (supplementary data). Porod's law is respected at higher  $q$  values for all three samples including the  
455 sample altered for only 11 days. The quantity of secondary phases on these samples altered for a short  
456 duration is negligible (TEM images (not shown here) of AVM6 samples altered for 90 days at 50°C and  
457 95% RH show that the surface precipitates are visually much less denser than the AVM6-180 samples).  
458 Therefore, the porosity, pore-size and specific surface area of the gel layer can be calculated. The  
459 porosity, pore diameter and specific surface area of AVM6-11 are 66%, 4.4 nm and 328  $\text{m}^2/\text{g}$   
460 respectively; that of AVM6-31 are 47%, 4.5 nm and 235  $\text{m}^2/\text{g}$  respectively; and that of AVM6-90 are 11%,  
461 4.8 nm and 58.2  $\text{m}^2/\text{g}$ . These values are recapitulated in table 4. It can be noticed that porosity decreases  
462 with time, while pore size increases. The  $I_{corr}$  vs.  $q$  plot of AVM6-11 is distinctly different than that of  
463 the other AVM6 samples. The shoulder corresponding to the highest intensity is at a higher  $q$  for the  
464 AVM6-11 sample. This translates to a smaller average pore size than the other glasses [74]. However, the  
465 porod regimes of the AVM6 samples altered for larger duration is shifted towards much higher  $q$ . This  
466 suggests the presence of smaller pores in the samples that were altered for a duration longer than 11  
467 days, even though the average pore-size increases with increase in duration of alteration.

468 AVMV4 and QMg:  $I_{corr}$  vs.  $q$  plot of these two glasses are similar in the sense that, neither of them  
469 displays a porod's regime. The plots are shown in figure S 22 (supplementary data). The exponent  $D$   
470 ( $I(Corr) \propto q^{-D}$ ) decreases with increase in duration of alteration, suggesting an increase in the  
471 roughness of the pore-interface. It can be considered that the reason for the absence of a porod's  
472 regime in the SAXS diagram is the interference of poorly crystallized precipitates. This means that the  $D$   
473 value, which varies between 3.4 to 2.6, is not representative of a rough pore-interface in the gel layer,

474 but rather a distortion of signal due to the presence of almost equal proportions of gel layer and poorly  
475 crystalline precipitates.

476 Q and QCa: The  $I_{corr}$  vs.  $q$  plot of these two glasses exhibit a porod's regime (figure 7). The absence of a  
477 substantial amount of secondary precipitates on the SEM and TEM images of the monolith samples  
478 validate the use of these measurements to calculate the porosity, pore size and specific surface area of  
479 pores. The porosity of Q-180 is 65% and decreases to 44% in the Q-557 sample. The pore diameter  
480 increases from 4.3 nm in the Q-180 sample to 5 nm in the Q-557 nm. The surface area of pores also  
481 decrease from 451 m<sup>2</sup>/g in the Q-180 sample to 264 m<sup>2</sup>/g in the Q-557 sample. The porosity of QCa-180  
482 is 27%, which decreases to 9% in the QCa-557 sample. The pore diameter increases from 5.1 nm in QCa-  
483 180 to 7.5 nm in QCa-557. The surface area of pores decrease from 158 m<sup>2</sup>/g in QCa-180 to 37.6 m<sup>2</sup>/g in  
484 QCa-557. These calculated values are presented in table 4. Contrary to AVM6 and AVM10 samples  
485 altered for 180 days and 557 days each, the high  $q$  porod's regime shift towards lower  $q$  at longer  
486 duration of alteration. This indicates an increase in the average pore size with time. The higher pore sizes  
487 of the QCa sample than the Q sample and the factor of increase in pore-size with time correspond well  
488 with the magnitude of the shift in high- $q$  porod's regime to lower  $q$  values for these samples as shown in  
489 figure 7.

### 490 3.4 Hydration kinetics

#### 491 3.4.1 FTIR spectroscopy

492 The hydration kinetics is followed by studying the evolution of the increase in the absorbance of the  
493 band attributed to the OH stretching mode in SiOH molecules. For this, the absorbance around 3600 cm<sup>-1</sup>  
494 (OH stretching) measured at a given time of alteration (A) is reduced by the absorbance for the pristine  
495 glass (A<sub>0</sub>). Figure 8 shows the increase of (A-A<sub>0</sub>) over time for all the six glasses until 557 days of  
496 alteration. Figure 8(a) shows the difference in the increase of (A-A<sub>0</sub>) versus time according to the glass  
497 stoichiometry. The increase in absorbance of AVM6 glass is approximately twice that of AVM10, 10 times  
498 that of QCa and 15 times that of AVMV4, Q and QMg. By correlating the increase in the absorbance of  
499 the SiOH band to the thickness of altered layer formed and the vapor hydration rate, it seems that there  
500 is an inflexion in the vapor hydration rate of all six glasses around approximately 6 months in the given  
501 conditions. For the AVM10 glass, it seems that this inflexion occurs at 4 months. In figure 8(d), it seems  
502 that there is acceleration in the vapor hydration rate between 60 and 120 days of alteration, followed by  
503 a strong slowdown of the vapor hydration rate. Figures 8(c) shows the strikingly similar behavior of the  
504 AVMV4 and QMg glasses. The inflexion seems to occur around 120 days of alteration. There also seems

505 to be a decrease in the absorbance after approximately 380 days of alteration. Figure 8(b) shows the  
506 evolution of  $(A-A_0)$  vs. time of the glasses Q and QCa. The inflexion seems to occur approximately around  
507 180 days for the samples Q, QCa and AVM6. The factor by which the rate of increase of  $(A-A_0)$  drops after  
508 six months vary from 7.5 (AVM6) to 15 (AVM10).

### 509 **3.4.2 Alteration kinetics based on the different measurements of thickness**

510 The measurements of the thickness of the altered layers formed by ToF-SIMS and SEM/TEM images after  
511 180 days and 557 days of vapor hydration of the six glasses are presented in table 3. It can be noticed  
512 that the thickness measured by ToF-SIMS is lower than the thickness measured by SEM/TEM images for  
513 four of the six glasses (AVMV4, Q, QCa and QMg). This is likely due to the fact that in ToF-SIMS, the layer  
514 of precipitates and the gel layer might get abraded faster than the pristine sample due to the difference  
515 in composition and their lower density. But the same speed of abrasion was used whatever the layer  
516 considered. As a result, the thicknesses of the altered layers, which are a combination of the gel layers  
517 and precipitate layers, are underestimated. Nevertheless, the thicknesses measured by ToF-SIMS and  
518 TEM images are in the same order of magnitude. A second similarity between the thicknesses measured  
519 by both techniques is that the sample Q has the smallest thickness among the four samples altered for  
520 180 days and the thickness of the samples Q, QMg and AVMV4 are similar among the samples altered for  
521 557 days. Therefore, it can be stated that the two techniques corroborate each other. In the case of the  
522 glasses AVM6 and AVM10, which have an irregular alteration, ToF-SIMS provides an average altered  
523 layer thickness in a relatively larger zone ( $50 \times 50 \mu\text{m}^2$ ) and the SEM/TEM images have shown that the  
524 thickness could vary from a few tens of nm to a few  $\mu\text{m}$ . The average thickness provided by ToF-SIMS is  
525 useful to identify the relative durability of glasses. In addition, according to the FTIR results, the glasses  
526 AVM6 and AVM10 alter 10-20 times faster than the other four glasses. This result is very well  
527 corroborated by the ToF-SIMS results. While studying the alteration kinetics based on ToF-SIMS and  
528 SEM/TEM images, the rate of formation of altered layer (in nm/day) after 180 days and 557 days  
529 calculated by assuming linear alteration kinetics shows that the rate has decreased between 180 days  
530 and 557 days of vapor hydration. This result is also explained very well by the FTIR spectroscopy, which  
531 shows an inflexion in the rate of increase in  $(A-A_0)$  with time after about 120-200 days of alteration. Thus  
532 the alteration kinetics measured by three different techniques are coherent.

## 533 4. Discussion

534 **4.1 Morphology of the altered layer**

535 Figure 9 shows a schematic description of the different morphologies of the altered layer for all  
536 six glasses altered under the same conditions. All six glasses present a homogeneous gel layer of tens of  
537 nm thickness adjacent to the pristine glass. AVM6 and AVM10 present irregularly shaped, discontinuous  
538 and more porous altered zones beneath the continuous gel layer. These two glasses contain significant  
539 amount of well-developed Mg-rich smectites and needle-shaped precipitates (AVM6 has more of it than  
540 AVM10). AVMV4 and QMg also present a layer of poorly-crystalline Mg-rich layer of precipitates on the  
541 surface above the gel layer. However, the SEM images have shown that they are present in a much lesser  
542 quantity than in AVM6 and AVM10. SEM images have not revealed any irregularly altered zones in these  
543 glasses. Q and QCa glasses also contain precipitates on the surface of the gel layer, but unlike in the Mg-  
544 containing glasses, they do not cover the glass surface. They are rather present in the form of crystals,  
545 which are either isolated or in clusters.

546 The morphology of AVM6 and AVM10 altered samples is rather surprising, particularly because  
547 of the presence of porous irregular altered zones beneath the homogeneous gel layer. Irregular  
548 alteration has been noticed in literature [75-78], especially in atmospheric alteration studies. The  
549 formation of a heterogeneous altered layer and craters are often attributed to a localized chemical  
550 attack due to surface defaults such as cracks/scratches/fissures or deposit of dust particles/matter from  
551 exposure to atmosphere or formation of hygroscopic salts locally on the surface or preferential/irregular  
552 water condensation [22, 79, 80]. The unexpected part was the presence of the uniform and continuous  
553 gel layer in-between phyllosilicates and irregular more porous discontinuous altered zones. A similar  
554 dense gel layer formed in-between phyllosilicates and irregular porous zones could not be found in  
555 literature. The closest analogy found was the gel layer formed during the aqueous alteration of a Si-B-Na-  
556 Ca-Zr glass. In the cited studies, a dense gel layer was present on the altered surface and above a porous  
557 gel layer. This denser gel layer was associated with pore-closure with time and passivating effect of the  
558 gel layer [81-83]. However, in literature, a denser gel layer close to the unaltered glass and a porous gel  
559 layer towards the glass surface and beneath secondary phases have been noticed [84]. Two possibilities  
560 can be imagined in our study: (i) The hydration front is irregular; the pore closure due to reorganization  
561 of the gel occurs at the surface in the region of the "oldest" gel, as suggested in the above mentioned  
562 example [83]. (ii) The denser gel layer and the irregular, more porous, discontinuous altered zones were

563 formed or driven by two different mechanisms. The second assumption seems more likely and is  
564 discussed further in section 4.5.

#### 565 **4.2 Behaviour of elements (alkalis, Ca and B) in the altered zone**

566  
567 Boron is depleted in the gel layer of all six glasses (less than 20% retention). Although it is useful  
568 to estimate the altered layer thicknesses from ToF-SIMS profiles, its depletion is puzzling. It would be  
569 logical to expect that elements are not lost from the altered layer during vapor phase hydration. The  
570 depletion could mean that there is water condensation on glass surface followed by run-off. If this is the  
571 case, the loss of other soluble elements such as Na and Li can be expected as well. However, Na is  
572 retained to a higher extent than boron as can be seen in figure 6. The profiles of B, Na and Li do not  
573 resemble each other. Therefore, the possibility of evaporation of boric acid species at 50°C and 95% RH  
574 should also be investigated [85, 86].

575 Hence, a vapor hydration experiment was conducted with 0.6 g of borosilicate glass (QMg)  
576 powder of particle size 20-40  $\mu\text{m}$  (90°C, 98% RH, 153 days) using the protocol previously used on glass  
577 monoliths by Neeway et al. [28]. The glass powder was placed in a cup inside the reactor above NaCl  
578 solution that was used to impose relative humidity. The set-up was arranged in such a way that the  
579 water that condenses on glass powders in the cup cannot run-off. Despite the set-up,  $0.7\pm 0.1$  mg of  
580 boron was present in the NaCl solution at the end of the experiment. The vapor hydration rate of QMg at  
581 90°C was estimated based on unpublished results and using this value, it was estimated that  $27\pm 6\%$  of  
582 boron from the altered layer was lost by evaporation. This experiment shows the possibility of  
583 evaporation of boron/boric acid species and indicates that at 50°C, probably only a small fraction of  
584 boron escapes due to volatility and a large fraction must be lost due to condensation and run-off.

585 Ca is depleted to a higher extent than boron in the QCa glass (<2% retention). It can be justified  
586 by the formation of calcite crystals on the surface of the glass, which may adhere poorly. For a glass that  
587 has only 52 nm thick altered layer, sufficient quantity of calcite had precipitated to be identified in XRD  
588 pattern. The depletion of Na towards the surface of the Q glass could probably be due to formation of  
589 carbonates (although undetected). In the other glasses, Na is well retained in the gel layer. In figure 6, a  
590 certain similarity can be observed in the profile of Na and H for all glasses. This suggests that Na is  
591 reactive and might be linked to inter-diffusion reaction. Despite being probably released from the glass  
592 network, Na is still well retained in the gel layer (except in Q). It may be present in porewater, form

593 precipitates or may participate in the hydrolysis of  $\equiv\text{Si-O-Si}\equiv$  bonds to form  $\equiv\text{Si-O}^-\dots\text{Na}^+$  bonds, as  
594 suggested in literature [39].

### 595 4.3 Porosity of the altered layer

596  
597 During the SAXS data treatment, it was assumed that the pores in the gel layer are filled with water. This  
598 assumption is supported by the calculation of the threshold pore-size by Kelvin's equation (equation  
599 4.3.1) [87], below which, water is expected to condense in pores due to capillary effect. This threshold  
600 pore-radius was calculated to be 9.2 nm at 50°C and 95% RH from equation 4.3.1. The maximum value of  
601 the pore-radius measured through SAXS is <4 nm. Therefore, it seems highly probable that the pores are  
602 filled with water. The porosity of the gels was also calculated by considering that the pores are filled with  
603 air, but in this case, the calculated porosity values were unrealistic. This further reinforces our  
604 assumption that the pores are filled with water. However, a certain uncertainty is associated with this  
605 assumption. Even if it is considered that the pores are indeed filled with water during the experiment, it  
606 is unclear if the water stays in the pores during characterization or it evaporates/escapes into the  
607 atmosphere once the sample is removed from the humid and hot atmosphere (95% RH & 50°C). Data  
608 analysis has been carried out despite this uncertainty by considering that water remains inside the pores,  
609 since the samples were not exposed to high temperatures or desiccators during storage until  
610 characterization. Specific studies to carefully assess the impact of this uncertainty on data treatment are  
611 a necessary perspective.

$$612 \ln \frac{P}{P_0} = -\frac{2HyV_l}{RT} \quad (\text{Equation 4.3.1})$$

613 The values of the porosity, specific surface area of the pores and the pore-radiuses are in the same order  
614 of magnitude as those observed in published aqueous alteration experiments of borosilicate glasses [63,  
615 88, 89]. 66% porosity of the gel layer of Q-180 and AVM6-11 (table 4) seem relatively high, especially  
616 while comparing with TEM images of Q-180, which do not show a very porous altered layer. This means  
617 that either the porosity measured by SAXS is overestimated or there is some other unknown mechanism  
618 that could explain such high porosity values, which needs further investigation of the gel layer formed on  
619 these glasses. This porosity value may be overestimated due to the volume fraction of gel used in data  
620 treatment, which is reasonably assumed based on altered layer thicknesses of the gel layer formed on  
621 monoliths. This being said, such high porosity values have also been reported during aqueous alteration  
622 of glasses [63, 89].

623 From table 4, all three glasses show a decrease in porosity and surface area of pores with time and an  
624 increase in the average pore size with time. This evolution in our vapor hydration study is similar to the  
625 results of an aqueous alteration study conducted by Girard et al., who altered glasses containing Si, B,  
626 Na, Ca and Zr in aqueous medium at an SA/V (surface area of glass/solution volume) ratio of  $3000 \text{ m}^{-1}$  at  
627  $90^\circ\text{C}$  for time periods up to 96 h [89]. According to their results, the porosity, depending on composition,  
628 increased rapidly to a maximum value within a few hours of glass alteration. After reaching maxima, the  
629 porosity and specific surface area of pores decreased with increasing time of alteration, probably due to  
630 a shrinking gel and the pore-size increased due to either coalescence of pores or further dissolution at  
631 the pore walls. The initially high porosity after a few hours of glass leaching was attributed to leaching of  
632 Si from the solution without re-condensation until the solution becomes saturated with respect to Si.  
633 This theory was based on the calculation of an estimated porosity from leachate composition. In this  
634 study, the leachate cannot be sampled since it is a vapor phase alteration. Therefore, an acceptable  
635 estimated porosity cannot be calculated using the leached fraction of soluble elements such as B and Na,  
636 as was done in literature [89]. However, an estimated porosity was calculated based on the retention  
637 factor R of elements in the gel layer calculated from ToF-SIMS profiles of monoliths and the volume  
638 fraction occupied by oxides  $\phi_i$  as shown in section 8 of the supplementary data.

639 The estimated porosity values thus calculated vary between 14% and 25% (table S 1-supplementary  
640 data). For all six glasses, the estimated porosity value at 557 days is less than the estimated porosity  
641 value at 180 days. This decrease in this estimated porosity is coherent with the SAXS results.  
642 Nevertheless, the values of porosity calculated by SAXS for the glass Q is 3.2 to 3.9 times higher than the  
643 hypothetical values estimated by depleted elements (based on ToF-SIMS results). It can be supposed  
644 that the porosity estimated by retention of elements in the gel layer calculated based on ToF-SIMS  
645 analysis is probably underestimated, because it considers that the elements present in the porewater of  
646 the gel layer are a part of the gel layer network. There is the possibility of overestimation of porosity  
647 values by SAXS as well. In the cases in which the SAXS porosity is lower than the porosity estimated from  
648 SIMS data, different hypotheses such as a shrinking gel or precipitation of colloids or secondary phases  
649 (calcite) in the pores could be proposed based on literature [89, 90].

#### 650 **4.4 Hydration Kinetics**

651 Overall, the relative durability of the glasses identified by the increase in absorbance of the SiOH  
652 molecules in FTIR spectra are coherent with that measured by other characterization techniques. These  
653 results reinforce the argument that FTIR spectroscopy is a good method to follow vapor hydration



654 kinetics, in the absence of sampling techniques to determine soluble element concentrations in the  
655 leachate. All glasses showed an inflexion in the vapor hydration kinetics after 120 or 180 days of  
656 alteration. The cause for this inflexion has not yet been investigated. But such inflexion has been  
657 observed earlier in literature, notably in the experiments conducted on CSD-B (inactive simulant of  
658 intermediate-level long lived waste glass) and SON68 glasses after about 100-200 days of alteration (at  
659 35-90°C) [29, 58].

#### 660 **4.5 Influence of glass composition and insights into vapor hydration mechanisms**

661  
662 The difference in the vapor hydration kinetics of AVM6, AVM10 and AVMV4 is an indication of the  
663 significant effect of glass composition on glass hydration. The effect of stoichiometry on the relative  
664 durability of AVM glasses in aqueous medium was already investigated [46, 47]. According to these  
665 studies, the three major parameters affecting glass durability in water under a given condition were pH,  
666 Mg and Al concentration. When  $\text{pH}_{50^\circ\text{C}} > 9$ , alteration rates increase due to precipitation of Mg-  
667 aluminosilicates. Moreover, AVM glasses contain very little Ca. Therefore, it is considered that the role of  
668 charge compensating atoms of  $[\text{AlO}_4]^-$  units is preferentially occupied by Mg (the preference in gels  
669 decreases in the order  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$ ). Thus, a higher quantity of Al in the gel layer probably retains  
670 higher quantity of Mg in the gel, thereby, increasing the passivation properties of the gel layer [46, 47].  
671 This interpretation was used to explain the highest relative durability of AVM10 glass in aqueous  
672 medium, since it contains the highest Al concentration among the three glasses.

673 In our vapor hydration study, AVM10 glass is one of the two least durable glasses. Therefore, the glass  
674 durability is not simply linearly dependent on Al concentration. The reason for this could be that the  
675 AVM10 glass contains higher MgO molar concentration than  $\text{Al}_2\text{O}_3$  (i.e. molar ratio of  $\text{Al}_2\text{O}_3/\text{MgO} < 1$ ).  
676 Therefore, as an extreme case, if it is considered that all the  $[\text{AlO}_4]^-$  units in the gel layer are charge  
677 compensated by  $\text{Mg}^{2+}$  ions, there is still an excess of Mg that can saturate the molecular water  
678 layers/porewater to form Mg-silicates, thus driving the glass alteration. The difference in the relative  
679 durability of AVM10 between aqueous medium and vapor phase could be due to the possibly higher pH  
680 of the very small volume of water in vapor phase, thereby promoting the precipitation of Mg-silicates  
681 during vapor hydration and not as much during aqueous alteration.

682 The lower durability of AVM6 glass in this vapor hydration study can also be explained using the same  
683 interpretation (i.e. molar ratio of  $\text{Al}_2\text{O}_3/\text{MgO} < 1$ ). The extensive alteration of AVM6 and AVM10, which is  
684 manifested as irregularly altered zones, could be driven by the precipitation of a significant amount of  
685 Mg-silicates. On the other hand, this ratio is equal to 1 for AVMV4 and is greater than 1 for QMg,

686 suggesting that, Mg could be principally occupying the role of charge compensating atom and therefore  
687 be less available for participation in the formation of secondary phases. As a result, the vapor hydration  
688 of these two glasses may not be accelerated due to the precipitation of Mg-silicates.

689

690 The lack of structural study to support this assumption definitely needs to be acknowledged. The  
691 distribution of coordination number of Al in the gel layer was not studied. Incidentally, recent  
692 publications have shown that due to the high cation field strength of Mg, the presence of this element in  
693 the glass network increases the fraction of <sup>(v)</sup>Al and <sup>(vi)</sup>Al and <sup>(iii)</sup>B, and thus contributes to glass  
694 depolymerisation [91, 92]. As a matter of fact, the fraction of <sup>(iv)</sup>B in the Mg containing glasses in our  
695 study were lower than that in the glasses Q and QCa (section 2.1). It is also suggested that some of the  
696 Mg could be acting as a network former [92]. Therefore, there is a need to better understand the role of  
697 Mg in the glass as well as in the gel, its impact on the gel structure and especially the competition  
698 between ions to compensate the charge of  $[AlO_4]^-$  units.

699

700 In order to understand the specific effect of Ca and Mg on vapor hydration of glasses, the results of the  
701 simplified glasses Q, QCa and QMg need to be focused upon. Table 3 shows that QCa and QMg alter 1.6  
702 to 1.7 times faster than Q, among the samples altered for 180 days. This can be construed to be a  
703 negative effect of Ca and Mg, due to the precipitation of calcite and Mg-rich precipitates. However, the  
704 NBO fraction (table 1) indicates that these two glasses have higher fraction of NBOs than the glass Q.  
705 From figure S 23 in supplementary data, it can be seen that, among the glasses altered for 180 days, the  
706 higher the NBO fraction, the higher the thickness of the altered layer formed. This relation seems to be  
707 linear for the glasses AVMV4, Q, QCa and QMg and a sharp rise is noted for the glasses AVM6 and  
708 AVM10, which have undergone extensive alteration due to secondary phases precipitation. Therefore,  
709 the slightly higher altered layer thicknesses of the glasses QCa and QMg in comparison to Q could be due  
710 to the lower resistance to network hydrolysis and not a negative effect of Ca or Mg. This suggests that  
711 network-hydrolysis could be the rate limiting mechanism of formation of the uniform gel layer.

712 Among the samples altered for 557 days, the altered layer thickness of QCa is twice that of Q and QMg.  
713 This change in the relative durability of glasses with a longer duration can be explained by considering  
714 the presence of a passivating altered layer. The SAXS results also hint at a reorganization of the  
715 homogeneous gel layer, at least in the case of Q, QCa and AVM6. The inflexion in the vapor hydration  
716 kinetics (FTIR spectroscopy) after 180 days approximately strongly suggests the presence of a passivation

717 mechanism of the gel layer in all six glasses. After six months, the altered layer of QMg (and AVMV4)  
718 could have become more passivating than that of Q and QCa. This presumption is based on ToF-SIMS  
719 profiles, which show that the retention of Ca in the gel layer is less than 1% and Na is less retained in the  
720 gel layer of Q. The gel layer of QMg (and AVMV4) retains a higher quantity of Mg. It has already been  
721 shown that the retention of Mg increases the passivation properties of the gel layer [46]. This implies  
722 that the rate-limiting vapor hydration mechanism changes, probably to diffusion of species through the  
723 gel layer, after the inflexion of vapor hydration rate due to the formation of a passivating altered layer.  
724 This is in agreement with the structure discussion above for AVMV4 and QMg.

725 In brief, the specific effect of Ca or Mg could not be seen in this vapor hydration study because the  
726 excessive concentration of Al (molar ratio of  $\text{Al}_2\text{O}_3/(\text{MgO} \text{ or } \text{CaO}) \geq 1$ ) has masked the possible negative  
727 effect that Ca or Mg could have due to secondary phase precipitation. The presence of Al in the glass  
728 increases its resistance to network hydrolysis since  $\equiv\text{Si-O-Al}\equiv$  bonds require more energy to be broken  
729 than  $\equiv\text{Si-O-B-}$  or  $\equiv\text{Si-O-Si}\equiv$  bonds [54, 93].

730 The interpretation of the results suggests that the rate-limiting mechanism of formation of the gel layer  
731 in vapor hydration is network hydrolysis in this study. This conclusion is reinforced by the fact that  
732 AVM10, which has the highest Al content in the pristine glass, has the lowest thickness of the  
733 homogeneous gel layer (15-30 nm in TEM), even if the overall alteration layers cumulate to larger  
734 thickness after secondary phases form.

735 The formation of irregularly shaped (few tens of nm to few  $\mu\text{m}$  thick), discontinuous, more porous  
736 altered zones behind the homogeneous gel layer in AVM6 and AVM10 glasses seem to be driven by  
737 precipitation of significant quantities of Mg-silicates. During vapor hydration, extensive alteration due to  
738 secondary phase precipitation is naturally local (and hence irregular). Thus, it is possible that in AVM6  
739 and AVM10, the two types of altered zones were formed by two parallel mechanisms.

740 The precipitated secondary phases found at the surface in the other four glasses (AVMV4, Q, QCa and  
741 QMg) are probably a consequence of the release of alkaline-earth elements from glass network and do  
742 not drive the formation of their homogeneous gel layer.

#### 743 4.6 Vapor hydration vs. aqueous alteration

744 Glass AVM6 was found to be the glass of lowest durability of the series in aqueous leaching and in the  
745 present vapor phase alterations. However, a reversal of glass durability in vapor phase and aqueous  
746 medium has been observed between the glasses AVM10 and AVMV4. The residual alteration rates of the  
747 three complex glasses in aqueous medium (initially pure water, 50°C,  $\text{SA}/\text{V}=5500 \text{ m}^{-1}$ , values measured  
748 between 5-10 years of alteration) are: AVM6-  $5.1 \times 10^{-4} \text{ g}/\text{m}^2/\text{day}$ ; AVM10-  $9 \times 10^{-5} \text{ g}/\text{m}^2/\text{day}$ ; [46]; AVMV4-

749  $5.6 \times 10^{-4}$  g/m<sup>2</sup>/day (personal communication-value estimated based on a statistic interpolation model).  
750 The difference may be due to changes in the solution chemistry of the very low volume of water  
751 available for glass dissolution in vapor phase. This small volume of water may get rapidly saturated with  
752 respect to secondary phases that are clearly different than those that precipitate during aqueous  
753 alteration.

754 The smectites formed during vapor hydration, as identified through STEM-EDX analyses (see sub-section  
755 of 3.1.1), seem to be different than those that form during aqueous alteration of the same glasses. A tri-  
756 octahedral smectite was identified on AVM6 altered in aqueous medium [46], while a di-octahedral  
757 smectite (type montmorillonite) was identified during this vapor hydration study of AVM6. The  
758 phyllosilicate formed in vapor phase contained 75% lower Al, 40% lower Mg and 10 times higher Fe  
759 content.

760 The phyllosilicate composition obtained on AVM10 in this study was compared with the phyllosilicate  
761 composition obtained during the aqueous alteration of AVM10 in the study conducted by Thien et al.  
762 (SA/V 5500 m<sup>-1</sup>, 50°C, 2500 days, initially pure water and 400 mg/L of MgCl<sub>2</sub>·6H<sub>2</sub>O added after 114 days)  
763 [94]. The concentration of Al in the phyllosilicate of our study was 25% lower than the Al concentration  
764 in the smectite identified by Thien et al [94]. Similarly, the concentration of Mg was 30% lower and the  
765 concentration of Fe was three times higher.

766 This shows that caution needs to be taken while extrapolating aqueous alteration results to  
767 vapor hydration by considering that vapor hydration is equivalent to aqueous alteration at a very high  
768 SA/V ratio. Certain studies conducted vapor hydration tests in extreme conditions (150-200°C, 100% RH)  
769 to predict the secondary phases that would form during long-term aqueous alteration of glasses [36].  
770 Here, it is clearly shown that the same phases do not precipitate in both media.

771 One similarity between aqueous alteration and vapor hydration studies of glasses is the texture  
772 of the gel layer. SAXS data indicated that the porosity, pore-size and specific surface area values are in  
773 the same order of magnitude and evolve similarly with time in the two glasses of different compositions  
774 and in different alteration conditions [88, 95]. This could imply a similar mechanism of formation of the  
775 gel layer.

## 776 5. Conclusion

777 In order to study the influence of glass composition on vapor hydration kinetics, three complex glasses  
778 (>20 oxides) and three simplified glasses (4 or 5 oxides) were altered in vapor phase (at 50°C and 95%

779 RH) for a period of 180 days and 557 days. Based on the analysis of the characterization results of the  
780 altered samples, it seems that network hydrolysis is the rate limiting mechanism of formation of the gel  
781 layer during vapor hydration of these glasses. Under conditions that are favorable for the precipitation of  
782 secondary phases, it seems that the vapor hydration kinetics is accelerated in a localized manner, leading  
783 to the formation of irregularly shaped, discontinuous altered zones that could be up to a few  $\mu\text{m}$  thick.  
784 The presence of alkaline-earth elements (such as Mg or Ca) seems to make the glass more reactive, since  
785 they actively participate in the formation of secondary phases. However, the negative effect of these  
786 elements is attenuated by the presence of Al, since Al increases the resistance to hydrolysis of glass  
787 network and its presence in the gel layer retains alkaline-earth elements to compensate  $[\text{AlO}_4]^-$  entities.  
788 Therefore, when the molar ratio of  $\text{Al}_2\text{O}_3/(\text{MgO or CaO}) \geq 1$ , the positive effect of Al prevails over the  
789 expected negative effect of Ca or Mg and therefore the glass is relatively more durable. When the ratio is  
790  $< 1$ , the negative effect of Ca or Mg prevails. For this reason no specific effect of Ca or Mg on vapor  
791 hydration of the three simplified glasses could be seen (molar ratio of  $\text{Al}_2\text{O}_3/(\text{MgO or CaO}) \geq 1$ ).

792 Apart from this principal result, two types of altered layer morphologies have been identified. The  
793 porous texture of the gel layer of a vapor hydrated glass has been investigated using SAXS. The measured  
794 pore-diameters vary between 4.3-7.5 nm, similar to the pore-sizes found in the gel layer formed on  
795 various similar glasses during aqueous alteration.

796 It has been shown that the vapor hydration mechanism changes with glass composition and time. The  
797 rate of vapor hydration evaluated in FTIR showed a decrease between 180 days and 300 days, which  
798 validate the formation of a passivating layer.

799 Based on this study, a few perspectives have been identified. The structural role of Mg in the glass and  
800 gel and its capability to compensate negative charge of  $[\text{AlO}_4]^-$  units needs to be investigated to  
801 understand the positive effect of Al that prevails over the negative effect of Mg on glass durability.  
802 Aqueous alteration of the same glasses at very basic pH ( $\text{pH}_{50^\circ\text{C}} > 11$ ) may provoke the precipitation of  
803 similar secondary phases in order to observe the relative durability of these glasses. This might help to  
804 affirm or refute the hypothesis of importance of molar ratio of  $\text{Al}_2\text{O}_3/\text{MgO}$  on glass durability.

805 It would also be interesting to conduct vapor hydration experiments of the same glasses at a higher  
806 temperature ( $> 90^\circ\text{C}$ ) to study if possibly favorable conditions for secondary phase precipitation drives  
807 vapor hydration or if the rate-controlling mechanism is network-hydrolysis as in low temperatures  
808 ( $50^\circ\text{C}$ ). It is also necessary to investigate if the gel layers formed during vapor hydration have any

809 protective effect against aqueous alteration, since it is expected that a vapor hydrated nuclear waste  
810 glass would eventually be altered in groundwater of the repository site.

#### 811 Acknowledgements

812 We would like to thank Laurent Duffours (PrimeVerre) for preparation of the polished glass monoliths,  
813 Géraldine Parisot (CEA) for ICP-OES analysis of glass powders, Jean-Pierre Mestre (CEA) and Marie Fenart  
814 (CEA) for the SEM images, Myriam Chartier (CEA) for XRD patterns, Laurent Dupuy and Elodie Chauvet  
815 (TESCAN Analytics) for the ToF-SIMS profiles and Jeremy Causse (ICSM) for SAXS data acquisition. This  
816 study was supported by CEA and EDF (Electricité de France). We would like to particularly thank Florent  
817 Tocino and Hélène Schneider (EDF) for their support. We also thank the two anonymous reviewers for  
818 their helpful comments and constructive feedback.

#### 819 Data Availability

820 The SEM and TEM data supporting the findings are available within the article and the supplementary  
821 information. The processed data of SAXS, ToF-SIMS, NMR spectroscopy and XRD apparatuses are also  
822 available within the article and supplementary information. The raw data of SAXS, ToF-SIMS, NMR  
823 spectroscopy and XRD apparatuses required to reproduce these findings cannot be shared at this time  
824 due to technical and time limitations. However, they can be shared by the corresponding author upon  
825 reasonable request.

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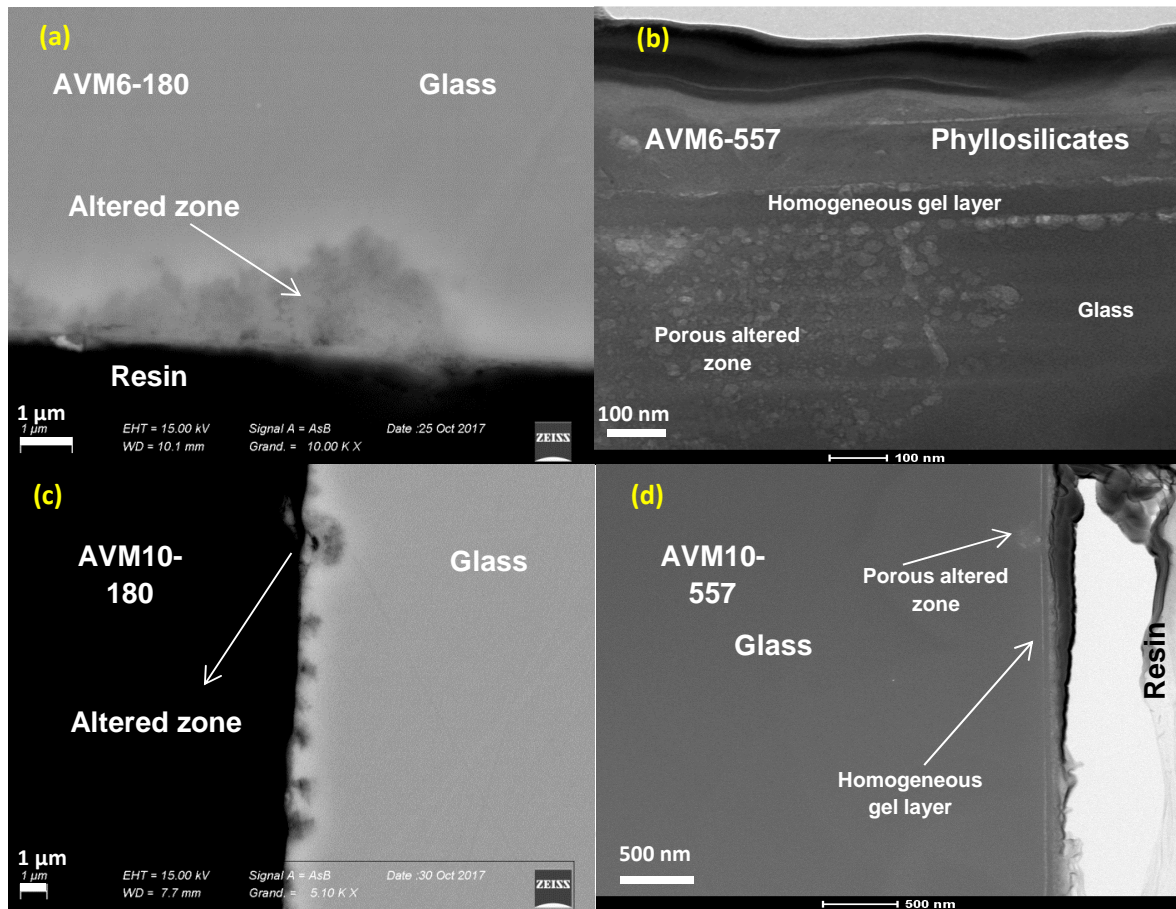
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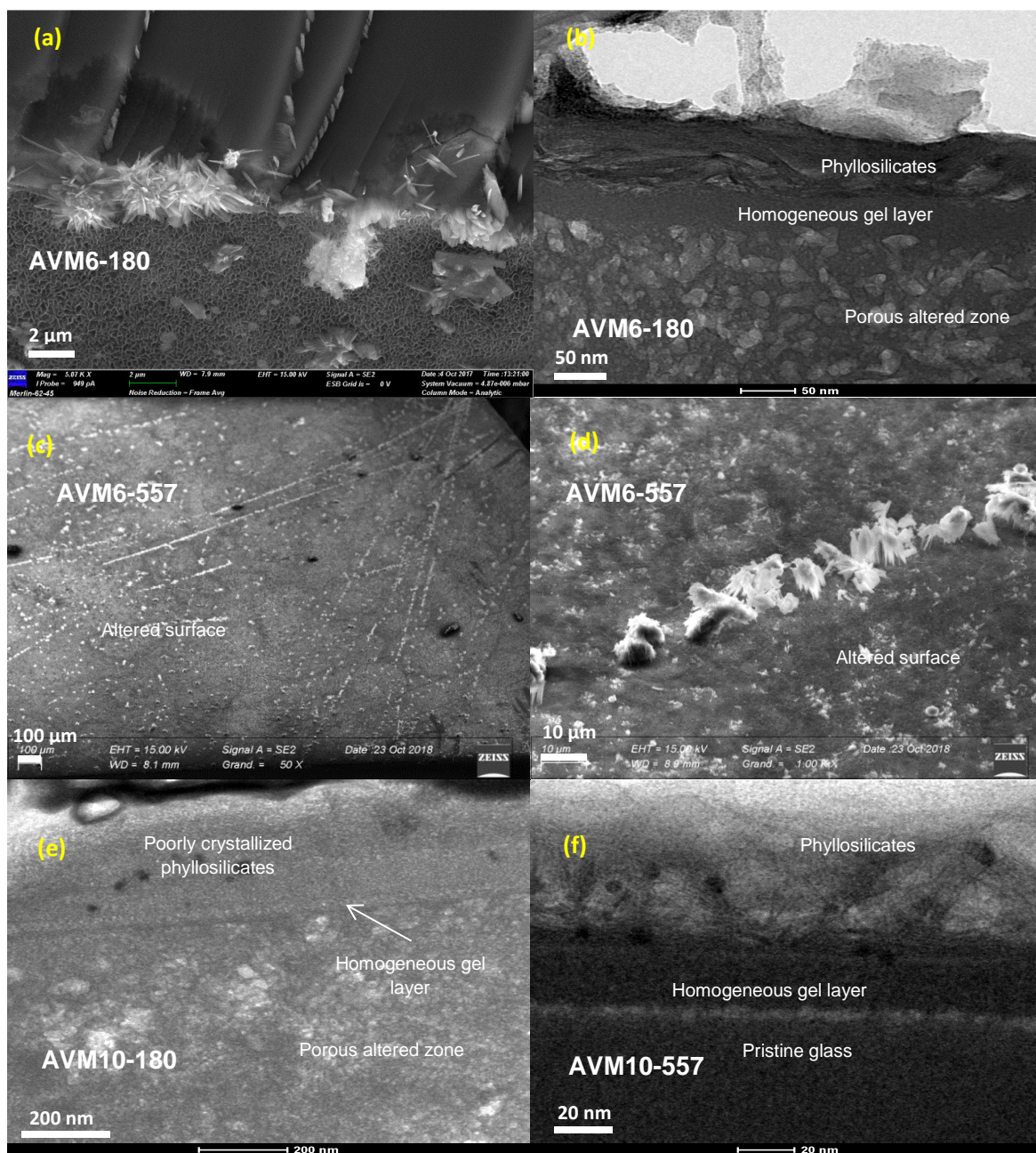
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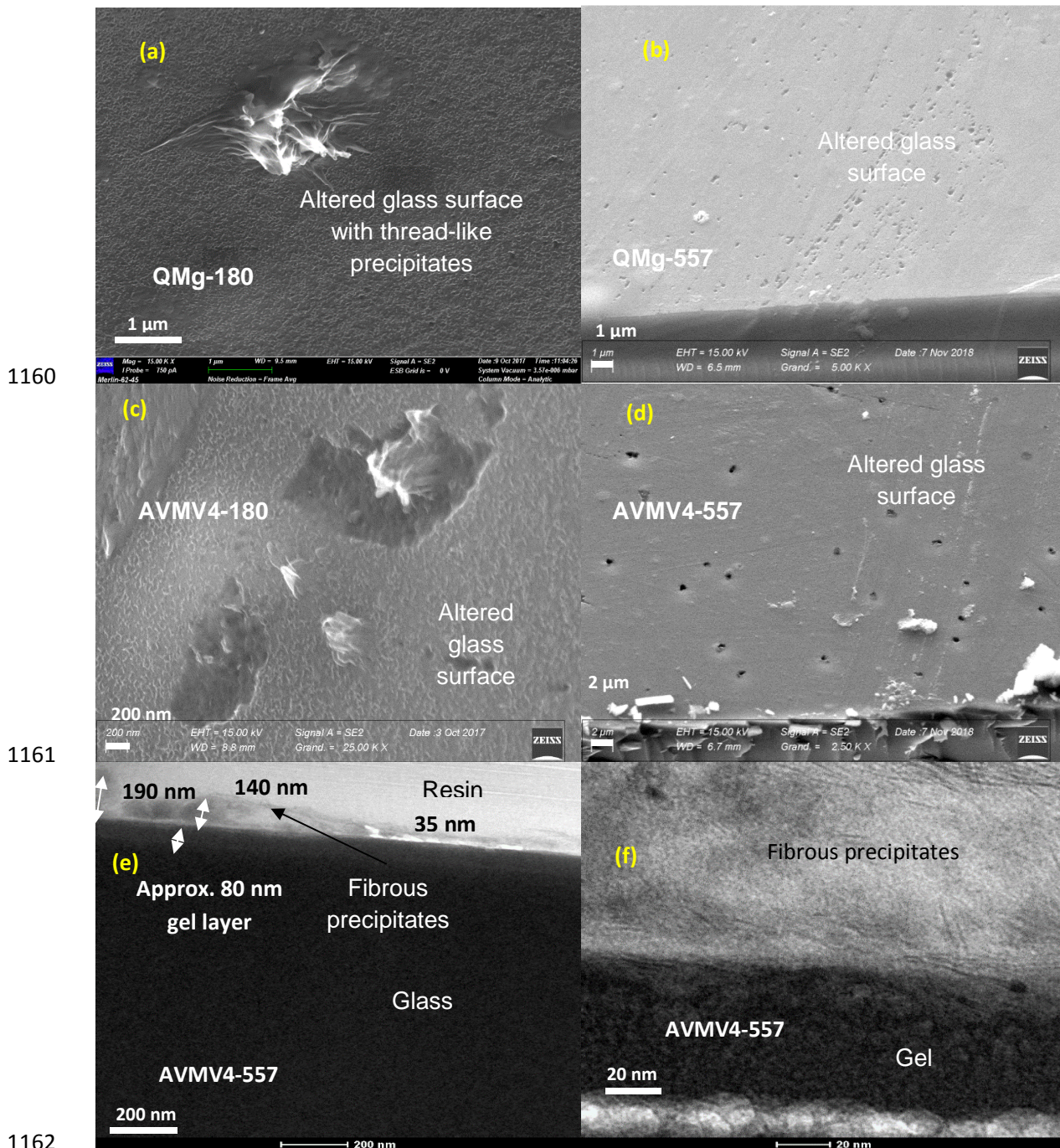


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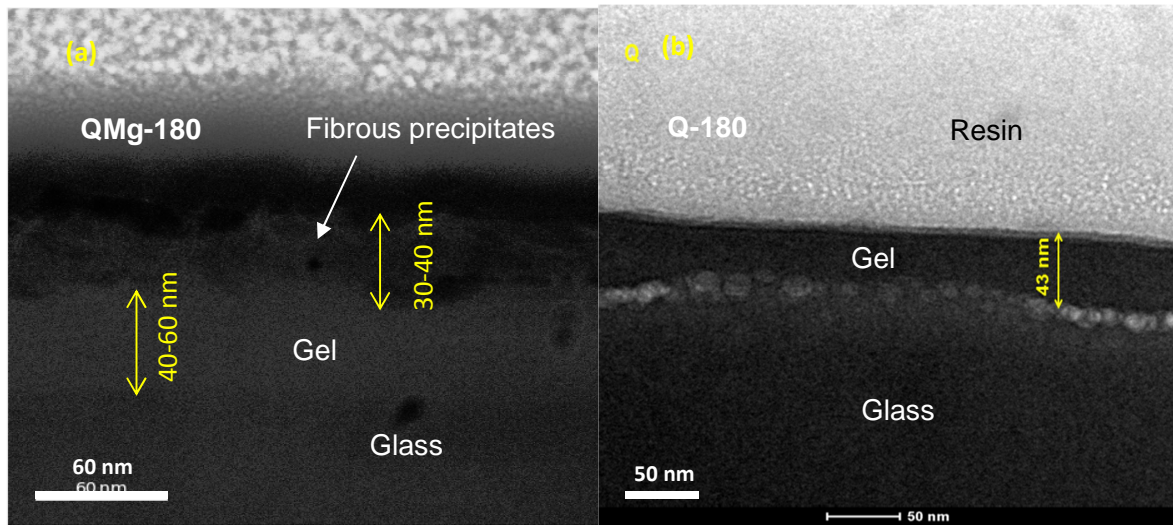
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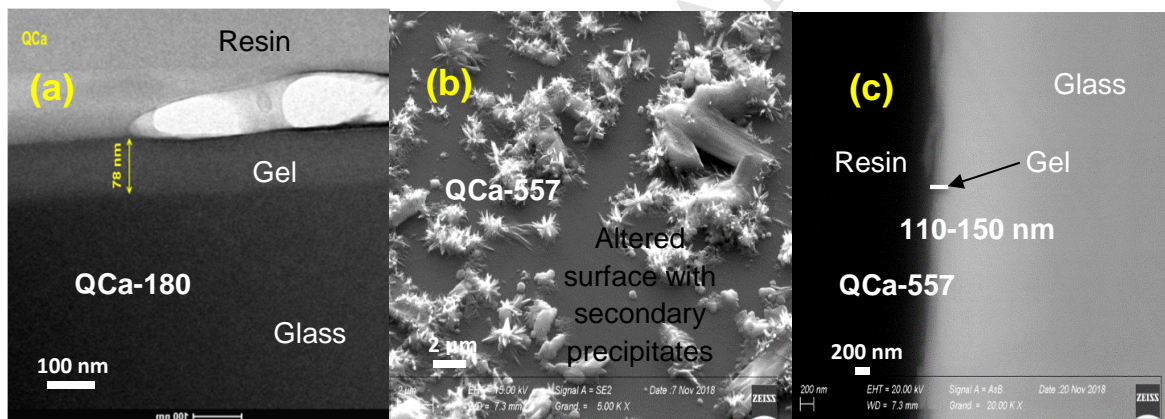
1163 *Figure 3 (a) SEM image of QMg (altered for 180 days at 50°C and 95% RH) showing a carpet of thread-like precipitate and fibrous*  
 1164 *cluster of secondary precipitates; (b) SEM image of QMg (altered for 557 days) showing a gnawed appearance at the altered*  
 1165 *sample surface; (c) SEM image of AVMV4 (altered for 180 days) showing a similar altered surface to QMg altered for the same*  
 1166 *duration; (d) SEM image of AVMV4 (altered for 557 days) showing holes/pits of size 400-500 nm; (e) TEM image of AVMV4-557*  
 1167 *(cross-section) showing a layer of phyllosilicates of varying thickness on altered glass surface and a uniform homogeneous gel*  
 1168 *layer of approx. 80 nm thickness; (f) A zoom of image (e), showing the homogeneous gel layer with a mixture of amorphous and*  
 1169 *crystalline precipitates on the altered surface. There appear to be more crystallized precipitates towards the surface and at the*  
 1170 *interface of gel-layer precipitate-layer*





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 1172 *Figure 4 (a) STEM image of QMg (cross-section) (altered for 180 days at 50°C and 95% RH); (b) TEM image of Q (cross-section)*  
 1173 *(altered for 180 days)*

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 1176 *Figure 5 (a) TEM image of QCa (cross-section) altered for 180 days at 50°C and 95% RH; (b) SEM image of QCa altered for 557*  
 1177 *days at 50°C and 95% RH; (c) SEM image of cross-section of QCa altered for 557 days*

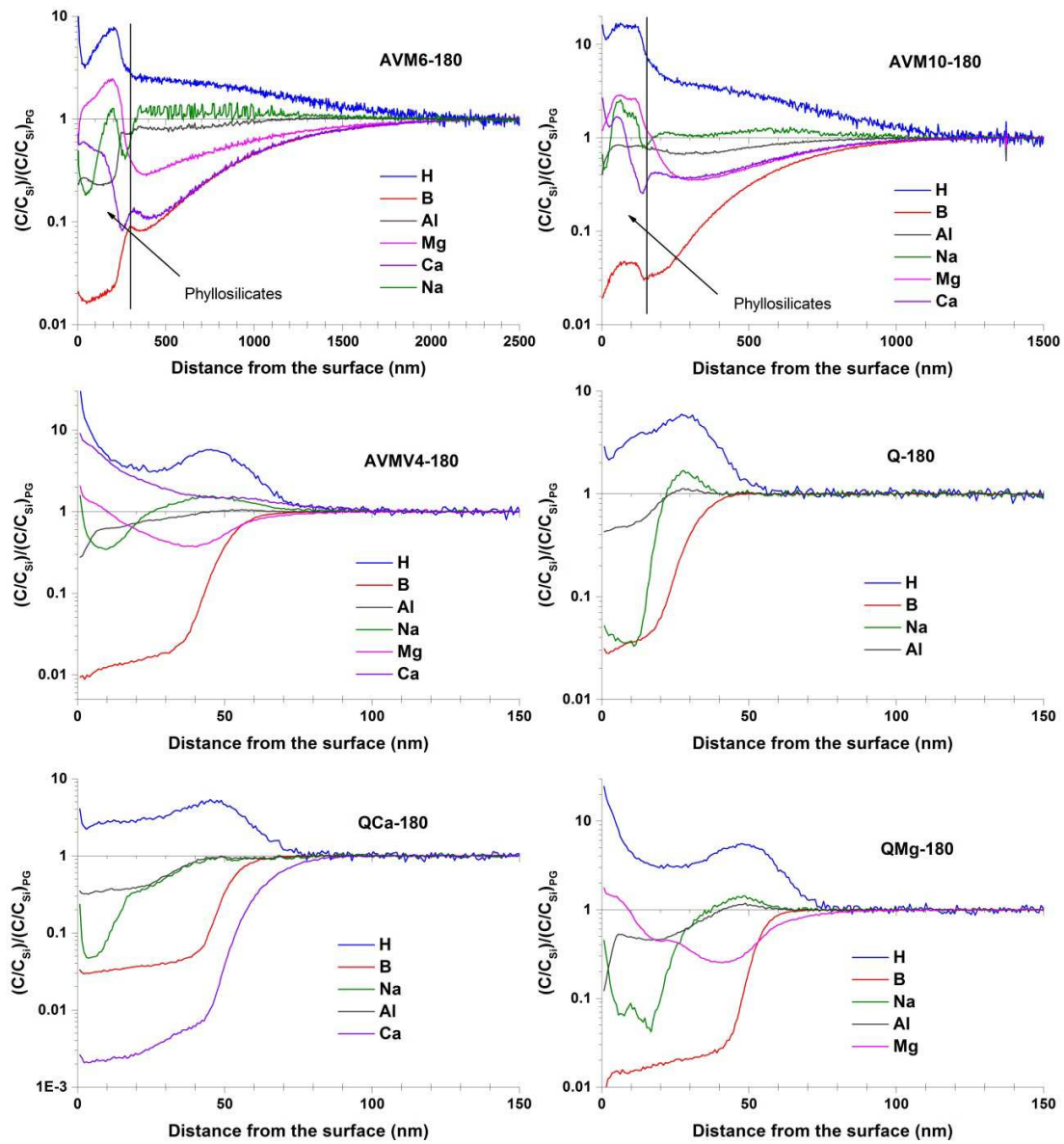
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1184 *Figure 6 ToF-SIMS profiles of all six glasses altered at 50°C and 95% RH for 180 days; The profiles of only the major elements of*  
 1185 *the AVM glasses are shown here*

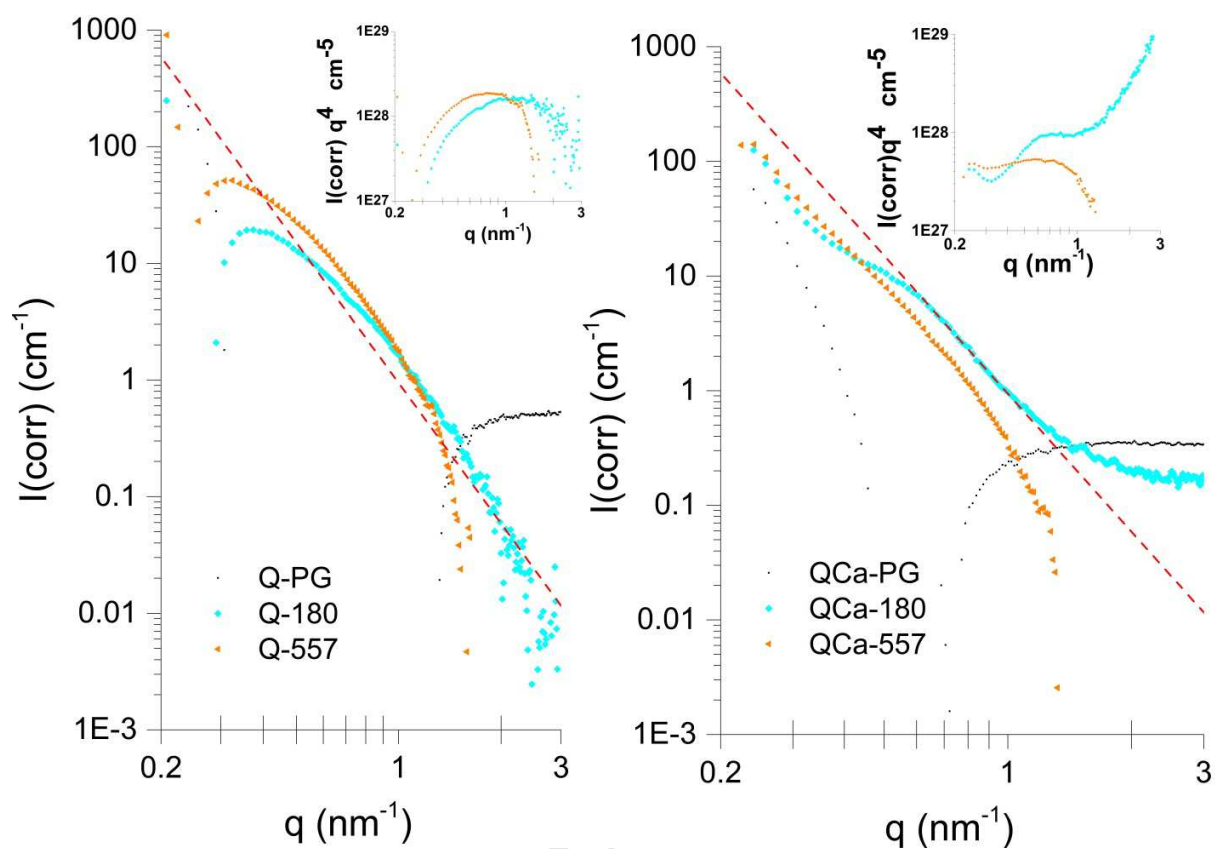
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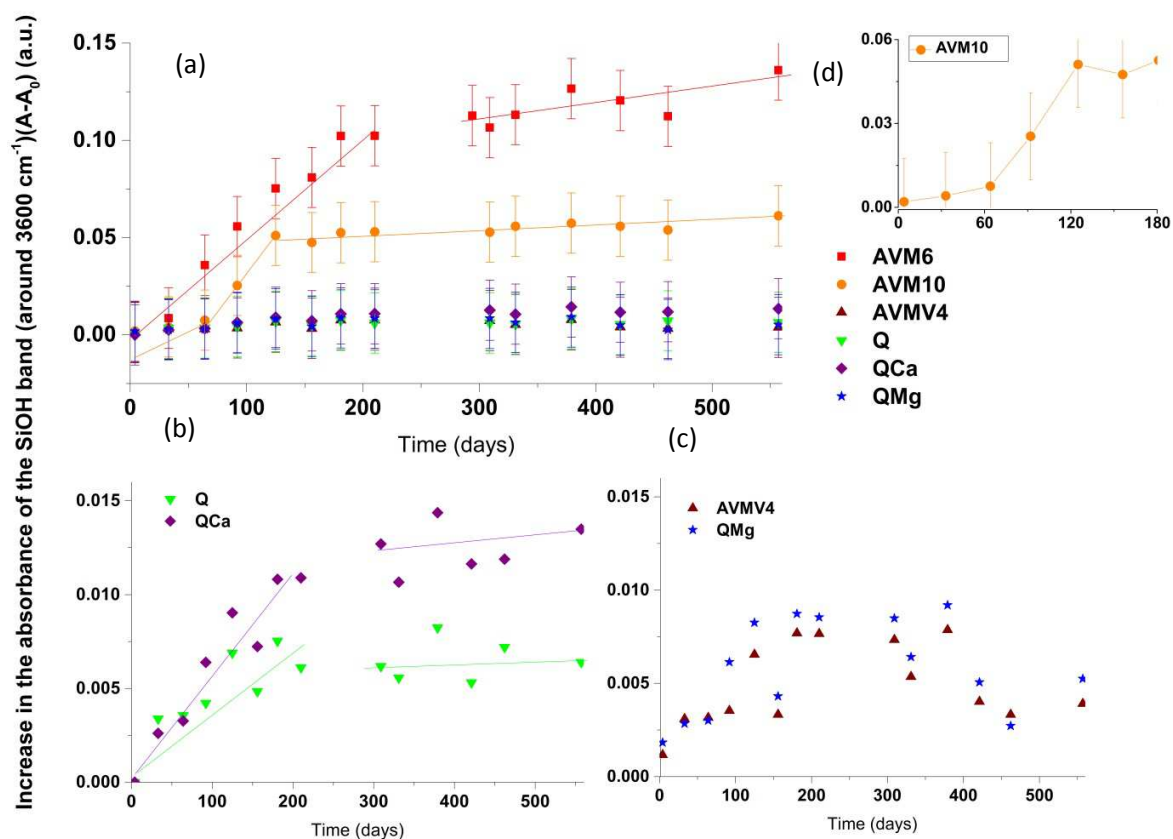


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1192 Figure 7 SAXS spectra of the glasses (a) Q and (b) QCa that were unaltered (black squares), altered for 180 days (blue circles) and  
 1193 557 days (orange triangles); The red dotted lines represent  $I \propto q^{-4}$ ; The inset graphs show the plot of  $(I(\text{corr}) \cdot q^4)$  vs.  $q$  highlighting  
 1194 the shift of the porod regime towards lower  $q$  with increasing duration of alteration;  $I(\text{corr})$  is a result of data treatment to  
 1195 separate the intensity scattered by grain envelopes and the inner pores of the gel layer

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1199 *Figure 8 Evolution of  $(A-A_0)$  with time; (i. e.) The increase in the absorbance of the SiOH band at 3600 cm<sup>-1</sup> of deconvoluted FTIR*  
 1200 *spectra of glasses altered at 50°C and 95% RH until 557 days (A) with respect to the absorbance of the SiOH band of the*  
 1201 *deconvoluted FTIR spectrum of the unaltered glass monolith ( $A_0$ ). (a) Evolution of  $(A-A_0)$  for all six glasses; (b) Evolution of  $(A-A_0)$*   
 1202 *of the glasses Q and QCa; (c) Evolution of  $(A-A_0)$  of the glasses AVMV4 and QMg; (d) A zoom of image (a) to observe closely the*  
 1203 *evolution of  $(A-A_0)$  of AVM10 glass until 180 days*

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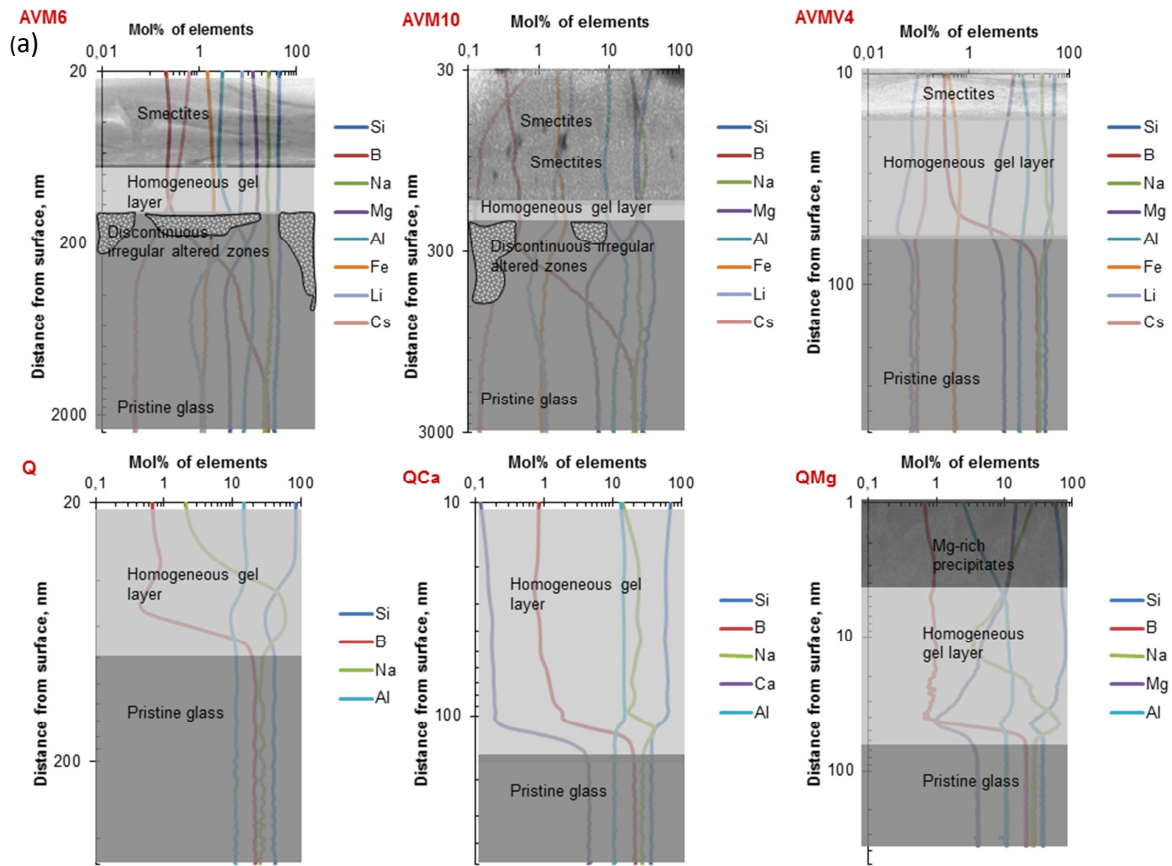
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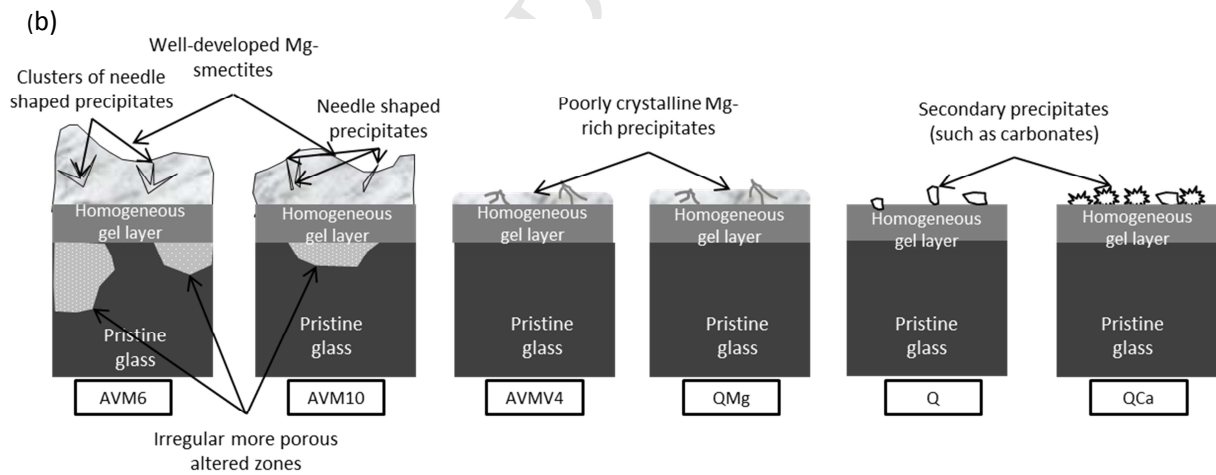
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1213 Figure 9 (a) Description of the altered layer morphology of the six glasses that were vapor hydrated at 50°C and 95%RH for 180  
 1214 days and 557 days; This description was constructed based on TEM images and ToF-SIMS profiles at 557 days; X-axis is the mol%  
 1215 of elements (without considering O) calculated from ToF-SIMS intensities based on Pons-Corbeau method ([96]); y-axis is the  
 1216 distance from the surface in nm; The portions of the ToF-SIMS profiles that correspond to pristine glass, homogeneous gel layer  
 1217 and smectites were chosen approximatively by a combined analysis of TEM images and ToF-SIMS profiles; (b) Schematic  
 1218 description of the morphology of the altered glasses

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1220 *Table 1 Glass compositions (mol% of oxides) (measured by ICP) (error 3%) and fraction of Non-Bridging Oxygen*  
 1221 *atoms (NBO) and percent of boron in 4-coordination (<sup>IV</sup>B) (error 3-8%)*

	<b>AVMV4</b>	<b>AVM6</b>	<b>AVM10</b>	<b>Q</b>	<b>QCa</b>	<b>QMg</b>
<b>SiO<sub>2</sub></b>	48.16	49.29	43.39	57.48	52.67	52.6
<b>Al<sub>2</sub>O<sub>3</sub></b>	7.15	5.88	8.30	8.07	7.49	7.74
<b>B<sub>2</sub>O<sub>3</sub></b>	16.71	18.64	16.29	15.28	14.6	15.02
<b>Na<sub>2</sub>O</b>	18.61	16.65	16.39	19.17	19.01	18.83
<b>CaO</b>	0.04	0.24	0.24	0	6.23	0
<b>MgO</b>	7.15	6.28	10.38	0	0	5.81
<b>Li<sub>2</sub>O</b>	0.05	0.89	0.91	0	0	0
<b>ZrO<sub>2</sub></b>	0.22	0.10	0.29	0	0	0
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.38	0.79	0.81	0	0	0
<b>NiO</b>	0.13	0.27	0.27	0	0	0
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.09	0.20	0.20	0	0	0
<b>P<sub>2</sub>O<sub>5</sub></b>	0.08	0.00	0.81	0	0	0
<b>SrO</b>	0.06	0.03	0.08	0	0	0
<b>Y<sub>2</sub>O<sub>3</sub></b>	0.02	0.01	0.02	0	0	0
<b>MoO<sub>3</sub></b>	0.29	0.13	0.39	0	0	0
<b>MnO</b>	0.10	0.05	0.13	0	0	0
<b>Ag<sub>2</sub>O</b>	0.02	0.01	0.03	0	0	0
<b>CdO</b>	0.05	0.26	0.26	0	0	0
<b>TeO<sub>2</sub></b>	0.03	0.01	0.03	0	0	0
<b>Cs<sub>2</sub>O</b>	0.07	0.03	0.09	0	0	0
<b>BaO</b>	0.06	0.03	0.08	0	0	0
<b>La<sub>2</sub>O<sub>3</sub></b>	0.05	0.02	0.06	0	0	0
<b>Ce<sub>2</sub>O<sub>3</sub></b>	0.05	0.02	0.07	0	0	0
<b>Pr<sub>2</sub>O<sub>3</sub></b>	0.02	0.01	0.03	0	0	0
<b>Nd<sub>2</sub>O<sub>3</sub></b>	0.14	0.04	0.10	0	0	0
<b>RuO<sub>2</sub></b>	0.17	0.08	0.22	0	0	0
<b>PdO</b>	0.11	0.05	0.15	0	0	0
<b>Fraction of NBO</b>	0.134	0.158	0.162	0.036	0.111	0.115
<b>Percent of <sup>IV</sup>B</b>	39	20	27	48.5	46.5	37

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1225 Table 2 Composition (normalized to 4 moles of Si) of phyllosilicates measured by STEM-EDX analyses (at least 12% relative error)

	O	Mg	Al	Si	Ca	Cr	Fe	Nd	
<b>AVM6-180</b>	13.60	1.51	0.18	4.00	0.07	0.01	0.18	0.01	
<b>AVM6-557</b>	15.62	1.72	0.20	4.00	0.06	0.03	0.16	0.00	
	O	Mg	Al	Si	P	Ca	Cr	Fe	Nd
<b>AVM10-180</b>	35.00	3.44	1.09	4.00	0.21	0.10	0.00	0.27	0.08
<b>AVM10-557</b>	20.82	2.01	1.06	4.00	0.17	0.16	0.01	0.23	0.00

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1227 Table 3 Thickness (in nm) of the altered layer (altered at 50°C and 95% RH for 180 days and 557 days each); (ToF-SIMS) is  
1228 measured from equation 2.4.4.2; (TEM) is measured based on the density difference between pristine glass and gel layer in TEM  
1229 images

Duration of alteration	180 days		557 days	
	(ToF-SIMS)	(TEM)	(ToF-SIMS)	(TEM)
<b>AVM6</b>	1060	(70 nm homogeneous layer + Irregular alteration + surface precipitates)	900	(70 nm homogeneous layer + Irregular alteration + surface precipitates)
<b>AVM10</b>	630	(~30 nm homogeneous layer + Irregular alteration + surface precipitates)	905	(~30 nm homogeneous layer + Irregular alteration + surface precipitates)
<b>AVMV4</b>	52	-	64	(~80 nm homogeneous altered layer + surface precipitates)
<b>Q</b>	31	~43 nm homogeneous altered layer	66	~76 nm homogeneous altered layer
<b>QCa</b>	52	~78 nm homogeneous altered layer	121	110-150 nm homogeneous altered layer (SEM)
<b>QMg</b>	53	(~60 nm altered layer + ~30 nm fibrous precipitates)	66	(~76 nm homogeneous altered layer + surface precipitates)

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1232 *Table 4 Porosity, pore-size and surface area of gel calculated from SAXS data;  $\phi_{gel}$  corresponds to the volume fraction of gel*  
 1233 *calculated from ToF-SIMS profiles of monoliths that were used to calculate the porosity of the gel formed on glass powders*

	Time (days)	Porosity (%)	pore diameter, nm	Surface area of pores, m <sup>2</sup> /g	$\phi_{gel}$
<b>Q</b>	180	65	4.3	451	0.05
	557	44	5	264	0.1
<b>QCa</b>	180	27	5.1	158	0.08
	557	9	7.5	37.6	0.19
<b>AVM6</b>	11	66	4.4	328	0.06
	31	47	4.5	235	0.15
	90	11	4.8	58.2	0.64

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## Highlights

- Rate-controlling vapor hydration mechanism is dependent on glass composition
- The molar ratio of  $\text{Al}_2\text{O}_3/\text{MgO}$  affects glass alteration kinetics in vapor phase
- $(\text{Al}_2\text{O}_3/\text{MgO}) < 1$  seems to result in significant precipitation of Mg-smectites
- Difference between relative glass durability in aqueous medium and vapor phase
- Porosity and pore-size of altered layer is similar in the two alteration media