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# Influence of zirconium on cation mobilities in Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> melts: a multicomponent diffusion and XANES study

M. Ficheux<sup>a,b</sup>, E. Burov<sup>a</sup>, L. Cormier<sup>b,\*</sup>, E. Guillard<sup>a</sup>, N. Trcera<sup>c</sup>

<sup>a</sup>*Surface du Verre et Interface (UMR 125), CNRS/Saint-Gobain Research Paris, 39 quai Lucien Lefranc, 93300 Aubervilliers, France*

<sup>b</sup>*Sorbonne Université, CNRS UMR7590, MNHN, IRD, Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC), 4 place Jussieu, F-75005 Paris, France*

<sup>c</sup>*Synchrotron SOLEIL, F-91192, Gif Sur Yvette, France*

## Abstract

High temperature cation mobilities, based on the multicomponent diffusion method, have been coupled with a structural investigation in the Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub> (NCASZ) system at 1200°C and 1250°C. From structural investigation using X-ray absorption spectroscopy (XANES), zirconium was determined in six-fold coordinated sites in the reduced glass composition range of our study and no significant structural changes have been evidenced compared to a quaternary Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (NCAS) glass with a similar composition. Additionally, the diffusion experiments revealed that adding zirconium in the quaternary melt has no influence on the dominant eigenvectors that correspond to exchange between calcium and sodium. Despite the expected mobility decrease resulting from a viscosity increase upon the addition of zirconium, the dominant eigenvalue calculated in this study is higher when Zr is introduced in the melt structure. This result strongly suggests that the sodium mobility is enhanced by the presence of Zr, which is explained by a change in the structural role of sodium from network modifier associated to Q<sup>3</sup>(Si) sites in NCAS melts to charge compensator associated with [ZrO<sub>6</sub>]<sup>2-</sup> sites in NCASZ melts. This modification generates lower bond strengths between sodium and other cations in the melt, thus favoring an enhancement in mobility. Moreover, the diffusion matrix was applied to predict diffusion profiles between zirconium-bearing crystals and melts. We observed that even far from the composition field used for the matrix determination, predictions of zirconium diffusion profiles may be relevant and demonstrate the potential of this approach to evaluate crystal/melt dissolution behavior.

\*Corresponding author. Tel.: +33 1 44 27 52 39

E-mail address: laurent.cormier@sorbonne-universite.fr (L. Cormier)

## 1. INTRODUCTION

Zirconium is an important component in silicate glasses and melts of geological or industrial interests. In geology, zirconium has been frequently studied to understand the formation of zircon ( $\text{ZrSiO}_4$ ), which is an important mineral in geochronological studies and in inferring paleo-formation conditions (Valley et al., 2005). The growth shape and content of radioisotopes of those crystals may be used to deduce eruption history and magma chamber residence time (Simon et al., 2008). One of the main parameters on the formation and survival of zircon is the diffusivity of Zr within silicate melts, which has been extensively investigated (Baker and Watson, 1988)(Behrens and Hahn, 2009)(Boehnke et al., 2013)(Harrison and Watson, 1983)(Mungall et al., 1999)(Zhang and Xu, 2016). Concerning industry, a major benefit to add zirconium within glass compositions is to enhance the chemical durability. Even a small amount (about 2 wt%  $\text{ZrO}_2$ ) increases significantly acid and alkaline durability of a glass (Dimbleby and Turner, 1926). This chemical durability is particularly useful for long term disposal of nuclear wastes (Galoisy et al., 1999)(Gin et al., 2013) where the borosilicate-based glass containing few wt%  $\text{ZrO}_2$  has to stand against water and alkali leaching for a very long time scale. Higher contents of  $\text{ZrO}_2$  (about 16 wt%) are also used in commercial glass fibers for cement reinforcement where a very high alkaline durability is desired (Larner et al., 1976). Another major use of Zr is in the formation of glass-ceramics. Its structural role as nucleating agent promotes bulk crystallization of nano-phases that serve as local heterogeneities for the crystallization (Dargaud et al., 2010)(Dargaud et al., 2011). However, the ability of zirconium oxide to crystallize may also induce problems in other domains. For example, during industrial float glass production, zirconium may leave the furnace walls to enter in the melted glass (Manfredo and McNally, 1984)(Rahimi et al., 2011). Local points in the melt with high Zr concentration may crystallize (Heitz, 1999), creating defects for the final glass products.

In the aforementioned domains, phase separation and crystallization mechanisms must be mastered in order to control the properties of the melt. Unfortunately, in our knowledge no studies focusing on industrial melts are available. In rhyolitic melts, past investigations show that a zircon crystal grows until  $925^\circ\text{C}$  while it dissolves above this temperature (Zhang and Xu, 2016). These high-temperature mechanisms are controlled by chemical diffusion of the elements in the melt (Bouttes et al., 2015)(Chen and Zhang, 2008)(Edwards and Russell, 1996)(Mazurin and Streltsina, 1972)(Roskosz et al., 2006). Most of the time, the chemical diffusion of the slowest diffusing element drives the mechanism. Studies on Zr diffusion, based on simple Fick's law, enable to determine Zr diffusion coefficients ( $D_{\text{Zr}}$ ) depending on temperature, pressure, water content, but they are only valid for the specific studied composition (LaTourrette et al., 1996)(Zhang et al., 2010). As an example, Zr diffusion in dry rhyolite melts is around  $10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ , while Na diffusion coefficient in same conditions can reach  $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  at  $1200^\circ\text{C}$  (Zhang et al., 2010). Such studies give accurate results but are strictly limited to one specific glass/melt composition. Moreover, microscopic diffusion mechanisms remain unclear.

In order to describe the mobility of each element and be more flexible concerning the compositional field where diffusions coefficients are relevant, previous authors have studied the chemical diffusion in melts through a multicomponent approach (Claireaux et al., 2016)(Guo and Zhang, 2016)(Guo and Zhang, 2018)(Liang, 2010)(Liang et al., 1996b). This multicomponent diffusion approach describes mobility of each element considering interactions with others, allowing the description of complex diffusion phenomena like uphill diffusion (i.e., diffusion of a component in a direction opposite to its concentration gradient)

89 (Liang et al., 1996b). In this latter case, an initially flat concentration profile becomes a  
90 gradient generated by strong coupling with another element. The multicomponent diffusion  
91 approach takes into account interactions between elements assuming a linear model and  
92 determines a diffusion matrix which contains cross diffusion coefficients. The matrix describes  
93 the mobility of an element under its own gradient of chemical potential as driving force  
94 (diagonal terms) and the impact of the other elements on this driving force by the coupled  
95 diffusion coefficients (off-diagonal terms). The eigenvectors of the diffusion matrix give  
96 information on the coupling between species in the form of exchange reactions and  
97 eigenvalues give the occurrence coefficients of those reactions (Chakraborty et al.,  
98 1995b)(Chakraborty et al., 1995a). Several studies have been carried out at high temperatures  
99 for silicate melts in various systems: Na<sub>2</sub>O-CaO-SiO<sub>2</sub> (NCS) (Trial and Spera, 1994), K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-  
100 SiO<sub>2</sub> (KAS) (Chakraborty et al., 1995b)(Chakraborty et al., 1995a)., MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (MAS) and  
101 CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) (Kress and Ghiorso, 1993)(Richter et al., 1998), CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>  
102 (CAS) (Liang et al., 1996b)(Sugawara et al., 1977) and recently Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (NCAS)  
103 (Claireaux et al., 2016)(Claireaux et al., 2019). Guo and Zhang investigated multicomponent  
104 diffusion in more complex systems with a 7-components haplobasalt and a 8-components  
105 basalt (Guo and Zhang, 2016)(Guo and Zhang, 2018). A recent paper focused on the ternary  
106 Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (NBS) (Pablo et al., 2017).

107 In this work, we study multicomponent diffusion in NCAS melt with the addition of  
108 ZrO<sub>2</sub>. Using the multicomponent approach, the determination of the diffusion matrix requires  
109 that no structural changes occur along a diffusion profile. However, addition of zirconium  
110 within the glass structure may result in different local Zr environments. After saturation (Kato  
111 and Araki, 1986), Zr may crystallize in ZrO<sub>2</sub>, occurring in 7-fold coordination <sup>[7]</sup>Zr for  
112 monoclinic/tetragonal phases and in 8-fold coordination <sup>[8]</sup>Zr for the cubic high temperature  
113 phase (Howard et al., 1988). In NAS glass, from low concentration to saturation, Zr is usually  
114 6-fold coordinated <sup>[6]</sup>Zr (Cormier et al., 2015). Zr in 7-fold coordinated environment has been  
115 evidenced in CMAS glasses (Cormier et al., 2015) and minor amounts of <sup>[7]</sup>Zr are also observed  
116 in sodo-borosilicate glasses with increasing ZrO<sub>2</sub> content (McKeown et al., 1999). In order to  
117 address a possible Zr coordination change with compositions in the studied glasses/melts, X-  
118 ray absorption spectroscopy is a well-suited method (Cormier et al., 2015)(McKeown,  
119 2000)(Galoisy et al., 1999), providing high spatial resolution and enabling *in situ*  
120 measurements.

121 In order to prevent any crystallization, we have studied a system with a low amount of  
122 ZrO<sub>2</sub> (about 3 wt%). Na cations were introduced in excess of (Zr+Al) to ensure complete charge  
123 compensation of these elements, thereby limiting possible coordination changes observed for  
124 Zr (Calas et al., 2014) or Al (Neuville et al., 2006) when insufficient charge compensation is  
125 provided by alkali/alkaline earth cations.

## 126 2. EXPERIMENTAL

### 127 2.1. Sample composition and preparation

128 The composition domain investigated here is centered on the peralkaline composition  
129 C<sub>0</sub> = 62.5 wt% SiO<sub>2</sub>, 12.9 wt% Na<sub>2</sub>O, 10.5 wt% CaO, 10.9 wt% Al<sub>2</sub>O<sub>3</sub>, 3 wt% ZrO<sub>2</sub> (66.4SiO<sub>2</sub>-  
130 13.3Na<sub>2</sub>O-11.95CaO-6.8Al<sub>2</sub>O<sub>3</sub>-1.55ZrO<sub>2</sub> in mol%). This C<sub>0</sub> glass has a composition close to a



131 window glass (typically 75SiO<sub>2</sub>-15Na<sub>2</sub>O-10CaO), with the addition of Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Excess of  
132 aluminium and zirconium in industrial glass is often observed at the interface between the  
133 melt and the refractory. C<sub>0</sub> is also a composition similar to the NCAS glass (without ZrO<sub>2</sub>)  
134 previously studied by Claireaux *et al.* (Claireaux et al., 2016)(Claireaux et al., 2019), allowing  
135 direct comparison to understand the influence of Zr on the diffusion properties. Around this  
136 C<sub>0</sub> central composition, 14 different glasses have been synthesized and compositions of the  
137 diffusion couples are summarized in Table 1. Glasses are gathered in pairs, now designated as  
138 glasses couples to create a diffusion exchange between two elements. For example, AZ glass  
139 is enriched by 2 wt% Al<sub>2</sub>O<sub>3</sub> and depleted by 2 wt% ZrO<sub>2</sub> compared to C<sub>0</sub>. It is coupled with ZA  
140 glass which is enriched by 2 wt% ZrO<sub>2</sub> and depleted by 2 wt% Al<sub>2</sub>O<sub>3</sub>.

141

142

143 Table 1. Measured composition in weight% of C<sub>0</sub> central composition, glass couples, ZrSiO<sub>4</sub> zircon crystal and G1 synthesized glass composition.  
 144 T<sub>g</sub> values are obtained using Fluegel's model (Fluegel, 2007). An error of ± 0.05 wt% may be considered on these values.

	C <sub>0</sub>	AN	NA	AC	CA	NC	CN	NZ	ZN	SZ	ZS	AZ	ZA	ZC	CZ	ZrSiO <sub>4</sub>	<sup>145</sup> G1
<b>Na<sub>2</sub>O</b>	12.9	9.5	14.2	12.7	12.1	14.4	10.3	13.3	11.4	12.2	11.9	12.3	12.4	12	13.7	0	14.4
<b>CaO</b>	10.5	9.8	11.1	8.6	11.4	8.47	14.8	9.9	9.1	9.9	9.6	9.4	10	9.6	12.9	0	9.9
<b>ZrO<sub>2</sub></b>	3	2.8	2.6	2.8	2.5	2.8	2.7	0.9	4.5	0.9	4.4	0.9	4.2	4.4	1.1	67	0
<b>Al<sub>2</sub>O<sub>3</sub></b>	10.9	14.1	9.5	13.2	9.5	11.6	11.7	11.4	11.4	11.0	11.4	12.7	9.2	11.5	11.5	0	0.6
<b>SiO<sub>2</sub></b>	62.5	63.7	62.5	64.2	65.2	61.3	60.1	63.3	63.7	65.4	62.1	61.5	61.2	62.5	61.3	33	75
<b>T<sub>g</sub></b>	612	654	597	623	612	602	638	603	633	609	629	616	615	629	602		

146

147 Viscosities of each glass were measured from 1100°C to 1600°C, using a high  
148 temperature Couette rheometer (Fig. S1 in the Supplementary file). The glass transition  
149 temperatures  $T_g$  were estimated using Fluegel's model (Fluegel, 2007) and reported in Table  
150 1. The values are close to those reported in a similar system without  $ZrO_2$  (Claireaux et al.,  
151 2019).  $T_g$  values vary around the  $C_0$  composition and increase by about +40°C for the  $Al_2O_3$   
152 and  $ZrO_2$  rich compositions, and decrease by about -20°C for the glasses with more  $Na_2O$   
153 content and less  $Al_2O_3$  and  $ZrO_2$  content. However, the deviations of the  $T_g$  values are low  
154 compared to the experimental uncertainties and their influence on the diffusion processes is  
155 weak.

156 After diffusion through thermal treatment, this method allows us to investigate only  
157 one exchange per profile. A maximum of 4 wt% concentration difference has been chosen in  
158 order to keep the mass conservation assumption and a constant diffusion matrix through the  
159 diffusion profiles, in accordance with Fick's second law. Glasses have been synthesized using  
160 the following raw materials: Ronceveaux sand ( $SiO_2 > 99.7$  wt%), Saint-Germain Limestone  
161 ( $CaCO_3 > 99.8$  wt%), sodium carbonate from Novacarb ( $Na_2CO_3 > 99.9$  wt%), calcined alumina  
162 ( $Al_2O_3 > 99.9$  wt%) from Keraglass and zirconia ( $ZrO_2 > 99.9$  wt%) from Zirpro. Some ppms of  
163 coke have also been introduced in order to improve glass homogeneity. For each couple, one  
164 of the two glasses is colored in blue by adding 200 ppm of cobalt oxide (that is the range of  
165 impurity content of used raw materials) for several reasons: the interface between two glasses  
166 (one doped with Co and the other one undoped) is easily found optically and any macroscopic  
167 convection occurring at high temperature between the two glasses is immediately observed.  
168 Glasses have been melted in a platinum crucible at 1550°C for 8h, mechanically agitated for  
169 homogeneity every hour and finally poured on a metallic table. An annealing step of 50 min  
170 at 20°C above  $T_g$  has been carried out to relieve residual internal stresses, which allows the  
171 glass to stand against various mechanical sollicitation for sample sizing before diffusion  
172 experiment.

## 173 2.2. Diffusion experiments

174 Two temperatures have been selected: 1200°C and 1250°C. They are as close as  
175 possible to the temperature of interest for industrial and geological issues; these are also  
176 temperatures at which experiments are feasible, avoiding convection and nucleation  
177 phenomena. The risk of formation of convection cells can be estimated, in accordance with  
178 the Rayleigh number  $Ra$  defined as:

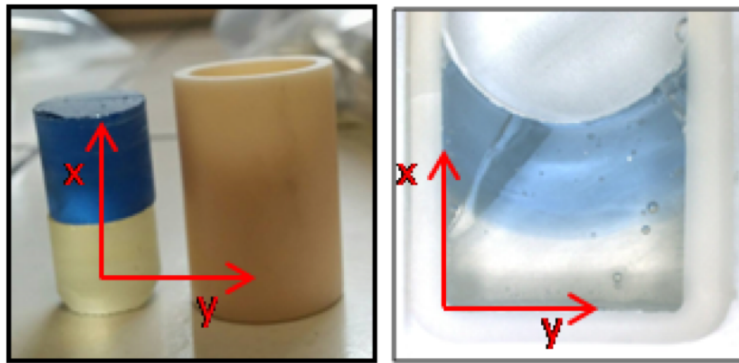
$$179 \quad Ra = \frac{g \cdot \Delta T \cdot l^3 \beta}{\eta \cdot \alpha} \quad (1)$$

180 where  $g$  is the constant of gravity,  $\Delta T$  the temperature variation in sample,  $l^3$  the sample  
181 volume,  $\beta$  the thermal dilatation of the melted glass,  $\eta$  the dynamic viscosity,  $d$  the density  
182 and  $\alpha$  its thermal diffusivity. When  $Ra$  is higher than 1700-2000, a convection cell is expected  
183 to appear. In order to avoid convections,  $Ra$  can be lowered by reducing the sample size  $l^3$ .  
184 Cylinder-shaped glass samples were used with 8 mm diameter and 4mm height (Fig. 1). The  
185 contact face of each cylinder is mechanically polished until surface asperity sizes are below  
186 5  $\mu m$ , avoiding significant bubble trapping that disturbs diffusion. The glasses couple is piled  
187 in an alumina crucible with 8 mm inner diameter, 2 mm thickness and 15 mm height (Fig. 1).

188 For each couple, the denser glass is placed at the bottom of the crucible in order to limit  
189 convection. Additionally, considering that alumina diffuses at high temperature from the  
190 crucible to the glass, we have not considered data that are close to the alumina crucible.

191 The choice of diffusion times results from a trade-off between two contradicting  
192 conditions. A long diffusion profile is needed to acquire enough points that will give an  
193 accurate spatial resolution to follow chemical composition variations along the concentration  
194 profile while, in order to avoid the apparition of convection cells, the diffusion time has to be  
195 limited. The crucibles containing samples are introduced in a preheated electric furnace then  
196 removed after 20 min. Samples are finally annealed in another furnace preheated at 10°C  
197 above T<sub>g</sub> during 50 min. The furnace is then turned off and the samples are slowly cooled  
198 down to room temperature. Table S1 in the supplementary file summarizes the couples that  
199 were measured and the experimental conditions.

200



201

202 Fig. 1. Sample before heat treatment and ready for microprobe analysis.

203

### 204 2.3. Chemical diffusion profiles

205 The chemical concentration profiles of the diffusion couple samples were determined  
206 by Electron Probe Micro-Analysis (EPMA) using a Cameca SX-Five electron microprobe at the  
207 CAMPARIS center (Sorbonne University, Paris) and at Saint-Gobain Research Paris. The  
208 operating conditions were 15 kV accelerating voltage, 10 nA beam current and only 5 s  
209 counting time in order to limit the migration of light elements such as Na during acquisition.  
210 After encapsulation in epoxy resin, samples are cut and polished to 1 μm by using a series of  
211 diamond pastes. Optical microscopy was used to check that no convection cells appeared. To  
212 avoid any Na migration under the beam, the beam area has been defocussed to 5 μm<sup>2</sup>, which  
213 reduces the received energy per μm<sup>2</sup>. The microprobe beam was stopped during focalization  
214 before each measurement, which limits the exposition time. It was also necessary to start each  
215 new acquisition point with Na as the first analyzed element. This procedure minimizes the  
216 exposition time of the analyzed surface before collecting Na data and allows a standard  
217 deviation of Na of 0.1 wt%. Considering that this is the order of magnitude of composition  
218 inhomogeneities that we might find in our glass, we are satisfied with such accuracy.

219 In theory, only (n-1) experiments with (n-1) profiles are required to determine the (n-  
220 1)<sup>2</sup> coefficients of the diffusion matrix. In our case, only 4 experiments should be necessary.

221 However, we experimentally had reproducibility problems in the diffusion coefficients of the  
222 matrix with this limited number of profiles. We then reached an experimental setup with 7  
223 profiles that solved our problems and gives a good reproducibility in the results. It was  
224 especially necessary to increase the number of acquired data in the exchange profile between  
225 slowly diffusing elements, such as Al, Si, Zr.

## 226 **2.4. Structural profiles**

227 The Zr L<sub>2,3</sub> edges are due to transition from 2p to 4d states. In Oh symmetry, the two  
228 peaks in the Zr L<sub>2</sub> and L<sub>3</sub> edges are associated with the crystal field splitting of the 4d states  
229 into t<sub>2g</sub> and e<sub>g</sub> empty states. The filling of these empty states change their energy position,  
230 which can be measured through XANES (X-ray Absorption Near Edge Spectroscopy). The  
231 XANES data at the Zr L<sub>2,3</sub>-edges were acquired at the SOLEIL synchrotron source on the LUCIA  
232 beamline (Saint-Aubin, France) using a Si(111) double crystal monochromator. Data were  
233 recorded in fluorescence mode at ambient conditions (T = 22°C) using a silicon drift diode  
234 detector. Each spectrum is the average of at least two spectra with an energy step of 0.1 eV  
235 at a counting time of 3 seconds. After normalization of the high energy side using Athena  
236 software (Ravel and Newville, 2005), a residual background was subtracted by fitting an  
237 arctangent function. The background-free spectra have then been fitted with pseudo-Voigt  
238 functions. The parameters of the pseudo-Voigt functions give information on the 4d energy  
239 level that are related to the coordination number. XANES spectra were obtained for crystalline  
240 references containing Zr in different environments: Baghdadite (Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub>) with Zr  
241 coordination number N = 6 (<sup>6</sup>Zr), Baddeleyite (monoclinic ZrO<sub>2</sub>) with N = 7 (<sup>7</sup>Zr) and zircon  
242 (ZrSiO<sub>4</sub>) with N = 8 (<sup>8</sup>Zr). Using a spot size area of ~10 μm<sup>2</sup>, XANES spectra were acquired  
243 through several diffusion profiles, with a position accuracy of ~1 μm.

244 Raman spectroscopy was also used to determine the average changes in network  
245 connectivity induced by the different chemical exchanges. Raman spectra were acquired using  
246 a Renishaw Qontor machine and a green laser with a wavelength of 532 nm and a power of  
247 50 mW. The spot was focused with x50 lens and the acquisition time per spectra was 1 s. The  
248 excited zone is about 5 μm<sup>2</sup>, which is comparable with EPMA. Principal Component Analysis  
249 (PCA) treatment was performed thanks to the constructor software. The temperature and  
250 frequency dependencies were corrected using the Long correction (Long, 1977) and  
251 normalized using the total area under the spectrum. The Raman spectra have been acquired  
252 along each concentration profiles. We have carefully acquired Raman spectra along the EPMA  
253 profiles in order to correlate each spectrum with its associated composition. Thereby, we can  
254 couple both composition and structural information along the same diffusion profile.

## 255 **2.5. Mathematical analysis of diffusion profiles**

256 The cooperative nature of species mobility in a multicomponent system has been  
257 analyzed using a matrix diffusion approach where eigenvectors describe coupling between  
258 species. Details about the theoretical background of the matrix approach has been discussed  
259 by Liang (Liang, 2010). The numerical procedure to determine diffusion coefficients from  
260 diffusion-couple experiments, taken as the eigenvalues of the diffusion matrix, can be found  
261 in Claireaux *et al.* (Claireaux et al., 2016).

262 Firstly, for each temperature, the diffusion matrix was obtained from the least-square  
263 minimization of the difference between all available experimental diffusion profiles and the  
264 theoretical diffusion profiles given by:

265 
$$\tilde{C}_i(x, t) = \Delta\tilde{C}_i \operatorname{erf}\left(\frac{x}{\sqrt{2\alpha_i t}}\right) \quad (2)$$

266 where  $\alpha_i$  is an eigenvalue of the diffusion matrix,  $\Delta\tilde{C}_i$  is the initial concentration step in the  
267 eigen-basis and  $\tilde{C}_i(x, t)$  is the projection of the concentration profiles of the different species,  
268 along the direction of the eigen-vector  $i$ .

269 Secondly, we fitted the diffusion profiles at two temperatures using a common basis  
270 of eigenvectors. As discussed in Claireaux *et al.* (Claireaux et al., 2019), since the estimated  
271 direction of eigenvectors does not change much with temperature, the obtained set of  
272 eigenvalues is likely to be more accurate.

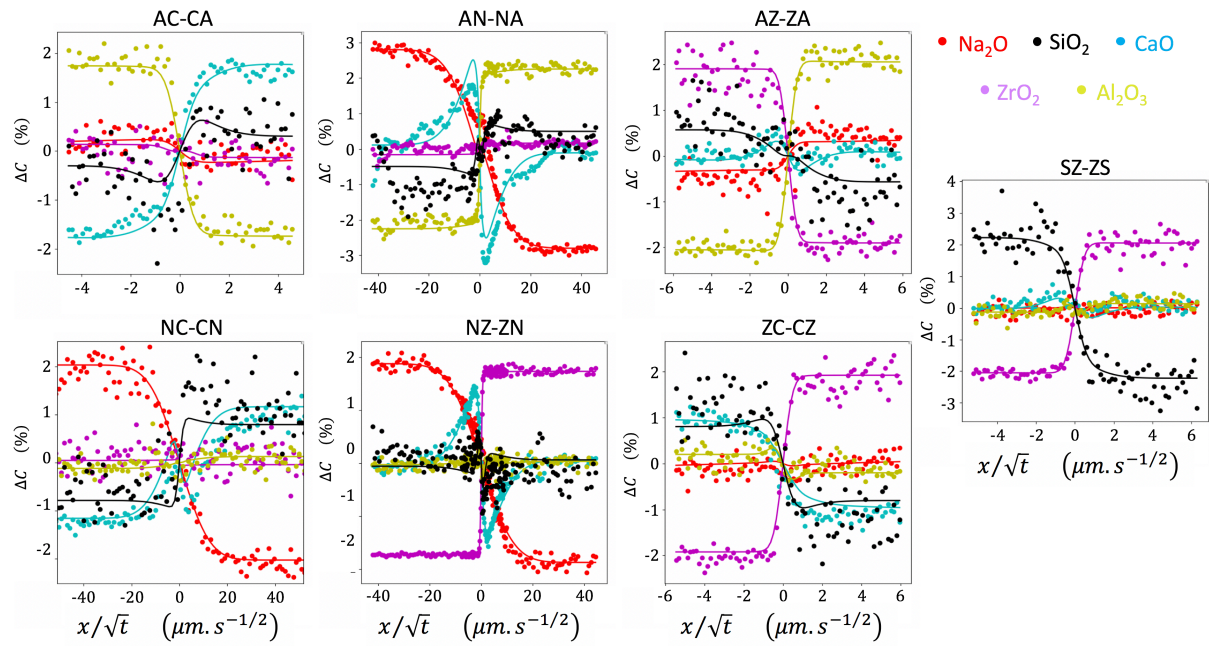
273 The least-square error was computed in the eigenbasis of the diffusion matrix, using  
274 the open-source code *multidiff* (<https://pythonhosted.org/multidiff/>).

### 275 3. EXPERIMENTAL RESULTS

276 The seven concentration profiles obtained at 1200°C and 1250°C are given in Fig. 2 and  
277 Fig. 3, respectively. The interface composition  $C_i$  of each diffusion couple is listed in Table S2  
278 in the supplementary file. The diffusion distance is normalized by  $\sqrt{t}$  in order to make our  
279 results independent of time. Each concentration profile is plotted relatively to the central  
280 composition  $C_0$  for better readability ( $x/\sqrt{t} = 0$  and concentrations = 0). In a concentration  
281 profile, the two glass compositions should differ for the two elements that are added or  
282 removed compared to the composition  $C_0$ . However, small variations for other components  
283 are sometimes observed compared to the target composition (Table. 1). Most of these  
284 variations concern  $\text{SiO}_2$  concentration, causing a small variation compared to the total  $\text{SiO}_2$   
285 content. These variations imply concentration gradients that can create interactions between  
286 elements during diffusion. To avoid this problem, all profiles are fitted altogether and the real  
287 concentration differences are taking into account.

288 Diffusion profiles are very similar at 1200°C (Fig. 2) and 1250°C (Fig. 3). As previously  
289 observed (Claireaux et al., 2016)(Guo and Zhang, 2016)(Guo and Zhang, 2018)(Liang, 2010),  
290 the exchanges between Na and Ca are much more extended in space than other ones. Na is  
291 the most mobile element and its diffusion distance does not seem to be highly impacted by  
292 the element it is exchanged with. As Na cations do not have network forming role in the melt  
293 structure, they are able to move freely within the silicate framework. The second fastest  
294 diffusing element is Ca. Its diffusion distance strongly depends on the element it is exchanged  
295 with, from very fast exchange with Na to very slow with Zr or Al. The very well-known uphill  
296 diffusion of Ca under Na/Al exchange (Liang et al., 1996a)(Zhang et al., 1989) is observed also  
297 in our system for both temperatures. An interesting point is the apparition of the same Ca  
298 strong uphill diffusion when Zr is exchanged with Na (Fig. 2,3 ZN|NZ). This uphill diffusion  
299 comes from a different mobility of Na compared to Al and Zr. From structural considerations,  
300 an exchange between two network modifiers is easier than between element with different  
301 structural roles (network modifier vs network former). This aspect will be detailed in the  
302 discussion part.

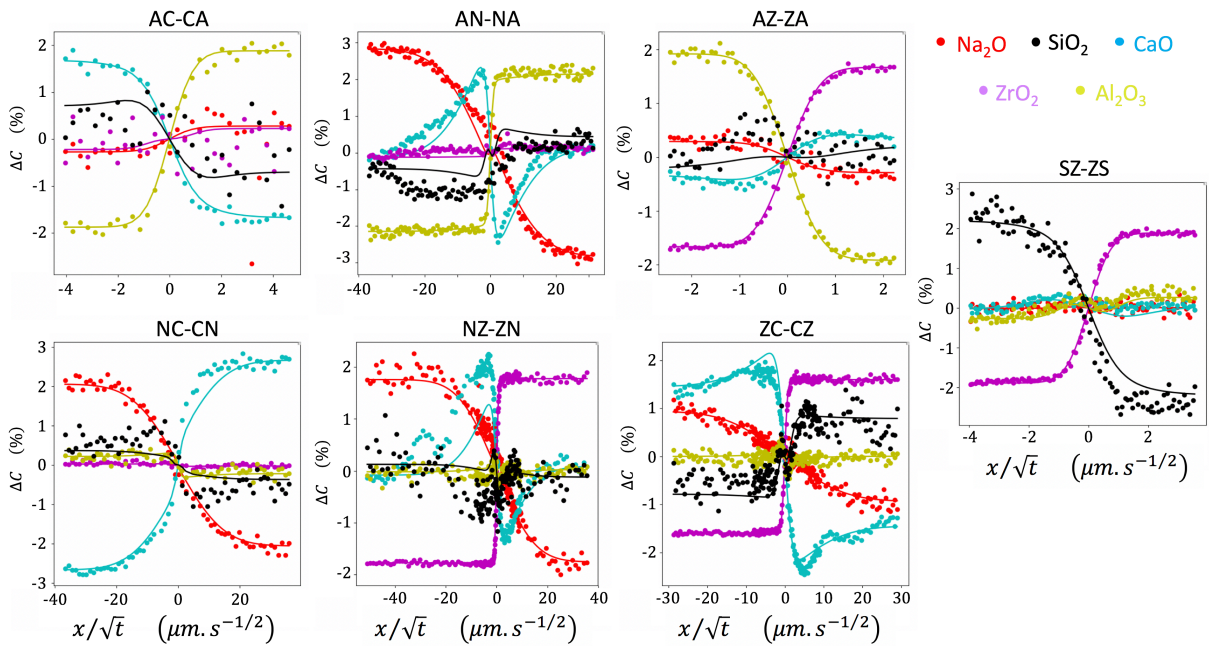
303



304

305 Fig. 2. Concentration profiles for all diffusion couples at 1200°C. The dots correspond to  
 306 measurement when the solid lines correspond to the fit for diffusion matrix determination.

307



308

309 Fig. 3. Concentration profiles for all diffusion couples at 1250°C. The dots correspond to  
 310 measurement when the solid lines correspond to the fit for diffusion matrix determination.

311

### 312 3.1 Eigenvectors and eigenvalues

313 The theoretical diffusion profiles obtained with the best-fit diffusion matrix correspond  
 314 to the solid lines plotted behind experimental data in Fig. 2 and Fig. 3. The agreement between

315 experimental and theoretical profiles is very good. However, the Ca uphill profile is not well  
316 described when it is asymmetric. The eigenvectors and eigenvalues calculated for the diffusion  
317 matrix allow us to determine exchange reactions. The eigenvectors give the stoichiometry of  
318 the reaction and indicate exchange diffusion mechanisms (Guo and Zhang, 2016)(Guo and  
319 Zhang, 2018). Their associated eigenvalues indicate the rate of these reactions (Chakraborty  
320 et al., 1995b)(Chakraborty et al., 1995a). In order to obtain those eigenvectors and  
321 eigenvalues, the fit of each profile has been set up through different steps. We first proceed  
322 calculations for each temperature, independently. The obtained diffusion matrix for 1200°C  
323 and 1250°C with SiO<sub>2</sub> as a dependent component is given in Table 2 and the eigenvalues and  
324 eigenvectors are reported in Table 3. Those eigenvectors are expressed in wt% eigenbasis. It  
325 has already been observed that eigenvectors are almost constant with temperature  
326 (Chakraborty et al., 1995a)(Kress and Ghiorso, 1993)(Mungall et al., 1998). Our calculations  
327 confirm this result with very small changes occurring for the eigenvectors. Then, the fit of all  
328 profiles for the two temperatures was performed in a common basis of eigenvectors. The  
329 eigenvectors and the eigenvalues are given in Table 4 and compared with the results  
330 previously obtained on a similar NCAS glass without ZrO<sub>2</sub> (Claireaux et al., 2016). We observe  
331 that the major exchange direction is the Na/Ca exchange. The second eigenvector corresponds  
332 to Ca exchanging with network formers. The 3<sup>rd</sup> and 4<sup>th</sup> reactions are more complex and will  
333 be developed in the discussion part. Concerning the eigenvalues, their evolution follow  
334 common sense with increasing values between 1200°C and 1250°C reflecting the enhanced  
335 diffusion at higher temperatures.

### 336 **3.2 XANES Spectroscopy**

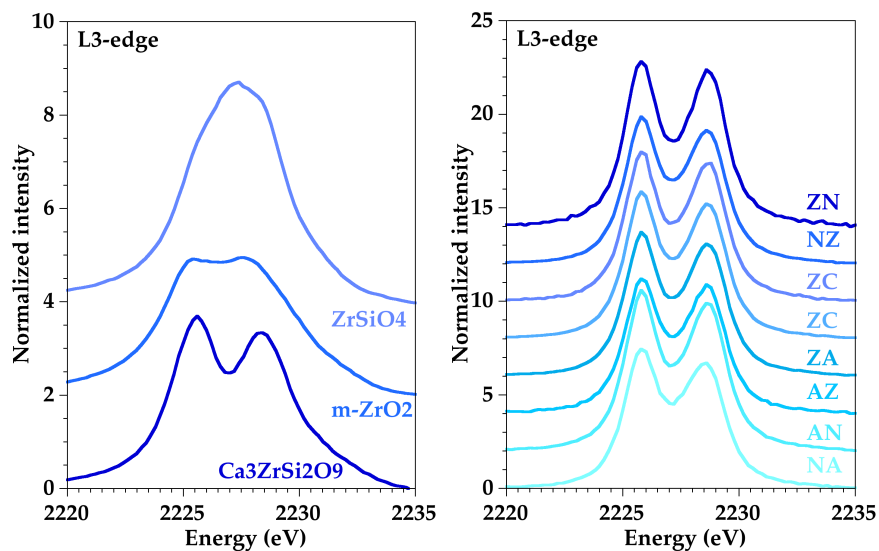
337 The Zr L<sub>3</sub> edge XANES spectra are plotted in Fig. 4.a for crystalline references containing  
338 <sup>[6]</sup>Zr, <sup>[7]</sup>Zr and <sup>[8]</sup>Zr, showing a strong influence of the Zr coordination number and the site  
339 geometry (Bouvier et al., 2001)(Howard et al., 1988)(Wyckoff, 1963). In baghdadite, Zr occurs  
340 in a slightly distorted octahedron ZrO<sub>6</sub> and the spectrum presents two well-resolved peaks. In  
341 baddeleyite and zircon, the two components are poorly resolved due to the low site symmetry  
342 for <sup>[7]</sup>Zr and <sup>[8]</sup>Zr sites.

343 XANES spectra have been measured along four diffusion profiles corresponding to the  
344 couple exchanges NZ/ZN, ZC/CZ, AZ/ZA, that all include a zirconium concentration gradient,  
345 and the couple exchange AN/NA to assess possible interactions between Zr, Al and Na. The  
346 apparent crystal field splitting and relative intensities indicate that Zr is mostly in an  
347 octahedral symmetry in all glasses and along all diffusion profiles. As the changes occurring in  
348 spectra are limited along a profile, we only plot the spectra of all glass couples in Fig. 4.b. Each  
349 spectrum was fitted using two pseudo-voigt functions in order to determine the evolutions of  
350 the energy positions and full widths at half maximum (FWHM) for both peaks. No change is  
351 observed in the energy position (not shown) but the FWHM is slightly changed along several  
352 profiles (Fig. 5). It is especially clear on the NZ/ZN and AN/NA diffusion couples (Fig. 5.a and  
353 Fig 5.b). The width of the peaks increases with increasing Zr or Al content and decreases with  
354 increasing Na content. It has been recognized that charge compensation of Zr and Al sites is  
355 preferentially achieved by Na rather than Ca (Angeli et al., 2010)(Cormier et al., 2000)(Quintas  
356 et al., 2009)(Quintas et al., 2017). The narrower peaks imply better defined Zr-sites that are  
357 present when more Na atoms are available. This probably results for a better charge  
358 compensation of Zr sites that are less distorted. Conversely, when the number of Al or Zr



359 atoms increase, a small Zr site deformation is observed, resulting from the competition  
 360 between Al and Zr for charge compensation by Na.

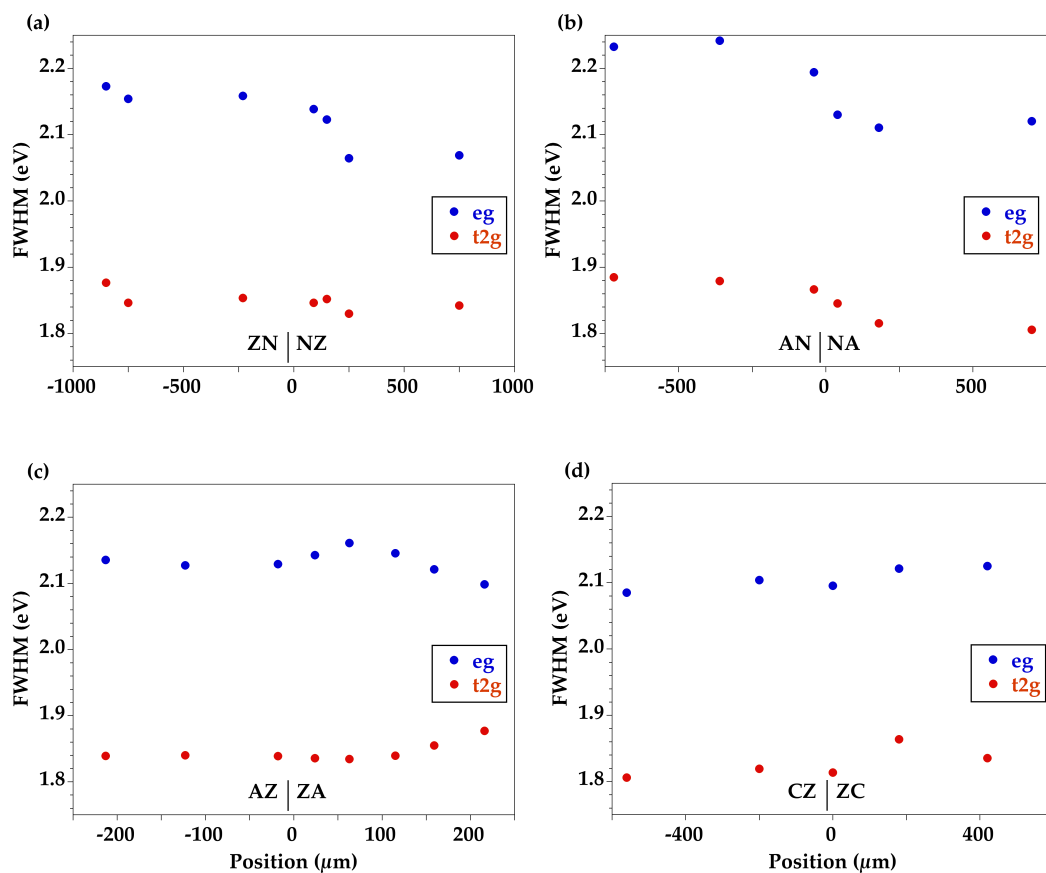
361



362

363 Fig. 4. Left: L<sub>3</sub> edge XANES references. Right: L<sub>3</sub> edge XANES spectra for studied coupled glass.

364



365

366

367 Fig. 5. Width at the middle height of Zr L<sub>3</sub>-edge XANES profiles, corresponding to Zr site  
368 deformation through t<sub>2g</sub> (first peak) and e<sub>g</sub> (second peak) energy position.

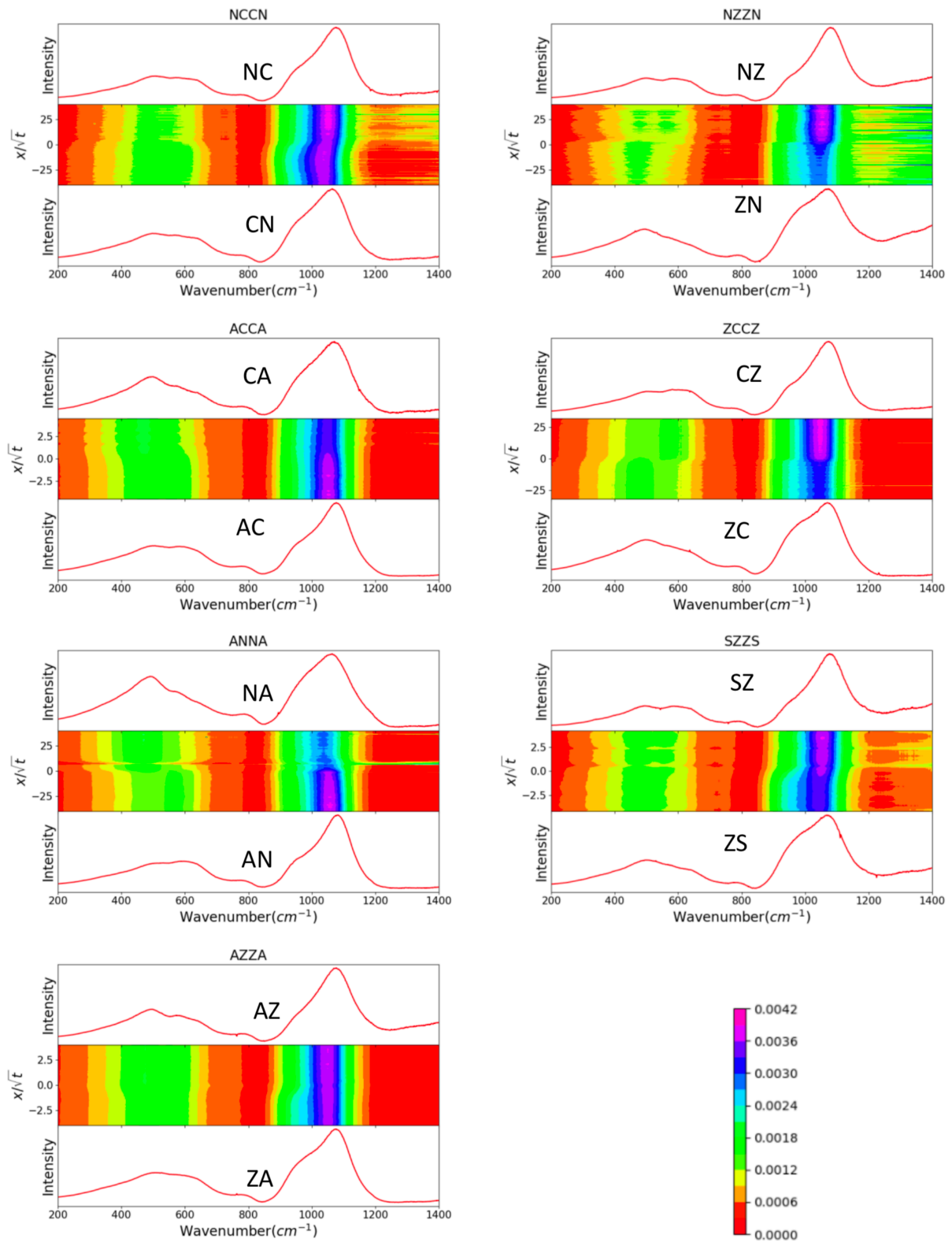
369

### 370 **3.3 Raman spectroscopy**

371 Raman spectra profiles were acquired on each diffusion profile and each glass couple  
372 endmember after diffusion during 20 min at 1250°C (Fig .6). In order to detect small variations  
373 along profiles, the Raman spectra have been plotted as measured intensity (color scale) for  
374 each wavenumbers (x axis) depending on position along the diffusion profile (y axis). These  
375 plots allow a comparison of the structural changes depending on the concentration profile.  
376 We can follow the modifications through recognition of some well-known Raman vibration  
377 bands according to literature. The position of these bands is given upon and below each  
378 colormap.

379 On the NC/CN profile (Fig. 6.a), when Ca content increases and Na content decreases,  
380 the band at 1100 cm<sup>-1</sup>, usually related to Q<sup>3</sup> units (with Q<sup>n</sup> corresponding to SiO<sub>4</sub> species with  
381 *n* bridging oxygens), decreases in intensity and the one at 980 cm<sup>-1</sup>, usually related to Q<sup>2</sup> units,  
382 increases in intensity (Schaller, 1999). These changes indicate a network depolymerization due  
383 to the introduction of Ca within the alumino-silicate network.

384



385

386 Fig. 6. Raman spectra intensity profiles acquired along diffusion profiles. Spectra of coupled  
 387 glass before diffusion are also plotted upon and above color map.

388

389 The structural modification due to Al exchange with a non-network former cation can  
390 be followed with the exchange AC/CA and AN/NA (Fig. 6.c and Fig. 6.e), respectively. In both  
391 cases, the  $Q^3$  unit band ( $1100\text{ cm}^{-1}$ ) intensity increases with Al content that indicates an  
392 increase in network connectivity. The Raman band in the  $400\text{-}800\text{ cm}^{-1}$  region are usually  
393 attributed to inter-tetrahedral T-O-T linkages (with T = Si/Al) (McMillan and Piriou,  
394 1982)(Mysen et al., 1982)(Neuville et al., 2004)(Petrescu et al., 2012). The aluminum exchange  
395 with both Ca and Na significantly impacts this region. The intensity of the band at  $480\text{ cm}^{-1}$   
396 that corresponds to Si-O-Si bending (Petrescu et al., 2012) decreases when Al content  
397 increases. At the same time, the intensity of the band at  $570\text{ cm}^{-1}$  increases and this band is  
398 attributed to the presence of Al-O-Al bridges (Neuville et al., 2006). Similar structural  
399 evolutions with compositions in aluminosilicates glasses have been previously reported and  
400 no major changes are observed due to the presence of 3 wt%  $\text{ZrO}_2$ .

401 Other profiles involving Zr exchange show common specific changes (Fig 6.b, d, f, g).  
402 We first detect a band appearing at  $980\text{ cm}^{-1}$  with increasing Zr content. Such a band has been  
403 observed in Zr-bearing glasses and it is attributed to Zr-O-Si stretching vibrations (Angeli et al.,  
404 2010). Some authors proposed that the Zr site is linked to  $Q^3(\text{Si})$  units in borosilicates (Quintas  
405 et al., 2017). At the same time, for ZN/NZ (Fig. 6.b), ZC/CZ (Fig. 6.d) and SZ/ZS (Fig. 6.f)  
406 exchange couples, the band at  $1100\text{ cm}^{-1}$  attributed to  $Q^3(\text{Si})$  linked with Na decreases in  
407 intensity with Zr content. In these exchanges, we expect that Zr diffusion is associated with a  
408 structural change as  $Q^3(\text{Si})\text{-Na}$  is replaced by  $Q^3(\text{Si})$  linked with Zr polyhedra. This structural  
409 reorganization implies a repolymerization of the alumino-silicate network. On the contrary,  
410 when zirconium is exchanged with aluminum (Fig 6.g), we do not observe any changes on the  
411  $Q^3(\text{Si})$  band. This seems to indicate that Zr and Al have a similar role in the glass structure. This  
412 conclusion is in agreement with our XANES results. The increase of the characteristic band of  
413 Al-O-Al at  $570\text{ cm}^{-1}$  is also observed when Al content increases.

## 414 4. DISCUSSION

### 415 4.1. Influence of zirconium on mobility in NCASZ glass

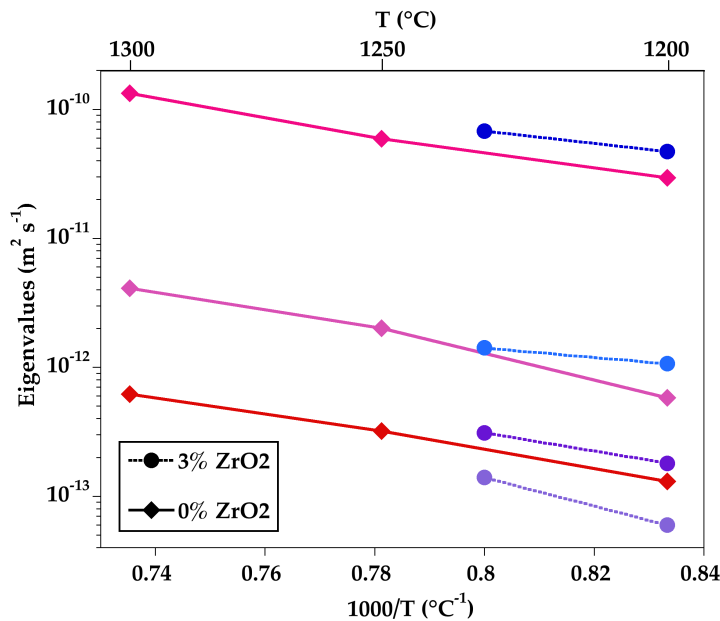
416 In order to rationalize the effect of Zr on chemical mobility in NCASZ glass, discussion  
417 will be based on a comparison of our results with previous ones obtained in the NCAS system  
418 with similar compositions. Considering the eigenvectors determined in NCAS and NCASZ  
419 (Table 4), addition of  $\text{ZrO}_2$  does not strongly modify the two main eigenvectors that are  $V_1$  and  
420  $V_2$ . Indeed, influence of zirconium is weak and more related to minor eigenvectors such as  $V_3$   
421 and  $V_4$ . The eigenvalues of NCASZ are roughly 262 times lower for  $V_3$  compared to  $V_1$ . The  
422 observation of the same eigenvectors for NCAS and NCASZ glasses allows a comparison of the  
423 eigenvalues for the two systems for different temperatures (Fig. 7). At the same temperature  
424 ( $1200^\circ\text{C}$ ), the eigenvalues corresponding to the first and second eigenvectors are higher by  
425  $\sim 1.6$  factor for  $V_1$  and 1.84 factor for  $V_2$  when 3 wt%  $\text{ZrO}_2$  is added, which indicates that  
426 diffusion along these eigenvectors is accelerated by the addition of  $\text{ZrO}_2$ . As far as we know,  
427 this phenomenon has not been observed previously. However, a recently published study  
428 (Zhang et al., 2018) showed that a small amount of  $\text{ZrO}_2$  in  $2\text{SiO}_2\text{-Na}_2\text{O}$  binary glasses increases  
429 Na mobility in terms of ionic conductivity in the temperature range of  $200\text{-}400^\circ\text{C}$ . Our present  
430 study could reflect the same phenomenon with chemical potentials and not electrical

431 potentials as driving forces. This result is counterintuitive if we consider diffusivity related to  
 432 viscosity variation as stated in the Eyring model (Eyring, 1936):

$$433 \quad D^E = \frac{k_B T}{\eta d} \quad (3)$$

434 where  $\eta$  is the melt viscosity, and  $d$  is a typical jump distance corresponding to a diffusive step.  
 435  $d$  is usually taken as the oxygen-oxygen interatomic distance  $d = 2.8 \text{ \AA}$  (Lesher, 2010)(Ni et al.,  
 436 2015)(Zhang et al., 2010). Concerning  $\eta$ , we used the measured viscosity values for NCAS  
 437 (Claireaux et al., 2016), and our own measured viscosity data for NCASZ (Fig. S1 in the  
 438 Supplementary file). As expected, due to the large bond strength of the Zr-O bond, addition  
 439 of  $\text{ZrO}_2$  increases viscosity. The diffusion coefficients derived from Eq. 3 (Fig. 8) match self-  
 440 diffusivities of network formers in high temperature melts (Zhang et al., 2010). The solid lines  
 441 are the Eyring diffusion coefficients for NCAS endmembers while the dotted lines represent  
 442 the diffusion coefficients for the same NCAS with 3 wt%  $\text{ZrO}_2$ . We observe (Fig. 8) that adding  
 443  $\text{ZrO}_2$  decreases Eyring diffusivities of all network formers. For example the AN value of  
 444 diffusivity is always higher than the  $\text{AN}_{\text{Zr}}$  value of the same glass with  $\text{ZrO}_2$ . In conclusion, if  
 445 diffusion is ruled by viscosity only, the diffusivity should decrease as  $\text{ZrO}_2$  content increases.

446



447

448 Fig. 7. Eigenvalues obtained for diffusion matrix and corresponding to the exchange reactions.  
 449 The dotted lines with circles are the eigenvalues of this study when the triangles correspond  
 450 to the values in Claireaux et al. (Claireaux et al., 2016, 2019) for higher temperatures.

451

452 In order to understand this contradiction that diffusivity of some elements increase  
 453 with viscosity, we correlate structural changes with diffusion paths. To this purpose, the  
 454 eigenvectors (Table 4) can be interpreted as exchange reactions between ions (Chakraborty  
 455 et al., 1995a) and we convert weight concentration in Table 4 to mole concentration in the  
 456 following equations. This conversion results in the following reactions:

457 
$$V_1 = 1.1CaO \leftrightarrow 0.95Na_2O \quad (4)$$

458 
$$V_2 = 1.1CaO \leftrightarrow 0.8SiO_2 + 0.1Al_2O_3 \quad (5)$$

459 
$$V_3 = 0.9 SiO_2 + 0.7CaO \leftrightarrow 0.65Al_2O_3 + 0.2ZrO_2 + 0.15Na_2O \quad (6)$$

460 
$$V_4 = 0.5 ZrO_2 + 0.3CaO \leftrightarrow 0.6Al_2O_3 + 0.2SiO_2 + 0.15Na_2O \quad (7)$$

461 The first reaction (Eq. 4) can be easily interpreted as an exchange of non-network  
 462 formers in the melt structure. This exchange was observed repeatedly in previous studies  
 463 (Claireaux et al., 2016)(Trial and Spera, 1994). This reaction has also the highest eigenvalue,  
 464 indicating that it is the fastest homogeneous melt reaction. This is consistent with the high  
 465 mobility of alkalis and alkaline earths in melts compared to network formers (Si, Al and Zr in  
 466 the present case).

467

468 Table 2. Diffusion matrix obtained separately for temperatures at 1200°C and 1250°C with SiO<sub>2</sub>  
 469 as dependent component. Coefficient are given in 10<sup>-12</sup>m<sup>2</sup>.s<sup>-1</sup>. Errors on the values are less  
 470 than 5% (Claireaux et al., 2019).

471

	1200°C				1250°C			
	Na <sub>2</sub> O	CaO	ZrO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO	ZrO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Na <sub>2</sub> O	45.35	-0.52	0.02	-6.85	65.57	-0.75	0.04	-9.87
CaO	-48.44	1.69	0.24	7.89	-67.03	2.24	2.39	1.12
ZrO <sub>2</sub>	-0.63	-0.09	0.04	0.05	-0.88	-0.10	0.14	0.11
Al <sub>2</sub> O <sub>3</sub>	-1.36	-0.12	0	0.22	-1.9	-0.13	0.07	0.47

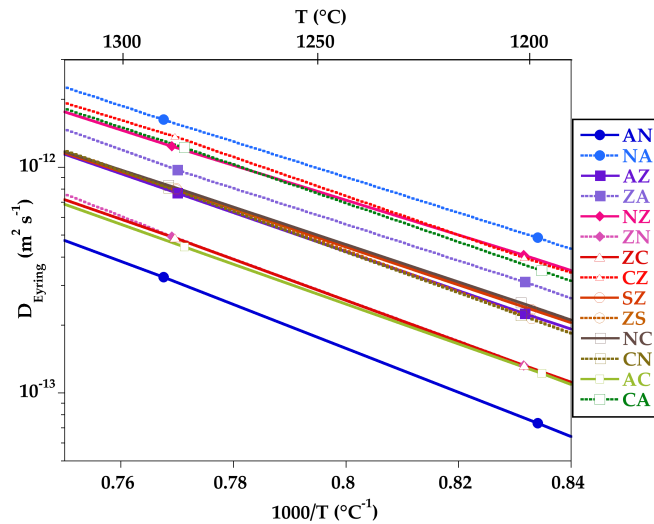
472

473 Table 3. Eigenvectors and eigenvalues (10<sup>-12</sup>m<sup>2</sup>.s<sup>-1</sup>) obtained by fitting experimental data  
 474 separately for temperatures at 1200°C and 1250°C in independent eigenbasis.

	NCASZ – 1200°C				NCASZ – 1250°C			
	V1	V2	V3	V4	V1	V2	V3	V4
Na <sub>2</sub> O	-0.97	-0.06	0.18	-0.15	-0.82	-0.04	0.08	-0.06
CaO	1	1	-0.59	0.13	1	1	-0.71	0.22
ZrO <sub>2</sub>	0.02	-0.03	0.09	1	-0.02	0.10	0.45	1
Al <sub>2</sub> O <sub>3</sub>	0.05	-0.15	1	-0.78	-0.01	-0.17	1	-0.69
SiO <sub>2</sub>	-0.1	-0.75	-0.68	-0.19	-0.17	-0.76	-0.83	-0.46
α <sup>1200</sup>	38.2	0.83	0.12	0.06				
α <sup>1250</sup>					65.41	1.39	0.32	0.13

475

476



477

478 Fig. 8. Eyring diffusivity for different NCASZ endmembers with  $ZrO_2$  (dash line) and without  
 479  $ZrO_2$  (solid line).

480

481 Table 4. Eigenvectors and eigenvalues ( $10^{-12}m^2.s^{-1}$ ) obtained by fitting experimental data for  
 482  $1200^\circ C$  and  $1250^\circ C$  in common eigenbasis for NCASZ and given by Claireaux et al.(Claireaux et  
 483 al., 2016) for NCAS.

	NCASZ				NCAS		
	V1	V2	V3	V4	V1	V2	V3
<b>Na<sub>2</sub>O</b>	-0.96	0.06	0.14	-0.14	1	0.02	-0.15
<b>CaO</b>	1	1	-0.69	0.25	-0.92	1	0.98
<b>ZrO<sub>2</sub></b>	0.00	-0.02	0.39	1	X	X	X
<b>Al<sub>2</sub>O<sub>3</sub></b>	0.05	-0.15	1	-0.96	0.02	-0.47	-1
<b>SiO<sub>2</sub></b>	-0.09	-0.89	-0.84	-0.14	-0.09	-0.52	0.17
<b><math>\alpha^{1200}</math></b>	47.20	1.07	0.18	0.06	29.5	0.58	0.13
<b><math>\alpha^{1250}</math></b>	67.69	1.42	0.31	0.14			
<b><math>\alpha^{1280}</math></b>					59.1	2.01	0.32
<b><math>\alpha^{1360}</math></b>					133	4.1	0.62

484

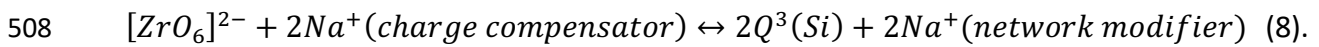
485

486 The second reaction (Eq. 5) is an exchange between a non-network former (Ca) and  
 487 network formers (Si and Al). The same reaction has been evidenced in CAS (Liang et al., 1996a)  
 488 and NCAS (Claireaux et al., 2016) but with different stoichiometric numbers for Al and Si.  
 489 Addition of Zr in NCAS tends to increase the number of Si exchanged with Ca. The  
 490 corresponding eigenvalue is also higher in NCASZ compared to NCAS.

491 The third reaction (Eq. 6) describes the exchange of alumina for silica which is  
 492 accompanied by an associated flux of Na and Ca cations. This reaction was also observed in  
 493 the NCAS system (Claireaux et al., 2016). However, the corresponding stoichiometric numbers  
 494 are different and, in the present case, there is also a minor amount of Zr that is involved in the

495 exchange for Si and Ca. The fourth reaction (Eq. 7) is the major reaction involving Zr. It  
 496 corresponds to the exchange of Zr for Al and a minor Si amount, with again including Ca and  
 497 Na cations. Furthermore, it has the smallest eigenvalue and highest uncertainty. Thereby,  
 498 there is a minor influence of this exchange on the overall diffusion processes.

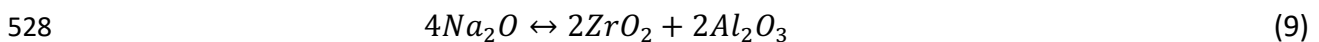
499 If now we consider the observed structural behavior of each element in the melt  
 500 structure along the diffusion profile, we can better understand the propensity of Zr to  
 501 accelerate Na mobility in the reaction V<sub>1</sub>. Indeed [ZrO<sub>6</sub>]<sup>2-</sup> octahedra preferentially need to be  
 502 charge compensated by nearby Na<sup>+</sup> atoms (Angeli et al., 2010)(Cormier et al., 2000)(Quintas  
 503 et al., 2017). According to Raman spectra along diffusion profiles (Fig 6), the number of Q<sup>3</sup>(Si)  
 504 decreases when ZrO<sub>2</sub> is exchanged with SiO<sub>2</sub> (Fig 6.f). Consequently, as a ZrO<sub>6</sub> octahedra is  
 505 formed, two Na<sup>+</sup> cations initially close to a non-bridging oxygen belonging to a Q<sup>3</sup> species (role  
 506 of network modifier) move near a Zr atom to ensure charge compensation of the [ZrO<sub>6</sub>]<sup>2-</sup> site.  
 507 The overall behavior can be described as:



509 To our knowledge, no data exist on Na-O bond lengths when Na is charge  
 510 compensating [ZrO<sub>6</sub>]<sup>2-</sup>. However, concerning other negatively charged polyhedra ([AlO<sub>4</sub>]<sup>-</sup>,  
 511 [BO<sub>4</sub>]<sup>-</sup>), the Na-O distance is generally larger when Na is charge compensator rather than  
 512 network modifier (Angeli et al., 2010). The electrostatic binding energy of alkali being inversely  
 513 proportional to the Na-O distance (Greaves and Ngai, 1995), a shorter Na-O distance implies  
 514 a deeper depth of the Coulomb well and important trapping of alkalis that consequently  
 515 reduces their mobility. Indeed, the negative charge that Na<sup>+</sup> cations compensate as a network  
 516 modifier is spatially localized for a NBO on a Q<sup>n</sup> species and more delocalized for a [ZrO<sub>6</sub>]<sup>2-</sup> site.  
 517 Na<sup>+</sup> cations in charge compensating role are less trapped near [ZrO<sub>6</sub>]<sup>2-</sup> site than Na<sup>+</sup> cations  
 518 near NBOs, which could lower the activation energy for diffusive step and increase mobility of  
 519 Na<sup>+</sup> in presence of Zr, inducing an enhancement of Na-Ca exchange ratio.

## 520 **4.2. Validation of matrix diffusion model in the initial composition field**

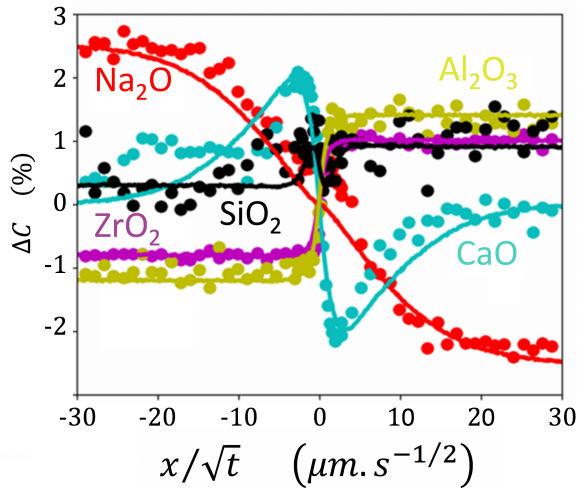
521 The matrix diffusion model has only been determined from binary exchanges. In  
 522 geological and industrial domains of interest, multicomponent diffusion often involves more  
 523 than two composition gradients. To examine the predictive capabilities of our eigenvectors  
 524 and eigenvalues, additional experiments have been performed for a more complex  
 525 composition change. The exchange of three oxides, Na<sub>2</sub>O, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, has been considered  
 526 between two glasses corresponding to the following equation in weight%. It correspond to an  
 527 exchange between NA and ZN glasses (Table 1) :



529 Fig. 9 shows the diffusion exchange between these two glasses at 1200°C for 20 min. The  
 530 calculations deduced from the diffusion matrix (solid line) are in very good agreement with  
 531 EPMA experiments (dotted line). This result indicates that the diffusion matrix can be  
 532 successfully used to predict diffusion exchanges. The prediction error is comparable with  
 533 fitting errors. Additionally, we also observe that the CaO diffusion profile contains an uphill  
 534 diffusion appearing with both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> having small concentration gradients.

535





536

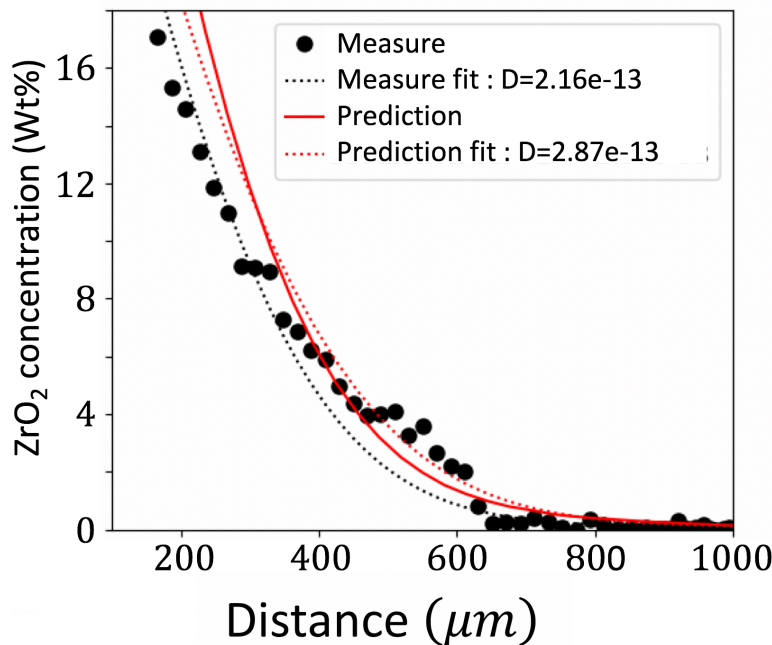
537 Fig. 9. Diffusion experiment at 1200°C for 20 min between NA and ZN glass. Solid lines  
 538 represent the predicted diffusion profile when the dots are related to EMPA measurements.

539

#### 540 4.3. Diffusion at the crystal-melt interface

541 The test of the diffusion matrix is also pursued far outside the composition field  
 542 centered around  $C_0$ . Doing that, we consider that a change in fully accounts for diffusivities in  
 543 the entire NCASZ phase diagram. It is certainly not valid for all compositions but it allows us  
 544 to get a good estimation of diffusion processes.

545



546

547 Fig. 10. Diffusion exchange for 40.5 h at 1250°C between  $ZrSiO_4$  and G1 (Table 1). The dots  
 548 represent the EMPA measures when the cyan triangle represents the prediction. The red solid  
 549 line is the  $D(Zr)$  obtained through experimental profile fit with eq. 10.

550

551 We were interested in the interaction of crystals with highly viscous melts to reproduce  
552 partial dissolution of a mineral. Zircon crystal ( $ZrSiO_4$ ) was investigated and behaves as an  
553 infinite reservoir for Zr. The glass in contact with the crystal is a Zr-free NCAS glass of  
554 composition G1 (Table 1).

555 We investigated Zr diffusivity that should control crystal dissolution (and crystal  
556 growth) due to the slow Zr diffusion (Bindeman and Melnik, 2016). The diffusion matrix has  
557 been used to predict Zr diffusion from zircon crystal towards the G1 glass. A diffusion  
558 experiment has also been performed to compare with the matrix predictions. The experiment  
559 takes place at 1250°C for 40.5 hours. Composition profiles have been acquired with EPMA. In  
560 order to make our results comparable with previous studies, the predicted profiles of  $ZrO_2$   
561 calculated using the diffusion matrix have been fitted with the equation usually used for  
562 simple diffusion coefficient determination (Zhang et al., 1989):

563 
$$\frac{C - C_\infty}{C_{zircon} - C_\infty} = \text{erfc}\left(\frac{x}{2\sqrt{Dt}} - a\right) / \text{erfc}(-a) \quad (10)$$

564 and the parameter  $a$  satisfies the relation:

565 
$$\frac{C_{zircon} - C_\infty}{C_s - C_0} = \sqrt{\pi} a e^{a^2} \text{erfc}(-a) \quad (11)$$

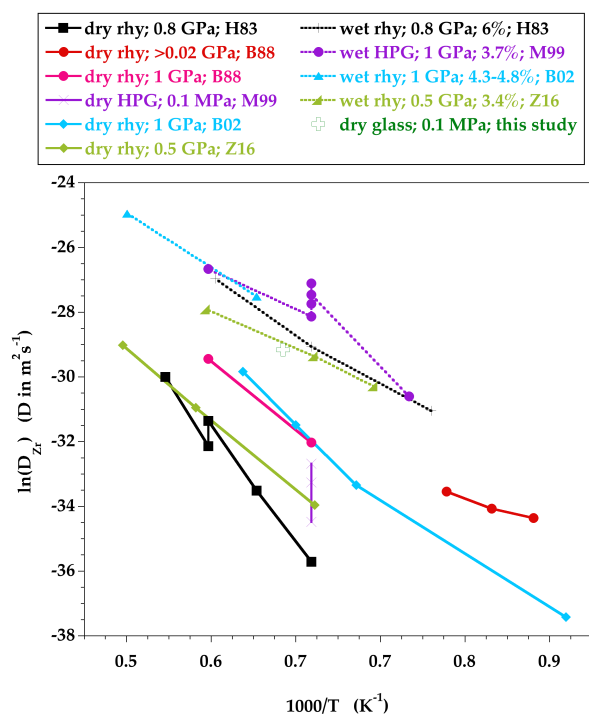
566

567  $C_{zircon}$  represents the initial concentration in the crystal,  $C_s$  corresponds to saturation  
568 concentration in glass at the interface and  $C_\infty$  represents the studied element concentration  
569 far from the interface.

570 Fig. 10 presents the diffusion profile of  $ZrO_2$  from zircon towards G1 glass. Both  
571 calculations and experiments show similar behaviors: the Zr concentration in the melt is  
572 highest at the immediate boundary with the crystal and decreases with increasing distance  
573 from the crystal.

574 The rate of Zr diffusion is described by the apparent diffusion coefficient  $D(Zr)$  in the  
575 melt that can be calculated using Eq.10 for both the EPMA measurements and the matrix  
576 predictions. The  $D(Zr)$  obtained from EPMA profile is  $2.16 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$ . This value can be  
577 compared to the one extracted from the matrix predictions:  $2.87 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$ . Matrix  
578 predictions and EPMA experiments differ roughly by a factor of 1.30. The diffusion matrix  
579 overestimates the diffusion coefficient. This discrepancy could be partially due to the large  
580 viscosity gradient along the diffusion profile that is not taken into account in our diffusion  
581 model determined in a very limited composition field. Along a diffusion profile, we expect that  
582 there is no change in the exchange reaction (eigenvectors) but the eigenvalues will be  
583 affected.

584



585

586 Fig. 11. Diffusion coefficient of zirconium determined in previous studies for different  
 587 pressure, water content (dry = solid line) and composition. rhy legend correspond to a rhyolitic  
 588 melt when HPG is related to basaltic one : HW83(Harrison and Watson 1983); BW88 (Baker  
 589 and Watson 1988), M99 (Mungall et al 1999); B02 (Baker et al 2002); Z16 (Zhang et al 2016).  
 590 The current study is also represented.

591

592 We then compare our predicted coefficients with previous studies (Fig. 11). We did not  
 593 represented our experimental values of  $D(\text{Zr})$  because values would be superimposed with  
 594 predicted ones. Due to the variable compositions, water contents and pressures between our  
 595 study and the classical geological ones, large differences may occur between the different  
 596  $D(\text{Zr})$  coefficients. Nevertheless, two groups tend to appear, reflecting mainly the very strong  
 597 influence of water content on  $D(\text{Zr})$ . Zr diffusion coefficients are systematically higher for  
 598 hydrous melts, due to the formation of hydroxyls and non-bridging oxygens resulting in an  
 599 increase ability to create charge-balanced polyhedra (Freda and Baker, 1998). Surprisingly, the  
 600  $D(\text{Zr})$  values obtained in the present study are close to those for the hydrous melts group  
 601 though G1 is a dry glass. However, G1 glass contains a significant  $\text{Na}^+$  content contrary to  
 602 geological glasses in Fig. 11. Those  $\text{Na}^+$  cations may play the same role as protons  $\text{H}^+$  and  
 603 increase diffusion in our system, shifting our  $D(\text{Zr})$  value from the dry to the hydrated group.  
 604 A similar mechanism for diffusion, requiring no readjustments of the network topology, has  
 605 been proposed for water and alkalis by Mungall (Mungall, 2002), pointing to the parallel  
 606 behavior for  $\text{Na}^+$  and  $\text{H}^+$  cations.

607

## 5. Conclusion

608 Using diffusion-couple experiments, the diffusion matrix was determined in a Zr-  
609 bearing NCAS glass at 1200°C and 1250°C. The studied system is centered on the composition  
610  $C_0$ ,  $66.4\text{SiO}_2$ - $13.3\text{Na}_2\text{O}$ - $11.95\text{CaO}$ - $6.8\text{Al}_2\text{O}_3$ - $1.55\text{ZrO}_2$  (NCASZ). A strong coupling between  
611 sodium and calcium has been evidenced. A CaO uphill diffusion was showed when  $\text{ZrO}_2$  is  
612 exchanged with  $\text{Na}_2\text{O}$ . This uphill diffusion was already well known when  $\text{Al}_2\text{O}_3$  is exchanged  
613 with  $\text{Na}_2\text{O}$ . Diffusion matrices have been interpreted using their eigenvalues and eigenvectors.  
614 The eigenvectors determined in the present study are remarkably similar to those obtained  
615 previously for a similar system without  $\text{ZrO}_2$  (Claireaux et al., 2016). On the contrary,  
616 eigenvalues are different and reveal higher eigenvalues for NCASZ for at least the two main  
617 exchanges, suggesting that a small amount of  $\text{ZrO}_2$  in melts tends to increase diffusivity. It is  
618 surprising that Zr increases diffusivity and viscosity in melts because those two characteristics  
619 show usually opposite trends. Indeed, the diffusion coefficients of network formers calculated  
620 from measured viscosity through Eyring relation indicate that adding zirconium should  
621 decrease the diffusion coefficients.

622 Our structural study, coupled with our diffusion one, helped us to understand this  
623 phenomenon. Using X-ray absorption spectroscopy (XANES), Zr atoms are determined to be  
624 in 6-fold coordinated sites,  $[\text{ZrO}_6]^{2-}$ , in NCASZ glass and these sites are preferentially charge  
625 compensated by  $\text{Na}^+$ . XANES spectra also reveal a competition between  $[\text{AlO}_4]^-$  and  $[\text{ZrO}_6]^{2-}$   
626 for charge compensation by  $\text{Na}^+$ . Raman spectroscopy gave further structural insights,  
627 showing that adding  $\text{ZrO}_2$  yields a decrease of the number of  $\text{Q}^3(\text{Si})$  units. This decrease is  
628 correlated to the increase of  $[\text{ZrO}_6]^{2-}$  sites, which indicates a structural change in the role of  
629  $\text{Na}^+$ . Initially associated with the non-bridging oxygen of  $\text{SiO}_4$  polyhedra,  $\text{Na}^+$  becomes  
630 associated with  $[\text{ZrO}_6]^{2-}$  sites as charge compensator. The increase of diffusivity may be  
631 partially explained by the weak Na-O bond strength when  $\text{Na}^+$  atoms charge compensate  
632  $[\text{ZrO}_6]^{2-}$  polyhedra compare to Na-NBO bond strength. Indeed, activation energy should be  
633 lower for Na displacement when it has weaker bond.

634 Finally we compare the applicability of our diffusion matrix to more general cases, far  
635 from the composition field for which the diffusion matrix has been determined. We were able  
636 to estimate the diffusion coefficient of zirconium with an error factor of 1.3 which is  
637 reasonable considering the large extent of  $D(\text{Zr})$  values found in literature.

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645

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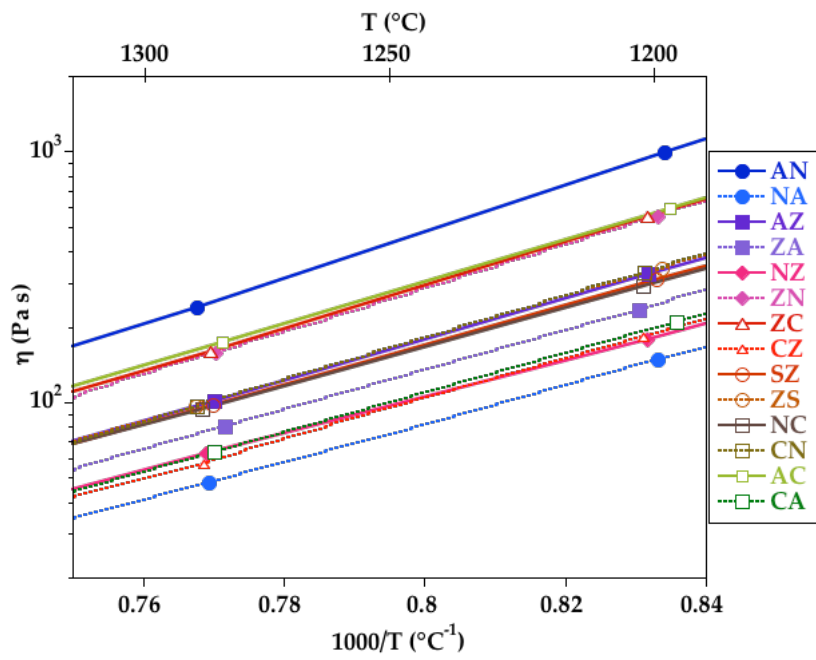
## SUPPLEMENTARY INFORMATION

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821 Fig. S1. Viscosity of end-member melts obtained from rotating-cylinder viscometry.  
822 Experimental points (symbols) are fitted with a Vogel–Fulcher–Tammann law.

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828 Table S1. List of experiments and experimental diffusion conditions.

	M <sub>1</sub>	M <sub>2</sub>	T(°C)	t
Exp 1	AC	CA	1200-1250	20min
Exp 2	NA	AN	1200-1250	20 min
Exp 3	ZA	AZ	1200-1250	20 min
Exp 4	NC	CN	1200-1250	20 min
Exp 5	NZ	ZN	1200-1250	20 min
Exp 6	CZ	ZC	1200-1250	20 min
Exp 7	SZ	ZS	1200-1250	20 min
Exp 8	NA	ZN	1200	20 min
Exp 9	ZrSiO <sub>4</sub>	G1	1250	40.5 h

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830 Table S2. Interface (average) compositions of each diffusion couple (weight%).

	Na <sub>2</sub> O	CaO	ZrO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
C <sub>0</sub>	12.9	10.5	3	10.9	62.50
AC-CA	12.4	10.00	2.65	11.35	64.70
AN-NA	11.85	10.45	2.70	11.8	63.10
AZ-ZA	12.35	9.7	2.55	10.95	61.35
NC-CN	12.35	11.64	2.75	11.65	60.7
NZ-ZN	12.35	9.5	2.70	11.40	63.50
ZC-CZ	12.85	11.25	2.75	11.50	61.90
SZ-ZS	12.05	9.75	2.65	11.20	63.75
Average	12.39	10.35	2.72	11.34	62.69
Standard deviation	0.36	0.77	0.13	0.32	1.33

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