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Atomic mobility in calcium and sodium aluminosilicate melts at 1200°C

Corinne Claireaux^a, Marie-Hélène Chopinet^a, Ekaterina Burov^a, Emmanuelle Gouillart^a, Mathieu Roskosz^b,
Michael J. Toplis^c

^aSurface du Verre et Interfaces (UMR 125), CNRS/Saint-Gobain Recherche, 39 quai Lucien Léfranc, 93300 Aubervilliers, France

^bMuséum National d'Histoire Naturelle, Institut de Minéralogie, de physique de la matière condensée et de cosmochimie, Sorbonne University, Paris, France

^cLaboratoire Dynamique Terrestre et Planétaire (UMR 5562), Observatoire Midi-Pyrénées, 14 avenue Belin, Toulouse, 31400, France

Abstract

Multicomponent chemical diffusion in liquids of the quaternary system CaO–Na₂O–Al₂O₃–SiO₂ has been studied. Diffusion-couple experiments were performed at 1200°C and for different durations around a central composition of 64.5 wt%SiO₂, 13.3 wt%Na₂O, 10.8 wt%CaO, 11.4 wt%Al₂O₃, leading to an overconstrained system of equations that was used to determine the diffusion matrix of the system. The dominant eigenvector of the diffusion matrix was found to correspond to the exchange between sodium and calcium, consistent with the results of the ternary soda-lime silica system. On the other hand, neither of the other two eigenvectors of the diffusion matrix of the quaternary system involve sodium. Given a factor of 50 between the dominant and second eigenvalue, diffusion couples involving the exchange of sodium oxide and a network-forming oxide result in strong uphill diffusion of calcium. The second eigenvector, corresponding to the exchange of calcium with silicon and aluminum, is close to the dominant eigenvector found in previous studies of ternary alkaline-earth aluminosilicate systems. Our results therefore suggest that simple systems may be used to understand diffusive mechanisms in more complex systems.

1. Introduction

Chemical diffusion in silicate and aluminosilicate melts plays a key role in mass transfer processes of importance in the Earth and planetary sciences, as well as in applied fields such as industrial glass making (Schaeffer, 1984). Diffusive mechanisms involved in crystal-melt interactions have been studied both for mineral dissolution (Edwards and Russell, 1996; Liang, 1999; Acosta-Vigil et al., 2002, 2006; Chen and Zhang, 2008), refractory corrosion (Samaddar et al., 1964; Oishi et al., 1965; Sandhage and Yurek, 1990) or crystal nucleation and growth (Roskosz et al., 2005, 2006). In addition, the link between diffusive and viscous transport has received considerable attention (Mungall, 2002; Njiokepe et al., 2008; Ni et al., 2015), and diffusion has also been shown to influence isotope fractionation (Richter et al., 1999, 2008), onset of boundary layer convection (Spera et al., 1984; Liang et al., 1994), melt oxidation (Cooper et al., 1996; Smith and Cooper,

2000; Behrens and Stelling, 2011) and phase separation (Mazurin and Porai-Koshits, 1984).

The multicomponent nature of chemical diffusion is a key element of diffusion in silicate melts, as underlined by phenomena such as uphill diffusion (Liang et al., 1996a) or the mixed-alkali effect (Imre et al., 2002). In a polymerized silicate or aluminosilicate network, the common picture of random jumps of individual particles converts to consideration of cooperative rearrangements that involve several species (Mungall, 2002). Although effective binary diffusion coefficients may provide a convenient representation of some diffusive mechanisms, a more thorough description is provided by the *diffusion matrix* (Zhang, 2010; Liang, 2010), that links the flux of a given element to all the independent concentration gradients. The eigenvectors of the diffusion matrix provide a macroscopic indication of the exchange chemistry that dominates at the microscopic level, while the associated eigenvalues provide an indication of the relative frequencies of those exchanges (Zhang, 2010; de Koker and Stixrude, 2010).

Due to the large amount of experimental data required, studies that determine the complete diffusion matrices in silicate melts represent a small

Email address:

emmanuelle.gouillart@saint-gobain.com (Emmanuelle Gouillart)

44 fraction of the large body of literature that exists
 45 concerning diffusion in molten silicates. Of those
 46 studies, work has concentrated on $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$,
 47 a simplified system of wide geological interest (Liang
 48 and Davis, 2002; Liang et al., 1996b; Oishi et al.,
 49 1982; Sugawara et al., 1977). Other studies in
 50 ternary systems have been performed in the sys-
 51 tems $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Kress and Ghiorso, 1993;
 52 Richter et al., 1998), $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Chakraborty
 53 et al., 1995a,b) and $\text{SrO}-\text{SiO}_2-\text{K}_2\text{O}$ (Varshneya and
 54 Cooper, 1972) and in $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ (Wakabayashi
 55 and Oishi, 1978; Trial and Spera, 1994), a soda-
 56 lime composition of interest to glass-makers. Very
 57 few studies have addressed more complex systems,
 58 exceptions being $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Kress
 59 and Ghiorso, 1993; Richter et al., 1998) and
 60 $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ (Mungall et al.,
 61 1998). Surprisingly, no aluminosilicate composition
 62 containing both alkali and alkaline earth has been
 63 explored to determine its diffusion matrix, despite the
 64 fact that geological melts contain aluminum as well
 65 as alkali and alkaline-earth elements, and despite the
 66 industrial interest of the $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$
 67 system. Furthermore, the link between preferential
 68 exchanges expressed by eigenvectors in simplified
 69 (such as ternary) systems, and exchanges in more
 70 complex systems, remains to be studied.

71 The objective of this work is to determine the diffu-
 72 sion matrix of the quaternary $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$
 73 system, in the peralkaline domain. From the diffusion
 74 matrix, we aim at deriving its eigenvectors in order to
 75 understand diffusive transport in this quaternary system,
 76 and to compare its eigenspaces with other silicate and
 77 aluminosilicate systems.

78 2. Theoretical background on chemical diffusion

79 A description of the formalism of multicompo-
 80 nent chemical diffusion can be found in several refer-
 81 ences (Gupta and Cooper, 1971; Trial and Spera, 1994;
 82 Brady, 1995; Zhang et al., 2010; Liang, 2010). We re-
 83 produce the main arguments here, for the sake of com-
 84 pleteness.

85 *Self-diffusion* -. Chemical diffusion of a single species,
 86 often considered to be a dilute tracer inside a matrix, is
 87 described by Fick's first law

$$88 \quad \mathbf{j} = -D\nabla C, \quad (1)$$

89 that proposes a linear relation between the flux \mathbf{j} and
 the concentration gradient ∇C . The linear coefficient D

90 is called the diffusion coefficient or diffusivity of the el-
 91 ement. Fick's first law can be derived from microscopic
 92 principles, by computing the flux of individual partic-
 93 les (atoms, ions, molecules...) subject to thermally-
 94 activated random motion. Assuming that diffusion is the
 95 only source of local concentration changes, i.e. in the
 96 absence of convection (Richter et al., 1998) or chemical
 97 reaction (Cooper et al., 1996; Smith and Cooper, 2000),
 98 and that the diffusion coefficient does not vary with the
 99 concentration of the species, one obtains Fick's second
 100 law:

$$\frac{\partial C}{\partial t} = D\nabla^2 C, \quad (2)$$

also known as the diffusion equation. In sili-
 cate melts, diffusion of single species has been mea-
 sured (Jambon and Carron, 1976; Jambon, 1982; Liang
 et al., 1996a; LaTourrette et al., 1996; Zhang et al.,
 2010; Leshner, 2010; Wu et al., 2012) and mode-
 led (Mungall, 2002; Zhang, 2010) for a large variety
 of compositions and elements.

Diffusion matrix-. The motion of species in silicate
 melts depends on their environment, so that a complete
 description of diffusion has to take into account cou-
 plings between species. For a mixture of n species, such
 couplings may be described by a *diffusion matrix*, that
 extends Fick's first law to its vectorial formulation:

$$\mathbf{j} = -\mathbf{D}\nabla\mathbf{C}, \quad (3)$$

where $\mathbf{C} = (C_1, \dots, C_n)$ is the vector of local con-
 centrations, $\mathbf{j} = (\mathbf{j}_1, \dots, \mathbf{j}_n)$ represents the fluxes, and \mathbf{D}
 is the $n \times n$ diffusion matrix. With this formalism, the
 flux of one species depends on the gradient of all com-
 ponents:

$$\mathbf{j}_i(\mathbf{x}) = - \sum_k D_{ik} \nabla C_k(\mathbf{x}). \quad (4)$$

A more complex formulation could include even
 more components than the n chemical concentrations,
 for example by distinguishing between the possible spe-
 ciations of network formers, that influence the local dis-
 placement of ions. Nevertheless, since chemical con-
 centrations are more easily accessed with a good spatial
 resolution than other quantities, only chemical concen-
 trations are usually considered as components.

Furthermore, it is possible to reduce the dimension-
 ality of the diffusion matrix for systems satisfying the
 conservation of mass. If the C_i are mass concentrations,

130 and if we neglect variations of density with composition
131 (an approximation that will be made here), then

$$\sum_i C_i(\mathbf{x}) = 100. \quad (5)$$

132 Taking the spatial derivative of the above equation re-
133 sults in

$$\sum_i \nabla C_i(\mathbf{x}) = 0. \quad (6)$$

134 Because of the above constraint, the gradient vector
135 $\nabla \mathbf{C}$ belongs to a hyperspace of dimension $n - 1$. Since
136 \mathbf{D} can only be measured through its effect on $\nabla \mathbf{C}$, it is
137 only possible to measure $(n - 1) \times (n - 1)$ independent
138 coefficients of \mathbf{D} . Therefore, \mathbf{D} is often defined as an
139 $(n - 1) \times (n - 1)$ matrix. The n^{th} species is considered to
140 be dependent on the others; it is usually chosen among
141 network formers, that are less mobile, although formally
142 any species can be chosen as the dependent one.

143 Finally, a vector formulation of Fick's second law is
144 obtained, under the assumption that \mathbf{D} is independent of
145 concentrations

$$\frac{\partial \mathbf{C}}{\partial t} = \mathbf{D} \nabla^2 \mathbf{C}. \quad (7)$$

146 *Measuring the diffusion matrix* -. The diffusion ma-
147 trix is typically computed from 1-D diffusion experi-
148 ments between two melts of different initial composi-
149 tions, with a flat interface. At $t = 0$, the concentration
150 gradient is therefore nonzero only at the interface be-
151 tween the two liquids:

$$\nabla \mathbf{C} = \Delta \mathbf{C} \delta(x), \quad (8)$$

152 where $\Delta \mathbf{C}$ is the step of concentration between the
153 two slabs, the interface is taken at $x = 0$, and

$$\delta(x) = \begin{cases} 1 & \text{if } x = 0 \\ 0 & \text{if } x \neq 0. \end{cases} \quad (9)$$

154 Eq. (7) with the initial condition of Eq. (8) can be
155 solved analytically in the eigenbasis of the diffusion ma-
156 trix. Let us define

$$\mathbf{D} = \mathbf{P} \mathbf{\Lambda} \mathbf{P}^{-1}, \quad (10)$$

157 with

$$\mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & \dots & \dots \\ \vdots & \ddots & \dots \\ \vdots & \vdots & \lambda_{n-1} \end{pmatrix} \quad (11)$$

158 the diagonal matrix of eigenvalues λ_i , and $\mathbf{P} =$
159 $(\mathbf{v}_1, \dots, \mathbf{v}_{n-1})$ is the block matrix of the eigenvectors \mathbf{v}_i .
160 Therefore,

$$\mathbf{\Lambda} \mathbf{v}_i = \lambda_i \mathbf{v}_i. \quad (12)$$

161 Defining $\tilde{\mathbf{C}} = \mathbf{P}^{-1} \mathbf{C}$ and $\tilde{\Delta} \mathbf{C} = \mathbf{P}^{-1} \Delta \mathbf{C}$, respectively
162 the concentration and the initial concentration step in
163 the eigenbasis of \mathbf{D} , Eq. (7) can be written as

$$\frac{\partial \tilde{\mathbf{C}}}{\partial t} = \mathbf{\Lambda} \nabla^2 \tilde{\mathbf{C}}. \quad (13)$$

164 Since $\mathbf{\Lambda}$ is a diagonal matrix, all equations of (13) are
165 independent and have similar solutions to that obtained
166 for the diffusion of a single species:

$$\tilde{C}_i(x, t) = \tilde{\Delta} C_i \operatorname{erf} \left(\frac{x}{\sqrt{2 \lambda_i t}} \right). \quad (14)$$

167 Note that the above solution is valid for an infinite
168 medium, *i.e.* when the width of the diffusing interface
169 is much smaller than the width of each sample. From an
170 experimental set of concentration profiles, the diffusion
171 matrix is obtained by fitting theoretical profiles of Eq.
172 (14) to the experimental profiles.

3. Materials and methods 173

3.1. Experimental methods 174

175 *Glass compositions* -. We choose to measure the dif-
176 fusion matrix in a composition domain centered on
177 the peralkaline composition $\mathbf{C}_0 = 64.5 \text{ wt\%SiO}_2$
178 , $13.3 \text{ wt\%Na}_2\text{O}$, 10.8 wt\%CaO , $11.4 \text{ wt\%Al}_2\text{O}_3$
179 (corresponding to $\mathbf{C}_0 = 67.4 \text{ mol\%SiO}_2$, 13.5
180 $\text{mol\%Na}_2\text{O}$, 12.1 mol\%CaO , $7.0 \text{ mol\%Al}_2\text{O}_3$, or
181 $\text{Si}_{2.02}\text{Na}_{1.62}\text{Ca}_{0.73}\text{Al}_{0.28}\text{O}_6$). With this central compo-
182 sition, all compositions of diffusion-couple glasses lie
183 in the peralkaline domain, while the concentration of
184 all four oxides is important enough to allow for ac-
185 curate measurements of the composition using elec-
186 tron microprobe analysis. Compared to window-glass
187 soda-lime compositions, this composition is aluminum-
188 enriched, a fact that generally increases the strength of
189 the glass (Eagan and Swearengen, 1978). Indeed, the
190 composition studied here is close to industrially-used
191 high-strength glass compositions (Karlsson et al., 2010;
192 Danielson et al., 2016), such as compositions used in
193 the aeronautic industry (Chopin et al., 2001).

194 We prepared a set of glasses centered on \mathbf{C}_0 for the
195 diffusion couple experiments. Choosing the concentra-
196 tion difference in a diffusion couple is a trade-off be-
197 tween two contradicting aspects: we expect the diffu-
198 sion matrix to be independent of concentration only in

199 a small domain, while increasing the signal over noise
 200 ratio of concentration profiles requires to have a larger
 201 initial step of concentration. Here we choose a maxi-
 202 mal concentration difference of 5wt%. We prepared 12
 203 different glasses, each of them being enriched in one ox-
 204 ide and depleted in another one with respect to C_0 . For
 205 example, we denote as AN a composition with 2.5wt%
 206 more alumina, and 2.5wt% less sodium oxide than C_0 .

207 Glasses were synthesized from raw materials of indus-
 208 trial grade, using Ronceveaux sand and Tacon lime-
 209 stone from Samin, hydrated alumina from Dadco, and
 210 sodium carbonate from Novacarb. 0.3wt% of sodium
 211 sulfate and 300 ppm of coke were added as fining
 212 agents. In addition, 100 ppm of cobalt oxide were
 213 added to one glass in each diffusion couple, in order
 214 to detect convection. Raw materials were weighed and
 215 mixed for several minutes in a Turbula-type mixer, and
 216 melted for 6h in a 800 mL platinum crucible in a Joule-
 217 heated furnace at 1500°C. Melts were mixed for one
 218 hour with a platinum stirrer to improve homogeneity.
 219 Melts were then quenched on a metallic plate, and an-
 220 nealed at 600° C for one hour. Compositions of the
 221 different glasses are given in Table 1. We have also
 222 reported in Table 1 densities of the different composi-
 223 tions estimated at 1200°C using the models of (Bottinga
 224 et al., 1982), (Spera, 2000), (Priven, 2004) and (Fluegel
 225 et al., 2008). Values given in Table 1 correspond to
 226 the average of density values for the different models.
 227 The standard deviation of the density between models
 228 is smaller than 0.02 for all models, and the standard de-
 229 viations of the difference of density between endmem-
 230 bers is smaller than 0.007 for all experiments but one
 231 (AC/CA, with a standard deviation of 0.017). Relative
 232 variations of calculated density between diffusion end-
 233 members are all smaller than 2.5%, confirming the val-
 234 idity of mass conservation along a diffusion profile.

235 *Diffusion experiments* -. We performed diffusion exper-
 236 iments for each couple intersecting at C_0 , resulting in
 237 6 different diffusion couples: NA/NA, CA/AC, AS/SA,
 238 CN/NC, CS/SC, and NS/SN (using the notation defined
 239 above, with the first letter denoting the element in ex-
 240 cess and the second letter the element that is depleted).
 241 Therefore, only two oxides have a significant concentra-
 242 tion difference between the two endmembers of a given
 243 diffusion couple.

244 In theory, only $(n-1)$ experiments with $(n-1)$ profiles
 245 each are required to determine the $(n-1)^2$ coefficients of
 246 the diffusion matrix. However, more experiments than
 247 this bare minimum are useful to overconstrain the solu-
 248 tion in the case of noisy data. Furthermore, our set of
 249 experiments is completely symmetrical with respect to

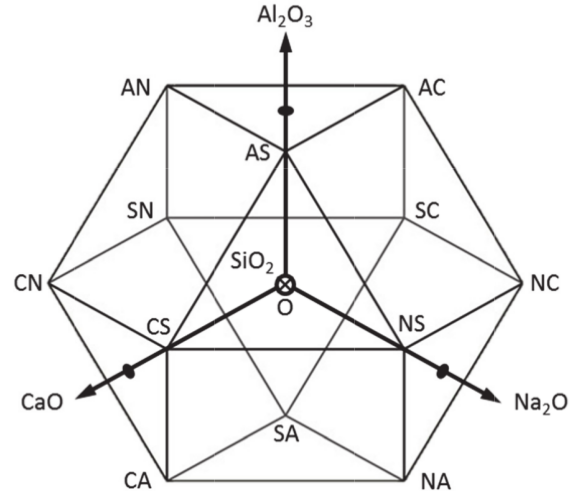


Figure 1: Schematic of diffusion-couple compositions.

250 the different oxides, so that we explore all the possible
 251 directions of exchange between oxides.

252 Diffusion experiments were made at 1200°C, a tem-
 253 perature low enough to avoid convection and high
 254 enough to avoid crystallization. Square slabs of dimen-
 255 sions $15 \times 15 \times 5$ mm³ of the different glasses were cut;
 256 a coarse polishing of surfaces ensured a good contact be-
 257 tween the two slabs, limiting the formation of bubbles.
 258 Slabs were put in vitreous silica crucibles of 25-mm di-
 259 ameter, the denser glass being placed below the lighter
 260 one. The space between the crucible and the glass slabs
 261 was filled with quartz sand to limit slumping of the melt,
 262 and to mitigate the formation of cracks during quenching.
 263 Crucibles were introduced into an electric furnace
 264 preheated at 1200°C. Samples reached 1200°C about 20
 265 minutes after being put inside the furnace. Therefore,
 266 we define $t = 0$ as the end of this 20-minute period.
 267 Counting from this point, isothermal treatments of dura-
 268 tions of 20 minutes, 1 hour and 3 hours were performed
 269 for all diffusion couples. Samples were then quenched
 270 in air and annealed at 600° C for one hour to avoid frac-
 271 ture during subsequent sample preparation. They were
 272 then mounted in epoxy resin, cut perpendicularly to the
 273 interface, and polished to optical quality for further ob-
 274 servation.

275 *Diffusion profiles* -. The absence of convection was
 276 verified using optical microscopy (using color contrast
 277 thanks to cobalt oxide) as well as scanning electron mi-
 278 croscopy in back-scattered mode, on a Zeiss Gemini
 279 DSM 982 FEG-SEM. Although convection was absent
 280 in most experiments, two of the 3-hour experiments had
 281 to be discarded because of interfaces disturbed by con-

	C_0	AC	AN	AS	CA	CN	CS	NA	NC	NS	SA	SC	SN
Na ₂ O	13.3	13.7	10.8	13.5	13.6	10.5	13.3	16.0	15.9	15.4	13.6	13.2	10.4
CaO	10.8	7.8	10.7	10.2	13.7	13.8	13.6	10.7	7.9	11.7	10.6	6.9	10.6
Al ₂ O ₃	11.4	13.4	13.3	13.5	8.4	12.0	11.4	8.9	11.6	10.8	8.9	11.7	11.7
SiO ₂	64.5	65.1	65.4	62.1	64.3	63.6	61.7	64.3	64.6	62.0	66.9	66.7	66.8
density		2.35	2.38	2.37	2.36	2.40	2.40	2.37	2.35	2.38	2.36	2.34	2.37

Table 1: Compositions (in weight percents) and calculated densities ($\times 10^3 \text{ kg.m}^{-3}$) of glasses used in diffusion couples. Chemical compositions were measured for each glass from the average of 20 electron microprobe analysis measurements. C_0 is a theoretical composition (no glass of composition C_0 was synthesized).

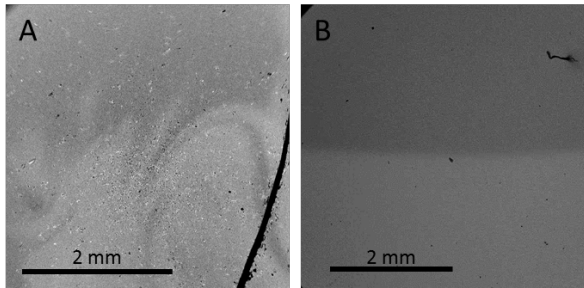


Figure 2: SEM images of interfaces between diffusion endmembers. (a) Interface destabilized by convection, that is discarded. (b) Stable interface for which diffusion only has been at play.

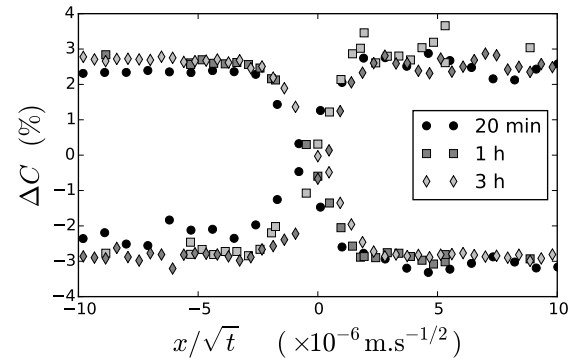


Figure 3: CS-SC exchange - Calcium oxide and silica concentration versus normalized distance to the interface x/\sqrt{t} , for diffusion experiments of 20 minutes, 1 hour and three hours.

vection (see Fig. 2). Diffusion profiles were measured using a Cameca SX-100 electron microprobe at the University of Lille. Analyses were performed for 20 seconds with an acceleration voltage of 15 kV, a current of 15 nA and a spot size of 20 microns in order to reduce the charge density on the sample. For an accurate measurement of sodium concentration, four counting intervals of 5 seconds were used, and a regression performed to extrapolate decreasing concentrations back to the initial concentration. Measurement accuracy on sodium oxide is of the order of 1 wt%, while that of the other elements is of the order of 0.2 wt%. Along a diffusion profile, two measurement points were always separated by at least 30 microns to limit the impact of sodium migration at one point on adjacent measurements.

3.2. Mathematical analysis of diffusion profiles

We first verified that diffusion profiles obtained for different durations on the same diffusion couple could be overlain when plotting concentrations versus rescaled distance x/\sqrt{t} . A typical example is plotted in Fig. 3, for the SC/CS diffusion couple, where a good agreement is observed between the different times. Rescaled profiles corresponding to the shortest time (20 minutes) are slightly shifted compared to rescaled profiles for one and three hours. This small difference likely originates from the uncertainty concerning the

starting time. Therefore, in the following we only use the 1- and 3-hour experiments to obtain the diffusion matrix, corresponding to a set of 10 experiments.

In order to obtain the diffusion matrix, we perform a least-square minimization of the difference between experimental concentration profiles, and concentrations resulting from Eq. (14). Least-square minimization is the standard method to fit diffusion matrices (Trial and Spera, 1994; Liang et al., 1996a; Acosta-Vigil et al., 2002; Liang, 2010), since it allows one to fit, at the same time, a large number of profiles. It is also more robust to noise than direct methods such as the Boltzmann-Matano method (Kress and Ghiorso, 1995; Lesher, 1994; Saggiaro and Ziemath, 2006; Liang, 2010; Vielzeuf and Saül, 2011), that requires the calculation of spatial derivatives of the profiles.

We use the optimization routine `optimize.leastsq` provided by the Python package `scipy`, that implements the Levenberg-Marquardt algorithm. The difference to be minimized is computed in the eigenbasis of the diffusion matrix. Therefore, at each iteration of the minimization procedure, a new set of eigenvectors and eigenvalues of \mathbf{D} is obtained, allowing one to trans-

form experimental concentration profiles to profiles in the new eigenbasis, that are compared to theoretical profiles defined by Eq. (14). Silica is used as the dependent species. Since the fitting procedure involves 9 parameters, and the non-linear function to be minimized is not convex and can have several local minima, special care is required for the initialization of \mathbf{D} . Initial parameters for \mathbf{D} are selected visually from a rough adjustment of experimental and computed concentration profiles.

4. Results

4.1. Diffusion profiles

Fig. 4 represents diffusion profiles for all diffusion couples, for a thermal treatment of one hour. Several observations can be made from this set of profiles. Diffusion distances from a few hundreds of microns to one millimeter are observed, confirming that the electron microprobe is a technique perfectly adapted to our experiments. Also, the maximum diffusion distance is of the order of one millimeter, much smaller than the height of the original glass sample (5 mm), so that the approximation of diffusion in an infinite medium is valid here. Experiments with an initial difference of sodium oxide show a larger diffusion width than experiments with the same concentration of sodium oxide for the two melts. Sodium being the most mobile species, this result is to be expected. Uphill diffusion of calcium is observed in the case of exchange between sodium and a network formers, that is for the NA/AN and NS/SN couples. Uphill diffusion of calcium is also observed for the AS/SA couple, for which there exists as well a small concentration difference in sodium oxide between end members. In such experiments, diffusion profiles of different elements have very different diffusion widths, the diffusion distance of sodium and calcium being much greater than that of silicon and aluminum.

4.2. Diffusion matrix

Using the optimization procedure described in the previous section, we obtained the diffusion matrix from concentration profiles available for 1- and 3-hour experiments at 1200° C. With SiO_2 as the dependent component, the matrix \mathbf{D} is given by

$$\mathbf{D} = \begin{pmatrix} 25.55 & -4.45 & -8.29 \\ -22.86 & 4.85 & 8.00 \\ 0.33 & -0.29 & -0.02 \end{pmatrix},$$

where the lines of \mathbf{D} give the fluxes of Na_2O , CaO , and Al_2O_3 respectively, and coefficients are in $10^{-12}\text{m}^2\cdot\text{s}^{-1}$ units. Since coefficients of the fitted 3×3 matrix \mathbf{D}

represent differences between the “true” coefficients of the unknown 4×4 matrix, we also give here the eigenvalues and eigenvectors of \mathbf{D} , that are the same regardless of the choice of the dependent species. Eigenvalues and eigenvectors are shown in Table 2. Since the coefficients of eigenvectors can be multiplied by any constant value, we set the principal coefficient to 1, for the sake of clarity. Uncertainties on the different coefficients were obtained using a procedure known as *bootstrapping* in statistics, relying on random sampling with replacement: one profile is excluded in turns from the set of profiles, in order to compute different estimations of the diffusion matrix. We selected the excluded profiles in the set of experiments for which we had both data for 1 and 3 hours, in order to keep data corresponding to all diffusion couples within the fitting set. Excluding a diffusion couple resulted in a larger deviation for eigenvalues and eigenvectors; this observation validates our experimental strategy to use all 6 diffusion couples, although in theory 3 would have been enough to constrain the fitting procedure. While previous studies (Chakraborty et al., 1995a,b) have suggested that a minimum number of profiles is sufficient to determine the diffusion matrix, we believe that a smaller set of experiments comes at the cost of large uncertainties on the diffusion matrix (Liang, 2010).

Table 2: Eigenvalues ($\times 10^{-12}\text{m}^2\cdot\text{s}^{-1}$) and eigenvectors

	\mathbf{v}_1	\mathbf{v}_2	\mathbf{v}_3
α_i	$29.5 \pm .2$	0.58 ± 0.02	$0.3 \pm .06$
Na_2O	1	0.02 ± 0.01	-0.15 ± 0.01
CaO	-0.92 ± 0.005	1	0.98 ± 0.04
Al_2O_3	0.02 ± 0.01	-0.47 ± 0.06	-1 ± 0.03
SiO_2	-0.09 ± 0.02	-0.52 ± 0.08	0.17 ± 0.05

4.3. Eigenvectors and eigenvalues

The dominant eigenvector of the diffusion matrix, associated to the fastest diffusion process, is found to correspond to the exchange of sodium and calcium. The second eigenvector corresponds to the exchange of calcium with silicon and aluminum, while the third eigenvector is dominated by the exchange of calcium and aluminum. Therefore, the two diffusion processes highlighted by the minor eigenvectors involve no or very little sodium, and they are much slower. The ratio between the first and the second eigenvalue is on the order of 50. For silicates, such high ratios between eigenvalues have only been reported in systems with alkalis: Trial and Spera (Trial and Spera, 1994) found a ratio of 24 in the NCS system, and also had a first eigenvector

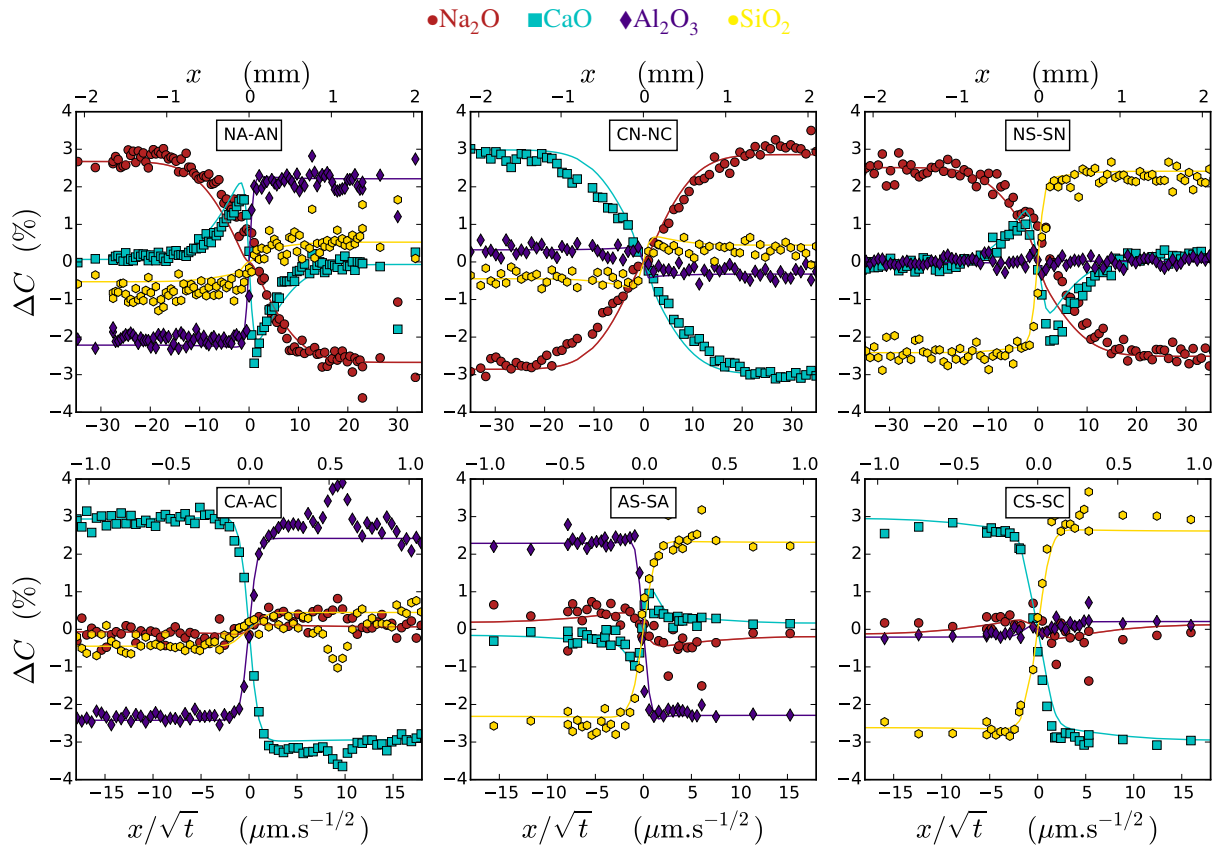


Figure 4: Concentration profiles for all diffusion couples at 1200°C and 1-hour treatments. Note the different spatial scale for diffusion couples involving sodium (first line) and not involving sodium (second line). Spatial coordinates are given both in mm and in rescaled units.

411 colinear to sodium-calcium exchange. Chakraborty et al. (Chakraborty et al., 1995a,b) found ratios between 5 and 270 for the KAS system. Nevertheless, the latter experiments used only one diffusion couple to fit a diffusion matrix, making it hard to quantify the terms of the diffusion matrix accurately, all the more for an ill-conditioned matrix (with very different eigenvalues). In contrast, systems involving only alkaline-earth network modifiers (Kress and Ghiorso, 1993; Liang et al., 1996b; Richter et al., 1998), including systems involving both Ca and Mg (Kress and Ghiorso, 1993; Richter et al., 1998), have been found to have eigenvalues of the same order of magnitude, with a ratio smaller than 5 between the largest and second largest eigenvalues.

425 The decoupling between α_1 and α_2 has important consequences for all diffusion paths, that is the set of compositions linking endmembers in the course of a diffusion experiment. In Fig. 5, we have represented the diffusion paths in the 3-D space of compositions (the 4th component being known from mass conserva-

431 tion). All diffusion paths cross at C_0 , the average composition. We have also represented the three eigenvectors of the diffusion matrix. As shown in Fig. 5, for any diffusion couple with a non-null projection on the dominant eigenvector (that is, any diffusion couple with $\Delta C_{Na} \neq 0$), the diffusion path is mostly colinear to the dominant eigenvector (direction represented by the thick orange arrow). In other words, diffusion paths are aligned with the dominant eigenvector in regions where ΔC_{Na} is substantial, while they are aligned with the other eigenvectors (involving network formers) only when ΔC_{Na} is small.

5. Discussion

5.1. Validity of the diffusion-matrix formalism

444 While the overall quality of the fit of experimental data is satisfying, it can be noted in Fig. 4 that there is a slight asymmetry in the profiles of sodium and calcium, in the case of a difference of sodium concentration in

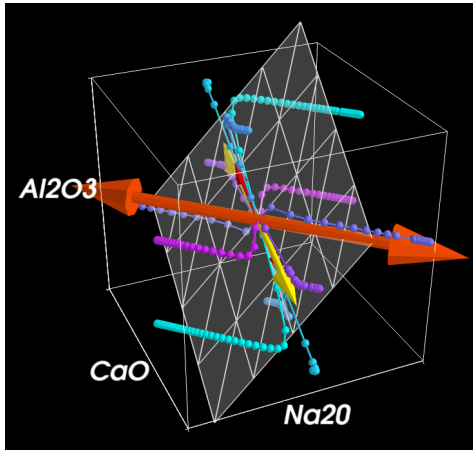


Figure 5: 3-D visualization of diffusion paths, centered around concentration C_0 . Concentrations can be represented in a 3-D Cartesian space, since the fourth concentration value can be deduced from the three other concentrations. The three axis represent a difference in Na_2O , CaO , and Al_2O_3 , as shown by labels on the axes. The shaded white plane represents $\Delta C_{\text{Na}_2\text{O}} + \Delta C_{\text{CaO}} + \Delta C_{\text{Al}_2\text{O}_3} = 0$, so that deviations out of this plane represent a difference in silica concentration. Arrows (in orange, yellow and red) represent the directions of the eigenvectors of the diffusion matrix. Note that diffusion couples involving a difference in sodium oxide concentration are parallel to the dominant eigenvector at the two ends of the diffusion path.

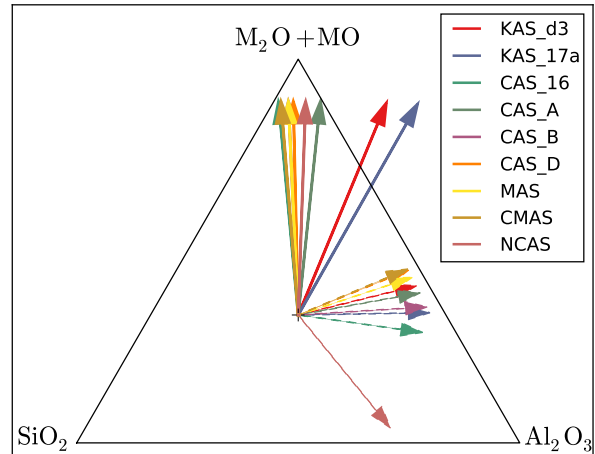


Figure 6: Directions of diffusion eigenvectors of Table 3, projected in the plane $\Delta C_{\text{SiO}_2} + \Delta C_{\text{Al}_2\text{O}_3} + \Delta C_{\text{M}_2\text{O}+\text{MO}} = 0$. Note that we have grouped together alkali M_2O and alkaline-earth MO oxides for more clarity, so that the dominant eigenvector of our NCAS system is not represented here. For all systems, the dominant eigenvector is represented with a solid line, while other(s) eigenvectors are represented with a dashed line. Note the persistence of an eigenvector corresponding to the exchange of alkali-earth oxides with an equal proportion of silica and alumina.

449 the diffusion couple. This asymmetry is probably due to
 450 variations of diffusion coefficient along the profile, pos-
 451 sibly correlated to variations in melt viscosity generated
 452 by the composition gradient (i.e. Mungall (2002)). Ac-
 453 counting for the observed asymmetry would therefore
 454 require fitting diffusion profiles using a concentration-
 455 dependent diffusion matrix. Nevertheless, such refine-
 456 ment would only slightly modify the diffusion matrix
 457 quantified here, and was not attempted.

458 5.2. Comparison with other systems

459 In order to compare the eigenvectors of our quater-
 460 nary system to other systems, the findings of several
 461 previous studies, in ternary or more complex systems
 462 are summarized in Tab. 3. For a graphical representa-
 463 tion, we have plotted the directions of eigenvectors in
 464 Fig. 6.

465 Our dominant eigenvector, corresponding to the ex-
 466 change of sodium and calcium, is similar to the principal
 467 eigenvector of the NCS system of Trial and Spera (Trial
 468 and Spera, 1994). Furthermore, this eigenvector has a
 469 much larger eigenvalue than the second eigenvector, in
 470 the two systems. In contrast, systems that have two al-
 471 kalis (like the NKASH system of (Mungall et al., 1998))
 472 or two alkaline-earth species (like the CMAS system
 473 of (Richter et al., 1998)) do not have an eigenvector

474 corresponding to the fast exchange of these two alkali
 475 or two alkaline-earth species. This difference might be
 476 paralleled with slower transport properties (such as elec-
 477 trical conductivity) associated to the so-called mixed-
 478 alkali (Isard, 1969; Swenson and Adams, 2003) and
 479 mixed-alkaline-earth (Roling and Ingram, 2000; Kjeld-
 480 sen et al., 2013) effects. These mixed effects have been
 481 assigned to a discrepancy between the sites of two al-
 482 kali or two alkaline-earth species, with the consequence
 483 that the two species are “blocking” each other. It is also
 484 of note that the exchange between sodium and calcium
 485 was also found to be predominant in more complex ge-
 486 ological melts (Lundstrom, 2003).

487 Moreover, sodium is present only in the domi-
 488 nant eigenvector, so that its diffusion is decoupled
 489 from network formers. This behaviour contrasts
 490 with systems with alkali species but no alkaline-earth
 491 species (Chakraborty et al., 1995b; Mungall et al.,
 492 1998), where alkalis exchange preferentially with sil-
 493 ica rather than with alumina. However, an exchange
 494 of sodium with network formers might be followed by
 495 the faster exchange of calcium with sodium, along the
 496 direction of the dominant eigenvector, so that the ex-
 497 change of sodium with network formers can be de-
 498 scribed by a combination of the two first eigenvectors.

499 As for our second eigenvector, corresponding to the
 500 exchange of calcium with similar quantities of sil-
 501 ica and alumina, this exchange is close to the domi-

experiment	eigenvectors	eigenvalues ($\times 10^{-12} \text{m}^2 \cdot \text{s}^{-1}$)	T (° C)	reference
NCS	$\text{Na}_2\text{O} \leftrightarrow 0.85\text{CaO} + 0.15\text{SiO}_2$ $0.27\text{Na}_2\text{O} + 0.73\text{CaO} \leftrightarrow \text{SiO}_2$	105 4.4	1200	Trial and Spera (1994)
KAS D-3	$\text{K}_2\text{O} \leftrightarrow 0.14\text{Al}_2\text{O}_3 + 0.86\text{SiO}_2$ $0.75\text{Al}_2\text{O}_3 + 0.25\text{K}_2\text{O} \leftrightarrow \text{SiO}_2$	0.07 1×10^{-3}	1400	Chakraborty et al. (1995b)
KAS 17a	$\text{K}_2\text{O} \leftrightarrow 0.01\text{Al}_2\text{O}_3 + 0.99\text{SiO}_2$ $0.98\text{Al}_2\text{O}_3 + 0.02\text{K}_2\text{O} \leftrightarrow \text{SiO}_2$	10.8 0.04	1400	Chakraborty et al. (1995b)
KAS 23	$\text{K}_2\text{O} \leftrightarrow 0.02\text{Al}_2\text{O}_3 + 0.98\text{SiO}_2$ $0.8\text{Al}_2\text{O}_3 + 0.02\text{K}_2\text{O} \leftrightarrow \text{SiO}_2$	14.4 0.08	1600	Chakraborty et al. (1995b)
NKASH	$\text{Na}_2\text{O} \leftrightarrow \text{SiO}_2$ $\text{K}_2\text{O} \leftrightarrow \text{SiO}_2$ $\text{Al}_2\text{O}_3 + 0.08\text{K}_2\text{O} + 0.21\text{Na}_2\text{O} + 0.28\text{H}_2\text{O} \leftrightarrow 1.57\text{SiO}_2$ $\text{H}_2\text{O} \leftrightarrow \text{SiO}_2$	550 540 3.4 280	1600	Mungall et al. (1998)
CAS 16	$\text{CaO} \leftrightarrow 0.58\text{Al}_2\text{O}_3 + 0.42\text{SiO}_2$ $\text{Al}_2\text{O}_3 \leftrightarrow 0.15\text{CaO} + 0.85\text{SiO}_2$	99 23	1500	Liang et al. (1996a)
CAS A	$\text{CaO} \leftrightarrow 0.41\text{Al}_2\text{O}_3 + 0.59\text{SiO}_2$ $0.81\text{Al}_2\text{O}_3 + 0.19\text{CaO} \leftrightarrow \text{SiO}_2$	34 8.3	1500	Liang et al. (1996a)
CAS B	$\text{CaO} \leftrightarrow 0.54\text{Al}_2\text{O}_3 + 0.46\text{SiO}_2$ $0.93\text{Al}_2\text{O}_3 + 0.07\text{CaO} \leftrightarrow \text{SiO}_2$	47 23	1500	Liang et al. (1996a)
CAS D	$\text{CaO} \leftrightarrow 0.52\text{Al}_2\text{O}_3 + 0.48\text{SiO}_2$ $0.62\text{Al}_2\text{O}_3 + 0.38\text{CaO} \leftrightarrow \text{SiO}_2$	36 11	1500	Liang et al. (1996a)
MAS	$\text{MgO} \leftrightarrow 0.54\text{Al}_2\text{O}_3 + 0.46\text{SiO}_2$ $0.68\text{Al}_2\text{O}_3 + 0.32\text{MgO} \leftrightarrow \text{SiO}_2$	70 20	1550	Richter et al. (1998)
CMAS	$\text{CaO} \leftrightarrow 0.36\text{MgO} + 0.32\text{Al}_2\text{O}_3 + 0.32\text{SiO}_2$ $\text{MgO} \leftrightarrow 0.07\text{CaO} + 0.53\text{Al}_2\text{O}_3 + 0.4\text{SiO}_2$ $0.13\text{CaO} + 0.26\text{MgO} + 0.61\text{Al}_2\text{O}_3 \leftrightarrow \text{SiO}_2$	59 26 3.2	1500	Richter et al. (1998)
NCAS	$\text{Na}_2\text{O} + 0.02\text{Al}_2\text{O}_3 \leftrightarrow 0.92\text{CaO} + 0.09\text{SiO}_2$ $\text{CaO} + 0.02\text{Na}_2\text{O} \leftrightarrow 0.47\text{Al}_2\text{O}_3 + 0.52\text{SiO}_2$ $\text{CaO} + 0.17\text{SiO}_2 \leftrightarrow 0.99\text{Al}_2\text{O}_3 + 0.15\text{Na}_2\text{O}$	29.5 0.58 0.3	1200	this study

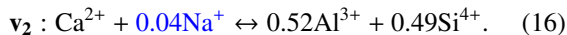
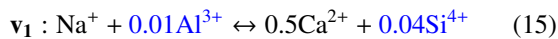
Table 3: Diffusion eigenvectors and eigenvalues from the literature.

502 nant eigenvector found in CAS (Liang et al., 1996a)
 503 and MAS (Richter et al., 1998) compositions. Also,
 504 the two dominant eigenvectors of the CMAS system
 505 in (Richter et al., 1998) correspond to the exchange of
 506 alkaline-earth species with silica and alumina. Since
 507 the environment of aluminum is expected to be differ-
 508 ent with or without sodium, with a fraction of aluminum
 509 tetrahedra being compensated preferentially by sodium
 510 ions (Cormier and Neuvill, 2004; Lee and Sung, 2008),
 511 it is quite surprising that the dominant eigenvector of the
 512 CAS system transposes to our NCAS system. A strik-
 513 ing result of our study is therefore that in our quaternary
 514 system, the two most important eigenvectors of the dif-
 515 fusion matrix correspond to the dominant eigenvectors
 516 of the ternary sub-systems. This robustness of eigenvec-
 517 tors to compositional changes and the addition of new
 518 species could be used to design experimental strategies
 519 to determine the diffusion matrix of complex systems.

520 The slowest eigenvector in Table 2 corresponds to the
 521 exchange of calcium and aluminum oxides, with only
 522 small couplings with silica and sodium oxide. There
 523 is no direct equivalent of this eigenvector in the stud-
 524 ies summarized in Table 3. However, our composition
 525 is richer in silica than most compositions of Table 3,
 526 in particular CAS compositions. Moreover, our third
 527 eigenvector is determined with much less accuracy than
 528 the other two, due to the large difference between the
 529 first and last eigenvalues. In order to improve the ac-
 530 curacy of the third eigenvector, diffusion couples with
 531 a zero projection on the first eigenvector would be re-
 532 quired.

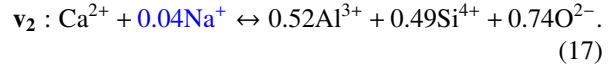
533 5.3. Microscopic interpretation of exchange reactions

534 Eigenvectors can be interpreted as exchange reactions
 535 between ions (Chakraborty et al., 1995b), converting
 536 first from weight concentration to molar concentration
 537 of oxides, and from oxide to ionic concentration. This
 538 conversion results in the following reactions



In the above equations, terms highlighted in blue have very small coefficients, and probably stem from numerical errors. Therefore, we neglect these terms in the following. Note that even if charge does not appear to be conserved in (16), charge is compensated by oxygen anions, not represented in the exchange reactions. Eq. (16)

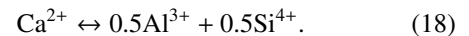
could equally be written as



542 However, it is interesting to observe that the fastest re-
 543 action (15) is charge-balanced by cations. 540

541 Equations such as (15) and (16) can be interpreted
 542 in terms of microscopic exchange reactions. For the
 543 first one involving one Na^+ and half a Ca^{2+} , a possi-
 544 ble mechanism is illustrated on Fig. 7 (a), involving two
 545 silica tetrahedra. At the beginning of the exchange,
 546 one calcium ion is bound to two oxygens on two different
 547 tetrahedra, one of which has an additional non-bridging
 548 oxygen associated with a sodium ion (see Fig. 7 (a)).
 549 Let us suppose that the calcium ion breaks one of its
 550 two bonds to move closer to the sodium ion, and that
 551 the sodium ion moves close to the oxygen ion initially
 552 bound to the calcium ion. At the end of the exchange,
 553 the calcium ion is bound to two oxygen ions of the same
 554 tetrahedron, while the sodium ion is a modifier of a dif-
 555 ferent tetrahedron than initially. This sequence is a possi-
 556 ble mechanism to account for reaction (15). The ex-
 557 change of sodium and calcium is likely to take place
 558 in the so-called Greaves channels (Greaves, 1985; Jund
 559 et al., 2001; Meyer et al., 2002; Bauchy and Micoulaut,
 560 2011; Tilocca, 2010). Moreover, this mechanism in-
 561 volves only non-bridging oxygens, so that no Si – O
 562 or Al – O bound is broken. Therefore, such exchanges
 563 are more frequent than reactions involving network form-
 564 ers, as (16).

As for the second eigenvector, we have sketched a possible mechanism in Fig. 7 (b). The proposed exchange involves two silicon tetrahedron and one aluminum, that is 4-coordinated at the beginning and at the end of the reaction. The aluminum is charge-compensated by a calcium ion, that also acts as a modifier for one of the silicon tetrahedron. Then, the aluminum becomes 5-coordinated when a new Al – O – Si is formed, and the calcium only compensates the aluminum (Fig. 7 (b) center). Finally, the calcium moves closer to another silicon tetrahedron and break an Al – O – Si bond in order to act both as a modifier and charge compensator. This exchange describes how calcium progresses through the network of silicon and aluminum tetrahedra by breaking Al – O – Si bonds, and is therefore consistent with the exchange



566 As for network formers, the above reaction requires
 567 to break a Al – O bound, which takes more time than
 568 breaking a chemical bound between oxygen and a net-
 569 work modifier. Therefore, the frequency of the second

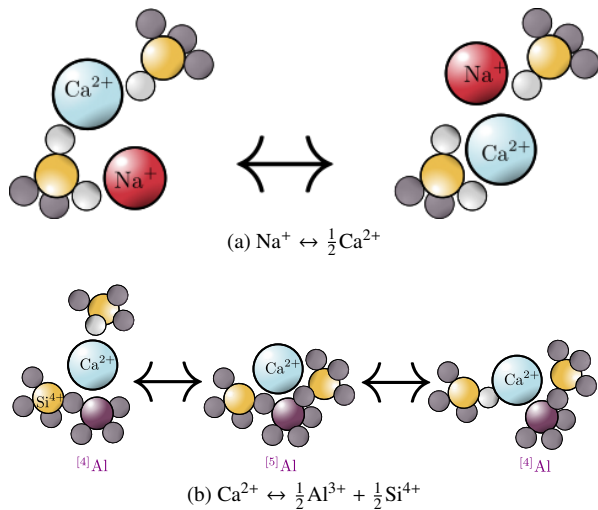


Figure 7: Schematic drawing of local exchanges with a stoichiometry corresponding to eigenvectors of the diffusion matrix. Sodium cations are represented in red, calcium in blue, silicon in yellow, aluminum in purple, bridging oxygens in dark gray and non-bridging oxygens in light grey. (a) Exchange between sodium and calcium, corresponding to Eq. (15). (b) Exchange between calcium, and silicon and aluminum, corresponding to Eq. (16).

569 reaction mechanism is expected to be much lower than
 570 for the first exchange, in agreement with experimental
 571 eigenvalues.

572 We have not attempted to find a reaction mechanism
 573 for the third eigenvector, since we believe that the un-
 574 certainty on the direction of the eigenvector is large, be-
 575 cause of the ill-conditioning of the diffusion matrix.

576 We do not claim that the reactions sketched in Fig. 7
 577 are the only possible exchanges leading to the stoe-
 578 chiometry of Eqs. (15-16). It is possible that other con-
 579 figurations could result in a similar chemical balance.
 580 However, writing diffusion eigenvectors as simple local
 581 exchanges has several advantages. First, identify-
 582 ing such exchanges makes it possible to look for their
 583 signature using either molecular-dynamics or ab-initio
 584 simulations (Tilocca, 2010) or exchange rates computed
 585 from *in situ* NMR measurements (Stebbins et al., 1995;
 586 Gruener et al., 2001; Kanehashi and Stebbins, 2007).
 587 Second, identifying possible configurations responsible
 588 for the chemical exchanges helps to understand why
 589 the direction of eigenvectors does not vary much with
 590 composition (Liang et al., 1996a): if a discrete number
 591 of possible exchanges dominates mass transport, eigen-
 592 vectors of the diffusion matrix should correspond to the
 593 most frequent exchanges and be invariant over concen-
 594 tration domains where the frequency ranking of reac-
 595 tions stays the same.

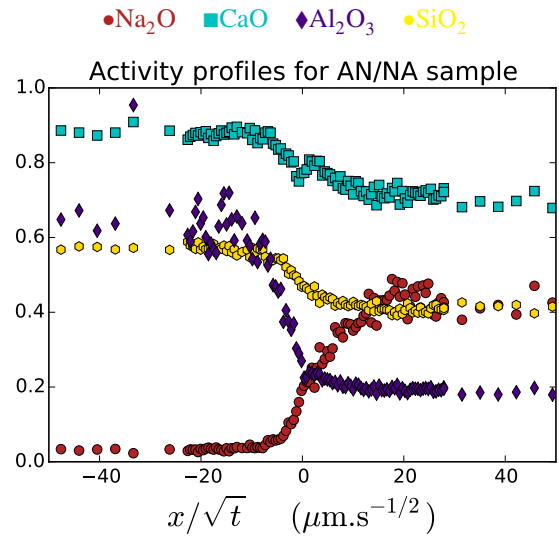


Figure 8: Activity profiles for the AN/NA sample, for a heat treatment of 1h at 1200°C. In order to represent all activity profiles on the same plot, we have used arbitrary scaling coefficients and represented $10^9 \times a(\text{Na}_2\text{O})$, $2.10^4 \times a(\text{CaO})$ and $5.10^4 \times a(\text{Al}_2\text{O}_3)$.

5.4. Activity variations across diffusion profiles

596 From a thermodynamic perspective, diffusion of a
 597 given species is driven by the gradient in the activ-
 598 ity of that species, rather than its concentration (Liang
 599 et al., 1997). In other words, phenomena such as the
 600 uphill diffusion of Ca described here and in the litera-
 601 ture (e.g. (Zhang et al., 1989; Liang et al., 1996a)) may
 602 be considered as the macroscopic consequence of sig-
 603 nificant variations in activity coefficient across a given
 604 diffusion profile. In this case, the complex variations in
 605 concentration should correspond to a simple variation
 606 in activity across the profile, with no local extrema in
 607 the latter. Direct determination of the relevant activity
 608 coefficients has not been made in the portion of the qua-
 609 ternary system studied here, but thermodynamic models
 610 available in the literature may be used to estimate how
 611 activities vary across our diffusion profiles. For this pur-
 612 pose we have used the FactSage programme (Bale et al.,
 613 2002, 2009), a commercially available thermodynamic
 614 calculator constructed from databases in systems of in-
 615 creasing compositional complexity. We note that in al-
 616 most all cases smooth and continuous variations in activ-
 617 ity (with no maxima) are calculated across our pro-
 618 files for all elements. For example, for the diffusion
 619 couple AN/NA, which shows the most prominent uphill
 620 diffusion of calcium concentration (c.f. Fig. 4a), calcu-
 621 lated activities of CaO (Fig. 8) indicate that: i) despite
 622 the fact that initial concentrations of CaO were identi-
 623

624 cal across the profile, the activity of CaO was different
625 in each starting glass, and ii) that a perfectly continu-
626 ous decrease in CaO activity is calculated, a behaviour
627 also found for the three other oxide components in this
628 sample (Fig. 8). A detailed analysis and interpretation
629 of all the calculated activities derived from our data-set
630 is outside the scope of the present contribution, but this
631 preliminary analysis clearly shows that consideration of
632 oxide activities may be used to rationalize even highly
633 non-linear concentration gradients that show multiple
634 extrema.

635 5.5. Geological implications

636 Assuming that eigenvectors are not a significant func-
637 tion of temperature, the results obtained here provide
638 some qualitative insights into the conditions that would
639 favour uphill diffusion in geological systems (i.e. that
640 will lead to concentration profiles that cannot be con-
641 sidered in terms of effective binary diffusion). For ex-
642 ample, we find that complex gradients in Ca content
643 are generated when sodium diffuses against network-
644 forming cations such as Si and Al (Fig. 4). However,
645 this situation is not commonly encountered in geologi-
646 cal systems. For example, dissolution of very Ca-rich
647 plagioclase may result in opposing concentration gra-
648 dients of Na and Al around dissolving grains, but in
649 that case there will also be significant gradients in Ca
650 that may obscure the effects of off-diagonal terms of
651 the diffusion matrix. Furthermore, for the case of the
652 Moon (one of the most potentially important contexts
653 for anorthite dissolution) the concentrations of Na are
654 so low that no non-linear effects on Ca-diffusion have
655 been described (e.g. (Morgan et al., 2006)). On the other
656 hand, dissolution of albite-rich plagioclase should result
657 in strong gradients of Na with only weak associated gra-
658 dients of CaO. However, in this case, gradients of Na, Si
659 and Al may all be positively correlated around the dis-
660 solving grain, again limiting the development of uphill
661 diffusion of Ca. We do note, however, that weak up-hill
662 gradients have been described around dissolving plagi-
663oclase grains (in SiO₂ for the experiments of (Morgan
664 et al., 2006), and Na₂O for (Yu et al., 2016)) indicat-
665 ing that knowledge of the complete diffusion matrix is
666 necessary when modeling the detailed behaviour of ge-
667 ological systems. However, we also stress that quantita-
668 tive application of our results to systems of geochemical
669 interest must await quantification of the temperature de-
670 pendence of the diffusion matrix and confirmation that
671 the eigenvectors derived here are indeed applicable over
672 relevant temperature ranges.

673 Conclusion

674 Using diffusion-couple experiments, we determined
675 the diffusion matrix in the soda-lime aluminosili-
676 cate system, in the vicinity of a composition of
677 64.5 wt%SiO₂, 13.3 wt%Na₂O, 10.8 wt%CaO, 11.4
678 wt%Al₂O₃. We used a large number of diffusion experi-
679 ments in order to overconstrain the determination of the
680 diffusion matrix, for a better robustness to measurement
681 noise and ill-conditioning of the matrix. Indeed, we
682 found a factor of 50 between the largest eigenvalue, cor-
683 responding to the exchange of sodium and calcium, and
684 the second largest eigenvalue, corresponding to an ex-
685 change involving network formers. Our study therefore
686 showed that the diffusion of sodium is largely decou-
687 pled from that of network formers, since sodium only
688 appears in the exchange reaction with calcium.

689 This first study of multicomponent diffusion in a qua-
690 ternary aluminosilicate glass containing both alkali and
691 alkaline-earth cations permits comparisons with previ-
692 ous studies in ternary systems. The dominant eigenvec-
693 tor, corresponding to the exchange of sodium and cal-
694 cium, plays the same role in our quaternary system as
695 in the ternary soda-lime system. Moreover, the second
696 eigenvector, corresponding to the exchange of calcium
697 with network formers, is the dominant eigenvector in
698 ternary CAS systems. The diffusion matrix of the NAS
699 system has not been determined yet in the literature, but
700 the eigenvectors of the KAS system (transposing Na for
701 K) do not seem to play a role in the NCAS system. In-
702 deed, we observed in our system a calcium-mediated
703 decoupling between sodium and network formers. Fu-
704 ture studies adding a fifth element, such as magnesium
705 or potassium, could reveal the extent to which complex
706 systems can be modeled using a decomposition in sim-
707 pler systems.

708 Finally, the ability to model diffusion over a large
709 composition domain with a single set of eigenvectors
710 and eigenvalues, and the persistence of eigenvectors
711 with the addition of elements, suggests that eigenvec-
712 tors can be interpreted as cooperative rearrangements of
713 multiple species. We attempted to give a microscopic
714 interpretation of these rearrangements. In order to probe
715 the existence of such mechanisms at the atomic level,
716 molecular dynamics would be required, in order to ex-
717 tract collective dynamic patterns responsible for the dif-
718 fusion of species.

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723 Marc Flesselles and William Woelffel.

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