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► **To cite this version:**

Daniel R. Neuville, Charles Le Losq. Link between medium and long-range order to macroscopic properties of silicate glasses and melts. *Reviews in Mineralogy and Geochemistry*, 2022, 87 (1), pp.105-162. 10.2138/rmg.2022.87.03 . hal-03857133

HAL Id: hal-03857133

<https://hal.science/hal-03857133>

Submitted on 17 Nov 2022

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4 **Link between medium and long-range order to macroscopic properties of**
5 **silicate glasses and melts**

6
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15 **Abstract:** Understanding the cationic network and the medium range order of glasses and melts allows
16 rationalization of each elements role in terms of the network former, charge compensator or network
17 modifier concepts. Such knowledge can be combined with further details, e.g. regarding the role of highly
18 coordinated network former elements, to model the macroscopic properties of glasses and melts, like
19 their molar volume, density, configurational entropy and viscosity. In this chapter, we present recent
20 advances on such work, which open new avenues for the production of useful and precise models of
21 geologic and industrial glasses and melts.

22
23
24 *1. Introduction*

25 The two first chapters of this volume focus on the structure of magmas at different scales: short and
26 medium range order. A quick review of the glass literature, from the 90's or older, reveals that most
27 published papers focused on the structure of glasses, or on properties of glasses or melts. Depending on
28 their original discipline, the work of the scientific community in those areas are different. Physicists
29 published papers on glass structure, including the structure of SiO₂, GeO₂, B₂O₃ as seen by X-Ray or
30 neutron diffraction and Raman spectroscopy for example ([Wright 1990](#), [Gaskell et al., 1991](#), [Galeener et
31 al., 1983](#)). Chemists worked on more complex glass compositions, like chalcogenide ([Poulain and Lucas,
32 1970](#), [Poulain 1983](#)), or focused their work on specific properties of glasses like refractive index, density
33 or the oxidation state of multivalent elements ([Schreiber, 1986](#)). Earth scientists worked on properties of

34 melts involved in geologic phenomena, like diffusivity, heat capacity, density or viscosity (Ryan and
35 Blevins, 1987, Carmichael et al. 1977, Bacon 1977; Robie et al., 1979, Bottinga and Weill 1970, 1972).
36 This has changed over time. Since the 2000's, it is easier to simultaneously investigate the structure and
37 properties of glasses. Industrial and technological needs evolved, and the interest of the Earth sciences
38 community became more and more focused on the acquisition and interpretation of *in situ* data to address
39 problems requiring insights about silicate melts at high temperature and high pressure. As a result, the
40 scientific community became more unified, performing more and more studies that simultaneously
41 investigated the structure and properties of glasses and melts. Presently, we have reached a point where
42 it is possible to link together experimental and structural/thermodynamic data to build models for solving
43 industrial or Earth sciences problems. The aim of this chapter is to show how this is possible.

44 45 *1.1 Glass structure versus macroscopic properties*

46 Among the most important questions about glasses and melts, one is critical for many applications
47 and studies: how the melt/glass structure affects macroscopic properties? For Doremus (1973), a glass is
48 an amorphous solid. The term solid implies a high viscosity, usually greater than 10^{10} Pa.s. This viscosity
49 therefore limits the flow of the body. The amorphous term implies the absence of long-range order (see
50 Figure 5A in the previous chapter, Drewitt et al., 2021), which reveals an analogy with the liquid state.
51 So, a glass is a solid whose properties are similar to those of liquids. Parks and Huffman (1926) even talk
52 about "a fourth state of matter". However, no consensus exists regarding glass, and the nature of glass
53 and the glass transition are two fundamental questions that remain open in condensed matter physics
54 (e.g., see the different definitions in and debate between Zanotto and Mauro, (2017), Popov (2018),
55 Schmelzer and Tropin, (2018)).

56
57 An important point is that glasses can exhibit very different chemical compositions and can be
58 prepared by different means. Mineral (i.e. silicate), oxide, non-oxide, metal and organic glasses exist (see
59 for an exhaustive description in Musgraves et al. (2019)). In fact, glasses are found regardless of the type
60 of chemical bonds that link the atoms they contain: covalent, ionic, metallic, Van der Waals or hydrogen
61 bonding. The glassy state is a characteristic of condensed matter. Glasses can be obtained by the rapid
62 quench of liquids, or of a gas by solid condensation, by amorphization of a crystalline phase or by sol-
63 gel methods (Descamps 2017). The most common method for obtaining a glass is by the rapid quench of
64 a liquid¹. During the quench, viscosity continuously increases up to a value so high that the final state
65 can be considered as solid. One can therefore imagine the structure of the glass as being similar to that

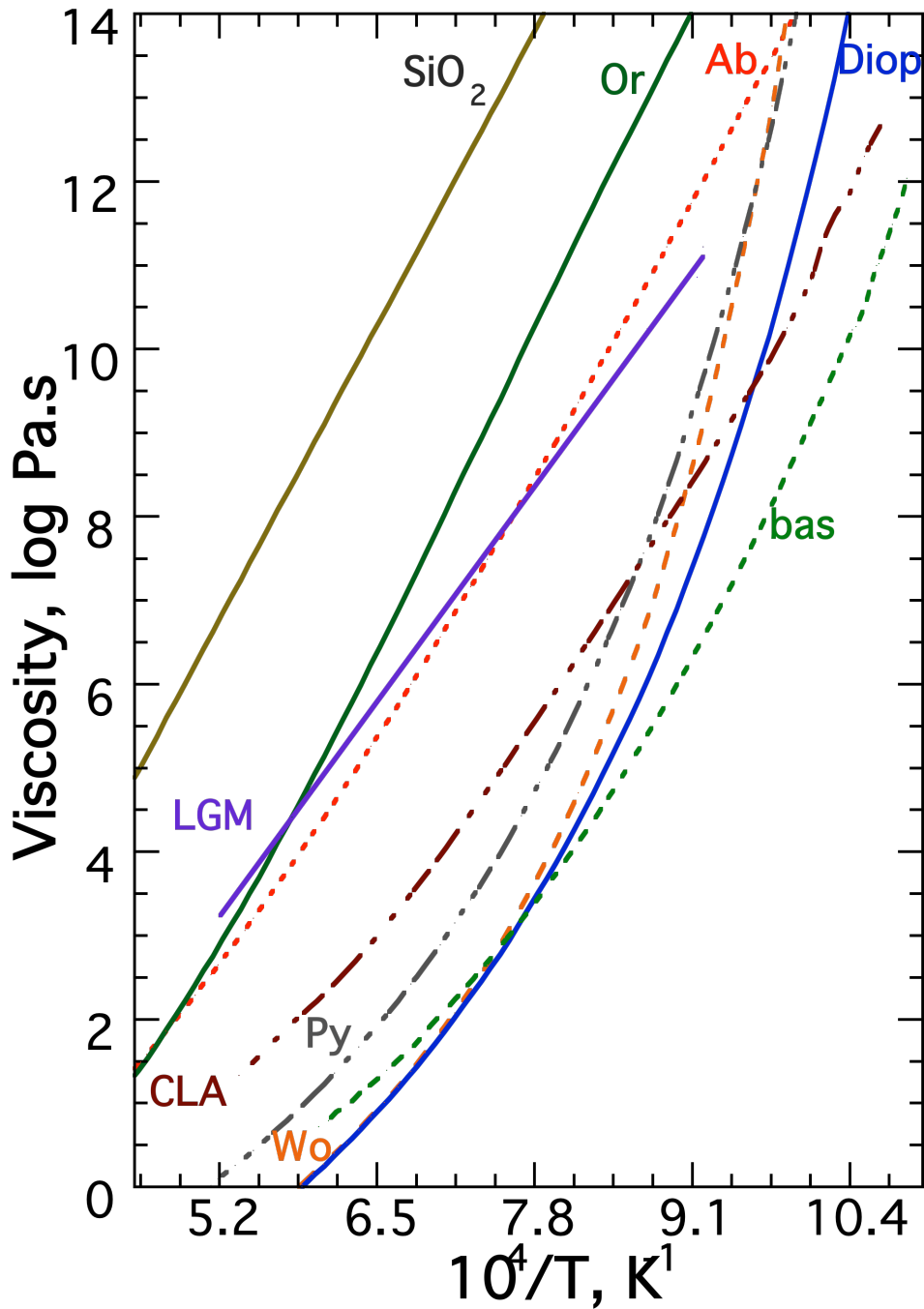
¹ rapid cooling rate means 15°/min, the term classic cooling rate is also used.

66 of a liquid whose movements are hindered. Glasses, like undercooled liquids, have a disordered structure
67 that was frozen in at the glass transition temperature.

68

69 A fundamental question is *what happens when a liquid crosses the glass transition temperature?* The
70 latter is the temperature (often abbreviated T_g , and more realistically it is a small temperature interval) at
71 which second order thermodynamic properties like heat capacity show a transition, revealing the locking-
72 in of the atoms in fixed (but undetermined) positions. In essence, T_g is the temperature at which a number
73 of thermodynamic properties go from liquid-like to solid-like values.

74 Unlike a crystallized solid, it is not possible to introduce the term of melting temperature for the glassy
75 state. The solidification of a liquid into glass is accompanied, in fact, by a continuous and gradual increase
76 in viscosity upon cooling, without the appearance of a crystalline structure (Figure 1). This behavior
77 remains true regardless of the glass/melt chemical composition (silicate, aluminosilicate, borate,
78 borosilicate, germanate, chalcogenate, tellurate, metallic, organic... see for details regarding each glass
79 family the [Musgraves et al., 2019](#)). This shows the continuous transition from glass to liquid for a
80 property such as viscosity ([Tamman, 1925](#); see Figure 1). The glass transition is a dynamic phenomenon
81 that characterizes the loss of internal thermodynamic equilibrium. Indeed, the properties of a glass no
82 longer depend solely on pressure and temperature, but also on the temperature at which the glass
83 transition occurs. Finally, Tamman ([1925](#)) sums the concept as “*The viscosity of a liquid increases with
84 increasing undercooling, and in a rather narrow temperature interval it increases very rapidly to values
85 characteristic of solid crystals. A brittle glass is thus formed from an easily mobile liquid. This change
86 in viscosity does not correspond to the behavior of the other properties, which in this temperature interval
87 change relatively only slightly. The change in viscosity is a continuous one and no temperature can be
88 chosen as the freezing-point, the point at which the liquid becomes solid. Glasses are undercooled
89 liquids.*”



90

91 *Figure 1: Viscosity versus $1/T$ curves for different melt compositions. LGM and CLA are rhyolite and*
 92 *andesite melts from [Neville et al. \(1993\)](#), bas is a basalt melt from [Villeneuve et al. \(2008\)](#), SiO_2 is silica*
 93 *melt from [Heterington et al. \(1964\)](#) and [Urbain et al., \(1982\)](#), Ab and Or are albite, $\text{NaAlSi}_3\text{O}_8$, and*
 94 *orthoclase, KAlSi_3O_8 melts from ([Le Losq and Neville, 2013](#); [Le Losq et al., 2017](#)); Py, Wo, Diop, are*
 95 *Pyrope, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, Wollastonite, CaSiO_3 , and Diopside, $(\text{CaMg})\text{SiO}_3$, melt compositions ([Neville](#)*
 96 *and [Richet, 1991](#)).*

97

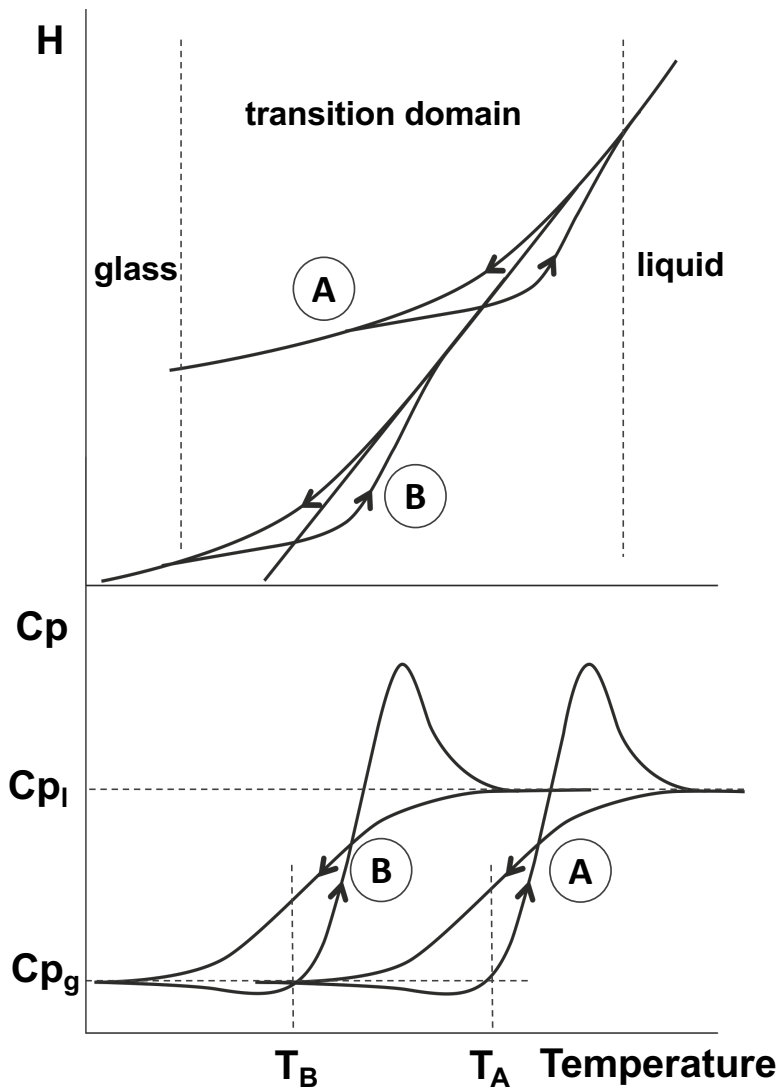
98 The simplest and earliest characterization of the glass transition is due to Parks and Huffmann
99 (1927), who investigated organic liquids. They note Nernst (1911), has stated that heating a glass
100 “externally it has the properties of a solid, owing to great viscosity and considerable rigidity, produced
101 by strong mutual action of the molecules. An amorphous body differs from a crystal, however, in its
102 complete isotropy and absence of a melting point; on heating, it passes continuously from the amorphous
103 to the usual liquid state, as its properties show steady change with rise of temperature, and no breaks
104 anywhere.”

105 In fact, Parks and Huffmann (1927) stated “While there is no definite temperature, comparable
106 to the melting point of a crystal, at which all properties undergo a sharp change, there is nevertheless a
107 temperature interval, definite and reproducible, in which a number of properties change with a rapidity
108 approaching that observed in the case of the melting process of a crystal. In brief, there is a softening
109 region instead of a melting point. The glass as it exists below this softening region differs so markedly
110 from the liquid existing above that it might well be considered as a different state of the substance.”

111 From an energetic point of view, Moynihan et al. (1974) showed that the variations in relative
112 enthalpy and heat capacity with temperature for two different cooling or heating speeds exhibit a sudden
113 change in temperature and corresponds to a dampened variation of these two properties. They showed
114 that for the same liquid, the glass transition temperature varies with the cooling or heating rate. The higher
115 the cooling rate, the higher relative enthalpy or heat capacity (Figure 2). The glass transition thus
116 corresponds to a small temperature and pressure interval upon which properties such as heat capacity
117 undergo a second order transition (Moynihan et al., 1974). This interval is at higher temperatures at high
118 cooling rates (situation A in Figure 2), and moves to lower temperatures at slower cooling rates (situation
119 B in Figure 2).

120 It is theoretically possible to obtain identical variations for all properties as a function of time at the
121 same temperature (thermal expansion, viscosity for example) but it is not necessary (Moynihan, et al.,
122 1974). With sudden changes in temperature, variations of the liquid properties linked to atomic mobility
123 require some time to reach a new equilibrium. This time is called the relaxation time, τ . A liquid has a
124 large number of different configurational states (Goldstein 1969; 1976). Each state corresponds to a
125 minimum in potential energy and when temperature decreases, the number of possible configurations
126 decreases as the domains for structural rearrangement become larger and larger. As a result, the time for
127 structural relaxation, τ , of the liquid increases. Crossing the glass transition leads to the atoms trapped
128 in given but disorganised positions. This results in quenching the liquid into a glass. The configuration
129 state of the glass does not change from T_g to 0 K, as shown by the fact that the residual entropy of glass
130 remains constant below T_g (e.g., see Tequi et al., 1993; Richet et al., 1991; Richet and Neuville, 1992;
131 Richet et al., 1986; Goldstein, 2011; Schmelzer et al. 2018 and references cited therein). It should be

132 noted that Raman and infrared vibrational spectroscopy data suggest that the structure of a glass is an
 133 image of the instantaneous configuration of the liquid at T_g (Kashio et al, 1980; Kusabiraki and Shiraishi,
 134 1981; Kusabiraki 1986; Sharma et al., 1978; Shevyakov et al., 1978, Neuville and Mysen, 1996).
 135



136
 137 *Figure 2: relative enthalpy and heat capacity versus temperature for 2 different cooling rates, A and*
 138 *B correspond respectively to fast and low temperature change (redrafted from Moynihan et al., 1974).*
 139 *Cp_l and Cp_g correspond to the heat capacities of the liquid and the glass, respectively. T_B and T_A*
 140 *correspond to the glass transition at the two different rates A and B, respectively.*
 141

142

143 The uniform cooling of a liquid at a rate $q=dT/dt$ can be likened to a series of instant temperature
144 jumps $\Delta T = T_{fi} - T_i$, where T_{fi} and T_i are the final and initial temperatures, each jump being followed by
145 a Δt period during which the temperature remains constant and equal to T_{fi} . Just after each jump, the
146 viscosity of the liquid, η_l , is still worth η_{Ti} and differs from $\eta_{Tfi} - \eta_{Ti}$ from the new balance value, η_{Tfi} .
147 This is called relaxation, the process by which the liquid tends to reach the state of equilibrium associated
148 with the final temperature T_{fi} . To characterize the kinetics of this evolution, we can define a viscous
149 relaxation time τ_η as equal to:

$$150 \quad \tau_\eta = \eta_l - \eta_{Tfi} / (\delta\eta / \tau_\eta). \quad (1)$$

151 Experimentally, τ_η increases when T decreases. Three cases can be distinguished:

152 $\Delta\tau \gg \tau_\eta$, the substance has a relatively long time to equilibrate its structure at the new
153 temperature. We are in the liquid state or in a glass state at the thermodynamic equilibrium for which the
154 equilibrium viscosity is reached almost instantaneously. During cooling, the viscosity increases to its
155 equilibrium value.

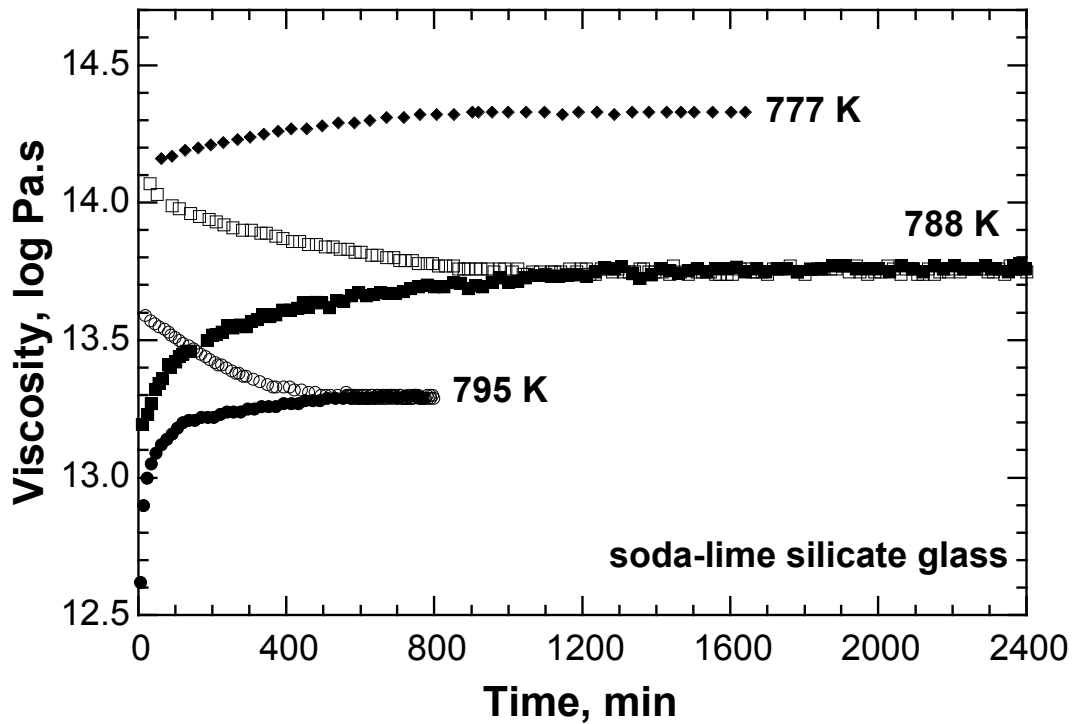
156 $\Delta\tau \sim \tau_\eta$, this corresponds to the glass transition domain. Viscosity depends on both the time and
157 temperature to which the glass was previously subjected.

158 $\Delta\tau \ll \tau_\eta$, the relaxation time is much higher than the measurement time. No configurational
159 rearrangement is then possible. The liquid freezes. Only the vibrational part of the heat capacity remains,
160 which is close to the heat capacity of the crystal.

161

162 Relaxation times depend heavily on temperature (Rehson, 1975; 1989, Simmons et al., 1970; 1974,
163 Dingwell and Webb, 1990), as well as on the structure and therefore glass composition; e.g. borosilicate
164 glasses have higher relaxation times than silicate or aluminosilicate glass compositions (Sipp et al., 1997).
165 Figure 3 shows, for a soda-lime silicate glass, that relaxation time increases with decreasing temperature:
166 e.g. equilibrium is reached after 500, 1200, 1600 min respectively at 795, 788 and 777 K.

167



168

169 *Figure 3: Viscosity versus time for a soda-lime silicate glass at different temperatures (redrafted from*
 170 *Sipp et al., 1997). We can note that increasing viscosities represent relaxation after previous*
 171 *measurements performed at higher temperatures, whereas decreasing viscosities indicate relaxation*
 172 *after annealing at lower temperatures.*

173

174 However, it is important to note that there is no reason why the relaxation times of the various
 175 properties should be identical at equal cooling speeds. Moynihan et al. (1976a) indicate that “for example,
 176 the enthalpy changes occurring during the approach to equilibrium of a network glass following a change
 177 in temperature could be considered to arise from the breaking of some of the network bonds, while the
 178 volume changes are due to rearrangement of the structure into less densely packed configurations. One
 179 cannot say a priori, however, which of these two processes should on the average occur earlier in time.
 180 That is, bond breaking might be a necessary precursor to volume-changing rearrangements of the
 181 structure, so that one would expect H to relax faster than V . On the other hand, configurational
 182 rearrangements leading to large volume changes might occur early in time, stressing the network and
 183 leading to subsequent bond breaking, so that one would expect V to relax faster than H .” In practice, it
 184 appears that the differences in relaxation time between volumetric and calorimetric relaxation times are
 185 relatively small, if not almost non-existent, and are essentially due to differences in cooling or heating

186 rates (Sasabe et al., 1977; Moynihan and Gupta, 1978; Dingwell and Webb, 1990). Differences between
187 relaxation times for the same material but determined with methods sensitive to different properties are
188 clearly visible when comparing data from dilatometry, calorimetry and viscosimetry. For example, in the
189 case of alkaline-earth aluminosilicate glass compositions, drop calorimetry T_g are generally found at
190 temperatures at which viscosities are of $10.7 \pm 0.5 \log \text{ Pa.s}$, a value lower than that of $\sim 12 \log \text{ Pa.s}$ that
191 is known to be the reference for the determination of the viscous T_g (Neuvville and Richet 1991; Tequi et
192 al., 1991).

194 *1.2 Thermodynamic approach to glass transition*

195 We have seen that temperature and pressure are not sufficient parameters to characterize the state of
196 glass. Tool and Eichlin (1931) introduced the concept of fictive temperature, T_{fic} , to characterize a glass
197 at constant pressure. It can be defined as the temperature at which the glass would be in an equilibrium
198 state (as a melt) if it could be heated and measured instantly. The fictive temperature can be defined
199 during cooling in dilatometry or calorimetry, as the glassy transition temperature.

201 It is possible to give a formal thermodynamic definition of the fictive temperature, considering it as
202 an order parameter. Moynihan et al. (1974, 1976a,b) discussed fictive temperatures, their influence on
203 enthalpy properties and order parameters. It can be recalled, that the glass transition looks like a second-
204 order transition for which volume, enthalpy and viscosity are continuous functions of T but not heat
205 capacity, dilatation and compressibility coefficients. For the latter parameters, a steep transition is
206 observed when temperature crosses the glass transition.

208 In reality, fictive temperature is a critical parameter as it reflects how viscosity, hence relaxation time,
209 can show non-equilibrium behavior and can depend on time in the supercooled domain. In Figure 3, the
210 effect of fictive temperature is clearly visible. The downward curve is obtained from a sample that has a
211 fictive temperature below the measurement temperature. Similar behaviors are visible for density, or
212 refractive index (Winter, 1943, Ritland, 1954). When the fictive temperature of the glass is higher than
213 the measurement temperature, the glass has a more disordered configurational state than the state it should
214 have if the glass were in thermodynamic equilibrium, i.e. its "fictive" configuration entropy is too high.
215 It has a lower viscosity than its equilibrium viscosity, so its viscosity increases over time until the fictive
216 temperature equals the measurement temperature. For a fictive temperature lower than that of
217 measurement, the viscosity decreases until the establishment of the thermal equilibrium characterized by
218 the equality of the two temperatures. In Figure 2, the relaxation curves over time for the cases of cooling

219 or heating are asymmetrical. This is because a liquid increases its entropy faster with an increase in
 220 temperature (Rehson, 1980, Dingwell and Webb, 1990; Sipp et al., 1997)².

221
 222 *1.3 Viscosity and glass transition*

223 The glass transition is closely related to transport phenomena and more specifically to viscosity (Adam
 224 and Gibbs 1965; Gibbs and Dimarzio, 1958; Goldstein, 1969; Grest and Cohen, 1980; Scherer 1984,
 225 Richet, 1984), one of the fundamental properties of liquids that intervenes in transport processes. For the
 226 experimentalist, liquid viscosity also can be considered as a structural probe. Many models attempt to
 227 describe the variation of viscosity with temperature. Among them, we can cite the empirical Arrhenius and
 228 Tamman-Vogel-Flucher (TVF) equations, or the thermodynamic Adam-Gibbs (AG) model (see also
 229 section 2) allows linking melt mobility to its thermodynamic properties such as heat capacity and
 230 configurational entropy, and can be used for viscosity predictions and extrapolations (Neuville and
 231 Richet, 1990). Le Losq and Neuville (2017) further showed that the AG model allows linking melt
 232 structural knowledge to thermodynamic properties and viscosity, in order to build complete, extensive
 233 models for property predictions.

234
 235 *1.4 Configurational properties and glass structure*

236 Configuration properties are the key to understand the difference between liquids and glasses. To
 237 illustrate the importance of such configurational aspects, consider the second order thermodynamic
 238 properties of crystal, glass and liquid pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$).

239
 240 TABLE 1: Heat capacity of pyrope and $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, glass and liquid in $\text{J mol}^{-1} \text{K}^{-1}$. Data are from
 241 Tequi et al. (1991).

T(K)	Crystal	Glass	Liquid
298	325,6	327,8	
1020	492,2	504,4	665,7
1700	522,6		689,5

242
 243 Above room temperature, the glass and crystalline phase have similar heat capacities, C_p . On the
 244 contrary, the C_p of the liquid is 25% higher than that of solids (crystal or glass). Moreover, it should also
 245 be noted that the C_p of the liquid usually increases with temperature of the liquid and cannot be
 246 considered as a constant. These differences can have a significant impact when you integrate with

² A fictive pressure, P_{fic} , can be defined as the pressure at which the glass would be in an equilibrium state if it were subjected instantly to pressure equal to P_{fic} , at constant temperature.

247 temperature or pressure, as shown by the example of pyrope and $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ liquid. For instance, a
 248 simple extrapolation of the heat capacity of the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ liquid to low temperatures would produce
 249 a liquid with a lower entropy than that of its crystalline form below 694 K (Figure 4A). This temperature
 250 actually corresponds to the Kauzmann temperature, a temperature below which the liquid entropy would
 251 become lower than that of a crystal with the same composition. Such a system does not exist because a
 252 property of a liquid like the entropy should always remain higher than that of its crystalline form at a
 253 given temperature. The violation of this idea is known as the Kauzmann paradox (Kauzmann, 1948)³.
 254 The pyrope example shows that configuration terms play an important role on the properties of liquids.
 255 It is therefore necessary to understand how configurational properties vary, and their link to melt and
 256 glass structure. Figure 4A shows the variation of the entropy of a crystal, glass and liquid for the
 257 $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ composition as a function of temperature. It is clear that the residual entropy corresponds
 258 to the difference between the entropy of the glass and that of the crystal at 0 K. This residual entropy is
 259 very small compared to the entropy of glass, crystal and liquid. This residual entropy is called
 260 configurational entropy, S^{conf} , and it is the key to understanding glasses and liquids. To determine S^{conf} ,
 261 it is necessary to solve the entropic cycle represented in Figure 4A. However, this is only possible for
 262 minerals that melt congruently, and with a composition that can exist in a stable form as crystal, liquid
 263 and glass. Measuring the heat capacity of the crystal, C_{pc} , from 0 K to the melting temperature, T_m , allows
 264 determining its absolute entropy S_c at T_m :

$$265 \quad S_c = \int_0^{T_m} \frac{C_{pc}}{T} dt. \quad (2)$$

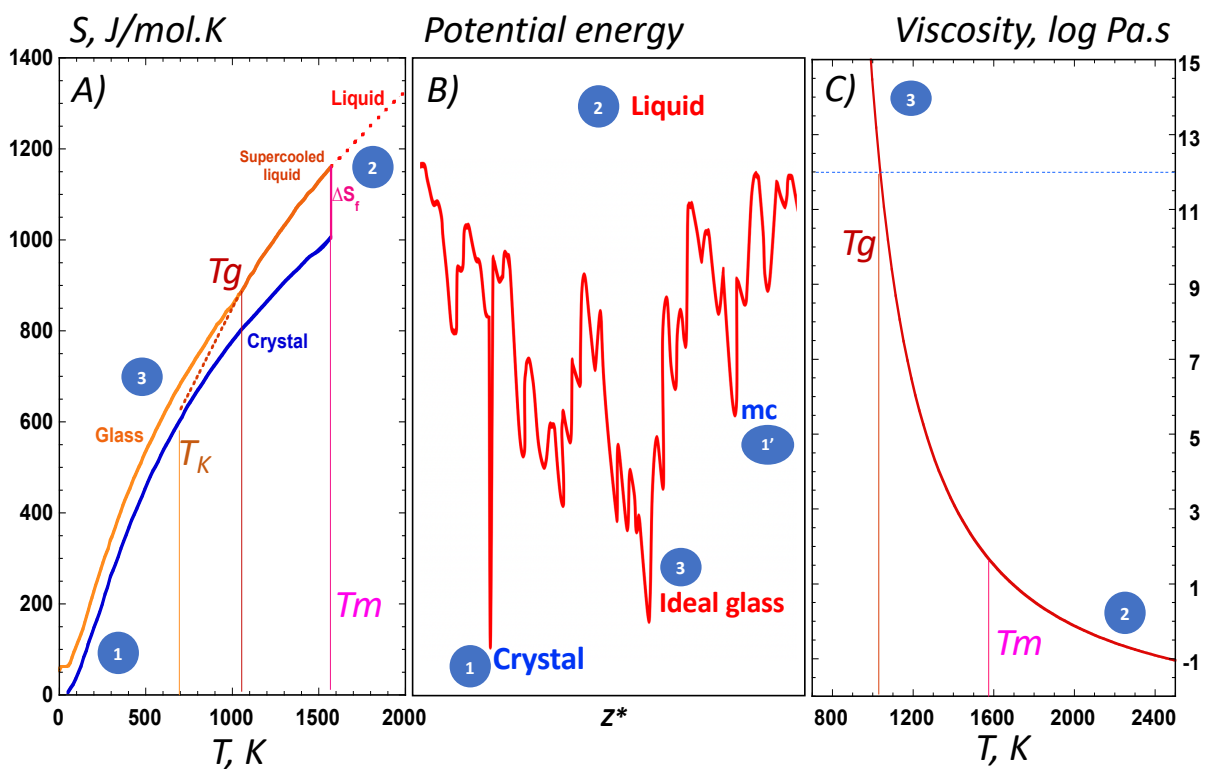
266 By adding the entropy of fusion of the crystal, ΔS_f , to S_c , the entropy of the liquid S_l is then obtained
 267 at T_m . Measuring the heat capacity between the melting temperature, T_m , and the glass transition
 268 temperature, T_g , allows determining the heat capacity of the liquid and the supercooled liquid, C_{pl} . The
 269 measurement of the heat capacity of the glass between T_g and 0 K provides C_{pg} . Finally, the residual
 270 entropy, also known as the so-called configurational entropy S^{conf} , is obtained at 0 K via:

$$271 \quad S^{conf}(0\text{ K}) = \int_0^{T_m} \frac{C_{pc}}{T} dt + \Delta S_f + \int_{T_m}^{T_g} \frac{C_{pl}}{T} dt + \int_{T_g}^0 \frac{C_{pg}}{T} dt. \quad (3)$$

272 This calculation is illustrated in Figure 4A for a composition of $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Tequi et al.,
 273 1991). As this Figure shows, S^{conf} represents a small difference between large numbers, and its value will
 274 be affected by a very large error if calorimetric measurements are not made with the highest possible
 275 accuracy. For this purpose, the studies focused on determining S^{conf} from calorimetry measurements
 276 require high-precision measurements of thermal capacity: heat capacities need to be determined better

³ this well-known paradox in temperature is recently proposed via pressure, but without any
 experimental basis see papers of Schmelzer et al., (2016) and Mauro (2011).

277 than 0.2 % by adiabatic calorimetry between 0 K and ambient, and better than 0.5 % by high-temperature
 278 drop calorimetry (e.g. Tequi et al., 1991). Aside from the time and the difficulty of performing such high
 279 precision heat capacity measurements, one of the main drawbacks of the calculation of the
 280 configurational entropy through the thermodynamic cycle is the necessity to study minerals that melt
 281 congruently, with compositions existing as glass, liquid and crystal as stated previously. Only a few
 282 chemical compositions can be studied in this way. Fortunately, as we shall see later, S^{conf} can be
 283 determined through the use of the Adam and Gibbs model combined with viscosity measurements.



284
 285 *Figure 4: A) entropy versus temperature (Tequi et al., 1991), B) schematic representation of the com-*
 286 *plex higher dimensional potential energy hypersurface of an N -particle system in terms of a two-dimen-*
 287 *sional diagram of chemical potential versus some collective configuration coordinate Z^* , which defies*
 288 *precise definition, but the width of the funnel represents entropy (Angell, 1991; Mossa et al. 2002),*
 289 *and C) viscosity versus temperature for the $Mg_3Al_2Si_3O_{12}$ composition (Neuville and Richet, 1991). The*
 290 *same numbers are all connected together in the three figures. 1 is the Pyrope crystal that presents the*
 291 *minimum potential energy. 1' is a metastable crystal, mc, that can have a potential energy higher than*
 292 *that observed for the glass. 2 is the liquid with a low viscosity, high entropy and high potential energy,*
 293 *in which atoms can move rapidly from one position to one other. 3 is the glass, in which atoms can*
 294 *move very slowly, there is a relaxation time, viscosity increase and entropy decrease, and the atom can*
 295 *fall in different potential energy minima and stay inside or jump to another with a lower potential en-*
 296 *ergy. T_m is melting temperature, T_g , glass transition temperature, T_K Kauzmann temperature, ΔS_f en-*
 297 *tropy of melting at the melting temperature. Supercooled liquids are liquids between melting tempera-*
 298 *ture and glass transition temperature.*

299
300
301

302 Figure 4B schematically illustrates the positions of atoms in a crystal as a function of the collective
303 configuration coordinate, as determined by local minima of interatomic potentials that are at specific
304 positions, allowing the building of a repetitive pattern characterized by long range order. In a glass, the
305 bond angles and interatomic distances are not constant but extend over a range of relatively close values.
306 Long-range order does not exist, and one can represent the interatomic potentials as a plane showing
307 minima separated by barriers with varying shapes and heights. As a result, glass entropy is higher than
308 that of crystal at given temperature (point 3, Figure 4). The ideal glass with the minimum potential exists,
309 but also other minima can exist with higher potential for the glass state or even the metastable crystal
310 (point 1'). Now suppose that a certain amount of heat is brought instantly to the glass. Below the glass
311 transition, the thermal energy brought upon increasing temperature is accommodated as vibrations, via
312 an increase in average vibration amplitudes. The specific heat is vibrational in nature and the material
313 behaves like a solid. At and above T_g , the thermal energy becomes important enough to allow the atoms
314 to cross the energy barriers that separate the different configurational states (Richet and Neuville, 1992).
315 This configurational contribution is necessarily positive, and the liquid or glass states can be defined by
316 the existence or absence of this contribution (Davis and Jones, 1953). In a way, the glass transition can
317 be seen as the beginning of the exploration by atoms of positions corresponding to the highest values of
318 interatomic potential (Goldstein, 1969). This distribution of configurations over increasingly high
319 potential energy states is the main characteristic of atomic mobility and low viscosity or relaxation time
320 (point 2, Figure 4).

321 If we now look at the changes in volume in an amorphous material, we notice that a general
322 characteristic of interatomic potentials is their anharmonic nature, i.e. that the forces applied to the
323 vibrational atoms are not exactly proportional to the movements in relation to the equilibrium positions
324 of these atoms (Richet and Neuville, 1992). An increase in vibration amplitudes therefore leads to an
325 increase in interatomic distances. Like solids, liquids also have such anharmonic vibrational expansion,
326 but higher-energy patterns that begin to be explored over the glass transition are generally associated
327 with increased interatomic distances. This is why the thermal expansion coefficient generally increases
328 significantly at the glass transition (Richet and Neuville 1992).

329

330 *1.5 pressure-temperature space*

331 As we have mentioned before, there is a glassy transition pressure (Rosenhauer et al., 1979), which
332 allows one to place the glass transition in a pressure-temperature plane for a given cooling or heating

333 rate. However, the effects of pressure and temperature on the properties of glasses are actually different.
334 High pressure can produce irreversible configurational changes. So, for given experimental quench rates
335 or measurement time scales, the kinetics of configurational changes are markedly different depending on
336 whether they are caused by pressure or temperature. The main reason for this difference is that the shape
337 of potential energy wells varies little with temperature but significantly with pressure. If high kinetic
338 energy is required to cross the potential barriers at constant pressure, changes in these barriers with
339 pressure can lead to new configurational states at lower temperatures, if the pressure is high enough. The
340 processes occurring at high pressure in glasses are likely similar to those that occur in liquids. Since the
341 2000's, many papers have shown significant changes in the glass structure with increasing pressure, more
342 or less linked to changes in their properties (e.g. [Poe et al., 2001](#), [Suzuki et al., 2002](#), [Wang et al., 2014](#)).
343 In this volume, an exhaustive chapter can be found on the effect of pressure on the structure and properties
344 of melts and glasses by Sakamaki and Ohtani (2021).

346 2. Silicate glasses and melts

347 2.1 Alkali or earth alkaline silicate glasses and melts

348 As depicted in the previous two chapters, silica glass is a material well-connected at the molecular scale,
349 built from a three-dimensional network of tetrahedral units composed of covalently bonded central Si
350 and apical O atoms (a.k.a. Bridging Oxygens or BO). However, contrary to α -quartz that forms perfect
351 trigonal crystals, SiO_2 glass is built by SiO_4 tetrahedra distributed disorderly yet not totally randomly
352 (e.g. see Figure 5A in chapter 3, this volume). The relative density d of silica glass equals 2.20 (molar
353 volume $V_m = 27.311 \text{ cm}^3$), a value lower than that observed for α -quartz ($d = 2.65$, $V_m = 22.673 \text{ cm}^3$) that
354 presents a compact and well-ordered structure. This implies that silica glass presents a rather porous
355 structure, with possibly a minor amount of Non-Bridging Oxygen (NBO, see Chapter 2, this volume)
356 atoms not connected to 2 Si atoms ([Brückner 1970](#); [Fanderlik, 1990](#)). The fraction of NBO in silica is
357 usually considered as negligible, making the silica structure a very strong one.

358 As an alkali oxide is added, Na_2O for example, more and more NBO are created until reaching the
359 possibility to create isolated SiO_4 tetrahedra linked together by only ionic Na-O bonds. For alkali
360 silicates, this corresponds to a theoretical view because Na_4SiO_4 glasses do not exist. However, in the
361 Ba-silicate system, it is possible to obtain glasses with 33% and 37% silica with classic cooling rate
362 ([Bender et al., 2002](#)), while in the Mg-silicate system it is possible to obtain glasses up to 62 MgO in
363 mole percent (38% SiO_2) but below 50 percent of silica, it is necessary to use a fast cooling rate as shown
364 in Raman spectra ([Neuville et al., 2014](#)). Glass formation in the SiO_2 - Na_2O system is actually not possible
365 for amounts of Na_2O lower than that of the metasilicate composition Na_2SiO_3 ([Schairer and Bowen,](#)
366 [1956](#)). At higher Na_2O contents, up to 58 mole percent, it is possible to obtain Na silicate glasses only

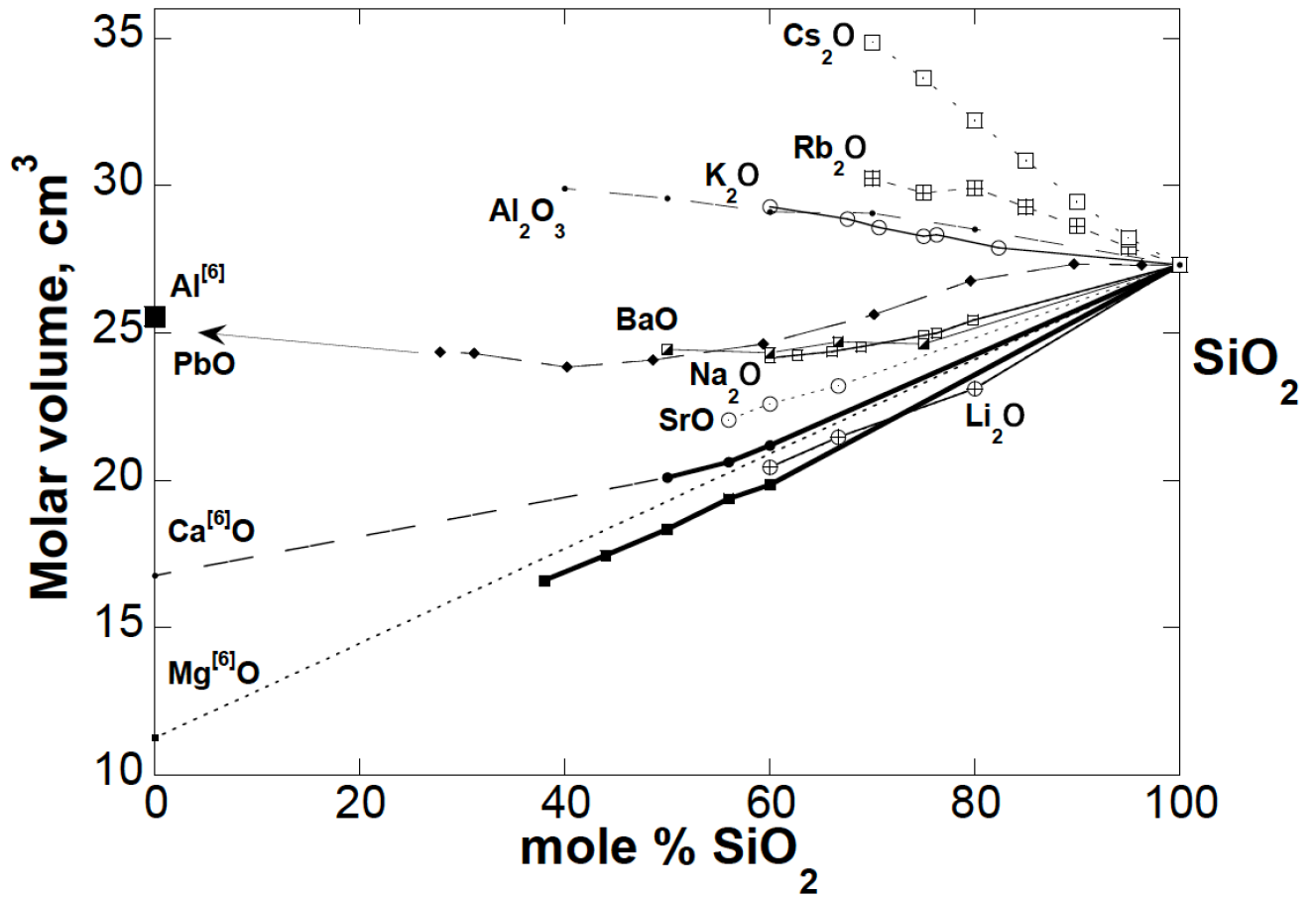
367 via high-speed quenching of a small quantity of melt (a few grams; [Imaoka and Yamazaki, 1963](#)). Stable,
368 large pieces of glass cannot be formed below 60 mol% of SiO₂ in this system ([Neuvillle, 2006](#)). For other
369 alkali-silicate glasses, it is possible to make glasses up to 35 and 55 mole % of Li₂O and K₂O, respectively
370 ([Imaoka and Yamazaki, 1963](#), [Levin et al., 1964](#)).

371
372 To summarize, alkali silicate glasses can be easily obtained at normal cooling rates in the 60 to 99
373 mole % SiO₂ range (see Raman spectra of silicate glasses in [Neuvillle et al., \(2014\)](#)), and alkaline-earth
374 silicate glasses between 33 and 75 mol% SiO₂, particularly with heavy alkaline-earth elements like Ba.
375 For Mg, the glass forming domain is smaller, and ranges between 37 and 55 mole % SiO₂ ([Imaoka and
376 Yamazaki, 1963](#), [Richet et al., 2009](#)). In the CaO-SiO₂ system between 1 and 62 mole % SiO₂, the melts
377 at temperatures just above the liquidus consists of two immiscible phases ([Imaoka and Yamazaki, 1963](#),
378 [Levin et al., 1964](#), [Hudon and Baker 2002ab](#); [Neuvillle 2006](#)).

379
380 Alkali or alkaline-earth silicate glasses show almost linear variations in molar volume with addition
381 of M₂O or M²⁺O in silica glasses (Figure 5). Molar volumes obtained from density measurements for
382 CaO-Al₂O₃-SiO₂ and Na₂O-Al₂O₃-SiO₂ are also available in the literature ([Seifert et al., 1982](#), [Doweidar
383 1998, 1999](#)) but we have chosen not to report them on the figures for two reasons: -i) they show similar
384 trends to ours, - ii) they are made with different cooling rate than ours (not mentioned in the articles).
385 The molar volume (V_m) of silicate glasses increases or decreases as a function of the cation size⁴. In the
386 case of cations presenting an ionic radius larger than O²⁻ (132 pm), like Cs⁺, Rb⁺ or K⁺, the glass molar
387 volume increases with cation addition. For cations presenting an ionic radius lower than that of O²⁻, like
388 Na⁺ and Li⁺, V_m of silicate glasses decreases both with the cation size and its amount. A similar behavior
389 is observed in alkaline-earth silicate glasses. In Ca and Mg silicate glasses, V_m varies almost linearly with
390 the glass SiO₂ (Figure 5). In Figure 5, a dotted straight line is drawn between SiO₂ and MgO with MgO
391 with Mg in 6-fold coordination, and it is clearly observed that the V_m of Mg-silicate glasses are below
392 this line, which suggests that the CN of Mg is significantly less than 6 in amorphous magnesium silicates.
393 Such an interpretation agrees with ²⁵Mg Nuclear Magnetic Resonance (NMR) spectroscopy that shows
394 that Mg is essentially in four-fold coordination in silicate glasses ([Fiske and Stebbins, 1994](#); [Georges and
395 Stebbins, 1998](#), [Kroeker and Stebbins, 2000](#), [Shimoda et al., 2007a,b](#)), as well as with XANES at the Mg
396 K-edge ([Trcera et al., 2009](#)) while Ca is essentially in six fold coordination in silicate glasses as shown
397 by XANES at the Ca K-edge ([Neuvillle et al., 2004b](#), [Cormier and Neuvillle, 2004](#); [Ispa et al., 2010](#);
398 [Cicconi et al., 2016](#)). These gentle variations may indicate that Ca and Mg remain almost in the same

⁴Cation size are given in [Whittaker and Muntus \(1970\)](#) and molar volumes are from [Robie et al. \(1979\)](#).

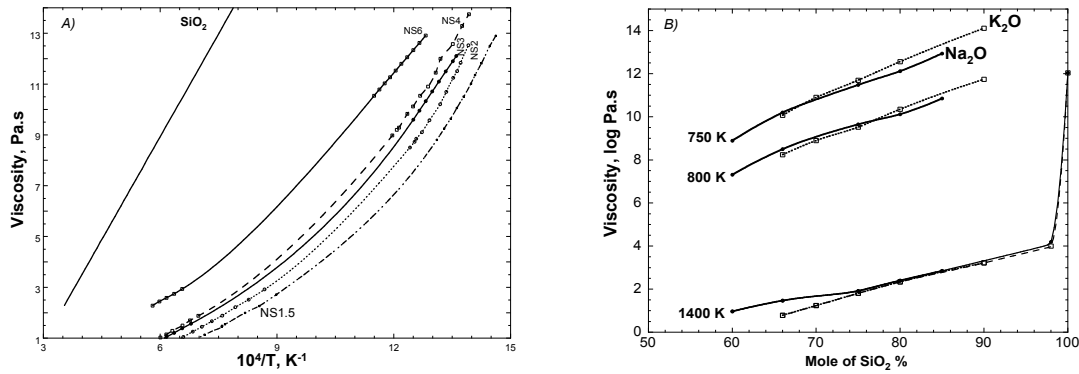
399 coordination number, CN, in silicate glasses, this CN being slowly affected by the SiO₂ content or by the
 400 variation in the number of bridging oxygens around Si.
 401



402
 403
 404 **Figure 5:** Molar volume of glasses at room temperature: data for Ca, Mg, Na, K, Li silicate glasses
 405 are original data from Neuville, Sr and Ba Novikov (2017) Rb, Cs O'Shaughnessy et al., (2017, 2020);
 406 Pb-silicate (Ben Kacem et al., 2017) and Al-silicate glasses (Wang et al., 2020). Molar volume of ^[6]Al
 407 corresponds to Al₂O₃, and MgO and CaO are from Robie et al. (1979). Density of MA44.00 and MA38.00
 408 glasses are respectively 2,807 and 2,881, Raman spectra of these two glasses are given by Neuville et al.
 409 (2014).

410
 411
 412 *Viscosity of silicate melts*

413 In Figure 6A, the viscosity of SiO₂ and soda silicate melts are plotted as a function of reciprocal
 414 temperature. Silica shows the highest viscosity of all glass compositions, as well as a strongly linear
 415 behavior indicating an Arrhenian behavior (slope is equal to an activation energy).



416

417 **Figure 6:** A) viscosity versus reciprocal temperature (SiO₂ NS6, NS4, NS3, NS2, NS1.5, data from
 418 [Neville, 2006](#), and [Le Losq et al., 2014](#)). NSx: x corresponds to the ratio of SiO₂/Na₂O in mole percent
 419 (e.g. NS4: x = 4 = 80/20 - 80 % SiO₂ and 20 % Na₂O); B) viscosity versus SiO₂ content for Na- and K-
 420 silicate glasses (data from [Poole, 1948](#), [Bockris et al., 1955](#), [Neville, 1992](#), [2006](#)).

421

422 The fact that silica easily forms a glass, albeit a strong one with a very high viscosity, directly indicates
 423 that Si is a network former cation. Other elements, presenting lower valence and larger ionic radius, can
 424 play different roles in the glass structure. For instance, the introduction of Na₂O in silica glass yields to
 425 breaking the covalent Si-O-Si bridges, and, hence, to the formation of Non-Bridging Oxygens, NBO. Na
 426 is considered, in this case, as a network modifier cation. Na fits into the glass structure as cations linked
 427 to the surrounding oxygens by bonds that are much more ionic and thus weaker than Si-O covalent bonds.
 428 Thus, the structure of sodium silicate glasses is weaker than that of vitreous silica. This translates into a
 429 lowering of the viscosity at given temperature when adding Na₂O in SiO₂ (Figure 6A). Furthermore, the
 430 introduction of Na₂O in silica glass produces a non-Arrhenian behavior that increases with x for the NSx
 431 glass; x corresponds to the ratio of SiO₂/Na₂O in mole percent (Figure 5A). When viscosity varies with
 432 1/T following an Arrhenian behavior, it follows this equation:

433

$$434 \quad \text{Log } \eta = A + B/T, \quad (4)$$

435

436 with A the viscosity at infinite temperature and B an activation energy. This equation can only be used
 437 for a few chemical compositions like SiO₂, GeO₂, NaAlSi₃O₈ or KAlSi₃O₈. An Arrhenian behavior
 438 implies that the activation energy, B, is independent of temperature, and, hence, that the process
 439 underlying melt viscous flow remains the same regardless of temperature. For melts showing a strong
 440 non-Arrhenian behavior like NS3, the activation energy term, B, decreases from 2000 kJ mol⁻¹ at 1000
 441 K down to 300 kJ mol⁻¹ at 1800 K. In such conditions, it is no longer possible to use the Arrhenian

442 equation. For this reason, Tamman, Vogel and Fulcher proposed the so-called TVF equation (Vogel,
443 1921; Fulcher, 1925, Tamman and Hesse, 1926) to link viscosity and temperature:

$$444 \quad \text{Log } \eta = A + B/(T-T_1), \quad (5)$$

446
447 A , B and T_1 are just fitting parameters without physical meaning. The TVF equation is very useful to
448 fit and interpolate viscosity data at low and/or at high temperature (Neuville and Richet, 1990). This
449 equation has been used in many different papers and is at the basis of several viscosity models (Bottinga
450 and Weill, 1971; Shaw, 1972; Persikov 1991; Giordano et al., 2008; Giordano et Russell, 2018). The
451 empirical parameters A , B , T_1 can be linked to glass structure (Giordano and Russell, 2018). However,
452 while finding very practical applications, this equation remains purely empirical.

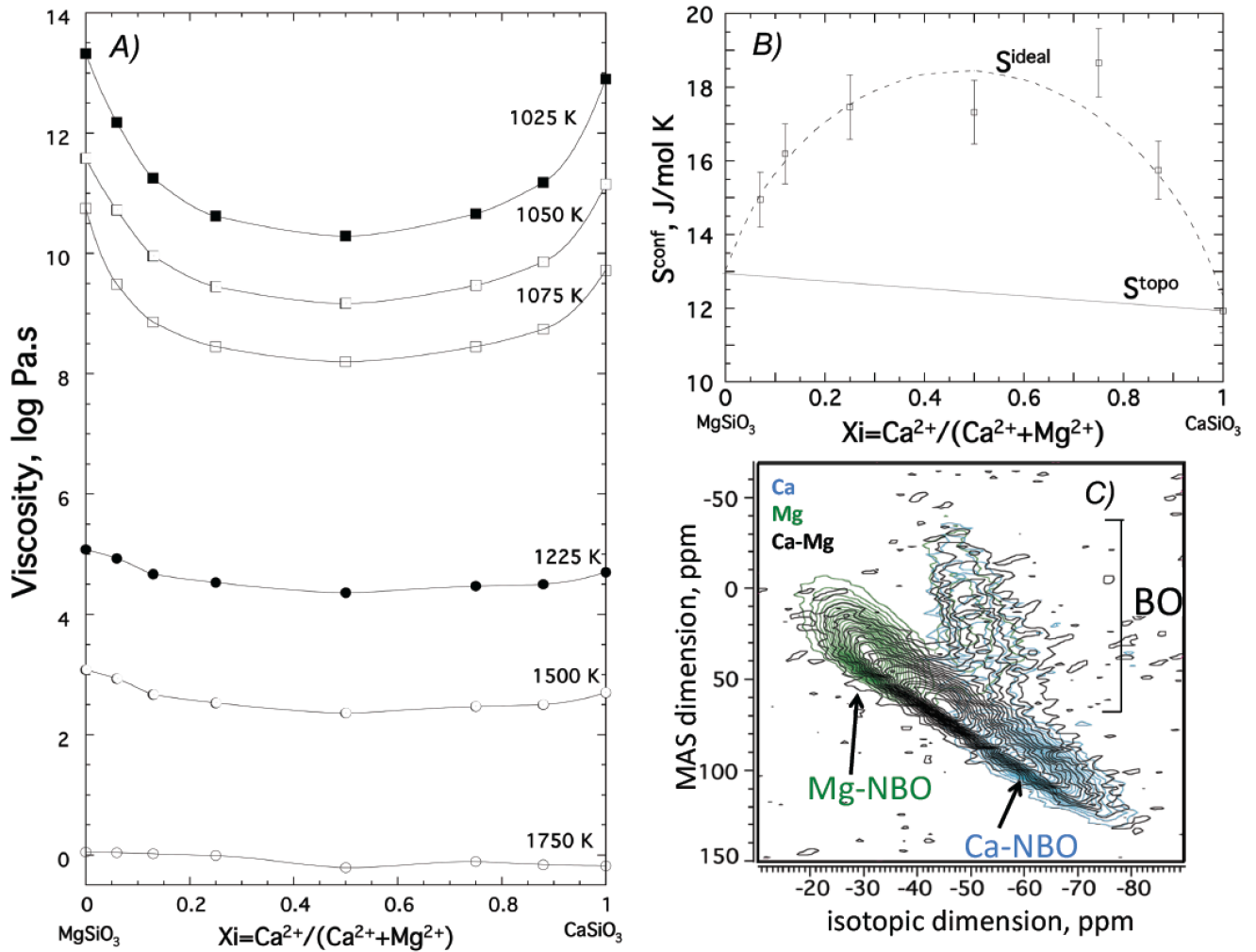
453
454 Aside from the empirical Arrhenius or TVF equations, the Adam-Gibbs equation, derived from the
455 theory of Adam and Gibbs (1965), is one of the best candidates to fit and extrapolate viscosity
456 measurements for silicate melts (Urbain, 1972, Wong and Angel, 1976; Scherer, 1984, Richet 1984,
457 Neuville and Richet, 1990; 1991, Mauro et al., 2009). The strength of this equation is that it allows
458 relating viscosity measurements to heat capacity and configurational entropy data (Urbain, 1972; Wong
459 and Angell, 1976; Scherer, 1984, Richet, 1984). The Adam-Gibbs theory and equation will be discussed
460 in more details in the next section. No other equation allows relating thermodynamic to dynamic variables
461 in a simple way.

462
463 The variations observed and described previously for sodium silicate glasses are similar for all alkali
464 oxides, as for instance visible for K_2O in Figure 6B. Generally, the addition of a few percent of alkali in
465 silica glass produces an important viscosity decrease of a few orders of magnitude (Lecko et al., 1977).
466 Ten mole percent of alkali oxides decreases the viscosity by ~ 10 orders of magnitude at 1400 K, this
467 decrease being larger at low temperature near the glass transition temperature. After 10 mol% of added
468 alkali oxides, the decrease in viscosity with increasing alkali content becomes less pronounced and the
469 viscosity varies almost linearly at high temperature. These viscosity variations for more than 10% of
470 added alkali are well correlated with increases in thermal expansion and heat capacity of the liquid which
471 vary almost linearly as a function of chemical change at high temperature (Bockris et al., 1955; Lange
472 and Carmichael, 1987; Lange and Navrotsky 1992).

474 *2.2 ideal mixing: mixing alkali or alkaline-earth in silicate glasses and melts*

475 In section 2.1, we observed that molar volumes, as well as viscosity and glass transition temperature
476 of alkali and alkaline-earth silicate glasses all changes with the addition of network modifiers. Mixing
477 different metal cations (like Ca and Mg, or Na and K) in silicate glasses results in large variations in their
478 properties, such as large decreases of their glass transition temperatures or large increases in their
479 electrical conductivity (Day, 1976). This is the so-called mixed alkali effect, MAE, reviewed many times
480 (Richet, 1984, Neuvillle and Richet, 1991, Allward and Stebbins, 2004; Cormier and Cuello, 2013, Le
481 Losq and Neuvillle, 2013, Le Losq et al., 2017, Bødker et al., 2020) in the literature for alkali silicate
482 glasses since the work of Day (1976).

483
484 In this section, we show and introduce some terminology about mixing elements and their effect on
485 the structure and macroscopic properties of melts and glasses. Ca and Mg are very important elements in
486 Earth and material sciences, and it thus it is particularly important to understand how they mix in silicate
487 melts. To understand this, we can look at how viscosity varies along the CaSiO_3 - MgSiO_3 binary. Neuvillle
488 and Richet (1991) have shown that at constant temperature, the viscosity of $(\text{Ca,Mg})\text{SiO}_3$ composition is
489 always lower than the viscosity of the end-member, CaSiO_3 or MgSiO_3 (Figure 7A).



491
 492 **Figure 7:** A) Viscosity versus $x_i = Ca^{2+}/(Ca^{2+} + Mg^{2+})$ at constant temperature and B) configurational
 493 entropy for Ca/Mg mixing data from dashed line correspond to the total configurational entropy and
 494 full line to the topological variation of the entropy see text (Neville and Richet, 1991) C) ^{17}O triple-
 495 quantum NMR spectrum redrafted from Allwardt and Stebbins (2004).
 496

497 By using the Adam-Gibbs equation, it is possible to determine the configurational entropy, S^{conf} .
 498 Adam and Gibbs (1965) theory of relaxation processes is based on the idea that transporting matter in a
 499 viscous liquid requires a cooperative change in the fluid configuration. A liquid with zero configuration
 500 entropy would be analogous to a perfect crystal, and no material displacement could occur since a single
 501 configuration would be available. The viscosity would then be infinite. If only two configurations were
 502 possible, a movement of matter could only occur if all the atoms of the liquid changed position
 503 simultaneously. The probability of such a cooperative movement would be very low and viscosity
 504 extremely high, but no longer infinite. More generally, as S^{conf} grows, cooperative configurational
 505 changes can occur independently of each other in increasingly smaller volumes of the liquid. At the same
 506 time, viscosity decreases and is predicted by:

$$\log \eta = A_e - B_e/TS^{conf}(T), \quad (6)$$

where A_e is a pre-exponential term and B_e a measure of the Gibbs-free energy barriers hindering configurational rearrangements in the liquid. $S^{conf}(T)$ can be written as:

$$S^{conf}(T) = S^{conf}(T_g) + \int_{T_g}^T \frac{C_p^{conf}(T)}{T} dt, \quad (7)$$

And

$$C_p^{conf}(T) = C_{pl}(T) - C_{pg}(T_g), \quad (8)$$

where C_{pl} and C_{pg} are the heat capacity of the liquid and the glass.

C_p^{Conf} is the melt configurational heat capacity, equal to the difference between the heat capacity of the liquid C_{pl} and the heat capacity of the glass at T_g , $C_{pg}(T_g)$ (Richet et al., 1986). Those values can be measured or modelled with the existing parametric equations (Stebbins et al., 1984; Richet and Bottinga 1984; Richet 1987; Tangeman and Lange 1998; Russell and Giordano 2017), see for examples and details Neuville (2005, 2006), Le Losq et al. (2014) and Le Losq and Neuville (2017). One may also note that $C_{pg}(T_g) \sim 3R$, the Dulong and Petit limit (Petit and Dulong, 1819), such that it can be easily estimated from this simple calculation (Richet, 1987). The configurational heat capacity is a very important term, in particular, the higher C_p^{conf} is, the faster S^{conf} increases with T, and the lower the B_e/S^{conf} ratio.

The importance of these differences between configurational C_p is illustrated in Figure 1, where in the case of $\text{NaAlSi}_3\text{O}_8$, the liquid C_p^{conf} represents less than 10% of that of the glass, and deviations from Arrhenius behavior are small. On the contrary, CaSiO_3 or $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ have a C_p^{conf} representing 30% of the C_p of the glass, and the viscosity versus $1/T$ curves depart significantly from a straight line. Because of the importance of C_p^{conf} , it is therefore imperative to know the heat capacity of liquids and glasses for a given temperature and chemical composition. We can note that the configurational heat capacity $C_p^{conf}(T)$ depends essentially on the heat capacity of the liquid, C_{pl} , and in the case of alkaline-earth silicate melts, C_{pl} is independent of T and varies mostly linearly with melt composition (Stebbins et al., 1984, Richet and Bottinga, 1985, Lange and Navrotsky, 1992). This explains the pseudo-linear variations of viscosity observed at high temperature (1750 K, Figure 7A).

However, near T_g , the melt viscosity depends strongly on $S^{conf}(T_g)$, which shows large non-linear variations with melt composition. This explains the large, non-linear viscosity changes at supercooled temperature upon mixing alkaline-earth elements in silicate melts (Figure 7A). Using equation 6 in conjunction with viscosity data and heat capacity values (from data or models), S^{conf} can be calculated. S^{conf} along the CaSiO_3 - MgSiO_3 binary is plotted in Figure 7B. To reproduce S^{conf} variations with composition, it is necessary to look at the contributions to $S^{conf}(T_g)$ in equation 7. S^{conf} records topological contributions from the melt structure (bond angle and inter-atomic distance distributions, etc.) as well as

540 excess entropy arising from chemical mixing effects. It thus is common to express S^{conf} as the addition of
541 those two sources (Neuville and Richet, 1991):

$$542 \quad S^{conf}(T_g) = S^{topo} + S^{mix} \quad (9)$$

543 with S^{mix} the term embedding all mixing contributions and S^{topo} the entropy arising from the topology
544 of the glass network. The topology of the network for the two end-members is distinctly different and is
545 also different compared to the crystalline analogues.

546 S^{topo} , the topological configuration entropy can be approximated as a linear variation of the
547 configurational entropy of the end-members and calculated as $\sum x_i S^{conf}_i(T_g)$, with $S^{conf}_i(T_g)$ the
548 configurational entropy of CaSiO_3 and MgSiO_3 glasses (Neuville and Richet, 1991). This S^{topo} term
549 corresponds to a mechanical mixing between the two end-members without necessary chemical or
550 physical interaction. S^{topo} can be expressed from the glass structure and varies linearly with composition
551 (Le Losq and Neuville, 2017).

552 S^{mix} corresponds to a chemical mixing term that can be ideal or non-ideal. In the case of Ca/Mg mixing,
553 the simplest hypothesis that can be made is that $S^{mix} = S^{ideal}$, and thus can be written as:

$$554 \quad S^{ideal} = -n \sum R x_i \ln x_i, \quad (10)$$

555 where R is the perfect gas constant and n is the number of atoms exchanged per formula units, 1 in
556 this case, $x_i = \text{Ca}^{2+}/(\text{Ca}^{2+} + \text{Mg}^{2+})$. From a thermodynamic point of view, the ideal solution implies that
557 end-members components mix randomly in solution.

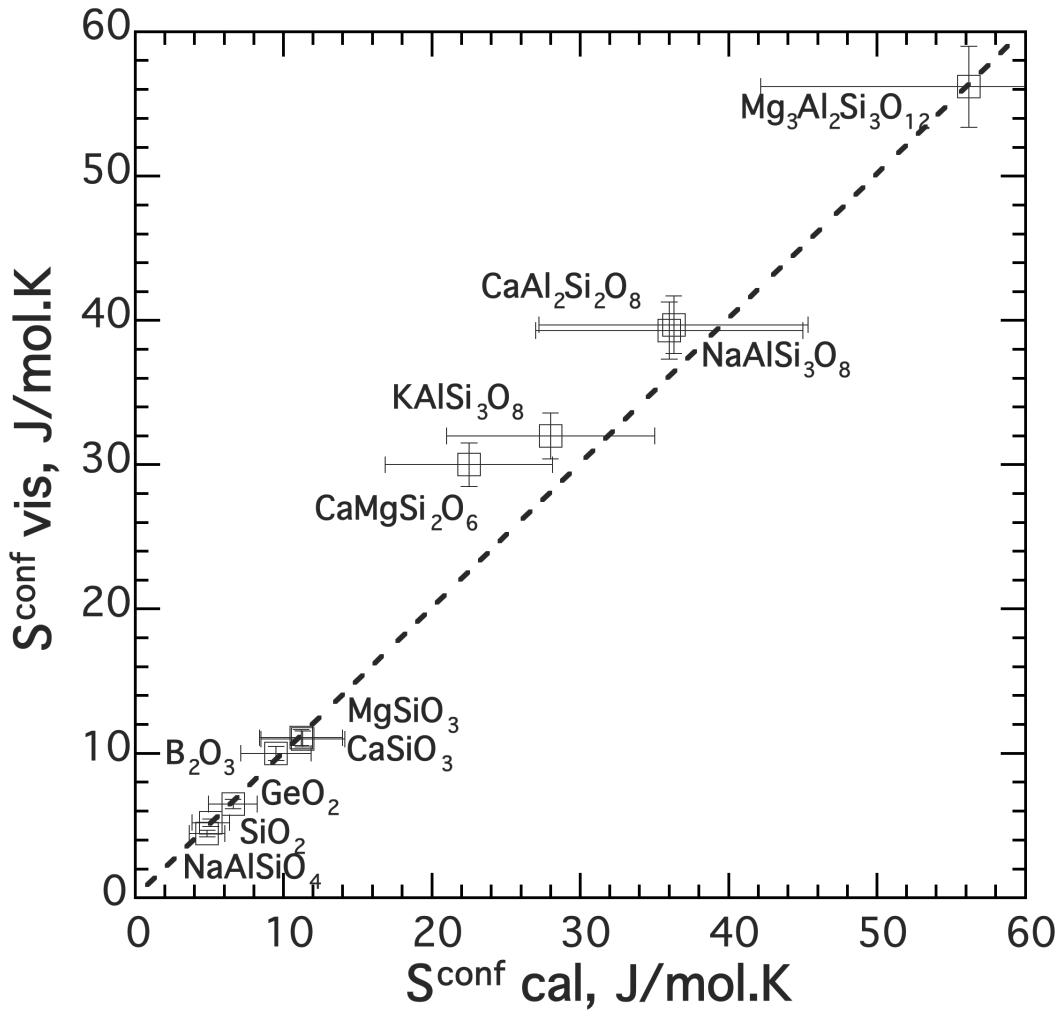
558 The excellent agreement (Figure 7B) between entropies obtained from viscosity measurements and
559 values predicted using eqs 6 to 10 shows that the ideal mixing hypothesis for Ca/Mg is consistent with
560 the data. It should be noted that the mixing effect is predominant near T_g . The configuration entropy of
561 the intermediate compositions is therefore much higher than that of the end-members, explaining the
562 minimum in viscosity observed upon Ca/Mg mixing. When temperature increases, the entropy of the
563 end-members increases rapidly and S^{mix} , which is constant, eventually becomes small compared to $\sum x_i$
564 $S^{conf}_i(T_g)$ in eq. (9). Therefore, at high temperatures, S^{mix} is negligible and this results in a quasi-linear
565 variations in viscosity, driven by the linear variation of C_{pl} upon Ca/Mg mixing.

566 These macroscopic conclusions about Ca/Mg mixing are in very good agreement with nanoscale
567 investigations made by ^{17}O NMR (Allwardt and Stebbins, 2004) and neutron diffraction and RMC
568 (Cormier and Cuello, 2013). From neutron diffraction, the silicate network shows small but significant
569 changes with the Mg/Ca exchange and a significant intermixing of Ca and Mg can be observed (Cormier
570 and Cuello, 2013). From another point of view, ^{17}O NMR spectra of the diopside glass $(\text{CaMg})\text{SiO}_3$
571 shows that only one broad non-bridging oxygen atom (NBO) peak is visible, and encompasses the entire
572 range of chemical shifts ranging from Ca-NBO to Mg-NBO. Comparison of the isotropic projections
573 from 3QMAS NMR to 1D spectra predicted using a random model show that Ca/Mg mixing in Ca/Mg-

574 silicate glasses is generally highly disordered (Allwardt and Stebbins, 2004), except maybe near the glass
 575 transition temperature where a more ordered glass is possible as shown by neutron diffraction made on
 576 CaSiO₃ glass by Gaskell et al. (1985).

577
 578 *Validity of the viscosimetry approach to determine $S^{conf}(T_g)$*

579 We have just shown that it is possible to determine configurational entropies using viscosity
 580 measurements and the AG theory. Are those values of $S^{conf}(T_g)$ truly representative of the glass residual
 581 entropy? To answer this question, we can compare $S^{conf}(T_g)$ obtained from calorimetric measurements to
 582 those obtained from fitting viscosity data. Data from 11 very different compositions, including B₂O₃,
 583 SiO₂ or KAlSi₃O₈, show very good agreement between $S^{conf}(T_g)$ values retrieved from viscosity
 584 measurements or calorimetric measurements (Figure 8). This thus validates the use of eq. 6 to determine
 585 $S^{conf}(T_g)$ of melts.



586
 587 *Figure 8: viscosimetry configurational entropy versus calorimetry configurational entropy for 10*
 588 *different oxide glasses for which determination of calorimetric measurements are possible. Calorimetry*

589 data are from Richet (1984) for SiO_2 , $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , de Ligny and Westrum (1996) for GeO_2 and
590 B_2O_3 , Richet et al. (1991) for NaAlSiO_4 , Tequi et al. (1991) for $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and Richet et al. (1986)
591 for MgSiO_3 , CaSiO_3 , $\text{CaMgSi}_2\text{O}_6$ and $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$. Viscosity data are from Hetherington et al. (1964)
592 and Urbain et al. (1982) for SiO_2 , Neuville and Richet (1991) and Le Losq and Neuville (2013) and Le
593 Losq et al. (2017) for alkali and alkaline-earth silicate and aluminosilicate compositions, from Fontana
594 and Plummer (1966) for GeO_2 , and from Eppler (1966), Macedo et Litovitz. (1965), Napolitano et al.
595 (1965) for B_2O_3 .

596

597 In the case of Na/K mixing in silicate melts, only one set of measurements is available from Poole
598 (1948). Using those data, Richet (1984) proposed that an ideal, random Na/K mixing occurs in silicate
599 melts, and viscosity can be modelled using the ideal mixing calculation of S^{conf} ; some differences
600 between calculated and measured viscosity in the supercooled silicate melts are visible in Richet (1984)
601 work, however they arise from the way the data and model are represented. The more recent study of Le
602 Losq and Neuville (2017) resolved this, showing that it is clearly possible to model the viscosity of Na-
603 K silicate melts while assuming a random mixing of the alkalis (see section 2.4).

604

605 2.3 Mixing alkali and alkaline-earth elements in silicate glasses

606 Most industrial and geologic glasses are silicate and aluminosilicate glasses containing a mixture of
607 alkali and/or alkaline-earth elements. Igneous rocks (Morey and Bowen, 1925) as well as nearly 90 % of
608 industrial glasses contain mixtures of alkali and alkaline-earth elements. We can cite the particular case
609 of soda-lime silica glasses, extensively used for the construction of conventional windows and container
610 glasses. The importance of $\text{M}^{2+}\text{O}-\text{M}^+\text{O}-\text{SiO}_2$ glasses (with M^+ an alkali and M^{2+} an alkaline-earth
611 element) further increased recently because they also are used for the development of bioactive glasses
612 (Hench, 1991 and Kim et al. 1995, Clupper and Hench, 2003, Hill and Brauer, 2011; Brauer, 2015).
613 Given the importance of alkali and alkaline-earth metal cations in glasses, many studies were performed
614 to understand the $\text{M}^{2+}\text{O}-\text{M}^+\text{O}$ mixing in silicate glasses. They are essentially focused on the glass
615 mechanical properties or devitrification (Morey, 1930; Frischat and Sebastian, 1985; Koike and
616 Tomozawa, 2007, Koike et al., 2007), on glass structure (Buckerman and Müller-Warmuth, 1992, Jones
617 et al., 2001; Lockyer et al., 1995; Lee and Stebbins, 2003; Lee et al., 2003, Neuville 2005, 2006, Hill and
618 Brauer, 2011; Brauer, 2015; Moulton and Henderson, 2021 and reference therein) or thermodynamic
619 properties (Natrup et al., 2005; Neuville 2005, 2006, Richet et al., 2009b; Inaba et al., 2010, Sugawara et
620 al., 2013). Given the above-mentioned importance of $\text{M}^{2+}\text{O}-\text{M}^+\text{O}-\text{SiO}_2$ glasses, we will in this section
621 bring new insights to the effect of $\text{M}^{2+}\text{O}-\text{M}^+\text{O}$ mixture on the properties of silicate glass and melt.

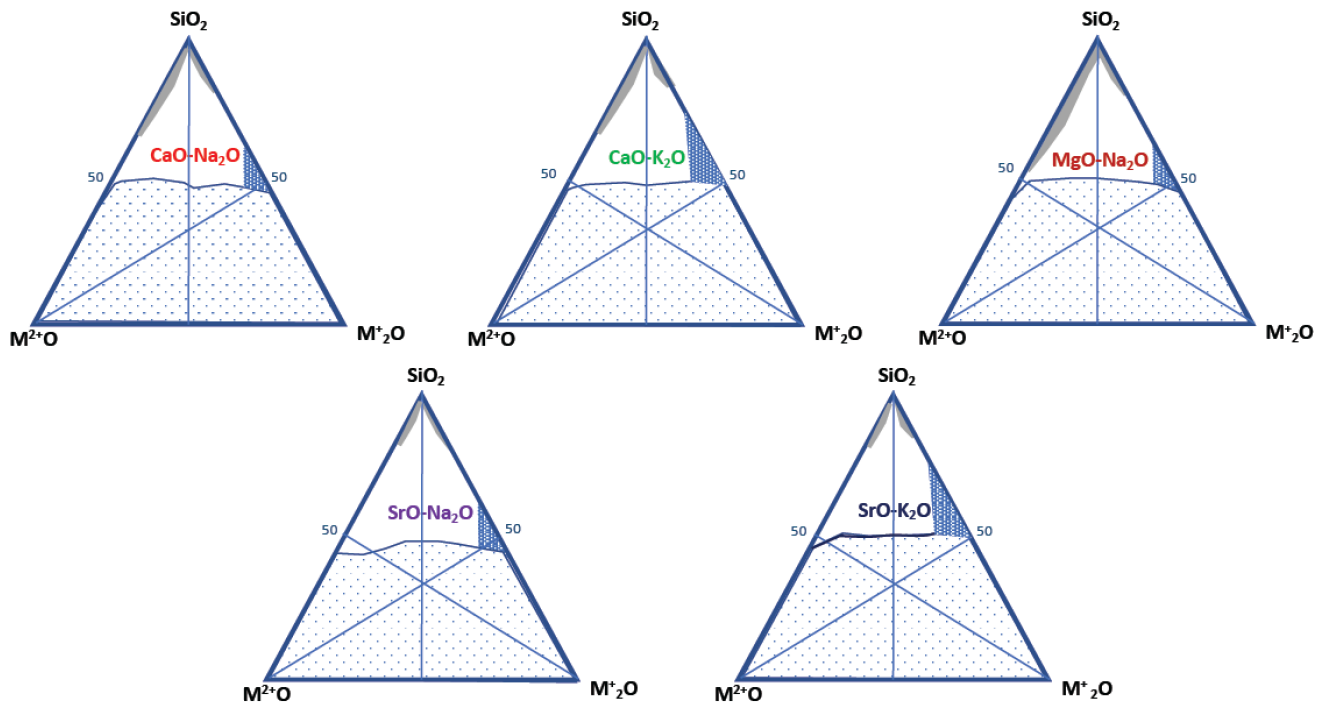
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2.3.1 Glass formation domains

The substitution of alkali elements by alkaline-earth elements allows extending the glass forming domain of silica glasses to lower silica contents (Figure 9), and, more generally, it allows improving many glass properties (Moore and Carey, 1951, Imaoka and Yamazaki 1963, Tomozawa, 1978; 1999; Gahay and Tomozawa 1989, 1984, Neuville, 2005, 2006). For $M^{2+}O$ and M^+O_2 bearing silicate glasses, the vitrification domain starts near 50 mol% silica in most cases. For Mg silicates, it starts at 45.7 mol% (Moore and Carey, 1951). It was generally accepted that the presence of Mg-O bonds allows preserving somehow the continuity of the silicate network, with Mg acting to some extent as a network former (Moore and Carey, 1951), an idea in agreement with the low coordination number of Mg discussed previously. In the case of CaO-Na₂O-SiO₂ glasses, the first phase diagram was made by Morey and Bowen (1925). It revealed the domain where glasses can be formed, but also an immiscibility domain in which phase separation is observed. This immiscibility domain is very large near the CaO-SiO₂ binary, extending between 62 and 100 mol% of silica. It decreases rapidly with addition of Na₂O in the glass (Morey and Bowen, 1925, Greig 1927, Hudon and Baker, 2002a,b). In the immiscibility domain, different phases exist: cristobalite, SiO₂, wollastonite CaSiO₃, sodium disilicate Na₂Si₂O₅, devitrite Na₂Ca₃Si₆O₁₆, and a non-defined compound Na₂Ca₂Si₃O₉. The proportion of these phases vary as a function of the bulk composition and the cooling rate (Morey and Bowen, 1925, Greig 1927, Tomozawa, 1978; 1999; Gahay and Tomozawa 1989; Hudon and Baker, 2002a,b; see also Schuller chapter in Neuville et al., 2017).

Similar observations can be made in the other $M^{2+}O$ - $M^{2+}O$ -SiO₂ systems, with $M^+=Li^+$, Na⁺, K⁺ and $M^{2+}=Mg^{2+}$, Ca²⁺, Sr²⁺, Ba²⁺. Generally, a pyrosilicate phase, $M^{2+}SiO_3$, and one or two phases $M^+_yM^{2+}_xSi_zO_u$ crystallize at high silica contents (> 70 mol%, x,y,z,u are different proportions of each crystalline phases), except for $M^{2+}=Ba^{2+}$ where the glass forming domain is large but mostly unconstrained. Bender et al. (2002) achieved the synthesis of Ba silicate glasses up to the BS7 (BaO/SiO₂=7 in mol %) composition, and Frantz and Mysen (1995) investigated some of those glass compositions by Raman spectroscopy.

To summarize, in all of the $M^{2+}O$ - $M^{2+}O$ -SiO₂ ternary diagrams, the glass forming domains are relatively small and essentially exist at silica contents higher than 50 mol%, with exception of barium silicates. In the case of sodium and potassium silicates, a large zone of high hygroscopicity exists below the glass forming domain, typically between 66 and 50 mol % of silica for sodium silicate glasses and between 70 and 50 mol % for potassium silicate glasses (Tomozawa, 1978; 1999; Gahay and Tomozawa 1989). In general, one should be careful with potassium silicate glasses that are always highly hygroscopic.



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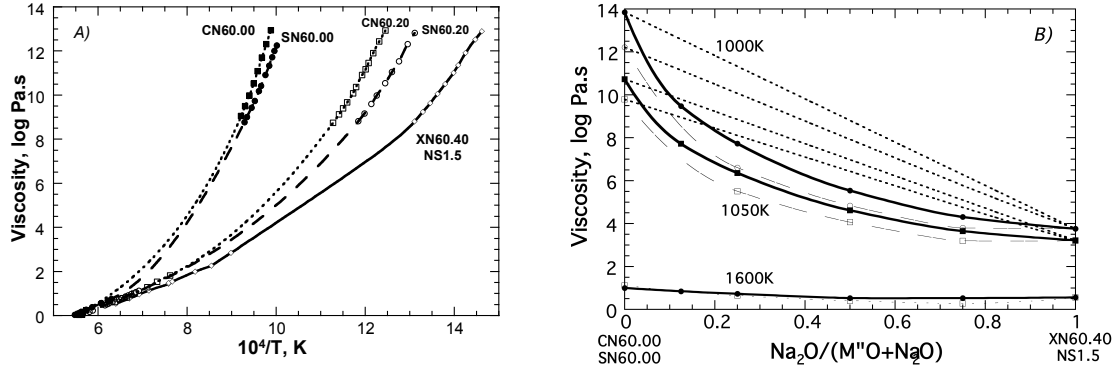
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Figure 9: The upper part of the ternary diagram corresponds to the glass forming region of glass between $M^{2+}O$ and M^+_2O , with $M^{2+}=Mg^{2+}$, Ca^{2+} , Sr^{2+} and $M^+=Na^+$, K^+ (redrafted from Imaoka and Yamazaki, 1963 and Levin et al., 1964). The white areas are the glass making domain, the light dotted areas are the crystallization domains, the dark dotted lines correspond to the glass making domain, but strongly hygroscopic, and the gray areas to unmixed glass.

2.3.2 Viscosity variations

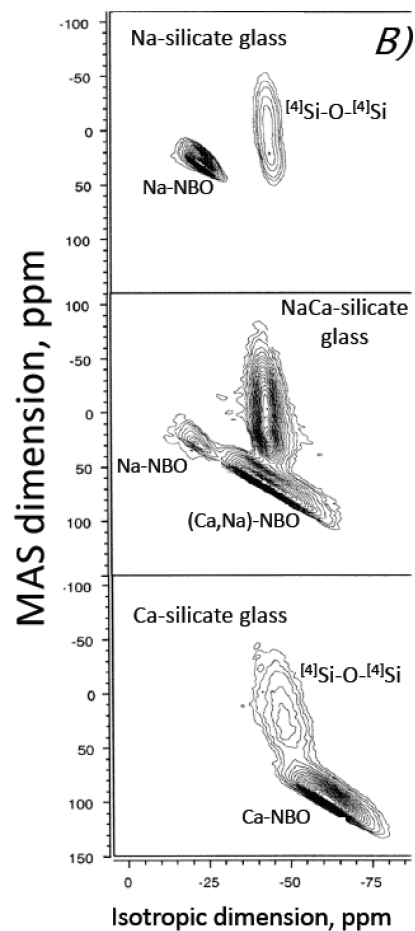
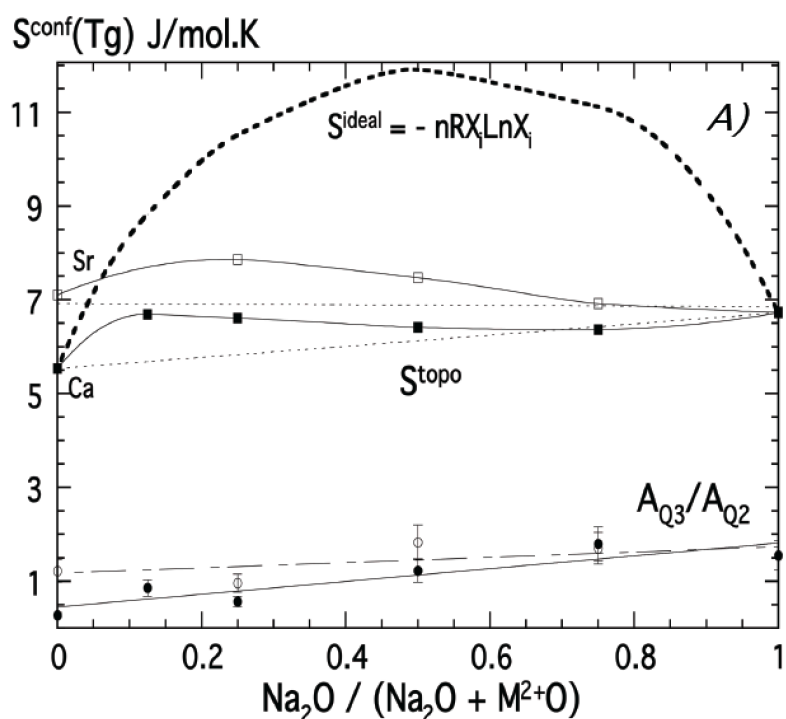
Figure 10A shows viscosity measurements of silicate melts for M^{2+} -Na mixing with $M^{2+} = Ca^{2+}$, Sr^{2+} . Ca- and Sr-silicate melts show similar behavior. The addition of those elements produces a large increase in melt viscosity at constant temperature, in agreement with previous measurements (English, 1923). The lack of measurement between 10^2 and 10^9 Pa·s results from the very rapid rate of crystallization in this viscosity-temperature range for mixed alkali and alkaline-earth silicate glasses (Meiling and Uhlmann, 1977; Mastelaro et al. 2000, Neuville, 2005, 2006). In the Figure 10B, we clearly observe that addition of 10 mole % Na_2O in an alkaline-earth silicate melt has a stronger effect on melt viscosity than addition of 10 mole % $M^{2+}O$ to a soda-silicate melt composition. This indicates that a sodium silicate glass network can incorporate alkaline-earth elements more easily than the opposite. A striking difference exists in the behavior of the viscosity between pure Na-silicate melts and pure alkaline-earth silicate melts (CN60.00 or SN60.00). Indeed, at constant viscosity and near T_g (Figure 10B), i.e. near 1000 K, the viscosity of the end-member compounds differ by 10 orders of magnitude. This difference decreases

678 with temperature: it is less than 0.5 order of magnitude at 1600 K. Furthermore, at 1600 K, the viscosity
 679 of the $\text{Na}_2\text{O}-\text{M}^{2+}\text{O}-\text{SiO}_2$ melts decreases almost linearly with $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{M}^{2+}\text{O})$. Similar behaviors
 680 were already observed by English (1923) in the same system with 75 mole % SiO_2 and 25 mole % Na_2O ,
 681 and with a substitution of Na_2O by up to 12 mole % CaO .



682
 683 **Figure 10:** A) Viscosity versus $1/T$ for silicate melts ranging from the pure alkaline-earth silicate
 684 melt) to pure soda silicate (XN60.40) composition names are: XN60.Y, X=C or S for the Ca or Sr system,
 685 Y correspond to Na_2O content, 60 to SiO_2 in mole percent, and $X=100-(60+Y)$ all in mole percent. B)
 686 Viscosities of Na/M^{2+} silicate melts versus $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{M}^{2+}\text{O})$ at constant temperature, $\text{M}^{2+}=\text{Ca}, \text{Sr}$,
 687 dashed lines correspond to the linear viscosity variation at 1000 K, 1050 K and 1600 K, solid and open
 688 symbols correspond to the $\text{CaO}-\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{SrO}-\text{Na}_2\text{O}-\text{SiO}_2$ systems, respectively compiled from
 689 Neuville (2006, 2005).

690
 691 The viscosity variations observed in Figure 10 can be understood using equations 6 to 9. It is possible
 692 to determine how configurational entropy varies upon the mixing of Na_2O with M^{2+} in the glasses (Figure
 693 11A). S^{conf} can be decomposed in S^{topo} and S^{mix} (eq. 9). S^{topo} is equal to the sum of endmembers. S^{mix} , in
 694 the case of M^+/M^{2+} mixing, has a complex expression that depends on the way the cations mix into the
 695 glass structure.



696
 697 **Figure 11:** A) $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{M}^{2+}\text{O})$ dependence of configurational entropy, $S^{\text{conf}}(T_g)$, A_{Q3}/A_{Q2} ratio for
 698 in black symbol CaO and in open symbol for SrO (entropy are in J/mol.K and A_{Q3}/A_{Q2} without units and
 699 are calculated from the Q^3 and Q^2 areas of the Raman spectra, see Neuvill (2005, 2006) for more detail).
 700 B) ^{17}O 3QMAS MAS spectra for Ca-Na silicate glasses at 9.4 T redrafted from Lee and Stebbins, (2003).
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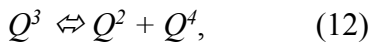
702 Between the calcium and sodium silicate glasses, $S^{\text{conf}}(T_g)$ varies non-linearly with $\text{Na}_2\text{O}/(\text{Na}_2\text{O}$
 703 $+\text{CaO})$. It increases rapidly with increasing $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{CaO})$ to 0.2, then it slightly decreases with
 704 further substitution Ca^{2+} by Na^+ . Similar observations are made in the SrO- Na_2O - SiO_2 system (Neuvill,
 705 2005). The observed variations strongly depart from the predictions made by the ideal model given in
 706 equation 10 (Figure 11A). In the case of Na^+ and Ca^{2+} , or of Na^+ and Sr^{2+} , it is clear that, as their $S^{\text{conf}}(T_g)$
 707 variations are close to linear trends, those atoms do not mix randomly in the silicate melts. The fits of
 708 $S^{\text{conf}}(T_g)$ presented in Figure 11A thus require the use of a non-ideal mixing model. To model S^{mix} in the
 709 case of a non-ideal mixing of alkali and alkaline-earth elements, Neuvill (2005, 2006) proposed to use
 710 the equation:

$$711 \quad S^{\text{mix}} = W_{NM} x_n y_c^3, \quad (11)$$

712 where $x_n = \text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{M}^{2+}\text{O})$ and $y_c = 1-x_n$, and W_{NM} is a constant.

2.3.3 Structure of mixed glasses

Equation (11) implies a significant change in the residual entropy that originates from a re-arrangement of the glass structure as Ca^{2+} is replaced by Na^+ . Spectroscopic methods that probe the glass structure allow us to investigate such structural changes. ^{23}Na and ^{17}O Nuclear Magnetic Resonance (NMR) spectroscopy data shown a non-random distribution in the case of Na^+ - Ca^{2+} mixing, with in particular a prevalence of Na^+ - Ca^{2+} pairs in the system (Figure 11B), and several partially resolved non-bridging oxygen peaks such as Na^+ -NBO, and mixed peaks (Na^+ , Ca^{2+})-NBO (Lee and Stebbins, 2003). The observed fractions of Na^+ -NBO are smaller than those predicted by random distributions of Na^+ and Ca^{2+} , suggesting preference for dissimilar pairs (Lee and Stebbins, 2003) which is also in good agreement (Florian et al., 1996; Lee 2005, Lee and Stebbins 2002 and Lee et al., 2003). In the previous chapter, Raman spectroscopy soda and lime silicate glasses were shown in Figure 9. Different Q^n contributions are visible in those spectra. From these Q^n contributions, the ratio of the area between Q^3 and Q^2 units, A_{Q3}/A_{Q2} can be calculated. Results of such calculation are plotted in Figure 11A. It shows that the fraction of Q^3 units in the glass increases with increasing the $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{M}^{2+}\text{O})$ ratio. M^{2+}O silicate glasses are thus richer in Q^2 and Q^4 units than alkali silicate glasses (Frantz and Mysen, 1995, Neuville 2005, 2006), because increasing the ionic field strength of metal cation in the glass shifts to the right the equilibrium of the reaction:



This observation will be used in section 2.4 for highlighting how one can build models of the structure, entropy and viscosity of silicate melts. Huang et al. (2016) investigated Ca_3SiO_5 composition by using $^{17}\text{O} \rightarrow ^{29}\text{Si}$ CP-HETCOR NMR experiment and they proposed that free oxygen can also play a small role structure and properties in the mixed glasses, what is possible but this experiment must be considered with caution, firstly it is a particularly difficult composition to manufacture and secondly, only the nominal compositions are given and not those analyzed.

2.3.4 Network polymerization

The substitution of 30 mol% of CaO by Na_2O in an alkaline-earth silicate glass results in a moderate increase of $\sim 0.9 \text{ J mol}^{-1} \text{ K}^{-1}$ of $S^{\text{conf}}(T_g)$ (Figure 11A). This indicates an increase in the structural disorder in the glass, possibly linked to change in the glass network polymerization. Structural changes that may account for the entropy behaviour may be discerned in the Raman spectra of the glasses. In particular, the ratio of the areas of Raman bands assigned to Q^3 and Q^2 units, A_{Q3}/A_{Q2} , varies with $\text{M}^{2+}\text{O}/(\text{M}^{2+}\text{O}+\text{M}^{2+}\text{O})$, indicating a change in the Q^n speciation distribution (Neuville, 2006). There is a distinct increase of this ratio with adding Na_2O in the alkaline-earth silicate glasses. In the case of Na/Ca

747 and Na/Sr mixing, Raman spectroscopy observations shown in Figure 11A are in good agreement with
748 previous observations by Raman spectroscopy (McMillan, 1984; McMillan et al., 1982; Frantz and
749 Mysen, 1995) and by ^{17}O NMR (Maekawa et al., 1991; Buckerman and Müller-Warmuth, 1992; Jones
750 et al., 2001, Lee and Stebbins, 2003, Lee et al., 2003), all showing a decrease in Q^3 fraction upon
751 substitution of alkali by alkaline-earth element in silicate glasses. Moreover, the increase in Q^2 units with
752 adding alkaline-earth elements in soda silicate glasses can be correlated to increasing Boson peak
753 frequency and intensity (Neuvville, 2006).

754 Note that below 250 cm^{-1} , there is only a scattering continuum and the Raleigh tail of the exciting line,
755 except at very low frequency where there is the so-called boson peak (Malinovsky and Sokolov, 1986;
756 Buchenau et al., 1986). This peak has been ascribed to excitations associated with rotational motions of
757 almost rigid tetrahedra (Buchenau et al., 1986; Helhen et al., 2000, 2002). Helhen et al. (2002) consider
758 that this peak, observed for different silicate glasses, increases in intensity and shifts to higher frequency
759 with higher distortion of the SiO_4 tetrahedra. Several others interpretations are proposed: - Champagnon
760 and collaborators proposed that Boson peak can be link with structural homogeneity in the glass
761 (Champagnon et al., 2009), and the other hand Chumakov and collaborators proposed that Boson peak
762 can be attributed to some fluctuation of disorder in glass (Chumakov et al., 2014) and finally Schirmacher
763 and collaborators proposed an intermediate interpretation by considering that the Boson peak can
764 corresponds to the spatial fluctuations of elastic constants caused by the structural disorder of the
765 amorphous materials (Schirmacher and Ruocco, 2020, Schirmacher et al., 2015). If we consider that
766 molecular dynamic simulations provided by Cormack and coworkers suggest that Si-NBO bond length
767 is about 0.05 \AA shorter than the Si-BO bond length (Henderson, 1995; Cormack and Du, 2001; Du and
768 Cormack 2004)⁵, we can propose that Q^2 units are more distorted than Q^3 or Q^4 units. This implies that
769 Q^4 and Q^0 units are regular tetrahedra with Q^4 bigger than Q^0 and they are less distorted than the Q^1 , Q^2 ,
770 Q^3 units species (Nakamura et al., 2013). It is probable that Q^2 units are the more distorted tetrahedra
771 with 2 distances T-BO and 2 distances T-NBO which can be in good agreement with the variation of the
772 frequency of boson peak. So, we proposed that the variation on the Boson peak observed as a function
773 of chemical change in simple systems with cation substitution can be attributed to tetrahedra distortion
774 as observed on SiO_2 glass with pressure. This variation can also result of structural heterogeneity produce

⁵ Du and Cormack (2004) proposed from MD simulation that when the alkali content vary between 10 and 50 mole percent the $d(\text{Si-BO})$ vary between 1.625 and 1.629 \AA and $d(\text{Si-NBO})$ varies between 1.559 and 1.579 \AA . Henderson (1995) proposed from EXAFS measurements that $d(\text{Si-O})$ equal $1.61\pm 0.02\text{ \AA}$ and $1.58\pm 0.02\text{ \AA}$ for NS1.5 glass which is in good agreement with MD.

775 by the fact that soda silicate glasses are richer in Q^3 species than lime-silicate glasses. These structural
776 heterogeneities can also be close the idea of percolation channels proposed by Greaves (1985).

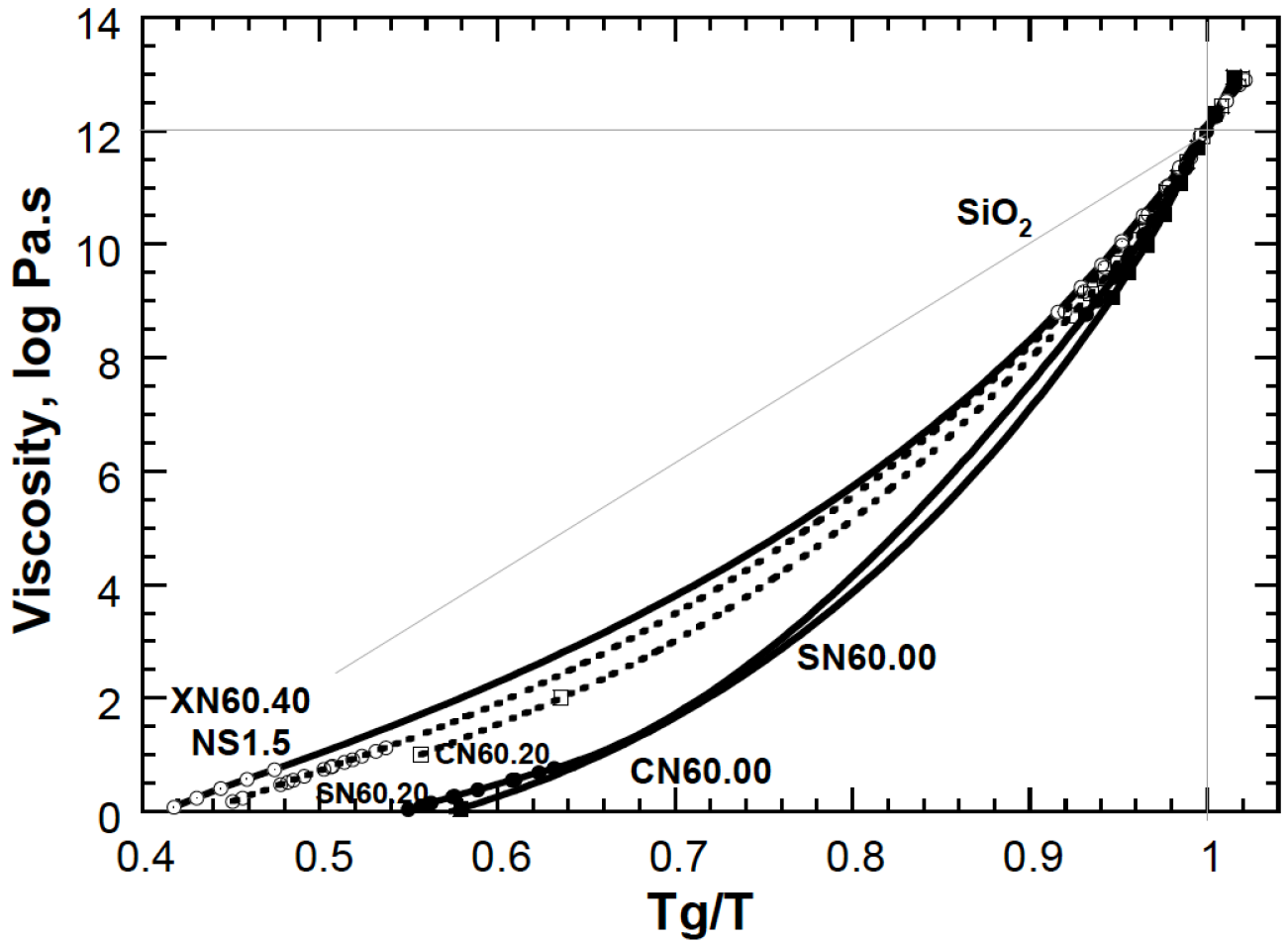
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778 2.3.5 Fragility

779 Angell (1991) proposed a classification of liquids between strong and fragile: a strong liquid shows a
780 linear variation like SiO₂ in the diagram $\log \eta$ versus T_g/T whereas this linear relation is not preserved in
781 a fragile liquid (Figure 12). The melt fragility, m , is related to its thermodynamic properties via the
782 relationship:

$$783 \quad m = B_e / S^{conf}(T_g) * T_g * (1 + C_p^{conf}(T_g) / S^{conf}(T_g)) \quad , \quad (13)$$

784 In the case of the M⁺₂O-M²⁺O-SiO₂ system, the viscosities of the alkali- alkaline-earth silicate melts
785 are plotted as a function of T_g/T in Figure 12. The strongest liquid is the pure soda silicate, XN60.40
786 (NS1.5), whereas the most fragile liquids are the pure alkaline-earth silicate melts. The Ca- and Sr-silicate
787 melts have similar fragility, despite the Ca-silicate melt being more viscous than Sr-silicate melt.
788 Intermediate chemical compositions mixing Na⁺ with Ca²⁺ or Sr²⁺ present an intermediate behavior
789 between end-members. The behavior of the melt fragility correlates well with melt C_p^{conf} values, which
790 decrease of ~ 20 % upon replacing M²⁺ with Na (M²⁺ = Ca²⁺ or Sr²⁺; Neuville, 2005, 2006). This
791 observation on the decrease of the C_p^{conf} is in good agreement with the increase of the $\Delta C_p = C_{pl} / C_{pg}(T_g)$
792 which varies between 1.2 for the Na-silicate glass up to 1.27 and 1.29 for Ca- and Sr-silicate glasses.
793 Note that, Angell (1991) proposed that ΔC_p vary between 1.1 and 1.3 for a strong and fragile liquid
794 respectively.



795

796 **Figure 12:** Viscosity of soda- $M^{2+}O$ silicate glasses versus T/T_g . Error bars are smaller than symbol
 797 size, from Neuville (2005, 2006).

798

799 **2.3.6 Melt configurational entropy, fragility, Q^n speciation, mobility and network connectivity**

800 The distribution of cations in the glass network can have important implications for transport properties
 801 such as conductivity, viscosity and fragility. In the case of the Na/Ca substitution in silicate melts, Roling
 802 and Ingram (2000) have shown that the mobility of Ca^{2+} cations is enhanced upon their replacement by
 803 Na^+ . This replacement of Ca^{2+} by Na^+ produces a positive coupling effect on the movements of divalent
 804 cations that correlates well with the increase in $S^{conf}(T_g)$ (Figure 11A). Conversely, the activation energies
 805 related to movements of Na^+ is slightly changed. The cation mobility strongly depends on the glass
 806 structure, and the structural changes taking place during the Na/Ca substitution in the Ca-silicate glass
 807 enhance the mobility of Ca^{2+} . The modification in network topology will provide new types of empty
 808 sites that could be used for Ca movements (Cornier and Neuville, 2004). The mobility of the divalent
 809 cation is then assisted by positive coupling with the more mobile monovalent cation (Magnien et al.,
 810 2004, 2008).

811

812 To summarize the observations made in the case of the mixing between alkali, M^+ , and alkaline-earth,
813 M^{2+} , elements in silicate glasses and melts:

- 814 - alkali and alkaline-earth cations do not mix randomly,
- 815 - increased alkali content increases the formation of Q^3 species,
- 816 - diffusivity increase with alkaline-earth element (Roling and Ingram, 2000),
- 817 - fragility increases with alkaline-earth content,
- 818 - the distortion of the tetrahedra suggested by the boson peak variation and the distortion of the
819 network increases with increasing MO content,
- 820 - the proportion of Q^2 species increases with $M^{2+}O$ content and in the same way, the intensity and the
821 frequency position of the boson peak increase. The fact, that the alkaline-earth silicate glasses around
822 than 60% of silica correspond to a mixing of Q^2 and a small amount of Q^4 species, may be the origin of
823 the unmixing observed for more than 60% of SiO_2 in the $M^{2+}O-SiO_2$ binary system (see Figure 9). These
824 two interconnected Q^n species can also be an image of the percolation channels (Greaves et al., 1981,
825 Greaves, 1985, Frischat et al., 2001, Le Losq et al., 2017).

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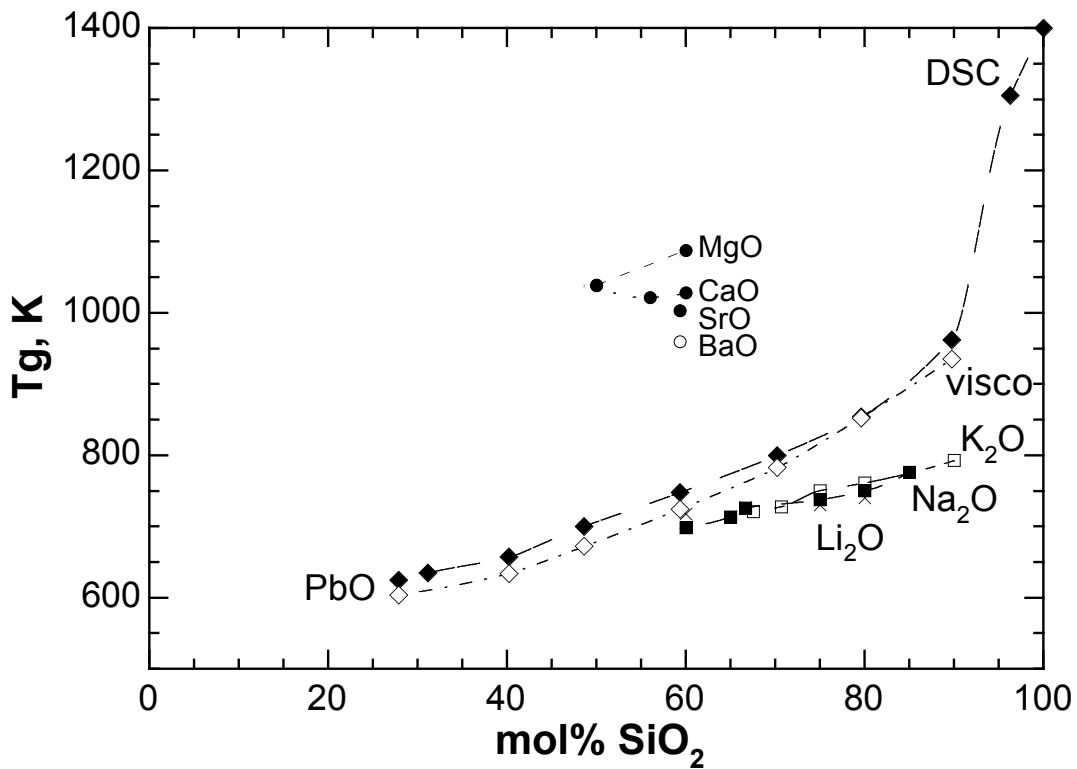
827 *2.4 Silicate glasses and others network formers*

828

829 *2.4.1 Lead*

830 The replacement of SiO_2 by PbO produces a small decrease in the glass molar volume until the Si/Pb
831 ratio reaches a value of 0.5. Further PbO addition results in a molar volume increase. The PbO amorphous
832 molar volume value can be obtained by extrapolation and is 25.0 cm^3 (Robie et al., 1979; see arrow in
833 Figure 5) which is similar to the molar volume of Litharge, PbO with Pb^{2+} in four-fold coordination.
834 Variations in the molar volume of lead silicate glasses correlate well with structural observations made
835 via Raman spectroscopy (chapter 2, this volume, and Ben Kacem et al., 2017). For small amounts of lead
836 oxide added to silica glass (<20 mole %), Pb is essentially in six-fold coordination and its introduction
837 into silica results in the formation of non-bridging oxygens, clearly visible in the Q^n species distribution
838 in the Raman spectra (Ben kacem et al., 2017). This is accompanied by a decrease in melt viscosity and
839 glass transition temperature. At PbO concentrations higher than 20 mol%, a mixture of essentially two
840 lead species, in 4- and 6-fold coordinations, exists. Kohara et al. (2010) and more recently Sampaio et al.
841 (2018) mentioned that Pb can be distributed between 3-, 4-, 5- and 6-fold coordination but recent X-Ray
842 diffraction shows that Pb is essentially distribute in 4- and 6-fold coordination (Drewitt et al., this issue).
843 Pb in four-fold coordination can be considered as a weak network former (Fayon et al., 1998, 1999; Feller
844 et al., 2010; Ben Kacem et al., 2017) as $^{[4]}Pb$ creates a network of interconnected tetragonal pyramid
845 PbO_4 (Morikava et al., 1982). This is visible in Raman spectra, where an intense band at 140 cm^{-1} can be

846 assigned to Pb-O-Pb covalent bonds (see chapter 3 and Ben Kacem et al., 2017). This band at 140 cm⁻¹
 847 is clearly at higher frequency than that observed in alamosite, PbSiO₃, at 110 cm⁻¹ and attributed to Pb in
 848 6-fold coordination (Worrell and Henshall, 1978; Ben Kacem, 2017, Pena et al., 2017). The coexistence
 849 of network former PbO₄ and network modifier PbO₆ entities agree with the pair correlation function
 850 obtained from the X-ray diffraction data (see chapter 3, Figure 6B (Drewitt et al. 2021)), which show that
 851 the proportion of PbO₄ increases with decreasing SiO₂/PbO. The mixing of the tetragonal pyramid PbO₄
 852 with SiO₄ tetrahedra is probably mechanical in nature, i.e. the two polyhedra cohabit and are
 853 interconnected but their mixture does not result in an excess of entropy as indicated by the linear
 854 decreases of the glass transition temperature between 30 and 80% of SiO₂ (Figure 13). The fast decrease
 855 in T_g upon addition of ~10 mol% PbO probably relates to the network modifier role of PbO₆ octahedra,
 856 containing some NBOs in their first coordination shell.



857
 858 **Figure 13:** Glass transition temperature as a function of the fraction of SiO₂ in PbO-SiO₂ glasses.
 859 Data for Ca²⁺, Mg²⁺, Na⁺, K⁺, Li⁺ silicate glasses are original data from Neuville, Ca50 and Mg50
 860 (Neuville and Richet, 1991), Ca60 and NS1.5, NS2, NS4 from Neuville (2006), NS3 from Le Losq et al.
 861 (2014); Sr60 from Neuville (2005) and Pb-silicate glasses open circle are from viscosity measurements
 862 and full circle are from DSC measurements. (Ben Kacem et al., 2017). Note that all T_g are obtained
 863 using viscosity measurements to be comparable except those obtained by Ben Kacem with DSC.

864

865 The introduction of PbO thus produces the transformation of Q^n units into Q^{n-1} units as PbO₆ are
866 network modifier units. The appearance of these Q^{n-1} species is documented by changes in the high
867 frequency envelope (800 - 1200cm⁻¹) of the Raman spectra of the glasses (Worrell and Henshall, 1978;
868 Ben Kacem et al., 2017). The Raman spectra of PbO-SiO₂ glasses corresponds to the combination of two
869 distinct endmember Raman signals: that of a lead-silicate glass network with Q^{n-1} species, and that of an
870 amorphous lead network characterized by a strong peak at 140 cm⁻¹. The relative abundances of these
871 signals, and of their associated networks, vary as a function of the SiO₂/PbO ratio and this is in good
872 agreement with observation made using ¹⁷O NMR by Lee and Kim (2015). Lee and Kim (2015) also
873 observed a small amount of free oxygen as early mention by Sampaio et al. (2018), but this small amount
874 cannot explain the T_g and viscosity variations.

875

876 In this sense, lead is an example of an amphoteric⁶ element that plays two different roles, network
877 former or network modifier, depending on melt chemical composition. Another example of an element
878 presenting such behavior is Fe³⁺, which, depending on its coordination, plays different structural roles
879 (Moretti, 2005). Indeed, while Fe³⁺ in 4- or 5-fold coordination can be considered as network formers,
880 Fe³⁺ in 6-fold coordination behaves as a network modifier in silicate melts. It can be found in the literature
881 that such elements are “intermediate” and often aluminum is associated with this terminology. However,
882 the story is more complex than this, and Al³⁺ does not really present amphoteric behavior per se as highly
883 coordinated Al species are not surrounded by NBOs such that ^[4]Al is exclusively a network former
884 element. Its behavior is however complex, as we shall see in the sections below.

885

886 2.4.2 Al in silicate glasses

887 A well-known feature of silicate mineral structures is that Si cations can be replaced isomorphously
888 by aluminum cations, provided that either mono or divalent cations can ensure charge compensation of
889 Al polyhedra to maintain local neutralization of electrical charges in the structure. As such, those mono
890 or divalent cations are called charge compensators. However, it is also possible to obtain alumina-silica
891 glasses without the presence of charge compensator cations. From a research point of view, this is very
892 interesting because Al₂O₃-SiO₂ glasses are important materials for the understanding of how network
893 former elements mix. Al₂O₃-SiO₂ glasses have a very high liquidus (Sossman, 1933), and are difficult to
894 synthesize except by fast quench or sol-gel methods (e.g. see Wang et al., 2020). With those methods, it
895 is possible to obtain Al₂O₃-SiO₂ glasses in three different regions, near 15 mol%, 50 mol% or 60 mol%

⁶ An amphoteric element can react both as an acid or a base; see Moretti (2005) for details on this concept for silicate melts.

896 of silica. The molar volume of $x\text{Al}_2\text{O}_3-(1-x)\text{SiO}_2$ glasses calculated from density measurement (Wang et
897 al., 2020) varies linearly between 27.3 up to 31 cm^3 for 60 % of Al_2O_3 (Figure 6).

898 From the data on Al_2O_3 (corundum), the molar volume of Al in six-fold coordination is 25.57 cm^3
899 (Robie et al., 1979). The molar volume of Al in five-fold coordination is unknown, but the extrapolation
900 of the Al_2O_3 - SiO_2 line in Figure 5 yields a value of $\sim 32 \text{ cm}^3$ at 0 mol % of SiO_2 . Poe et al. (1992) proposed
901 that Al_2SiO_5 glass is composed by 50% of $^{[5]}\text{Al}$, 40% of $^{[4]}\text{Al}$ and 10% of $^{[6]}\text{Al}$.

902 However, no information on the geometry of the $^{[5]}\text{Al}$ oxygen polyhedra is available: it could
903 be a tetragonal pyramid, or a trigonal bi-pyramid. The present data do not allow assessment of this
904 problem, but it is possible to make an assumption: the geometric shape of $^{[5]}\text{Al}$ will depend on the nearest
905 charge compensator cation. For example, the smaller the quadrupolar moment, Cq , observed in ^{27}Al
906 NMR is, the more $^{[5]}\text{Al}$ will look like a square base pyramid. The role of $^{[4]}\text{Al}$, $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ in the glass
907 and melt structure will be discussed later in section 3.

908

909 *2.5 Silicate melts: how can we use existing structural knowledge to model melt properties*

910 With the above information from the traditional glass forming ranges, we understand that we
911 know for silicate melts and glasses:

912 - the glass has a network of Q_n units, whose concentrations can be determined via NMR or
913 Raman spectroscopy (Farnan and Stebbins, 1990; Stebbins et al., 1992; Dupree et al., 1986; Maekawa et
914 al., 1991; Mysen, 1990; Mysen and Frantz, 1993; 1994; Ispa et al., 2010; Zhang et al., 1996; Sen et al.,
915 2003; Davis et al., 2010; O'Shaughnessy et al., 2020; Nesbitt et al., 2018, 2021)

916 - glass and melt heat capacities, which can be calculated, and

917 - their rheological properties.

918 It has been a longstanding goal to link those observations via a single model that could predict the
919 properties and structure of glasses and melts. A pioneering start was the work of Mysen (1995), who
920 proposed to calculate the melt configuration heat capacity from partial heat capacity values $C_p^{conf} Q_n$
921 assigned to each Q^n unit with a fraction x_{Q^n} :

$$922 \quad C_p^{conf} = \sum x_{Q^n} C_p^{conf} Q^n. \quad (14)$$

923 Links between melt thermodynamic parameters, rheology and structure were further established by
924 subsequent publications (Neuville and Mysen, 1996; Neuville 2006; Mysen 1990, 1995, Le Losq et
925 Neuville, 2013, 2017, Le Losq et al., 2015, 2017; Russell and Giordano 2017). Recently, Le Losq and
926 Neuville (2017) demonstrated how, using the Adam and Gibbs theory and Q^n values from NMR
927 spectroscopy, it is possible to determine with a high precision the viscosity of Na_2O - K_2O - SiO_2 melts. In
928 this section, we will show how such a model can be constructed, and what opportunities for extension

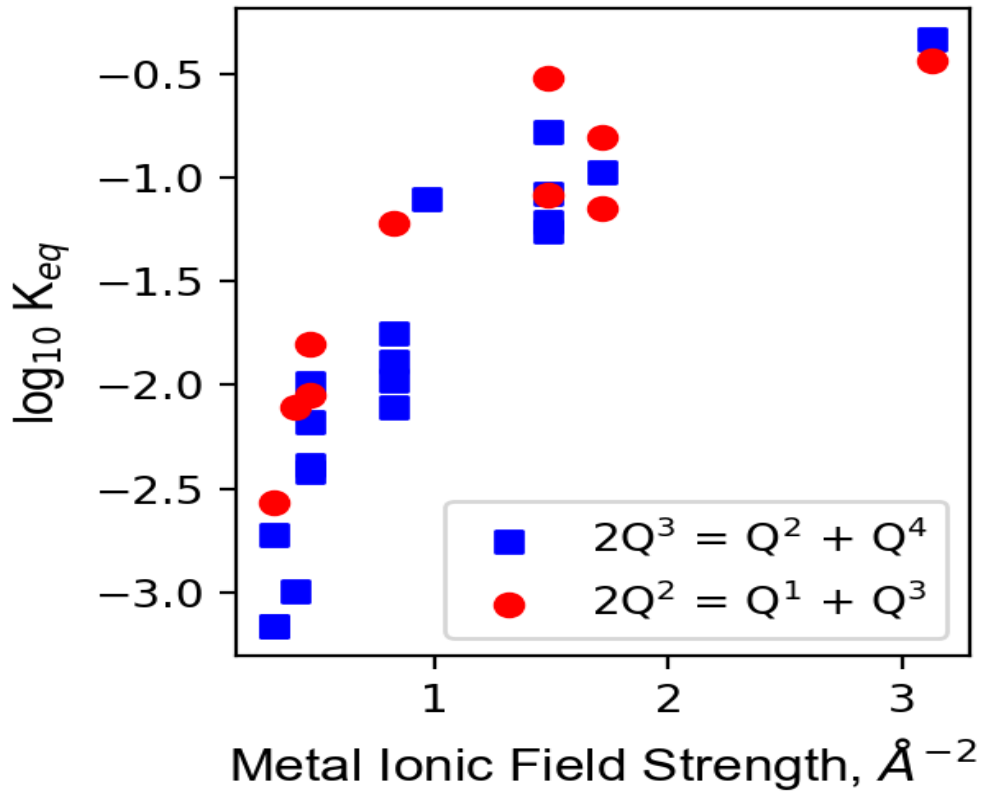
929 are envisioned. The application of such modeling for aluminosilicate melts will further be discussed in
930 section 3.

931
932 Using a principle similar to that of equation (14), we may be able to calculate values of $S^{conf}(T_g)$ and
933 B_e in eqs. 6 to 9 from partial values assigned to Q^n units in the glass, i.e. in the melt at the glass transition
934 temperature. This is possible because B_e is temperature-independent (Adam and Gibbs, 1965), and
935 $S^{conf}(T)$ can be estimated from $S^{conf}(T_g)$ and C_p^{conf} , which can be easily determined from viscosity data
936 and modeled in silicate melts, respectively. This implies that we can use glass structural data to build a
937 model for melts. However, we need to be able to model precisely how the distribution of Q^n units vary
938 with glass composition. Fortunately, the distribution of Q^n units mostly depends on (i) the glass silica
939 concentration, and (ii) the ionic field strength (IFS) of network modifier metal cations. Numerous ^{29}Si
940 NMR spectroscopy data were acquired on silicate glasses and allow us to know precisely how Q^n units
941 distribute depending on glass composition. They allow, in particular, determining the equilibrium
942 constants of the Q^n dissociation reactions

$$943 \quad Q^n = Q^{n-l} + Q^{n+l}, \quad (15)$$

944 which is at play in silicate glasses and melts. This explains the deviations of the Q^n distribution
945 measured compared to silicate minerals, where binary combinations of Q^n units are observed (e.g. Q^4 -
946 Q^3 , Q^3 - Q^2 , etc.). In glasses and melts, randomness implies that the Q^n distribution departs from the binary
947 model. The existing ^{29}Si NMR and Raman data allow one to estimate how the melt composition
948 influences such deviation. In Figure 14, we collected K_{eq} equilibrium constants for the dissociation of Q^3
949 units and of Q^2 units, and reported them as a function of the ionic field strength. In this Figure, most data
950 are from NMR spectroscopy because data interpretation from ^{29}Si NMR 1D and 2D methods (Edén,
951 2012) is less subject to debate, despite some possible complications that highlight that the determination
952 of Q^n unit distribution always is an arduous task (Pedone et al. 2010; Charpentier et al. 2013). Indeed,
953 Raman data requires the use of Raman cross sections, determined by calibration against ^{29}Si NMR data,
954 to transform the area of Raman peaks assigned to different Q^n units into concentrations of those Q^n units.
955 This is a first barrier as Raman cross-sections are not straightforward to obtain, a second one being the
956 fit of the spectra that can be a topic of debate (Nesbitt et al., 2018, 2021; Bancroft et al., 2018). The very
957 few K_{eq} values from Raman data used in Figure 14 do not come from possibly controversial traditional
958 peak fitting methods, but from the use of linear alternative least square methods to retrieve partial Raman
959 spectra for the different Q^n units in binary silicate glasses, a method developed by Zakaznova et al. (2007)
960 and Malfait et al. (2007, 2009). While it is very powerful for binary silicate glasses, it relies on
961 composition-specific, constant Raman signal shapes for the different Q^n units. This hypothesis is valid in
962 binary systems, but this method is limited because (i) partial Raman spectra for one binary system (e.g.

963 Na₂O-SiO₂) cannot be used for others and (ii) this starting hypothesis becomes void for ternary and more
 964 complex systems. This is because partial Raman spectra and Raman cross-sections differ depending on
 965 the network modifier present into the glass (e.g. Malfait et al., 2009; Woelffel et al. 2015).



966 **Figure 14:** Equilibrium constants of the dissociation of Q³ and Q² units represented as a function of the
 967 metal ionic field strength. Metal IFS was calculated assuming a coordination number of 6 and ionic
 968 radius from Whittaker and Muntus (1970). Equilibrium constants were calculated from the data of
 969 Emerson (1989), Emerson and Bray (1994), Maekawa et al. (1991), Bray et al. (1991), Zhang et al.
 970 (1996, 1997), Schneider et al., (2003), Voigt et al. (2005), Larson et al. (2006), Malfait et al. (2007),
 971 Zakaznova-Herzog et al. (2007), Sen et al. (2009), Malfait et al. (2009), Davis et al. (2010) and Herzog
 972 and Zakaznova-Herzog (2011).

973
 974
 975 An idea that arises when seeing Figure 14 is to parametrize the K_{eq} values as a function of the mean
 976 ionic field strength of metals cations in silicate glasses. Indeed, K_{eq} values for Q³ and Q² units change
 977 systematically depending on the ionic field strengths of the metal cation in the glass structure. It thus
 978 seems possible to calculate K_{eq} values from the mean ionic field strengths of metal cations in the glass.
 979 For ternary and more complex silicate glasses, this relies on the fact that mixing different cations in

980 silicate glasses affects linearly the distribution of Q^n units. Fortunately, this is a good approximation.
 981 Indeed, from ^{29}Si and ^{23}Na MAS NMR spectroscopy, the Q^n unit distribution upon Rb-Na mixing in
 982 alkali trisilicate glasses does not systematically change (Hater et al., 1989). This was also reported during
 983 Na and Li mixing in $(\text{Na,Li})_2\text{Si}_2\text{O}_5$ glasses (Ali et al., 1995, Sen et al., 1996). From ^6Li , ^7Li and ^{29}Si static
 984 NMR spectroscopy data, Bray et al. (1991) observed a linear change of the Q^3 units fraction upon mixing
 985 Li and K in disilicate glasses. The ^{29}Si static NMR data from Emerson and Bray (1994) further suggest
 986 a slight departure from linearity of the Q^3 unit fraction when mixing $\text{Na}_2\text{Si}_2\text{O}_5$ and $\text{Cs}_2\text{Si}_2\text{O}_5$ glasses. Such
 987 interpretation may be consistent with ^{17}O Dynamic Angle Spinning NMR data from mixed $\text{Na}_2\text{Si}_2\text{O}_5$ -
 988 $\text{K}_2\text{Si}_2\text{O}_5$ glasses (Florian et al., 1996), showing slightly non-linear changes of the fractions of Bridging
 989 (BO) and Non-Bridging (NBO) oxygen anions with changes in the glasses K/ (K + Na) ratios. Such
 990 observation agrees with the recent report of Le Losq and Neuville (2017), which showed that the Raman
 991 areas of Q^n units in alkali trisilicate glasses vary linearly within error bars.

992

993 From the above review, it thus should be possible to calculate K_{eq} values for Q^3 and Q^2 unit
 994 dissociation given the mean IFS of metal cations present in the silicate glass. However, despite a good
 995 correlation, scattering is visible in Figure 14. Such scattering results from second order effects that may
 996 be related to some local peculiarities of the effect of each cation on K_{eq} values as well as our lack of a
 997 perfect understanding of the coordination number of each cation. To circumvent this problem, we propose
 998 to calculate the mean K_{eq} values in silicate glasses based on the combination of K_{eq} values assigned to
 999 each cations (from their calculation in the binary $\text{M}^{x/2x}\text{O-SiO}_2$ systems):

000

$$001 \quad K_{eq} \text{ glass} = \sum K_{eq}^i x_i, \quad (16)$$

002 where x_i is the fraction of a given cation relative to the sum of all cations. Assuming linear variations
 003 in the Q^n unit fractions upon mixing different cations, a valid hypothesis given existing data as indicated
 004 previously, this will allow obtaining the most precise model for the variations in Q^n units in Al-free
 005 silicate glasses (the case of aluminium deserves its own section, such that its effect will be discussed in
 006 section 3). K_{eq}^i values determined for each system are provided in Table 1, based on the data reported in
 007 Figure 14.

008

Metal cation	$K_{eq} \ 2Q^3 = Q^2 + Q^4$	$K_{eq} \ 2Q^2 = Q^1 + Q^3$
Li	0.09(5)	0.2(2)
Na	0.012(4)	0.06(-)

K	0.006(3)	0.012(5)
Rb	0.001(-)	?
Cs	0.001(-)	0.003(-)
Mg	0.464(-)	0.364(-)
Ca	0.106(-)	0.156(-)
Ba	0.078(-)	?

Table 1: mean values of the K_{eq} coefficients for the dissociation of Q^3 or Q^2 units in M^+O_2 - SiO_2 or $M^{2+}O$ - SiO_2 glasses, calculated from the data presented in Figure 14. Standard deviations from the mean are provided in parenthesis, when possible.

Now that we can calculate the fractions of Q^n units for various silicate compositions, it opens doors to calculate the terms of the Adam and Gibbs equation: B_e and $S^{conf}(T_g)$. Le Losq and Neuville (2017) leveraged such ability for K_2O - Na_2O - SiO_2 melts with 60 to 100 mol% SiO_2 , taking into account the ideal mixing of Na and K in silicate melts (Richet, 1984) when developing equations for $S^{conf}(T_g)$ and B_e . For $S^{conf}(T_g)$, they assumed that, added to the topological entropy S^{topo} , excess entropies arise from the ideal Si mixing between the different Q^n units S^{mix}_{Si} and random mixing of Na and K into the glass network S^{mix}_{Na-K} , such that:

$$S^{conf}(T_g) = S^{topo} + S^{mix}_{Si} + S^{mix}_{Na-K}, \quad (17)$$

with

$$S^{topo} = \sum_{n=2}^3 x_{Q_{Naenv}^n} S_{Q_{Naenv}^n}^{conf} + \sum_{n=2}^3 x_{Q_{Kenv}^n} S_{Q_{Kenv}^n}^{conf} + x_{Q^4} S_{Q^4}^{conf}, \quad (18)$$

$$S_{Si}^{mix} = \frac{-x_{Si}}{x_O} * 2 * R * \sum_{n=2}^4 x_{Q^n} \ln(x_{Q^n}), \quad (19)$$

and

$$S_{Na-K}^{mix} = \frac{-(x_{Na} + x_K)}{x_O} * 2 * R * (X_K \ln(X_K) + (1 - X_K) * \ln(1 - X_K)), \quad (20)$$

with x_{Si} , x_O , x_{Na} and x_K the atomic fractions of Si, O, Na and K respectively, $X_K = K/(K+Na)$, R the gas constant, and x_{Q^n} the Q^n fractions. We note that, as Le Losq and Neuville (2017) investigated melts with NBO/T lower than 1.5, equations above were limited to Q^2 to Q^4 units. In addition, in the topological contribution (equation 18), Q_{Naenv}^n and Q_{Kenv}^n units with their associated $S_{Q_{Naenv}^n}^{conf}$ and $S_{Q_{Kenv}^n}^{conf}$ values are distinguished; those are the Q^n units, with $n < 4$, that have NBO bonded preferentially to Na or K, respectively. This is an approximation introduced to take into account the fact that Q^n units with NBO

033 bonded to Na or K may present different S^{conf} values, as shown by the difference of $S^{conf}(T_g)$ between
 034 sodic and potassic silicate glasses.

035

036 For the calculation of B_e , the link between $S^{conf}(T)$ and B_e needs to be considered. Indeed,

$$037 \quad B_e = \frac{\Delta\mu s_c}{k_B}, \quad (21)$$

038 and

$$039 \quad S^{conf}(T_g) = \frac{N_A}{z (T_g)} s_c, \quad (22)$$

040 with $\Delta\mu$ the Gibbs free-energy barrier opposed to the cooperative rearrangements of molecular
 041 subunits of size z (T_g) and intrinsic entropy s_c , k_B the Boltzmann constant and N_A the Avogadro
 042 constant (Adam and Gibbs, 1965; Richet, 1984). s_c represents the entropy of the molecular subunits
 043 involved in the melt viscous flow and relaxation process. It appears in both eqs. (21) and (22), yielding
 044 a strong correlation between $S^{conf}(T_g)$ and B_e (Neuville and Richet, 1991). From eqs. (20) and (22), we
 045 can write

$$046 \quad B_e = \frac{\Delta\mu z (T_g) S^{conf}(T_g)}{R}, \quad (23)$$

047 with R the perfect gas constant ($=N_A k_B$). From eq. (23) and considering that $\Delta\mu$ and s_c are
 048 temperature-independent (Richet, 1984), B_e should be expressed similarly to $S^{conf}(T_g)$, from the melt
 049 structure recorded at T_g in glasses. Considering that, Le Losq and Neuville (2017) assumed that B_e can
 050 be expressed as the sum of partial molar B_e terms for the different Q_{Menv}^n and Q^4 units, with additional
 051 non-linear contributions arising from the role of $S^{conf}(T_g)$ in eq. (23). The latter non-linear contributions
 052 are obtained by directly injecting eqs. (19) and (20) with K_1 and K_2 scaling terms in the expression of B_e :

$$053 \quad B_e = \sum_{n=2}^3 x_{Q_{Naenv}^n} B_{e_{Q_{Naenv}^n}} + \sum_{n=2}^3 x_{Q_{Kenv}^n} B_{e_{Q_{Kenv}^n}} + x_{Q^4} B_{e_{Q^4}} + K_1 S_{Si}^{mix} + K_2 S_{Na-K}^{mix} \quad (24)$$

054

055 Using this model, Le Losq and Neuville (2017) showed that it is possible to calculate the viscosity of
 056 the alkali silicate melt with a mean square error of 0.2 log Pa·s. This error is much lower than those of
 057 parametric models, typical presenting root mean squared errors on their parametrization datasets of ~ 0.6-
 058 0.7 log Pa·s (e.g. Hui and Zhang, 2017; Giordano et al., 2008).

059

060 Le Losq and Neuville (2017) used cubic splines for interpolation of the Q^n distribution in their model.
 061 With the approach presented in this chapter, it is possible to replace this by the K_{eq} -based model for Q^n
 062 distribution in silicate melts in order to improve the future deployment and development of such a
 063 thermodynamic viscosity model. Preliminary tests yield good predictions with standard errors of 0.3 log

064 Pa·s, a value slightly higher than the initial value of 0.2 log Pa·s from Le Losq and Neuville (2017). This
065 difference arises from the fact that the initial cubic spline modeling of the Q^n distribution in K_2O-Na_2O-
066 SiO_2 melts is slightly more accurate than the global structural model based on the K_{eq} values calculations.
067 Differences are in the range of 1-2%. This actually highlights how sensitive a model can be to melt
068 structure: an error of only 1-2 % alters measurable the accuracy of the model.

070 3. Aluminosilicate glasses and melts

071 Aluminum is a key element in Earth and material sciences because it is present, in various amounts,
072 in most geologic and industrial glasses, and it drastically affects their properties. Generally, a well-known
073 feature of the structure of silicate minerals is that silicon ions may be replaced isomorphously by
074 aluminum ions provided that either mono or divalent cations are available to maintain local neutralization
075 of electrical charges in the structure (Putnis, 1992). This feature is clearly visible in tectosilicates that
076 present an interconnected three-dimensional silica-like tetrahedral structure, in which the mono or
077 divalent cations are accommodated in the framework free volumes. In these minerals, the ratio
078 $R=M^+_2O/Al_2O_3$ or $M^{2+}O/Al_2O_3$ is unity. The metal cations play charge compensator roles, and no non-
079 bridging oxygens are present. This is also generally the case in tectosilicate glasses, albeit some possible
080 minor amounts of NBOs may be present (Stebbins and Xu, 1997). However, an additional complexity in
081 aluminosilicate glass is the variable coordination number of Al. Indeed, while Al mostly substitutes for
082 Si in the SiO_4 tetrahedra in silicate glass, it also is found in five and six-fold coordinations, in proportions
083 that depend on melt chemical composition, system pressure and temperature, and glass-forming cooling
084 rate (Ohtani et al., 1985; Risbud et al., 1987; Murdoch et al., 1985; Mc Millan, et al., 1982; Merzbacher
085 et al., 1990, 1991; Lacy, 1963; Merzbacher and White, 1991; Coté et al., 1992, Stebbins and Xu, 1997,
086 Sato et al., 1991; Allward and Stebbins, 2005a,b, 2007, Allwardt, et al., 2004; 2007; Stebbins et al., 2000,
087 2008; Stebbins, 2008; Henderson et al., 2007; Lee 2005, Lee and Stebbins, 2000, 2002, 2009; Neuville
088 et al., 2004ab, 2006, 2008a,b, 2010; Le Losq et al., 2014). The varying coordination number of Al raises
089 the question of its role in the melt structure depending on its coordination. Indeed, following the
090 terminology proposed by Zachariassen (1932), while Al in four-fold coordination is a network former, Al
091 in six-fold coordination should be a network modifier, and Al in five-fold coordination should probably
092 also be considered as a network modifier. We will review such questions, and more generally the
093 connection between aluminosilicate melt structure and properties in this section.

095 3.1 Molar volume, coordination number and structure

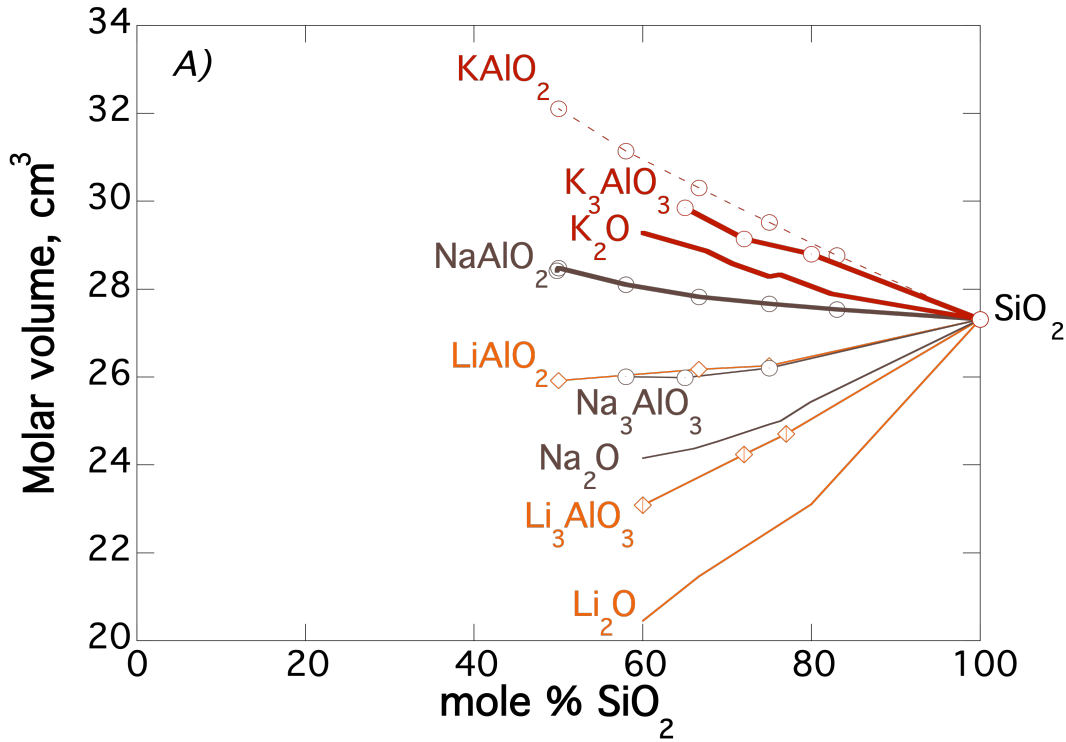
096 Density and molar volume are properties easy to measure in glasses, and bring important pieces of
097 information regarding their internal structure, and by extension, that of the melt at the glass transition.

098 Variations in the molar volumes of alkali and alkaline-earth silicate and aluminosilicate glasses as a
099 function of silica concentration show similar trends, except for the heaviest elements, like potassium,
100 cesium and rubidium (Figure 15). From silica glass with $V_m=27,31\text{cm}^3$, it is found that generally the
101 molar volume decreases with the decrease in SiO_2 , except for K-, Cs-, Rb- silicate glasses. For the same
102 SiO_2 content, the magnitude of the decrease of the molar volume depends on the ionic field strength of
103 the metal cation: it is moderate for Na^+ and very important for Mg^{2+} (for example V_m of Ca silicate
104 $=21,21\text{cm}^3$ and $24,14\text{cm}^3$ for Na-silicate, both at 60 mol % of SiO_2 – note that we compare Ca and Na
105 silicate glass and not Mg-silicate at 60 of silica, because this glass is made with a high cooling rate, and
106 its fictive temperature is probably very different than that for the Na-silicate glass). In the case of
107 potassium, V_m always increases regardless of the glass aluminum content. For other cations, V_m variations
108 in aluminosilicate glasses are more complex. First, the M^{2+}/Al or M^+/Al ratio directly influences the
109 variations of V_m with the glass silica concentration. Secondly, a general concave trend of the V_m versus
110 SiO_2 relationship is observed according to previous work (Seifert et al., 1982, Doweidar et al., 1999,
111 Doweidar 1999). Taking the SiO_2 - CaAl_2O_4 binary mixture as an example, and starting from silica, V_m
112 decreases with silica decrease until 50 mol% SiO_2 ($V_m=25,81\text{cm}^3$ for anorthite glass), and then increases
113 up to a value of $\sim 27\text{cm}^3$ for the pure CaAl_2O_4 end-member for example. Such non-linear V_m trends
114 indicate that V_m modelling in aluminosilicate glasses cannot be obtained from a linear combination of
115 partial V_m values assigned to the different oxides. To circumvent this problem, several papers have
116 modelled the density of glass and melts as a function of their expected Q^n speciation (Doweidar, 1999,
117 Doweidar et al., 1999) or other entities like partial volume of oxide components (Lange, 1996, 1997,
118 Bottinga and Weill, 1970).

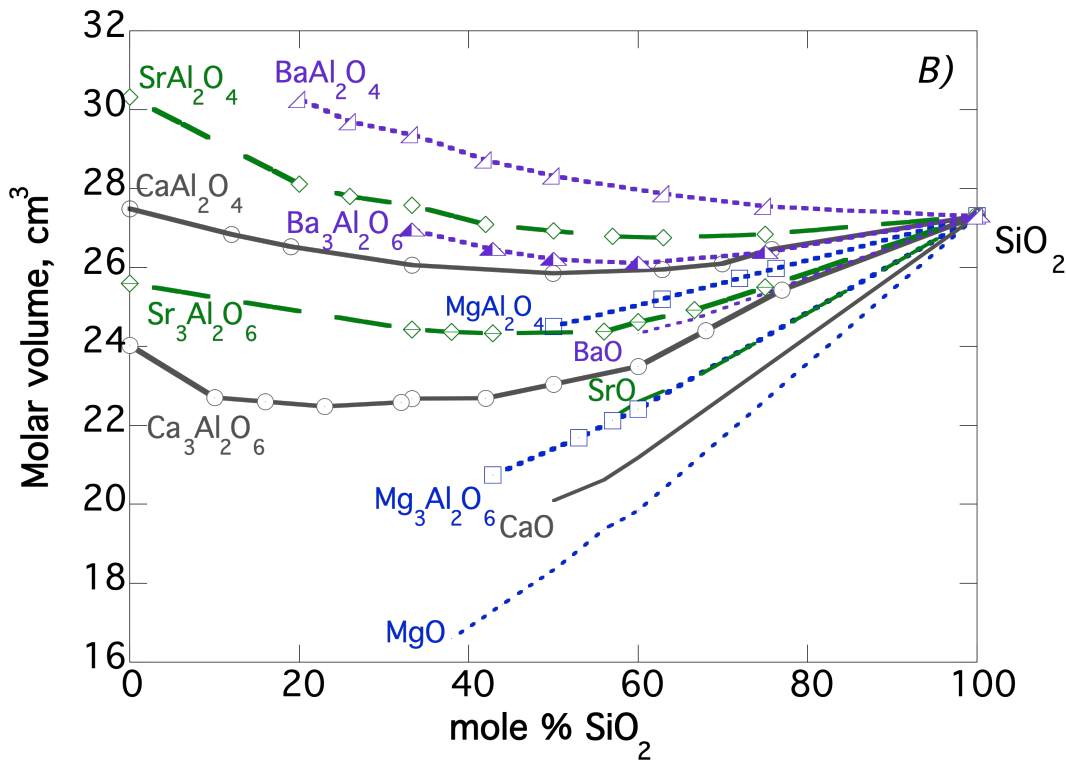
119 One of the most important pieces of information arising from V_m data analysis is the possibility to
120 provide knowledge regarding the coordination numbers of metal cations as well as aluminum. We have
121 mentioned, in section 2.1 (Figure 5), that metal cations' CNs remain almost constant in silicate glasses.
122 It is also well known that the molar volume of the SiO_4^{4-} tetrahedra doesn't change a lot as a function of
123 the Q^n species because the $d(\text{Si-BO})$ or $d(\text{Si-NBO})$ vary less than 0.05\AA (Cormack and Du, 2001; Du and
124 Cormack 2004). This variation corresponds to a variation of around 3% on the distance between Si-BO
125 and Si-NBO which causes a variation of the volume of the tetrahedra between 12.4 and 9.3% as a function
126 of the amount of alkali content respectively 10 and 50%, if we used the distances given by Cormack and
127 collaborators. In the case of aluminum, the molar volume of AlO_4^{5-} tetrahedra doesn't change because
128 Al-O distances stay almost constant as a function of the different Q^n species for Al^7 , and the most
129 important change in the molar volume of Al units come from the change in the coordination of Al and

⁷ The distance Al-O increases from 1.76 up to 1.86 \AA when the coordination number of Al changes from 4 to 6 (Cormier et al., 2000, 2003, Hennet et al., 2016). This implies that Al-O distance vary smaller when Al change of Q^n species in tetrahedra.

130 not of the Q^n species of Al. If we consider that the volumes vary very slightly in the ternary diagrams this
 131 implies that the molar volume variation observed between silicates and aluminosilicates glasses is
 132 produced essentially by changes in coordination number of alkaline or alkaline-earth. Before discussing
 133 this, we will quantify the different proportions of aluminum.



134



135

136

137 **Figure 15:** A) molar volume for alkali and B) for alkaline-earth silicate and Al-silicate glasses, data
138 for NAS, KAS compositions (Le Losq et al. 2017, 2015, Neuvill, 1991, 2006), LAS (Strukelj, 2008), MAS,
139 CAS system (Neuvill, 1992), SAS data from Novikov et al., (2017), BAS original data and from Novikov
140 (2017).

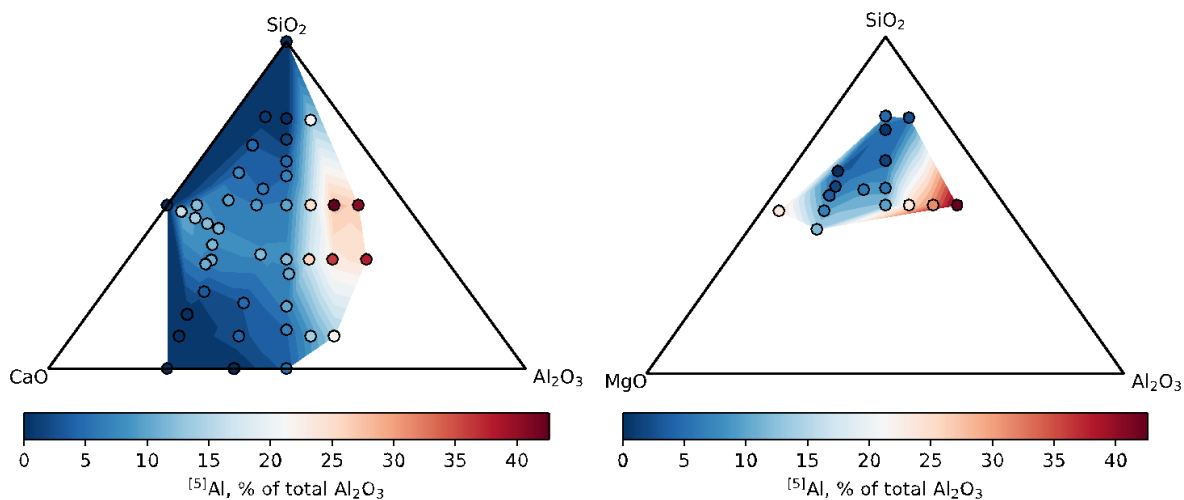
143 3.2 Proportion of Al in five-fold coordination

144 Given the role of Al coordination on V_m and other melt/glass properties, it is clear that Al coordination
145 should be quantified. Fortunately, through ^{27}Al NMR spectroscopy, several studies allow drawing a
146 picture of Al coordination variations with composition, temperature and pressure.

147 The presence of $^{[5]}\text{Al}$ is systematically observed in the middle of the ternary diagrams of Li
148 aluminosilicate, and alkaline-earths aluminosilicate, including peralkaline glasses in which Al in five-
149 fold coordination is not expected considering the stoichiometry (Neuvill et al., 2006, 2007, 2008b,
150 2010). Moreover, the proportion of $^{[5]}\text{Al}$ is always maximum for glasses with about 50 mol % of SiO_2
151 (Neuvill et al, 2004, 2006, 2008, Novikov et al., 2017). On the contrary, Na or K tectosilicate and
152 peraluminous glasses have small concentrations of Al in five-fold coordination, which becomes
153 undetectable in peralkaline compositions (Stebbins and Farnan, 1992; Allwardt et al., 2005a,b; Lee et al.
154 2009; Le Losq et al., 2014). The variation of NMR chemical shift values for $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ sites with
155 SiO_2 content are less dependent on silica content than $^{[4]}\text{Al}$ sites (Figure 13b, from the previous chapter).
156 The NMR chemical shift values are directly related to the inter-tetrahedral angle or the first-neighbor
157 cations (Stebbins and Farnan, 1992). This can imply that $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ sites are more connected with Al
158 in four fold coordination than with Si in different Q^n species which does not respect the Lowenstein
159 rule's, but in the majority of studies this rule is avoided (Neuvill et al., 2008a, 2010, Lee and Stebbins,
160 2009, Hiet et al., 2009). 2D NMR ^{27}Al - ^{29}Si correlations (Lee and Stebbins, 2009, Hiet et al., 2009) show
161 that $^{[5]}\text{Al}$ is more connected with Si than with Al in lanthanum aluminosilicate glasses (Florian et al.,
162 2007). Highly coordinate Al species, especially $^{[5]}\text{Al}$, are likely to have a positive formation enthalpy and
163 their abundance in the melt is expected to increase with increasing temperature as observed by some
164 authors (Neuvill et al., 2008b; Stebbins, 2008). However, the ^{27}Al NMR spectra at high temperature
165 shifts to lower ^{27}Al chemical shift values with increasing temperature, this can be interpret as resulting
166 from the appearance of $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ contributions located at lower chemical shifts than that of $^{[4]}\text{Al}$
167 (Kanehashi and Stebbins, 2007, Thompson and Stebbins, 2011, 2012, 2013). Signatures of Al in high
168 coordination are also clearly visible using X-ray absorption spectroscopy at the Al K-edge (Neuvill et
169 al., 2008b). In the case of CA50.25 (anorthite melts composition), Neuvill et al (2008b) show an increase
170 from 8% up to 22% of $^{[5]}\text{Al}$ between room temperature and 1900 K, in good agreement with high

171 temperature Al NMR (Stebbins, 2008). A significantly higher proportion of $^{[5]}Al$ is observed in
 172 magnesium aluminosilicate glasses than in the others aluminosilicate systems on the tectosilicate join
 173 (Neuvillle et al., 2008b, Novikov et al., 2017, Figure 23B) which can be explained by the promotion of
 174 highly coordinated Al species with the presence of metal cations with relatively high ionic field strength,
 175 as shown in boroaluminate by Bunker et al., (1991) and in La-aluminosilicate glass compositions (Florian
 176 et al. 2007). Such an idea agrees with the increase in the disorder when the cation field strength decreases
 177 (Mysen et al., 1982; Murdoch et al., 1985; Sharma et al, 1985; Navrotsky et al., 1982, 1985; Lee and
 178 Stebbins 2000, 2002, Neuvillle et al. 2008a, Wu and Stebbins, 2009; Lee et al., 2016, Le Losq et al.,
 179 2017).

180
 181 Several papers on ^{27}Al NMR spectroscopy have shown that, for $R = M/Al$ varying between infinity
 182 and 1 (silicate to tectosilicate compositions), Al is essentially in four-fold coordination (Risbud et al.,
 183 1987, Murdoch et al., 1985; Merzbacher et al., 1990, 1991; Merzbacher and White, 1991; Coté et al.,
 184 1992, Stebbins and Xu, 1997, Stebbins et al., 2000, 2008; Neuvillle et al., 2004ab, 2006, 2007, 2008a,
 185 McMillan and Kirkpatrick, 1992; Massiot et al., 2008; Lee and Stebbins, 2009, 2016; Richet et al.,
 186 2009a; Le Losq et al., 2014; Novikov et al., 2017; Florian et al., 2018, Charpentier et al., 2018). In the
 187 CAS system, 93 % of Al is in 4-fold coordination, and the proportion of $^{[5]}Al$ increases slowly up to 7%
 188 for the anorthite glass composition on the tectosilicate join (Neuvillle, et al., 2006). In the MAS system,
 189 the proportion of $^{[5]}Al$ is a little higher, 12% for Mg-anorthite glass (Neuvillle et al., 2008a). For all others
 190 M^+ or M^{2+} Al-silicate systems, the proportion of $^{[5]}Al$ is lower and the amounts decrease with increasing
 191 z/r (z : cation charge and r atomic radius, see Neuvillle et al., 2008a or Stebbins et al., 2008, Novikov et
 192 al., 2017). Figure 16 A and B show the total amount of $^{[5]}Al$ in mol % in the CAS and MAS system.



193
 194 **Figure 16:** Percentage of $^{[5]}Al$ of total Al_2O_3 in the CAS (left) and MAS (right) systems. Data from
 195 Neuvillle et al. (2004, 2006, 2007, 2008b, 2010, Massiot et al., 2008; Licheron et al., 2011).

196

197 3.3 Molar volume, AlO_4^{4-} and implications for the coordination number of metal cations

198 In the previous sections, we saw that the molar volume of Si in the different Q^n species can vary by
199 less than 10% when n varies from 4 to 0 and that the molar volume of Al stays almost constant for Al in
200 four-fold tetrahedra. Despite this, the molar volume V_m of a lime aluminosilicate glass with 50% of SiO_2
201 (wollastonite to anorthite glasses) can vary from 20 to 25.9 cm^3 between the wollastonite and anorthite
202 compositions, this represents an increase of 25 %. This increase is 12 % between silicate glasses and the
203 glasses on the $R = 3$ join, and of 12 % again between the join $R = 3$ and the join $R = 1$ with $R=MO/Al_2O_3$
204 with $M=Mg, Ca$. This huge increases of V_m is a maximum at 50 mol % silica.

205 In the case of calcium aluminate glasses, the molar volume difference between C3A ($Ca_3Al_2O_6$) and
206 CA ($CaAl_2O_4$) glasses is only 6.8 % (Figure 15B). In Figure 15B, the increase of molar volume between
207 join $R=3$ and 1 can also result from a change in the coordination number of calcium because the aluminum
208 stays in four-fold coordination between C3A and CA glasses. In this case, Ca varies between regular
209 octahedra where Ca is in 6-fold coordination to a distorted site in 7-8-fold coordination (Cormier et al.,
210 2001, 2003, Neuvillle et al., 2008b, 2010, Cicconi et al., 2016; Drewitt et al., 2012, 2017, Jakse et al.,
211 2012; Takahashi et al., 2015; Hennet et al., 2016).

212

213 Generally, the coordination number of alkali or alkaline-earth elements is difficult to determine, but
214 changes in the V_m of a glass can inform us about CN changes. For instance, the abovely variation in the
215 CN of Ca is in good agreement with the changes observed via XANES at the Ca K -edge in Ca
216 aluminosilicate glasses (Neuvillle et al., 2004b, 2008, Cormier and Neuvillle, 2004; Cicconi et al., 2016).
217 In particular, Cicconi et al. (2016) observed a shift to greater energy and a decrease in intensity of the
218 pre-edge in the XANES spectra at the Ca K -edge between wollastonite to anorthite glasses. This shift
219 can also be correlated with the new peak ω_2 observed in the depolarized Raman spectra, VH, (see Figure
220 13, chapter 3 this volume, Drewitt et al., 2021). The peak ω_2 decreases when R goes from infinity to 1
221 (to silicate to tectosilicate glasses)

222

223 In the case of the NAS system ($Na_2O-Al_2O_3-SiO_2$), the peak ω_2 is also clearly visible for silicate
224 glasses in the VH Raman spectra and it disappears for $R=Na_2O/Al_2O_3=1$ (Hehlen and Neuvillle, 2015).
225 This peak ω_2 exists in all silicate glasses with $M^+=Na, K$ and $M^{2+}=Mg, Ca, Sr, Ba$ (Hehlen and Neuvillle,
226 2015, 2020) and it's intensity decreases when Al replaces M^+ or M^{2+} . In the NAS glass system, a shift is
227 also observed in the chemical shift, δ , of ^{23}Na NMR between NS3 and albite glass (Le Losq et al., 2015)
228 following a trend that can be correlated with variations in XANES at the Na K -edge between the NS3
229 and albite glasses (Neuvillle et al., 2004).

230

231 In the case of the SAS (SrO-Al₂O₃-SiO₂) system, Novikov et al. (2017) also observed some change in
232 the first XANES oscillation which can also be attributed to a change in CN of strontium.

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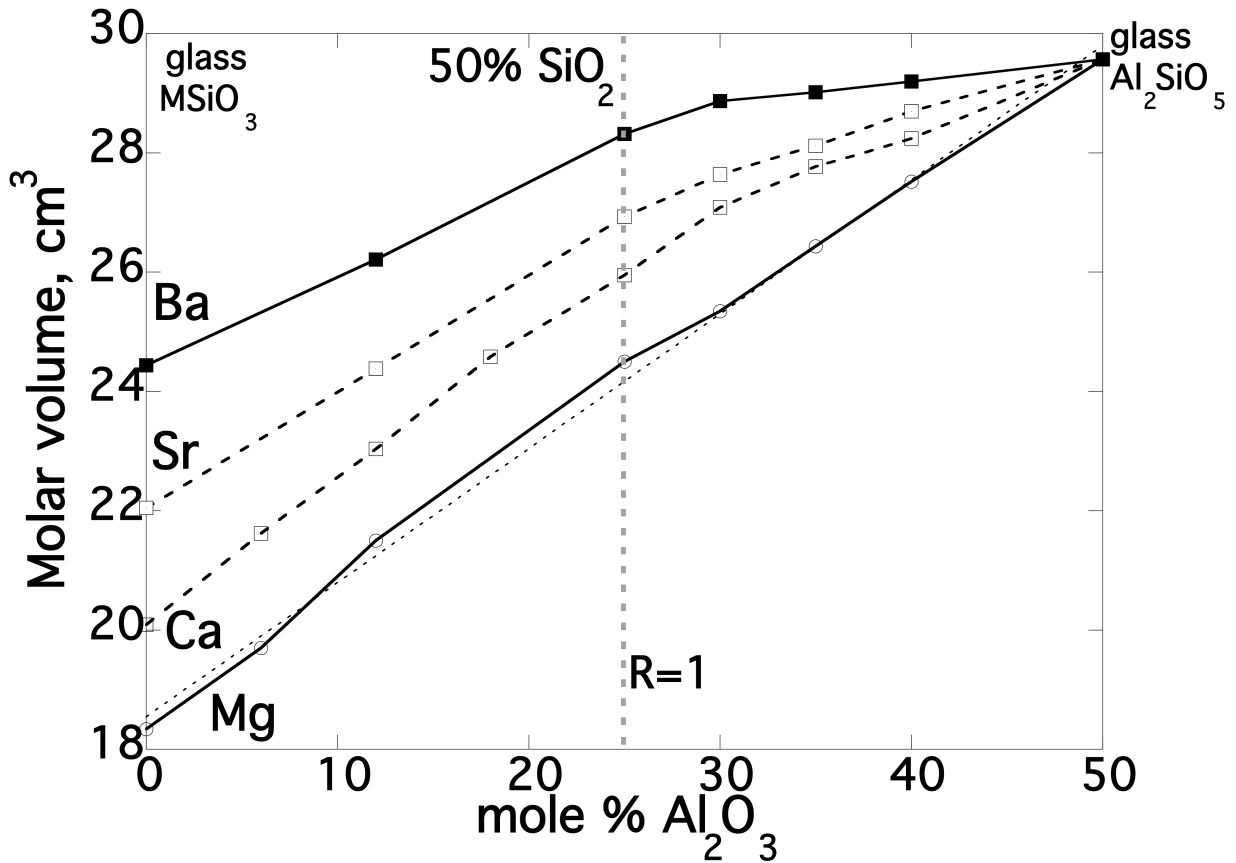
234 To summarize, ²³Na NMR, XANES at the Na, Sr, Ca K-edge, and depolarized Raman spectra, (VH),
235 all show changes that can be correlated with an observed increase in the molar volume between silicate
236 and tectosilicate glasses. V_m varies between 4% and 16% with changing the M⁺/Al or M²⁺/Al ratio at a
237 given silica content and depends clearly on the metal cation size. The V_m changes can be assigned to
238 changes in the coordination of metal cations as their role in the aluminosilicate network varies with the
239 M/Al ratio. Similarly, features observed in NMR, XANES or Raman spectroscopies can be directly
240 correlated with such change in the role of alkali or alkaline-earth elements between network modifier and
241 charge compensator. The concept of network modifier and charge compensator was introduced by
242 Zachariazen but never really demonstrated. Now, with the technical evolution of spectroscopy methods,
243 but with measuring the molar volume determined from density measurements, it is possible to have an
244 idea of the role alkaline elements.

245

246 In Figure 17, the molar volume of various glasses is shown as a function of mole percent of Al₂O₃ at
247 constant silica. The glass compositions vary between MSiO₃ up to Al₂SiO₅, M=Mg, Ca, Sr, Ba. Four
248 trends are clearly visible for the four alkaline-earth aluminosilicate glass families. In the case of MgSiO₃-
249 Al₂SiO₃, the molar volume varies almost linearly with Al₂O₃ (the linear variation corresponds to the
250 dashed line). This can imply:

- 251 - i) that the coordination number of Mg is almost constant in this system and is not really affected by
252 the Mg/Al substitution, an idea in good agreement with XANES at the Mg K-edge (Trcera et al., 2009);
253 -ii) that the molar volume depends on the proportion of Al in five-fold coordination.

254



255

256 *Figure 17: molar volume at constant $\text{SiO}_2 = 50 \text{ mol}\%$ for four alkaline-earth aluminosilicate glass*
 257 *compositions. (The dashed line between MgSiO_3 and Al_2SiO_5 glasses correspond to this equation*
 258 *$18.547 + 0.22497 * \text{Al}_2\text{O}_3$). Values are calculated from density measurements from Neuville (1992) for Ca*
 259 *and Mg system peralkaline compositions, Neuville et al. (2006, 2008) for Ca and Mg Per-aluminate*
 260 *compositions, Novikov et al. (2017) for Sr compositions, Novikov (2017) for Ba compositions and Al_2SiO_5*
 261 *are from Wang et al. (2020).*

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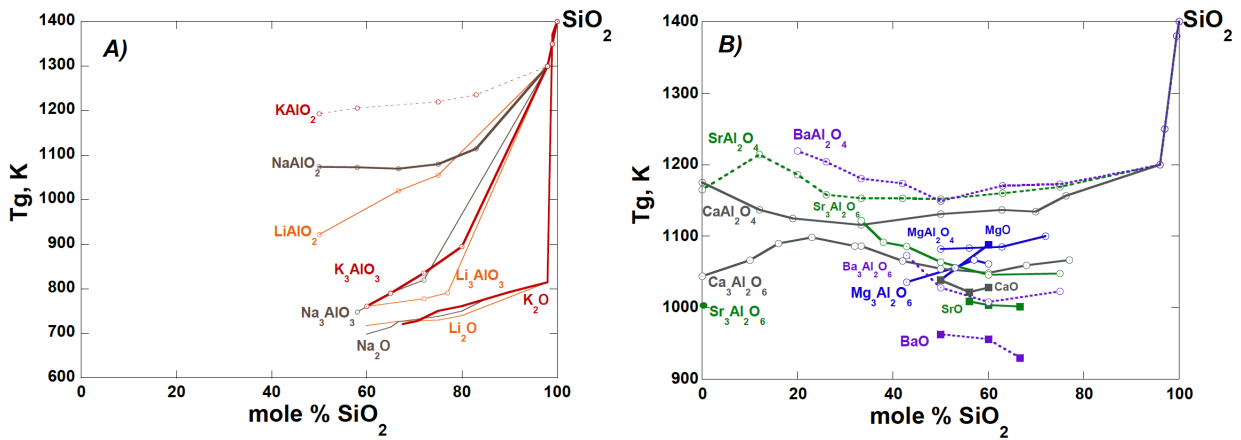
263 For the Ca, Sr and Ba aluminosilicate glasses the changes observed in the slopes near 25 mol % of
 264 Al_2O_3 correspond to the tectosilicate line ($R = M^{2+}O / \text{Al}_2\text{O}_3 = 1$), characterized by an increase in the
 265 proportion of $^{[5]}\text{Al}$ in the glass (Neuville et al., 2006, 2008, Novikov et al., 2017, Novikov 2017). This
 266 Figure clearly shows two domains, one where V_m is affected by aluminum, the peraluminous domains,
 267 and one where V_m depends on an increase in the coordination of the alkaline-earth element, the peralkaline
 268 domain (Cicconi et al., 2016; Novikov et al., 2017).

269

270 3.3 Glass transition temperature

271 In general, a decrease in T_g occurs with decreasing SiO_2 content at all R ratios ($R = M^{2+}O_2 / \text{Al}_2\text{O}_3$ or
 272 $M^{2+}O / \text{Al}_2\text{O}_3$) (Figure 18). It is particularly important at silica contents between 100 and ~75 mol%. In

273 detail, this T_g decrease is more significant in Al-free silicate melts than in tectosilicate glasses; the lower
 274 R , the lower the effect of changing SiO_2 on T_g . Typically, at $R=1$ in tectosilicate compositions, the
 275 decrease in T_g is of ~ 300 K for $\text{MAl}_2\text{Si}_2\text{O}_8$ glasses, and 200 K and 300 K for respectively KAlSiO_4 and
 276 NaAlSiO_4 glasses. The large contrast between T_g variations in Al-free silicate and tectosilicate glass
 277 compositions results from the changing role of metal cations upon aluminum addition into the melt
 278 network. Indeed, while in silicate glasses, alkali and alkaline-earth elements are network modifiers that
 279 break the 3D tetrahedral network, in aluminosilicate glasses they ensure the charge compensation of
 280 AlO_4^- tetrahedral units and thus participate in increasing melt polymerization. This translates to higher
 281 T_g along the $\text{M}^+\text{AlO}_2\text{-SiO}_2$ or $\text{M}^{2+}\text{Al}_2\text{O}_4\text{-SiO}_2$ binaries than along the $\text{M}^+\text{O}_2\text{-SiO}_2$ or $\text{M}^{2+}\text{O-SiO}_2$ binaries.



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283

284 *Figure 18: Glass transition temperature T_g , in K, of silicate and aluminosilicate glasses with alkali*
 285 *elements (A) and alkaline-earth elements (B). The glass transition temperatures were determined from*
 286 *viscosity measurements, i.e. they correspond to the temperature at which $\log \eta = 12$ Pas. Data from*
 287 *Neuville (1991) for Li, K silicates; Neuville (2006) and Le Losq et al. (2014) for sodic systems, (Neuville,*
 288 *1992) for Ca and Mg, Novikov et al. (2017) for Sr and Novikov (2017) for Ba.*

289

290 3.4 Link between structure and properties of aluminosilicate melts: example of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ 291 system

292 To discuss and illustrate the links between glass structure and glass/melt properties, the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$
 293 SiO_2 (CAS) glass system will be taken as an example in the following. The CAS system has the advantage
 294 having the largest glass forming domain (Neuville et al., 2006). The observations and interpretations
 295 made in this system can be extended to other ternary system. In general, in the CAS system, an important
 296 decrease in T_g is observed with decreasing SiO_2 content, which results from network depolymerization,
 297 except at $R = 1$. In the latter case, melt polymerization is almost constant and the decrease in T_g results
 298 from the formation of weaker Si-O-Al bonds as Al substitutes for Si in Q^4 units (Navrotsky et al., 1985;

299 [Neuvville et al., 2004](#), [Cormier et al., 2001, 2005](#), [Hennet et al., 2016](#)). T_g varies by about four hundred
300 degrees between pure SiO_2 ($T_g \sim 1480$ K; [Richet and Bottinga 1984](#)) and the center of the ternary system
301 ($T_g = 1115$ K for $\text{CA}33.33$, $\text{M}^{2+}\text{AX.Y}$ where M^{2+} =alkaline-earth element and $\text{A}=\text{Al}_2\text{O}_3$, $\text{X} = \text{SiO}_2\%$ i.e.
302 33.3 mol%, $\text{Y} = \%\text{Al}_2\text{O}_3$ and $\text{M}^{2+}\text{O}=(100-(\text{X}+\text{Y}))$ in this case, $\text{CaO}=33.3\%$). At $R=1$, glasses with less
303 than 30 mol% SiO_2 display a continuous increase in T_g upon decreasing SiO_2 content, and T_g reaches a
304 new local maximum for the CaAl_2O_4 composition at 1175 K; the minimum in T_g at $R=1$ is centered
305 between 40 and 50 mol% SiO_2 . The observed behavior in T_g at $R = 1$ results from the competition between
306 Si and Al as network formers. As indicated by the difficulty of forming glasses at high Al concentrations
307 (e.g. along the SiO_2 - Al_2O_3 binary) as well as a lowering of T_g with addition of Al. Al can be considered
308 as a relatively poor network former compared to Si. This is further corroborated by variations in the melt
309 fragility (i.e. the derivative of the melt viscosity as a function of T at T_g): the strongest existing melt is
310 SiO_2 , and Al-rich melts have higher fragility, with the most fragile being CaAl_2O_4 in the CAS system
311 (Figure 19). This is also in good agreement with the variation of the C_p^{conf} of SiO_2 and CaAl_2O_4 , which
312 varies between 8.2 to 13.8 J/mol K. This ΔC_p between liquid and glass at T_g can be expressed in term of
313 C_{pl}/C_{pg} ratio as proposed by [Angel \(1991\)](#). This ratio varies between 1.1 for SiO_2 , the strongest melt to
314 1.37 for CaAl_2O_4 , the more fragile melt in Figure 19.

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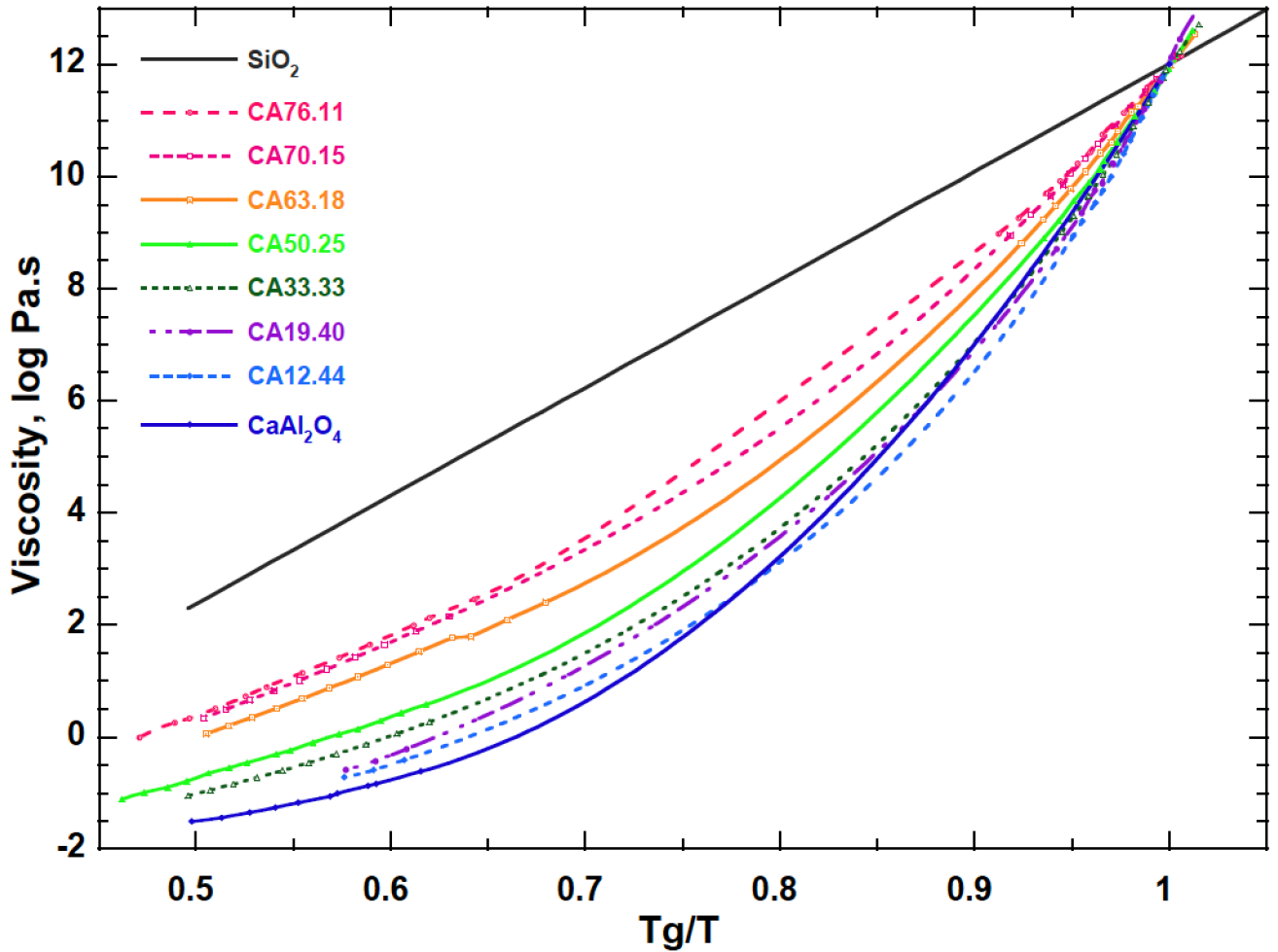
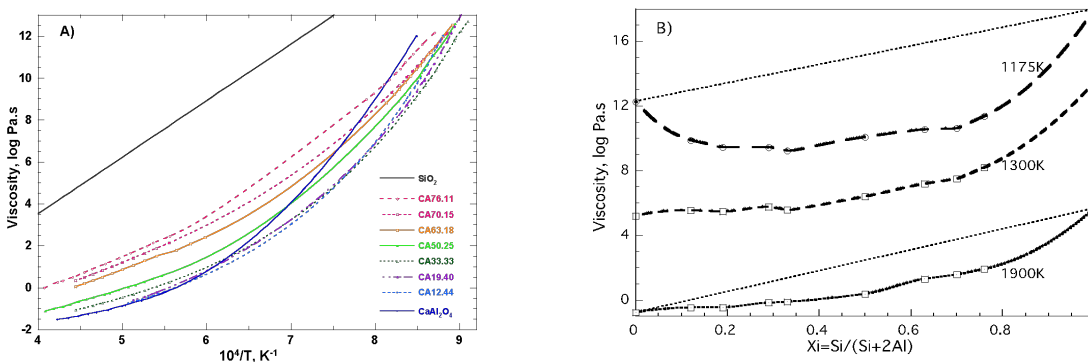


Figure 19: "Angel plot" showing $\log \eta$ versus T_g/T for melts with $R=CaO/Al_2O_3=1$ in the CAS system.

As mentioned previously, the CAS system presents one of the largest glass-forming domains. Indeed, it is possible to quench glasses even without silica, e.g. like the C12A7 composition (CXAY with C=CaO, A=Al₂O₃, X and Y are their relative proportions), using classic quench rates. With increasing quench rates, e.g. via laser levitation heating, it is possible to make glasses between C3A and CA1.5 (from 75 down to 40 mol% CaO). In this condition, the addition of a small amount of SiO₂ in CaO-Al₂O₃ glasses extends the glass forming ability and lowers the melt liquidus temperature. Other macroscopic properties are also markedly changed with silica introduction in CaO-Al₂O₃ melts/glasses, suggesting extensive structural modifications. For instance, an anomalous behavior of T_g is clearly observed at low silica content, with a maximum in T_g visible at ~20 mol% SiO₂ along the Ca₃Al₂O₆-SiO₂ binary (Figure 18B; Higby et al., 1990; Neuville 1992; Neuville et al., 2004; Cormier et al., 2005; Neuville et al., 2010). Note that this anomalous behavior of T_g results from the change in the polymerization of Al which varies between Q^2 to Q^4 species along the join $R=3$ between C3A and CA20.40 glasses (Neuville et al., 2004, Cormier et al., 2001, 2003, 2005).

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To explore further the properties of CAS glass compositions, viscosity along the join $R=1$ (CaAl_2O_4 – SiO_2 binary) is plotted in Figure 20. At high temperatures, viscosity decreases constantly with addition of CaAl_2O_4 (Figure 20B). At supercooled temperatures, near T_g , melt viscosity decreases by ~ 7 orders of magnitude with adding 30 mol% CaAl_2O_4 to silica, then a further addition of 30 mol% CaAl_2O_4 yields a decrease in viscosity of 1 order of magnitude. Between 40 and 0 mol% SiO_2 , melt viscosity increases ~ 5 orders of magnitude. The deviation from a linear variation (Figure 20B) is 4 orders of magnitude at 1175 K, and less than 2 orders of magnitude at 1900 K. It thus decreases with increasing temperature. These changes thus deviate strongly and negatively from a linear variation, particularly at undercooled conditions. Such behavior may originate from mixing between Si and Al in Q^4 units that occurs in such tectosilicate melts (Seifert et al., 1982), this mixing resulting in excess entropy and leading to non-linear, convex variation of the melt viscosity as a function of the $\text{Si}/(\text{Si}+\text{Al})$ ratio (e.g., Neuvillle and Mysen, 1996).



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Figure 20: A) Viscosity of melts between silica and CaAl_2O_4 compositions, CAX.Y mean: $X=\text{SiO}_2$ %, $Y=\text{Al}_2\text{O}_3$, $\text{CaO}=100-(X+Y)$. B) viscosity at constant temperature, 1150, 1200, 1800 K as a function of $X_i=\text{Si}/(\text{Si}+2\text{Al})$. SiO_2 data are from Hetherington et al. (1964) Leko, (1979) and Urbain et al. (1982), CaAl_2O_4 from Urbain (1983), Neuvillle (1992).

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In all others glass systems, alkali or alkaline-earth aluminosilicate, viscosity shows similar behavior along the join $R=1$, an important decrease between 100 and 70% of SiO_2 , and for lower silica content, a smaller decrease of the viscosity (Alkaline see Le Losq et al., 2017, Mg, Neuvillle 1992, Sr, Novikov et al 2017, Ba, Novikov 2017).

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As already mentioned, the configurational heat capacity, C_p^{conf} , is required in order to determine the configurational entropy, $S^{\text{conf}}(T)$, from equations (6) and (7). In the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, the

359 configurational heat capacity can be determined from the difference between the heat capacity of the melt
 360 at T and that of the glass at T_g (equation 8). Several models exist, like those of Richet (1987) and Richet
 361 and Bottinga (1985), and allow one to calculate the configurational heat capacity with precision. The
 362 more recent works of Courtial (1993) and Richet and Neuville (1992) allow refining the heat capacity
 363 modelling in the CaO-Al₂O₃-SiO₂ system, with using the following partial molar heat capacity equations
 364 (J mol⁻¹ K⁻¹) for the glass and liquid (the estimated uncertainties is about 1% for the partial molar heat
 365 capacities following Courtial and Richet, 1993):

$$366 \quad C_{pg \text{ SiO}_2} = 127.2 - 0.010777T - 431270/T^2 - 1463.9/T^{0.5}, \quad (25)$$

$$367 \quad C_{pg \text{ Al}_2\text{O}_3} = 175.46 - 0.005839T - 1347000/T^2 - 1370/T^{0.5}, \quad (26)$$

$$368 \quad C_{pg \text{ CaO}} = 39.159 + 0.01865T - 152300/T^2, \quad (27)$$

$$369 \quad C_{pl \text{ SiO}_2} = 81.37, \quad (28)$$

$$370 \quad C_{pl \text{ Al}_2\text{O}_3} = 85.78 - 130.216T, \quad (29)$$

$$371 \quad C_{pl \text{ CaO}} = 86.05. \quad (30)$$

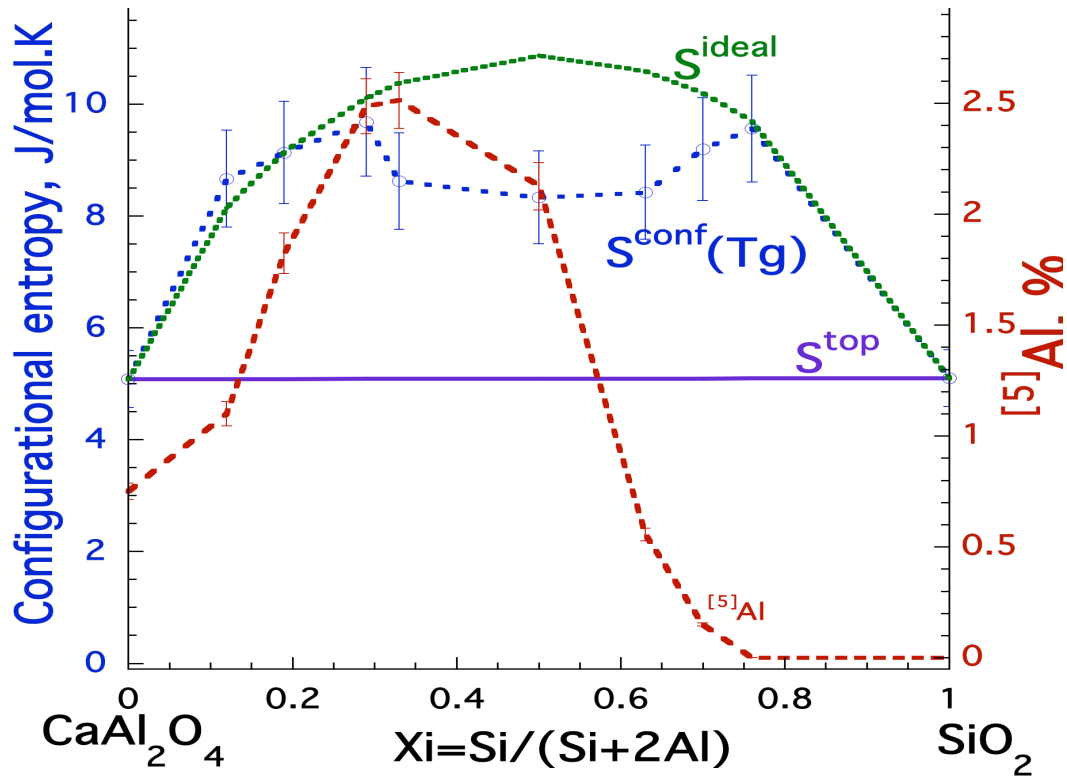
372

373 With these partial molar heat capacity terms, $C_p^{conf}(T_g)$ can be calculated easily and used for the
 374 calculation of $S^{conf}(T_g)$, which are plotted in Figure 21. It is clearly visible that $S^{conf}(T_g)$ of silica glass is
 375 almost the same than that of CaAl₂O₄, CA glass. Assuming that $S^{conf}(T_g)$ can be decomposed into
 376 topological and excess terms, we can model the observed variations as

$$377 \quad S^{topo} = X_{\text{SiO}_2} S^{conf}(T_g)_{\text{SiO}_2} + (1 - X_{\text{SiO}_2}) S^{conf}(T_g)_{\text{CaAl}_2\text{O}_4}, \quad (31)$$

378 S^{topo} is thus assumed to vary linearly between the two end-members SiO₂ and CaAl₂O₄ glasses. This
 379 term S^{topo} , is independent of temperature and corresponds to a simple mechanical mixing between two
 380 entities. The term S^{ideal} , defined in equation 10, can be taken as equal to the entropy obtained from an
 381 ideal random mixing of two species, in this case Si and Al. At high or low concentration of silica, $S^{conf}(T_g)$
 382 variations seem to follow the ones predicted assuming such an ideal mixing between Si and Al. This
 383 suggests that CaAl₂O₄ randomly replace Si₂O₄ in the melt/glass structure. However, between 33 and 75
 384 percent of silica, $S^{conf}(T_g)$ variations depart from the predictions of this ideal mixing model. In this silica
 385 concentration range, a decrease of ~25 % in $S^{conf}(T_g)$ is observed, and there is a maximum difference of
 386 ~2.5 J mol⁻¹ K⁻¹ between $S^{conf}(T_g)$ values and the ideal model at around 50 mol% SiO₂ (Figure 21).

387



388

389 *Figure 21: Configurational entropy at the glass transition temperature, $S^{conf}(T_g)$ (Neuville, 1992), and*
 390 *real proportion of $^{[5]}Al$ in mole percent in glasses along the SiO_2 - $CaAl_2O_4$ binary (Neuville et al., 2004,*
 391 *2004). Each $S^{conf}(T_g)$ value was calculated from the viscosity data obtained for each composition.*

392

393 The observed $S^{conf}(T_g)$ variations (Figure 21) suggest that :

394

-i) at low or high silica concentrations, Si and $^{[4]}Al$ mix almost randomly in the melt/glass structure,

395

-ii) a deviation from ideal mixing exists at intermediate silica contents. The latter deviation can be

396

rationalized upon considering that Al in five-fold coordination represents around 2,5 % of total Al in the

397

CA50.25 glass.

398

Excess $^{[5]}Al$ tends to decrease $S^{conf}(T_g)$ and in parallel increase the glass transition temperature, as

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shown by Le Losq et al. (2014) in the Na_2O - Al_2O_3 - SiO_2 system. A similar effect is potentially observed

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here, with the presence of $^{[5]}Al$ possibly producing a decrease in $S^{conf}(T_g)$ and also an increase in T_g

401

because $^{[5]}Al$ and $^{[4]}Si$ do not interact and do not mix randomly. One should be careful with extrapolating

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such behavior because it is only valid close to the glass transition. Indeed, at high temperatures (close or

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above the liquidus), Neuville et al (2008b) proposed that $^{[5]}Al$ plays a role similar to $^{[5]}Si$, a transient

404

species ensuring the exchange of O atoms during viscous flow according to Stebbins (1991). Similarly,

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in polymerized aluminosilicate networks, we can infer that five-fold coordinated network formers (Si or

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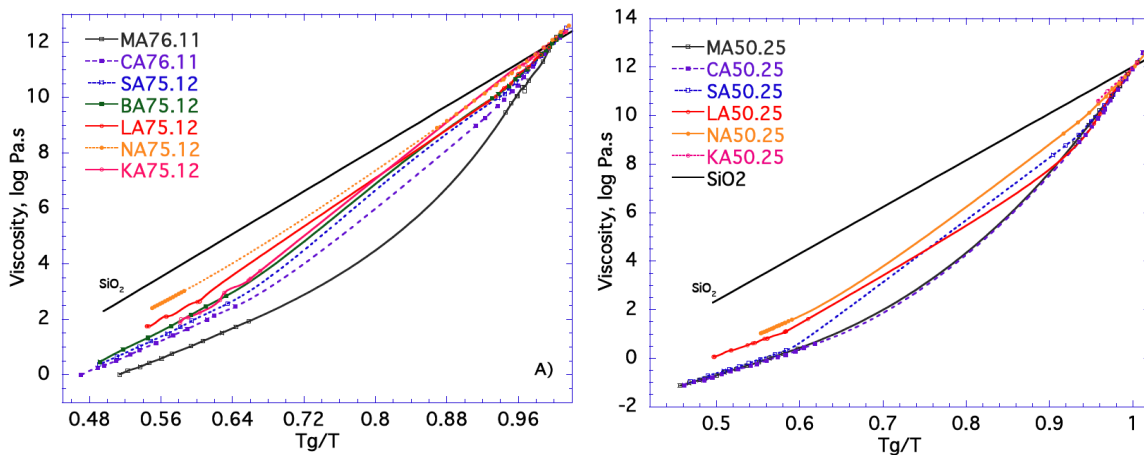
Al) ensure cationic mobility at high temperature. In depolymerized networks, Q^1 , Q^2 and Q^3 units ensure

407 network mobility (Stebbins, 1991; Farnan and Stebbins, 1990, 1994; Neuville et al., 2008b, Le Losq et
 408 al., 2014). Such assumptions agree well with the data near the C3A domain (see section 4). From Figure
 409 21, it is further possible to make the assumption that ^{51}Al plays a different role in silica-rich or alumina-
 410 rich glasses and melts. Indeed, in silica-rich networks (>60 mol% SiO_2), ^{51}Al increases network
 411 connectivity and this results in a decrease in $S^{conf}(T_g)$. In an aluminate-rich network, a few percent of ^{51}Al
 412 plays a role similar to ^{41}Al , which exchanges randomly with Si.

413
 414 Other systems show behaviors along the tectosilicate join similar to that previously presented for
 415 $\text{CaAl}_2\text{O}_4\text{-Si}_2\text{O}_4$. In particular, Raman spectra along all tectosilicate joints in the LAS, NAS, KAS, MAS,
 416 SAS, BAS systems show similar variations. They all present a linear decrease in the frequency of the
 417 bands assigned to T-O symmetric and asymmetric stretching of Q^4 units with decreasing SiO_2
 418 concentration. This correlates very well with increasing ^{27}Al NMR chemical shifts with decreasing silica
 419 content in tectosilicate glasses (see Figure 12 previous chapter, Drewitt et al., 2021). Those Raman and
 420 NMR variations arise from the variation of the T-O distance between Si-O and Al-O, as the Si-O distance
 421 is shorter than the Al-O distance.

422
 423 In the Figure 22, the viscosities of tectosilicate melts with 75 and 50 mol % silica are plotted as a
 424 function of T_g/T . The strongest glass in the Angell plot corresponds to the SiO_2 composition, and the
 425 more fragile the composition, the greater the curvature. The fragility of melts decreases from Mg, Ca, Sr
 426 to Ba for the alkaline-earth elements. Alkali tectosilicate compositions show similar fragilities at 50 mol
 427 % silica (Figure 22B). At 75 mol % (Figure 22A), Li and K tectosilicate compositions also present a
 428 similar fragility while the Na-tectosilicate composition is the strongest one.

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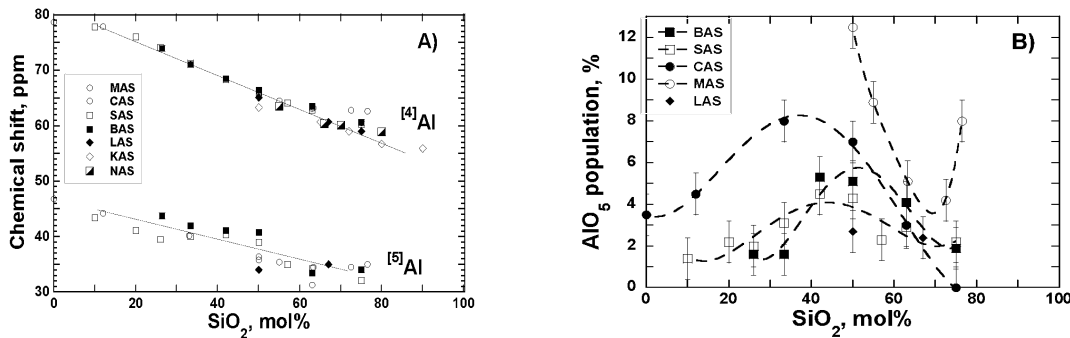


430
 431 *Figure 22: Viscosity of MAX.Y melts versus T_g/T , with $M = \text{Li}_2, \text{Na}_2, \text{K}_2, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$. $X = \text{SiO}_2$,*
 432 *$Y = \text{Al}_2\text{O}_3$, and $MO=100-(\text{SiO}_2+\text{Al}_2\text{O}_3)$ in mole%, A) for 75 mole % of SiO_2 , and B for 50 mole % of*

433 SiO_2 . (data are from *Le Losq, 2012 for LAS, Le Losq et al., 2017, for NAS and KAS, Neuville 1991 for*
 434 *CAS and MAS, Novikov et al.2017, for SAS, and Novikov, 2018 for BAS).*

435
 436 *3.5 From the CAS system to other chemical systems*

437 For tectosilicate glasses and melts, the structure seems to present a random distribution and random
 438 substitution between SiO_4^{4-} and AlO_4^{5-} units, in violation of the Loewenstein's aluminum avoidance
 439 principle (*Loewenstein, 1954*). The Si/Al substitution is clearly confirmed by the linear variation of the
 440 chemical shift of the ^{27}Al NMR and of the frequency of the Raman band in the $800 - 1200\text{cm}^{-1}$ domain.
 441 We can propose that alkali or alkaline-earth elements are in the free-volumes of the $\text{Al}_x\text{-Si}_{(1-x)}\text{O}_2$ network,
 442 ensuring the charge compensation of AlO_4^{5-} units. The Figure 23 shows the proportion of $^{[5]}\text{Al}$ in
 443 tectosilicate glasses versus SiO_2 content. The proportion of $^{[5]}\text{Al}$ is a maximum in the middle of the
 444 ternary system, in the peraluminous domain for all ternary systems MAS (with $\text{S}=\text{SiO}_2$, $\text{A}=\text{Al}_2\text{O}_3$,
 445 $\text{M}=\text{Li}_2\text{O}$, Na_2O , K_2O , MgO , CaO , SrO , BaO), and increases with the decrease of z/r^2 (*Lee and Stebbins,*
 446 *1999, 2000, Allward et al, 2003, 2007, Stebbins, 2008, 2016; Stebbins and Farnan, 1992; Stebbins et al.,*
 447 *1999; Neuville et al., 2004, 2006, 2008, 2010, Le Losq et al., 2017, Lee et al., 2016; Novikov et al., 2017,*
 448 *Stebbins et al., 2008, Lee et al., 2009, Hiet et al., 2009, Alu et al., 2018*). In the NAS and KAS system,
 449 $^{[5]}\text{Al}$ is not detected in tectosilicate compositions, and it is only present in peraluminous domain
 450 (*Allwardt, et al., 2003; Le Losq et al., 2014*).



451
 452 *Figure 23: A) NMR chemical shift of $^{[4]}\text{Al}$ and $^{[5]}\text{Al}$ and B) proportion of $^{[5]}\text{Al}$ in LAS, MAS, CAS,*
 453 *SAS, BAS system along the join $R=1$, the tectosilicate join (note that there is not $^{[5]}\text{Al}$ in Na and K*
 454 *tectosilicate glasses). Data from *Le Losq (2012), Neuville et al., (2008, 2006), Novikov et al., (2017),*
 455 *Novikov, (2017)*. Error bar are smaller than symbol size.*

456
 457 In tectosilicate glasses, the NMR chemical shifts of $^{[5]}\text{Al}$ and $^{[4]}\text{Al}$ decrease linearly with the silica
 458 content (*Figure 23A*), due to an increase in the mean T-O-T inter-tetrahedral angle as Al substitutes for
 459 Si in tetrahedral units (*Stebbins and Farnan, 1992; Neuville et al., 2006, 2008*). At a given silica content,

460 small variations in the ^{27}Al NMR chemical shift are observed, and correlate with the electronegativity
461 and size of the first-neighbor metal cations in the glass structure. These variations arise from small
462 changes in the Si/Al distribution and in the mean inter-tetrahedral T-O-T angle as the metal cation field
463 strength and property changes.

464
465 In peralkaline glasses, the degree of polymerization plays a small role on the ^{41}Al environment. Mysen
466 et al. (2003) showed that, in sodium aluminosilicates, Al remains mostly in Q^4 units. Using Raman and
467 viscosity data, Le Losq et al. (2014) corroborated such a view for this system. Other studies suggest that
468 this remains true probably in most aluminosilicate compositions at silica contents higher than 40 mol%
469 (Neuvill et al., 2004b, 2008, Novikov et al., 2017); a strong preference of ^{41}Al for the most polymerized
470 structural units is expected according to experimental (Mysen et al., 1981; Cormier et al., 2000; 2005,
471 Neuvill et al., 2004b, 2008, Novikov et al., 2017) and numerical studies (Cormier et al., 2003, Cormier
472 2019).

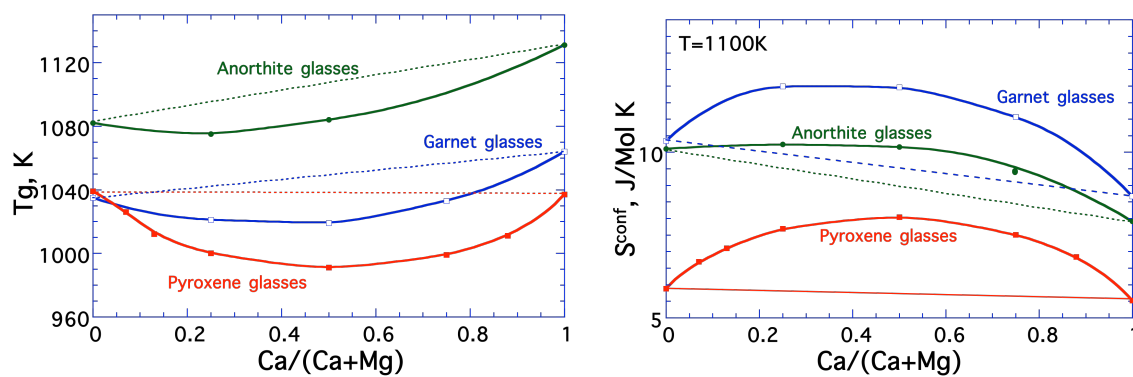
474 *3.6 Alkaline-earth mixing in aluminosilicate glasses and melts*

475 The substitution of one alkaline-earth element by another has little affect on glass Raman spectra
476 (Merzbacher and White, 1991, Neuvill et al. 2008b). The Si/Al substitution actually has a greater
477 influence on the aluminosilicate network than the alkaline-earth element substitution (see also chapter 3,
478 this volume). In the case of Ca-Mg aluminosilicates, this agrees with an ideal mixing of Ca and Mg in
479 aluminosilicates as inferred from macroscopic viscosity measurements (Neuvill and Richet, 1991). This
480 random distribution was confirmed by ^{17}O NMR data, which show that NBOs, are equally associated
481 with Mg or Ca cations (Farnan and Stebbins, 1990, 1994; Allwardt and Stebbins, 2004). However, the
482 network is more perturbed by the presence of Mg than by Ca because of the higher ionic field strength
483 of Mg (Navrotsky et al., 1982; Roy and Navrotsky, 1985) and the Ca/Mg coordination number should
484 play an important role. The coordination number of Mg is well characterized (Kroeker and Stebbins,
485 2000, Trcera et al. 2009, Fiske and Stebbins, 1994): it is 4 in silicate glasses, and increases up to 5-6 in
486 aluminosilicate glasses, in agreement with glass molar volumes variations (Figure 15). Turning to Ca, in
487 silicate glasses it is mainly located in distorted sites with 6-7 oxygen neighbors (Cormier et al., 2003,
488 Neuvill et al., 2004b, 2008, Cicconi et al., 2016). Its CN increases with substitution by Al as shown by
489 the variation of the molar volume between CaSiO_3 and Al_2SiO_5 glasses (Figure 17). At high Al_2O_3
490 content ($R \geq 1$), in Ca/Mg aluminosilicate glasses, Ca is in 7-8 fold coordination (Shimoda et al., 2007a)
491 whereas Mg is in 6-fold coordination (Shimoda et al., 2007b, Trcera et al. 2009), as corroborated by data
492 like molar volume, X-ray diffraction spectra, XANES spectra at the Ca and Mg K-edge, and ^{43}Ca and
493 ^{25}Mg NMR experiments (Kroeker and Stebbins, 2000, Trcera et al. 2009, Fiske and Stebbins, 1994).

494 The above discussion raises a paradox: Ca and Mg always have different coordination numbers but
495 seem to mix randomly in silicate and aluminosilicate melts and glasses. First, this may highlight the
496 difficulty determining alkali or alkaline-earth environments that are loosely held in large sites with fairly
497 irregular coordination (Cormier and Neuvill, 2004, Neuvill et al., 2008). Nevertheless, there is a
498 general consensus for lower coordination for Mg than Ca. The low Mg coordination number and the
499 possibility to have MgO₄ tetrahedra in Mg-silicate glass suggest that Mg will not be available for charge
500 compensation of Al in tetrahedral position. Alternatively, its small size favors its localization in network
501 tetrahedral cavities, yielding important distortions of the aluminosilicate network to accommodate such
502 Mg coordination, which could result in the formation of highly-coordinated Al. This interpretation might
503 justify the modifier role played by Mg despite their low coordination (Shimoda et al., 2007b, Guignard
504 and Cormier, 2008, Trcera et al. 2009), in agreement with recent NMR data suggesting that substitution
505 of Na by Mg in aluminosilicates in glass promotes melt depolymerisation (Sreenivasan et al. 2020).
506 Similar observations can be made regarding the role of Zn in silicate or aluminosilicate glasses (Novikov,
507 2017). The fact that the viscosities of the Mg or Zn glass compositions are lower than that of Ca glass
508 compositions for the same amount of SiO₂, confirms the role of network modifier of Mg and Zn while
509 they are preferably in 4-fold coordination. (Neuvill, 1992; Neuvill and Richet, 1991; Toplis and
510 Dingwell, 2004, Neuvill et al., 2008).

511
512 In mixed CMAS glasses, Raman, NMR and neutron diffraction data (Allwardt and Stebbins, 2004,
513 Allwardt et al., 2003, Lee et al., 2003, Lee and Stebbins, 2003; Neuvill et al., 2006, 2008, Guignard and
514 Cormier, 2008; Cormier and Coello, 2013, Cormier 2019) are in good agreement with random mixing
515 between Ca and Mg in the melt structure, as initially proposed by Neuvill and Richet (1991). This
516 implies that intermediate CMAS melts can be considered as being derived from the random mixing of
517 their CAS and MAS end-members, e.g. Ca₃Al₂Si₃O₁₂ - Mg₃Al₂Si₃O₁₂ for garnet-like glasses and
518 CaAlSi₂O₈ - MgAlSi₂O₈ for anorthite-like compositions. An interesting observation is that Ca/Mg mixing
519 shows a random distribution and the network polymerization is not really affected by the Ca/Mg
520 substitution, but the proportion of ⁵¹Al increases with the Ca/Mg substitution (Neuvill et al., 2008b).

521
522



523

524 *Figure 24: A) glass transition temperature and B) configurational entropy at 1100 K upon Ca/Mg*
 525 *mixing in pyroxene ($CaSiO_3$ - $MgSiO_3$), garnet ($Ca_3Al_2Si_3O_{12}$ - $Mg_3Al_2Si_3O_{12}$) and anorthite ($CaAl_2Si_2O_8$ -*
 526 *$MgAl_2Si_2O_8$) glass compositions, with respectively 0, 12.3 and 25.0 mol% Al_2O_3 . Data for pyroxene and*
 527 *garnet glasses are from Neuville and Richet (1991) and original data for anorthite glasses.*

528

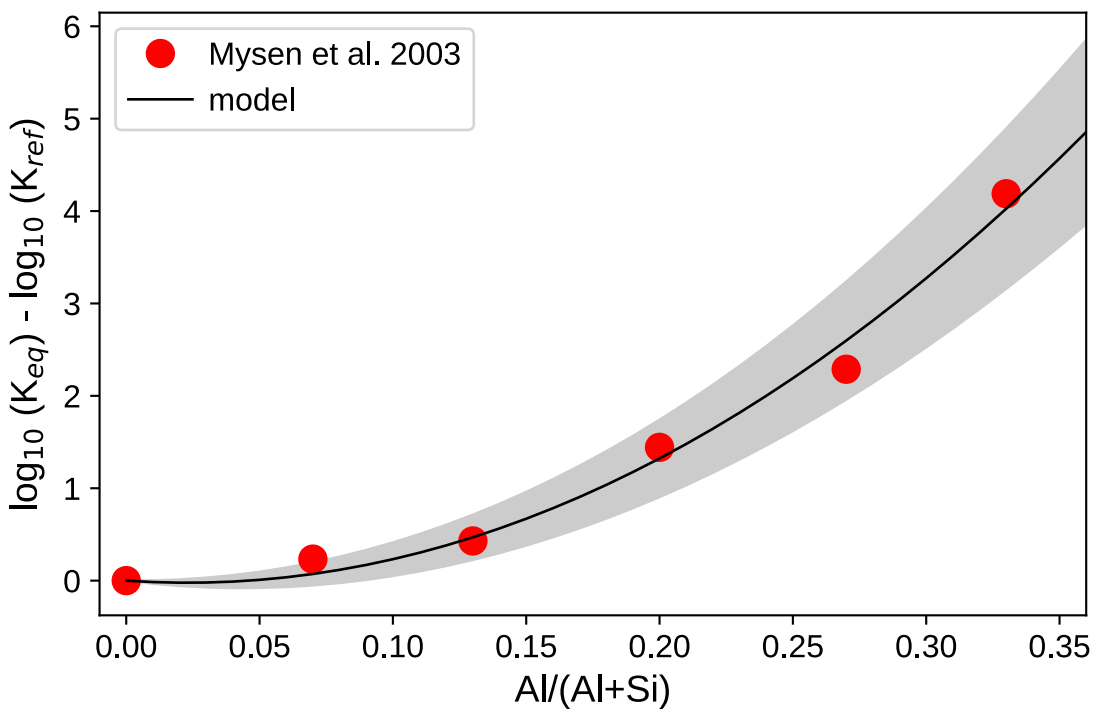
529 Unfortunately, knowledge regarding the mixing between Sr/Ca, Ba/Mg or more generally between an
 530 alkali with an alkaline-earth element in aluminosilicate compositions remain scarce, and it is not possible
 531 to propose a general conclusion. It is possible to say that Si and Al are almost randomly distributed in
 532 tectosilicate glass compositions, and metal cations are located in cavities of the 3D polyhedral network
 533 and ensure the charge compensation of the AlO_4^{5-} tetrahedra. This assumption is in good agreement with
 534 the linear variation of the $T-O$ distances from 1.66 up to 1.76 Å between SiO_2 and $CaAl_2O_4$ glasses
 535 (Figure 13b, chapter 3, this issue). The $T-O$ distances are also well correlated with the linear variation of
 536 the NMR chemical shift of ^{27}Al and the linear variation of the frequency of the Q^f species along the
 537 tectosilicate joint (compiled in Figure 13a,b chapter 3, this issue). They may mix randomly like Ca and
 538 Mg, but a non-random distribution with increasing network segregation has also been reported in alkali
 539 tectosilicate melts (Le Losq et al., 2017). This highlights the complexity of the structure of
 540 aluminosilicate melts and glasses, a problem when considering the modelling of their properties. Other
 541 problems are the presence of excess NBOs, $[^5]Al$ and tri-coordinated oxygens (Stebbins and Xu, 1997,
 542 Le Losq et al. 2014). For instance, the presence of $[^5]Al$ can be important, reaching concentrations up to
 543 12% of the Al_2O_3 in the middle of the MAS ternary system, and the presence of $[^5]Al$ results in increasing
 544 the glass transition temperature and decreasing configurational entropy. Metal cations could be located
 545 in cavities of the 3D polyhedral network, in a manner consistent with the Compensated Continuous
 546 Random Network model (Greaves and Ngai, 1995; Greaves and Sen, 2007; Le Losq et al., 2017); they
 547 ensure the charge compensation of the AlO_4^{5-} tetrahedra. In the potassium aluminosilicate ternary, a non-
 548 random distribution of Si and Al between framework units may be accompanied by an increasing
 549 segregation of metal cations in clusters or channels. This has been proposed to explain the variations in

550 the structure and properties of potassium tectosilicate melts, for instance (Le Losq and Neuville, 2013;
 551 Le Losq et al., 2017). This is a problem when considering the modelling of their properties, and a large
 552 number of approximation may be necessary as we shall see in the later section.

553

554 3.7 Models for alkali aluminosilicate melts

555 The above sections allow us to have a glimpse into the complexity of aluminosilicate melts. Even
 556 leaving aside the potential effects of parameters like $^{[5]}Al$, there is no data for the distribution of Q^n
 557 species in aluminosilicate melts because ^{29}Si NMR spectroscopy loses resolution with aluminosilicate
 558 compositions due to Si-Al interactions resulting in significant signal broadening and increased
 559 complexity of the peaks. Mysen et al. (2003) quantified the fractions of the different Q^n species in Na
 560 aluminosilicate glasses by modelling the ^{29}Si NMR data. Their findings allow us to constrain the K_{eq}
 561 value for the dissociation $2 Q^3 = Q^2 + Q^4$ in sodium aluminosilicate glasses (Figure 25). We observe that
 562 Al introduction into the glass network promotes the dissociation of Q^3 units.



563

564 *Figure 25: Relative value of the equilibrium constant K_{eq} of the reaction $2 Q^3 = Q^2 + Q^4$ obtained*
 565 *from Q^n data in Na aluminosilicate melts calculated by Mysen et al. (2003), reported as a function of the*
 566 *$Al/(Al+Si)$ ratio of glasses. K_{ref} is the value of K_{eq} in the glass without Al. The black line represents a*
 567 *polynomial modelling of the data, and the grey areas are the two-sigma confidence interval of the model*
 568 *predictions. Using this model, it is possible to estimate the Q^n distribution in alkali aluminosilicate*
 569 *glasses, but one must note that such relation remains unknown for other elements like K, Ca or Mg.*

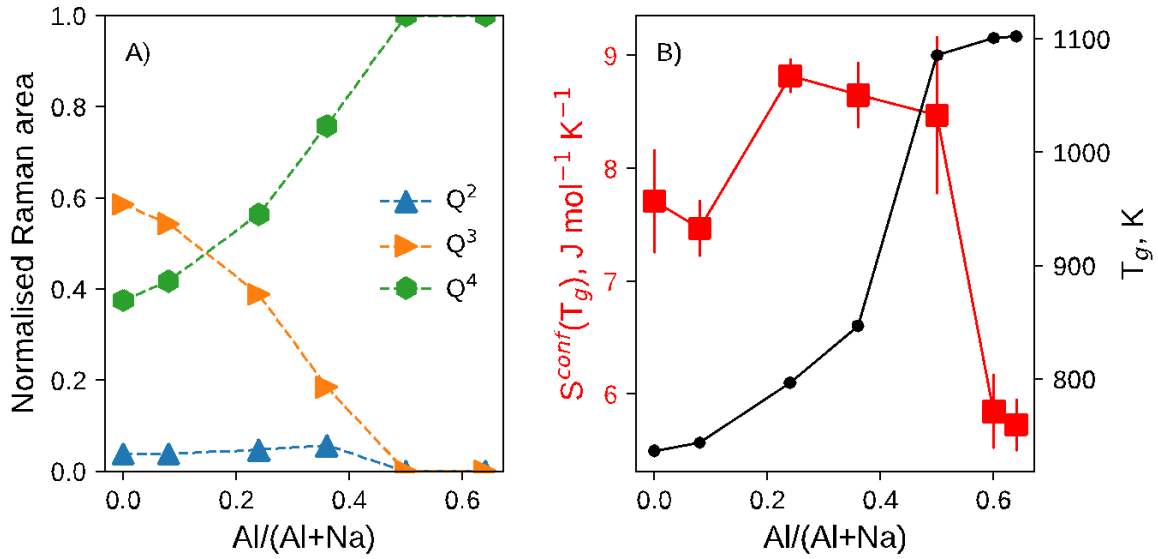
570

571 This result is the only experimental one to the knowledge of authors that could be used to model the
572 Q^n distribution in aluminosilicates based on the principle of using partial K_{eq} values as highlighted in
573 section 2.5. Other models (Doweidar, 1999 for example), like the associate solution one, are purely
574 theoretical and remain unconstrained by experimental data, as they are not available. This does not
575 prevent one from building models of glass and melt properties. For instance, Doweidar (1999) simply
576 used a binary model for calculating the density of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses from partial molar values of
577 different Na- Q^n units. The structural model employed there is clearly not appropriate, but interestingly,
578 this does not prevent a good prediction of glass densities. A better attempt to link melt composition,
579 structure and viscosity is that of Starodub et al. (2019), who calculated the Q^n distribution in $\text{Na}_2\text{O}-\text{K}_2\text{O}-$
580 $\text{Al}_2\text{O}_3-\text{SiO}_2$ melts from an associate solution model, and then linked the fractions of Q^n units and the
581 concentrations of cations to the parameters of the Avramov-Milchev equation for calculation of melt
582 viscosity. This is an interesting model, but it suffers from two problems. First, they did not select the
583 viscosity data used for fitting their model, as they used the large SciGlass database, and the results of
584 their model will thus suffer from the propagation of large errors affecting some experimental data.
585 Secondly, the Avramov-Milchev (Avramov and Milchev, 1988) equation works well but it is less
586 attractive than the Adam-Gibbs theory because it does not allow one to link the chemical, structural,
587 thermodynamic and dynamic dimension of the problem.

588

589 An extension of the model presented in section 2.5 could allow one to circumvent such caveats. We
590 will explore if such a model is possible to implement below for the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. A
591 first step would be to combine the silicate structural model (section 2.5) to the relationship presented in
592 Figure 25. This will allow one to approximate the Q^n speciation in aluminosilicate glasses. Then, we need
593 to know the effects of Na-K mixing in aluminosilicate melts and of Al concentration on the glass
594 configurational entropy. Combining viscosity and Raman data with thermodynamic calculations, Le
595 Losq et al. (2014) have shown that Al introduction in NaSi_2O_7 yields a rapid network polymerisation
596 (Figure 26A) that is accompanied by a jump in glass configurational entropy and an increase in glass T_g
597 (Figure 26B). At $\text{Al}/(\text{Al}+\text{Na})$ higher than 0.5, we see a continuous decrease in $S^{conf}(T_g)$ that is
598 accompanied by increasing T_g .

599



600

601 *Figure 26: A) Fractions of the Q^n units Raman signal, and B) entropy and glass transition temperature*
 602 *of Na aluminosilicate glasses with 75 mol% SiO_2 but varying $Al/(Al+Na)$ ratios. Data from Le Losq et*
 603 *al. (2014).*

604

605 Variations in $S^{conf}(T_g)$ are thus complex functions of the melt $Al/(Al+M)$ ratio. As an approximation,
 606 one could assume that Al and Si mix randomly in Q^4 units in the silicate network, as proposed for Na
 607 tectosilicate melts by Neuville and Mysen (1996). Note that it is important to remember that unlike the
 608 Ca or Mg aluminosilicate system, the ternary system $Na_2O-Al_2O_3-SiO_2$ does not contain Al in 5-fold
 609 coordination except in the peraluminous domain (Lee et al., 2003, Le Losq et al., 2014). This hypothesis
 610 implies that the Lowenstein Al-O-Al avoidance rule will not be respected, and is thus in contradiction
 611 with the interpretation of NMR data of Na aluminosilicate glasses (Lee and Stebbins, 1999, Lee et al.,
 612 2003). However, this hypothesis allows reproduction of the variations in configurational entropy
 613 observed when Al substitutes Si in Na aluminosilicate melts (Neuville and Mysen, 1996; Le Losq, 2012).
 614 One may thus consider it as adequate for the aim of building a model of configurational entropy
 615 variations. An additional point is to consider that Q^4_{Al} charged-balanced by Na ($Q^4_{Al,Naenv}$) or K ($Q^4_{Al,Kenv}$)
 616 probably present different partial configurational entropies (respectively $S^{conf}_{Q^4_{Al,Naenv}}$ and $S^{conf}_{Q^4_{Al,Kenv}}$). S^{topo}
 617 (eq. 16) could then be written as:

618

$$\begin{aligned}
 619 \quad S^{topo} = & \sum_{n=2}^3 x_{Q^n_{Si,Naenv}} S^{conf}_{Q^n_{Si,Naenv}} + \sum_{n=2}^3 x_{Q^n_{Si,Kenv}} S^{conf}_{Q^n_{Si,Kenv}} + x_{Q^4_{Si}} S^{conf}_{Q^4_{Si}} + \\
 620 \quad & x_{Q^4_{Al,Naenv}} S^{conf}_{Q^4_{Al,Naenv}} + x_{Q^4_{Al,Kenv}} S^{conf}_{Q^4_{Al,Kenv}}. \quad (32)
 \end{aligned}$$

621

622 From this equation, we need to discriminate the fraction of charge-compensator and network modifiers
623 (Na, K), in order to calculate the variation in the fractions of the Q^n units. This could be done easily
624 assuming that the fractions of charge-compensator and network modifiers Na and K are just equal to the
625 weighted average fractions of Na and K. This assumes no preference of Na and K to specific
626 environments, an hypothesis that surely could be challenged.

627
628 We see that many hypotheses have been already proposed in order to start building a model to express
629 $S^{conf}(T_g)$. This is without even considering the calculation of any entropy resulting from cationic mixing,
630 S^{mix} . The picture becomes even more complex at this point. Indeed, while variations of $S^{conf}(T_g)$ upon
631 mixing Na and K in silicate melts can be explained by a random mixing of those cations (Richet, 1984;
632 see section 2.4, eq. 18): mixing Na and K in the presence of Al results in a different behaviour. Entropy
633 variations upon mixing Na and K in tectosilicate melts (R=1) are far from ideal (Le Losq and Neuville,
634 2013). Viscosity, Raman, NMR and molecular dynamic simulation data all indicate that Na and K
635 actually are present in different environments in tectosilicate melts (Le Losq et al., 2017), with K tending
636 to be present in large percolation channels in the polyhedral Al-Si network. This was recently challenged
637 by a new analysis of viscosity data along the SiO_2 -(Na,K)AlO₂ binary by Robert et al. (2019). Those
638 authors fitted viscosity data of mixed Na-K tectosilicate melts, leaving the A_e parameter (eq. 6) free. This
639 yields results where it is possible to fit viscosity upon Na-K mixing in tectosilicate melts assuming a
640 random Na-K distribution, like in silicate melts. In such cases, most of the variations in viscosity seemed
641 to be explained by variations in A_e . While this is an interesting take on this problem, this is probably not
642 a good representation of the reality. Indeed, many authors demonstrated that the pre-exponential term in
643 viscosity equations converge to a singular value (Persikov, 1991; Giordano and Dingwell, 2003,
644 Giordano et al., 2008, Giordano and Russell 2018). The A_e parameter is unlikely to vary largely in
645 aluminosilicate melts (e.g. Russell and Giordano, 2005, 2017 and references therein). It thus seems
646 improbable that A_e varies largely upon substitution of Na by K at fixed SiO_2 and Al_2O_3 contents. Raman
647 spectroscopy data and molecular dynamic simulations (Le Losq and Neuville, 2013; Le Losq et al., 2017,
648 Le Losq et al., 2019) further indicate that Na tectosilicate and K tectosilicate melts do not have the same
649 structure, such that Na and K do not mix randomly in such systems. The mixing of Na- and K-
650 tectosilicates thus appears to be of a mechanical mixing, and should accordingly yield a pseudo-linear
651 variation of $S^{conf}(T_g)$. This agrees with conclusions from Le Losq and Neuville (2013) as well as Le Losq
652 et al. (2017), which report pseudo-linear variations in $S^{conf}(T_g)$ upon Na-K mixing.

653
654 Considering that mixing Na and K compensators does not affect entropy, we need to consider
655 three sources for the calculation of S^{mix} : (i) the ideal mixing of Si between different Q^n units, (ii) the

656 ideal mixing of Si and Al in Q^4 units and (iii) the ideal mixing of Na and K network modifiers. We thus
 657 have:

$$658 \quad S_{Si-Al}^{mix} = -2 \frac{x_{Si \in Q^4} + x_{Al}}{x_o} R \left[\frac{Al}{Al+Si} \log \frac{Al}{Al+Si} + \left(1 - \frac{Al}{Al+Si}\right) \log \left(1 - \frac{Al}{Al+Si}\right) \right], \quad (33)$$

660 with $x_{Si \in Q^4}$ the mole fraction of Si in Q^4 units,

$$661 \quad S_{Si}^{mix} = \frac{-x_{Si}}{x_o} * 2 * R * \sum_{n=2}^4 x_{Q_{Si}^n} \log(x_{Q_{Si}^n}), \quad (34)$$

662 and assuming a distribution of Na and K as charge-compensator and network modifier that varies
 663 linearly with Al/(Al+M), we finally have

$$664 \quad S_{Na-K modifiers}^{mix} = MODS \times \left[-2R \frac{x_{Na} + x_K}{x_o} (X_K \log(X_K) + (1 - X_K) \log(1 - X_K)) \right], \quad (35)$$

665 with MODS the fraction of modifiers contributing to S^{mix} ; MODS is equal to $(1 - Al/(Na+K))$ for $Al <$
 666 $(Na+K)$, and is equal to 0 for $Al \geq (Na+K)$.

667 The sum of equations 32 to 35 allows the calculation of $S^{conf}(T_g)$. B_e can be calculated following a
 668 similar logic to that used for silicate melts (section 2.5):

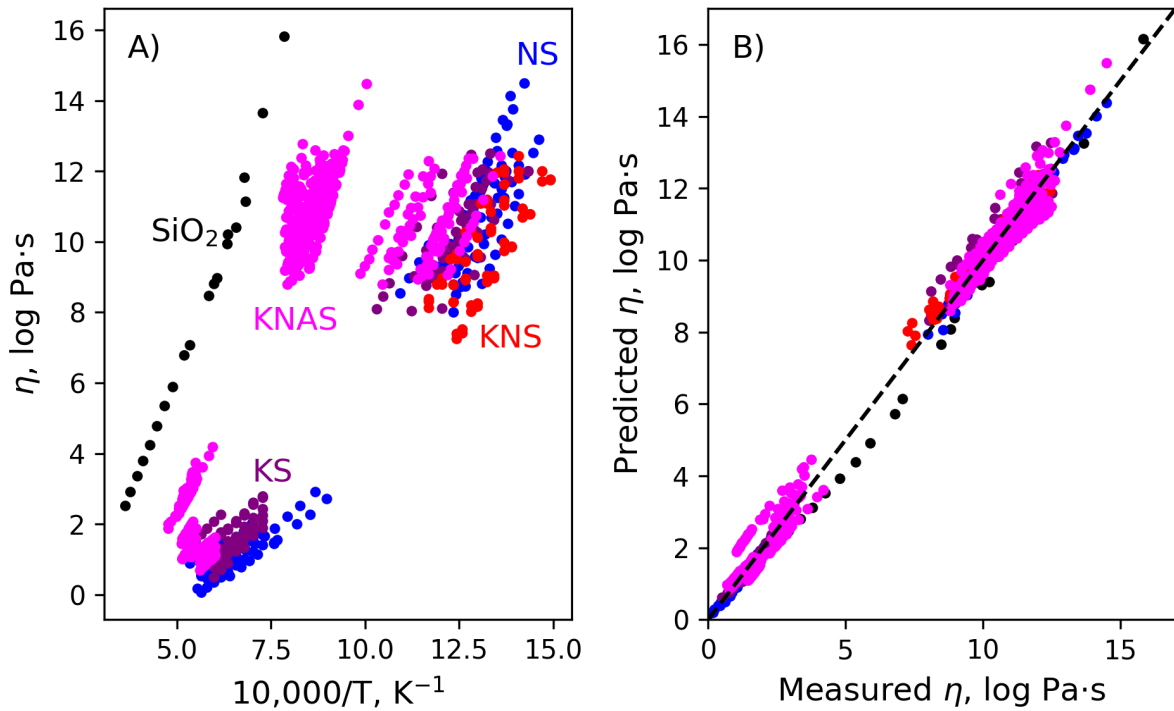
$$669 \quad B_e = \sum_{n=2}^3 x_{Q_{Si,Naenv}^n} B_{e Q_{Si,Naenv}^n} + \sum_{n=2}^3 x_{Q_{Si,Kenv}^n} B_{e Q_{Si,Kenv}^n} + x_{Q_{Si}^4} B_{e Q_{Si}^4} +$$

$$670 \quad x_{Q_{Al,Naenv}^4} B_{e Q_{Al,Naenv}^4} + x_{Q_{Al,Kenv}^4} B_{e Q_{Al,Kenv}^4} + K_1 S_{Si}^{mix} + K_2 S_{Na-K modifiers}^{mix} + K_3 S_{Si-Al}^{mix}, \quad (36)$$

671 with K_1 , K_2 and K_3 being proportionality constants accounting for the influence of the intrinsic entropy
 672 in B_e (section 2.4; Le Losq and Neuville, 2017). A_e is left as a common parameter.

673 Using the equations described above, and selecting viscosity data from the literature for parameter
 674 tuning via least-square (see Figure 27), we are able to build a model for the viscosity of melts in the
 675 $Na_2O-K_2O-SiO_2-Al_2O_3$ system, with compositions from 50 mol% (in aluminosilicates; 60 in silicates) to
 676 100 mol% SiO_2 , and NBO/T ranging from 0 to 1.33. Root-mean-square-errors between viscosity
 677 predictions and measurements are equal or lower than 0.5 log Pa·s. This demonstrates that building a
 678 structural model of the properties of aluminosilicate melts is possible. However, the above model is

688 incomplete because it relies on many hypotheses, and does not take into account (yet) many specifics
 689 like the role of $^{[5]}Al$ on $S^{conf}(T_g)$. Despite this, this is an encouraging step toward the construction of
 690 structural models that usually achieve a high degree of precision in the predictions they make. New
 691 developments in modelling the melt structure and in linking it with melt properties will surely allow
 692 improvements of such structural models in the future.
 693



694
 695 *Figure 27. A) Viscosity data used for the model calibration. Data (n=817) are those compiled by Le*
 696 *Losq and Neuville (2017) for silicates (NS, KS, KNS and SiO₂), and for aluminosilicates (KNAS) they*
 697 *were compiled from Riebling (1966), Taylor and Rindome (1970), Urbain et al. (1982), Le Losq (2012),*
 698 *Le Losq and Neuville (2013), Le Losq et al. (2014), and Le Losq et al. (2017). The model parameters*
 699 *were optimised by No-U-Turn Markov Chain Monte Carlo sampling via the PyMC3 Python library. The*
 700 *root-mean-squared error between predictions and measurements is around 0.36 log unit.*

701
 702 *4. Aluminate glasses and melts*

703 Aluminate glasses and melts are of interest from a fundamental structural point of view: they contain
 704 only Al as a network former and, hence, allow better understanding of the role of Al in glasses and melts.
 705 The study of aluminate materials is also very important to understand the formation and evolution of
 706 parental bodies in the universe (Leger et al., 2009; Batalha et al., 2011). Aluminate materials further
 707 represent a technological material of interest because of their good IR transmission and ultralow optical
 708 losses (Higby et al., 1990) that make them attractive candidates for low loss optical fibers such as infrared

709 waveguides (Lines et al., 1989, King and Shelby, 1996). In addition, calcium aluminate glasses have been
710 found to be photosensitive to ultraviolet radiations, leading to potential applications in photometric
711 devices for information storage purposes (Hosono et al., 1985). They also have excellent mechanical
712 properties, such that calcium aluminate glass fibres have been proposed for the reinforcement of cement
713 composites (Wallenberger et al., 2004, El Hayek, 2017).

714 Looking at aluminate glasses allows one to better understand the fundamental role of aluminum in
715 glasses and liquids, a task somehow difficult in aluminosilicate compositions because of the
716 superposition of many complexities (see section 3). Numerous studies have probed the structure of
717 calcium aluminate crystals, glasses and melts (e.g. McMillan and Piriou, 1983, Hannon and Parker, 2000,
718 Benmore et al., 2003; Neuville et al., 2008, 2010, Licheron et al., 2011, Drewitt et al., 2012, 2017). From
719 those, it appears that four compositional “domains” can be distinguished: Al_2O_3 , Al_2O_3 -CA, CA-C3A
720 and C3A-CaO with $\text{CA}=\text{CaAl}_2\text{O}_4$, $\text{C3A}=\text{Ca}_3\text{Al}_2\text{O}_6$.

722 4.1 Al_2O_3

723 Crystalline Al_2O_3 has corundum structure with Al in 6-fold coordination (Rankin, 1915). Several
724 studies, using ^{27}Al NMR at high temperature show that Al_2O_3 liquid is a mixture of 60% $^{[6]}\text{Al}$ - 40% $^{[4]}\text{Al}$.
725 This was confirmed more recently by XANES at the Al *K*-edge and FDMNES simulation (Neuville et
726 al., 2009). Recently, Shi et al. (2019) proposed, from new X-ray diffraction at high temperature
727 measurements, that Al is essentially in five-fold coordination in the Al_2O_3 liquid; this interpretation is
728 based on the Al-O distance. The ^{27}Al NMR chemical shift is 53 ppm (Couture et al., 1990; Florian et al.,
729 1995, Ansell et al., 1997), a value that can be interpreted as $^{[5]}\text{Al}$, or as a mixture of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$. When
730 assuming a mixture of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$, the high temperature ^{27}Al NMR data allow determining an Al NMR
731 relaxation time in excellent agreement with the relaxation time obtained from viscosity measurements
732 (Urbain, et al. 1982). Besides, when comparing XANES data at the Al *K*-edge measured at high
733 temperature in the liquid state to spectra simulated using the FDMNES code (Joly, 2001), the assumption
734 of a mixture of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ provides the best reproduction of the experimental data (Neuville et al.,
735 2009). From all the high temperature NMR and XANES spectroscopies and/or neutron diffraction
736 measurements, it is at the moment preferable to consider that, in liquid alumina, Al is present as a mixture
737 of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$.

738 We have essentially mentioned Al_2O_3 in its crystalline or liquid forms, however, some studies have
739 shown that it is possible to obtain Al_2O_3 in its amorphous form, it is usually obtained by fast quenching
740 and in thin film form (Lee et al., 2010; Kim et al., 2014). In that case, Al is essentially a mix of 4- and 5-
741 fold coordination with a small amount of 6-fold coordination (Lee et al., 2010; Kim et al., 2014). The

742 difference between the Al coordination between glass and liquid state can be easily explained by the high
743 cooling rate.

744 4.2 Al_2O_3 - $CaAl_2O_4$ compositions.

746 With the introduction of calcium (or others alkaline-earth elements) in alumina liquid, a first
747 crystalline phase can be found: grossite, $CaAl_4O_7$, called CA2, with AlO_4 tetrahedra only in Q^4 units
748 although one of the O atoms forms an “oxygen tricluster” which links three AlO_4 tetrahedra (Stebbins et
749 al, 2001, Iuga et al., 2005, Neuville et al., 2010). With increasing Ca content up to the $CaAl_2O_4$ crystal
750 composition, the amount of tricluster oxygen decreases and Al stays in four fold coordination. The
751 $CaAl_4O_7$ composition always crystallizes while $CaAl_2O_4$ (CA) can be quenched to a glass by fast quench
752 methods. In the CA glass, ^{41}Al is dominant and ^{51}Al representing 3,5 % of total Al (Neuville et al., 2006).
753 In the CA liquid, ^{41}Al remains dominant but the proportion of ^{51}Al increases up to around 40 mol % near
754 2000 K, as observed from XANES at the Al K-edge and neutron diffraction (Neuville et al., 2008a,
755 Drewitt et al., 2012). Oxygen triclusters also probably are present but remain unquantified during these
756 changes. The coordination of calcium, which is 7-fold in the glasses, increases in the melts as indicated
757 by the evolution of the pre-edge of Ca K-edge XANES spectra between room temperature and
758 superliquidus temperatures (Neuville et al., 2008a).

760 4.3 CA-C3A compositions.

761 For compositions between $50 > Al_2O_3 > 25$ mol%, Al is only in tetrahedral coordination in both the
762 glasses and the crystals, with a number of bridging oxygens varying between 4 to 2 respectively for CA
763 and C3A (McMillan and Piriou, 1983, Neuville et al., 2004, 2006, 2010, Licheron et al. 2011, Drewitt et
764 al., 2017). In C3A crystal or glass ($Ca_3Al_2O_6$), Al can be found in Q^2 units, and, with increasing
765 temperature, Al K-edge XANES show very small changes (Neuville et al., 2008a). The later observation
766 implies that Al stays in Q^2 species with increasing temperature without creation of ^{51}Al . The cationic
767 mobility is only insured by Q^2 species, and not by highly coordinated units as proposed by Stebbins and
768 Farnan (1992) for polymerized melts. Calcium cations in crystalline C3A and glass is in 6-fold
769 coordination, and, near 2000 K, a small pre-edge in Ca K-edge XANES spectra is observed; this implies
770 that the Ca coordination increases with increasing temperature (Neuville et al., 2008a).

772 4.4 C3A-CaO compositions

773 For compositions with $Al_2O_3 < 25$ mol%, no glass or stable crystalline phases are observed. The
774 knowledge of Al and Ca coordination in such conditions remains very scarce, if not non-existent.

4.5 Link with observations in other binary systems

In SrO-Al₂O₃ and BaO-Al₂O₃ systems, the liquidus temperatures are higher than in the CaO-Al₂O₃ system. This observation seems logical since there is agreement with an increase of liquidus temperature with increasing the size of the alkaline-earth elements in alkaline-earth aluminosilicate systems (Méducin et al., 2004, Licheron et al., 2011, Shan et al., 2018). Turning to MgO-Al₂O₃, Mg²⁺ forms a very stable spinel with alumina; it is not possible to quench the MgAl₂O₄ composition or other magnesium aluminate composition even with using fast-quench methods. In MgAl₂O₄ crystals, Mg and Al are in 4 and 6-fold coordinations, respectively, at room temperature and that can change with temperature (Andreozzi et al., 2000, Neuville et al., 2009).

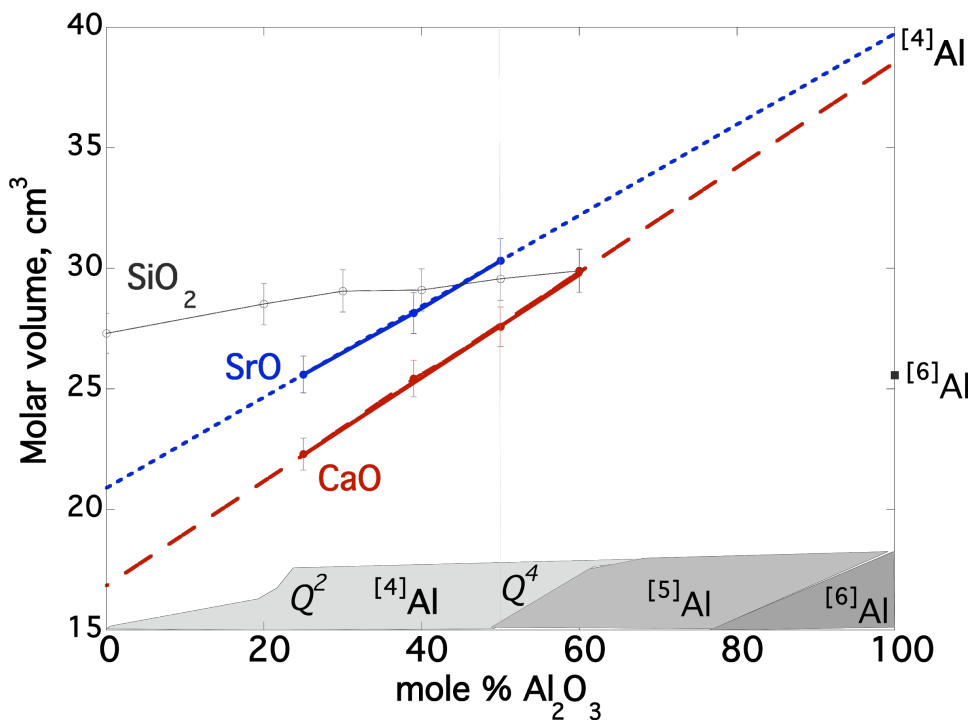
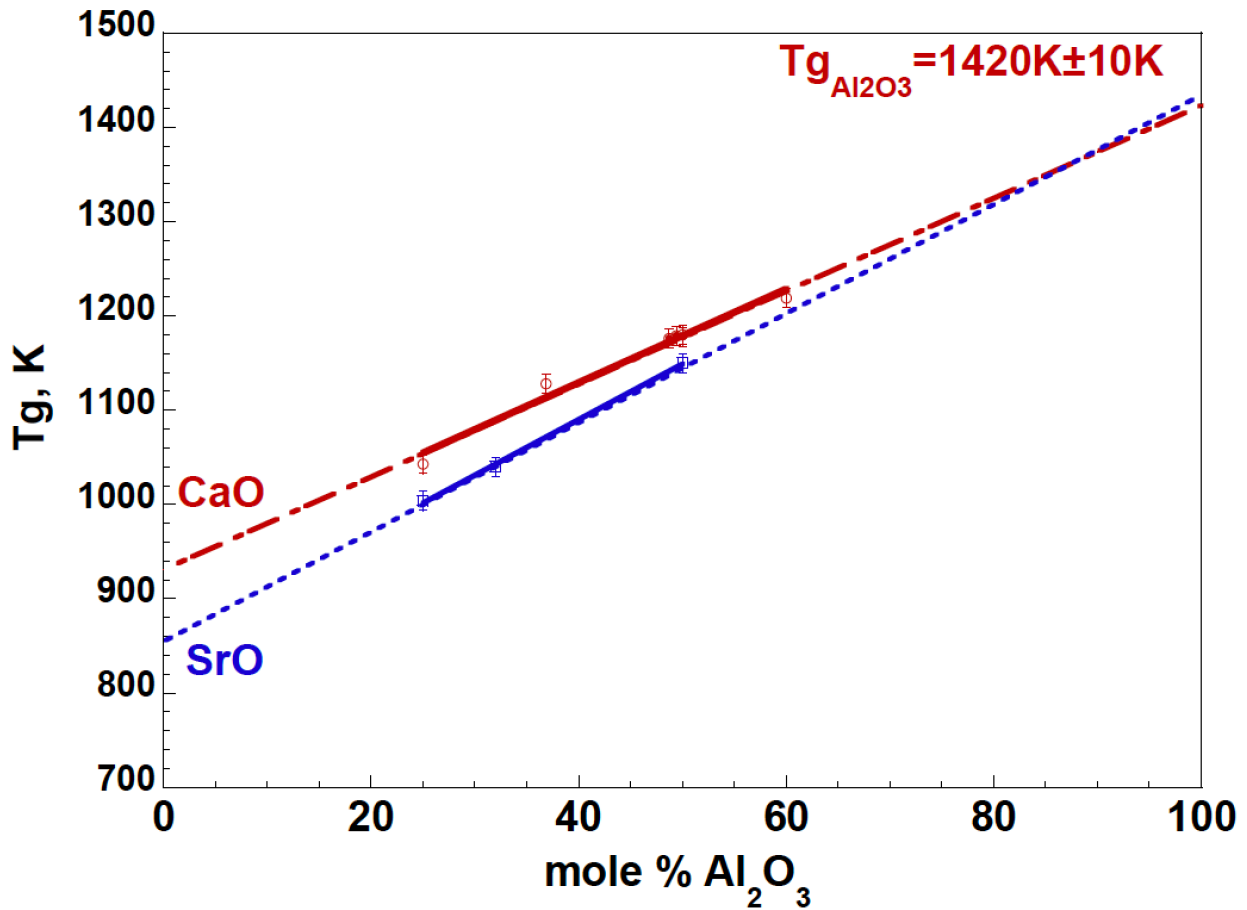


Figure 28: Coordination of Al between MO-Al₂O₃ and variation of molar volume of aluminate glasses. Molar volumes are calculated from the density measurements for Al₂O₃-SiO₂ (Wang et al., 2020), Al₂O₃-CaO (Neuville et al., 2006, 2010, Licheron et al., 2011), and Al₂O₃-SrO (Licheron et al., 2011). Solid lines correspond to fits of the data with a line, and dashed lines show the extrapolation of those fits to end members.

Figure 28 summarizes the evolution of the Al coordination in aluminate glasses and also shows how the molar volume of glass changes with Al₂O₃ content. The glasses CxA or SxA, with x varying between 3 and 1, are made by levitation and fast quench, and all these glasses show Al in 4-fold coordination (Neuville et al., 2006, 2008b, 2010, Licheron et al., 2010). For Ca or Sr aluminates, a linear variation of

797 the molar volume with the alumina content is observed between 25 and 50 mole percent of alumina, and
 798 Ca is in 6-fold coordination and Al in 4-fold coordination (Neuville et al., 2008b). If we consider linear
 799 extrapolations of these trends, it is possible to propose, considering only Al in four-fold coordination and
 800 Ca and Sr in 6-fold coordinations, that the respective partial molar volumes of Al₂O₃, CaO and SrO are
 801 respectively of 39.1, 17.0 and 21.0 cm³ mol⁻¹. Such estimations are in very good agreement with the
 802 values proposed by Robie (1978) for the molar volume of CaO and SrO.
 803



804
 805 *Figure 29: Glass transition temperature obtained from DSC measurements with and heating rate of*
 806 *10°/min for aluminate glasses. Full line corresponds to linear variation fitting datas and dashed line*
 807 *corresponds to extrapolation up to end members.*

809 To complete the observations made on the molar volume, the glass transition temperatures for C_xA
 810 and S_xA glasses were measured and plotted in Figure 28. The glass transition temperature of the different
 811 C_xA and S_xA glasses were obtained by DSC measurements with a heating rate of 10 °/min. Two linear
 812 trends are observed along the binaries CaO-Al₂O₃ and SrO-Al₂O₃. They converge to similar values when
 813 extrapolated to the alumina end-member. From this, we can propose an “apparent” partial glass transition
 814 temperature for Al₂O₃ at 1420 ± 10 K. Following this logic, we also propose partial T_gs for CaO and SrO

815 in 6-fold coordination at 932 ± 10 and 857 ± 10 K. The estimated T_{g_i} for Al_2O_3 with Al in four-fold
816 coordination is in very good agreement with calculation of phase diagrams using CALPAHD program
817 (Pitsch, et al. 2021 submitted).

818 Recently Shan et al (2018) made some calcium-strontium peraluminous glasses at 58% mole of Al_2O_3
819 using levitation device and fast cooling rate. They investigated macroscopic properties of these glasses
820 and they showed that an ideal mixing term between Ca and Sr clearly exist to explain Vickers micro-
821 hardness and glass transition temperatures variation between Ca/Sr aluminate glasses.

822

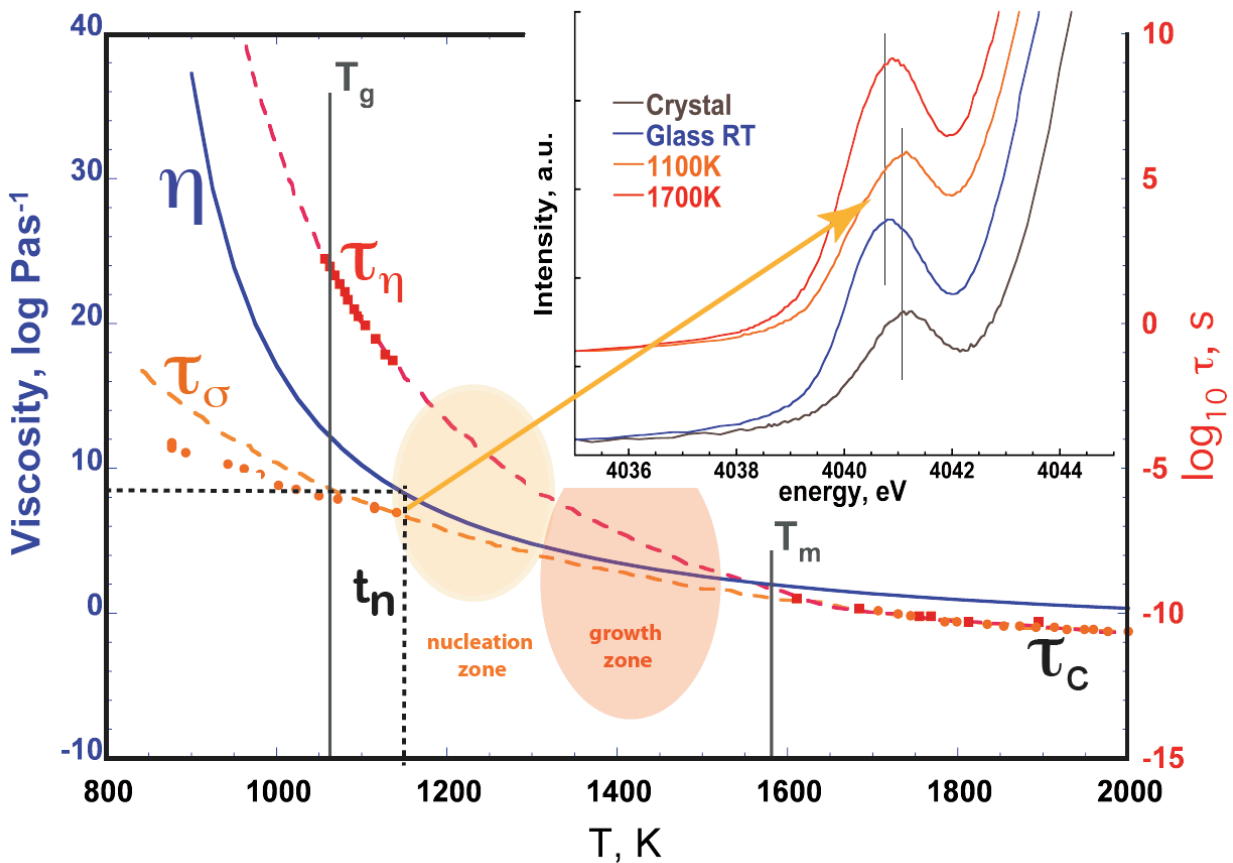
823 5. Conclusion and perspectives

824 Since the 1980s, it has been possible to study the structure of a liquid at high temperature by
825 several spectroscopic methods: Raman, NMR, X-ray absorption and X-ray and neutron diffraction
826 techniques. This allows us to understand the local order and the medium range order directly in the liquid
827 state and thus be able to link the high temperature structure to the measurements of properties directly
828 accessible at high temperature, like heat capacity, viscosity, conductivity, diffusivity. We have seen that
829 this kind of approach is very promising because it allows us to have a global view of a glass and a liquid
830 and thus to better understand the structural changes that take place in a liquid. This improved
831 understanding of silicate glasses and liquids has great applications in both volcanology and geochemistry
832 where we are better able to understand changes in eruptive dynamism, mass transfers and also chemical
833 balances during crystallization processes for example. But this work allows also a better understanding
834 of industrial processes during melting, glass-forming or even during the processes of glass-ceramic.

835 To summarize the changes that can occur in a cooling liquid, Figure 30, obtained for a
836 composition of $Ca_3Al_2Si_3O_{12}$ liquid, shows both the changes that occur in the liquid state and during its
837 cooling. We can see that at high temperature, beyond the liquidus, T_m , 1580K, the relaxation times
838 obtained from the ^{27}Al NMR, τ_{NMR} , measurement of conductivity, τ_σ , or viscosities, τ_η converge and are
839 similar. It simply means that in the liquid state all cations whatever their roles in the melts, move in
840 relation to each other. From structural point of view, it is a liquid state, characterized by the particularly
841 intense pre-edge of the XANES spectra at the Ca K -edge at high temperature. On the other hand, when
842 the temperature decreases, there is a decoupling between the various relaxations, this means that the
843 atoms begin to move differently, the network modifiers like Ca, continue to move as shown by the
844 relaxation τ_σ , while the relaxation calculated from the viscosity measurements, τ_η , shows a strong
845 increase, meaning that the tetrahedral network composed of tetrahedral SiO_4 and AlO_4 moves more
846 slowly, which translates into an increase in the viscosity curve. This decoupling between the various
847 families of atoms appears at about 1100K for this chemical composition, several orders of magnitude

848 separate the relaxation times obtained from the conductivity measurements, τ_σ , from those obtained from
 849 viscosity measurements, τ_η . These differences show, on the one hand, that the aluminosilicate network
 850 freezes with a significant increase of τ_η , and viscosity and that calcium atoms put themselves in a position
 851 close to that which they will have in the crystalline phase, as shown by the changes observed in the pre-
 852 edge of the XANES spectra at the Ca K-edge. In the end, we find that close to T_g , the Ca is probably in a
 853 crystallographic site almost identical to the one it will have in a crystal.

854



855

856 *Figure 30: viscosity of $Ca_3Al_2Si_3O_{12}$ liquid from Neuville and Richet (1991), relaxation τ_η is calculated*
 857 *from viscosity measurements, τ_σ and τ_{NMR} , are from Gruener et al., (2001) and pre-edge XANES spectra*
 858 *at the Ca K-edge are from Neuville et al., (2008b)*

859

860 Figure 30 completes the Figure 4 of this chapter, which helped to understand the links between potential
 861 movements in a liquid, various entropic states and viscosity, but this latter figure indicates that at high
 862 temperature all atoms can move quickly relative to each other and that at lower temperatures, atoms are
 863 in different potentials energy states and that changes will take more time.

864

865 In 2021, it is therefore possible and necessary to understand the structure and properties of a
 glass or/and a liquid throughout its history during a natural or industrial process. The current

866 computational techniques discussed in the following chapters can show and predict these different states,
867 and it is easy to imagine that the new techniques based on Machine Learning will allow modeling of the
868 structure, and physical properties and be able to predict them globally (Le Losq et al., 2021), this will
869 have great consequences for both earth sciences and materials sciences.

870

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