

21 **Ca Neighbors from XANES spectroscopy: a tool to investigate structure, redox and**
22 **nucleation processes in silicate glasses, melts and crystals.**

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29 **ABSTRACT**

30 In this study Ca K-edge X-ray Absorption Spectroscopy (XAS) has been employed to study
31 the Ca structural role in a set of silicate glasses. For the first time the accurate analysis of the
32 Ca pre-edge peak has been performed, providing information about the different Ca local
33 environments, and on its structural role.

34 This approach was tested on Ca-aluminosilicate glasses (CAS system) with constant SiO₂
35 content (50mol% and 76mol%), ranging from percalcic to peraluminous domains. In alkali-
36 earth aluminosilicate glasses Al and Si are network formers in a large range of compositions,
37 whereas calcium should act either as network modifier and charge compensator. The results
38 obtained show a different Ca behaviour as a function of Al content, which in turn is related to
39 the Al local environment. For example, we observe changes in the pre-edge peak centroid
40 energies depending on the changes in the role of Ca as a network modifier (Al = 0 mol%), to
41 charge compensator (aluminosilicate join) to a more complex role in the peraluminous
42 domain, depending on the fraction of ^{[4],[5],[6]}Al. This approach was further applied to study
43 Fe-bearing glasses and, a diopside (CaMgSi₂O₆) composition at different temperatures. It was
44 possible to correlate the variations occurring in the Ca pre-edge peak centroid positions with
45 both redox state and crystal nucleation mechanism.

46

47 **Introduction**

48 Calcium is a very important element in Earth and materials sciences. It can be found in
49 all natural processes, i.e. mechanisms of sedimentation, magmatic processes, redox
50 mechanisms, nucleation and growth crystallization mechanisms (Magnien et al. 2008;
51 Neuville et al. 2008, 2014) and that implies that calcium plays a key role in the formation of
52 materials. The structure of calcium aluminosilicate glasses is of great interest for
53 technological or geological applications. These glasses are attractive materials due to their
54 highly refractory nature and their excellent optical and mechanical properties (Lines et al.
55 1989; Wallenberger and Brown 1994). They can also be considered as frozen approximations
56 of melts, for which a detailed knowledge of the structure is needed to better constrain the
57 modeling of magmatic processes. The phase diagram CaO-Al₂O₃-SiO₂ (CAS) investigated for
58 the first time by Rankin (1915) is very important for glasses, glass-ceramics, ceramics,
59 concrete and Earth Sciences. In the CAS system Ca can play different roles as a function of
60 the Al₂O₃ content. Ca can act as network modifier (NM) or as charge compensator (CC)
61 depending upon what role Al plays in the glass. The CAS system is remarkable because
62 glasses from pure SiO₂ to calcium aluminate can be synthesized using normal quench rates
63 (10°/s), contrary to alkali or Mg aluminosilicate glasses (Neuville et al. 2008). Moreover,
64 recently Helhen and Neuville (2015) have demonstrated a change in the role of Ca as a
65 function of chemical composition by investigating changes in the VV/VH Raman signature.
66 Here we investigate the Ca environment using X-Ray Absorption Spectroscopy at the Ca K-
67 edge (4038.5 eV).

68

69 **Experimental Methods**

70 Ca K-edge X-ray Absorption Near Edge Structure (XANES) spectra were obtained at
71 the Soft X-rays Spectroscopy (SXS) beam line at the Brazilian Synchrotron Light Laboratory,
72 LNLS (electron energy of the storage ring is 1.37 GeV). The SXS beamline equipped with a

73 Si₁₁₁ monochromator (the spectral resolution ΔE is ~ 0.65 eV) had a focused beam of 2.5 mm^2
74 spot size, and the spectra were recorded in Total Electron Yield (TEY) detection mode, with
75 the sample compartment pressure at 10^{-8} mbar. Measurements were done with sample
76 surfaces normal to the beam. The pre-edge peak region was scanned in 0.1 eV (± 0.015) steps,
77 whereas the edge region was scanned in 0.25 eV (± 0.03) energy steps, and the energies were
78 calibrated using a Ti foil. XANES spectra were reduced by background subtraction with a
79 linear function and then normalized for atomic X-ray absorption on the average absorption
80 coefficient of the spectral region from 4100 to 4300 eV. The threshold energy was taken as
81 the first maximum of the first derivative of the spectra, whereas the main peak positions were
82 obtained by calculating the second derivative of the spectra. In addition to the position of the
83 main edge, particular attention has been given to the analysis of the pre-edge peak. This small
84 feature is attributed to the transition of the Ca $1s$ electron to the unoccupied Ca $3d/O 2p$
85 hybridized states. The intensity of the components of the pre-edge peak is thus related both to
86 quadrupole transitions and to the p -like components of the t_{2g} and e_g orbitals (Bianconi et al.
87 1978; de Lazaro et al. 2007). XANES normalization and pre-edge extraction have been
88 carried out following previous work made on iron by Cicconi et al. (2015 and references
89 therein). After the background subtraction the pre-edge peaks have been fitted by a sum of
90 pseudo-Voigt (pV) functions. The centroid position of the pre-edge peak represents the
91 energy position of the deconvoluted components weighted by their integrated area.

92 To the best of our knowledge this study presents the first detailed analysis of Ca pre-
93 edge peaks. Indeed, up to now observation were only done on the shape and/or on the relative
94 intensities of the Ca pre-edge peaks.

95 Glass samples in the ternary system CaO-Al₂O₃-SiO₂ (CAS) have been investigated.
96 The viscosity, transition temperatures and the thermodynamic parameters are given elsewhere
97 (Neuvill 1992; Neuvill et al. 2004a,b). We studied Ca-aluminosilicate glasses (CaX.Y,
98 where X represents the Si content and Y the Al content) with constant SiO₂ content (50 and

99 76 mol%, respectively named Ca50 and Ca76 series), ranging from percalcic (Ca50.00,
100 Ca55.18, and Ca76.11), to the tectosilicate join (50.25, 50.30) and into the peraluminous
101 domain (Ca50.40, and, Ca76.17) (Neuvill et al. 2004b, 2006). Moreover, we studied the role
102 of Ca in soda-lime-silicate glasses (WG series) for two Fe-bearing glasses - one fully oxidized
103 (WG1-Ox), and one reduced (WG1-Rd) - and for a Fe-free WG base glass.

104

105 **RESULTS**

106 The study of the XANES features has been done for Ca-aluminosilicate glasses
107 ranging from percalcic to peraluminous domains (with Al₂O₃ content between 11 and 17% for
108 Ca76 glasses and between 0 up to 40% for Ca50 glasses). The full XANES spectra for Ca50
109 glasses are plotted in Figure 1a, however we focused our attention more on the analysis of the
110 pre-edge peaks, which are plotted in Figures 1b-d, respectively for the Ca-aluminosilicate
111 glasses and for three window glasses. The pre-edge peaks show several differences in their
112 shapes. Nevertheless three main positions (letters “a-c” in Figs. 1b-d) can be clearly
113 identified, which also correspond to the average position of the pV components used (average
114 value at 4039.3 eV for “a”, 4040.13 eV for “b” and 4040.74 eV for “c”). The analysis of the
115 different components shows changes that can be correlated to the Ca local environment,
116 following the knowledge of the structure of these glasses (Neuvill et al. 2004a-b, 2006). In
117 the joins at 50 and 76 mol% of silica, from the percalcic to the tectosilicate join and into the
118 peraluminous domain there is a marked modification of both intensity and energy position of
119 the pre-edge peaks (Fig. 1b-c). Glasses in the WG series present mainly variations on the
120 relative intensity and energy positions for the components “a” and “b” (Fig. 1d) depending on
121 the presence of iron, or on Fe redox state.

122

123 **DISCUSSION and mechanism assumption**

124 *Charge compensator versus network modifier*

125 Ca K-edge XANES spectra have several features (capital letters A, B, C in Fig. 1a)
126 that clearly vary depending on the glass chemistry. In an early work, Sowrey and coauthors
127 (2004), by studying XANES spectra of Ca-crystalline phases, linked the edge position (B in
128 Fig. 1a) or the intensity of the shoulder (C in Fig. 1a) to the Ca coordination numbers. But
129 their correlations show a large spread of data and did not take into account the pre-edge
130 peaks. Indeed, from the study of some model compounds (not presented here) we observed
131 that there is not a simple trend correlating the main edge position (B) with the Ca local
132 environment. However there are systematic changes of the pre-edge peak centroid energies.
133 We observed that pre-edge peak centroid positions can be successfully correlated to the
134 different Ca behaviour, and in turn, to modifications in coordination and $\langle\text{Ca-O}\rangle$ distances,
135 for all the glasses here analysed (Fig. 2). Indeed, the distributions of the centroid for silicate
136 glasses follow a trend strictly related to the differing roles of Ca in the silicate network. In a
137 glass completely depolymerized (Ca50.00), Ca acts entirely as Network Modifier (NM in Fig.
138 2), whereas in the highly polymerized anorthite glass (Ca50.25) Ca is a Charge Compensator
139 (CC in Fig. 2). The increase in the centroid energy position for glass Ca50.25 can be
140 explained in terms of increasing coordination and longer $\langle\text{Ca-O}\rangle$ distances, in agreement
141 with NMR studies (Shimoda et al. 2007; Angeli et al. 2007) and this can be directly correlated
142 to the change of Ca behaviour in glasses as also recently observed comparing Raman spectra
143 in VV and VH polarization (Helhen and Neuville 2015). In the peraluminous domain
144 (Ca50.40, Ca76.17) the higher atomic packing density and therefore the presence of greater
145 percentages of higher coordinated aluminum ($^{[5],[6]}\text{Al}$) implies an increasing need of charge
146 compensation, and then Ca CC role is even more reinforced. Furthermore, differently from
147 the other glasses, Ca50.40 and Ca76.17 pre-edge peaks show the presence of the component
148 “c” at higher energy (Figs.1b-c). We propose that Ca occurs in two different sites to balance
149 respectively $^{[4]}\text{Al}$ and $^{[5],[6]}\text{Al}$. This trend that brings centroid positions to higher energy (Fig.

150 2), due to the appearance of the “c” component, is similar in both Ca50 and Ca76 series (Figs.
151 1b c) and thus it could be related to two different local Al environments in the glass network.

152 All the results obtained point to a different behaviour of Ca as a function of the change
153 of its role between network modifier, charge compensator, and possibly, charge compensator
154 of highly coordinated aluminum. The centroid variation could alternatively be related to a
155 change in oxygen coordinations and/or in <Ca-O> distances. Ca compensating ^[4]Al, and even
156 more for ^{[5],[6]}Al, has a higher <Ca-O> distance than Ca as NM.

157

158 *Signature of redox changes*

159 Further studies have been done on glasses of soda-lime-silicate compositions (WG
160 series) with and without iron. The Fe-free WG glass lies in the region assigned to the network
161 modifier role of calcium (NM shadow area in Fig. 2) because the system is fully
162 depolymerized by Na and Ca which implies that Ca neighbors are almost the same as in
163 Ca50.00 glass (Fig. 2). Indeed the two Fe-free glasses WG and Ca50.00 have almost the same
164 centroid position. If now some iron is added with different oxidation states, as we see in
165 Figure 1d, the position of the “a” and “b” components increase, showing the same trend than
166 in aluminosilicate glasses.

167 The oxidized glass WG1-Ox ($Fe^{3+}/\Sigma Fe = 0.99$) lies in the area assigned to the Ca as
168 charge compensator (CC shadow area in Fig. 2). This confirms that Fe^{3+} 4-fold coordinated
169 acts as a structural analogue of Al^{3+} as proposed for other glass compositions (Cicconi et al.
170 2015). On the other hand, the almost fully reduced Fe-glasses (WG1-Rd, $Fe^{3+}/\Sigma Fe < 0.1$) lies
171 between the two grey intervals reported in Fig. 2. When the redox changes, the surrounding of
172 Fe is going to change as well. It is suggested that Fe^{2+} will present then a mixture of different
173 coordinations (4-, 5- and/or 6-fold coordinated) reflecting the results obtained from the Fe K-
174 edge of these glasses and from other previous studies on silicate glasses (e.g. Cicconi et al.
175 2015). By changing coordination and valence, the Fe needs for charge compensation will be

176 modified, thus causing variations in the Ca local environment. The role played by Ca is then
177 strongly related to Fe speciation. It can also be inferred that Fe^{3+} prefers tetrahedral
178 coordination when sufficient alkali/alkali-earth are available for charge compensation, as in
179 the case of aluminum.

180

181 *Understanding nucleation process*

182 The pre-edge peak centroid energy positions have been successfully used to observe
183 Ca modifications depending on the glass structure in Ca-aluminosilicate glasses (Ca50, Ca76
184 series) or on the Fe speciation (WG series). In addition we investigated the Ca K-edge XAS
185 signals obtained from previous in-situ studies at High Temperature (HT) (see [Neuvillle et al.](#)
186 [2008, 2014](#)) in an Al/Fe free system in which Ca has, theoretically, a more restricted number
187 of sites. The starting material was a diopside ($\text{CaMgSi}_2\text{O}_6$) crystal, investigated from room
188 temperature (cryst in [Fig. 2](#)), to first the liquid state, 1700K ($T_m = 1664\text{K}$), then rapidly
189 quenched (glass in [Fig. 2](#)), and finally heated at 1050K, a temperature higher than the glass
190 transition temperature ($T_g = 991\text{K}$, [Neuvillle and Richet 1991](#)) and then kept at this
191 temperature for 1 hour. As reported in the original study for this composition ([Neuvillle et al.](#)
192 [2008](#)), after 20 minutes at T_g no changes occurred in XANES or EXAFS regions, whereas the
193 pre-edge peak show clear variations.

194 Similar centroid energy positions were found for the melt and the quenched glass ([Fig.](#)
195 [2](#)). However, a noticeable energy shift is observed between the pre-edge peak of the liquid at
196 1700 K and that of the crystalline phase. This variation in the pre-edge position has been
197 associated with changes in the number of O neighbors around Ca in the crystal compared to
198 the glass or the liquid. In the latter, Ca is in a polyhedron with a lower O coordination (6-,7-
199 fold) than in the crystal (8-fold) ([Prencipe and Tribaudino 2000](#); [Cormier et al. 2003](#);
200 [Shimoda et al. 2007](#)). The glass, after 1 hour around T_g (1050K), does not show signs of
201 crystallization, but it is in a probable nucleation state. It shows a centroid with an intermediate

202 position between the liquid and the crystal (Fig. 2). These observed changes in the centroid
203 position could be explained by the higher mobility of Ca atoms compared to Si/O atoms, just
204 above the glass transition temperature. Hence, in a short time Ca reaches an intermediate
205 environment (a pre-nucleus site) closer to that of the crystal, whereas at the same time Si/O
206 atoms maintain the initial glassy structure. Gruener et al. (2001) already observed that Ca, in
207 aluminosilicate glasses, has a higher mobility at the glass transition temperature, and these
208 possible faster movements of Ca have been also associated with changes in electrical and
209 physical properties at Tg (Gruener et al. 2001).

210 Here again the centroid position of the Ca pre-edge peaks presents a high sensitivity to
211 modifications in the local environment around Ca atoms, even at high temperatures.

212

213 **IMPLICATIONS**

214 XAS data at the Ca K-edge is a promising tool to reflect the complexity of the Ca
215 environment in glasses/melts. Ca XANES and especially pre-edge peaks contain information
216 on Ca oxygen coordination and local environment. However, a precise understanding of the
217 Ca environment goes far beyond a simple local structure information and we verified that Ca
218 pre-edge peak analysis can provided insights about:

219 - the role of Ca in a silicate glass network. The change of Ca role between network
220 modifier (NM) to charge compensator (CC) is fundamental to better understand the large
221 variations of physical properties previously observed in aluminosilicate glasses (Neuville
222 1992; Le Losq et al. 2014). Indeed, Ca as NM breaks Si-O-Si bonds, consequently decreases
223 polymerization, viscosity, and Tg. At the same time, Ca as CC is close to Al³⁺ in 4 or 5-fold
224 coordination, and it helps the Al to be incorporated into the network, and consequently the
225 polymerization, the viscosity and the Tg increase.

226 - redox impact on silicate structure modifications. Magnien et al. (2008) have shown
227 that, at low temperature, the redox mechanism is mainly controlled by the movement of

228 divalent cations. Unfortunately, direct studies on Fe do not provide convincing information on
229 the network connectivity. However, from the Ca pre-edge peak analysis, changes of the role
230 of Ca from NM to CC could be identified depending on the presence or on the speciation of
231 Fe. This variation of the role of Ca is associated with the need of Fe³⁺ to be compensated, and
232 it indicates that Fe³⁺ acts in the network in a similar manner as Al³⁺. Furthermore, the large
233 variations of the oxygen distribution around Ca could explain the large variations of the redox
234 mechanisms in silicate melts.

235 - The Ca environment can be a key to understanding nucleation processes. Indeed the
236 nucleation process is very difficult to follow and needs highly sensitive tools. In fact, Ca is
237 expected to move at lower temperatures compared to the atoms involved in the glass network,
238 in agreement with observations on relaxation processes ([Gruener et al. 2001](#)). As a
239 consequence, the Ca environment should be quickly modified during nucleation processes.
240 [Neuvillle et al. \(2008\)](#) observed that, in a diopside composition, Ca pre-edge peak was
241 modified and associated it with a change of Ca site from an “amorphous” one, to a “pre-
242 nucleus” one. The quantitative approach of the Ca pre-edge centroid energy, presented here,
243 has the sensitivity required to further study nucleation.

244 **Acknowledges**

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248

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308

309 **Figure Captions**

310

311 Figure 1: (a) XANES spectra at the Ca K-edge for glasses with 50mol% SiO₂. Shifts in all the
312 main features (capital letters A to C) are clearly visible. (b-c) Ca pre-edge peaks for glasses in
313 the CAS system and for (d) soda-silica-lime (WG) glasses. The pre-edge peaks show three
314 main components (rectangles and small letters “a” to “c”).

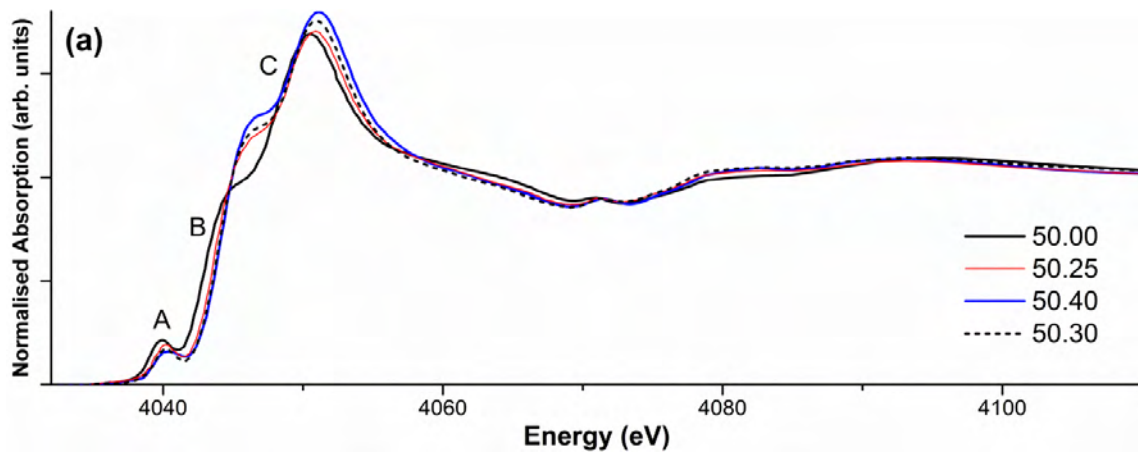
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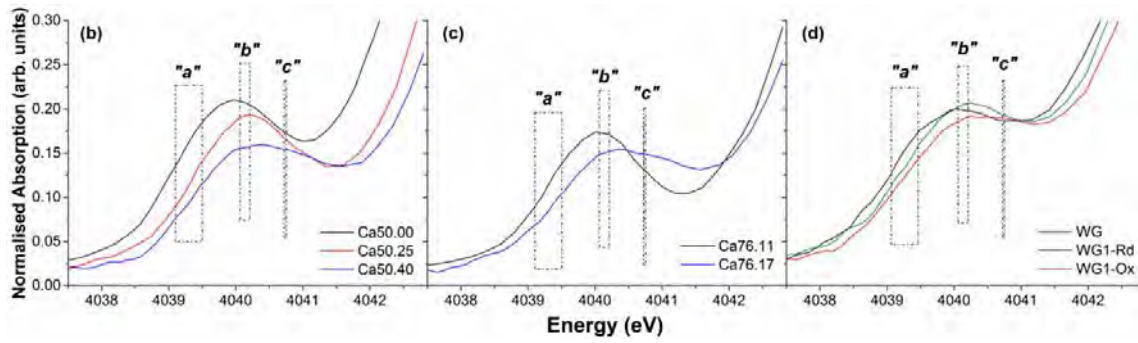
317 Figure 2: Plot of the Ca pre-edge peak centroid energy positions for aluminosilicate glasses in
318 the CAS system with constant Si molar content (Ca50 and Ca76), and for Fe-free (WG) and
319 Fe-bearing (WG1Rd and WG1Ox) soda-lime-silicate glasses. Moreover, a diopside
320 composition (CM50) studied from room temperature to liquidus is reported (see text). The
321 grey intervals indicate the regions where Ca is considered to behave only as network modifier
322 (NM) or charge compensator (CC).

323

324 Figure 1a-d



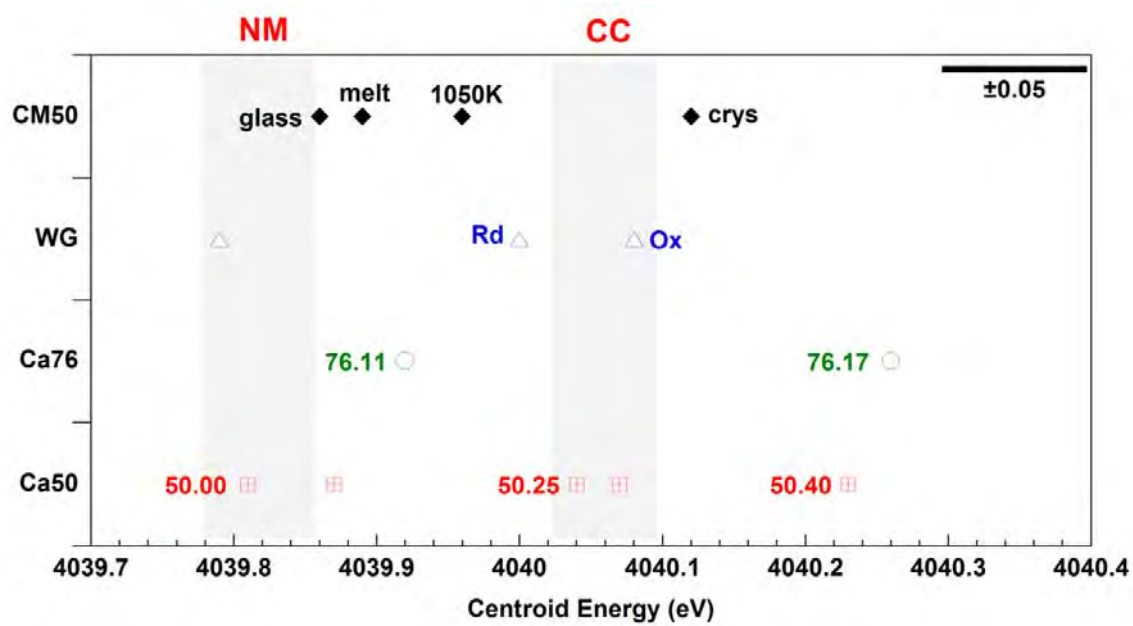
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327

328 Figure 2



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