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

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ABSTRACT

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

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

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

Experimental Methods

Ca K-edge X-ray Absorption Near Edge Structure (XANES) spectra were obtained at the Soft X-rays Spectroscopy (SXS) beam line at the Brazilian Synchrotron Light Laboratory, LNLS (electron energy of the storage ring is 1.37 GeV). The SXS beamline equipped with a
Si$_{111}$ monochromator (the spectral resolution $\Delta E$ is $\sim 0.65$ eV) had a focused beam of 2.5 mm$^2$ spot size, and the spectra were recorded in Total Electron Yield (TEY) detection mode, with the sample compartment pressure at $10^{-8}$ mbar. Measurements were done with sample surfaces normal to the beam. The pre-edge peak region was scanned in 0.1 eV ($\pm 0.015$) steps, whereas the edge region was scanned in 0.25 eV ($\pm 0.03$) energy steps, and the energies were calibrated using a Ti foil. XANES spectra were reduced by background subtraction with a linear function and then normalized for atomic X-ray absorption on the average absorption coefficient of the spectral region from 4100 to 4300 eV. The threshold energy was taken as the first maximum of the first derivative of the spectra, whereas the main peak positions were obtained by calculating the second derivative of the spectra. In addition to the position of the main edge, particular attention has been given to the analysis of the pre-edge peak. This small feature is attributed to the transition of the Ca 1$s$ electron to the unoccupied Ca 3$d$/O 2$p$ hybridized states. The intensity of the components of the pre-edge peak is thus related both to quadrupole transitions and to the $p$-like components of the $t_{2g}$ and $e_g$ orbitals (Bianconi et al. 1978; de Lazaro et al. 2007). XANES normalization and pre-edge extraction have been carried out following previous work made on iron by Cicconi et al. (2015 and references therein). After the background subtraction the pre-edge peaks have been fitted by a sum of pseudo-Voigt (pV) functions. The centroid position of the pre-edge peak represents the energy position of the deconvoluted components weighted by their integrated area.

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

Glass samples in the ternary system CaO-Al$_2$O$_3$-SiO$_2$ (CAS) have been investigated. The viscosity, transition temperatures and the thermodynamic parameters are given elsewhere (Neuville 1992; Neuville et al. 2004a,b). We studied Ca-alumino-silicate glasses (CaX.Y, where X represents the Si content and Y the Al content) with constant SiO$_2$ content (50 and...
76 mol%, respectively named Ca50 and Ca76 series), ranging from percalcic (Ca50.00, Ca55.18, and Ca76.11), to the tectosilicate join (50.25, 50.30) and into the peraluminous domain (Ca50.40, and, Ca76.17) (Neuville et al. 2004b, 2006). Moreover, we studied the role of Ca in soda-lime-silicate glasses (WG series) for two Fe-bearing glasses - one fully oxidized (WG1-Ox), and one reduced (WG1-Rd) - and for a Fe-free WG base glass.

RESULTS

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

DISCUSSION and mechanism assumption

Charge compensator versus network modifier
Ca K-edge XANES spectra have several features (capital letters A, B, C in Fig. 1a) that clearly vary depending on the glass chemistry. In an early work, Sowrey and coauthors (2004), by studying XANES spectra of Ca-crystalline phases, linked the edge position (B in Fig. 1a) or the intensity of the shoulder (C in Fig. 1a) to the Ca coordination numbers. But their correlations show a large spread of data and did not take into account the pre-edge peaks. Indeed, from the study of some model compounds (not presented here) we observed that there is not a simple trend correlating the main edge position (B) with the Ca local environment. However, there are systematic changes of the pre-edge peak centroid energies.

We observed that pre-edge peak centroid positions can be successfully correlated to the different Ca behaviour, and in turn, to modifications in coordination and <Ca-O> distances, for all the glasses here analysed (Fig. 2). Indeed, the distributions of the centroid for silicate glasses follow a trend strictly related to the differing roles of Ca in the silicate network. In a glass completely depolymerized (Ca50.00), Ca acts entirely as Network Modifier (NM in Fig. 2), whereas in the highly polymerized anorthite glass (Ca50.25) Ca is a Charge Compensator (CC in Fig. 2). The increase in the centroid energy position for glass Ca50.25 can be explained in terms of increasing coordination and longer <Ca-O> distances, in agreement with NMR studies (Shimoda et al. 2007; Angeli et al. 2007) and this can be directly correlated to the change of Ca behaviour in glasses as also recently observed comparing Raman spectra in VV and VH polarization (Helhen and Neuville 2015). In the peraluminous domain (Ca50.40, Ca76.17) the higher atomic packing density and therefore the presence of greater percentages of higher coordinated aluminum ([5],[6]Al) implies an increasing need of charge compensation, and then Ca CC role is even more reinforced. Furthermore, differently from the other glasses, Ca50.40 and Ca76.17 pre-edge peaks show the presence of the component “c” at higher energy (Figs.1b-c). We propose that Ca occurs in two different sites to balance respectively [4]Al and [5],[6]Al. This trend that brings centroid positions to higher energy (Fig.
due to the appearance of the “c” component, is similar in both Ca50 and Ca76 series (Figs. 1b c) and thus it could be related to two different local Al environments in the glass network.

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

Signature of redox changes

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

The oxidized glass WG1-Ox (Fe$^{3+}$/ΣFe = 0.99) lies in the area assigned to the Ca as charge compensator (CC shadow area in Fig. 2). This confirms that Fe$^{3+}$ 4-fold coordinated acts as a structural analogue of Al$^{3+}$ as proposed for other glass compositions (Cicconi et al. 2015). On the other hand, the almost fully reduced Fe-glasses (WG1-Rd, Fe$^{3+}$/ΣFe < 0.1) lies between the two grey intervals reported in Fig. 2. When the redox changes, the surrounding of Fe is going to change as well. It is suggested that Fe$^{2+}$ will present then a mixture of different coordinations (4-, 5- and/or 6-fold coordinated) reflecting the results obtained from the Fe K-edge of these glasses and from other previous studies on silicate glasses (e.g. Cicconi et al. 2015). By changing coordination and valence, the Fe needs for charge compensation will be
modified, thus causing variations in the Ca local environment. The role played by Ca is then strongly related to Fe speciation. It can also be inferred that Fe$^{3+}$ prefers tetrahedral coordination when sufficient alkali/alkali-earth are available for charge compensation, as in the case of aluminum.

Understanding nucleation process

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

Similar centroid energy positions were found for the melt and the quenched glass (Fig. 2). However, a noticeable energy shift is observed between the pre-edge peak of the liquid at 1700 K and that of the crystalline phase. This variation in the pre-edge position has been associated with changes in the number of O neighbors around Ca in the crystal compared to the glass or the liquid. In the latter, Ca is in a polyhedron with a lower O coordination (6-,7-fold) than in the crystal (8-fold) (Prencipe and Tribaudino 2000; Cormier et al. 2003; Shimoda et al. 2007). The glass, after 1 hour around Tg (1050K), does not show signs of crystallization, but it is in a probable nucleation state. It shows a centroid with an intermediate
position between the liquid and the crystal (Fig. 2). These observed changes in the centroid position could be explained by the higher mobility of Ca atoms compared to Si/O atoms, just above the glass transition temperature. Hence, in a short time Ca reaches an intermediate environment (a pre-nucleus site) closer to that of the crystal, whereas at the same time Si/O atoms maintain the initial glassy structure. Gruener et al. (2001) already observed that Ca, in aluminosilicate glasses, has a higher mobility at the glass transition temperature, and these possible faster movements of Ca have been also associated with changes in electrical and physical properties at Tg (Gruener et al. 2001).

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

IMPLICATIONS

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

- the role of Ca in a silicate glass network. The change of Ca role between network modifier (NM) to charge compensator (CC) is fundamental to better understand the large variations of physical properties previously observed in aluminosilicate glasses (Neuville 1992; Le Losq et al. 2014). Indeed, Ca as NM breaks Si-O-Si bonds, consequently decreases polymerization, viscosity, and Tg. At the same time, Ca as CC is close to Al$^{3+}$ in 4 or 5-fold coordination, and it helps the Al to be incorporated into the network, and consequently the polymerization, the viscosity and the Tg increase.

- redox impact on silicate structure modifications. Magnien et al. (2008) have shown that, at low temperature, the redox mechanism is mainly controlled by the movement of
divalent cations. Unfortunately, direct studies on Fe do not provide convincing information on the network connectivity. However, from the Ca pre-edge peak analysis, changes of the role of Ca from NM to CC could be identified depending on the presence or on the speciation of Fe. This variation of the role of Ca is associated with the need of Fe$^{3+}$ to be compensated, and it indicates that Fe$^{3+}$ acts in the network in a similar manner as Al$^{3+}$. Furthermore, the large variations of the oxygen distribution around Ca could explain the large variations of the redox mechanisms in silicate melts.

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

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References


Neuville, D.R. and Richet, P. (1991) Viscosity and mixing in molten (Ca,Mg) pyroxenes and

and Ca environment in calcium aluminosilicate glasses and crystals by Al and Ca K-edge


aluminosilicate glasses: effects of composition determined by 27Al MQ-MAS NMR and

Environments around Al, Si, and Ca in aluminate and aluminosilicate melts by X-ray
absorption spectroscopy at high temperature. American Mineralogist 93, 228-234.

applied to earth and material sciences. Reviews in Mineralogy and Geochemistry, 78, 509-
541.

diopside at 10 K. Canadian Mineralogist, 38, 183–189.

1–79.

Sowrey, F.E., Skipper, L.J., Pickup, D.M., Drake, K.O., Lin, Z., Smith, M.E., and Newport,
calcium K-edge XANES. Physical Chemistry Chemical Physics, 6, 188-192.

environments in silicate glasses by high-resolution 43Ca MQMAS NMR technique at high
Figure Captions

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

Figure 2: Plot of the Ca pre-edge peak centroid energy positions for aluminosilicate glasses in the CAS system with constant Si molar content (Ca50 and Ca76), and for Fe-free (WG) and Fe-bearing (WG1Rd and WG1Ox) soda-lime-silicate glasses. Moreover, a diopside composition (CM50) studied from room temperature to liquidus is reported (see text). The grey intervals indicate the regions where Ca is considered to behave only as network modifier (NM) or charge compensator (CC).
Figure 1a-d

(a) Normalised Absorption (arb. units)

Energy (eV)

(b) Normalised Absorption (arb. units)

Energy (eV)
Figure 2