

# Local Al site distribution in aluminosilicate glasses by $^{27}\text{Al}$ MQMAS NMR

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## Abstract

Coordination and local environment around Al in glasses and liquids is a long-standing question, which has been a controversial issue in geochemistry and glass science. Nuclear magnetic resonance at high-field (750 MHz) was employed to investigate the geochemically and industrially important CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system. We show that Al remains mainly in tetrahedral position in glasses, however, the presence of five-fold coordinated aluminum is the general rule throughout the ternary CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> system, except for the low silica percalcic region. The proportion of five-fold (Al<sup>V</sup>) and six-fold (Al<sup>VI</sup>) coordinated Al was quantified to determine the effects of composition overall the peralkaline part. Moreover our results indicate that Al may occupy more polymerized positions than Si. These two findings do put new questions to the modeling/understanding of these glasses and their parent liquids.

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## 1. Introduction

The structure of glasses remains a fundamental open question to understand physical properties of interest for earth sciences, glass and glass–ceramic industries. The CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (CAS) ternary system is important for geological and technological applications, due in particular to their high refractory, good optical [1] and mechanic properties [2]. In aluminosilicate glasses, it is generally concluded that both Si and Al are in tetrahedral coordination to oxygen. These (Si, Al)O<sub>4</sub> tetrahedra are corner-sharing through bridging oxygens (BO), forming aluminosilicate frameworks with varying degree of polymerization [3]. The structural role of Al is more complex due to the charge balancing requirement of the AlO<sub>4</sub><sup>−</sup> tetrahedra, which is usually achieved by a charge compensating alkali or alka-

line-earth cations [4]. The non-framework cations can also depolymerize the aluminosilicate networks by forming non-bridging oxygen (NBO), which play essential roles in many dynamic properties of melts [5]. However, it has been recently shown that this simple picture must be questioned since NBO [6] and Al<sup>V</sup> [7–10] do exist in tectosilicate compositions contrary to simple stoichiometric considerations. The presence of Al<sup>V</sup> has been shown experimentally [7], and 7% of Al<sup>V</sup> have been measured in a glass of anorthite composition (CaAl<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>) [8] even with different quench rates. This high amount of Al<sup>V</sup> implies that the presence of tricluster [11] to understand rheological variations around the M/Al = 1 join, is not ascertained for such composition. A tricluster corresponds to a tri-coordinated oxygen linked with three (Si, Al)O<sub>4</sub> tetrahedra. Though the existence of such triclusters has long been proposed to explain some physical properties of aluminosilicate glasses, considerable controversy exists because this species is very difficult to be detected. Only recently, the first direct

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evidence of triclusters in a  $0.50\text{CaO} \cdot 0.50\text{Al}_2\text{O}_3$  glass has been observed by NMR using a  $\{^{17}\text{O}\}^{27}\text{Al}$  Heteronuclear Multiple Quantum Correlation technique [12].

In the peraluminous glass composition [13] and on the  $\text{SiO}_2\text{--Al}_2\text{O}_3$  join [14] NMR and Raman spectroscopies evidence that excess aluminum yield the presence of  $\text{Al}^{\text{V}}$  and  $\text{Al}^{\text{VI}}$  with increasing proportions as  $\text{Al}_2\text{O}_3$  content increases. For these glasses,  $\text{Ca}^{2+}$  ions are not available for charge compensating the  $\text{AlO}_4$  tetrahedra and the glass neutrality is achieved by Al coordination change. In the per-alkaline-earth part, previous investigations concluded for the exclusive presence of  $\text{Al}^{\text{IV}}$  [4].

In this letter, we present a complete investigation of the Al environment in the CAS ternary system. Due to the increase sensitivity of high-field NMR, we show the possibility to detect small amounts of high-coordinated Al even in the per-alkaline-earth part. The proportion has been carefully obtained showing important variations with composition and the presence of such high-coordinated species should have important implications to explain physical properties such as transport of glasses and melts.

## 2. Experimental procedures

Per-alkaline-earth CAS glasses can be synthesized by classical techniques from pure aluminate to high-silica content, which make this ternary a model system to investigate structural parameters and physical implications of interest for other glass systems. The studied glasses (Fig. 1) were prepared by melting  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$  using classic and rapid quenching method. Glasses are labelled according to the chemical composition as  $\text{CA}x \cdot y$ , with  $x = \text{SiO}_2$ ,  $y = \text{Al}_2\text{O}_3$  and  $\text{CaO} = 100 - (x + y)$ . We mixed about 100 g of the appropriated mixture of  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  (Rectapur from Merck) for 1 h under alcohol in an agate mortar. The powder was heated slowly to decompose the carbonate and then heated up to 1900 K in covered Pt-alloy crucibles to avoid contamination, for a few hours in atmospheric condition. The sample was quenched in few seconds from high temperature by dipping the bottom of the platinum crucible into distilled water. From this method, quench rate was typically close than 15 K/s. Two sets of glasses (CA42.14 and CA50.25) were melted using aerodynamic levitation device using air as flowing gas and  $\text{CO}_2$  laser as a heating source [15]. With this device, estimated cooling rate was one order faster than previous quenching rate, 300 K/s.

$^{27}\text{Al}$  nuclear magnetic resonance (NMR) spectra have been obtained at high-field (17.6 T–750 MHz) using a Bruker AVANCE instruments equipped with high speed MAS probeheads (spinning rates of 30 to 33 kHz, aluminum free zirconia rotors of 2.5 mm diameter). The multiple quantum magic angle spinning (MQ-MAS) [16] experiments have been acquired using the shifted-echo pulse sequence with acquisition and processing of the full echo [17] and synchronized acquisition of the indirect dimension [18].

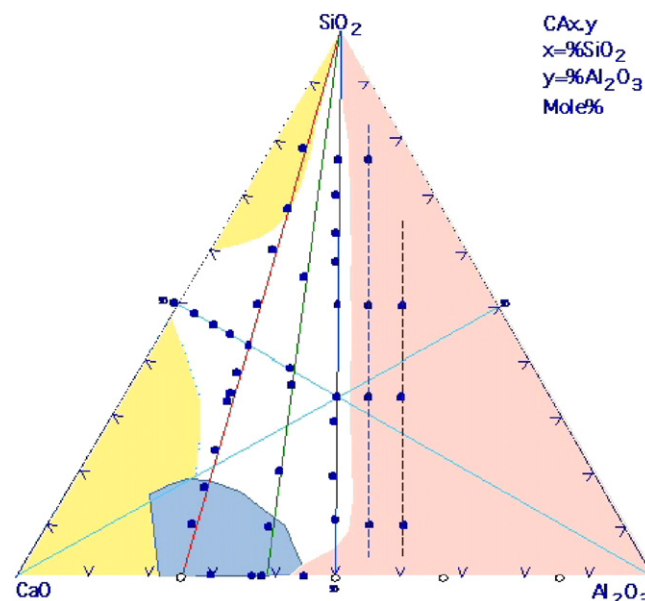


Fig. 1.  $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$  ternary system. Glasses are labelled according to the chemical composition as  $\text{CA}x \cdot y$  with  $x = \text{SiO}_2$ ,  $y = \text{Al}_2\text{O}_3$  and  $\text{CaO} = 100 - (x + y)$  in mol%. Glasses can only be obtained within the white zone using classic quenching method, while hyper-quenched glasses are in the rose region (in yellow zones, glasses can not be prepared). The blue zone near the  $\text{CaO--Al}_2\text{O}_3$  join, indicates the region where Al is observed in  $\text{Q}^2$  species (see text). In this region, few or no  $\text{Al}^{\text{V}}$  species are detected. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

## 3. Results and discussion

$^{27}\text{Al}$  2D NMR spectra of four glasses along the join  $R = 3$  (CA60.10, CA42.14, CA16.21 and CA0.25) are shown in Fig. 2. In previous studies carried out at moderate magnetic fields, quadrupolar broadening were so severe that they caused strong overlap, obscuring the spectral resolution, and preventing detection of minor species. The use of the 17.6 T high-field allows reduction of second-order quadrupolar broadening and enhances chemical shift distribution, which enables a more accurate description of the Al environment.

The CA60.10 and CA42.14 spectra present two distinct contributions: a dominant contribution centered at  $\delta_{\text{iso}}$  63.4 and 68.9 ppm and a second one centered at 38.7 and 33.6 ppm respectively for the two glass compositions. These two signals are assigned to  $\text{Al}^{\text{IV}}$  (higher chemical shift) and  $\text{Al}^{\text{V}}$  (lower chemical shift) [19], respectively. A careful evaluation [20,21] of the proportion of each species indicates 8 and 5% of  $\text{Al}^{\text{V}}$  in CA42.14 and CA60.10 glasses, respectively. On the contrary for the glasses containing low-silica (CA16.21 and CA0.25), Al is present only in tetrahedral sites with no detectable amount of high-coordinated species. Moreover, the chemical shifts for  $\text{Al}^{\text{IV}}$  appear at significantly higher values, 80.4 and 82.8 ppm for CA16.21 and CA0.25, respectively.

The isotropic chemical shift,  $\delta_{\text{iso}}$ , for  $\text{Al}^{\text{IV}}$  presents a strong dependence with composition and similar variations

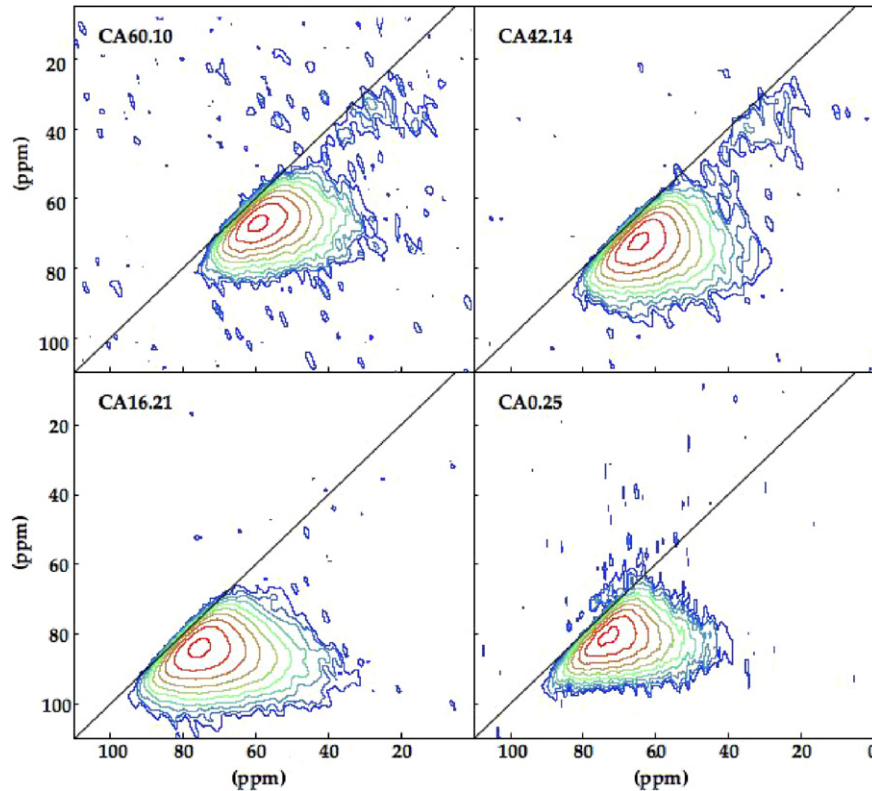


Fig. 2. Contour plots of  $^{27}\text{Al}$  3QMAS NMR spectra collected at 17.6 T for CA60.10, CA42.14, CA16.21, CA0.25 glasses. The plain curve represents chemical shift axis.

for all joins (Fig. 3). At high-silica content ( $\text{SiO}_2 > 45$  mol%), the  $\text{Al}^{\text{IV}}$  chemical shift increases with decreasing silica content but present close values for the different joins. Chemical shifts are well known to be affected not only by local ordering but also by intermediate-range structure. The decrease of the  $\text{Al}^{\text{IV}}$   $\delta_{\text{iso}}$  can thus be simply related

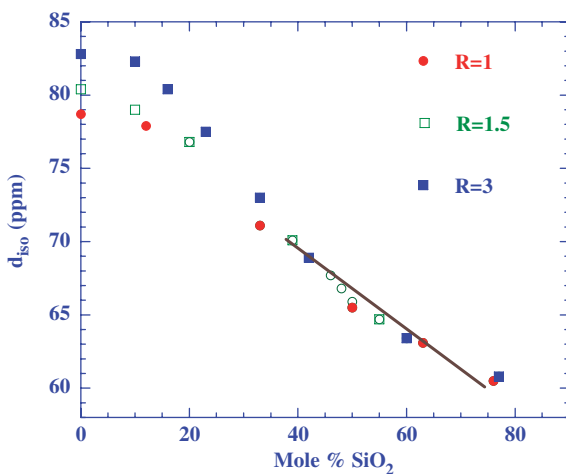


Fig. 3. Dependence of the isotropic chemical shifts,  $\delta_{\text{iso}}$ , for  $\text{Al}^{\text{IV}}$  as a function of  $\text{SiO}_2$  content for the three joins  $R = \text{CaO}/\text{Al}_2\text{O}_3 = 1, 1.5$  and  $3$ . The line is only a guide for the eye showing the linear dependence with  $\text{SiO}_2$  content of  $\delta_{\text{iso}}$ , for more than 45 mol%  $\text{SiO}_2$ . Errors are estimated to be  $\pm 0.5$  ppm and are the size of the symbols.

to changes in the nature of second Si/Al neighbors around  $\text{AlO}_4$  tetrahedra. The similar values for the three joins are consistent with the high polymerized nature of the aluminosilicate network involving Al mainly in  $\text{Q}^4$  species [22], with lower  $\delta_{\text{iso}}$  values for high number of Si neighbors, like in the case of Si  $\text{Q}^n$  species.

At lower  $\text{SiO}_2$  content ( $\text{SiO}_2 < 45$  mol%), the  $\text{Al}^{\text{IV}}$  isotropic chemical shift follows a linear variation but with different slopes depending on the join considered: higher values are observed as the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio increases. Since only along the join  $R = 1$ , aluminosilicate network can be considered as fully polymerized, variations for the two other joins should have a different origin than the substitution of Si by Al as second neighbors around  $\text{AlO}_4$  tetrahedra.

Three calcium aluminate glasses were prepared (CA0.25, CA0.39 and CA0.50) using high and low quench-rate.  $\text{Al}^{\text{IV}}$  chemical shift for these three glasses are 82.8, 80.4 and 78.7 ppm, respectively, which corresponds to a linear variation as a function of  $\text{Al}_2\text{O}_3$  content. X-ray absorption spectroscopy has shown that Al is present in distinct environment in these glasses [23]: in CA0.25, Al is in depolymerized species  $\text{Q}^2$ , while, in CA0.39, Al is in more polymerized sites  $\text{Q}^3$  and  $\text{Q}^4$  and, in CA0.50, Al is in fully polymerized  $\text{Q}^4$  species. Therefore, the chemical dependence of the  $\text{Al}^{\text{IV}}$   $\delta_{\text{iso}}$  (Fig. 3) can be related to Al present in different  $\text{Q}^n$  species. These findings are thus a likely evidence for a relationship between the  $\delta_{\text{iso}}$  values and the  $\text{Q}^n$

speciation of Al in glasses. It could provide valuable information on the polymerization state of the aluminosilicate network in relation with physical properties. For instance, in glasses with low-silica content, previous experimental and theoretical studies [23,24] have shown speciation of Al in different  $Q^n$  species with composition, which has been related to anomalous variations in the glass transition temperature [24].

Unexpectedly,  $Al^V$  is observed in all the glass forming region, except in the very low-silica ( $SiO_2 < 16\%$ ) – CaO rich percalcic part. The proportion of  $Al^V$  shows a clear dependence with the glass composition. A maximum of  $Al^V$  is found for all joins between 30 and 50 mol%  $SiO_2$  (Fig. 4). The smaller amount of  $Al^V$  is found along the join  $R = 1.5$ . For peraluminous glasses ( $R < 1$ ), the proportion of  $Al^V$  is higher than in the per-calcic region, which is expected given that not enough Ca is present to ensure charge compensation of  $AlO_4$  tetrahedra. In Fig. 4, it is clear that the highest proportion of  $Al^V$  is found for 50 mol%  $SiO_2$  (CA50.40). With excess aluminum ( $R < 1$ ), the quantity of  $Al^V$  increases noticeably, and most of the Al atoms in excess are encountered in  $Al^V$  sites. These results are in good agreement with those observed on Mg peraluminous glasses where up to 6% of  $Al^V$  were detected [10]. The concentration of  $Al^V$  systematically increases with decreasing the CaO/ $Al_2O_3$  ratio at constant silica content. A small amount of  $Al^{VI}$  (2.6%) is detectable for the CA33.50 and CA50.40 peraluminous glasses and more surprisingly for the CA48.03 glass (1.9%) that is the composition the closest to wollastonite glass (CA50.00). The minor amount of  $Al^{VI}$  is in good agreement with earlier prediction [11] that rejected this possibility on the basis of packing arguments. However, the existence of  $Al^{VI}$  has been detected in CAS glasses near the  $SiO_2$ – $Al_2O_3$  join [13,14].

We can propose a model for the distribution of Al in CAS glasses as a function of  $SiO_2$  content and R:

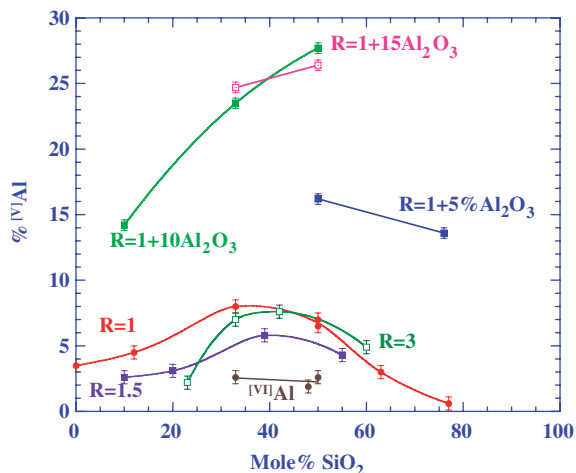


Fig. 4. Proportion of  $Al^V$  and  $Al^{VI}$  as a function of  $SiO_2$  content. Lines are guide for the eye only.

- $x > 40$  mol%  $SiO_2$ , and  $1 < R < 3+$  (join 3 and wollastonite glass with very low amount of  $Al_2O_3$ ): Al is in  $Q^4$  species with 7–8% of  $Al^V$  in all glasses without quenching rate effect (15 or 300°/s)[25].
- $x < 40$  mol%  $SiO_2$ , and  $R = 1.5$ : along this join Al is in  $Q^4$  species at high-silica content, and progressively in  $Q^3$  species with decreasing  $SiO_2$  content. For these glasses, less than 5% of  $Al^V$  were found except for the CA0.39 where only  $Al^{IV}$  is present.
- $x < 40$  mol%  $SiO_2$ , and  $R = 3$ : along this join Al is in  $Q^4$  species at high-silica content, and progressively in depolymerized species ( $Q^2$ ) with decreasing  $SiO_2$  content. Only  $Al^{IV}$  is present for glasses containing less than 16 mol% of  $SiO_2$ .
- For peraluminous glasses,  $Al^{IV}$  is present in  $Q^4$  species and is the dominant species but the content of  $Al^V$  species increases with excess alumina up to 20%.

The presence of  $Al^V$  is important to understand the macroscopic dynamics of the liquid state. In glasses near the tectosilicate compositions, the proportion of  $Al^V$  suggests that the existence of O triclusters is not required to explain the variations in viscosity observed for Na aluminosilicate melts [10]. Furthermore, Si and Al with extra O neighbors have often been suggested as transition states in viscous flow in silicate liquids [5,26]. These defects or transient species facilitate the local redistribution of bridging and non-bridging oxygens and are probably fundamental species by which viscous flow occurs, at least in melts with high content of network forming oxides. The important amount of  $Al^V$  detected in our study can be explained by the fact that Al cations are larger than Si cations and generally have less net positive charge so that Al–O bonds are generally weaker and even more likely to be broken during flow than Si–O bonds. Moreover, the presence of  $Al^V$  within the aluminosilicate framework can have an influence on the rheological properties at the glass transition temperature ( $T_g$ ). Since this species is preserved during the quench at the  $T_g$ , it is likely that they would be more abundant at higher temperature as expected for a high-energy defect.

At low-silica and high CaO content, such high-coordinated species are no more observed and this could be the first evidence for a different mechanism for liquid relaxation and flow. These glasses are characterized by a high number of NBO and a highly depolymerized network that can be viewed as polymerized clusters whose surfaces would consist primarily of  $Q^2$  or  $Q^3$  sites associated with weak bonds between NBO and  $Ca^{2+}$  ions. The relative motion of these clusters could explain viscous flow with little (Si, Al)–O bond breaking or silicate species exchange, contrary to relatively rich silica melts. This peculiar behavior could be of interest for designing new environmental friendly glass fibers [2].

A few percent of  $Al^{VI}$  have been evidenced in Na-aluminosilicate glasses by MAS NMR, though resolution at that time prevents a direct observation of  $Al^V$  contribution that could be blurred by the  $Al^{IV}$  one [27]. This indicates

that the presence of high-coordinated species is likely to be present, in minor amounts, in most aluminosilicate glasses. Therefore, the tetrahedral Al coordination must clearly be taken as a first approximation in glass models. A correct calculation of average  $Q^n$  species or NBO to tetrahedral ratio is thus complicated by the presence of  $Al^V$  and/or  $Al^{VI}$ . We have seen that these species control macroscopic transport properties in the liquids but they also contribute to the topological disorder of the glassy network, which may affect some physical properties. Other defects may also exist in some part of the ternary diagram and, for instance, the presence of tricluster has been recently evidenced in a CA0.50 glass by  $^{17}O$  NMR [12]. The chemical dependence of the proportion of  $Al^V$  along a join (Fig. 3) is unclear and it would be desirable to understand which factors are important in stabilizing this species. The role of  $Al^V$  and  $Al^{VI}$  as possible network former still remains a controversial issue that will need further investigation. These new data strengthen the presence of high-coordinated Al species in glasses and challenge classical models of oxide glasses, to understand physical and thermodynamical properties of glasses and melts.

#### 4. Conclusions

$^{27}Al$  Nuclear magnetic resonance spectra at high-field (750 MHz) were obtained on glasses in the ternary  $CaO-Al_2O_3-SiO_2$  system. These spectra indicate that Al is mainly present in tetrahedral position in these CAS glasses. Variations of the  $^{41}Al$  chemical shifts with compositions are related to different polymerized environment around  $AlO_4$  tetrahedra. Small amounts ( $\sim 5\%$ ) of five-fold coordinated aluminum are found in all the ternary system, except for the low-silica percalcic region. Important variations of  $^{51}Al$  with compositions have been carefully quantified. The amount of  $^{51}Al$  does not seem dependent of the quenching rate. This high-coordinated species is important to understand the transport properties of these glasses and melts and their absence for the low-silica glasses, which are highly depolymerized, could evidence a viscous flow process associated with non-bridging oxygens. These findings show that Al has a complicated environment in glasses that should be taken into account in glass models since the presence of high-coordinated species should affect their physical or thermodynamics properties.

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