Contents lists available at ScienceDirect

### **Chemical Geology**

journal homepage: www.elsevier.com/locate/chemgeo

# Structure of type A CAI-like melts: A view from multi-nuclear NMR study of melilite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>-Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) glasses



Sun Young Park<sup>a,b,\*</sup>, Changkun Park<sup>a</sup>, Hyun Na Kim<sup>c</sup>, Seoyoung Lee<sup>d</sup>, Sung Keun Lee<sup>d</sup>

<sup>a</sup> Division of Earth-System Sciences, Korea Polar Research Institute, Incheon 21990, Republic of Korea

<sup>b</sup> Oil & Gas Research Center, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Republic of Korea

<sup>c</sup> Department of Earth Environmental Sciences, Kongiu National University, Gongiu 32588, Republic of Korea

<sup>d</sup> School of Earth and Environmental Sciences, Seoul National University, Seoul 08826, Republic of Korea

### ARTICLE INFO

Keywords: Melilite glasses and melts Structure and disorder High-resolution solid-state nuclear magnetic resonance Viscosity and diffusivity

### ABSTRACT

Exploring the polymerization and structural disorder of Ca-Al-rich inclusion (CAI)-like melts is a key question in cosmochemistry due to strong implications for macroscopic properties of melts (i.e., viscosity and diffusivity). Here, we report experimental results showing the effect of composition on the structure of mellilte glasses and melts [åkermanite (Åk, Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) - gehlenite (Gh, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>)] in type A CAIs with varying composition using high-resolution solid-state nuclear magnetic resonance (NMR). The <sup>27</sup>Al magic angle spinning (MAS) and 3Q (triple quantum) MAS NMR spectra of mellilte glasses show predominant <sup>[41</sup>Al. A non-negligible fraction of <sup>[51</sup>Al is observed in Åk<sub>50</sub>Gh<sub>50</sub> and Åk<sub>72</sub>Gh<sub>28</sub> glasses and it slightly increases with increasing åkermanite content. The <sup>17</sup>O 3QMAS NMR spectra of mellilte glasses show that bridging oxygens (BOS, Si–O–Si, Al–O–Al, and Si–O–Al) and non-bridging oxygens (NBOs, Ca–O-Si, Ca–O-Al, and mixed {Ca, Mg}–NBO) are partially resolved. Despite the strong preference of Si over Al for NBOs, for the first time, Ca–O-Al is observed in natural melts (i.e., gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses and melts). The results show that Al-NBO (~150 ppm in MAS dimension) can be distinguished from Si-NBO (~110 ppm) in melilite glasses and melts. The fraction of NBO increases with increasing åkermanite content. The experimental results suggest that composition-induced structural changes should be considered to interpret the melt viscosity, diffusivity, and oxygen isotopic composition of CAI-like melts in the early Solar System.

### 1. Introduction

Ca-Al-rich inclusions (CAIs), submillimeter to centimeter-sized clasts in chondrite, are known to be the oldest objects in the Solar System, thus probing the formation process of CAI provides insight into understanding the early evolution of our Solar System (MacPherson et al., 2005, and references therein). After the formation of CAIs at the early evolution of the Solar System, repeated melting and secondary alteration occurs in the nebular and on asteroidal parent bodies (MacPherson et al., 2005). The history of these events can be obtained from the oxygen isotopic composition of CAIs. CAIs are classified into type A, B, and C with composition. Spinel and melilite are predominant in type A CAIs and diopside is additionally observed in type B CAIs. Type C CAIs are anorthite and pyroxene-rich and melilite-poor (MacPherson, 2014, and references therein). The precursor melts of CAIs are inferred as Ca-rich Ca–Mg aluminosilicate system based on their mineral assemblage. The crystallization sequence for type A CAI

melts is known to spinel followed by melilite (Stolper, 1982, and references therein). Thus, the composition of remaining melts represents the composition of the melilite after the spinel crystallizes. The melilite in CAIs is binary solid-solution gehlenite (Gh, Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) - åkermanite (Åk, Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>) with thermal minimum at ~72 mol% of åkermanite. The composition of melilite in CAIs is relatively simple comparing to terrestrial igneous melilite mineral including iron and sodium (Grossman, 1975). According to the phase diagram of melilite, the Alrich melilite crystallizes first, thus the composition of remaining melts becomes åkermanite-rich as the temperature decreases (Osborn and Schairer, 1941).

One of the unsolved questions in type A CAIs is the variable oxygen isotopic compositions of melilite and spinel. Oxygen isotopic compositions of spinel in type A CAIs are uniformly <sup>16</sup>O-rich, whereas those of melilite are relatively <sup>16</sup>O-poor and variable. In some igneous type A CAIs, melilite shows oxygen isotopic variation in a single crystal, which has been explained by oxygen isotope exchange either between gas and

\* Corresponding author at: Oil & Gas Research Center, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Republic of Korea. *E-mail address:* sunyoung@kigam.re.kr (S.Y. Park).

https://doi.org/10.1016/j.chemgeo.2020.119894

Received 2 March 2020; Received in revised form 8 September 2020; Accepted 15 September 2020 Available online 16 September 2020 0009-2541/ © 2020 Elsevier B.V. All rights reserved. melt in the solar nebula (Aléon et al., 2007; Yurimoto et al., 1998), or between melilite crystal and aqueous fluid on the CV parent body (Krot et al., 2019). Nevertheless, the origin of variable isotopic composition in melilite has not been fully understood yet. In addition, the changes in viscosity and diffusivity of melilite melts with composition have not been considered to understand the variable isotopic composition in melilite melts.

The relationship between the macroscopic properties and atomic scale structures of silicate melts has been well known (Kelsey et al., 2008; Le Losq and Neuville, 2017; Lee, 2011; Malfait et al., 2012; Mysen and Richet, 2019: Navrotsky et al., 1983: Neuville et al., 2006: Neuville et al., 2008: Toplis and Dingwell, 2004: Xue and Kanzaki, 2008, and references therein). For examples, the network connectivity of silicate melts plays an essential role in determining the viscosity and diffusivity, which can be quantified with the fraction of non-bridging oxygens (NBOs) in melts (e.g., Bottinga et al., 1995; Giordano et al., 2009; Lee et al., 2004). The fraction of NBO in silicate melts varies with their composition. For instance, previous nuclear magnetic resonance (NMR) studies for atomic structure of model basaltic [CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) and CaO-MgO-Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>] and andesitic (CaO-MgO-Na2O-Al2O3-SiO2) melts have shown that the fraction of NBO increases with increasing Mg content (Park and Lee, 2012, 2014, 2018). Those studies suggest that the viscosity of model basaltic and andesitic melts would decrease with increasing Mg content, and thus NBO fraction. The trend is consistent with experimental data on the viscosity for CMAS melts in diopside-anorthite join (Gaudio and Behrens, 2009). Diffusivity of network former in silicate melts also depends on the composition (Lesher, 2010, and references therein). The results have shown that the oxygen diffusivity of silicate melts increases with NBO/T (Lesher, 2010, and references therein). The CAI-like melts would also show similar results: their viscosity and oxygen diffusivity should depend on their composition, especially Mg content in melilite composition. The objective of this study is to unveil the atomic structures including the degree of network connectivity, and structural disorder in type A CAI-like melts (i.e., melilite melts) with varying composition to reveal the relationship between structures and properties (e.g., viscosity and oxygen diffusivity). This allows us to constrain the oxygen isotopic variations within type A CAI minerals with respect to the isotope diffusion rate in the melts.

The most common approach to understanding melt structure is to study glasses quenched from liquids. A glass captures the structure of the liquid at the glass transition temperature, although the effect of temperature on the glass structure has been probed, which often shows minor but detectable structural differences (Stebbins et al., 2008). High-resolution solid-state NMR spectroscopy is effective in probing the atomic structures of silicate glasses including complex multi-component Ca-Mg aluminosilicate glasses (Allu et al., 2018; Glatz et al., 2019; Jaworski et al., 2016; Lee and Lee, 2020; Park and Lee, 2018; Sukenaga et al., 2017). The results for those multi-component glasses include the bonding preference between network-modifying cations and NBOs and/ or bridging oxygens (BOs) (Kelsey et al., 2008; Lee and Sung, 2008; Park and Lee, 2018, and references therein), coordination numbers of framework cations (e.g., Al) (Bista et al., 2015; Lee and Lee, 2020; Malfait et al., 2012; Neuville et al., 2006; Neuville et al., 2008; Park and Lee, 2014; Xue and Kanzaki, 2008). Previous <sup>27</sup>Al and <sup>29</sup>Si magic angle spinning (MAS) NMR study for melilite-based CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses suggested that <sup>[4]</sup>Al and <sup>[4]</sup>Si are predominant and significant fraction of Si-O-Al and NBOs are expected (Allu et al., 2018).

Despite the progress, there are still unsolved structural problems in multi-component silicate glasses and melts. For examples, NBOs in the silicate glasses studied so far are mainly bonded to Si instead of Al (Allwardt et al., 2003; Mysen and Richet, 2019; Stebbins et al., 2001). Nevertheless, a significant fraction of Al-NBO is observed in Si-poor and Ca-rich aluminosilicate glasses (Allwardt et al., 2003) and rare earth element (REE) bearing aluminosilicate glasses (Iftekhar et al., 2012; Jaworski et al., 2016). Recent simulation studies also predicted a significant fraction of Al-NBO (up to ~12%) in CMAS glasses (38.7CaO-9.7MgO-12.9Al<sub>2</sub>O<sub>3</sub>-38.7SiO<sub>2</sub> and 48.6CaO-8.3MgO-8.4Al<sub>2</sub>O<sub>3</sub>-34.7SiO<sub>2</sub>) (Ganisetti et al., 2019; Gong et al., 2019). However, it is not yet known whether Al-NBO exists in natural type A CAI-like melts.

In this study, we reveal the Al coordination environments, bonding preference of NBOs between Si and Al (i.e., Ca-O-Al and Ca-O-Si), and the role of cations (i.e.,  $Mg^{2+}$  and  $Ca^{2+}$ ) in melilite glasses with varying composition using high-resolution  $^{27}Al$  and  $^{17}O$  solid-state NMR. Finally, we discuss the structural evolution of melilite glasses and melts with varying composition with the implication for the changes in melt structures and properties. We explore the change of NBO fraction with åkermanite content to predict the change of viscosity with composition. Additionally, the viscosity and the diffusivity are inversely related, we try to reveal the origin of variable isotopic compositions observed in type A CAIs (Aléon et al., 2007), through the change of  $O^{2-}$  diffusivity in the melts.

### 2. Experimental methods

#### 2.1. Glass synthesis

A series of <sup>17</sup>O-enriched melilite glasses along the åkermanite–gehlenite join containing 0, 25, 50, 72, and 100 mol% åkermanite components were synthesized from carbonate (CaCO<sub>3</sub>) and oxide powders (MgO, Al<sub>2</sub>O<sub>3</sub>, <sup>17</sup>O-enriched SiO<sub>2</sub>) using high-temperature furnace at Kongju National University. The <sup>17</sup>O-enriched SiO<sub>2</sub> was prepared by hydrolyzing SiCl<sub>4</sub> in 40% <sup>17</sup>O-enriched water. The Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> powders were dried at 300 °C; MgO and <sup>17</sup>O-enriched SiO<sub>2</sub> were dried at 1000 °C for 1 h in an Ar environment. The weighed powders were mixed by grinding in an agate mortar during 10 min, and then decarbonated in a Pt crucible at 800 °C for 30 min. The samples were then melted above their melting temperature (1550–1700 °C) for 30 min, in an Ar environment and quenched into glasses by plunging the bottom of the Pt crucible into a water bath.

### 2.2. Electron microprobe (EPMA) analysis

The compositions of synthetic melilite glasses were measured with a field emission EPMA (FE-EPMA, JEOL JXA-8530F) at the Korea Polar Research Institute, using 15 keV accelerating voltage, 20 nA beam current, and beam size of ~5  $\mu$ m. Natural mineral standards from Smithsonian and JEOL including periclase (MgO), quartz (SiO<sub>2</sub>), anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), and wollastonite (CaO) were used as standards for silicate minerals. Counting times on peak were 20 s. The  $\phi(\rho Z)$  method of Armstrong/Love Scott were used to correct background and matrix effects (Armstrong, 1988). Element detection limits (3 $\sigma$ ) with JXA-8530F (wt%) were SiO<sub>2</sub> (0.02), Al<sub>2</sub>O<sub>3</sub> (0.01), MgO (0.01), and CaO (0.005). Table 1 shows the nominal compositions and the chemical compositions of melilite glasses determined by EPMA, which are close to the nominal compositions.

### 2.3. NMR spectroscopy

The <sup>27</sup>Al and <sup>17</sup>O MAS and triple quantum (3Q) MAS NMR spectra of glasses were collected using a Varian solid-state NMR 400 system (9.4 T) at 104.229 MHz with a 3.2 mm Varian double-resonance probe (Seoul National University, Korea). The relaxation delay for <sup>27</sup>Al MAS NMR were 0.8 s and the radio frequency (rf) pulse strength was 0.3  $\mu$ s. A fast amplitude modulation (FAM)-based shifted echo pulse sequence (consisting of two hard pulses with durations of 3.0 and 0.7  $\mu$ s and a subsequent soft pulse with a duration of 15  $\mu$ s) was used in <sup>27</sup>Al 3QMAS NMR (e.g., Baltisberger et al., 1996). Approximately 192–2688 scans were averaged to achieve the signal-to-noise ratio shown in the 3QMAS NMR spectra. The spectra were referenced to 0.3 M AlCl<sub>3</sub> (aq). Sample spinning speeds of 18 kHz were used. The <sup>17</sup>O MAS and 3QMAS NMR spectra of melilite glasses were collected at a Larmor frequency of

#### Table 1

Composition (mol%)		CMAS mol% (Nominal composition)				CMAS mol% (Determined by EPMA)				
		CaO	MgO	$Al_2O_3$	$SiO_2$	NBO/T <sup>a</sup>	CaO	MgO	$Al_2O_3$	$SiO_2$
X <sub>Åkermanite</sub>	0	50.0	0.0	25.0	25.0	0.7	50.0	0.0	25.1	24.9
	25	47.1	5.9	17.6	29.4	1.1	47.2	6.1	17.6	29.1
	50	44.4	11.1	11.1	33.3	1.6	44.5	11.0	11.1	33.4
	72	42.4	15.3	5.9	36.4	2.1	42.5	15.1	5.9	36.5
	100	40.0	20.0	0.0	40.0	3.0	40.2	20.0	0.0	39.8

Nominal composition and EPMA analyses of melilite (åkermanite-gehlenite join) glasses. Xåkermanite is the mole fraction of åkermanite.

<sup>a</sup> NBO/T = 2 \* { $X_{(CaO+MgO)} - X_{Al2O3}$ } / [1 - { $X_{(CaO+MgO)} - X_{Al2O3}$ }].

54.229 MHz, using a 4 mm Doty double-resonance probe. The relaxation delay for <sup>17</sup>O MAS NMR were 1 s and the radio frequency pulse strength was 0.4  $\mu$ s. Sample spinning speeds of 14 kHz were used. In the 3QMAS NMR experiment at 9.4 T, a FAM-based shifted echo pulse sequence with a hard pulse of duration 4.5  $\mu$ s for multiple-quantum excitation and two 1.1  $\mu$ s pulses for single quantum reconversion, a soft pulse of duration approximately 20  $\mu$ s, and an echo time of approximately 500  $\mu$ s (integer multiple of a rotor period) was used with a relaxation delay of 1 s. Approximately 4980–8064 scans of free-induction decay (FID) were averaged to achieve the signal-to-noise ratio shown in the <sup>17</sup>O 3QMAS NMR spectra. Approximately 60 FIDs were collected to construct the 2D spectra. The spectra were referenced to external tap water. The rf field strengths for hard pulses for <sup>27</sup>Al 3QMAS and <sup>17</sup>O 3QMAS NMR are approximately 125 and 75 kHz, respectively.

### 3. Results

## 3.1. Al environments of melilite ( $Ca_2Al_2SiO_7$ - $Ca_2MgSi_2O_7$ ) glasses and melts: <sup>27</sup>Al MAS and 3QMAS NMR results

Fig. 1 shows the <sup>27</sup>Al MAS NMR spectra for melilite glasses with varying åkermanite content. A single asymmetric peak, generally centered at ~60 ppm is observed in all spectra suggesting that <sup>[4]</sup>Al is dominant in all the glasses. The peak maximum of <sup>27</sup>Al MAS NMR spectra slightly decreases with increasing åkermanite content from ~62 ppm at gehlenite glass to ~59 ppm at Åk<sub>72</sub>Gh<sub>28</sub> glass. The long tails extending to lower frequency are due to the distributions of the



Fig. 1.  $^{27}$ Al MAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite.

quadrupolar coupling constant (C<sub>a</sub>) and the isotropic chemical shift  $(\delta_{iso})$  of Al environments in the glasses. Because the <sup>27</sup>Al MAS NMR spectra are obtained at 9.4 T, the effect of quadrupolar interaction can be dominant. Nevertheless, those results indicate that the extensive disorder is observed in melilite glasses because the observed peak width (~46 ppm) in MAS dimension of melilite glasses is much broader than that for Ca-Na aluminosilicate glasses (Lee, 2011; Lee et al., 2005). Fig. 2 shows <sup>27</sup>Al 3QMAS NMR spectra for melilite glasses with varying mole fractions of åkermanite. The predominant <sup>[4]</sup>Al and a small fraction of <sup>[5]</sup>Al are observed. Current peak assignments are based on the previous NMR studies for aluminosilicate glasses (Baltisberger et al., 1996, and references therein). <sup>[4]</sup>Al is observed at  $\sim -45$  ppm and <sup>[5]</sup>Al is observed at  $\sim -25$  ppm in isotropic dimension. The  $^{27}$ Al 3QMAS NMR spectra of gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses show only <sup>[4]</sup>Al and those of  $Åk_{50}Gh_{50}$  and  $Åk_{72}Gh_{28}$  glasses show a non-negligible fraction of <sup>[5]</sup>Al. The fraction of <sup>[5]</sup>Al slightly increases from  $Åk_{50}Gh_{50}$  to Åk72Gh28 glass. While [6]Al is not clearly shown in the 27Al 3QNMR spectra, there could be a minor fraction of <sup>[6]</sup>Al in Åk<sub>72</sub>Gh<sub>28</sub> glass (i.e., Mg-rich composition). Previous study for glasses in diopside-Catschermakite join showed non negligible intensity at  $\sim -5$  ppm in isotropic dimension (the expected peak positions for <sup>[6]</sup>Al) in Mg-rich composition (the mole fraction of diopside is 0.75) (Park and Lee, 2012). A minor fraction of <sup>[6]</sup>Al is not resolved in Åk<sub>72</sub>Gh<sub>28</sub> glass due to ~0.5% detection limit in 2D NMR spectra. The peak maximum of [4]Al moves from  $\sim -62$  ppm (Ak<sub>0</sub>Gh<sub>100</sub>) to  $\sim -59$  ppm (Åk<sub>72</sub>Gh<sub>28</sub>) in the isotropic dimension.

Fig. 3 shows the total isotropic projections of the <sup>27</sup>Al 3QMAS NMR spectra for melilite glasses with varying åkermanite content. The figure confirms that <sup>[4]</sup>Al is dominant in all the glasses. The peak maximum of <sup>[4]</sup>Al in the isotropic projection slightly shifts towards higher frequency (from  $\sim -49$  ppm to  $\sim -46$  ppm) with increasing åkermanite content. Those shifts are due to the increase of  $Q^4_{Al}(4Si)$  and/or  $Q^4_{Al}(3Si)$  with increasing Si/Al ratio in the glasses from 2.0 at Åk<sub>0</sub>Gh<sub>100</sub> glass to 12.3 at  $Åk_{72}Gh_{28}$  glass based on the peak position of  $Q_{A1}^{n}(mSi)$  (Lee and Stebbins, 2000). Here, Q<sup>n</sup><sub>Al</sub>(mSi) refers to a Al species with n bridging oxygens and m (0-4) Si as the next nearest neighbors. The peak position of Q<sup>4</sup><sub>Al</sub>(mSi) in isotropic dimension decreases with increasing m (0-4) (Lee and Stebbins, 2000, and references therein). The similar results were observed for CMAS glasses in diopside-Ca-tschermakite join (Park and Lee, 2012). The measured peak width for <sup>[4]</sup>Al in the isotropic projection slightly increases from ~13 ppm at Åk<sub>0</sub>Gh<sub>100</sub> glass to ~16 ppm at Åk72Gh28 glass with increasing åkermanite content. Those results are from an increase of dispersion in Q<sub>Al</sub><sup>4</sup> species distribution (Park and Lee, 2012).

### 3.2. Effects of composition on network connectivity in melilite glasses and melts: insights from <sup>17</sup>O MAS and 3QMAS NMR results

The peak assignments for the oxygen clusters in the <sup>17</sup>O MAS and 3QMAS NMR spectra are based on the previous reports on binary, ternary, and quaternary silicate glasses (Allwardt et al., 2003; Lee et al., 2016; Park and Lee, 2012). While NBO and BO peak positions slightly vary with composition, peaks positions for three types of BOs (Si–O–Si,



Fig. 2. <sup>27</sup>Al 3QMAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite. Contour lines are drawn at 5% intervals from relative intensities of 8% to 88% with added lines at 2%, 3%, and 5%.

Al–O–Al, and Si–O–Al) in <sup>17</sup>O 3QMAS NMR spectra for quaternary silicate glasses at 9.4 T have been well constrained (Kelsey et al., 2008; Park and Lee, 2012, 2018). The peak positions and structurally relevant NMR parameters (i.e.,  $C_q$  and isotropic chemical shift) for various NBOs (Ca-O-Al, Ca–O–Si, {Ca, Mg}–O–Si, and Mg-O-Si) in silicate glasses were also reported in the previous <sup>17</sup>O NMR study for ternary Ca–Mg silicate glasses, Ca-aluminosilicate glasses, quaternary Ca–Mg aluminosilicate glasses, and complex multi-component silicate glasses (Allwardt et al., 2003; Allwardt and Stebbins, 2004; Kelsey et al., 2008; Park and Lee, 2012, 2014, 2018; Stebbins and Xu, 1997).

Fig. 4 shows the <sup>17</sup>O MAS NMR spectra for melilite glasses with varying åkermanite content. The <sup>17</sup>O MAS NMR spectrum of gehlenite glass shows the presence of Si-NBO (Ca–O–Si) peak at ~99 ppm consistent with previous study (Allwardt et al., 2003; Lee and Stebbins, 2006). Similarly, a non-negligible fraction of NBO has been observed in a fully polymerized Ca-aluminosilicate glasses including anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) (Stebbins and Xu, 1997) and Ca-tschermakite (CaAl<sub>2</sub>SiO<sub>6</sub>) (Park and Lee, 2012; Stebbins et al., 1999) composition glasses. In addition to the typical NBO peak (Ca-O-Si), an additional broad shoulder feature at ~150 ppm is observed in gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses. The peak is possibly due to Al-NBO (Ca-O-Al) (Allwardt et al.,

2003; Lee et al., 2009). In this study, the first  $^{17}$ O MAS NMR spectra for melilite glasses reveal that Al-NBO can be generated in CAI-like melts despite higher energy penalty (see Section 4.3 for the detailed discussion).

Si–O–Si and {Ca, Mg}-mixed NBO are partially resolved in the <sup>17</sup>O MAS NMR spectrum for åkermanite glass. NBO peak positions move to lower frequency from Ca–O–Si (~107 ppm) to Mg–O–Si (i.e., Mg–NBO at ~35 ppm) (Allwardt and Stebbins, 2004; Lee et al., 2016). Those in quaternary CMAS glasses at the intermediate composition show varying fractions of Ca–O–Si and {Ca, Mg}–O–Si (Allwardt and Stebbins, 2004; Park and Lee, 2012). As Mg–O–Si peak overlaps with other NBO and BO peaks in the glasses, those are not resolved in all the glasses. The peak shape and width for each oxygen sites change with increasing åkermanite content, suggesting changes in oxygen cluster populations. As considerable overlaps among BO and NBO peaks make it difficult to estimate quantitatively the changes in their fractions, those predictions are qualitative.

Fig. 5 shows <sup>17</sup>O 3QMAS NMR spectra for melilite glasses with varying åkermanite content, providing enhanced resolution among the oxygen peaks compared to that obtained in <sup>17</sup>O MAS NMR spectra (Fig. 4). These spectra show multiple oxygen sites including Si–O–Si, Al-



Fig. 3. Total isotropic projection of  $^{27}$ Al 3QMAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite.



Fig. 4.  $^{17}$ O MAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite. The arrows are from the peak positions in the 2D  $^{17}$ O 3QMAS NMR spectrum (Fig. 5).

O-Al, Si–O–Al, Ca-O-Si, {Ca, Mg}-O-Si, and Ca–O–Al peaks. The oxygen peak from 150 to 0 ppm in the MAS dimension stems from different types of NBOs [Ca-O-Al, Ca–O–Si, mixed-{Ca, Mg} NBO, and Mg–O–Si]. Ca–O–Si peak is well resolved at ~ – 66 ppm in the isotropic dimension in all glasses suggesting prevalence of Ca–NBO in the quaternary silicate glasses studied here. Ca-O-Al is partially resolved at ~ – 87 ppm in isotropic dimension in gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses. The fraction of Ca-O-Al could not be obtained quantitatively, but it was confirmed that those peaks are clearly distinguished from Ca-O-Si in melilite glasses. The Mg–O–Si and mixed-NBO peaks partially overlap with other BO

peaks. The mixed-NBO peaks shift to a higher frequency in the isotropic dimension with increasing åkermanite content. The proportion of each BO and NBO changes with åkermanite content. The fraction of Al-O-Al and Si-O-Al apparently decreases and that of Si-O-Si increases with increasing åkermanite content. The prevalence of Si–O-Al peak in all the melilite glasses suggests a substantial mixing between Si and Al (Park and Lee, 2012, 2014, 2018). Al–O-Al peak is partially resolved at  $\sim -38$  ppm in the isotropic dimension and it decreases with increasing åkermanite content. The intensities of Si–O-Si peak ( $\sim -55$  ppm in the isotropic dimension) and {Ca, Mg}-mixed NBOs peak also increase with increasing åkermanite content up to endmember åkermanite glass.

Fig. 6 shows the total isotropic projection of 2D  $^{17}$ O 3QMAS NMR spectra for melilite glasses. Al–O–Al and Si–O–Al peaks are partially resolved in the gehlenite glass, whereas these peaks are overlapped with the mixed NBO peaks with increasing åkermanite content. Note that a small but non-negligible fraction of Ca-O-Al is observed at  $\sim -85$  ppm in gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses and Ca-O-Si peak is clearly resolved at  $\sim -66$  ppm in all the glasses. The spectra qualitatively show that the fraction of NBOs and Si–O–Si increases with increasing åkermanite content, whereas the Si–O–Al and Al-O-Al peak intensities decrease (increasing Si/Al ratio).

### 4. Discussion

### 4.1. Effects of composition on Al coordination environments

The fraction of <sup>[5]</sup>Al increases with increasing åkermanite content as shown in Fig. 2. The observed trend in the <sup>27</sup>Al MAS and 3QMAS NMR spectra in melilite glasses and melts confirms that the <sup>[5]</sup>Al is derived from the presence of  $Mg^{2+}$ . The trend is consistent with previous NMR studies for aluminosilicate glasses, where the fraction of <sup>[5]</sup>Al increases with increasing field strength of non-network forming cations (Kelsey et al., 2008; Le Losq et al., 2014; Neuville et al., 2008; Park and Lee, 2018, and references therein). Previous study suggests that the threshold value of the average cationic potential of non-network forming cations [  $< c/r >_{ave} = \sum_{i} x_i \alpha_i$ , where  $x_i$  is the mole fraction of each cation; and  $\alpha_i$  is the cationic potential {charge (c)/ionic radius (r)} of each non-network cation] is  $\sim 2$  to form the <sup>[5]</sup>Al (Park and Lee, 2014). The  $< c/r > _{ave}$  of melilite glasses slightly increases from 2 (at gehlenite glass) to 2.2 (at  $Åk_{75}Gh_{25}$  glass). The threshold  $< c/r > _{ave}$ value to generate <sup>[5]</sup>Al is ~2.2 in melilite glasses. The increased <sup>[5]</sup>Al with increasing åkermanite content indicates that the structural disorder (configurational disorder) increases with increasing åkermanite content (Park and Lee, 2018). The formation of highly coordinated Al (e.g., <sup>[5]</sup>Al and <sup>[6]</sup>Al) leads to an increase in configurational entropy in multi-component silicate glasses due to the rearrangement of atomic configurations (Lee et al., 2020). While <sup>[4]</sup>Al in gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glass is not fully polymerized due to observed Al-NBO, <sup>[4]</sup>Al in Åk<sub>50</sub>Gh<sub>50</sub> and Åk<sub>75</sub>Gh<sub>25</sub> glass is polymerized (evidenced by the lack of Al-NBO).

## 4.2. Si-Al disorder and preferential interaction between NBO and network modifying cations

The <sup>17</sup>O NMR results show that the fraction of Al–O–Al decreases with increasing åkermanite content as expected from the composition (i.e., an increase of Si/Al) and it is not observed in the Åk<sub>72</sub>Gh<sub>28</sub> glass under detection limit (Figs. 5 & 6). The degree of intermixing between Al and Si may range between a random distribution and chemical order. Al-avoidance rule, also called Loewenstein's rule is that Al-O-Si is more favorable than Si-O-Si and Al-O-Al (Loewenstein, 1954). The observed Al–O–Al ensures that the distributions of Si and Al in the melilite glasses and melts deviate from perfect chemical ordering (i.e., Al-avoidance rule). Current results are consistent with previous studies for Mg-aluminosilicate glasses (Lee et al., 2016), glasses in diopside-Ca-tschermakite join (Park and Lee, 2012), glasses in diopside-jadeite join (Park



Fig. 5. <sup>17</sup>O 3QMAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite. Contour lines are drawn at 5% intervals from relative intensities of 3% to 83% with added lines at 87%, 93%, and 98%.

and Lee, 2014), and iron-free model basaltic glasses (Park and Lee, 2018) where the fraction of Al-O-Al also tends to decrease with decreasing  $Al_2O_3/(MgO + Al_2O_3)$ .

As mentioned above, Fig. 5 shows that Si-NBO (Ca-O-Si) is observed

at ~107 ppm in MAS dimension in the spectra of melilite glasses. The <sup>17</sup>O 3QMAS NMR spectra (Fig. 6) show that Ca-O-Si is observed in all glasses at ~ -66 ppm in isotropic dimension. Total isotropic projection (Fig. 6) also shows prominent Ca-O-Si in all glasses. A previous NMR



Fig. 6. Total isotropic projection of <sup>17</sup>O 3QMAS NMR spectra for melilite glasses at 9.4 T with varying mole fraction of åkermanite.

study for diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) glass has shown that Ca-O-Si were not resolved due to the small fraction and overlapping with other peaks (i.e., mixed-NBO peaks) (Park and Lee, 2012) whereas it is still observed at  $\sim -67$  ppm (in isotropic dimension) in åkermanite glass (Mgrich composition). This is because the Ca/Mg ratio of åkermanite glass is 2 while that of diopside glass is 1. Previous NMR study for CMAS glasses in diopside-Ca-tschermakite join suggested that preferential partitioning of Ca<sup>2+</sup> and Mg<sup>2+</sup> and/or unmixing of these cations between NBOs and BOs may occur (Park and Lee, 2012). Similarly, two possibilities can be considered in this study. The first possibility is preferential interaction between Ca<sup>2+</sup> and NBO (Park and Lee, 2012). Additionally, those anomaly (i.e., preference of Ca-NBO) is due to the spatial proximity of  $Mg^{2+}$  with Si-O-<sup>[4,5]</sup>Al (Lee et al., 2016). Second, the current results with the prevalence of Ca-O-Si peak in all the glasses also imply a clustering of  $Ca^{2+}$  and  $Mg^{2+}$ . The current results, together with our previous studies on multi-component silicate glasses, corroborate that Ca<sup>2+</sup> and Mg<sup>2+</sup> show a non-random distribution around NBO and BO. Those results are not fully consistent with previous suggestion of Ca-Mg random mixing in glasses in Mg3Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>-Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> join inferred from viscosity measurement data (Neuville and Richet, 1991). While the origin is not clear, the inconsistency may be due to the difference in sample composition.

### 4.3. Formation of Al-NBO in Ca-rich natural melts (type A CAI-like melts)

The reported <sup>17</sup>O NMR results show that Al-NBO is present in melilite glasses. Al-NBO (Ca-O-Al) is observed in gehlenite and  $Åk_{25}Gh_{75}$ glasses at ~150 ppm in MAS dimension (~ -87 ppm in isotropic dimension) (see Figs. 5 and 6). Previous studies suggested that Si has a strong preference over Al for NBO in aluminosilicate glasses and melts (Allwardt et al., 2003; Engelhardt et al., 1985; Ganster et al., 2004; Lee et al., 2009; Lee and Stebbins, 2006; Petkov et al., 2000; Stebbins et al., 2001). For example, previous density functional theory (DFT) calculation study for Ca-aluminosilicate glass has shown that the energy penalty is higher for forming Al-NBO (108 kJ/mol) than Si-NBO (72 kJ/ mol) (Lee and Stebbins, 2006). Nevertheless, Al-NBO has been observed in several composition of silicate glasses including high Al content (i.e., Al/Si > 3) and REE bearing silicate glasses as mentioned before (Allwardt et al., 2003; Iftekhar et al., 2012; Jaworski et al., 2016; Neuville et al., 2006). The significant fraction of Ca-O-Al is also expected by MD simulations in Si-rich and Al-poor CMAS glasses (Al/Si = 0.66 and 0.48) (Ganisetti et al., 2019; Gong et al., 2019). In this study, the first <sup>17</sup>O MAS and 3QMAS NMR spectra for melilite glasses reveal that Ca-O-Al is present in gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses (i.e., Al/Si = 2 and 1.2, respectively). This indicates that Al is not fully polymerized in melilite glasses and melts (i.e., gehlenite and Åk<sub>25</sub>Gh<sub>75</sub> glasses can be generated by high field strength cations (i.e., Ca<sup>2+</sup>).

### 4.4. Implications for viscosity, diffusivity, and variable oxygen isotopic compositions of melilite in type A CAIs

The NBO fraction of melilite glasses and melts observed from <sup>17</sup>O 3QMAS NMR spectra increases with an increase in Mg content, in agreement with the NBO/T values estimated from the composition (Table 1). Here, NBO/T (the number of NBOs per tetrahedral network cation) is a very important parameter because numerous melt properties are correlated with this parameter (Mysen and Richet, 2019). The viscosities of silicate melts negatively correlate with the degree of melt polymerization ( $\eta \propto \exp[A/(B + X_{NBO})]$ , where A and B are constants depending on the composition of melts) (e.g., Bottinga et al., 1995; Giordano et al., 2009; Lee et al., 2004). Though it is qualitative, an increase of the NBO fraction suggests that the viscosity of melilite melts decreases with increasing åkermanite content. The viscosity of melts is inversely proportional to  $O^{2-}$  diffusion coefficient (Lesher, 2010, and references therein). This relationship can be represented by the Eyring equation (D =  $kT/\eta\lambda$ , here D is diffusivity, k is Boltzmann constant,  $\lambda$  is jump distance, T is temperature, and  $\eta$  is viscosity) (Eyring, 1936). Here, we estimated  $O^{2-}$  diffusivity in melilite melts from viscosity in melts in diopside-anorthite join using Eyring equation because both system are Ca–Mg aluminosilicate. Fig. 7A shows that the viscosity (at  $\sim$ 1300 K) of melts in diopside-anorthite join decreases with increasing NBO/T (Gaudio and Behrens, 2009). Fig. 7B shows the estimated O<sup>2</sup> diffusivity (log D, cm<sup>2</sup>/s) of melts in diopside-anorthite join (black circles) from viscosity of those melts using Eyring equation [where  $\lambda$  is 2.8 Å (oxygen interatomic distance) at constant temperature (~1300 K)]. Taking into consideration the effect of composition (NBO/ T) on the diffusivity in melt, the  $O^{2-}$  diffusivity of melilite melts (blue rectangles) is estimated. The trend line is predicted using the diffusivity of melts in diopside-anorthite join with NBO/T. The diffusivity of melilite melts is estimated using NBO/T estimated from the composition (Table 1). The results show that the estimated  $O^{2-}$  diffusivity increases with increasing NBO/T (åkermanite content). The current trend would certainly allow us to predict the diffusivity in the diverse silicate glasses and melts at constant temperature when the compositions of the melts are known (as shown in Fig. 7B).

Although there are several factors including temperature to affect the  $O^{2-}$  diffusivity, here we only consider the change of melt structure (NBO fraction) with composition to explain variable oxygen isotopic composition in constituent minerals in type A CAIs (Aléon et al., 2007; Ito et al., 2004). If the precursor materials of type A CAIs having <sup>16</sup>Orich compositions experienced melting in the <sup>16</sup>O-poor nebular gas, spinel can retain its <sup>16</sup>O-rich composition because either spinel could not melt due to the high melting temperature (~2378 K) (Hallstedt, 1992) or it could have been isolated from oxygen isotopic exchange due to its very sluggish oxygen isotopic diffusivity (Ryerson and McKeegan, 1994). The gehlenitic melilite (the first phase crystallized from the partial melt of type A CAI precursors or remained melt after crystallization of spinel) may have a similar isotopic composition to that of spinel (<sup>16</sup>O-rich) because it could have crystallized before oxygen isotope exchange between the melt and <sup>16</sup>O-poor gas due to its relatively slow oxygen isotope diffusivity. As fractional crystallization proceeds,



**Fig. 7.** (A) Experimental viscosity data of melts at 1300 K in diopside-anorthite join with NBO/T. (B) Estimated  $O^{2-}$  diffusivity of melts at 1300 K in diopside-anorthite join and melilite melts with NBO/T.

remained melt composition becomes more Mg-rich, resulting in lower viscosity and faster oxygen diffusivity. Thus the melilite with higher åkermanite content may show <sup>16</sup>O-poor composition similar to the surrounding gas composition, as the oxygen diffusion rate in melts increased. We note again that the current model considers the effect of composition (and therefore NBO content) at constant temperature on  $O^{2-}$  diffusivity. The current proposal of NBO-dependent diffusivity of CAI-like melts is, therefore, qualitative, as the effect of temperature has not been explicitly taken into consideration. More extensive future modeling efforts with varying temperature condition during fractional crystallization remain to fully account for the isotope composition of melilite in type A CAIs.

### 5. Conclusion

We clarified the structural details of the atomic environments around Al and O in melilite glasses and melts including the distribution of cations around NBOs and BOs, network connectivity, and extent of disorder. The <sup>27</sup>Al MAS and 3QMAS NMR spectra for the glasses clearly show predominant <sup>[4]</sup>Al. A non-negligible fraction of <sup>[5]</sup>Al is observed in Mg-rich glasses (i.e.,  $Åk_{50}Gh_{50}$  and  $Åk_{72}Gh_{28}$  glasses) and it slightly increases with increasing åkermanite content. These results bring an increase of the structural (i.e., configurational and topological) disorder in melilite glasses and melts.

The <sup>17</sup>O MAS and 3QMAS NMR spectra unveiled diverse structural disorder in melilite glasses. A partially resolved Ca-O-Si is observed in all the glasses confirming non-random distributions of  $Ca^{2+}$  and  $Mg^{2+}$ around NBOs and BOs in multi-component CMAS glasses and melts. Especially, Ca-O-Si is still observed in åkermanite glass due to the high Ca/Mg ratio (i.e., 2). Despite the strong bonding preference of Si over Al for NBOs the first <sup>17</sup>O MAS and 3QMAS NMR spectra for melilite glasses reveal that Al-NBO (i.e., Ca-O-Al) can be generated in natural CAI-like melts (gehlenite and Åk<sub>25</sub>Gh75 glasses and melts). The fraction of Ca-O-Al could not be obtained quantitatively, but it was confirmed that those peaks are clearly distinguished from Ca-O-Si in CMAS melilite melts. In addition, Al-O-Al peak is partially resolved and it decreases with increasing åkermanite content. Those results indicate that Al-avoidance rule is not obeyed in melilite glasses and melts and the mixing of Si and Al deviates from perfect chemical ordering. In spite of the formation of Al-O-Al and Al-NBO is energetically less preferred, a non-negligible fraction of Al-O-Al and Al-NBO is observed in melilite glasses and melts. The structural disorder can be derived from a high amount of high field strength cations (i.e.,  $Ca^{2+}$  and  $Mg^{2+}$ ).

The intensity for NBO peak apparently increases with åkermanite content suggesting the decrease of polymerization in melts. Though qualitative, the observed increase in NBO fraction with increasing åkermanite content indicates an obvious decrease in melt viscosity. Additionally, the diffusion of oxygen is also affected by the melt polymerization thus the diffusivity of  $O^{2-}$  in melilite melts decreases with increasing åkermanite content. Although the effect of temperature and cooling rate should be considered, changes in  $O^{2-}$  diffusivity could explain the variable oxygen isotopic compositions of melilite minerals in type A CAIs.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgement

This work was supported by Korea Polar Research Institute project (PE20200), a research grant (2017R1A2A1A17069511) to S.K.L. from the National Research Foundation of Korea, and basic research fund of the Korea Institute of Geoscience and Mineral Resources (GP2020-006). One anonymous reviewer and Charles Le Losq for their comments and Prof. Balz Kamber for editorial handling are kindly acknowledged.

### References

- Aléon, J., Elgoresy, A., Zinner, E., 2007. Oxygen isotope heterogeneities in the earliest protosolar gas recorded in a meteoritic calcium–aluminum-rich inclusion. Earth Planet. Sci. Lett. 263, 114–127.
- Allu, A.R., Gaddam, A., Ganisetti, S., Balaji, S., Siegel, R., Mather, G.C., Fabian, M., Pascual, M.J., Ditaranto, N., Milius, W., Senker, J., Agarkov, D.A., Kharton, V.V., Ferreira, J.M.F., 2018. Structure and crystallization of alkaline-earth aluminosilicate glasses: prevention of the alumina-avoidance principle. J. Phys. Chem. B 122, 4737–4747.
- Allwardt, J.R., Stebbins, J.F., 2004. Ca-Mg and K-Mg mixing around non-bridging O atoms in silicate glasses: an investigation using <sup>17</sup>O MAS and 3QMAS NMR. Am. Mineral. 89, 777–784.
- Allwardt, J.R., Lee, S.K., Stebbins, J.F., 2003. Bonding preferences of non-bridging O atoms: evidence from <sup>17</sup>O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses. Am. Mineral. 88, 949–954.
- Armstrong, J.T., 1988. In: Newbury, D.E. (Ed.), Quantitative Analysis of Silicate and Oxide Materials: Comparison of Monte Carlo, ZAF and φ(ρZ) Procedures. Microbeam

Analysis San Francisco Press, San Francisco, CA, pp. 239–246.

- Baltisberger, J.H., Xu, Z., Stebbins, J.F., Wang, S.H., Pines, A., 1996. Triple-quantum twodimensional <sup>27</sup>Al magic-angle spinning nuclear magnetic resonance spectroscopic study of aluminosilicate and aluminate crystals and glasses. J. Am. Chem. Soc. 118, 7209–7214.
- Bista, S., Stebbins, J.F., Hankins, W.B., Sisson, T.W., 2015. Aluminosilicate melts and glasses at 1 to 3 GPa: temperature and pressure effects on recovered structural and density changes. Am. Mineral. 100, 2298–2307.
- Bottinga, Y., Richet, P., Sipp, A., 1995. Viscosity regimes of homogeneous silicate melts. Am. Mineral. 80, 305–318.
- Engelhardt, G., Nofz, M., Forkel, K., Wihsmann, F.G., Maegi, M., Samoson, A., Lippmaa, E., 1985. Structural studies of calcium aluminosilicate glasses by high resolution solid state <sup>29</sup>Si and <sup>27</sup>Al magic angle spinning nuclear magnetic resonance. Phys. Chem. Glasses 26, 157–165.
- Eyring, H., 1936. Viscosity, plasticity, and diffusion as examples of absolute reaction rates. J. Chem. Phys. 4, 283–291.
- Ganisetti, S., Gaddam, A., Kumar, R., Balaji, S., Mather, G.C., Pascual, M.J., Fabian, M., Siegel, R., Senker, J., Kharton, V.V., Guenole, J., Krishnan, N.M.A., Ferreira, J.M.F., Allu, A.R., 2019. Elucidating the formation of Al-NBO bonds, Al-O-Al linkages and clusters in alkaline-earth aluminosilicate glasses based on molecular dynamics simulations. Phys. Chem. Chem. Phys. 21, 23966–23977.
- Ganster, P., Benoit, M., Kob, W., Delaye, J.M., 2004. Structural properties of a calcium aluminosilicate glass from molecular-dynamics simulations: a finite size effects study. J. Chem. Phys. 120, 10172–10181.
- Gaudio, P.D., Behrens, H., 2009. An experimental study on the pressure dependence of viscosity in silicate melts. J. Chem. Phys. 131, 044504.
- Giordano, D., Ardia, P., Romano, C., Dingwell, D.B., Di Muro, A., Schmidt, M.W., Mangiacapra, A., Hess, K.U., 2009. The rheological evolution of alkaline Vesuvius magmas and comparison with alkaline series from the Phlegrean Fields, Etna, Stromboli and Teide. Geochim. Cosmochim. Acta 73, 6613–6630.
- Glatz, P., Comte, M., Montagne, L., Doumert, B., Cormier, L., 2019. Quantitative determination of the phosphorus environment in lithium aluminosilicate glasses using solid-state NMR techniques. Phys. Chem. Chem. Phys. 21, 18370–18379.
- Gong, K., Ozccelik, V.O., Yang, K., White, C., 2019. Density functional modeling and total scattering analysis of the atomic structure of a quaternary CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS) glass: uncovering the local environment of magnesium. *arXiv*. Mater. Sci. 1–35. https://arxiv.org/abs/1909.13351.
- Grossman, L., 1975. Petrography and mineral chemistry of Ca-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta 39, 433–454.
- Hallstedt, B., 1992. Thermodynamic assessment of the system MgO–Al<sub>2</sub>O<sub>3</sub>. J. Am. Ceram. Soc. 75, 1497–1507.
- Iftekhar, S., Pahari, B., Okhotnikov, K., Jaworski, A., Stevensson, B., Grins, J., Edén, M., 2012. Properties and structures of RE<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> (RE = Y, Lu) glasses probed by molecular dynamics simulations and solid-state NMR: the roles of aluminum and rare-earth ions for dictating the microhardness. J. Phys. Chem. C 116, 18394.
- Ito, M., Nagasawa, H., Yurimoto, H., 2004. Oxygen isotopic SIMS analysis in Allende CAI: details of the very early thermal history of the solar system. Geochim. Cosmochim. Acta 68, 2905–2923.
- Jaworski, A., Stevensson, B., Edén, M., 2016. The bearings from rare-earth (RE = La, Lu, Sc, Y) cations on the oxygen environments in aluminosilicate glasses: a study by solidstate <sup>17</sup>O NMR, molecular dynamics simulations, and DFT calculations. J. Phys. Chem. C 120, 13181–13198.
- Kelsey, K.E., Allwardt, J.R., Stebbins, J.F., 2008. Ca-Mg mixing in aluminosilicate glasses: an investigation using <sup>17</sup>O MAS and 3QMAS and <sup>27</sup>Al MAS NMR. J. Non-Cryst. Solids 354, 4644–4653.
- Krot, A.N., Nagashima, K., Fintor, K., Pál-Molnár, E., 2019. Evidence for oxygen-isotope exchange in refractory inclusions from Kaba (CV3.1) carbonaceous chondrite during fluid-rock interaction on the CV parent asteroid. Geochim. Cosmochim. Acta 246, 419–435.
- Le Losq, C., Neuville, D.R., 2017. Molecular structure, configurational entropy and viscosity of silicate melts: link through the Adam and Gibbs theory of viscous flow. J. Non-Cryst. Solids 463, 175–188.
- Le Losq, C., Neuville, D.R., Florian, P., Henderson, G.S., Massiot, D., 2014. The role of Al<sup>3+</sup> on rheology and structural changes in sodium silicate and aluminosilicate glasses and melts. Geochim. Cosmochim. Acta 126, 495–517.
- Lee, S.K., 2011. Simplicity in melt densification in multicomponent magmatic reservoirs in Earth's interior revealed by multinuclear magnetic resonance. Proc. Natl. Acad. Sci. U. S. A. 108, 6847–6852.
- Lee, A.C., Lee, S.K., 2020. Network polymerization and cation coordination environments in boron-bearing rhyolitic melts: Insights from <sup>17</sup>O, <sup>11</sup>B, and <sup>27</sup>Al solid-state NMR of sodium aluminoborosilicate glasses with varying boron content. Geochim. Cosmochim. Acta 268, 325–347.
- Lee, S.K., Stebbins, J.F., 2000. The structure of aluminosilicate glasses: high-resolution <sup>17</sup>O and <sup>27</sup>Al MAS and 3QMAS NMR study. J. Phys. Chem. B 104, 4091–4100.
- Lee, S.K., Stebbins, J.F., 2006. Disorder and the extent of polymerization in calcium silicate and aluminosilicate glasses: O-17 NMR results and quantum chemical molecular orbital calculations. Geochim. Cosmochim. Acta 70, 4275–4286.
- Lee, S.K., Sung, S., 2008. The effect of network-modifying cations on the structure and disorder in peralkaline Ca-Na aluminosilicate glasses: O-17 3QMAS NMR study. Chem. Geol. 256, 326–333.
- Lee, S.K., Cody, G.D., Fei, Y.W., Mysen, B.O., 2004. Nature of polymerization and properties of silicate melts and glasses at high pressure. Geochim. Cosmochim. Acta 68, 4189–4200.

- Lee, S.K., Cody, G.D., Mysen, B.O., 2005. Structure and the extent of disorder in quaternary (Ca-Mg and Ca-Na) aluminosilicate glasses and melts. Am. Mineral. 90, 1393–1401.
- Lee, S.K., Deschamps, M., Hiet, J., Massiot, D., Park, S.Y., 2009. Connectivity and proximity between quadrupolar nuclides in oxide glasses: insights from through-bond and through-space correlations in solid-state NMR. J. Phys. Chem. B 113, 5162–5167.
- Lee, S.K., Kim, H.-L., Kim, E.J., Mun, K.Y., Ryu, S., 2016. Extent of disorder in magnesium aluminosilicate glasses: insights from <sup>27</sup>Al and <sup>17</sup>O NMR. J. Phys. Chem. C 120, 737–749.
- Lee, S.K., Mosenfelder, J.L., Park, S.Y., Lee, A.C., Asimow, P.D., 2020. Configurational entropy of basaltic melts in Earth's mantle. Proc. Natl. Acad. Sci. U.S.A. 202014519.
- Lesher, C.E., 2010. Self-diffusion in silicate melts: theory, observations and applications to magmatic systems. Rev. Mineral. Geochem. 72, 269–309.
- Loewenstein, W., 1954. The distribution of aluminum in the tetrahedra of silicates and aluminates. Am. Mineral. 39, 92–96.
- MacPherson, G.J., 2014. Calcium–aluminum-rich inclusions in chondritic meteorites. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry 2nd. Pergamon, Oxford, pp. 1–47.
- MacPherson, G.J., Simon, S.B., Davis, A.M., Grossman, L., Krot, A.N., 2005. Calciumaluminum-rich inclusions: major unanswered questions. In: Krot, A.N., Scott, E.R.D., Reipurth, B. (Eds.), Chondrites and the Protoplanetary Disk, ASP Conference Series. Astronomical Society of the Pacific, San Francisco, pp. 225–250.
- Malfait, W.J., Verel, R., Ardia, P., Sanchez-Valle, C., 2012. Aluminum coordination in rhyolite and andesite glasses and melts: effect of temperature, pressure, composition and water content. Geochim. Cosmochim. Acta 77, 11–26.
- Mysen, B.O., Richet, P., 2019. Silicate Glasses and Melts: Properties and Structure, second ed. Elsevier, Amsterdam.
- Navrotsky, A., Zimmermann, H.D., Hervig, R.L., 1983. Thermochemical study of glasses in the system CaMgSi<sub>2</sub>O<sub>6</sub>-CaAl<sub>2</sub>SiO<sub>6</sub>. Geochim. Cosmochim. Acta 47, 1535–1538.
- Neuville, D.R., Richet, P., 1991. Viscosity and mixing in molten (Ca, Mg) pyroxenes and garnets. Geochim. Cosmochim. Acta 55, 1011–1019.
- Neuville, D.R., Cormier, L., Massiot, D., 2006. Al coordination and speciation in calcium aluminosilicate glasses: effects of composition determined by Al-27 MQ-MAS NMR and Raman spectroscopy. Chem. Geol. 229, 173–185.
- Neuville, D.R., Cormier, L., Montouillout, V., Florian, P., Millot, F., Rifflet, J.C., massiot, D., 2008. Structure of Mg- and Mg/Ca aluminosilicate glasses: <sup>27</sup>Al NMR and Raman spectroscopy investigations. Am. Mineral. 93, 1721–1731.
- Osborn, E.F., Schairer, J.F., 1941. The ternary system pseudo wollastonite-äkermanitegehlenite. Am. J. Sci. 239, 715–763.
- Park, S.Y., Lee, S.K., 2012. Structure and disorder in basaltic glasses and melts: insights from high-resolution solid-state NMR study of glasses in diopside-Ca-tschermakite join and diopside-anorthite eutectic composition. Geochim. Cosmochim. Acta 80, 125–142.
- Park, S.Y., Lee, S.K., 2014. High-resolution solid-state NMR study of the effect of composition on network connectivity and structural disorder in multi-component glasses in the diopside and jadeite join: Implications for structure of andesitic melts. Geochim. Cosmochim. Acta 147, 26–42.
- Park, S.Y., Lee, S.K., 2018. Probing the structure of Fe-free model basaltic glasses: a view from a solid-state <sup>27</sup>Al and <sup>17</sup>O NMR study of Na-Mg silicate glasses, Na<sub>2</sub>O-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses, and synthetic Fe-free KLB-1 basaltic glasses. Geochim. Cosmochim. Acta 238, 563–579.
- Petkov, V., Billinge, S.J.L., Shastri, S.D., Himmel, B., 2000. Polyhedral units and network connectivity in calcium aluminosilicate glasses from high-energy X-ray diffraction. Phys. Rev. Lett. 85, 3436–3439.
- Ryerson, F.J., McKeegan, K.D., 1994. Determination of oxygen self-diffusion in åkermanite, anorthite, diopside, and spinel: implications for oxygen isotopic anomalies and the thermal histories of Ca-Al-rich inclusions. Geochim. Cosmochim. Acta 58, 3713–3734.
- Stebbins, J.F., Xu, Z., 1997. NMR evidence for excess non-bridging oxygen in an aluminosilicate glass. Nature 390, 60–62.
- Stebbins, J.F., Lee, S.K., Oglesby, J.V., 1999. Al-O-Al oxygen sites in crystalline aluminates and aluminosilicate glasses: high-resolution oxygen-17 NMR results. Am. Mineral. 84, 983.
- Stebbins, J.F., Oglesby, J.V., Kroeker, S., 2001. Oxygen triclusters in crystalline CaAl<sub>4</sub>O<sub>7</sub> (grossite) and in calcium aluminosilicate glasses: <sup>17</sup>O NMR. Am. Mineral. 86, 1307.
- Stebbins, J.F., Dubinsky, E.V., Kanehashi, K., Kelsey, K.E., 2008. Temperature effects on non-bridging oxygen and aluminum coordination number in calcium aluminosilicate glasses and melts. Geochim. Cosmochim. Acta 72, 910–925.
- Stolper, E., 1982. Crystallization sequences of Ca-Al-rich inclusions from Allende: an experimental study. Geochim. Cosmochim. Acta 46, 2159–2180.
- Sukenaga, S., Florian, P., Kanehashi, K., Shibata, H., Saito, N., Nakashima, K., Massiot, D., 2017. Oxygen speciation in multicomponent silicate glasses using through bond double resonance NMR spectroscopy. J. Phys. Chem. Lett. 8, 2274–2279.
- Toplis, M.J., Dingwell, D.B., 2004. Shear viscosities of CaO-Al<sub>2</sub>O<sub>3</sub>-SiO2 and MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> liquids: implications for the structural role of aluminium and the degree of polymerisation of synthetic and natural aluminosilicate melts. Geochim. Cosmochim. Acta 68, 5169–5188.
- Xue, X.Y., Kanzaki, M., 2008. Structure of hydrous aluminosilicate glasses along the diopside-anorthite join: a comprehensive one- and two-dimensional <sup>1</sup>H and <sup>27</sup>Al NMR study. Geochim. Cosmochim. Acta 72, 2331–2348.
- Yurimoto, H., Ito, M., Nagasawa, H., 1998. Oxygen isotope exchange between refractory inclusion in allende and solar nebula gas. Science 282, 1874–1877.