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LETTER

Structural investigation of Mg local environments in silicate glasses by ultra-high field ^{25}Mg 3QMAS NMR spectroscopy

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ABSTRACT

Structural information on divalent cations such as Mg^{2+} should have important implications for magmatic liquids because of their abundance in the Earth's interior; nevertheless, little is confirmed about their coordination environments. We here apply a ^{25}Mg triple-quantum magic-angle spinning (3QMAS) NMR technique at an ultra-high magnetic field (21.8 T) and successfully show the occurrence of multiple Mg sites in $MgSiO_3$ glass. We find that these sites are distinguished by the degree of polyhedral distortion, not by the coordination number. The present study concludes that the highly distorted MgO_6 species occur in $MgSiO_3$ glass, in strong contrast with a recent radial distribution study.

Keywords: Mg local environment, $MgSiO_3$ glass, ^{25}Mg 3QMAS NMR, ultra-high magnetic field

INTRODUCTION

Alkali and alkaline earth cations act as network modifiers in silicate melts and glasses. Most studies on their structures have focused on SiO_4 and AlO_4 tetrahedral networks, whereas the lack of local information about the monovalent or divalent cations has been a long-standing problem in understanding the complete picture of amorphous structures. Some researchers have examined the local environments of the Mg^{2+} ion in $MgSiO_3$ and $CaMgSi_2O_6$ glasses, which are still controversial issues. The coordination number, one of the most important factors affecting dynamic properties, of Mg in such glasses was concluded as fourfold coordination in some studies (Tabira 1996; Wilding et al. 2004) and fivefold (Ildefonse et al. 1995; Li et al. 1999) or sixfold in others (Kroeker and Stebbins 2000).

NMR spectroscopy is a robust tool for collecting structural information focused on a specific element in multi-component systems. Unfortunately, ^{25}Mg NMR has been difficult to apply because of its low resonance frequency (18.4 MHz at 7.0 T) and relatively low natural abundance (10.1%). Using a high magnetic field and ^{25}Mg isotopic enrichment drastically alleviates these shortcomings. Nevertheless, ^{25}Mg MAS NMR further suffers from the large second-order quadrupolar broadening. To overcome this, we here applied the ^{25}Mg 3QMAS technique to Mg-containing silicate glasses and clarified the detailed environments surrounding the Mg^{2+} ions in these glasses.

EXPERIMENTAL PROCEDURE

A series of ^{25}Mg-enriched glass samples ($MgSiO_3$, $CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, $Mg_3Al_2Si_3O_{12}$, $Na_2MgSi_2O_6$, and $K_2MgSi_2O_6$ glasses) and diopside ($CaMgSi_2O_6$) and åkermanite ($Ca_2MgSi_2O_7$) crystals were prepared from appropriate mixtures of 99%-enriched ^{25}MgO, $Ca(OH)_2$, K_2CO_3, Al_2O_3, and SiO_2 reagents. The $MgSiO_3$, $CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, and $Mg_3Al_2Si_3O_{12}$ glasses were obtained by melting the powder mixtures at 1500–1700 °C and quenching in air or water, but $Na_2MgSi_2O_6$ and $K_2MgSi_2O_6$ glass was melted at 1300 °C. XRD indicated that they were amorphous. Diopside and åkermanite were prepared by melting at 1500 °C and subsequent annealing at 1000 °C for 6 hours.

The ^{25}Mg NMR measurements were conducted on a JNM-ECA930 spectrometer (21.8 T) at the National Institute for Materials Science. The working frequency was 56.9 MHz. The 90° pulse lengths were optimized to 1.6–1.8 μs for the glasses. Spin-lattice relation times T_1 were estimated to be less than 0.5 s by the saturation recovery method. All the MAS spectra were acquired with a spin-echo sequence (a pulse length of 1.8 and 3.6 μs) to avoid acoustic ringing, and a recycle delay of 0.5 s. Longer delays did not influence the peak shape.

The ^{25}Mg 3QMAS spectra were acquired with a z-filter sequence and a delay of 0.5 s. Triple-quantum excitation and subsequent conversion pulses were optimized to 6.0 and 2.5 μs, respectively. Samples set in 4 mm MAS rotors were rotated at a spinning rate of 18 kHz. Chemical shifts were externally referenced to $MgSO_4$ solution at 0.0 ppm.

A series of FID signals in the 3QMAS measurements were Fourier-transformed and sheared to obtain the separate isotropic (F1) and anisotropic (F2) dimensions. The isotropic chemical shift δ_{CS} and quadrupolar product P_Q were derived from the sheared two-dimensional spectra with the following equations (Amoureux et al. 2002);

$$\delta_{CS} = \frac{17}{27}\delta_{F1} + \frac{10}{27}\delta_{F2},$$

$$P_Q = \sqrt{\frac{170}{81}\frac{[4S(2S-1)]^2}{[4S(S+1)-3]}(\delta_{F1}-\delta_{F2})}\cdot\nu_0\cdot 10^{-3},$$

where δ_{F1} and δ_{F2} are the chemical shifts in F1 and F2 dimensions, ν_0 is the Zeeman frequency, and S is the spin number. The P_Q is also related to the quadrupolar coupling constant C_Q with the equation of $P_Q = C_Q\sqrt{1+\eta^2/3}$, where η is the asymmetry parameter (η = 0 to 1).

RESULTS AND DISCUSSION

Figure 1 shows the MAS spectra for Mg-containing silicate glasses. There are apparent differences between $MgSiO_3$, $CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, $Mg_3Al_2Si_3O_{12}$ glasses (Figs. 1a–1d)

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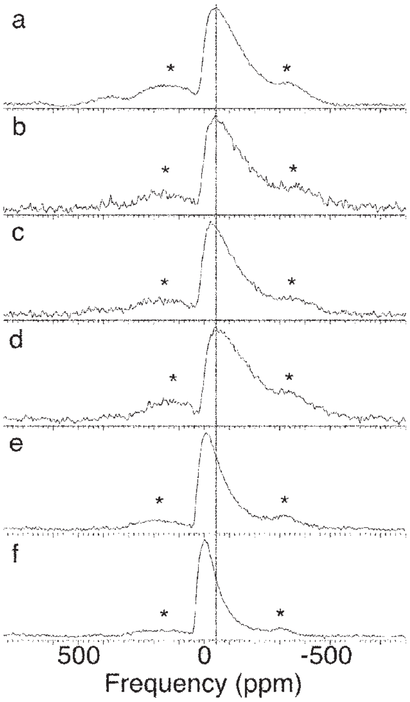

Figure 1. ^{25}Mg MAS NMR spectra at 21.8 T for (**a**) $MgSiO_3$, (**b**) $CaMgSi_2O_6$, (**c**) $Ca_2MgSi_2O_7$, (**d**) $Mg_3Al_2Si_3O_{12}$, (**e**) $Na_2MgSi_2O_6$, and (**f**) $K_2MgSi_2O_6$ glasses. 22 000–96 000 transients were averaged with relaxation delays of 0.5 s. The asterisks refer to spinning side bands. The vertical line is a guide for the eye.

Table 1. Estimates of isotropic chemical shift δ_{CS} and quadrupolar product P_Q from ^{25}Mg 3QMAS spectra at 21.8 T

		δ_{CS} (ppm)*	P_Q (MHz)*
$MgSiO_3$ glass	site A	10	3.5
	site B	24	3.3
	site C	9	5.8
	site D	1	7.3
$K_2MgSi_2O_6$ glass		37	2.8
diopside (^{VI}Mg crystal)		6	2.2
åkermanite (^{IV}Mg crystal)		49	2.9

* Errors are within 3 ppm and 0.5 MHz, respectively. The estimates for the crystals were from 3QMAS spectra at 700 MHz (not shown).

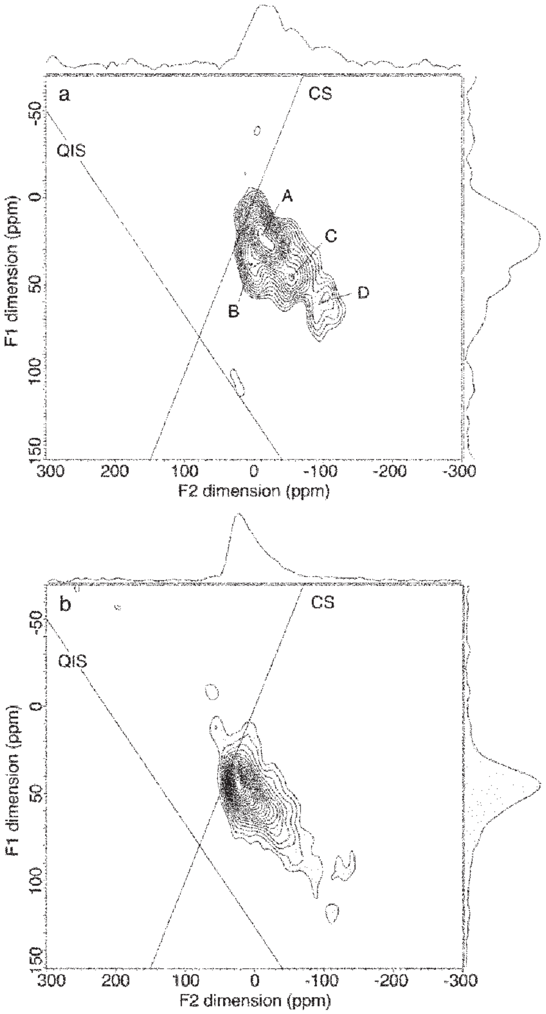

Figure 2. ^{25}Mg 3QMAS spectra at 21.8 T for (**a**) $MgSiO_3$ and (**b**) $K_2MgSi_2O_6$ glasses. 52 800 and 14 400 transients were collected for each 16 t_1 increment with delays of 0.5 s, respectively. Contour levels are equally drawn at 5% to 95% with an increment of ca. 5.3%, and 4% to 96% with an increment of ca. 4.2%, respectively.

and $Na_2MgSi_2O_6$, $K_2MgSi_2O_6$ glass (Figs. 1e and 1f). The observed peak maxima are at –47.1, –46.3, –25.7, –44.6, –3.4, and –0.9 ppm, respectively. In this case, the peak maxima are not isotropic chemical shifts due to quadrupolar interactions, and from the MAS data at a single field, the isotropic shifts cannot be obtained for quadrupolar nuclei in glasses. Also, the signal widths (FWHM) of the former group of glasses (140–190 ppm) are significantly larger than the latter (90–110 ppm). These results imply that the Mg local environments in the former glasses are different from those in the latter.

Figures 2a and 2b show the ^{25}Mg 3QMAS spectra of $MgSiO_3$ and $K_2MgSi_2O_6$ glasses, respectively. The multiple-quantum (MQ) MAS technique is an excellent method for observing high-resolution NMR spectra, free from second-order broadening of half-integer quadrupolar nuclei (Frydman and Harwood 1995). Figure 2a shows four Mg sites in the $MgSiO_3$ glass structure, in contrast to a single site for $K_2MgSi_2O_6$ glass. The estimated isotropic chemical shifts (δ_{CS}) and quadrupolar products (P_Q) for the glasses, diopside (a ^{VI}Mg site) and åkermanite (a ^{IV}Mg site), are listed in Table 1. The values for diopside and åkermanite agree with those reported by Kroeker and Stebbins (2000). MacKenzie and Meinhold (1994) reported the ^{25}Mg MAS spectrum for the fivefold Mg site in grandidierite. Its δ_{CS} was estimated to be 55 ppm, which is higher in frequency than that for the fourfold site in åkermanite. This may imply that the Mg site is largely affected by neighboring cations (BO_3 and AlO_5). The δ_{CS} of an eightfold Mg mineral such as pyrope is also unclear (Dupree and Smith 1988). MacKenzie and Meinhold (1994) mentioned that the δ_{CS} of sixfold Mg-containing silicates ranges from 5 to 14 ppm. Thus, we consider that in $MgSiO_3$ glass the sites A, C, and probably D are due to sixfold Mg species with different environments. Site B may be from a fivefold environment. In the case of $K_2MgSi_2O_6$ glass, we obtained only a single peak with a broad distribution along the quadrupolar-induced shift

(QIS) axis. The δ_{CS} of 37 ppm is less positive in frequency than that for åkermanite, but within the rough estimate for crystalline $K_2{}^{IV}MgSi_5O_{12}$ (30–50 ppm) (Kroeker and Stebbins 2000). We here conclude that the Mg^{2+} ions occur in a tetrahedral environment, but might be fivefold as deduced previously (Fiske and Stebbins 1994; George and Stebbins 1998). The linewidth of the F2 projections of the 3QMAS spectra for the both glasses are narrower than the corresponding MAS spectra, although they are identical in principle. This may result from the C_Q-dependence of MQ excitation efficiency. Other sites could exist with larger C_Q (P_Q), but they are not observed here.

Our conclusion that $K_2MgSi_2O_6$ glass has a single MgO_4 site supports the results of X-ray emission (Kawazoe et al. 1981) and MAS NMR (Kroeker and Stebbins 2000). The difference in the coordination state between $K_2MgSi_2O_6$ and $MgSiO_3$ glasses is explained by the effect of cation field strength. The cation field strength, Z/d^2 (Z is the charge and d is M-O distance) increases in the order of K (0.12), Na (0.18), Ca (0.36), and Mg (0.46–0.53) (Brown et al. 1995). This indicates an increase in bond strength in the order of K-O, Na-O, Ca-O, and Mg-O. Thus, in the $K_2MgSi_2O_6$ glass, Mg^{2+} ions strongly and effectively bind with oxygen atoms over competing K^+ ions to reduce the overall Mg coordination number (Kroeker and Stebbins 2000). If we consider that the MgO_4 tetrahedra partly act as weak network formers in $K_2MgSi_2O_6$ glass, they may influence bulk viscosity. Indeed, $K_2MgSi_5O_{12}$ melt shows a decrease in viscosity with an increase in pressure at constant temperature, whereas $CaMgSi_2O_6$ melt shows an increase in viscosity (Scarfe et al. 1979; Kushiro 1984; see also Wolf and McMillan 1995). The viscosity is most likely affected by the degree of network polymerization and cation coordination. Thus, this can be explained by the mechanism that the highly polymerized $(Mg,Si)O_4$ tetrahedral network involves an increase in the Mg coordination number with pressure, resulting in a decrease in viscosity. This may be supported by an ^{17}O 3QMAS study of K-Mg silicate glasses (Allwardt and Stebbins 2004), in which K^+ was found to bond with bridging oxygen atoms (^{IV}Mg-O-^{IV}Si in our definition), suggesting its charge balancing role. On the other hand, the less-polymerized $CaMgSi_2O_6$ melt is considered to take pressure-induced polymerization of SiO_4 tetrahedral network to effectively increase viscosity (Dickinson et al. 1990), probably with a small counteraction of the Mg coordination increase.

The ^{25}Mg MAS and 3QMAS spectra suggest that Mg^{2+} is mainly in octahedral coordination in $MgSiO_3$, $CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, and $Mg_3Al_2Si_3O_{12}$ glasses. For $CaMgSi_2O_6$ glass, the present study agrees with the previous MAS NMR study (Kroeker and Stebbins 2000) rather than the XAS studies (Ildefonse et al. 1995; Li et al. 1999). The present study indicates that the Mg environments in $Ca_2MgSi_2O_7$ and $Mg_3Al_2Si_3O_{12}$ glasses are different from the crystalline counterparts, åkermanite and pyrope, where Mg^{2+} is in a fourfold and an eightfold site, respectively. Our result is also in contrast with X-ray and molecular dynamics studies for pyrope glass (Okuno and Marumo 1993; Okuno and Kawamura 1995). The MAS spectrum of $Ca_2MgSi_2O_7$ glass shows slightly higher frequency than those of the other three glasses. This may suggest a larger amount of fivefold Mg species. Moreover, Wilding et al. (2004) recently reported the Mg coordination number of 4.5 for $MgSiO_3$ glass, based on a reverse Monte Carlo (RMC) simulation with X-ray and neutron diffraction. Our study, however, contradicts their result. This may stem from the short cut-off distance in their study. They also insisted that the mean coordination number increased from 4.5 to 5.0 with an increase in MgO content from $MgSiO_3$ to Mg_2SiO_4 glass. Another RMC study for Mg_2SiO_4 glass estimated that MgO_4, MgO_5, and MgO_6 polyhedra were present in a ratio of 30%, 50%, and 20%, respectively (Kohara et al. 2004). In combination with the present study, we conclude that the Mg coordination decreases from 6 in $MgSiO_3$ glass to 5 in Mg_2SiO_4 glass. Insufficient numbers of SiO_4 tetrahedra (nominally no bridging oxygen atoms as in olivine) need some MgO_4 units as additional weak network formers to make a network structure in Mg_2SiO_4 glass.

The present 3QMAS NMR spectroscopy suggests the existence of several Mg environments in the $MgSiO_3$ glass structure (Fig. 2a). The multiple sites can be associated with the diversity of SiO_4 tetrahedral network connectivity. Several spectroscopic studies suggested that the alkaline earth silicate glasses have broad Q^n distributions (Murdoch et al. 1985; Kubicki et al. 1992; Schneider et al. 2003). Mg^{2+} ions should locate in the interstitial positions among the SiO_4 linkage, resulting in the environmental diversity. Another significance is that these sites (A, C, and D) should be distinguished by the degree of MgO_6 octahedral distortions rather than by the difference in coordination states. Site A has a small P_Q value, indicating relatively regular octahedral sites. On the other hand, the large-P_Q sites C and D are attributed to highly distorted octahedra with large electric field gradients (EFG) (MacKenzie and Meinhold 1994). Such polyhedral distortions are also confirmed by inspecting an asymmetrical Mg-O peak in a radial distribution function (Wilding et al. 2004), and Yin et al. (1983) have insisted that $MgSiO_3$ glass has four Mg-O bonds at 2.08 Å and two additional bonds at 2.5 Å, based on the quasi-crystalline model. The 3QMAS spectrum clearly shows such distorted sites in $MgSiO_3$ glass. On the other hand, the 3QMAS spectrum of $K_2MgSi_2O_6$ glass shows a single peak with a long tail along the QIS axis (Fig. 2b). This indicates that the Mg^{2+} ions, among the competing K^+ ions, locate in a regular site coordinated by four oxygen atoms, although additional distorted sites may be hidden in the tail.

In the upper mantle, olivine, pyroxene, and garnet are believed to be abundant mineral components. Thus, primitive magmas are Mg-rich liquids, and the structural contribution from Mg^{2+} ions, as well as SiO_4 tetrahedral connectivity, could be an important factor affecting the dynamic properties of the liquids. The increase in the Mg coordination number will easily occur compared with that of the Si atom at depth (Kubicki and Lasaga 1991; Shimoda and Okuno 2006). At moderate pressures where the Si coordination state remains unchanged, the Mg^{2+} ion may control the bulk viscosity of the liquids, involving the pressure-induced network polymerization discussed above (Dickinson et al. 1990). Our findings predict that the viscosity of $MgSiO_3$, $Ca_2MgSi_2O_7$, and $Mg_3Al_2Si_3O_{12}$ melts (containing MgO_6) increases, but that of $(K,Na)_2O$-MgO-nSiO$_2$ melts (containing MgO_4) decreases at low pressures.

Our results further predict that the high-Z/d^2 divalent cations such as Fe^{2+} (0.44–0.51) and Ni^{2+} (0.48–0.55) should have local environments similar to Mg^{2+}; they have highly distorted octahedral sites in silicate glasses with no (or less) alkali cations, and the tetrahedral sites in the alkali-containing glasses (Waychunas et al. 1988; Keppler 1992; Farges et al. 2001). Jackson et al. (1993) have reported the Fe^{2+} coordination number of 4 for Fe_2SiO_4 melt, in reasonable agreement with that for Mg_2SiO_4 glass (Kohara et al. 2004).

The present study illustrates the potency of the ^{25}Mg MQMAS NMR technique under an ultra-high magnetic field, which shows the first evidence of multiple Mg sites with several degrees of distortion. We conclude that the Mg^{2+} ions in $MgSiO_3$, $CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, and $Mg_3Al_2Si_3O_{12}$ glasses are mainly in MgO_6 octahedral sites, in strong contrast with some previous studies. The ^{25}Mg MQMAS technique offers a great opportunity for understanding Mg local environments and their roles in organic and inorganic complexes (Grant et al. 2000; Hatakeyama et al. 2005).

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