

Communication

Multiple Ca^{2+} environments in silicate glasses by high-resolution ^{43}Ca MQMAS NMR technique at high and ultra-high (21.8 T) magnetic fields

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Abstract

We here show the ^{43}Ca 5QMAS NMR spectra at high field (16.4 T) and the first 7QMAS spectrum at ultra-high field (21.8 T) for geologically important Ca-containing glasses. The high-resolution MQMAS spectra present a clear evidence of multiple Ca sites in the amorphous structures that have never been identified by other analytical methods. The present study suggests that the Ca^{2+} ions are mainly in 7- and 8-fold coordination sites. This will offer valuable insights for dynamic properties of magmatic liquids. The MQMAS NMR technique at high magnetic field is a unique tool to understand the detailed structural information on a specific element in solids including organic and inorganic compounds.

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1. Introduction

Alkaline earth cations, Mg^{2+} and Ca^{2+} , are abundant elements in the magmatic liquids. Most studies on their chemical structures have been focused on SiO_4 and AlO_4 tetrahedral networks [1,2], whereas the local environments around the divalent cations have been a long-standing question to understand a global picture of amorphous structures. Nuclear magnetic resonance (NMR) spectroscopy is an advantageous method to analyze the local chemical sites around a specific element in complex materials. Especially, double rotation (DOR) [3], dynamic angle spinning (DAS) [4], and multiple-quantum magic angle spinning (MQMAS) [5] techniques offer high-resolution spectra for half-integer spins such as ^{25}Mg ($I = -5/2$) and ^{43}Ca ($I = -7/2$). On the other hand, NMR studies on such cations have been suppressed because of low natural abun-

dance (0.145% for ^{43}Ca) and low Larmor frequencies [6–8]. In this study, we report the Ca^{2+} environments in several geologically relevant silicate glasses using high-resolution MQMAS NMR spectroscopy at high and ultra-high magnetic fields.

2. Experimental

CaSiO_3 , $\text{CaMgSi}_2\text{O}_6$, and $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses were prepared by melting adequate mixtures of SiO_2 , Al_2O_3 , $\text{Mg}(\text{OH})_2$, and CaCO_3 reagents at 1500–1600 °C. Calcium-43 isotope enrichment of these glasses was achieved by using a 66% ^{43}Ca -enriched CaCO_3 powder (Trace Sciences International Inc.). X-ray diffraction patterns showed their amorphous structures.

^{43}Ca MAS, 3QMAS and 5QMAS [9] NMR spectra were acquired on the JNM-ECA700 spectrometer (16.4 T) working at 47.1 MHz, whereas the JNM-ECA930 (21.8 T) with a resonant frequency at 62.6 MHz was used for a 7QMAS spectrum of the CaSiO_3 glass. Samples were spun at 18 kHz

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in 4-mm MAS rotors. ^{43}Ca chemical shifts were externally referenced to a saturated CaCl_2 solution at 0.0 ppm. The MAS spectra were acquired at 45° tip angle (1.0 μs ; the rf-field of 125 kHz) optimized for the glasses with a recycle interval of 25 s and 128 scans. We applied a z-filter sequence in MQMAS [10]. Spectra were acquired with the optimized excitation and conversion pulses of 4.2 μs and 1.5 μs (360 scans for each of 16 t_1 increments and an interval of 15 s) for 3QMAS, and 5.6 μs and 2.4 μs (960 scans for each of 16 t_1 increments and an interval of 15 s) for 5QMAS, respectively. The 7QMAS spectrum of CaSiO_3 glass was acquired at 21.8 T with the optimized pulses of 6.9 μs and 3.7 μs (7392 scans for each 8 t_1 increments and an interval of 5 s). We applied a universal ppm scaling [11], which enable us to compare directly between 3Q, 5Q, and 7QMAS spectra. The isotropic chemical shifts (δ_{CS}) and quadrupolar products (P_Q) were extracted from the sheared two-dimensional spectra [12];

$$\delta_{\text{CS}} = \frac{17}{27}\delta_1 + \frac{10}{27}\delta_2,$$

$$P_Q = \sqrt{\frac{170}{81} \frac{[4S(2S-1)]^2}{[4S(S+1)-3]}} (\delta_1 - \delta_2) \cdot \nu_0 \cdot 10^{-3},$$

where δ_1 and δ_2 are the shifts in the isotropic and MAS dimensions, ν_0 is the Zeeman frequency, and S is the spin number.

3. Results and discussion

Fig. 1 represents ^{43}Ca MAS NMR spectra of CaSiO_3 , $\text{CaMgSi}_2\text{O}_6$, and $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses. The spectra show a broad signal (FWHM of 70–80 ppm), indicating Ca^{2+} ions in the disordered structures. The peak positions are 11.4, 4.2, and -11.7 ppm, respectively.

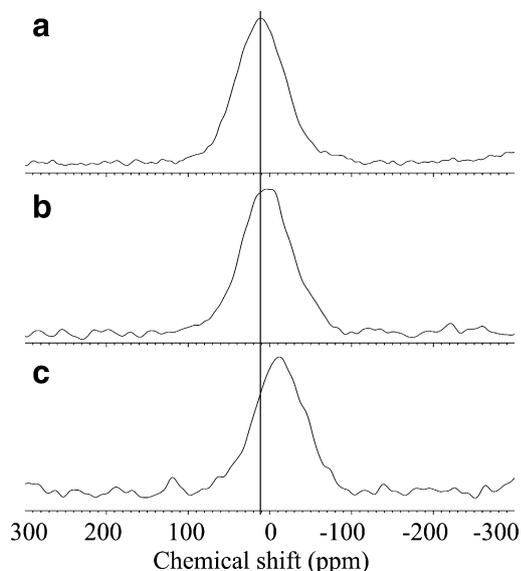


Fig. 1. ^{43}Ca MAS NMR spectra of (a) CaSiO_3 , (b) $\text{CaMgSi}_2\text{O}_6$, and (c) $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses at 16.4 T. The vertical line is a guide for the eye.

Fig. 2(a)–(f) show 3QMAS and 5QMAS spectra for the glasses. Although the 3QMAS spectra showed a single broad distribution as in their corresponding MAS spectra, the highly resolved 5QMAS spectra revealed several Ca sites in $\text{CaMgSi}_2\text{O}_6$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses. Since the 5QMAS spectrum of CaSiO_3 glass still showed a single peak, we thus performed the first 7QMAS measurement for the amorphous material at ultra-high magnetic field (Fig. 3). The highest septuple-quantum coherence pathway for ^{43}Ca provided the best resolved peaks due to the homogeneous effects [13] at the expense of the signal-to-noise ratio. All the spectra in Figs. 2 and 3 mostly align along the CS axis due to small P_Q values and the high magnetic fields we used, suggesting the distribution of chemical shifts, i.e., the diversity of Ca environments. According to the previous studies [6,8], the sites A ($\delta_{\text{CS}} = 14.9$ ppm, $P_Q = 3.9$ MHz), B (28.5 ppm, 3.4 MHz), and C (50.3 ppm, 2.6 MHz) for CaSiO_3 glass can be assigned to 8-, 7-, and 6-fold Ca species, respectively. Similarly, the sites A (13.9 ppm, 3.2 MHz), B (28.8 ppm, 3.3 MHz), and C (ca. 57.5 ppm, 3.2 MHz) for $\text{CaMgSi}_2\text{O}_6$ glass can be attributed to 8-, 7-, and 6-fold Ca states. For $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass, the sites B (9.2 ppm, 3.2 MHz) and C (ca. 27.0 ppm, 3.1 MHz) can be due to 8- and 7-fold species. The site A (-5.0 ppm, 3.0 MHz) may be from another 8-fold environment.

Assuming the small P_Q difference between the sites implying the similar efficiency in multiple-quantum excitation, the site populations were estimated by fitting the F1-projections of 5QMAS and 7QMAS spectra with three or four pseudo-Voigt components. The rough estimates obtained for sites A, B, and C were 21, 70, and 9% for CaSiO_3 glass, 40, 58, and 2% for $\text{CaMgSi}_2\text{O}_6$ glass, and 53, 38, and 8% for $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass (the fitting errors are within 1%). The average coordination numbers are calculated to 7.1, 7.4, and 7.8 with the above assignments. The incorporation of Mg^{2+} and Al^{3+} appears to increase highly coordinated species. The coordination increase in $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass when compared to CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses can be explained in terms of the network polymerization by introducing Al_2O_3 . Because there is less negative charge on the bridging oxygen (BO) than on the non-bridging oxygen (NBO), there are more oxygen atoms needed to balance the positive charge on the Ca^{2+} , thus higher coordination in the BO-rich, highly polymerized glass. This is consistent with a recent ^{23}Na NMR study [14]. In another perspective, the increase in the charge-compensating nature of Ca^{2+} ion may lead to higher coordination state with longer Ca–BO distances [15].

The crystalline polymorphs of CaSiO_3 (wollastonite, parawollastonite, and pseudowollastonite) have 6- to 8-fold Ca sites [16–18]. Diopside ($\text{CaMgSi}_2\text{O}_6$) has an 8-fold Ca site [19], and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) has 6- and 7-fold sites [20]. In the amorphous structures, the multiple environments on Ca^{2+} ion stem from the diversity of TO_4 ($T = \text{Si}, \text{Al}$) tetrahedral network connectivity Q^n , where the superscript n means the number of bridging oxygen

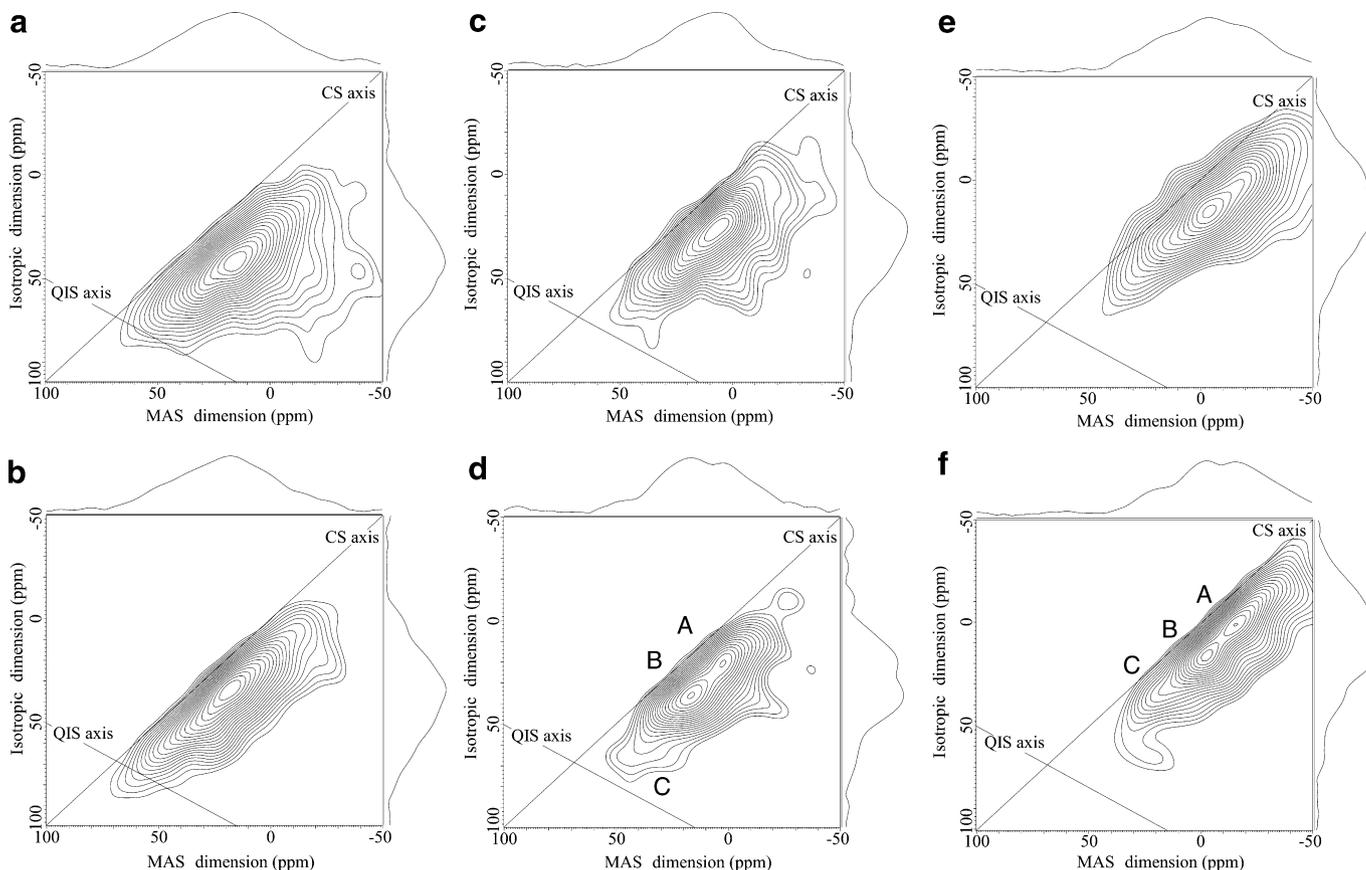


Fig. 2. (a) 3QMAS and (b) 5QMAS spectra for CaSiO_3 , (c) 3QMAS and (d) 5QMAS spectra for $\text{CaMgSi}_2\text{O}_6$, and (e) 3QMAS and (f) 5QMAS spectra for $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses at 16.4 T, respectively. Contours are plotted at 4–96% with an increment of ca. 4% for CaSiO_3 , 5–95% with an increment of ca. 5% for $\text{CaMgSi}_2\text{O}_6$, and 4.5–94.5% with an increment of ca. 4.5% for $\text{CaAl}_2\text{Si}_2\text{O}_8$ glasses, respectively. The spectra were treated with a Gaussian broadening of 400 Hz.

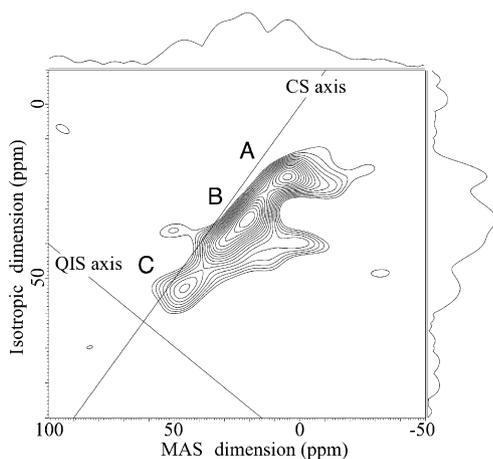


Fig. 3. 7QMAS spectrum of CaSiO_3 glass at 21.8 T. Contours are plotted at 6–94% with an increment of ca. 6%. The spectra were treated with a Gaussian broadening of 500 Hz and a long zero-filling as compensation for the short t_1 increment.

within a TO_4 tetrahedron. For example, Schneider et al. [1] reported ^{29}Si MAS spectra for CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ glasses, and deconvolved the signals into several Q^n contributions by Gaussian fitting.

It is interesting to note that we observed higher Ca coordinations in the $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass than those in “crystalline” anorthite. ^{27}Al and ^{17}O 3QMAS studies showed a small amount of 5-fold Al and NBO even in the $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass, although the conventional concept (stoichiometric consideration) shows only AlO_4 and no NBO, where Ca^{2+} ions act as charge balancers to locate around AlO_4^{5-} tetrahedra [21–24]. The additional oxygen in an AlO_5 pentahedron can result in the higher coordination states (8-fold) on Ca.

The Ca local environments in amorphous structures have not been well determined. Some X-ray RDF and EXAFS studies provided the coordination number of ~ 6 for Ca-containing silicate glasses [25–27]. Eckersley et al. [28] also concluded a well-defined CaO_6 species in the CaSiO_3 glass based on neutron diffraction with a Ca isotopic substitution technique. On the other hand, the present study suggests that the Ca^{2+} ions dominantly occur in the 7- and 8-fold coordination states. The discrepancy between the present and the previous studies may be due to the inadequacy of the coordination estimates from the radial distribution functions as reported by Cormier et al. [29], suggesting the existence of additional longer Ca–O pairs (i.e., polyhedral distortion). Recently, Neuvill et al. [30] reported Ca XANES spectra for $\text{CaO–Al}_2\text{O}_3\text{–SiO}_2$ glasses,

and suggested that Ca^{2+} ions were in distorted 7-fold environments as in anorthite. Our results partly support their study, but ^{43}Ca MQMAS NMR technique enables us to discuss the detailed site information including distribution of coordination states.

4. Conclusions

In conclusion, we successfully demonstrated the high-resolution MQMAS (especially 5QMAS and 7QMAS) NMR spectra that presented a clear evidence of multiple Ca sites for the geologically important Ca-containing glasses. The present study suggested that the Ca^{2+} ions were in 7- and 8-fold coordination states, in contrast with the previous studies. We thus expect that the MQMAS NMR technique, especially at higher magnetic fields, is a unique tool to understand the detailed structural information on such non-framework cations, which will offer valuable insights for dynamic properties of magmatic liquids.

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