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LETTER

Evidence for anomalously large degree of polymerization in Mg_2SiO_4 glass and melt

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ABSTRACT

Ab-initio molecular dynamics simulation of forsterite (Mg_2SiO_4) melt at 2273 K shows the presence of nearly 40% of the Si atoms as $(Si_2O_7)^{6-}$ dimers. This result is directly corroborated by the ^{29}Si nuclear magnetic resonance spectrum of bulk Mg_2SiO_4 glass, prepared by container-less levitation techniques. The presence of a large excess of bridging O atoms associated with the $(Si_2O_7)^{6-}$ dimers in forsterite glass and melt is in sharp contrast with their complete absence in crystalline forsterite. Such structural differences between the crystal and the melt can have important implications in understanding the dynamics of crystallization and segregation in a primordial magma ocean and the continuing chemical differentiation of the Earth.

Keywords: Ab initio molecular dynamics, forsterite, melt, glass, simulation, NMR, structure

INTRODUCTION

The mineral forsterite (Mg_2SiO_4) is one of the most important constituents of the terrestrial and lunar mantles and meteorites (e.g., Helfrich and Wood 2001; Tangeman et al. 2001). Glassy and crystalline Mg-rich end-members of the solid-solution series $(Mg,Fe)_2SiO_4$ are important ingredients of interplanetary and interstellar dust (Bradley et al. 1999; Molster et al. 1999). A fundamental understanding of the structure of glasses and melts of orthosilicate composition is essential to develop and test thermodynamic and dynamic models for the crystallization and segregation in the primordial magma ocean and for the large-scale chemical differentiation of the Earth and formation of the Moon (Stixrude and Karki 2005; Wilding et al. 2004; Herzberg and O'Hara 1998; Agee 1998). Unfortunately, structural studies of Mg_2SiO_4 glass have proved to be difficult in the past due to the experimental challenges involved in the synthesis of these glasses, arising primarily from their extremely poor glass-forming tendency.

Previous vibrational spectroscopic studies of orthosilicate glasses of pure forsterite and other compositions along the Mg-Fe and Mg-Mn joins synthesized by splat quenching techniques have shown that the structures of these glasses consist primarily of isolated SiO_4 tetrahedra, i.e., the Q^0 species (Williams et al. 1989; Durben et al. 1993). This result is consistent with the structures of crystalline orthosilicates which consist solely of Q^0 species. It is also in agreement with our conventional wisdom regarding the mechanism of formation of non-bridging O (NBO) atoms on introduction of modifier cations in SiO_2 which predicts that all O atoms in the glass structure would become NBO atoms at the orthosilicate composition (Eckert 1992). More interestingly, the Raman spectra of these splat-quenched glasses also showed the presence of a small concentration of $(Si_2O_7)^{6-}$ dimers or Q^1 species in the structure, which was suggested to be indicative of excess polymerization in the structure beyond that dictated by the stoichiometry. However, the relative fraction of such dimers could not be estimated from these vibrational spectra (Williams et al. 1989; Durben et al. 1993). Such estimation is particularly critical since the observation of dimers is also consistent with the analyzed compositions of these glasses which were found to be slightly off from the orthosilicate stoichiometry with ~34.3 mol% SiO_2 which implies that ~17% of Si would be present as Q^1 species (Williams et al. 1989).

Recent technological advances in laser-heated container-less levitation melting have allowed the synthesis of Mg_2SiO_4 and other high-MgO (>50 mol% MgO) silicate glasses in quantities of tens to hundreds of milligrams, that are largely free of crystals (Tangeman et al. 2001; Wilding et al. 2004; Kohara et al. 2004). Combined X-ray and neutron diffraction studies of such samples have shown that Mg-O coordination number increases from ~4 in Mg-silicate glasses with relatively low MgO content (50 mol% < MgO < 62 mol%) to ~5 for ~66.7% MgO, i.e., the Mg_2SiO_4 composition (Wilding et al. 2004; Kohara et al. 2004). This result is consistent with the presence of polymerized units in the Mg_2SiO_4 glass since at this stoichiometry any dimerization or other types of polymerization of SiO_4 tetrahedra would result in the formation of "free" O atoms. These O atoms would have to be bonded to Mg only, which would thereby increase the Mg-O coordination number in the glass (Kohara et al. 2004). However, the structural conclusions reported in these studies were based on the nominal compositions of the Mg-silicate glasses and exact chemical compositions of the samples were not reported. Besides, these experiments could not directly measure the extent of bulk polymerization of the Mg_2SiO_4 glass in terms of the Q-species make-up of the structure.

The ^{29}Si magic-angle-spinning nuclear magnetic resonance

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(MAS NMR) spectroscopic study of the Mg_2SiO_4 glass synthesized by container-less levitation techniques reported the presence of a single, relatively broad and slightly asymmetric peak centered at –70.4 ppm (Tangeman et al. 2001). This ^{29}Si MAS NMR peak was interpreted as indicating the presence of primarily Q^0 species that are likely to be sharing corners with the MgO_6 octahedra in the glass structure. The authors also noted that the ^{29}Si MAS NMR peak spanned the chemical shift range characteristic of Q^1 species in crystalline Ca-Mg-silicates (~ –72 to –82 ppm) and hence was consistent with the presence of small quantities of Q^1 species in the glass structure. However, chemical analyses of these glasses again indicated small but systematic deviation from the orthosilicate stoichiometry with ~34.4% SiO_2, which would dictate the presence of ~17% of the Si atoms as Q^1 species (Tangeman et al. 2001). Unfortunately, the lack of resolution in this ^{29}Si MAS NMR spectrum resulting from the presence of overlapping signals from the constituent Q-species due to the structural disorder did not allow a quantitative estimation of the degree of polymerization in the glass.

In light of this controversy, we have carried out an ab initio molecular dynamics (AIMD) simulation of Mg_2SiO_4 melt structure. The ^{29}Si NMR chemical shift parameters of the Si sites in this structure are calculated from first principles and have been compared with the experimental ^{29}Si NMR spectra of near-stoichiometric Mg_2SiO_4 glass synthesized via container-less levitation techniques. Here we present the results of this study that, when taken together, provide a consistent picture of the structure of Mg_2SiO_4 glass and liquid.

Experimental and simulation methods

Sample synthesis and ^{29}Si NMR spectroscopy

The Mg_2SiO_4 glass sample was synthesized from the constituent oxides using the container-less levitation melting technique. Although the glass sample studied here is a different batch compared to that used in a previous study by Tangeman et al. (2001), details of the synthesis procedure is identical to that reported in previous studies (Tangeman et al. 2001; Kohara et al. 2004). The glass sample consisted of spherical beads with diameters of ~0.5 mm. NMR spectroscopic measurements were made at ^{29}Si Larmor frequency of 99.3 MHz with Bruker probes and a Bruker Avance 500 spectrometer equipped with a widebore ultrashield magnet. The ^{29}Si static spectrum of the Mg_2SiO_4 glass was collected with a wideline probe. For MAS experiment the sample in the form of spherical beads was spun in a zirconia rotor without further crushing, in a 7 mm Bruker MAS probe. Radiofrequency (rf) pulses of duration 2.1 and 4.0 μs (both corresponding to 60° tip angle) were used for the ^{29}Si static and MAS experiments, respectively. Chemical shift for all ^{29}Si spectra are referenced to tetramethyl silane (TMS).

Ab initio molecular dynamics simulation and ^{29}Si NMR chemical shift calculation

The starting cell for AIMD simulations was cubic with 112 atoms (16 formula units of Mg_2SiO_4) and the cell volume was adjusted to the experimental density of Mg_2SiO_4 glass (~2.9 g/cm^3). Although this cell size is significantly smaller than those typically used for classical MD simulations (several thousand formula units), AIMD simulation is computationally intensive and requires several thousands of processor hours even for a cell with ~100 atoms. AIMD simulations were carried out using the density functional theory code CASTEP (Accelrys, Inc.) with the plane-wave pseudopotential method within the local density approximation (LDA) (Segall et al. 2002). The Perdew-Zunger exchange-correlation functionals (Perdew and Zunger 1981) modified after Ceperley and Alder were used (Ceperley and Alder 1980). A canonical ensemble was used with periodic boundary conditions and with Γ-point-only k-space sampling of the Brillouin zone. Ionic cores were described by ultra-soft Vanderbilt pseudopotentials with a cutoff energy of 310 eV (Vanderbilt 1990). An integration time step of 1 fs was used and temperature was controlled using a Nosé thermostat (Nosé 1984). The starting structure was melted at 6000 K for 1 ps. Subsequently the temperature of the resulting structure lowered incrementally to 4000 and 2000 K and allowing the structure to equilibrate at each temperature for 1 ps. The resulting structure was relaxed at 300 K for 2 ps within the generalized gradient approximation (GGA) simplified by the Perdew-Burke-Ernzerhof (PBE) functional (Segall et al. 2002). An energy cutoff of 600 eV for the plane wave basis expansions was used for this step.

First-principles calculations of ^{29}Si NMR chemical shift parameters of the Si sites in this simulated melt structure were carried out using the recently developed gauge-including projector augmented wave (GIPAW) method. The code CASTEP-NMR (Accelrys, Inc.) was used for these calculations within the GGA approximation with an energy cutoff of 600 eV. This method allows the reconstruction of the all-electron magnetic response from the pseudo-wave functions and is ideally suited for extended systems with periodic boundary conditions (Mauri et al. 1996). Recent studies have demonstrated the excellent accuracy of the GIPAW method in calculating the NMR parameters for ^{29}Si and ^{17}O nuclides in a variety of silicate crystals and glasses (Pickard and Mauri 2001; Balan et al. 2003; Farnan et al. 2003; Ashbrook et al. 2007). The Brillouin zone was sampled using the Monkhorst-Pack scheme and a $2 \times 2 \times 2$ k-point grid. These calculations yield the absolute shielding tensor components σ_{xx}, σ_{yy}, and σ_{zz}. The isotropic chemical shift δ_{iso} was obtained from isotropic shielding $\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$ using the experimentally determined ^{29}Si chemical shift of α-quartz as a reference. The chemical shift anisotropy (CSA) and asymmetry parameter η have been calculated using the relationships: $CSA = (\sigma_{zz} - \sigma_{iso})$ and $\eta = (\sigma_{yy} - \sigma_{xx})/(\sigma_{zz} - \sigma_{iso})$. We have assessed the accuracy of the GIPAW method by calculating the ^{29}Si NMR isotropic chemical shifts for the Si configurations reported for crystalline magnesium silicates and have found it to be within ±3 ppm (Gaudio et al. 2008).

Results and discussion

The simulated structure of the melt shows participation of ~40% of the Si atoms (6 out of 16 Si atoms in the simulation cell) in the formation of $(Si_2O_7)^{6-}$ dimers or Q^1 species with the concomitant formation of "free" O atoms (Fig. 1). The rest of the Si atoms form isolated Q^0 species. These free O atoms are typically shared by 4 Mg atoms with average Mg-O distances of ~2.03 ± 0.10 Å. The average Mg coordination number in the simulated melt structure has been calculated using a Mg-O cutoff distance of 2.4 Å and is found to be ~4.25. This coordination number is higher than that in the forsterite crystal where all Mg atoms are fourfold coordinated to O and is consistent with previous reports of an abrupt increase in the average Mg-O coordination number in Mg-silicate glasses near the forsterite composition as discussed

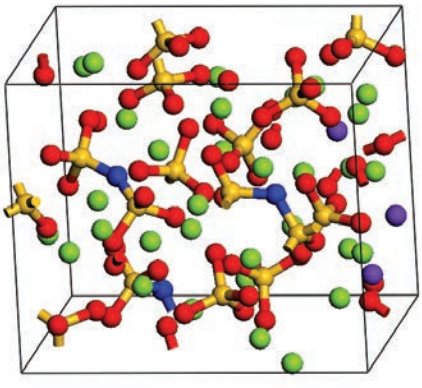

Figure 1. Structure of Mg_2SiO_4 melt obtained from AIMD simulation. Mg, Si, and O atoms in the simulation cell are shown in green, yellow, and red, respectively. Bridging O atoms in $(Si_2O_7)^{6-}$ dimers are shown in blue. Purple atoms are "free" O atoms shared only by Mg atoms.

above. However, this coordination number in the simulated melt structure (~4.25) as observed in this study is somewhat lower than its value (~4.7 ± 0.1) inferred previously from diffraction experiments (Wilding et al. 2004).

The ab initio ^{29}Si NMR chemical shift calculations yield the following ^{29}Si NMR chemical shift parameters for the Q^0 species in the simulated melt structure: average isotropic chemical shift δ_{iso} = –68 ppm, a CSA of –19 ± 4 ppm and η = 0.80 ± 0.15. This δ_{iso} value is similar to that of the Q^0 species in crystalline forsterite (~ –62 ppm) although the CSA of the latter is somewhat larger (–32.2 ppm) than that obtained for the Q^0 species in the simulated melt (Ashbrook et al. 2007). Corresponding parameters for the Q^1 species in the simulated melt are –75 ppm, 55 ± 5 ppm, and 0.60 ± 0.15, respectively. Hence, chemical shift calculations show only small differences in ^{29}Si isotropic chemical shifts of Q^0 and Q^1 sites in Mg_2SiO_4 melt, consistent with the lack of resolution of these two sites in previously published ^{29}Si MAS NMR spectra of a nominally Mg_2SiO_4 glass (Tangeman et al. 2001). However, the significant difference between the CSA parameters of these two sites, as expected from the difference in the site symmetries of Si atoms in these two Q-species, implies that better site resolution can possibly be obtained in the static ^{29}Si spectrum. The reason being, unlike MAS experiments, solid-state NMR spectra collected in the static mode, i.e., without sample spinning at the magic angle, preserves the site symmetry information for the nuclide under observation. Such information is typically lost in MAS NMR due to orientational averaging during magic angle spinning.

The ^{29}Si static NMR powder pattern of the Mg_2SiO_4 glass sample clearly reveals the presence of at least two Si sites and can be simulated well with a Gaussian peak centered at –66 ppm and a strongly non-axial powder pattern with δ_{iso} = –73 ppm, CSA = 45 ppm, and η = 0.9 (Fig. 2). These chemical shift parameters are consistent with the calculated values for Q^0 and Q^1 sites, respectively, in the simulated Mg_2SiO_4 melt structure. Hence, we assign the Gaussian peak and the non-axial powder pattern to Q^0 and Q^1 sites in the Mg_2SiO_4 glass. Integration of the areas under these line shapes directly yield the result that ~49 ± 4% of the Si atoms are present as Q^0 species in the Mg_2SiO_4 glass structure while ~51 ± 4% of the Si atoms are present as Q^1 species indicating a remarkably large degree of polymerization. The actual error bars for this Q-speciation are possibly somewhat larger due to the unknown contribution from unresolved signal corresponding to small amounts of Q^2 species and crystalline forsterite that may be present in the glass (vide infra). Moreover, Q-speciation obtained from NMR spectroscopy on the glass and AIMD simulation on the melt may not be directly comparable. Nevertheless, the experimental Q-speciation result is consistent with the observation made earlier that ~40% of the Si atoms in the simulated Mg_2SiO_4 melt structure form Q^1 species. Electron microprobe analyses of the Mg_2SiO_4 glass studied here indicate a small deviation from the orthosilicate stoichiometry, similar to that reported in a previous study (Tangeman et al. 2001) with ~34.5 ± 0.5 mol% SiO_2. However, the observation of ~51% of Si being present as Q^1 species in this glass clearly demonstrates the existence of a large excess of bridging O atoms beyond that demanded by this stoichiometry. When taken together, the experimentally observed Q-speciation and the concomitant formation of free O atoms in the simulated melt structure imply Q-species disproportionation according to the reaction: $2Q^0 = 2Q^1 + (O)^{2-}$ where $(O)^{2-}$ represents a free oxygen atom. Therefore, the presence of ~51% of Si atoms as Q^1 species would require the presence of ~6.25% of all O atoms as the $(O)^{2-}$ species in forsterite glass.

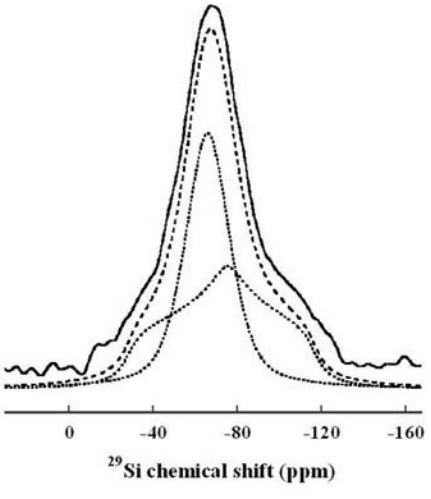

FIGURE 2. Experimental (solid line) and simulated (thick dashed line) ^{29}Si static NMR spectra of Mg_2SiO_4 glass with individual simulation components (thin dashed lines: Gaussian and non-Gaussian components correspond to Q^0 and Q^1 species, respectively). Experimental and simulated line shapes are vertically offset for clarity. Static spectrum represents an average of 154 000 transients collected with a delay of 10 s between pulses.

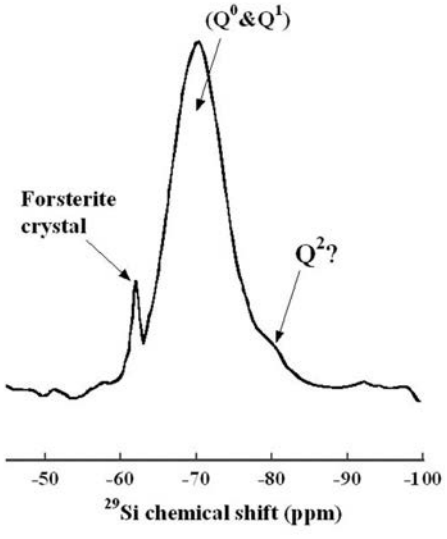

FIGURE 3. ^{29}Si MAS NMR spectrum of Mg_2SiO_4 glass. Sample was spun at a rate of 6 kHz and 9000 transients, collected with a delay of 10 s between pulses, were averaged to obtain the MAS spectrum. ^{29}Si MAS NMR spectra collected with longer delay times do not show any indication of differential relaxation between the signals for the crystal and the glass.

The ^{29}Si MAS NMR spectrum of this sample (Fig. 3) is similar to that published in a previous study (Tangeman et al. 2001). The sharp peak in this spectrum, centered at ~ –62 ppm corresponds to the presence of a small amount (~2.5%) of crystalline forsterite in the sample and is expected to have a nearly negligible effect (less than 1%) on Q-speciation. The chemical shift of the main peak in the ^{29}Si MAS spectrum at –70.4 ppm agrees within 1 ppm with the weighted average of the isotropic shifts of the Q^0 and Q^1 components in the static ^{29}Si spectrum indicating consistency of the spectral simulation (Fig. 2). The ^{29}Si MAS spectrum also displays a shoulder on the high-field side of the spectrum near –80 ppm that may correspond to the presence of a small amount (~9%) of Q^2 species in the glass structure. The crystalline forsterite and the Q^2 species in the glass are not directly detectable in the static ^{29}Si NMR spectrum due to their small concentrations combined with broad anisotropic line shapes. The shoulder corresponding to the Q^2 species in Figure 3 was not observed in the ^{29}Si MAS NMR spectrum of a glass of similar composition published in a previous study (Tangeman et al. 2001). Although no definitive argument can be made at this stage to explain such a difference, it may result from differences in cooling rates and hence in fictive temperatures of the two sets of samples.

A large concentration of excess bridging O atoms in silicate melts near the orthosilicate composition as observed in this study is expected to lead to rapid non-linear compositional variation in melt properties. Besides the structural effects on the configurational entropy and hence the fragility of the melt, the large excess of bridging O atoms in the orthosilicate melt will affect its transport properties such as diffusivity and viscosity and other physical properties, most notably compressibility. For example, the compressibility of a forsterite melt containing bridging Si-O-Si linkages is expected to be higher than that of the crystal with isolated SiO_4 tetrahedra as Si-O-Si bond angle is a highly compressible structural element in silicates (Burkhard 1997). Increasing compressibility at high pressure, may lead to magmas that are denser than the coexisting crystals (Lange and Carmichael 1990; Agee 1998). Such density reversal would allow for major chemical stratification of the mantle and would strongly influence the mechanisms and rates of mass and heat transport during planetary differentiation (Rigden et al. 1988; Heinz and Jeanloz 1987).

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