Different structural behavior of MgSiO₃ and CaSiO₃ glasses at high pressures

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Abstract

Knowledge of the structural behavior of silicate melts and/or glasses at high pressures provides fundamental information in discussing the nature and properties of silicate magmas in the Earth’s interior. The behavior of Si-O structure under high pressure conditions has been widely studied, while the effect of cation atoms on the high-pressure structural behavior of silicate melts or glasses has not been well investigated. In this study, we investigated the structures of MgSiO₃ and CaSiO₃ glasses up to 5.4 GPa by in-situ X-ray pair distribution function measurements, to understand the effect of different cations (Mg²⁺ and Ca²⁺) on high pressure structural behavior of silicate glasses. We found that the structural behavior of MgSiO₃ and CaSiO₃ glasses are different at high pressures. The structure of MgSiO₃ glass changes by shrinking of Si-O-Si angle with increasing pressures, which is consistent with previous studies for SiO₂ and MgSiO₃ glasses. On the other hand, CaSiO₃ glass shows almost no change in Si-Si distance at high pressures, while the intensities of two peaks at ~3.0 Å and ~3.5 Å change with increasing pressure. The structural change in CaSiO₃ glass at high pressure is interpreted as the change of the
fraction of the edge-shared and corner-shared CaO\textsubscript{6}-SiO\textsubscript{4} structures. The different high-pressure structural behavior obtained in MgSiO\textsubscript{3} and CaSiO\textsubscript{3} glasses may be structural origin of the difference in the properties such as viscosity between MgSiO\textsubscript{3} and CaSiO\textsubscript{3} melts at high pressures, implying the importance of the different structural behavior due to different cation atoms to discuss the nature and properties of silicate magmas in the Earth’s interior.

Keywords: glass structure, MgSiO\textsubscript{3}, CaSiO\textsubscript{3}, pair distribution function, high pressure

Introduction

Structures of silicate melts strongly influence physical properties such as density, viscosity, and diffusivity (e.g., Sakamaki et al., 2013; Sanloup et al., 2013; Wang et al., 2014; Bajgain et al., 2015), and therefore knowledge of the structural behavior of silicate melts and/or glasses under high pressure conditions is fundamental in understanding the nature and properties of silicate magmas in the Earth’s interior. Since structural investigation of silicate melts under in situ high pressure and high temperature condition is
still challenging, due to the technical difficulties, silicate glasses have been studied at high
pressures under room temperature condition as an analogue of silicate melts. Pressure-
induced structural changes of SiO$_2$ glass have been the most studied as the simplest silicate
composition by using in situ high-pressure techniques (e.g., Sato and Funamori, 2008;
Benmore et al., 2010; Murakami and Bass, 2010; Prescher et al., 2017; Lee et al., 2019;
Petitgirard et al., 2019; Kono et al., 2020; Andrault et al., 2020, Kono et al., 2022), which
provide important knowledge on the behavior of Si-O structure under high pressure
conditions. In addition, MgSiO$_3$ glass also has been studied by several researchers as a
representative composition of silicate magma in the Earth’s interior (e.g., Lee et al., 2008;
Kono et al., 2018; Salmon et al., 2019; Ryu et al., 2022). However, structural behavior of
other silicate glasses with different compositions remains not well investigated at in situ
high-pressure conditions.

In this study, we investigate structure of MgSiO$_3$ and CaSiO$_3$ glasses at high pressure
conditions up to 5.4 GPa by using in situ pair distribution function measurements, to
understand the effect of different cations (Mg$^{2+}$ and Ca$^{2+}$) on the high-pressure structural
behavior of silicate glasses. MgSiO$_3$ and CaSiO$_3$ glasses are the end-member pyroxene
compositions, and therefore knowledge of the structural behavior of MgSiO$_3$ and CaSiO$_3$
glasses at high pressures would provide important clues to understand structure and properties of silicate magmas in the Earth’s upper mantle. At ambient pressure condition, structures of MgSiO$_3$ and CaSiO$_3$ glasses have been studied by neutron diffraction (e.g., Cormier and Cuello, 2011), high energy X-ray diffraction (Kohara et al., 2011), Raman spectroscopy (e.g., Kalampounias et al., 2009), and nuclear magnetic resonance (NMR) spectroscopy (e.g., Kaseman et al., 2015) techniques. On the other hand, structural investigations of these glasses at in situ high pressure conditions are still limited, although there are several structural analyses for the high-pressure synthesized silicate glasses at ambient pressure condition (Shimoda et al., 2005). Nevertheless, structure of MgSiO$_3$ glass at in situ high pressure conditions has been studied by some previous studies using neutron diffraction (Salmon et al., 2019), X-ray diffraction (Kono et al., 2018; Ryu et al., 2022), and X-ray Raman scattering (Lee et al., 2008) measurements. In contrast, structure of CaSiO$_3$ glass has not been well studied at in situ high pressure conditions. To the best of our knowledge, only Kubicki et al. (1992) and Salmon et al. (2019) investigated the structure of CaSiO$_3$ glass at in situ high pressure conditions. Kubicki et al. (1992) conducted in-situ Raman spectroscopy and infrared absorption measurements on CaSiO$_3$ glasses in DAC (diamond anvil cell) at 11-35 GPa. Salmon et al. (2019) investigated the structure of
CaSiO₃ and MgSiO₃ glasses from ambient pressure to 17.5 GPa by using in-situ neutron
diffraction measurement and molecular dynamics (MD) simulation. Salmon et al. (2019)
showed that the M-O (M=Mg, Ca) coordination number of both CaSiO₃ and MgSiO₃
glasses increase at high pressures in a similar manner. The nearest neighbor Si-O and M-O
distances show slight increase with increasing pressure from ambient pressure to 17.5 GPa
(1.61 to 1.62 Å for Si-O distance of MgSiO₃ glass; 1.62 to 1.63 Å for Si-O distance of
CaSiO₃ glass; 1.99-2.02 Å for Mg-O distance in MgSiO₃ glass; 2.32-2.35 Å for Ca-O
distance in CaSiO₃ glass). Mg-O coordination number in MgSiO₃ glass changes from 4.50
at ambient pressure to 6.20 at 17.5 GPa, and Ca-O coordination number in CaSiO₃ glass
changes from 6.15 at ambient pressure to 7.41 at 17.5 GPa. These data indicate that the
nearest neighbor structures in MgSiO₃ and CaSiO₃ glasses change similarly with increasing
pressure. However, the study of Salmon et al. (2019) was limited only for the nearest
neighbor Si-O and M-O distances, due to weak scattering of Si and Ca in neutron
diffraction measurement, and the intermediate range structure such as Si-Si, Ca-Si and Ca-
Ca distances have not been investigated in Salmon et al. (2019).

In this study, we investigated structures of MgSiO₃ and CaSiO₃ glasses at high
pressures up to 5.4 GPa by using in-situ X-ray diffraction measurements to understand
effect of different cation (Mg and Ca) on the high-pressure structural behavior not only in
the nearest Si-O and M-O distances but also in the intermediate Si-Si, M-Si, and M-M
distances. We found different behavior in the intermediate range structures of MgSiO₃ and
CaSiO₃ glasses at high pressure conditions.

Experimental methods

CaSiO₃ and MgSiO₃ samples were prepared by mixing powders of SiO₂, CaCO₃,
and/or MgO. Powders of these oxides and carbonates were dried at 110 °C for >24 hours
before weighing with an electric balance, and were mixed in an agate mortar with ethanol
for 1-2 hours. Glass samples were prepared by an aerodynamic levitation furnace with CO₂
laser heating at ~1800-2100 °C at Geodynamics Research Center (GRC), Ehime University.
Chemical compositions of the synthesized glass samples were confirmed by using JEOL
JM-7000F field-emission scanning electron microscope (FE-SEM) with energy-dispersive
spectroscopy (EDS) at GRC (Table S1). Densities of the CaSiO₃ (2.80±0.05 g/cm³) and
MgSiO₃ (2.68±0.06 g/cm³) glasses were measured by Archimedes’ method.

High-energy X-ray diffraction measurements of the CaSiO₃ and MgSiO₃ glasses at
ambient pressure were conducted at the BL04B2 beamline of the SPring-8. The dedicated
X-ray diffractometer with six points detectors (four cadmium telluride detectors and two
 germanium detectors) at the BL04B2 beamline enables us to conduct accurate pair
distribution function (PDF) analysis with high-real space resolution (Ohara et al, 2020). We
used spherical glass samples of 1.8 mm diameter, which were placed in a vacuum chamber
under room temperature condition. High-energy X-ray diffraction measurements using
monochromatic X-ray of 61.4 keV were carried out by scanning the 2θ angle from 0.3 to 49
degrees, which covers the range of the momentum transfer $Q$ up to 25.5 Å$^{-1}$. The obtained
X-ray diffraction data were analyzed by using standard analysis procedures of the BL04B2
beamline (Kohara et al., 2007).

High-pressure experiments for CaSiO$_3$ and MgSiO$_3$ glasses were carried out by using
a Paris-Edinburgh (PE) press with a standard PE cell assembly of the 16-BM-B beamline in
the Advanced Photon Source (APS) (Kono et al., 2014). Cup-shaped WC anvils with the
cup diameter of 12 mm and the bottom diameter of 3 mm were used. The cell assembly
mainly consists of BN capsule surrounded by inner MgO ring and outer boron-epoxy (BE)
gaskets with ZrO$_2$ caps at the top and bottom the cell. Pressure was determined by X-ray
diffraction measurement of MgO ring with the equation of state of MgO (Kono et al., 2010)
for the CaSiO$_3$ glass experiment, and of Au foil, which is inserted between the MgO ring and BN capsule, using the equation of state of Tsuchiya (2003) for the MgSiO$_3$ glass experiment. Densities of CaSiO$_3$ and MgSiO$_3$ glasses at high pressure conditions are calculated based on the densities of CaSiO$_3$ (2.80±0.05 g/cm$^3$) and MgSiO$_3$ (2.68±0.06 g/cm$^3$) glasses measured at ambient pressure by Archimedes’ method and the pressure-volume relation of CaSiO$_3$ and MgSiO$_3$ glasses reported in Salmon et al. (2019).

Pair distribution function measurement of CaSiO$_3$ glass at high pressures was carried out by a multi-angle energy dispersive X-ray diffraction technique combined with the PE cell at the 16-BM-B beamline of the APS. A large Huber stage holding a germanium solid state detector allows precise control of 2θ angles, and energy dispersive X-ray diffraction measurements using fine collimation slits enables us to collect clean signals from glass sample without background noise from the surrounding pressure medium materials (Kono et al., 2014). We collected energy dispersive X-ray diffraction patterns at the 2θ angles of 3, 4, 5, 7, 9, 12, 16, 22, 28, and 35 degrees. The obtained energy dispersive X-ray diffraction spectra were analyzed by using an analysis program developed by Changyong Park and Rostislav Hrubiak at the 16-BM-B beamline (Kono et al., 2014). We obtained the S(Q) of CaSiO$_3$ glass at the Q range up to 17.0 Å$^{-1}$ under the pressure conditions from 0.8 GPa to
5.4 GPa at room temperature.

Pair distribution function measurement of MgSiO₃ glass at high pressures was conducted at the BL37XU beamline of the SPring-8. We used a monochromatic X-ray of 37.4 keV. The X-ray was focused from 1.0 to 0.2 mm in horizontal with 0.7-m-long horizontal-deflection mirrors so as to increase an available flux. The structure of MgSiO₃ glass was measured up to 5.2 GPa in the PE cell by high-energy X-ray diffraction measurement using a cadmium telluride point detector (Amptek X-123) with a double slit collimation setup in front of the detector. The double slit collimation setup yields collimation length of <1.8 mm at the sample position at 2θ angles higher than ~9°, to avoid background noises. Size of incident slit and two collimation slits were adjusted with varying 2θ angle to maximize intensity of signal by increasing collimation length within the diameter of MgSiO₃ glass sample. High-energy X-ray diffraction measurements for MgSiO₃ glass at high pressures were carried out by scanning the 2θ angle from 1 to 60 degrees. Analysis was conducted by using the method developed at the BL04B2 beamline of the SPring-8 (Ohara et al., 2020). We obtained the $S(Q)$ of MgSiO₃ glass at the $Q$ range up to 15.0 Å⁻¹ under the pressure conditions from 1.0 GPa to 5.2 GPa at room temperature.

It is important to note that both experiments at BL37XU beamline at SPring-8...
(MgSiO$_3$ glass experiment) and at 16-BM-B beamline at APS (CaSiO$_3$ glass experiment) used collimation slit setup in front of the detector. The collimation slit setup enables us to collect the XRD signal only from the sample at the $2\theta$ angle higher than $\sim 9^\circ$ for the MgSiO$_3$ glass experiment and at the $2\theta$ angle higher than $\sim 3^\circ$ for the CaSiO$_3$ glass experiment. Since the collimation slit setup eliminates back-ground noises not only from the high-pressure cell assemblies but also from different beamline component, we can obtain comparable data.

The pair distribution function $g(r)$ was obtained by Fourier transmission of the Faber-Ziman total structure factor $S(Q)$ (Faber and Ziman, 1965). The Lorch function was applied to remove the truncation effect on the final pair distribution function determination (Lorch, 1969). The positions of the peaks of the $g(r)$ showing discernible separation were determined by using simple Gaussian peak fitting. On the other hand, Si-Si, Mg-Si, and Mg-Mg peaks in MgSiO$_3$ glass, and Ca-O and O-O peaks in CaSiO$_3$ glass overlap each other. For the overlapping peaks, we used a multi-peak fitting method described in de Grouchy et al. (2017). In the de Grouchy et al.’s method, the $g(r)$ is the sum of all the individual ion-ion interactions within the sample, where each ion-ion contribution is represented by a Gaussian peak, $g(r)_{\text{ind}}$. The $g(r)$ is fit using the following equations:
\[ g(r) = \sum g(r)_{\text{ind}} = \frac{1}{n_0 S} \sum_i \frac{x_i A_i}{\sigma_i \sqrt{2\pi}} \exp \left( -\frac{(r - d_i)^2}{2\sigma_i^2} \right), \quad (1) \]

where

\[ A_i = \frac{C N_i}{4\pi \sigma_i^2} \int \frac{1}{\sqrt{2\pi}} \exp \left( -\frac{(r - d_i)^2}{2\sigma_i^2} \right) dr, \quad (2) \]

where \( CN_i \) is coordination number for individual ion-ion contributions, \( n_0 \) is number density, \( x_i \) is concentration of the species, and \( d_i \) is interatomic distance. \( \sigma_i \) is calculated from \( k \sqrt{d_i} \), which defines width and height of the individual Gaussian peak. \( k \) is an adjustable parameter (Hosemann and Bagchi, 1962), with values ranging from 0.06 to 0.15 depending on the ion-ion contribution.

**Results**

**Structure of MgSiO\textsubscript{3} and CaSiO\textsubscript{3} glasses at ambient pressure**

Figures 1a and 1b show the \( S(Q) \) and \( g(r) \) of MgSiO\textsubscript{3} glass at ambient pressure, respectively. The \( g(r) \) of MgSiO\textsubscript{3} glass shows peaks at \( r_1=1.621\pm0.002 \text{ Å}, r_2=2.030\pm0.004 \text{ Å}, r_3=2.618\pm0.009 \text{ Å}, \) and \( r_4=3.179\pm0.006 \text{ Å} \). A first-principles molecular dynamics simulation of MgSiO\textsubscript{3} glass reports bond distances of Si-O=1.63 Å, Mg-O=1.98 Å, O-O=2.68 Å, Si-Si=3.02 Å, Mg-Si=3.22 Å, and Mg-Mg=3.42 Å (Ghosh et al., 2014), indicating that the \( r_1, r_2, \) and \( r_3 \) peaks obtained in this study correspond to Si-O, Mg-O, and
O-O distances, respectively. The r₄ peak is considered as overlapping of Si-Si, Mg-Si, and Mg-Mg distances.

The S(Q) and g(r) of CaSiO₃ glass at ambient pressure are shown in Figs. 1c and 1d, respectively. The g(r) of CaSiO₃ glass shows the peak positions at r₁=1.622±0.001 Å, r₂=2.335±0.008 Å, r₃=2.623±0.012 Å, r₄=3.017±0.008 Å, and r₅=3.573±0.014 Å, which are considered as Si-O, Ca-O, O-O, Si-Si/Ca-Si, and Ca-Si/Ca-Ca distances, respectively (Cormier and Cuello, 2013; Mead and Mountjoy, 2006ab). According to a molecular dynamics simulation study (Mead and Mountjoy, 2006ab), Si-Si and Ca-Si distances overlap at the same distance at around 3.1 Å, and Ca-Si and Ca-Ca distances also overlap at around 3.6 Å.

**Structures of MgSiO₃ and CaSiO₃ glasses at high pressures**

Figures 2a and 2b show the S(Q) and g(r) of MgSiO₃ glass from 1.0 to 5.2 GPa. With increasing pressure, intensity of the first sharp diffraction peak (FSDP) of MgSiO₃ glass decreases, and the FSDP position shifts toward high Q (Figs. 2a and 3). The high-pressure behaviour of the FSDP is consistent with those reported in previous MgSiO₃ glass study (e.g., Ryu et al., 2022). On the other hand, the S(Q) of MgSiO₃ glass shows negligible
change at $Q > 3$ Å$^{-1}$ at high pressure conditions up to 5.2 GPa. The $g(r)$ of MgSiO$_3$ glass shows clear $r_1$ (Si-O) and $r_4$ (Si-Si/Mg-Si/Mg-Mg) peaks (Fig. 2b). On the other hand, the $r_2$ (Mg-O) peak is identified as a shoulder peak on the high r side of the $r_1$ (Si-O) peak, and the $r_3$ (O-O) peak is not visible. This is due to broadening of the peak width of $g(r)$ by narrower range of $Q$ (15 Å$^{-1}$) in the $S(Q)$ data obtained in the high pressure experiments. Fig. S1 shows the effect of the maximum $Q$ ($Q_{\text{max}}$) range on the $g(r)$ simulated by using the ambient pressure data. The resolution of the $g(r)$ is defined as $2\pi/Q_{\text{max}}$ (e.g., Lorch, 1969), and the peak width of $g(r)$ becomes broader by reducing the $Q_{\text{max}}$. In Fig. S1a, the $g(r)$ result simulated with the $Q_{\text{max}}=15$ Å$^{-1}$ shows the $r_2$ peak as the shoulder peak of the $r_1$ peak, similarly to the high-pressure experimental result, and it is difficult to identify the $r_3$ peak. On the other hand, the peak positions of $g(r)$ determined from the result of $Q_{\text{max}}=15$ Å$^{-1}$ ($r_1=1.619\pm0.003$ Å; $r_2=2.029\pm0.010$ Å; $r_4=3.183\pm0.003$ Å; $r_3$ is fixed at 2.618 Å) are comparable to those obtained from the data of $Q_{\text{max}}=25$ Å$^{-1}$ ($r_1=1.621\pm0.002$ Å; $r_2=2.030\pm0.004$ Å; $r_3=2.618\pm0.003$ Å; $r_4=3.179\pm0.003$ Å). Therefore, the peak positions of the $g(r)$ of MgSiO$_3$ glass at high pressures determined from the $S(Q)$ of $Q_{\text{max}}=15$ Å$^{-1}$ are considered to be comparable to those determined at ambient pressure. The $g(r)$ of MgSiO$_3$ glass at high pressures shows almost no change in the $r_1$ and $r_2$ peaks up to 5.2 GPa, while
the position of the r₄ peak decreases with increasing pressure (Fig. 2b).

Figures 2c and 2d show the S(Q) and g(r) of CaSiO₃ glass from 0.8 to 5.4 GPa. In contrast to the marked change in the FSDP of MgSiO₃ glass at high pressures, the S(Q) of CaSiO₃ glass shows only small change in the intensity and position of the FSDP at high pressures (Figs. 2c and 3). On the other hand, the second and third peak features in the S(Q) at around 4-6 Å⁻¹ shift toward high Q with increasing pressure (Fig. 2c). The g(r) of CaSiO₃ glass obtained at high pressures show clear r₁ (Si-O), r₂ (Ca-O), r₄ (Si-Si/Ca-Si), and r₅ (Ca-Si/Ca-Ca) peaks (Fig. 2d). The Ca-O peak of the g(r) in CaSiO₃ glass can be well identified even at the narrower range of Q_max (17 Å⁻¹) in the S(Q) of the high-pressure experiments (Fig. S1a), because of longer distance of Ca-O peak in CaSiO₃ glass compared to Mg-O peak in MgSiO₃ glass. In addition, comparison of the peak positions of CaSiO₃ glass at ambient pressure determined by the Q range of 17 Å⁻¹ (r₁=1.614±0.003 Å; r₂=2.358±0.008 Å; r₄=3.077±0.165 Å; r₅=3.560±0.021 Å) and 25 Å⁻¹ (r₁=1.622±0.001 Å; r₂=2.335±0.008 Å; r₄=3.017±0.008 Å; r₅=3.573±0.014 Å) show similar values. The r₁ and r₂ peaks of the g(r) of CaSiO₃ glass stay almost same up to 5.4 GPa, while there are marked changes in the intensity of the r₄ and r₅ peaks with increasing pressure (Fig. 2d). The intensity of the r₄ peak markedly increases with increasing pressure, accompanied with the decrease of the
intensity of the $r_5$ peak. The position of the $r_4$ peak stays almost same up to 5.4 GPa, while
the position of the $r_3$ peak slightly decreases with increasing pressure.

Table 1 summarizes the positions of the FSDP of $S(Q)$, the $g(r)$ peak positions, Si-O-Si angle of MgSiO$_3$ glass, and Si-O-Si/Ca-O-Si angles of CaSiO$_3$ glass from ambient to high pressures. Since the $r_3$ and $r_4$ peaks of MgSiO$_3$ glass are overlapped by O-O, Si-Si, Mg-Si, and Mg-Mg distances, we carried out multi-peak fitting procedure with the method of de Grouchy et al. (2017). We firstly fitted O-O, Si-Si, Mg-Si, and Mg-Mg peaks into the $r_3$ and $r_4$ peaks at ambient pressure (using the $Q_{max} = 15$ Å$^{-1}$ data) by referring the bond distances and the coordination numbers reported in Ghosh et al. (2014). The $g(r)$ at ambient pressure is well reproduced by the parameters of Ghosh et al. (2014) with minor adjustment for O-O and Si-Si distances (Fig. S2a). Then, the Si-Si and Mg-Si peak positions at high pressures were determined by fixing widths and heights of all peaks, and peak positions of O-O and Mg-Mg (2.65 and 3.42 Å, respectively) (Fig. S2). It has been reported in SiO$_2$ glass that O-O distance does not change at least up to 6.0 GPa, because of almost no change of Si-O tetrahedron structure (Kono et al., 2022). Since our observed Si-O distances of MgSiO$_3$ and CaSiO$_3$ glasses also do not change with varying pressure (cf. Fig. 4), we assumed no change in O-O peak distance in MgSiO$_3$ glass at the pressure range of this
study up to 5.4 GPa. For Mg-Mg distance of MgSiO$_3$ glass, MD simulations of Salmon et al. (2019) show that Mg-O bond distance and Mg-O-Mg angle do not change below 6 GPa, which indicates no change in Mg-Mg distance. We therefore assumed that the Mg-Mg distance have no pressure dependence at the pressure range of this study (< 5.2 GPa).

In addition, the Ca-O distances of CaSiO$_3$ glass at high pressure conditions are determined also by the peak-fitting method of de Grouchy et al. (2017), because the $r_3$ (O-O) peak of the $g(r)$ of CaSiO$_3$ glass is hidden around the right side shoulder of the $r_2$ (Ca-O) peak in the high-pressure data. Firstly, we fitted $r_2$ (Ca-O) and $r_3$ (O-O) peak positions at ambient pressure (using the $Q_{max}=25$ Å$^{-1}$ data) by fixing the coordination numbers reported in Mead and Mountjoy (2006b) and Bajgain et al. (2015). Our obtained Ca-O [2.302(±0.001) Å] and O-O [2.611(±0.007) Å] distances at ambient pressure condition are consistent with those reported in Mead and Mountjoy (2006b) and Bajgain et al. (2015). Then, we fitted $r_2$ (Ca-O) peak positions of CaSiO$_3$ glass at high pressures by fixing coordination number and O-O peak position obtained at ambient pressure (Figure S3).

**Discussion**

Figure 4 shows the nearest-neighbor Si-O and M-O (M=Mg, Ca) distances (Fig.4a)
and the intermediate range Si-Si and M-Si distances (Fig. 4b) of MgSiO$_3$ and CaSiO$_3$ glasses at high pressures. The Si-O peak positions of MgSiO$_3$ and CaSiO$_3$ glasses are same, while the positions of the M-O peaks are markedly different between MgSiO$_3$ and CaSiO$_3$ glasses (Fig. 4a). The difference between Mg-O and Ca-O distances in MgSiO$_3$ and CaSiO$_3$ glasses have also been observed in previous ambient pressure study, and is considered to be due to the different ionic radius of M cation (e.g., Cormier and Cuello, 2013). Our results show that the M-O peak positions of MgSiO$_3$ and CaSiO$_3$ glasses show almost no change with varying pressure. Similarly to our results, the experimental results of Salmon et al. (2019) also show almost no change in the M-O distances and coordination numbers at the pressure conditions below ~5 GPa, although Salmon et al. (2019) shows increase of M-O coordination number in MgSiO$_3$ and CaSiO$_3$ glasses at higher pressures than 6 GPa. These data indicate that nearest neighbor Si-O and M-O distances do not change at the pressure conditions of this study up to 5.4 GPa.

The intermediate range Si-Si distance of MgSiO$_3$ glass markedly decreases with increasing pressure (Fig. 4b), and it causes shrinking of Si-O-Si angle ($\theta = 2 \cdot \arcsin[\frac{|Si-Si|}{2}]/(|Si-0|]$) at high pressures (Fig. 5). It has been known that high-pressure structural change of SiO$_2$ glass occurs mainly by decreasing Si-O-Si angle at high
pressures (e.g., Sonneville et al., 2013). Similarly to SiO\textsubscript{2} glass, Ryu et al. (2022) has also reported decrease of Si-O-Si angle in MgSiO\textsubscript{3} glass with increasing pressure. We therefore consider that the pressure-induced structural change in MgSiO\textsubscript{3} glass up to 5.2 GPa is attributed to the decrease of Si-O-Si angle, as same as well-known compression behavior in SiO\textsubscript{2} glass (e.g., Sonneville et al., 2013). On the other hand, CaSiO\textsubscript{3} glass shows almost no change in the \( r_4 \) peak position with varying pressure (Fig. 4), which indicate both Si-Si and Ca-Si distances at \( \sim 3.0 \) Å do not change at high pressures. The calculated Si-O-Si and Ca-O-Si angles of the CaSiO\textsubscript{3} glass show almost no change with increasing pressure (Fig. 5), which is different from the marked decrease of the Si-O-Si angle in MgSiO\textsubscript{3} glass at high pressures. In exchange for the almost no change in Si-O-Si and Ca-Si-O angles, the \( g(r) \) of CaSiO\textsubscript{3} glass at high pressures show marked increase of the \( r_4 \) peak intensity accompanied with the decrease of the \( r_5 \) peak intensity (Fig. 2d). Although the \( r_5 \) (Ca-Si/Ca-Ca) peak position of CaSiO\textsubscript{3} glass slightly shortens with increasing pressure (0.8 \% between ambient and 5.4 GPa) (Fig. 4b), it is not as large as the shortening of the Si-Si peak position in MgSiO\textsubscript{3} glass at high pressures (1.8 \% between ambient and 5.2 GPa).

These data indicate marked difference in the high-pressure behavior of intermediate range structures of MgSiO\textsubscript{3} and CaSiO\textsubscript{3} glasses. There are two important
structural parameters to discuss intermediate range structure in silicate glasses. One is $Q^n$ species, which represents the number of bridging oxygens (n) connected with a tetrahedral cation (e.g., Mysen, 1990; Stebbins et al., 1992). Salmon et al. (2019) has shown pressure dependence of $Q^n$ species in MgSiO$_3$ and CaSiO$_3$ glasses calculated by MD simulations. The MD simulations of Salmon et al. (2019) show that both MgSiO$_3$ and CaSiO$_3$ glasses consist of ~50% of $Q^2$ species with ~25% of $Q^1$ and $Q^3$ species, which are consistent with those reported by $^{29}$Si NMR measurements at ambient pressure for MgSiO$_3$ (Sen et al. 2009; Davis et al., 2011) and CaSiO$_3$ (Zhang et al., 1997; Kaseman et al., 2015) glasses. The fractions of the $Q^n$ species in both MgSiO$_3$ and CaSiO$_3$ glasses show only little change with varying pressure at least below 10 GPa (Salmon et al., 2019). The data indicate that $Q^n$ species do not change in both MgSiO$_3$ and CaSiO$_3$ glasses at least in the pressure conditions of this study up to 5.4 GPa. We therefore consider that $Q^n$ species are not structural origin of our obtained different high-pressure behavior in the intermediate range structures of MgSiO$_3$ and CaSiO$_3$ glasses (Figs. 4 and 5).

Another important structural parameter to discuss pressure-induced structural change in silicate glasses is polyhedron connectivity (e.g., Lan et al., 2017; Hasmy et al. 2021). It has been reported in theoretical studies that SiO$_x$ polyhedrons of silicate glasses connect by...
corner-shared, edge-shared, and/or face-shared configurations, and the polyhedron connectivity may change with varying pressure (e.g., Lan et al., 2017; Hasmy et al. 2021). A molecular dynamics simulation study showed that CaSiO$_3$ glass has similar polyhedron connectivity structure to wollastonite (Mead and Mountjoy, 2006b). We therefore consider polyhedron connectivity in CaSiO$_3$ glass based on the wollastonite structure as a structural motif. In wollastonite, SiO$_4$ tetrahedra and CaO$_6$ octahedra forms corner-shared SiO$_4$-SiO$_4$ and edge-shared CaO$_6$-CaO$_6$ structures. These configurations yield the average Si-Si distance of 3.14±0.04 Å and the average Ca-Ca distance of 3.58±0.11 Å, respectively (Ohashi, 1984). On the other hand, there are two Ca-Si distances in wollastonite crystal structure formed by the corner-shared (3.65±0.16 Å) and edge-shared (3.10±0.03 Å) configurations of SiO$_4$ tetrahedron and CaO$_6$ octahedron (Ohashi, 1984). The two Ca-Si distances of the corner-shared and edge-shared CaO$_6$-SiO$_4$ configurations in the CaSiO$_3$ structural motif correspond to the $r_5$ and $r_4$ peak positions, respectively, in CaSiO$_3$ glass in this study. Then, our data imply that the change of the peak intensity between the $r_4$ and $r_5$ peaks obtained in the $g(r)$ of CaSiO$_3$ glass at high pressures (Fig. 2d) can be due to the structural change in the CaO$_6$-SiO$_4$ configuration. At low pressures up to 0.8 GPa, low $r_4$ peak intensity implies that the $r_4$ peak is mainly composed of the SiO$_4$-SiO$_4$ structure and
that the fraction of the edge-shared CaO$_6$-SiO$_4$ structure is low. The low contribution of the edge-shared CaO$_6$-SiO$_4$ structure on the $r_4$ peak is consistent with previous molecular dynamics simulation study of CaSiO$_3$ glass at ambient pressure (Mead and Mountjoy, 2006b). On the other hand, at high pressures, the intensity of the $r_4$ peak markedly increases accompanied with decreasing intensity of the $r_5$ peak (Fig. 2d). From the previous simulation study of SiO$_2$ glass (Hasmy et al., 2021), Si-Si coordination number does not change at the pressure conditions below 5.4 GPa. Furthermore, the Raman spectroscopy observations of CaSiO$_3$ glass below 5 GPa (Kubicki et al., 1992; Wolf and McMillan, 1995) show no change in the vibrational spectra related to SiO$_4$ polyhedral units with increasing pressure at least below 5 GPa, although it starts to change above 10 GPa. Therefore, we interpret the $r_4$ peak intensity change as the increase of the fraction of the edge-shared CaO$_6$-SiO$_4$ structure accompanied with decrease of the fraction of the corner-shared CaO$_6$-SiO$_4$ structure (the decrease of the intensity of the $r_5$ peak) at high pressures. The interpretation of the high-pressure structural behavior of CaSiO$_3$ glass at the pressure conditions less than 5.4 GPa is consistent with previous molecular dynamics simulations (e.g., Mead and Mountjoy, 2006a; Shimoda and Okuno, 2006). Mead and Mountjoy (2006a) investigated pressure-induced structural change in CaSiO$_3$ glasses at 0, 5, and 10
GPa, and showed that the intensity of the Ca-Si peak at ~3.1 Å increases with increasing pressure. In addition, Shimoda and Okuno (2006) also showed increase of the Ca-Si peak at ~3.1 Å accompanied with decrease of the Ca-Si peak ~3.6 Å between 0 and 7.5 GPa. Thus, our data suggest that compression of CaSiO$_3$ glass at high pressures up to 5.4 GPa occurs through the modification of the CaO$_6$-SiO$_4$ structure from the corner-shared configuration to the edge-shared configuration without changing the SiO$_4$-SiO$_4$ structure.

Implications

In this study, we observed different structural behavior in CaSiO$_3$ and MgSiO$_3$ glasses at high pressures. The different high-pressure structural behavior is also likely present in CaSiO$_3$ and MgSiO$_3$ melts, as Funamori et al. (2004) reported different behavior in the FSDP position at high pressures as same as our observations (Fig. 3). MgSiO$_3$ glass shows marked shift of the position of the FSDP with increasing pressure, while CaSiO$_3$ glass shows only small change in the FSDP position at high pressures (Fig. 3). The different behavior of the FSDP position in MgSiO$_3$ and CaSiO$_3$ glasses obtained in this study are similar to those in MgSiO$_3$ and CaSiO$_3$ melts reported in Funamori et al. (2004) (Fig. 3). These data imply possible presence of intrinsic high-pressure structural difference due to
different cation of Mg and Ca in both silicate glass and melt, and its importance in understanding nature and properties of silicate magmas in the Earth’s upper mantle. For example, it has been known that viscosity of supercooled liquid MgSiO₃-CaSiO₃ compositions show deep minima in the viscosity-composition relationship (Neuville and Richet, 1991), which is difficult to be interpreted by common viscosity-NBO/T (non-bridging oxygen (NBO) per tetrahedrally coordinated cation (T)) model (e.g., Bottinga and Weil, 1972; Shaw, 1972; Giordano and Dingwell, 2003). In addition, Cochain et al. (2017) reported different high-pressure behavior in the viscosity of MgSiO₃ and CaSiO₃ melts. CaSiO₃ melt (103.6 mPa s at 6.4 GPa and 2128 K) has markedly higher viscosity than MgSiO₃ melt (53.5 mPa s at 6.3 GPa and 2148 K) at high pressures. Furthermore, molecular dynamics simulations by Zhang et al. (2010) showed that the difference in viscosity between CaSiO₃ and MgSiO₃ melts becomes larger at 20 GPa. Our observed different high-pressure structural behavior between CaSiO₃ and MgSiO₃ glasses may be structural origin of the marked difference in the viscosity of CaSiO₃ and MgSiO₃ melts at high pressures.
Author Contributions

N.M.K and Y.K. devised the project, and wrote the manuscript. N.M.K. carried out the experiments with support from Y.K., I.O. and R.H. for the experiment at the beamline 16-BM-B in APS, and Y.K., K.O., K.N., and O.S. for the experiment at the beamline BL04B2 and BL37XU in SPring-8. All authors discussed the results on the manuscript.

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**Figure 1.** Structure factor, \( S(Q) \), and pair distribution function, \( g(r) \), of MgSiO3 glass (a, b) and of CaSiO3 glass (c, d) at ambient pressure. (b) \( r_1, r_2, r_3, \) and \( r_4 \) are Si-O, Mg-O, O-O, and Si-Si/Mg-Si/Mg-Mg distances, respectively. (d) \( r_1, r_2, r_3, r_4 \) and \( r_5 \) are Si-O, Ca-O, O-O, Si-Si, and Ca-Si/Ca-Ca distances, respectively.
**Figure 2.** Structure factor, $S(Q)$, and pair distribution function, $g(r)$, of MgSiO$_3$ glass (a, b) and CaSiO$_3$ glass (c, d) at high pressures. (b) $r_1$, $r_2$, and $r_4$ are Si-O, Mg-O, and Si-Si/Mg-Si/Mg-Mg distances, respectively. (d) $r_1$, $r_2$, $r_4$ and $r_5$ are Si-O, Ca-O, Si-Si, and Ca-Si/Ca-Ca distances, respectively.

**Figure 3.** Position of the first sharp diffraction peak (FSDP) in $S(Q)$ of CaSiO$_3$ and MgSiO$_3$ glasses at high pressures, compared with those of CaSiO$_3$ and MgSiO$_3$ melts reported in Funamori et al. (2004). Solid red squares and solid black triangles represent the FSDP positions of CaSiO$_3$ and MgSiO$_3$ glasses, respectively, obtained in this study. Sizes of the errors in CaSiO$_3$ glass results are smaller than the size of the symbol. Open red squares and open black triangles represent the FSDP positions of CaSiO$_3$ and MgSiO$_3$ melts, respectively, reported in Funamori et al. (2004). Vertical bars on the symbols represent the size of the error. Several data have the error bar smaller than the symbol size.

**Figure 4.** Peak positions in $g(r)$ of CaSiO$_3$ and MgSiO$_3$ glasses form ambient to around 5
GPa. Red solid squares and black solid triangles represent peak positions of CaSiO$_3$ and MgSiO$_3$ glasses, respectively. Vertical bars on the symbols represent the size of the error.

Several data have the error bar smaller than the symbol size.

**Figure 5.** Si-O-Si angle of MgSiO$_3$ glasses and Si-O-Si/Ca-O-Si angles of CaSiO$_3$ glass as a function of pressure. The Si-O-Si angle ($\theta$) was calculated by using simple sine relation ($\theta = 2 \cdot \arcsin(|\text{Si} - \text{Si}|/2)/|\text{Si} - \text{O}|$). Vertical bars on the symbols represent the size of the error. Several data have the error bar smaller than the symbol size.

**Table 1.** Positions of the first sharp diffraction peak (FSDP) of $S(Q)$, peak positions in $g(r)$, Si-O-Si angle of MgSiO$_3$, and Si-O-Si and Ca-O-Si angles of CaSiO$_3$ glasses at ambient and high pressure conditions.

<table>
<thead>
<tr>
<th>MgSiO$_3$ glass</th>
<th>Ambient</th>
<th>1.0 GPa</th>
<th>1.9 GPa</th>
<th>3.0 GPa</th>
<th>4.3 GPa</th>
<th>5.2 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSDP (Å$^{-1}$)</td>
<td>1.88(±0.01)</td>
<td>1.93(±0.01)</td>
<td>1.94(±0.01)</td>
<td>1.96(±0.01)</td>
<td>2.01(±0.05)</td>
<td>2.03(±0.06)</td>
</tr>
<tr>
<td>Si-O (Å)</td>
<td>1.621(±0.002)</td>
<td>1.613(±0.002)</td>
<td>1.618(±0.002)</td>
<td>1.616(±0.002)</td>
<td>1.605(±0.003)</td>
<td>1.614(±0.009)</td>
</tr>
<tr>
<td>Mg-O (Å)</td>
<td>2.030(±0.004)</td>
<td>2.026(±0.006)</td>
<td>2.004(±0.005)</td>
<td>2.050(±0.004)</td>
<td>2.027(±0.007)</td>
<td>2.055(±0.004)</td>
</tr>
<tr>
<td>O-O (Å)</td>
<td>2.65(fixed)</td>
<td>2.65(fixed)</td>
<td>2.65(fixed)</td>
<td>2.65(fixed)</td>
<td>2.65(fixed)</td>
<td>2.65(fixed)</td>
</tr>
<tr>
<td>Si-Si (Å)</td>
<td>3.179(±0.006)</td>
<td>3.171(±0.002)</td>
<td>3.168(±0.002)</td>
<td>3.134(±0.013)</td>
<td>3.113(±0.003)</td>
<td>3.122(±0.011)</td>
</tr>
<tr>
<td>Mg-Si (Å)</td>
<td>3.220(±0.006)</td>
<td>3.226(±0.006)</td>
<td>3.234(±0.008)</td>
<td>3.210(±0.006)</td>
<td>3.206(±0.007)</td>
<td>3.209(±0.004)</td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>3.42(fixed)</td>
<td>3.42(fixed)</td>
<td>3.42(fixed)</td>
<td>3.42(fixed)</td>
<td>3.42(fixed)</td>
<td>3.42(fixed)</td>
</tr>
<tr>
<td>Si-O-Si angle (°)</td>
<td>137.3(±0.8)</td>
<td>135.8(±0.5)</td>
<td>133.9(±0.6)</td>
<td>133.8(±0.6)</td>
<td>133.7(±0.9)</td>
<td>130.9(±1.4)</td>
</tr>
<tr>
<td>CaSiO$_3$ glass</td>
<td>Ambient</td>
<td>0.8 GPa</td>
<td>2.3 GPa</td>
<td>3.3 GPa</td>
<td>4.6 GPa</td>
<td>5.4 GPa</td>
</tr>
<tr>
<td>----------------</td>
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</tr>
<tr>
<td>FSDP (Å$^{-1}$)</td>
<td>2.137(±0.005)</td>
<td>2.154(±0.003)</td>
<td>2.168(±0.001)</td>
<td>2.177(±0.002)</td>
<td>2.189(±0.003)</td>
<td>2.200(±0.002)</td>
</tr>
<tr>
<td>Si-O (Å)</td>
<td>1.622(±0.001)</td>
<td>1.618(±0.003)</td>
<td>1.616(±0.003)</td>
<td>1.621(±0.003)</td>
<td>1.611(±0.003)</td>
<td>1.614(±0.003)</td>
</tr>
<tr>
<td>Ca-O (Å)</td>
<td>2.302(±0.001)</td>
<td>2.315(±0.004)</td>
<td>2.306(±0.004)</td>
<td>2.305(±0.004)</td>
<td>2.298(±0.004)</td>
<td>2.297(±0.004)</td>
</tr>
<tr>
<td>O-O (Å)</td>
<td>2.611(±0.007)</td>
<td>2.611(fixed)</td>
<td>2.611(fixed)</td>
<td>2.611(fixed)</td>
<td>2.611(fixed)</td>
<td>2.611(fixed)</td>
</tr>
<tr>
<td>Si-Si, Ca-Si (Å)</td>
<td>3.017(±0.008)</td>
<td>2.997(±0.026)</td>
<td>2.998(±0.032)</td>
<td>2.998(±0.014)</td>
<td>2.998(±0.018)</td>
<td>2.996(±0.001)</td>
</tr>
<tr>
<td>Ca-Si, Ca-Ca (Å)</td>
<td>3.573(±0.014)</td>
<td>3.569(±0.015)</td>
<td>3.550(±0.021)</td>
<td>3.557(±0.026)</td>
<td>3.554(±0.013)</td>
<td>3.554(±0.015)</td>
</tr>
<tr>
<td>Si-O-Si and Ca-O-Si angles (°)</td>
<td>136.8(±0.8)</td>
<td>135.6(±2.5)</td>
<td>136.2(±3.0)</td>
<td>135.4(±1.4)</td>
<td>137.0(±1.8)</td>
<td>136.3(±1.2)</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2
Figure 3
Figure 4

(a) Ca-O
Mg-O
Si-O
Si-Si

(b) Ca-Si, Ca-Ca
Mg-Si
Si-Si, Ca-Si
Si-Si

Peak position (Å)
Pressure (GPa)
Figure 5