

Studying the Structure of Magnesium Silicate Glasses by High-energy X-ray Diffraction

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Introduction

The magnesium silicate minerals $(\text{Mg,Fe})_2\text{SiO}_4$ (olivine) and $(\text{Mg,Fe})\text{SiO}_3$ (orthopyroxene) are the primary constituents of the Earth and lunar mantle [1]. Liquids produced by melting these mineral phases have influenced the evolution of the Earth and the Moon, resulting in the heterogeneous distribution of mantle phases that have been subject to subsequent melting processes, such as basalt volcanism. Little is known about the structure of liquids produced from magnesium silicates because the phases are very refractory. In addition, studying magnesium silicate glasses is difficult because these minerals are poor glass formers. In this work, a combination of high-energy x-ray diffraction and complementary neutron diffraction has been used to establish the change in structure that occurs with the change in composition of magnesium silicate glasses produced by containerless techniques. The results from this work provide new insight into the structure-dependent changes in thermodynamic and transport properties of the primary liquids produced by deep-Earth processes.

Methods and Materials

A series of five magnesium silicate glasses have been studied. These glasses range in composition from the magnesian orthopyroxene Mg_2SiO_6 (entstatite, which is 50% SiO_2) to the magnesian olivine Mg_2SiO_4 (forsterite, which is 33% SiO_2). Three intermediate glasses that were composed of 46%, 42%, and 38% SiO_2 were also made. The glasses were made by containerless synthesis, a technique that enables glasses to be made from refractory compositions and that is ideally suited to compositions considered to be poor glass formers. A bead of the crystalline precursor, levitated by a gas jet, is heated to high temperatures by a laser. Levitated liquids can be supercooled to temperatures several hundreds of degrees below the liquidus temperature by blocking the laser and glasses produced. Glasses are formed because the cooling rates are very rapid and because the absence of a container reduces the heterogeneous nucleation of crystalline phases. One important advantage of the containerless method is that glasses can be made at the composition of stoichiometric crystalline phases, and these glasses include those from magnesian olivine and magnesian

orthopyroxene compositions [2].

A series of x-ray diffraction measurements on the five magnesium silicate glasses were obtained at the BESSRC high-energy beamline station 11-ID-C at the APS [3]. These data were collected by using a beam energy of 114.92 keV. Data were collected for values of Q of up to 35 \AA^{-1} . The benefits of using high-energy x-rays for condensed matter research on disordered materials are many. These x-rays serve as a bulk probe because of their high penetration power, making the x-ray experiments analogous to conventional measurements and complementary to neutron diffraction measurements. The combination of high incident energy and low angles of scatter allows experimental access to a large Q range (currently 0.5 to $\sim 40 \text{ \AA}^{-1}$ is achievable). In addition, the important attenuation and multiple scattering corrections to measured liquid and glass data are very small when compared to those of conventional x-ray laboratory probes.

Neutron diffraction experiments were performed at the glass and amorphous materials diffractometer (GLAD) at ANL's IPNS. Diffraction data were collected for 6 hours on each sample. Four measurements were made on each sample. The diffraction data for the four individual runs were then summed, and the total structure factor was obtained by correcting for multiple scattering and absorption by using standard correction procedures.

Results

The total structure factor measurements obtained at the APS (11-ID-C) and at IPNS were Fourier-transformed to give real space pair correlation functions. These show prominent peaks that reflect Si-O, Mg-O, and O-O correlations. The integrated area beneath the Si-O peak confirms the four-fold coordination environment for Si-O, with a decrease in magnitude consistent with the compositional changes. The Mg-O coordination does not show a simple linear change in composition, but it does show a nonlinear increase in Mg-O coordination, from four-coordinate to five-coordinate Mg(II). Differences in the $S(Q)$ data confirm these real space changes.

To investigate the change in Mg-O coordination, the x-ray and neutron data can be combined to eliminate the

contribution of Si-O to the $S(Q)$, via the equation:

$$\Delta S(Q) = \frac{[S_N(Q) - 1] - \frac{W_N}{W_X(Q)} [S_X(Q) - 1]}{1 - \left(\frac{W_N}{W_X(Q)} \right)} \quad (1)$$

where W represents the Faber-Ziman weighting factors for neutrons W_N and for x-rays $W_X(Q)$. This difference function highlights changes in the Mg-O coordination as shown in Fig. 1. The coordination number for Mg-O is shown to be 4.0 for enstatite, increasing to 5.0 for forsterite. The increase in the Mg-O coordination number is nonlinear between the 0.62 MgO-0.38 SiO₂ glass and forsterite (0.67 MgO-0.33 SiO₂). The change in the Mg-O coordination number from 4.0 to 5.0 over this narrow composition range is unusual, since there is only a 3% decrease in oxygen abundance between the 38% SiO₂ glass and forsterite. There are also large changes in the O-O correlations as the shoulder at 3.2 Å discontinuously increases in intensity, suggesting that higher-order coordination exists in the forsterite glass (and liquid) than in the other glasses.

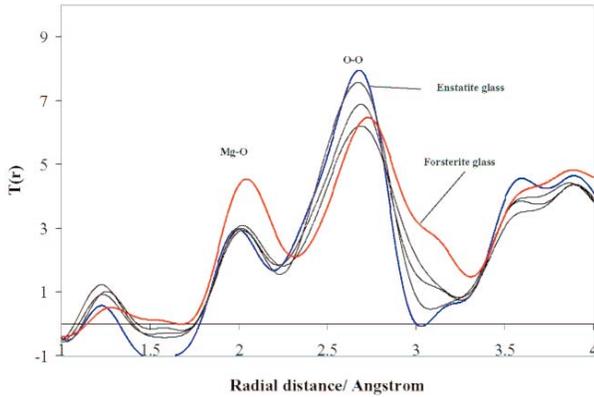


FIG. 1. The total pair correlation function $T(r)$ from a weighted difference between x-ray and neutron diffraction data for five Mg-silicate glasses when the Si-O correlation at 1.64 Å is eliminated. This plot highlights the similarity between the 50% MgO-50% SiO₂ glass sample (enstatite) and glass samples with silica contents as low as 38%. There is a major change in Mg-O coordination between 38% and 33% SiO₂ (forsterite) glass, as shown by the increase in the peak at 2.0 Å. There are also dramatic changes in the O-O correlation at 2.8 Å.

Discussion

The reverse Monte Carlo (RMC) technique [4] was used to model the structure of the forsterite and enstatite composition glasses; the x-ray and neutron diffraction

$[S(Q)]$ data were used as constraints. The neutron data constrained mainly the oxygen atom correlations, while the x-ray data simultaneously constrained the Si and Mg correlations. Additional constraints were used to ensure that the Mg and Si bonding arrangements were consistent with those obtained from the diffraction data. Although the simulation tends to give the most disordered structure consistent with the data, differences between the two glasses are quite evident. The model shows that the Mg coordination environment in the forsterite and enstatite composition glasses is very different. Mixtures of four-coordinate and five-coordinate Mg-O dominate the liquid and glass structure for compositions up to 38% SiO₂ (Fig. 2). For glasses with a silica content of less than 38%, the Mg-O coordination environment changes, and a distinct five-coordinate structural unit dominates (Fig. 3).

These structural trends suggest that there will be associated changes in the bulk thermodynamic properties of the corresponding liquids. The change in the coordination environment points to changes in the underlying potential energy landscape of the liquid, implying a nonlinear change in the configurational entropy and hence the rheology. More intriguing is that the stabilization of the five-coordinate Mg(II) may be expected to occur at moderately high pressures for glasses that are more silica-rich than Mg₂SiO₄, suggesting that the movement of silicate liquids in the Earth's mantle and crust may reflect pressure-induced changes in structure and structure-dependent properties, such as viscosity.

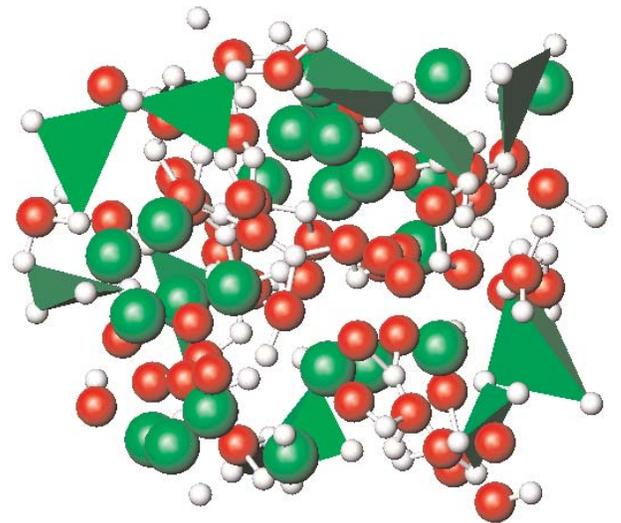


FIG. 2. Schematic illustration of results from RMC fit to combined diffraction data set for the glass containing 50% SiO₂. The dominantly four-coordinate Mg-O polyhedra are shown together with the discontinuous silicate framework

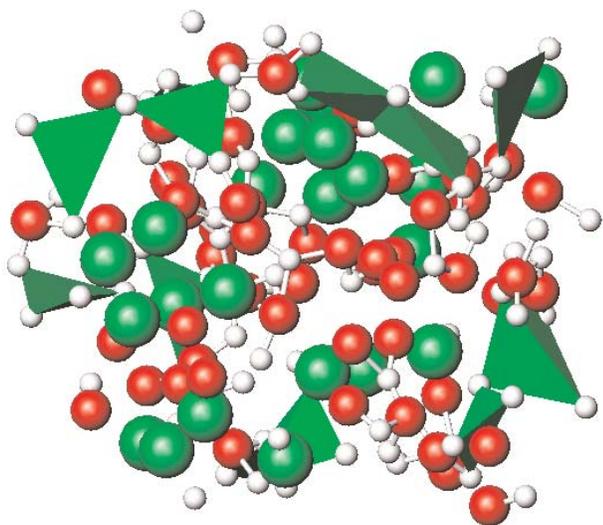


FIG. 2. Schematic illustration of results from RMC fit to combined diffraction data set for the glass containing 50% SiO_2 . The dominantly four-coordinate Mg-O polyhedra are shown together with the discontinuous silicate framework

Acknowledgments

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