

## Revision 2

# First principles molecular dynamics simulations of MgSiO<sub>3</sub> glass at high pressure

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## ABSTRACT

We report a first-principles molecular dynamics study of the equation of state, structural and elastic properties of MgSiO<sub>3</sub> glass at 300 K as a function of pressure up to 170 GPa. We explore two different compression paths: cold compression, in which the zero pressure quenched glass is compressed at 300 K, and hot compression, in which the liquid is quenched in situ at high pressure to 300 K. We also study decompression and associated irreversible densification. Our simulations show that the glass at the zero pressure is composed of primarily Si-O tetrahedra, partially linked with each other via the bridging oxygens (present in 35%; the remaining being the non-bridging oxygens). With increasing pressure, the mean Si-O coordination number gradually increases to 6, with 5-fold and subsequently 6-fold replacing tetrahedra as the most abundant coordination environment. The Mg-O coordination comprising of a mixture of four-,

five- and six-fold species at zero pressure picks up more high-coordination (seven- to nine-fold) species on compression and its mean value increases from 4.5 to 8 over the entire pressure range studied. Consistently, the anion-cation coordination numbers increase on compression with appearance of oxygen tri-clusters (three silicon coordinated O atoms) and mean O-Si coordination eventually reaching 2. Hot compression produces greater densities and higher coordination numbers at all pressures as compared with cold compression, reflecting kinetic hindrances to structural changes. On decompression from 6 GPa, the glass regains its initial uncompressed structure with almost no residual density. Decompression from 27 GPa produces significant irreversible compaction, and the peak-pressure of decompression significantly influences the degree of density retention with as high as 15 % residual density on decompression from 170 GPa. Irreversibility arises from the survival of high coordination species to zero pressure on decompression. With increasing pressure, the calculated compressional and shear wave velocities (about 5 and 3 km/s at the ambient conditions) of MgSiO<sub>3</sub> glass increase initially rapidly and then more gradually at high pressures. Our results suggest that hot-compressed glasses perhaps provide closer analog to high-pressure silicate melts than the glass on cold compression.

**Keywords:** Silicate glasses, first-principles study, structure, equation of state, high pressure

## INTRODUCTION

Silicate melts played a crucial role throughout the mantle pressure regime in the chemical

differentiation of the Earth in its early stages of accretion (Tonks and Melosh 1993; Labrosse et al. 2007). Melts are also thought to exist in the present day Earth at pressures well beyond the shallow magma genetic zone, including at the top of the transition zone (14 GPa, Song et al., 2004; Mookherjee et al., 2008) and at the core-mantle boundary (136 GPa, Williams and Garnero, 1996; Stixrude and Karki, 2005). In order to understand the origin and stability of these deep melts, and the role of high pressure melts in the earliest evolution of the Earth, knowledge of the physical properties of the silicate melts at the relevant pressure-temperature conditions is essential. A key quantity is the density of the silicate melt at high pressure, which determines whether the liquid is positively or negatively buoyant with respect to co-existing crystals. There is now substantial evidence that liquids can become denser than coexisting crystals at several crossover points throughout the mantle pressure regime, with important implications for chemical differentiation (Stolper et al., 1981; Agee and Walker, 1988; Stixrude and Karki, 2005; Sakamaki et al., 2006).

Silicate glasses have long been studied as experimentally accessible analogs of high pressure silicate liquids (Williams and Jeanloz, 1988; Kubicki et al., 1992; Meade et al., 1992). Silicate glasses can be studied at the ambient temperature, and have been examined spectroscopically to pressures beyond 100 GPa (Sato and Funamori, 2010; Murakami and Bass, 2010). However, because of the lack of data on silicate liquids, it is not known how closely the behavior of silicate glasses corresponds to that of liquids at high pressure. Experimental data on silicate liquids is still very limited at lower mantle conditions (Asimow and Ahrens, 2010), and measurements of silicate liquid structure are non-existent beyond a few GPa (Yamada et al., 2011).

Experimental studies of silicate glasses at high pressure show changes in local structure that are expected to occur in silicate liquids as well. Perhaps the most significant of these for

understanding deep liquid buoyancy is the change in Si-O coordination from dominantly four-fold at low pressure to dominantly six-fold at high pressure (Williams and Jeanloz, 1988). Understanding the nature of the coordination change is important because the higher coordinated state is more efficiently packed and therefore denser. However, direct comparisons between glass and liquid behavior are few because no experimental data exist on the pressure-induced Si-O coordination change in silicate liquids: the pressures that have so far been achieved for in situ x-ray diffraction studies are not high enough (Yamada et al., 2011). Considerable uncertainty remains therefore as to whether the structural changes seen in room temperature compression of glass correspond to those in the liquid state. Other changes in glass structure are known to occur that are important for compression at pressures lower than that of the coordination change including narrowing of the Si-O-Si angle (Hemley et al., 1986; Kubicki et al., 1992), changes in Q speciation (Xue et al., 1991), and changes in ring statistics (Stixrude and Bukowinski, 1991), and formation of oxygen tri-clusters (Lee et al., 2008).

A gradual four-fold to six-fold Si-O coordination change is also seen in first principles simulations of silicate liquids, although the pressure range over which it occurs appears to be somewhat lower than that found in room temperature compression of silicate glasses (Stixrude and Karki, 2005; Sun et al., 2011). Indeed, because of kinetic hindrances inherent in room temperature compression of glass, it has long been expected that the coordination change should occur at lower pressure in silicate liquids as compared with glasses (Williams and Jeanloz, 1988). Such kinetic hindrances are expected despite the apparent reversibility of the coordination change on decompression of the glass (Williams and Jeanloz, 1988). Actually, experimental studies suggest detectable amounts of high coordinated Si and/or Al in recovered glasses, indicating that the structural change is not entirely reversible (Xue et al., 1989; Allwardt et al. 2005; Kelsey et al., 2009). A limited number of experimental studies have attempted to overcome kinetic

hindrances via in situ high pressure quenching of melts to ambient conditions (Closmann and Williams, 1995). Another manifestation of kinetic hindrances in the response of glass to compression is irreversible compaction: a glass compressed to high pressure and then decompressed back to ambient pressure is typically denser than the initial uncompressed glass (Bridgman and Simon, 1953). Irreversible compaction and its dependence on composition, temperature, and decompression rate has been widely studied (Bridgman and Simon, 1953; Roy and Cohen, 1961; Meade and Jeanloz, 1987; Zha et al., 1994; Allwardt et al. 2005; Gaudio et al., 2008).

Another important source of uncertainty is the density of amorphous silicates at high pressure. While some data on the equation of state of silicate liquids have been collected via dynamic compression, measurements of the density of silicate glasses at lower mantle conditions are limited to a single study of silica glass (Sato and Funamori, 2008). Thus it is not yet possible to compare the density of silicate liquids and glasses directly on the basis of experimental measurements at lower mantle conditions. The reason is simple: techniques for measuring the density of crystals at high pressure, such as x-ray diffraction, cannot be used to measure the density of the glass. It has recently been proposed that measurements of sound velocities may be integrated to obtain the equation of state (Sanchez-Valle and Bass, 2010). However, important questions remain as to the suitability of this technique, in particular whether the bulk modulus computed from the measured velocities is the appropriate relaxed modulus, or instead the stiffer unrelaxed modulus, which does not contain complete information on pressure-induced structural re-arrangements (Zha et al., 1994; Smith et al., 1995).

First principles molecular dynamics simulations have been used to predict the structure and properties of silicate liquids throughout the mantle pressure regime (see Stixrude et al., 2009; Karki 2010 for a review). These simulations have shown remarkably good agreement with extant

experimental data and have provided predictions of properties and behavior outside of the experimentally measured regime that have influenced our ideas about the earliest evolution of Earth (Labrosse et al., 2007). First principles simulations have not yet been applied to silicate glasses at lower mantle pressure, although they have been used to examine the structure of silica glass at ambient pressure (Sarnthein et al. 1995; Kim et al. 2012). Theoretical studies of silicate glasses at high pressure have been limited to those based on semi-empirical force fields (e.g. pair potentials) (Kubicki and Lasaga 1991; Stixrude and Bukowinski, 1991; Morgan and Spera 2001; Shimoda and Okuno 2006). The pair-potentials method is less costly but has limited predictive power: results may depend sensitively on the design of the force field and how they are fit to experimental data (Stixrude, 2000). In contrast, first principles simulations are based on density functional theory which makes no assumptions regarding the shape of the charge density or the nature of bonding and requires no input from experiment.

Our simulations allow a direct comparison between the high pressure structure and equation of state of a silicate glass and a silicate liquid of the same composition at lower mantle conditions. We compare our simulations of  $\text{MgSiO}_3$  glass to our previous results on  $\text{MgSiO}_3$  liquid over the entire pressure regime of the mantle. Moreover, we explore and compare two different methods of synthesizing the glass, replicating previous experimental procedures: 1) cold compression. This is the most common procedure in experiments in which a glass synthesized at 1 bar is compressed isothermally at room temperature. 2) hot compression. This procedure attempts to overcome kinetic hindrances by quenching a liquid in situ at high pressure to room temperature. We also examine (ir-)reversibility of glass compression by comparing to the structure and equation of the glass on decompression.

## METHODOLOGY

We use first principles molecular dynamics simulation method within the local density approximation (Ceperley and Alder, 1980) as implemented in Vienna Ab initio Simulation Package (VASP) (Kresse and Furthmuller 1996). Projector augmented wave potentials (Kresse and Joubert 1999) were used with a cutoff energy of 400 eV and Gamma point Brillouin zone sampling. Cubic supercells containing 160 and 640 atoms (32 and 128 formula units, respectively) were used. The pulay stress varies from 4 to 8 GPa over the volume range studied and an empirical correction to account for the typical LDA over-binding is 2 GPa at each volume (Stixrude and Karki 2005; Karki and Stixrude 2010).

Initial configurations were taken from the liquid state at 3000 K, equilibrated for several picoseconds (we use a 1 fs time-step for all simulations). These liquid configurations were isochorically quenched down to 300 K. Quenching was performed by cooling in a series of finite temperature intervals, with 5 ps long equilibration at each temperature step. Various quench rates (1 and 0.5 K/fs, and also slower rates of 0.2 and 0.05 K/fs for 160 atom supercell) were considered. For each quench rate and system size, we determine the glass transition temperature by examining the variation of the enthalpy with temperature and finding the temperature at which the break in slope appears (e.g. Moynihan et al., 1974). Our quench rates are much faster than those used in experiments ( $10^2$ - $10^8$  K/s for silicate glasses, Wilding et al., 2004; Williams et al., 1989). However, they are typical rates used in computer simulations, especially in the case of intensive first-principles simulations. Once we reach 300 K, we run simulations sufficiently long for thermodynamic properties to reach equilibrium, typically several ps (Fig. S1).

The supercell sizes used here are typical or even larger than those used by other first-principles studies of glasses (Sarnthein et al. 1995; Kohara et al. 2011). Nevertheless, we

recognize that simulation cells of 160-640 atoms permit only a limited sampling of configuration space at 300 K over the feasible duration of our simulations. We have explored possible biases via the following method. We compare multiple quenches from different snapshots of the liquid state that are sufficiently far apart in time as to be uncorrelated with each other (typically at least 1 ps apart). We follow the same quench schedule for each snapshot and compare the resultant properties of the glass. This is a time consuming procedure that we have applied only to the 160 atom simulations. We assume that the standard deviation in the pressure that results from multiple quenches is representative of the 640 atom results as well. This is likely to be a conservative assumption as the 640-atom system captures a larger fraction of configuration space.

We investigate two simulation schedules for compressing the glass. First, *cold compression* refers to quenching an equilibrated liquid at the reference volume ( $V_X = 38.9 \text{ cm}^3 \text{ mol}^{-1}$ ) from 3000 K to 300 K and then subsequently compressing the quenched system. We then decrease the volume of the 300 K system sequentially from  $V/V_X = 1.0$  to  $V/V_X = 0.45$  at an interval of 0.05. Thus, the starting configuration at each volume is obtained from the equilibrated configuration at the previous volume along the compression path. Second, *hot compression* means that the glass system at each compressed volume was obtained by directly quenching a 3000 K liquid system at the corresponding volume. Thus, the actual compression is applied to liquid at high temperature (3000 K). The glass configuration at each volume along all three paths (hot compression, cold compression, and cold decompression) was equilibrated until the energy and structural convergences were reached (see Fig. S1).

Once we attain the smallest volume along the cold compression, we reverse the process. Our *decompression* schedule thus corresponds to sequentially decompressing the 300 K glass system from a certain compressed volume (such as  $V/V_X = 0.45$ ) to larger volumes with an interval of 0.05. A schematic representation of the simulation schedules is shown in Fig. 1 and



some relevant snapshots are shown in Fig. 2. We also discuss results for decompression from 6, 27, and 170 GPa.

We compute all partial (like and unlike atomic pair) radial distribution functions (RDF) given by

$$g_{\alpha\beta}(r) = \frac{1}{4\pi\rho_{\beta}r^2} \left[ \frac{dN_{\beta}(r)}{dr} \right] \quad (1)$$

where  $\rho_{\beta}$  is the number density of species  $\beta$  and  $N_{\beta}$  is the number of species  $\beta$  within a sphere of radius  $r$  around a selected atom of type  $\alpha$ . From the knowledge of RDF's, a number of other structural properties can be extracted as follows. The structure factors, which can be represented as the Fourier transform of the RDF's, are more readily comparable with experimental data from x-ray and neutron diffraction. The partial structure factor of species  $\alpha$  and  $\beta$  is written as:

$$S_{\alpha\beta}(q) = \delta_{\alpha\beta} + 4\pi\rho(c_{\alpha}c_{\beta})^{1/2} \int_0^{\infty} dr r^2 \frac{\sin qr}{r} (g_{\alpha\beta}(r) - 1) \quad (2)$$

where  $\delta_{\alpha\beta}$  is the Kronecker delta and  $C_{\alpha}$  is the concentration of species  $\alpha$ . The total structure factor can be derived by summing the partial structure factors as:

$$S(q) = \frac{\sum_{\alpha,\beta} b_{\alpha} b_{\beta} (c_{\alpha} c_{\beta})^{1/2} (S_{\alpha\beta}(q) + 1)}{\sum_{\alpha} c_{\alpha} b_{\alpha}^2} \quad (3)$$

where  $b_{\alpha}$  and  $b_{\beta}$  correspond to neutron ( $S_N(q)$ ) and X-ray ( $S_X(q)$ ) scattering lengths of species  $\alpha$  and  $\beta$ , respectively. Neutron scattering lengths were taken from Sears (1992) and the corresponding atomic numbers were used for the X-ray scattering lengths of the different species.

The bond length is calculated as a weighted average of all distances covered by the first peak in the RDF:

$$\langle r \rangle = \frac{\int_0^{r_{\min}} r g_{\alpha\beta}(r) dr}{\int_0^{r_{\min}} g_{\alpha\beta}(r) dr} \quad (4)$$

where  $r_{\min}$  is the position of the minimum after the first peak in the corresponding  $g_{\alpha\beta}(r)$ . The mean nearest-neighbor coordination for species  $\alpha$  with respect to  $\beta$  is calculated using

$$C_{\alpha\beta} = 4\pi\rho_{\beta} \int_0^{r_{\min}} r^2 g_{\alpha\beta}(r) dr, \quad (5)$$

where  $\rho_{\beta}$  is the number density of species  $\beta$ .

We also calculate the acoustic wave velocities from elastic coefficients, which can be derived from the stresses ( $\sigma_{ij}$ ) generated from the application of small strains ( $e_{kl}$ ) given by Hooke's law:

$$\sigma_{ij} = c_{ijkl} e_{kl}; \quad (i, j, k, l = 1, 2, 3) \quad (6)$$

where  $c_{ijkl}$ , is the fourth rank elastic tensor. We use a combination of tetragonal and triclinic strains of size  $e = \pm 2\%$ :

$$\begin{pmatrix} e & e/2 & e/2 \\ e/2 & 0 & e/2 \\ e/2 & e/2 & 0 \end{pmatrix} \quad (7)$$

In typical finite-strain static elasticity calculation, stress tensors obtained for the relaxed (strained) configurations are used. However, given the dynamic nature of the meta-stable glassy states in contrast to crystalline phases, the time averages of the properties of interest are necessary. For each strained configuration, we accumulate the time average components of the stress tensor over, at least 1 ps after an equilibration period.

Equation (6) gives  $\sigma_{xx} = c_{11}e$ ,  $\sigma_{yy} = \sigma_{zz} = c_{12}e$ ,  $\sigma_{yz} = c_{44}e$ ;  $\sigma_{zx} = c_{55}e$ ;  $\sigma_{xy} = c_{66}e$ , where  $c$ 's are in the Voigt notation. Ideally, glasses are isotropic and have only one set of independent elastic moduli: bulk modulus ( $K$ ) and shear modulus ( $G$ ).

Because of limited simulation system size, there can be non-negligible anisotropy. An averaging of  $c_{ij}$ 's (obtained from three symmetrically equivalent strains defined in Eq 7) is expected to be more meaningful. We first estimate three elastic constants,  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  as follows:

$$c_{11} = \frac{1}{3} \sum_{ii} c_{ii}; \quad c_{12} = \frac{1}{6} \sum_{ij}^{i \neq j} c_{ij} \quad \text{and} \quad c_{44} = \frac{1}{2} \left[ \frac{1}{2} (c_{11} - c_{12}) + \frac{1}{9} \sum_{mm} c_{mm} \right] \quad (8)$$

where  $i, j = 1, 2, 3$  and  $m = 4, 5, 6$ . The bulk and shear moduli are then given by

$K = (c_{11} + 2c_{12})/3$  and  $G = c_{44}$ , respectively. The compressional wave velocity ( $V_p$ ) and the shear wave velocity ( $V_s$ ) are given by

$$V_p = \sqrt{\frac{(K + 4G/3)}{\rho}} \quad \text{and} \quad V_s = \sqrt{\frac{G}{\rho}} \quad (9)$$

where  $\rho$  is the density of the glass. Uncertainties in the computed velocities include the standard deviation of the nominally symmetry-equivalent sets of elastic constants expressed in Eq. (8).

## RESULTS AND ANALYSIS

### Effects of quench rate and simulation cell size

For all simulation schedules used, we explore the effects of quench rate and system size on the final glass structure at 300 K. As expected from the analysis of Moynihan et al. (1976), the faster quench rate used in the simulations ( $T_g = 2030$  K, for a quench rate of  $\sim 0.03$  K/fs) yields a

higher glass transition temperature  $T_g$  as compared with experimental value (1039 K at 500 K/s) (Fig. S2). Similar results have been found in previous simulation studies. For example, for simulated amorphous silica,  $T_g$  was predicted to vary from 2900 to 3250 K for cooling-rates of 1 – 1000 K/ps (Vollmayr et al. 1996), whereas Della Valle and Andersen (1992) found  $T_g = 2200$  K for a quench rate of 0.025 K/fs. For simulated anorthite glass, Morgan and Spera (2001) estimated  $T_g \sim 2800$  K for a quench rate of 0.07 K/fs.

We observe a weak dependence of the structural properties on the quench rate. At the reference volume, the predicted structures for both simulation cell sizes and all quench rates agree well (Table 1). Also, the effects of the initial (quenching) temperature of the melt are not substantial (Table S1). The calculated mean coordination numbers, and the relative proportions of various coordination species are identical within the statistical uncertainty in these quantities. There is a slight tendency for the larger simulation cell to predict a larger proportion of odd-coordination defects. We believe that the slight dependence of structural details on the quench rate is due to the fact that we quench isochorically, in contrast to the isobaric cooling typical of experiments. We have previously argued that the difference between glass and liquid structures, when compared at the same volume, is small (Sun et al., 2011).

### **Pressure volume equation of state**

As shown in Fig. 3, starting at the same state point the cold and hot compression isotherms initially diverge with increasing pressure and then start to converge on further compression. The pressure-volume isotherm obtained along the decompression path lies below both cold and hot compression curves over most of the volume range studied. The difference between the cold compression and decompression isotherms is zero at  $V/V_x = 0.45$  by the design of our simulation

schedule, becomes the maximum at mid compression, and then gradually decreases at larger volume. The three sets of isotherms differ from each other with the hot compression curve being bounded from above and below, respectively, by the cold compression and decompression curves.

We compare the equation of state fit parameters with previous results in Table 2. The predicted equilibrium volume ( $V_0$ ) compares well with the available experimental results (Sanchez-Valle and Bass 2010). The predicted bulk modulus is significantly lower than the value obtained by Brillouin spectroscopy (Sanchez-Valle and Bass 2010). With increasing pressure, our calculated density diverges from the experimental equation of state obtained by integrating the Brillouin spectroscopy measurements. The experimental density is 18 % lower than the predicted density at the highest pressure (34 GPa) investigated in the experiments (Sanchez-Valle and Bass 2010) (Fig. 4). Our results disagree with a previous simulation study, which found density 16 % lower than ours at 93 GPa (Kubicki and Lasaga, 1991). We attribute this disagreement to the uncertainties associated with choosing the semi-empirical force field in the previous study. Our results are consistent with another previous MD study using a different semi-empirical force field, although the maximum pressure of that study was only 15 GPa (Shimoda and Okuno, 2006).

The predicted zero-pressure volume after decompression from 170 GPa is 15 % smaller than the uncompressed volume: a substantial residual densification (Fig. 3 & 4). When decompressed from 27 GPa, our simulated glass shows a residual densification of 9 %, in excellent agreement with experimental studies, which have measured irreversible density increases of 2 to 11 % depending on the pressure from which the glass was decompressed and also on the temperature, and up to maximum pressure of 10 to 33 GPa (Gaudio et al. 2008; Sanchez-Valle and Bass 2010). In our simulations, decompression from a maximum pressure of

6 GPa produced no residual densification, i.e., the compression was reversible up to this pressure.

## Glass structure

The calculated radial distribution functions (RDF's) show strong charge ordering, as expected, with sharp cation-anion first peaks, representing well defined cation-anion coordination shells, and like-charge (cation-cation and anion-anion) at larger distances (Fig. 5). In detail the agreement with experimental values of the mean inter-atomic distances and coordination numbers is excellent (Table 3). We note that when differences between theory and experiment appear, differences between different experiments also tend to be substantial. For example, our value of the O-O coordination number is essentially identical to the ideal meta-silicate value (5.8 vs. 6.0 in enstatite) in agreement with the value 5.7 from Waseda and Toguri (1977), whereas Yin et al. (1983) have found 4.3. Such differences between experimental values may result from differences in processing technique, particularly for weak x-ray scatterers such as O. A comparison with neutron diffraction data would be valuable as O scattering is much stronger than in x-rays, however, the one study available does not report values for coordination geometries (Wilding et al., 2004). The Wilding et al. (2004) study does report the spectra themselves, which show the Mg-O peak in the RDF at 2.0 Å, in excellent agreement with our value and significantly smaller than the two reported values from analysis of the x-ray diffraction data (2.08 to 2.14 Å). Our results support the Mg-O coordination number derived from diffraction studies (4.5) as opposed to the value inferred from NMR: 6-fold coordination with perhaps some 5-fold coordination (Shimoda et al., 2007). In agreement with our results, previous <sup>17</sup>O NMR studies of MgSiO<sub>3</sub> glass at the ambient pressure have showed that O-Si coordination number is 1.33, identical to the ideal meta-silicate value, i.e. NBO/T = 2/3 in enstatite (Lee et al. 2003; Allwardt and Stebbins 2004).

We find a small proportion of coordination defects, including 5-fold coordinated Si defects, and free oxygens (i.e. oxygens not bound to Si), and edge-sharing tetrahedra (1-2 %) that are not detected experimentally (Stebbins and McMillan 1993; Sen et al. 2009). We attribute this difference to the higher fictive temperature of our glass as compared with the experimental sample: small amounts of 5-fold coordination Si are detected in other uncompressed silicate glass compositions, and their proportion increases with increasing fictive temperature (Stebbins and McMillan, 1993); we suggest that the proportion of other coordination defects also increases with increasing fictive temperature.

We have also compared directly to the experimentally measured structure factor (Fig. 6). The agreement with experiment is good, and in particular we are able to confirm experimental identification of the main peaks via comparison with the partial structure factors. The first diffraction peak (FSDP) in neutron and x-ray scattering is due to cation-anion correlations. The second sharp peak in  $S_N(q)$  is due to O-O correlation, whereas in  $S_X(q)$  this feature appears as a small shoulder. The second prominent peak in  $S_X(q)$  is due to cation-cation correlations, which appear as the third sharp peak  $S_N(q)$ . On compression, the position of the FSDP moves out to larger  $q$  values (see Fig. S3), as is also seen in experimental measurements of  $\text{MgSiO}_3$  liquid up to 6 GPa (Funamori et al., 2004).

At high pressure, charge-ordering remains the dominant structural theme, with well-defined cation-anion coordination shells, albeit somewhat less sharply defined: RDF peak amplitudes are smaller than they are at zero pressure (Fig. 5). Cation-anion bond lengths vary significantly with increasing pressure (Fig. 7 and Fig. S4). The Si-O bond length initially increases on compression, a pattern also seen in experimental measurements of  $\text{MgSiO}_3$  liquid and  $\text{SiO}_2$  glass, as well as previous first principles simulations of liquids (Funamori et al., 2004;

Sato and Funamori, 2010; Sun et al., 2011). The somewhat counter-intuitive increase of bond length on compression is due to the increase in the Si-O coordination number, with larger coordination numbers being associated with longer bond-lengths (Sato and Funamori, 2010; Sun et al., 2011). The Mg-O bond length changes very slightly on compression initially, and then decreases with increasing pressure for  $P > 15$  GPa.

The mean Si-O coordination number increases monotonically on compression from 4-fold at ambient pressure to 6 at the highest pressure investigated. The Si-O coordination number changes more slowly for small compressions. The mean Mg-O coordination number increases from 4.5 at ambient pressure to a maximum of 8 at the highest pressure investigated. At each pressure, the glass contains a variety of coordination environments. The glass is almost perfectly tetrahedrally coordinated at the ambient pressure. Compression increases the proportion of 5-fold and 6-fold coordination environments. Five-fold is the most abundant coordination environment at intermediate compression, demonstrating that the structure of the glass differs qualitatively from that of any Mg-silicate crystal in which five-fold coordination does not occur. The variation of the Si-O coordination number with increasing pressure is broadly consistent with that seen in vibrational spectroscopy experiments, although it appears that the coordination increase occurs at somewhat lower pressure than had been proposed in the experimental studies (Williams and Jeanloz, 1988; Wolf and McMillan, 1995; Kubicki et al., 1992). In fact the study of Kubicki et al. (1992) did not find any octahedrally coordinated Si up to a maximum pressure of 45 GPa, in disagreement with our results and with the previous experimental study (Williams and Jeanloz, 1988). Detailed comparison is hindered by the fact that these vibrational spectroscopic studies are not quantitative with respect to speciation. In terms of O-Si coordination, our results show that upon increasing compression free oxygens disappear, the number of bridging oxygens increases at the expense of non-bridging oxygens, and oxygen tri-



clusters appear (Fig. 9). The presence of tri-clusters (oxygens coordinated with three silicons) has been seen experimentally in  $\text{MgSiO}_3$  glass at pressures above 12 GPa (Lee et al. 2008). In all cases, similar patterns have been seen in studies of silicate liquids (Stixrude and Karki, 2005, Sun et al., 2011).

The type of compression path: cold vs. hot, has a significant influence on glass structure (Figs. 7-9). In general, hot compression produces more rapid variation of the structure with increasing pressure. For example, the average Si-O coordination number reaches 5 at 12 GPa ( $V/V_x = 0.7$ ) on hot compression, but not until 25 GPa ( $V/V_x = 0.65$ ) on cold compression. In comparison, the liquid reaches 5-fold coordination at  $V/V_x = 0.68$  where the pressure at 3000 K is 39 GPa. The differences between hot and cold compression are most pronounced at low pressure. At pressure above 100 GPa, the structure of hot and cold compressed glasses are indistinguishable in terms of the average properties of coordination environments and within the uncertainty of our simulations.

To explore the relationship between the Si-O and O-Si coordination, we examine the distribution of the  $Q^n$  species. Here,  $n$  is the number of bridging oxygen (an oxygen atom which is also bonded to one or more silicon atoms) attached to a silicon atom, which can be in any coordination state in our case. The calculated distribution (Table 4) consists of a mixture of different species with  $Q^1$ ,  $Q^2$  and  $Q^3$  dominating in silicate glass (80 %). The  $Q^0$  species in 7 % represents isolated (free) tetrahedra. The distribution of  $Q$  species is more uniform than seen experimentally: our  $Q^2$  is less abundant than found experimentally and our  $Q^3$  and  $Q^1 + Q^0$  are more abundant (Sen et al., 2009). These differences are consistent with the higher glass transition temperature of our simulations: for example, the reaction  $Q^2 = Q^1 + Q^3$  is known to shift to the right with increasing fictive temperature (Sen et al., 2009). On compression the relative proportions of species change little over the range dominated by tetrahedral coordination ( $V/V_x \leq$

0.8). Further compression increases the proportion of high-order species implying an increase in connectivity of polyhedral network as the Si-O coordination number increases.

The structures along compression and decompression paths practically overlap when the decompression started from 6 GPa so there is no residual density. However, when the glass was decompressed from 27 GPa, the decompression path deviates from the compression path (Fig. 3 & 4) with the mean coordination numbers being slightly larger than those along the compression path. When the system was decompressed from a much higher pressure of 170 GPa, the difference between compression and decompression paths increases (Fig. 3 & 4) and more high coordination species are preserved (Fig. 9). When decompressed to zero pressure, the abundances of tetrahedra, pentahedra and octahedra are 63, 31 and 6 %, respectively, as compared to 95, 5 and ~0 %, along the compression path. Similarly, NBO, BO and O3 are present in 51, 46, 3 %, respectively, at the decompressed zero pressure compared to 62, 37 and ~0 % for the uncompressed one. Experimental measurements have also found high-coordinated species in the decompressed glass (Gaudio et al., 2008).

### **Wave velocities**

The acoustic wave velocities of MgSiO<sub>3</sub> glass were calculated using three elastic coefficients ( $c_{11}$ ,  $c_{12}$  and  $c_{44}$ ) obtained using the stress-strain relations (Table S2). Both the P- and S-wave velocities increase monotonically with increasing pressure at 300 K (Fig. 10). The calculated values of  $V_p$  and  $V_s$  of MgSiO<sub>3</sub> glass at 300 K and 0 GPa are ~5 and 2 km/s, respectively. These values are smaller by 20 to 30 %, respectively than experimental measurements at the ambient conditions (Sanchez-valle and Bass 2010). Our results are smaller than those experimentally measured over the entire pressure range investigated, with the difference between simulated and measured velocities diminishing at pressures greater than 10

GPa. Hot compression produces uniformly higher velocities than does cold compression. The transverse wave velocity on the hot compression path approaches the experimental value (Murakami and Bass 2011) nearly overlapping beyond 60 GPa. The experimental velocity measurements show abrupt changes in slope of the velocity-pressure profiles at various pressures (Sanchez-valle and Bass 2010; Murakami and Bass 2011). Our calculated velocity-pressure profiles do not show any conclusive evidence for such features.

## DISCUSSION

Our first principles results suggest that  $\text{MgSiO}_3$  glass is highly compressible so the predicted density varies substantially with pressure (Fig. 4). The pressure variation of density can be broadly separated in two regimes. The density increase is rapid in the low-pressure regime up to 20 GPa in which the density-pressure slope differs substantially between different schedules with the decompression paths giving systematically denser structure than both the compression paths. At zero pressure, the decompressed (from 170 GPa) glass density is larger than the uncompressed glass density by 15 %. The computed values of residual densities are 0 and 9 % when decompressed from 6 and 27 GPa, respectively. While other parameters such as high decompression rate, kinetic broadening, and input configuration can influence the residual density, our results suggest that the peak-pressure used for the decompression has a deterministic influence on the value of residual density. The predicted trend for the residual densification is consistent with the experimental observations of  $\text{MgSiO}_3$  glass (Gaudio et al. 2008; Sanchez-Valle and Bass 2010).

Our structural analysis detects about 10 % pentahedra (as compared to 5 % in the uncompressed volume) and no octahedra (30 % octahedra present at 27 GPa) in the glass

decompressed from 27 GPa while there is no significant change in coordination when decompressed from 6 GPa. This finding is consistent with the suggestion that the small residual density in decompressed glasses is perhaps due mostly to topological rearrangements. However, the decompressed (from 170 GPa) densified state at 0 GPa does possess significant amounts of high coordination species which are present at elevated pressures. For instance, 63 % Si-O tetrahedra are recovered in the decompressed glass compared to 95 % tetrahedra in the uncompressed glass; the remaining coordination polyhedra being pentahedra (31 %) and octahedra (6 %). Thus we infer that high remnant densification in decompressed glasses from high pressure is due mainly to the retention of high-coordination species.

The simulated  $\text{MgSiO}_3$  glass shows no clear sign of polyamorphic phase transition, which has been proposed to occur in other systems including silica glass (Zha et al. 1994). We find continuous structural changes along with a smooth increase (decrease) in density with compression (decompression). The pressure intervals over which we find the preponderance of the 4- to 6-fold coordination changes occur are consistent with that inferred from experiments: 20 to 37 GPa (Shim and Catalli 2009).

The calculated density of the glass is systematically larger than the experimental density at high pressure (Sanchez-Valle and Bass 2010). The discrepancy reaches 18 % at the maximum experimental pressure (34 GPa) compared with a discrepancy of 2 % at the ambient pressure. Similar trends have also been observed in case of vitreous silica (Zha et al. 1994; Della Valle and Venuti 1996). The cold-compressed glass from our simulations is thus much more compressible than the experimental glass. The predicted ambient bulk modulus is a factor of 3 less than the experimental value (Table 2). We attribute the discrepancies between the computations and experiments mainly to the frequency dependence of the bulk modulus of the glass. Whereas we determine the pressure-density relation directly from our simulations, the experimental equation

of state was determined from high frequency Brillouin measurements via

$$\rho(P, \omega) - \rho(P_0) = \int \frac{dP'}{V_B^2(P', \omega)} \quad (10)$$

where  $\rho$  is density,  $P$  is pressure, the bulk sound velocity

$$V_B^2 = \left( \frac{\delta P}{\delta \rho} \right)_\omega \quad (11)$$

and the equations are written to emphasize the dependence of quantities on the frequency,  $\omega$ . When the period of the probe is less than the relaxation time, one measures the unrelaxed bulk modulus. The unrelaxed bulk modulus is higher than the relaxed bulk modulus that governs static compression because the structure of the material does not have sufficient time to adjust to the compression during the period of the measurement probe.

Dispersion, which defines the dependence of the acoustic velocity on frequency, is well known from ultrasonic measurements of silicate liquids (Rivers and Carmichael 1987; Ai and Lange 2008). The low frequency relaxed modulus is measured when

$$\frac{1 \text{ GHz}}{f} > \left( \frac{\eta}{20 \text{ Pa s}} \right) \left( \frac{20 \text{ GPa}}{M} \right) \quad (12)$$

For most silicate melts near the ambient liquidus, this relationship is satisfied within the ultrasonic range of frequency ( $f = 1\text{--}10$  MHz), so that it is possible to measure the unrelaxed bulk modulus. For very viscous silicate liquids, dispersion becomes measurable and must be accounted for, either by performing measurements at lower frequency, or at higher temperature where the viscosity is lower. According to this analysis, Brillouin measurements on silicate glasses (Sanchez-valle and Bass 2010, Murakami and Bass 2011) measure the unrelaxed or high frequency bulk modulus. In glasses the viscosity is much higher than in silicate liquids ( $\eta > 10^{13}$  Pa s) while at the same time, the frequency of the Brillouin probe is higher (1–10 GHz) than in ultrasonic experiments. The Maxwell relaxation time is approximately 12 orders of magnitude

longer than the period of the Brillouin probe. The relationship (in Eq. 12) is therefore not satisfied for Brillouin measurements on glasses. Use of the higher unrelaxed Brillouin value of  $V_B$  in Eq. (10) leads to less apparent compression and lower density at high pressure, as we see in Fig. 4. Other studies have found similar discrepancies: Smith and coworkers (Smith et al. 1995) found that the density of  $\text{GeO}_2$  glass directly measured is 10 % greater than that computed from the high frequency bulk sound velocity via Eq. (10) at 6 GPa. Another experimental study also pointed out the pitfalls of using the unrelaxed bulk modulus to compute the equation of state (Zha et al., 1994).

Based on our results, we suggest that experimental studies of hot-compressed glasses perhaps provide closer analogs to high pressure silicate liquid properties than cold compression. We find that hot compression produces significantly greater density at the same pressure than cold compression. Similar type of behavior has also been observed in case of amorphous water/ice (Loerting et al. 2001, Giovambattista et al. 2005). The reason for this is that the high temperature liquid has access to a wider fraction of configuration space than the low temperature glass and is more readily able to accommodate its structure to high pressure conditions. The difference is often expressed in terms of kinetic hindrance to structure change in the glass, which is absent in the liquid state. On high pressure quenching, the structure of the high pressure liquid is largely preserved.

## IMPLICATIONS

This first principles study of the structure of  $\text{MgSiO}_3$  glass as a function of pressure can help us understand the atomistic origins of various physical properties including density, elasticity, viscosity, crystal-melt partitioning, etc. of silicate glasses and melts. The predicted glass structure, like melt structure, consists of a rich set of coordination species and the structural

changes occur continuously over the whole range of compression studied. Both Si and Mg display rapid increase in their mean coordination numbers with respect to O with compression up to 20 GPa beyond which the coordination increases become gradual. The anion-cation coordination numbers increase on compression, and eventually oxygen tri-clusters appear in large proportion at high pressure. The densification mechanism thus differs between low- and high-pressure regimes. Various cation-anion coordination states and oxygen tri-clusters may significantly affect the partitioning of incompatible elements between crystals and glasses (or melts). We anticipate that these trends will also appear in other divalent metal silicate compositions such as in Fe- and Ca-silicates. On decompression from low pressures, the system recovers most of its initial structural characteristics in terms of coordination and polyhedral arrangement. However, when decompressed from high pressure, it fails to revert back completely to the initial state, resulting in significant irreversible compaction primarily because of continuing existence of high coordination species to larger volumes. The magnitude of compression thus appears to control the magnitude of residual densification (and the degree of irreversibility). While our simulations are consistent with a large body of experimental measurements of glass structure and properties at ambient conditions, some significant discrepancies also appear. For instance, the predicted zero-pressure bulk modulus is much smaller than the experimental value, which we attribute mainly to the frequency dependence of the bulk modulus: whereas we compute the relaxed bulk modulus, Brillouin spectroscopy measures the unrelaxed bulk modulus. More computational studies are anticipated in the future in order to better understand such discrepancies and explain a rich set of existing experimental studies.

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**Table 1:** Predicted glass structures (expressed in terms of coordination environments,  $C_{\alpha\beta}$ 's, where  $\alpha$  and  $\beta$  represent atomic species under consideration) using 160- and 640-atom supercells for two quench rates. The numbers are presented within three significant figures. (FO: free oxygen, NBO: non-bridging oxygen, BO: bridging oxygen, O3: oxygen tricluster).

	640 atoms		160 atoms	
	1K/fs	0.5K/fs	1K/fs	0.5K/fs
$C_{\text{SiO}}$ (3-, 4-, 5-fold)	4.05 (0.00, 95, 4.9)	4.05 (0.00, 95, 5.0)	4.09 (0.00, 91, 8.9)	4.03 (0.00, 97, 3.1)
$C_{\text{OSi}}$ (FO, NBO, BO, O3)	1.35 (1.6, 62, 37, 0.00)	1.35 (1.6, 62, 37, 0.00)	1.36 (1.0, 62, 37, 0.02)	1.33 (0.00, 67, 33, 0.00)
$C_{\text{MgO}}$ (3-, 4-, 5-, 6-fold)	4.46 (3.3, 51.8, 41, 4.1)	4.60 (3.0, 42, 49, 6.0)	4.41 (1.8, 58, 38, 2.3)	4.60 (3.1, 45, 40, 12)
$C_{\text{OMg}}$ (0-, 1-, 2-, 3-, 4-fold)	1.49 (22, 19, 50, 8.0, 1.1)	1.53 (20, 20, 50, 9.3, 1.6)	1.47 (18, 25, 48, 7.8, 0.45)	1.53 (15, 23, 57, 5.5, 0.00)

**Table 2:** The fourth order equation of state parameters from three simulation schedules used in this study. Previous molecular dynamics results, MD1 (Kubucki and Lasaga 1991) and MD2 (Shimoda and Okuno 2006), and experimentally derived parameters, Expt. (Sanchez-Valle and Bass 2010) are shown for comparison.

	$V_0$ (cm <sup>3</sup> /mol)	$K_0$ (GPa)	$K'_0$	$K''_0$ (GPa <sup>-1</sup> )
Cold compression	35.9	27.2	3.5	-0.07
Hot compression	34.7	15.1	5.0	-0.23
Decompression	30.5	32.0	5.7	-0.25
MD1	37.0	24.1	5.4	
MD2	35.8	59.5		
Expt	36.5	78.4	4.8	

**Table 3: The calculated peak distances ( $R_p$ ) and average bond lengths ( $R_{av}$ ) in all partial radial distribution functions and the corresponding mean coordination numbers ( $C_{\alpha\beta}$ 's where  $\alpha$  and  $\beta$  represent atomic species under coordination consideration) at the ambient condition compared to the experimental data. The numbers in the parentheses are the calculated mean O-Si, O-Mg and Si-Mg coordination.**

	This study			Waseda and Toguri (1977)		Yin et al. (1983)	
	$R_p$ (Å)	$R_{av}$ (Å)	$C_{\alpha\beta}$	$R_p$ (Å)	$C_{\alpha\beta}$	$R_p$ (Å)	$C_{\alpha\beta}$
Si-O	1.63	1.64	4.0 (1.35)	1.62	3.7	1.63	4.1
Mg-O	1.98	2.05	4.6 (1.53)	2.14	4.5	2.08	4.1
O-O	2.68	2.71	5.8	2.65	5.7	2.66	4.3
Si-Si	3.00	3.02	2.1	3.14	3.5	3.05	2.0
Mg-Si	3.19	3.22	4.6 (4.6)				
Mg-Mg	2.92	3.42	4.5				

**Table 4:** The calculated abundances of  $Q^n$  species in  $MgSiO_3$  glass as a function of pressure on cold compression path compared with expt. (Sen et al. 2009).

$P$ (GPa), $V/V_x$	$Q^0$	$Q^1$	$Q^2$	$Q^3$	$Q^4$	$Q^5$	$Q^6$
-1.0, 1.0	7.0	21	28	31	12	0.4	0.00
Expt.	0.00	25	42	25.7	7.3	0.00	0.00
4.7, 0.9	6.0	22	28	31	11	1.5	0.00
7.3, 0.8	5.2	16	24	33	16	5.6	0.6
16, 0.7	0.78	6.2	18	25	24	17	9.4
38, 0.6	0.00	2.3	5.9	10	30	28	24
66, 0.55	0.00	0.83	2.0	8.6	24	33	31
109, 0.5	0.00	0.78	0.96	3.7	20	31	43

**Figure 1:** A schematic representation of three simulation schedules used.

**Figure 2:** Visualization snapshots of the  $\text{MgSiO}_3$  (640 atoms) glass structures at three different volumes (from left to right:  $V_x$ ,  $0.70V_x$ ,  $0.45V_x$ ) along hot compression (upper panel), cold compression (middle panel) and decompression (lower panel). The Si-O coordination polyhedra and Mg (spheres) atoms are color-coded to represent the coordination numbers (cyan for four-fold, blue for 5-fold, magenta for six-fold and white for seven-fold, pink for eight or higher). The atomistic visualization system of Bhattarai and Karki (2009) was used.

**Figure 3.** The calculated pressure–volume results (filled symbols) for  $\text{MgSiO}_3$  glass at 300 K fit to the fourth-order Birch-Murnaghan equation of state (lines) along the cold compression, hot compression and cold decompression paths. Here,  $V_x$  is the reference volume. Uncertainties are estimated from four different independent 160 atom configurations.

**Figure 4.** Pressure dependence of the  $\text{MgSiO}_3$  glass density (solid lines: *black* → cold compression; *red* → hot compression; *blue & green* → decompression) compared with the liquid (calculated at 3000 K) density and available experimental data (for glass and other relevant crystalline phases of  $\text{MgSiO}_3$ ). Legend details for the experimental data: (SV: Sanchez-Valle and Bass, 2010; GD: Gaudio et. al., 2008; SX: Saxena et. al., 1999; LZ: Li and Zhang, 2005).

**Figure 5.** The calculated partial radial distribution functions (RDF's) at different volumes ( $V_x$ ,  $0.6V_x$  and  $0.45V_x$ ) along the cold compression.

**Figure 6:** Total and partial structure factors,  $S_N(q)$  (neutron) and  $S_X(q)$  (X-ray), at the uncompressed volume ( $V_X$ ). Also shown are the experimental structure factors at the ambient pressure (Wilding et. al., 2004). The total structure factors have been shifted (by 1.5) in the Y-direction for the clarity. Dotted vertical (brown) lines are guide to estimate partial contributions to the total structure factor.

**Figure 7:** Pressure variations of the average Mg–O and Si–O distances along the cold (solid lines with symbols) and hot (dashed lines) compression. Uncertainties are estimated (cold compression) from four different independent 160-atom configurations.

**Figure 8.** The mean coordination numbers of different types as a function of pressure along the cold (solid lines with symbols) and hot (dashed lines) compression. Uncertainties are estimated (cold compression) from four different independent 160-atom configurations.

**Figure 9.** The Si–O, O–Si, Mg–O and O–Mg coordination numbers as a function of pressure along the cold (thick solid lines) compression, hot (thin solid lines) compression and decompression (dashed lines). Abundances of various coordination species (zero-fold to nine-fold) are indicated by the legends 0–9.

**Figure 10.** Pressure dependencies of the calculated bulk velocity,  $V_p$  and shear velocity,  $V_s$ . Corresponding experimental data are shown for comparison (SVB: Sanchez-Valle and Bass 2010; MB: Murakami and Bass 2011). Error bars represent the deviations of the three independently calculated  $G$  (or  $K$ ) values (employing eqn. 6 and 9) from the calculated mean  $G$  (or  $K$ ) values (employing eqn. 8 and 9). Red: hot compression. Black: cold compression.





















