

LETTER

The influence of atomic size and charge of dissolved species on the diffusivity and viscosity of silicate melts

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ABSTRACT

Molecular dynamics simulations are used to determine how a dissolved species alters the transport properties of a silicate melt. To identify the specific factors that affect the transport properties, we examine the effects of generic dissolved species for which the atomic interaction parameters can be systematically varied. We focus on the role of the size and charge of the dissolved species. Our results show that neutral dissolved species have negligible effects on the structure and bonding of the silica network, regardless of the size of the species. These neutral species are decoupled from the network, and can diffuse orders of magnitude faster than the network ions. In contrast, charged species strongly disrupt the silica network, which leads to significant enhancement of the transport properties (e.g., lower viscosity and higher diffusivity of the network ions). The effects of the charged dissolved species are strongly dependent on their size.

Keywords: Silicate, transport properties, diffusion, viscosity, magma

INTRODUCTION

The transport properties of silicate melts are strongly dependent on seemingly minor changes in composition. For example, when a silica-rich melt is mixed with just several weight percent of another oxide (e.g., MgO, Na₂O, etc.) or a volatile species (e.g., H₂O, F, CO₂, noble gases), the melt viscosity can be reduced by several orders of magnitude (Giordano and Dingwell 2003; Hui and Zhang 2007). Furthermore, the diffusivities of volatiles dissolved in a silicate melt can be many orders of magnitude greater than the diffusivities of the silicate ions, and can depend strongly on volatile concentration (Watson 1994). A detailed understanding of the compositional controls on the transport properties of silicate melts, and their relationship to changes in melt structure, is crucial for extrapolating melt property data to natural conditions and for understanding the diverse behaviors of magmas (Mysen 1988).

We use a novel simulation approach to elucidate the physical factors that underlie these changes in transport properties. Most studies aim to simulate accurately the properties of real systems, with interactions among atoms governed by empirically calibrated force fields (Lacks and Van Orman 2007; Ben Martin et al. 2009) or by ab initio treatments of the electronic structure (de Koker et al. 2008; Zhang et al. 2009). Here, our goal is not to address the properties of a particular system, but instead to gain insight into the fundamental roles of the size and charge of dissolved species on the transport properties of silicate melts. For this purpose, we examine “generic” dissolved species rather than actual chemical species so that we can vary their radii continuously without simultaneously varying other atomic properties.

COMPUTATIONAL METHODS

Molecular dynamics simulations are carried out for systems with silicon and O atoms as well as “generic” atoms that represent other dissolved species. Molecular dynamics simulations involve the numerical integration of Newton’s laws of motion (usually modified to impose constant temperature and pressure) for the atoms in the system, which interact through specified forces (Allen and Tildesley 1989).

The silicon and O atoms interact through the widely used BKS force field for silica (van Beest et al. 1990), modified in two ways: (1) a steep repulsive wall, which is significant only at short interatomic distances, is added to the interatomic potential to prevent nonphysical behavior inherent in the original BKS potential at short distances (Saika-Voivod et al. 2001); and (2) the non-coulombic potential is truncated at 5.5 Å and shifted in energy such that the energy is continuous at this cutoff distance (Horbach and Kob 1999), which leads to densities in better agreement with experiment and also reduces the computational burden of the simulations. While the non-coulombic forces are discontinuous at the cutoff distance, these forces are small in magnitude and the effect of the discontinuity is not significant. The generic atoms interact with all other atoms (e.g., silicon, oxygen and other generic atoms) via the potential:

$$\phi(r_{ij}) = \epsilon \left(\frac{\sigma}{r_{ij}} \right)^{30} + \frac{q_i q_j}{r_{ij}} \quad (1)$$

where r_{ij} is the distance between atoms i and j , $\epsilon = 1$ kcal/mol, σ is a constant that sets the size of the generic atom, and q_i is the charge of atom i . Note that σ has a common value for all types of interactions, i.e., with silicon, oxygen and other generic atoms. This common value is used to minimize the number of parameters characterizing the generic atom. The masses of the generic atoms are set at 30 g/mol, which is an arbitrary value with the appropriate order of magnitude for the dissolved species of interest; note that variations in mass have only a small influence on diffusion properties at the conditions of interest.

The simulations are carried out in a cubic simulation cell with periodic boundary conditions, in systems including 666 silicon atoms, 1332 O atoms, and 74 “generic” atoms. The system is initially held at zero pressure, to determine the zero-pressure volume of the system, and the remainder of the simulation is carried out at constant volume, at the appropriate zero-pressure volume. The simulations are carried out with the LAMMPS molecular simulation software (Plimpton 1995).

The viscosity, η_{sp} , is calculated from the Green-Kubo relation (Allen and Tildesley 1989), which involves the integral over time of the stress autocorrelation function for the off-diagonal components of the pressure tensor. Ensemble

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averaging is carried out by evaluating the integrand with different time origins, and the upper-limit of the integral is taken to be a time large enough that the integrand is zero. The statistical error in the viscosity is estimated from the variation in the results for η_{xy} , η_{yz} , and η_{zx} .

The diffusion constant, D , for each species is obtained from the Einstein relation (Allen and Tildesley 1989). The error is estimated from the variation in the results for D_x , D_y , and D_z (since liquids are isotropic with respect to diffusion).

RESULTS

The viscosity and diffusivity are examined for two types of silicate systems containing dissolved generic atoms, as a function of the size of the generic atom (i.e., σ in Eq. 1). In one case the generic atoms are neutral ($q_i = 0$ in Eq. 1), and in the other case the generic atoms are charged such that half have $q_i = +1$ and the other half have $q_i = -1$. Results are obtained at the temperature $T = 4000$ K, and at the zero-pressure volume for the particular system at this temperature (these volumes vary with σ and the charge on the atoms). The high temperature is used so that the atomic dynamics are sufficiently fast to allow convergence of results to high precision. The parameter σ is varied over the range 0 to 4 Å; note that for values of $\sigma < 1$ Å the corresponding atomic size is not physically meaningful, whereas for values of $\sigma = 2, 3$, and 4 Å the atomic radii determined from $g(r)$ results are $\sim 0.5, 1$, and 1.5 Å, respectively.

The simulation results for viscosity (Fig. 1) show that atomic charge fundamentally changes the way that the dissolved species alters the viscosity: the dissolved species acts to decrease the viscosity when the dissolved atoms are charged, but to increase the viscosity when the dissolved atoms are neutral. For small neutral dissolved atoms the viscosity changes are negligible, but as the size of the neutral atoms increases, the viscosity increases systematically. As discussed below, the neutral atoms do not alter the network structure of the melt; instead they clog the motion of the network atoms, thus increasing the viscosity. For charged solutes, the viscosity decreases with increasing atomic size for smaller dissolved atoms, but then increases with increasing atomic size for larger dissolved atoms.

The simulation results for diffusivity are shown in Figure 2. The influence of dissolved species on the diffusivity of Si and O is opposite to their influence on the viscosity, as expected based

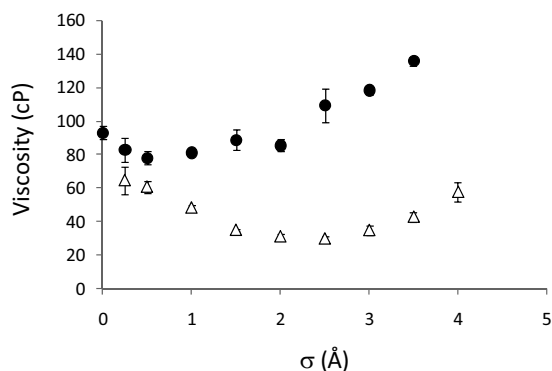


FIGURE 1. Viscosity of melts as a function of the size of the dissolved atoms, at 4000 K. Circles are results for systems with neutral dissolved atoms, and triangles are results for systems with dissolved atoms with charge +1, -1. Error bars are obtained as the standard error of the results obtained for the viscosity based on the xy , yz , and zx components of the stress tensor; when error bars are not visible, they are smaller than the symbols.

on the Eyring model of dynamics in liquids. Neutral solutes hinder the diffusion of Si and O, and charged solutes enhance their diffusion significantly. The changes in Si and O diffusivity with the size of the dissolved atoms are analogous to changes in the viscosity.

The diffusivities of the dissolved atoms depend strongly on their charge and size. At small size, the neutral atoms diffuse two orders of magnitude faster than the charged atoms. The diffusivity of the neutral solutes decreases exponentially with increasing size of the atom, in agreement with the experimental results of Lux (1987) for diffusion of noble gases in basaltic liquids. In contrast, the diffusivity of the +1 and -1 charged atoms has a complex dependence on atomic size, similar to the dependence observed for Si and O. The disruption of the silicate network induced by the charged solutes thus appears to enhance not only the diffusion of the network-forming Si and O atoms, but of the dissolved species as well. The small size dependence observed experimentally for diffusion of -1 ions (Alletti et al. 2007) may result in part from the complexity that results from the influence of ionic size on both the structure of the melt and the intrinsic diffusivity of the anionic species.

Interestingly, large charged atoms have nearly the same dif-

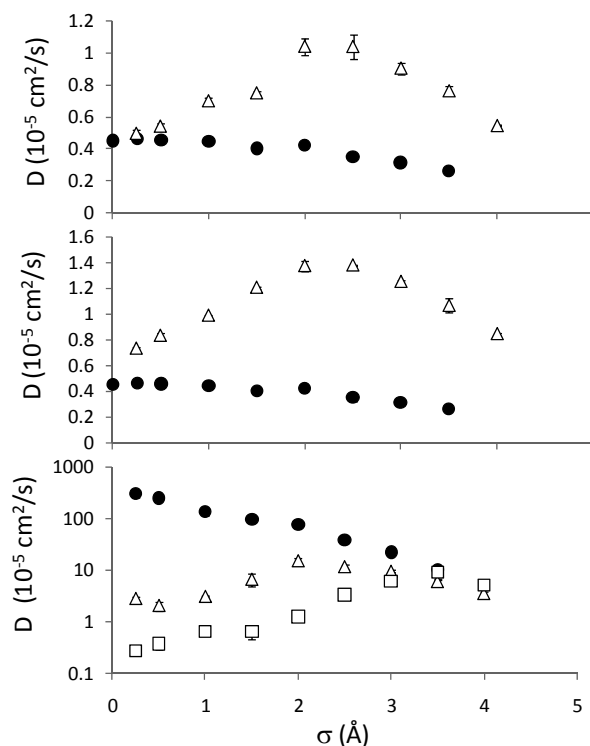


FIGURE 2. Diffusivity of species in melt as a function of the size of the dissolved atoms, at 4000 K. (a, b) Diffusivity of Si (a) and O (b); circles are results for systems with neutral dissolved atoms, and triangles are results for systems with dissolved atoms with charge +1, -1. (c) Diffusivity of dissolved atoms; circles are results for neutral dissolved atoms, triangles are results for dissolved atoms with charge +1, and squares are results for dissolved atoms with charge -1. Error bars are obtained as the standard error of the results obtained for the diffusivity based on the mean-squared displacements in the x , y , and z directions; when error bars are not visible, they are smaller than the symbols.

fusivity as neutral atoms of the same size. Charge is expected to become less important as the atomic size increases because the electrostatic force exerted on surrounding atoms decreases with the square of the distance.

Figure 3 shows the temperature dependence of diffusivities, for the system containing neutral dissolved atoms with $\sigma = 3$. For Si and O, diffusive motion is negligible below $T = 3000$ K; i.e., a glass transition occurs near this temperature (the glass transition temperature depends on the timescale of observation, and occurs at a higher temperature in simulations than in experiments due to the much shorter timescales). However, for the neutral atoms, the diffusive motion continues to be significant at temperatures far below the glass transition. There may be a change in the nature of the diffusion mechanism at the glass transition, as the results indicate there may be a change in slope of the diffusivity on the Arrhenius plot. It is not clear that the change in slope is significant, but if so it may indicate a transition from diffusive motion accommodated solely by thermal vibrations of the network atoms to motion that is assisted by diffusion of the network atoms at temperatures above the glass transition. Diffusion coefficients for the neutral species, which is similar in radius to He, are similar in magnitude and temperature dependence to those determined experimentally (Swets et al. 1961). The activation energy for O diffusion (455 kJ/mol) is nearly identical to that determined experimentally at lower temperatures (460 kJ/mol; Mikkelsen 1984), but significantly larger than the value determined from first-principles MD simulations over a similar temperature range (315 kJ/mol; Karki et al. 2007).

While neutral solutes have a negligible influence on melt structure, charged solutes significantly alter the structure in a way that varies with the atomic size (Fig. 4). Charged solutes depolymerize the melt, increasing the fraction of non-bridging O atoms significantly (Fig. 1b). This result is in agreement with the experimental finding that adding NaF to liquid silica increases the fraction of non-bridging oxygen (Mysen and Virgo 1985). Larger charged solutes are less effective at removing bridging O atoms from the melt network, and this probably explains why they are also less effective at reducing melt viscosity, and at enhancing Si and O diffusion. Charged solutes also alter Si coordination and the ring structure of the melt, but these changes are less pronounced than the changes in the fraction of non-

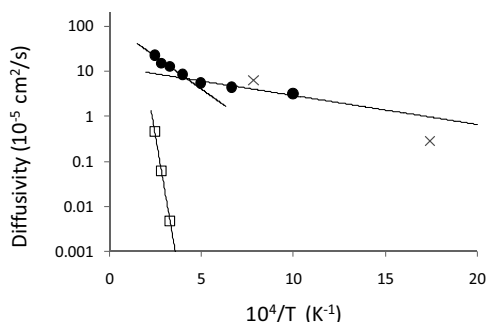


FIGURE 3. Diffusivities of oxygen (squares) and neutral atoms with $\sigma = 3$ (circles) in melt as a function of inverse temperature (the error bars are smaller than the symbols). The apparent activation energy for the neutral atoms is 12 kJ/mol in the low-temperature regime and 55 kJ/mol in the high-temperature regime. Experimental data for He diffusion in amorphous SiO_2 are shown as crosses.

bridging oxygen, and it is not clear whether these changes have a significant influence on melt transport properties.

DISCUSSION

We find that charged species enhance the transport properties of silicate melts, i.e., decrease the viscosity and increase the diffusivities (see Figs. 1 and 2). This result concurs with the model of Giordano and Dingwell (2003), in which adding structure-modifying oxides acts to decrease the viscosity. The changes in viscosity we find for charged solutes are much smaller than changes observed experimentally (e.g., a factor of two instead of several orders of magnitude) because the simulations are carried out at 4000 K and the experiments are typically carried out at 1000–2000 K; it is well known that the compositional dependence of viscosity increases in magnitude with decreasing temperature (Giordano and Dingwell 2003).

Whereas dissolved charged species enhance the transport properties, uncharged species do not (see Figs. 1 and 2). This result reinforces the inference that the decrease in viscosity observed in hydrous silicate melts (Stolper 1982; Lange 1994) comes about from the speciation of $\text{H}_2\text{O} + \text{O}^{2-} \rightarrow 2\text{OH}^-$; i.e., it is the hydroxide ions that cause the decrease in viscosity rather than the molecular water. The reason why the transport properties are not enhanced by neutral dissolved species is that the neutral

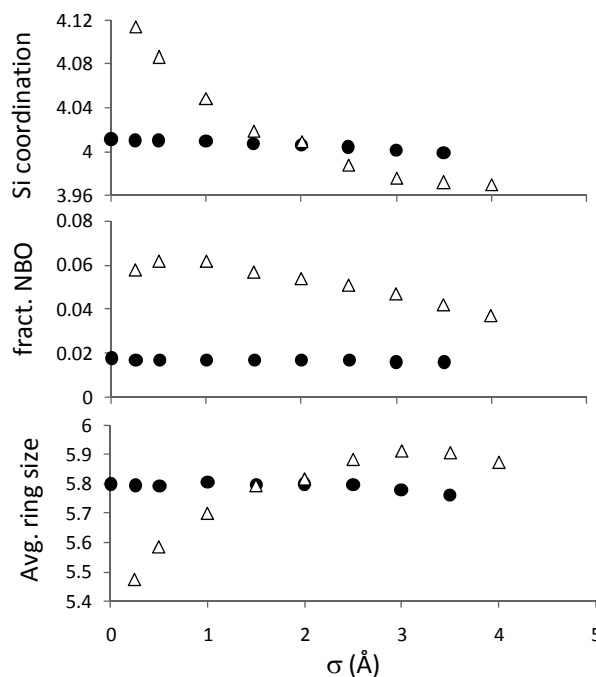


FIGURE 4. Structural properties of melts as a function of the size of the dissolved atoms. (a) Silicon coordination number (i.e., the average number of O atoms that are a nearest neighbor to a silicon atom); (b) fraction of O atoms that are non-bridging (defined as the fraction of O atoms with less than two nearest neighbor silicon atoms); (c) average silica ring size, where a ring is defined as the shortest closed loop of Si-O units that leaves an initial silicon ion via one Si-O unit and returns to the initial silicon ion via a different Si-O unit, and the ring size is the number of Si-O units in the ring. Circles are results for systems with neutral dissolved atoms, and triangles are results for systems with dissolved atoms with charge +1, -1.

dissolved atoms do not alter the silicate structure (see Fig. 4). Large neutral species have a modest inhibiting influence on melt transport properties, acting as passive barriers to the motion of network-forming species.

In their model for silicate melt viscosity, Giordano and Dingwell (2003) made the simplifying assumption that structure-modifying oxide species could be treated as having identical properties; i.e., no attempt was made to account for possible differences in the ability of different structure-modifying species to alter melt viscosity. The model was found to reproduce silicate melt viscosities quite well over the large range of compositions studied. On the other hand, there is experimental evidence that not all structure-modifying species influence the transport properties of silicate melts in the same way. For example, while OH^- and F^- severely reduce the viscosity of silicate melts, Cl^- appears to have little effect (Dingwell and Hess 1998). Our results suggest that the contrasting behavior of Cl^- relative to OH^- and F^- is due to the much larger size of Cl^- . The large size of dissolved CO_3^{2-} also may explain why it has little influence on silicate melt transport properties compared to OH^- and F^- (Lange 1994). Our results suggest that the Giordano and Dingwell model might be refined, and extended to an even broader range of compositions, by adding a simple parameterization based on the size of the structure-modifying species.

Our results show that neutral dissolved atoms can diffuse many orders of magnitude faster than network forming atoms in the same melt. The difference is particularly strong below the glass transition temperature, where the diffusivity of oxygen is effectively zero, while the diffusivity of the neutral species remains significant (see Fig. 3). This result agrees with previous experimental work that shows that He, CO_2 , and molecular H_2O are effectively “blind” to the glass transition, and have significant diffusivity at temperatures well below the glass transition temperature (Watson 1994; Zhang and Behrens 2000). In contrast to the neutral dissolved atoms, the charged solutes— anions in particular—have diffusivities generally similar to that of oxygen (see Figs. 2b and 2c). Water dissolves in silicate melts as both neutral molecular species and as charged hydroxyl species (Stolper 1982). Our results show that neutral species diffuse much faster than charged species; this would imply that molecular water is the primary diffusing species under most conditions, in agreement with inferences from experimental studies (Zhang and Behrens 2000). At very low water concentrations, relevant for example to the degassing of lunar magmas (Saal et al. 2008), hydroxyl groups may control water diffusion because they are present in much higher abundance (Stolper 1982). No experimental data exist on the diffusivity of OH^- in silicate melts, but F^- is similar in size and hence may provide a good analog for the diffusion of water in silicate melts at low concentrations. At high pressures, and/or high concentrations, water diffusion may involve many more than isolated hydroxyl and molecular species. Recent first-principles MD simulations demonstrate that several extended structures involving multiple H and O atoms may exist in hydrated silicate melts, and that proton transfer processes become dominant at high pressures (Mookherjee et al. 2008; Karki et al. 2009).

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