Usage Report for Fiscal Year 2018

Project Title:

Thermal Conductivity of Minerals in the Deep Earth and Planets

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Introduction

Transport properties such as diffusivity and viscosity of melts not only dictated the evolution of the early Earth's magma ocean but also control many geological processes from the dynamics of mantle convection to magma migration and volcanic activity. However, experimental measurements of melt diffusivity and viscosity at most of the mantle conditions remain impossible due to technical challenges. Herein we performed First Principles molecular dynamics simulation on the structure, density, diffusivity and viscosity of a model basaltic ($Ca_{11}Mg_7Al_8Si_{22}O_{74}$) melt at temperatures from 2200 and 3000K, and pressures from 0 to 80 GPa. As will be highlighted below we obtained new insights to the dynamics of the melts at high pressure and high pressure.

Methodology

Ab initio Molecular dynamics simulations were carried out on a model basaltic system. Constant volume and constant temperature (NVT) canonical ensemble has been employed along with Nosé thermostat. The simulations were carried using the VASP program, expanding electron orbitals in the plane wave (PAW) basis set. PBE functional was used keeping the kinetic energy cut-off of the plane wave 400 eV. The interatomic forces are computed for all the time steps from a fully self-consistent solution of the electronic structure to the Born-Oppenheimer surface, within the finite temperature formulation of density functional theory. The stoichiometry of the basaltic material studied was a mixture of seven diopside ($CaMgSi_2O_6$) and four anorthite ($CaAl_2Si_2O_8$): i.e., $Ca_{11}Mg_7Al_8Si_{22}O_{74}$. A cubic supercell with a total of 244 atoms was considered. Owing to the large size of the unit cell and computational limitations, we ran all the simulations using just one k-point (Γ) to sample the Brillouin Zone. For the melt system, simulations were performed at 0, 18, 23, 30, 38, 50, 62, 68 and 82 GPa and 2200/3000 K, similar to the experimental conditions. At each pressure, the melt was first equilibrated using constant-pressure-constant temperature (*NPT*) molecular dynamics at the desired temperature. A model cell was then determined from the average of the cell parameters from the *NPT* simulation in the equilibrated steps. The time step that was used for the integration of the equation of motions was chosen to be 2.0 fs. To ensure convergence in the calculated transport properties, depending on the thermodynamic conditions, AIMD simulations were performed for at 60,000 up to 120,000 time steps, equivalent to 0.12 to 0.24 ns. From monitoring the temporal evolution of the isotropic stress, temperature and total energy, it was found that most systems equilibrated after approximately 10000 steps. The remaining atomic trajectory from the MD calculations was used in the analysis.

Highlight of results

The structural changes of the basalt melt compressed at 2200K is succinctly summarized in the plot of the pressure-volume relation (Fig. 1) . We found the calculated data points cannot be fit to a single EOS. In fact, the calculated results seem to suggest there are into two regions of structural dissimilarity with a discontinuity at 30 GPa. As shown in the Fig.2 the use of two different EOS to the theoretical data produce a reasonable fit (blue and red lines in Fig. 1a). The discontinuity is reflected in the change in sound velocity in the melt (Fig. 1b)

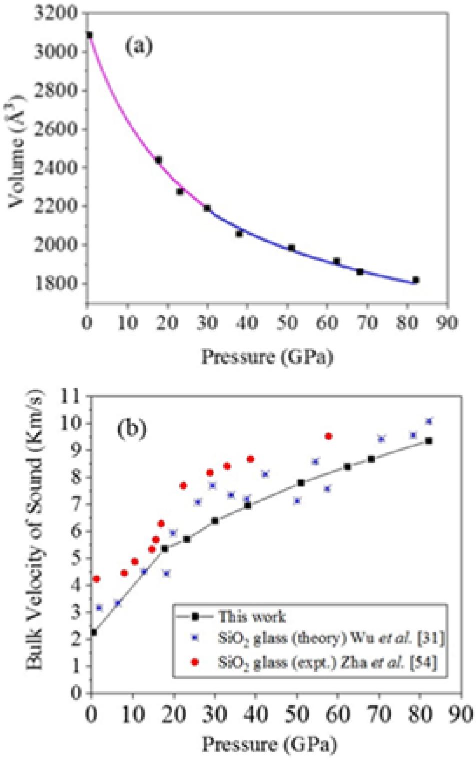

Fig. 1

Careful analysis of the Si-O and Al-O coordination numbers show the discontinuity is related to the change in local structure (Fig. 2). Moreover, it is found that the O atoms coordinated to Si and Al at high pressure is not permanent but there are lots of temporal fluctuations in bond breaking and forming from diffusive oxygen atoms. This phenomenon is clearly illustrated in the temporal evolution of the coordination numbers at 50 GPa and 2200 K of Si and Al in Fig. 4a and 4b, respectively.

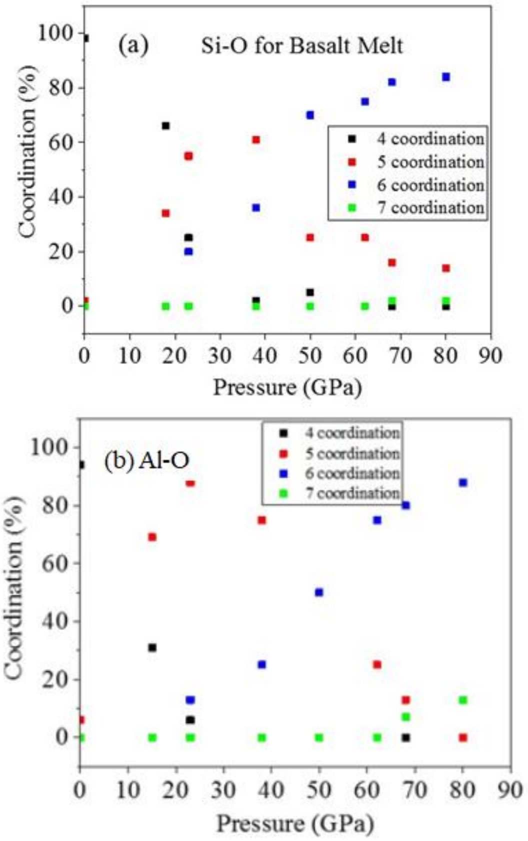

Fig. 3

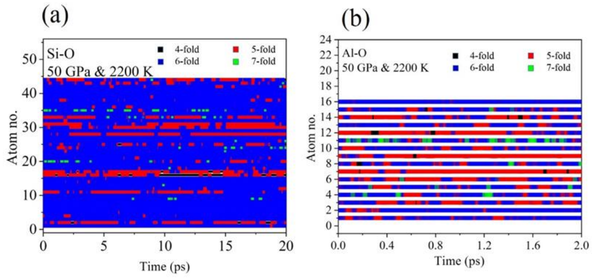

Fig. 4

The temporal bond breaking and formation has a significant effect on the viscosity of the melt. A summary of the viscosities of the basalt melt at 2200K and 3000K are depicted in Fig 5a. A great surprise and novel observation from this investigation is the reversal of viscosity at high pressure!!! This anomaly is observed both at 2200K and 3000Kand therefore, it is not an artifact of the calculation. More strikingly, a reversal in viscosity at similar depth as the theoretical simlations was reported recently. From the analysis of geophysical data (Fig. 5b).

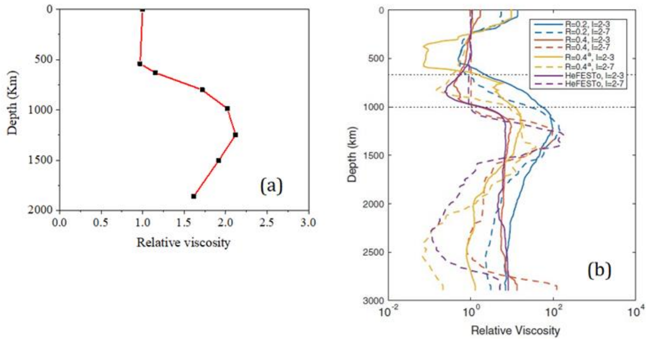

Fig. 5

Analysis of the MD trajectories show the reason for the viscosity trend and reversal at high pressure can be attributed to the change in Al-O coordination number. The predominance of fivefold coordination at intermediate compressed region has the following consequences. Firstly, it contributes to the gradual change in the mean Si–O and Al-O coordination number and the density with increasing pressure. Secondly, fivefold coordination has been proposed by Angell *et al.* as a key ingredient for facilitating diffusion and viscous flow. Experimentally, diopside melt shows an initial decrease in viscosity with increasing pressure, consistent with the growth of fivefold coordination. Ideally, a polymerized network aluminosilicate liquid should have four coordinated aluminium and silicon atoms, and 2 coordinated oxygen atoms. In such a melt system, all the oxygen atoms act as bridging oxygen (BO) atoms. Such systems have very high viscosity owing to the high activation barrier. On increasing the pressure, the coordination of the aluminium atoms increases to five very rapidly, weakening the Al-O bond, thus increasing the mobility of the atoms. However, Yarger *et al.* suggested that the bond angle changes of tetrahedral aluminosilicate network can also be a factor responsible for the decrease of the viscosity with compression. Although pure silica melts have been observed to have high viscosity, the addition of alkali and alkali earth elements act as network modifiers which reduce the viscosity drastically. The inclusion of alkali and alkali earth elements (Na, Ca, Mg, *etc.*) breaks the Si-O and Al-O linkages, giving rise to non-bridging oxygen (NBO) atoms. Previous studies have shown that the viscous flow in aluminosilicate melts is dependent on the oxygen exchange between polymeric units. Presence of the non-bridging oxygen atoms destroys the tetrahedral network structure resulting in the lowering of the activation energy for oxygen exchange. The low activation energy facilitates higher mobility, *i.e.* lower viscosity. In this study, between 0 and 18 GPa, the decrease in the viscosity can be attributed to the rapid increase in the aluminium coordination with oxygen. Interestingly, in our study, we found that the viscosity once again drops after 50 GPa (Fig. 5) for both 2200 and 3000 K. We have already seen that above 50 GPa, aluminium starts showing seven-fold coordination, thus weakening the Al-O bond further. Furthermore, on compression, the alkaline and alkaline earth metals in our system, *i.e.* Ca and Mg, also attain higher coordination, thus giving rise to more NBO and lowering the viscosity further. Fig. 5 shows the transition in the polyhedral structures for Si and Al. It is apparent that five-fold coordination and eventually even seven-fold coordination of the Si and Al atoms is the reason behind the anomalous viscosity.

Summary

In this work, we investigated the structural, thermodynamic, elastic, electronic and transport properties of both glass and molten model basalt. Our results on the melt structure and density match well with those obtained from previous experiments and theoretical calculations. In particular, the calculated viscosity of the model basaltic melt at 2200 K first decreases slightly from 49 mPa.s at 0 GPa to 48 mPa.s at 18 GPa, but then increases to 105 mPa.s at 50 GPa and drops to 80 mPa.s at 80 GPa. A similar trend including a reversal in viscosity at ~50 GPa is also predicted from the model basaltic melt at 3000 K.

The predicted trend in the viscosity of melt will have important implications to the mantle’s viscosity structure as well as the timescales of the early Earth’s magma ocean.

Status of the Project

This project has been successfully completed. Currently we are analyzing the trajectories in order to compute the ionic conductivity of basalt melt. A paper is under preparation and will be submitted for publication in the near future.

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Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

X. Du, Z. Wan, H. Wang, T. Iitaka, Y. Pan, H. Wang and J.S. Tse, Structures and Stability of Iron Halides at the Earth's mantle and core pressures: Implications for the missing halogen paradox, ACS Earth Space Chem., DOI: 10.1021/acsearthspace-chem.8b00034