



Available online at www.sciencedirect.com



Geochimica et Cosmochimica Acta

Geochimica et Cosmochimica Acta 312 (2021) 106-123

www.elsevier.com/locate/gca

# Carbon bearing aluminosilicate melt at high pressure

Suraj K. Bajgain\*, Mainak Mookherjee

Earth Materials Laboratory, Earth, Ocean and Atmospheric Sciences, Florida State University, Tallahassee, FL 32306, United States

Received 27 January 2021; accepted in revised form 30 July 2021; available online 4 August 2021

## Abstract

It is well known that volatiles such as water has significant influence on the properties of silicate melts. Carbon dioxide  $(CO_2)$  is also an abundant volatile in deep Earth, however the effect of  $CO_2$  on the properties of polymerized melts, particularly the transport properties, are poorly understood. This is crucial for better understanding of the generation and migration of carbon bearing silicate magma in deep crustal and mantle settings. In this study, we explore the structure and properties of carbon bearing aluminosilicate melt up to a pressure of ~25 GPa and temperature range of 2500-4000 K using *first principles* molecular dynamics (FPMD) simulation. Our results show that  $CO_2$  in the aluminosilicate melts dissolves as molecular  $CO_2$ and carbonate  $(CO_3^{2-})$  at lower pressures (~0-3 GPa). However, at higher pressures (>3 GPa) relevant to most of the upper mantle,  $CO_{2}^{2-}$  is predominant carbon species along with carbon in 4-fold coordination (CO<sub>4</sub>). Fraction of  $CO_{2}^{2-}$  increases with decreasing temperature and increasing pressure. We find that at the reference isotherm (2500 K), the density of the aluminosilicate melt is reduced by addition of  $CO_2$  (in wt.%) with  $\frac{d\rho}{dX_{CO_2}} = -0.0214$ . Effect of water on the density of melt is more pro-nounced with  $\frac{d\rho}{dX_{H_2O_2}} = -0.0422$ . Thus, the gravity-driven buoyancy of volatile rich magma will be greater than that of the magma without volatile components. The compressibility of the aluminosilicate melt is also affected by volatiles. For instance, both bulk modulus ( $K_{T0}$ ) and its pressure derivative ( $K'_{T0}$ ) for volatile bearing melts are respectively lower and higher than that of dry melt. Aluminosilicate melts are highly polymerized and show an anomalous pressure dependence of melt viscosity. Pressure dependence of viscosity at low pressure regime (P < 5 GPa) is significant with  $\frac{d\log(\eta)}{dP} = -2.06$ . Melt viscosity is further reduced by the addition of volatiles. Effect of volatiles on viscosity is more pronounced at low pressures and it minimizes at pressures where the melt viscosity exhibits minima. Due to the lower viscosity and larger buoyancy for both the  $H_2O$  and  $CO_2$ bearing aluminosilicate melts at crustal and upper mantle depths, magma mobility  $\left(\frac{\Delta n}{n}\right)$  is greater for volatile bearing melts. Thus, the residence time of such melts are expected to be shorter than volatile free melts in those settings. Like the mobility, electrical conductivity of aluminosilicate melts also increases when volatile is present in the silicate melt. We find that that as low as <1 vol.% volatile bearing aluminosilicate melt mixed with mantle matrix could be sufficient to explain the observed electrical conductivity anomalies in the upper mantle.

© 2021 Elsevier Ltd. All rights reserved.

*Keywords:* Carbon in deep Earth; Silicate melt, Melt viscosity; Carbon bearing aluminosilicate melts; Melt structure; First-principles calculations; Density of carboned silicate melts; Magma mobility; Electrical conductivity

# 1. INTRODUCTION

Silicate melts play a vital role in global carbon cycle by transporting carbon from the Earth's interior to the surface

\* Corresponding author. E-mail address: sbajgain@fsu.edu (S.K. Bajgain).

https://doi.org/10.1016/j.gca.2021.07.039 0016-7037/© 2021 Elsevier Ltd. All rights reserved. (Dasgupta, 2013). Similar to volatile such as water ( $H_2O$ ), carbon dioxide ( $CO_2$ ) also reduces the solidus temperature of the mantle rocks by hundreds of degrees and thus facilitating the partial melting at deep mantle conditions (Falloon and Green, 1989; Dasgupta and Hirschmann, 2006). This could result into the production of  $CO_2$ -rich silicate melts at the Earth's upper and lower mantle

Experimental studies indicate that the solubility of  $CO_2$ in silicate melts is typically low at lower pressures, but the solubility increases at higher pressures (Holloway, 1976; Dixon and Stolper, 1995; Guillot and Sator, 2011). It is well known that CO<sub>2</sub> solubility in magma is lower than that of  $H_2O$  by an order of magnitude. However, owing to the immiscibility of  $CO_2$  in an ascending column of magma, it exerts a greater influence in the outgassing process compared to  $H_2O$  which still remains soluble in the melt at similar depths (Gerlach, 1982; Spera, 1984; Brooker et al., 1999; Brooker et al., 2001; Lowenstern, 2001). Solubility of  $CO_2$  in silicate melts is affected not only by pressure, but also due to melt chemistry and melt structure (Brooker et al., 2001; Morizet et al., 2002). For instance, at low pressures (~2-3 GPa), CO2 solubility could be as high as ~18-19 wt.% for silica poor Ca/Mg melilitite melts (Brooker et al., 2001; Morizet et al., 2002). Solubility of  $CO_2$  is also influenced by degree of polymerization i.e., NBO/T where NBO is non-bridging oxygens and T is tetrahedrally coordinated network former cations. At low pressures of 1.5-2.0 GPa, for fully polymerized melts (NBO/  $T \sim 0$ , CO<sub>2</sub> solubility could be as low as 2.0 wt.%, however, for a fully depolymerized melt (NBO/T ~ 4.0),  $CO_2$  solubility could be as high as 16.0 wt.% (Brooker et al., 2001; Morizet et al., 2002). However, pressure also exerts a significant influence on the  $CO_2$  solubility, and even for a fully polymerized melt, it is expected that at pressures of ~10 GPa, CO<sub>2</sub> solubility could be ~10.0 wt.% (Brooker et al., 2001; Morizet et al., 2002).

Experimental and spectroscopic results have shown that molecular  $CO_2$  and  $CO_3$  are the most dominant species of carbon in silicate melts at lower pressures (Fine and Stolper, 1985; Brooker et al., 1999; Nowak et al., 2003; Morizet et al., 2013). However, carbon speciation and dissolution mechanism are poorly understood at high pressure owing to experimental challenges. Most melting experiments are followed by quenching of melt and the subsequent spectroscopic analysis on quenched products, which may not be representative of the local atomic arrangements i.e., speciation from higher pressures and temperature conditions (Nowak et al., 2003; Xue et al., 2018). In situ spectroscopic studies could provide insight into the speciation at simultaneous high pressures and temperatures. However, high temperatures are likely to also cause larger blackbody radiations and hence such studies also pose their own challenge (Konschak and Keppler, 2014).

Transport properties such as viscosity has a significant influence on the migration of magma in the Earth's interior. Volatile such as  $H_2O$  influences the atomistic scale structure and polymerization of silicate melt and in turn influences its viscosity (e.g., Whittington et al., 2000; Audétat and Keppler, 2004). However, the effect of  $CO_2$  on structure and properties of melt including viscosity is poorly understood (e.g., White and Montana, 1990; Bourgue and

Richet, 2001). For instance, in one set of experiments it was observed that 0.5 wt.% of CO2 leads to reduction of viscosity of aluminosilicate melts with stoichiometry NaAlSi3-O<sub>8</sub> and KAlSi<sub>3</sub>O<sub>8</sub> (Brearley and Montana, 1989; White and Montana, 1990). However, the melt viscosities are reported to be insensitive to  $CO_2$  content at temperatures >1000 K for potassium bearing silicate melts (43.1 mol% K<sub>2</sub>O and 56.9 mol% SiO<sub>2</sub>) and NaCaAlSi<sub>2</sub>O<sub>7</sub> melts (Brearley and Montana, 1989; Bourgue and Richet, 2001). More recent experiment on NaAlSi<sub>2</sub>O<sub>6</sub> melt reported 1-2 orders of magnitude reduction on viscosity in the presence of 0.5 wt.% CO<sub>2</sub> (Suzuki, 2018). However, the experiments were performed for a limited range of pressures, i.e., ~2-4 GPa at a fixed temperature of 1623 K. It is also known that transport properties such as diffusion and viscosity of highly polymerized aluminosilicate melts show an anomalous pressure dependent behavior i.e., viscosity decreases with increasing pressure upon initial compression (Kushiro, 1976; Funakoshi et al., 2002; Tinker et al., 2004; Suzuki et al., 2011). Temperature dependence of viscosity for various polymerized multi-component melts also show non-Arrhenian behavior at ambient pressures (e.g., Giordano and Dingwell, 2003; Giordano et al., 2008). How carbon affects the pressure and temperature dependence of viscosity is crucial to assess the mobility and kinematic viscosity of carbon bearing silicate melts at deep Earth conditions.

Molecular dynamics (MD) simulations have been successful in examining the solubility, density, structure, and transport properties of carbon bearing mafic/ultramafic silicate melts (e.g., Guillot and Sator, 2011; Vuilleumier et al., 2015; Ghosh et al., 2017; Solomatova et al., 2019; Karki et al., 2020; Solomatova and Caracas, 2020). However, the effect of carbon on structure and properties of polymerized silicate melt at high pressures and temperatures remains poorly understood. Owing to its importance in shallow, deep crustal, and deep mantle conditions, it is important to have a better insight into how carbon affects the atomistic scale structure and properties of silicate melt at these conditions. This is crucial for understanding how carbon is sequestered in the deep Earth and how it influences the mobility of melt i.e., how carbon is eventually transported and released back to the surface thus completing the deep Earth carbon cycle. In this study, we explore the effect of carbon on structure, equation of state, and transport properties of polymerized aluminosilicate melt.

#### 2. METHODS

We explore the structure and properties of carbon bearing aluminosilicate melt at high pressures using *first principles* molecular dynamics (FPMD) simulation with local density approximation (LDA) using the Vienna ab initio simulation package (VASP) (Ceperley and Alder, 1980; Kresse and Furthmüller, 1996). In FPMD simulations, the forces between atoms are estimated by approximately solving the Schrödinger equation using density functional theory (DFT) (Kresse and Hafner, 1993). Our simulation is based on canonical (NVT) ensemble with constant temperature provided by Nosé thermostat (Nosé, 1984). Our simulation cell is cubic i.e., a = b = c,  $\alpha = \beta = \gamma = 90^{\circ}$  and consists of 92 atoms. The projector augmented wave (PAW) method was implemented to represent the core electrons with kinetic energy cutoff of 400 eV (Blöchl, 1994). The Pulay stress corrections were made by comparing the difference in the stresses between 400 eV cutoff energy and 700 eV cut off energy at all volumes.

$$P = P_{400eV} + P_{Pulav} \tag{1}$$

where,  $P_{Pulav}$  is volume dependent Pulay correction given by  $(P_{700eV} - P_{400eV})$ .  $P_{700eV}$  and  $P_{400eV}$  are the pressures from simulation with energy cutoff of 700 eV and 400 eV, respectively. The convergence test shows that the effect of pressure is minimum when energy cutoff increases to 500 eV and more (Supplementary Fig. S1). However, the simulation time increases significantly when larger cutoff energies were used (Supplementary Fig. S1, inset). All simulations were performed using 400 eV energy cutoff and pressure was corrected using the Pulay correction (Eq. (1)). Comparison of corrected pressure with the pressures calculated using larger energy cutoff are similar for selected conditions (Supplementary Fig. S1). We also find that the structure and transport properties remains unaffected by the choice of cutoff energy i.e., 400 eV and 500 eV. Thus, all simulations were performed using 400 eV energy cutoff and pressure was corrected using the Pulav correction (Eq. (1)). We performed FPMD simulations on several cell volumes along three distinct isotherms: 2500 K, 3000 K, and 4000 K to explore a range of pressures from 0 to 25 GPa. The simulation cell consists of 8 formula units of NaAlSi2O6 and 4 formula units of CO2, i.e., ~9.8 wt.% CO2. This is consistent with the expected carbon content in natural silicate melt such as rhyolite, mid oceanic ridge basalt (MORB), and kimberlite melts at high pressures (Guillot and Sator, 2011). The simulation cell was first subjected to high temperatures of 6000 K, i.e., beyond the melting temperature for typical silicates which was followed by lowering of temperature to 4000 K. The temperature was subsequently reduced to 3000 K and finally to 2500 K. We performed the simulations for 30-100 picoseconds (ps). This is sufficient time for converged energy, stresses, and transport properties. We performed the simulations for ~350 ps are at lower temperature and pressure conditions (~0-3 GPa and 2500 K) where atomic scale dynamics are significantly more sluggish.

Prior studies on crystalline and silicate liquids have used FPMD simulations with  $\Gamma$ -point sampling (e.g., Zhang et al., 2013; Karki et al., 2018; Sun et al., 2020). These studies demonstrated that only  $\Gamma$ -point sampling is sufficient for simulation of liquids. Hence, following these prior FPMD studies on silicate liquids, we used  $\Gamma$ -point sampling to integrate the Brillouin-zone with a simulation time step of 0.5 femtoseconds. However, we have also tested the effect of k-point on the calculated properties by performing FPMD simulation at selected conditions using the 2  $\times$  2  $\times$  2 k-point sampling. We did not find any significant difference in the FPMD results with the 2  $\times$  2  $\times$  2 k-point sampling. Similarly, we have also tested the effect of cell size by simulating larger supercell with 184 atoms. Along 3000 K, we also performed simulation using generalized gradient approximation (GGA) pseudopotential to understand the role of exchange correlation functional on calculated properties.

The average of energy and pressure was computed using blocking method (Flyvbjerg and Petersen, 1989). We examined the radial distribution functions (RDF) (Supplementary Fig. S2) and the mean-square displacement (MSD) (Supplementary Fig. S3) to determine whether the melt exhibit the liquid state. The effect of supercell size on MSD and RDF are negligible (Supplementary Figs. S2-S3). RDF for the pair of atoms *i* and *j* is given by,

$$g_{ij}(r) = \frac{1}{4\pi\rho_j r^2} \left[ \frac{dN_j(r)}{dr} \right]$$
(2)

where  $\rho_j$  is the number density of species *j* and  $N_j$  is the number of species *j* within a sphere of radius *r* around a selected atom of type *i*. Similarly, the coordination number for atoms *i* with respect to atoms *j* in their nearest neighbor is calculated using-

$$C_{ij} = 4\pi \rho_j \int_0^{r_{min}} r^2 g_{ij}(r) dr$$
(3)

The self-diffusion of an ion x at each simulation steps can be estimated using the Einstein formulation-

$$D_x = \lim_{n \to \infty} \frac{1}{N_x} \sum_{i=1}^{N_x} \frac{\langle \left\{ \overrightarrow{r_i}(t_1) - \overrightarrow{r_i}(t_0) \right\}^2 \rangle}{6t}$$
(4)

where, term inside the parenthesis  $\langle \{\vec{r_i}(t) - \vec{r_i}(0)\}^2 \rangle$  represents the MSD,  $\vec{r_i}(t_0)$  and  $\vec{r_i}(t_1)$  are the position of the ion *x* at time  $t_0$  and its position after time  $\delta t = t_1 - t_0$ . To ascertain whether the simulation exhibits an ergodic behavior expected for silicate liquid, we examine the log–log plot of MSD vs time and evaluate whether magnitude of MSD > 10 Å<sup>2</sup> (Supplementary Fig. S3). Viscosity ( $\eta$ ) of silicate melt is given by the Green-Kubo relation (Allen and Tildesley, 1987).

$$\eta = \frac{V}{10k_B} \int_0^\infty \langle (\sum_{mn} P_{mn}(t_0 + \delta t) \cdot P_{mn}(t_0)) \rangle dt \tag{5}$$

where,  $P_{mn}$  is the symmetrized traceless portion of the stress tensor  $\sigma_{mn}$  from each simulation step given by  $P_{mn} = \frac{1}{2}(\sigma_{mn} + \sigma_{nm}) - \frac{1}{3}\delta_{mn}(\sum_{\lambda}\sigma_{\lambda\lambda})$ . Here,  $\delta_{mn}$  is the Kronecker delta. We use both the off-diagonal and diagonal components of stress tensor with different weighting factors of 1 and 4/3, respectively to calculate viscosity (Nevins and Spera, 2007; Chen et al., 2009). The integrand is stress autocorrelation function (ACF), which is averaged over time with different origin,  $t_0$  for better statistics. The ACF decays to zero and the viscosity shows a plateau (Supplementary Fig. S3).

Mobile charges in silicate melt could be associated with ionic/electrical conductivity which can be evaluated using the following relation

$$\sigma = \frac{1}{k_B T V} \lim_{n \to \infty} \frac{1}{6t} \left\langle \left[ \sum_{i=1}^{N} z_i \{ \overrightarrow{r_i}(t_1) - \overrightarrow{r_i}(t_0) \} \right]^2 \right\rangle$$
(6)

where  $k_B$  is the Boltzmann constant, T is the temperature, V is the volume of the cell and  $z_i$  is the charges of ion i. Since the bonds in silicate melt have partial covalent and ionic

character, the effective charges of each ion are likely to be smaller than their formal charges. The effective charges is estimated using the Bader charge analysis (Henkelman et al., 2006). We find that the effective charges do not vary significantly as a function of pressure, temperature and melt composition (Supplementary Fig. S4). So, we can use a constant effective charges (averaged over pressures, temperatures and compositions) for each species:  $Z_{Na} = +0.81e$ ,  $Z_{Al} = +2.40e$ ,  $Z_{Si} = +3.02e$ ,  $Z_O = -1.51e$ ,  $Z_C = +2.06e$ and  $Z_H = +0.67e$ . The effective charges are ~20–50% lower than corresponding formal charges. These values are similar to the effective charges of respective atoms reported in recent MD simulation studies for the range of silicate melts compositions (Vuilleumier et al., 2015; Ghosh and Karki, 2017; Dufils et al., 2018, 2020).

# 3. RESULTS

## 3.1. Thermodynamics

The equation of state (EOS) for carbon bearing jadeite melt can be described by third- order Birch Murnaghan equation of state (BM3) at reference isotherm  $(T_{ref} = 2500 \text{ K})$  (Fig. 1, Supplementary Table S1). Pressure and volume (density) relations along other isotherms are represented by the Mie Grüneisen thermal EOS

$$P(V,T) = P(V,T_{ref}) + \left(\frac{dP}{dT}\right)_{V}(T-T_{ref})$$
<sup>(7)</sup>

where,  $\left(\frac{dP}{dT}\right)_V$  is the volume dependent coefficient. Our results show that  $\left(\frac{dP}{dT}\right)_V$  increases with increasing density and are fitted with relation-

$$\left(\frac{dP}{dT}\right)_{V} = a + be^{-cu} \tag{8}$$

where,  $u = \frac{V}{V_{ref}} = \frac{\rho_{ref}}{\rho}$ , and *a*, *b*, and *c* are 0.39 MPa/K, 281.2 MPa/K and6.05, respectively. We find that the density of carbon bearing jadeite melt at 2500 K and ambient pressure is  $2.23 \pm 0.02$  g cm<sup>-3</sup> which is ~8% smaller than the density of volatile free jadeite melt at the same conditions (Bajgain et al., 2019). Carbon bearing melt is more buoyant than volatile-free melt. The isothermal bulk modulus ( $K_0$ ) of carbon bearing melt at 0 GPa and 2500 K is also lower than that of volatile free melt (Supplementary Table S1). However, the pressure derivative of bulk modulus ( $K'_0$ ) shows



Fig. 1. (a) Density-pressure relation for carbon bearing jadeite melt (Jd + 10 wt.% CO<sub>2</sub>) at 4000 K (red filled circles), 3000 K (green filled circles), and 2500 K (purple filled circles). Lines represent Birch Murnaghan equation of state (BM3EOS) fit along 2500 K isotherm and the Mie-Grüneisen thermal equation of state fit for other isotherms (Eq. (7)). Open diamonds represent the results from large simulation cell with 184 atoms. Inset shows the effect of 1 wt.% volatile in reducing the density of aluminosilicate melt at 2500 K, i.e.,  $\Delta \rho = \rho_{Jd} - \rho_{Jd+volatile}$ . Plot of (b) Thermal pressure coefficient,  $\left(\frac{dP}{dT}\right)_{V}$  and (c) Grüneisen parameter,  $\gamma$  as a function of density. Symbols in panels (b) and (c) shows mean values averaged over the temperature range 2500–4000 K for volatile free melts (green squares) and carbon bearing melts (blue circles). Lines represent fitted values (Eqs. (7), (8)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

a higher value which indicate the carbon bearing melt is more compressible than the volatile free melt. The  $\rho - P$ relationship along an isotherm shows that the density difference  $(\Delta \rho)$  between carbon bearing and volatile free melt reduces significantly with increasing pressure (Fig. 1). For instance,  $\Delta \rho$  is 0.11 g cm<sup>-3</sup> at 0 GPa and 2500 K which reduces to 0.05 g cm<sup>-3</sup> at ~5 GPa for jadeite melt with 10 wt.% CO2. Choice of exchange correlation functional, i.e., LDA or GGA also affects the melt density and thus the equation of state. We find that densities from GGA method are lower than that calculated using LDA method (Fig. 1). This is consistent with recent studies on aluminosilicate melt of albitic composition (Bajgain and Mookherjee, 2020). Our LDA results shows that the zero-pressure density of carbon bearing jadeite melt at 3000 K is  $2.15 \pm 0.05$  gcm<sup>-3</sup> which is 17% larger than the density estimated using GGA method (Supplementary Table S1).

At constant volume (density), both the pressure and energies increase linearly with increasing temperature. We estimate isochoric heat capacity  $(C_V)$  and Grüneisen parameter  $(\gamma)$  using the relations  $C_V = \left(\frac{dE}{dT}\right)_V$ , and  $\gamma = \frac{V}{C_V} \left(\frac{dP}{dT}\right)_V$ . Similar to  $\left(\frac{dP}{dT}\right)_V$ ,  $\gamma$  also varies non-linearly as a function of density-

$$\gamma = \gamma_{ref} + \gamma' e^{-\gamma \ u} \tag{9}$$

where,  $u = \frac{\rho_{ref}}{\rho}$  or  $\frac{V}{V_{ref}}$  and  $\rho_{ref} = 2.47 \text{ gcm}^{-3}$  ( $V_{ref} = 1207.95 \text{ Å}^3$ ),  $\gamma_{ref} = 0.10$ ,  $\gamma' = 33.74$  and  $\gamma'' = 5.03$ . Coefficient of thermal expansivity,  $\alpha = \frac{1}{V} \left(\frac{dV}{dT}\right)_P$  decreases asymptotically with pressure. At pressures up to ~4 GPa, the reduction in  $\alpha$  with pressure is quite steep. At pressures >~4 GPa,  $\alpha$  decreases more gradually and becomes insensitive to pressure at high pressures (Supplementary Fig. S5). The pressure dependence of  $\alpha$  for carbon bearing silicate melt is not much different than that of volatile free melt and hydrous silicate melts (Supplementary Fig. S5).

#### 3.2. Structure

The bond distances of all cation-oxygen pairs were estimated from the first minimum of partial radial distribution function (RDF) of each atomic pair (Supplementary Fig. S2). At 0 GPa and 2500 K, bond length for Na-O, Al-O, Si-O, O-O and C-O are 2.57 Å, 1.81 Å, 1.65 Å, 2.76 Å and 1.26 Å, respectively. At constant pressure, bond lengths increase with increasing temperature, but the effect of pseudopotential on the average bond length is small. For example, at 3000 K and ~0 GPa, average cation-oxygen bond lengths for atomic pair Na-O, Al-O, Si-O, O-O and C-O using LDA (GGA) pseudopotentials are 2.58 (2.59), 1.83 (1.83), 1.67 (1.68), 2.80 (2.83), 1.27 (1.26),respectively. Since both Al and Si are network former cations (Al, Si) and both have tetrahedral (T) coordination at ambient conditions, we also explore their behavior together as one species where T refers to (A1 + Si) taken together. Average T-O bond length at 2500 K and 0 GPa is 1.69 Å. At ambient pressure and 3000 K, T–O bond length using LDA (GGA) is 1.71(1.72) Å. Experiment at ~0 GPa and 1973 K reported lower T-O bond length of 1.63 A for volatile free jadeite melt at 1923 K (Sakamaki et al., 2012). Similarly, the X-ray diffraction study of the albite melt at 1473 K indicated the T–O bond length to be1.64 Å (Okuno and Marumo, 1982). This slight difference in the T–O bond length between our prediction and the experiment could be partly attributed to the temperature difference.

Average Na-O bond distance continuously decreases with increasing pressure. However, the average bond lengths for Al-O, Si-O and C-O increases upon compression (Supplementary Fig. S6). Average polyhedral coordination environment for all cation-oxygen pairs increases with increasing pressure (Supplementary Fig. S7). Upon compression till ~7 GPa, the average Na-O coordination  $(NaO_x)$  increases from 5-fold to 8-fold. Upon further compression till ~25 GPa, NaOx remains rather constant or slightly increases from 8-fold to 9-fold. Pressure dependence of O-Na coordination also shows a similar trend. We find the similar trend for the O-O coordination environment, i.e., an initial rapid increase in the coordination followed by a slower rate of increase in the coordination at higher pressure regime (Supplementary Fig. S7). The average coordination of network forming cations i.e.,  $AlO_X$ ,  $SiO_X$  increases continuously upon compression. The average  $TO_X$  (T = Al or Si) is ~4 at ambient pressure condition and increases upon compression to ~5.6 at 25 GPa (Supplementary Fig. S7). We note that the Si-O coordination remains nearly ~4 up to ~4 GPa, other coordination Na-O, O-O shows large increase at lower pressure regime (Supplementary Fig. S8). Average  $SiO_X$  at 2500 K change from 4.1 to 4.10 when pressure increases from ~0 GPa to ~3.6 GPa (Supplementary Fig. S8). At ~3.6 GPa, more than 90% silicon atoms are tetrahedrally coordinated with oxygens. We find similar behavior for volatile free and hydrous jadeite melts (Supplementary Fig. S8). Previous studies on silicate melts also exhibited this pressure dependent trend in Si-O coordination (Karki et al., 2007; Wang et al., 2014; Bajgain and Mookherjee, 2020). This behavior can be better understood in terms of the tetrahedral packing fraction (TPF) limit (Wang et al., 2014). Our results indicate that Si-O coordination remains unchanged till TPF ~0.6, i.e., corresponding to a packing fraction limit of randomly packed spheres (Torquato et al., 2000) (Supplementary Fig. S8). Upon further compression, i.e., at TPF > 0.6, the void space in between the polyhedral units cease to exist and further compression is accommodated by increase in Si-O coordination. Similar behavior has been reported in silicate melts with wide range of compositions (Wang et al., 2014). Melt densification at lower pressures is compensated by large decrease in inter-tetrahedral (T-O-T) bond angle (Bajgain et al., 2019; Bajgain and Mookherjee, 2020).

Pressure dependent increase in tighter packing of the atomistic scale structure is also manifested in the increased O–Na, O–Si, O–Al and O–C coordination with increasing compression (Supplementary Fig. S7). Effect of pressure on average coordination for each cation-oxygen pair is more pronounced compared to the effect of temperature. Upon isochoric heating, the mean coordination numbers remain nearly constant except for C–O coordination pair. Even though, the average C–O coordination ( $CO_X$ )

remains similar for 2500–3000 K, average  $CO_X$  along 4000 K isotherm are lower for all explored pressures (Supplementary Fig. S7). This is due to large abundance of CO and  $CO_2$  at 4000 K (Fig. 2).

The average coordination number is mostly affected by pressure and is rather insensitive to temperature. However, we observe that at a constant pressure, the relative abundance of the different coordination species is affected by temperature (Supplementary Fig. S9). For example, at ambient pressures, the abundance of  $AlO_4$  species is ~83% at 2500 K, ~74% at 3000 K and ~53% at 4000 K. Similarly. the abundances of  $AlO_3$  ( $AlO_5$ ) are ~5 (~12), ~11 (~15) and ~15 (~26)% at 2500, 3000 and 4000 K, respectively. Effect of carbon is negligible on the fraction of Al-O, Si-O and T-O coordination species (Supplementary Fig. S9). However, the carbon bearing aluminosilicate melt shows reduction in the average O-T coordination as well as the fraction of the O-T species. The carbon bearing melt shows that the fraction of the different O-T species varies widely over the explored range of pressures and temperatures (Supplementary Fig. S10). At ambient pressures and 4000 K, we find ~18% of  $OT_1$  and ~10%  $OT_0$  species.  $OT_0$ are the oxygen atoms which are not connected to any of the network forming cations but could be connected to network modifiers such as Na ions. Previous NMR studies reported the presence of  $OT_0$  or "free oxygens" in less polymerized silicate melts (Stebbins, 2017; Nesbitt et al., 2020). At similar pressure conditions, the abundance of nonbridging oxygen atoms (NBOs) decreases with decreasing temperatures i.e., ~14% at 3000 K and ~6% at 2500 K. Higher fractions of NBOs at higher temperatures is consistent with the depolymerization of melt with increasing temperature. However, the abundance of  $OT_0$  species at

ambient pressure are similar at all explored temperatures (Supplementary Fig. S10). The lower fraction of  $OT_1$  at lower temperature are compensated by larger fraction of  $OT_2$ . At ambient pressures, the abundance of  $OT_2$  atoms increase with decreasing temperature, i.e., ~63% at 4000 K, ~72% at 3000 K and ~80% at 2500 K.

Upon compression, the fractions of  $OT_0$ ,  $OT_1$ , and  $OT_2$ species decrease at the expense of oxygen tri-cluster  $(OT_3)$ species where an oxygen atom is attached to 3 Al/Si atoms. Decrease in  $OT_1$  or non-bridging oxygens with increasing pressure is well documented in previous experiments on silicate melts and glasses (e.g., Lee, 2011; Lee et al., 2020). Fraction of OT<sub>3</sub> species at ~0 GPa are ~9%, ~5% and ~2% at 4000 K, 3000 K and 2500 K. Abundance of  $OT_3$ species increases with increasing compression, and we find more than 30% oxygen tri-cluster species at the highest pressure (~25 GPa) explored in this study (Supplementary Fig. S10). Comparison of our results with volatile free jadeite melt indicate that  $OT_1$  species are more abundant in carbon bearing melts (Bajgain et al., 2019). Thus, the effect of  $CO_2$  is somewhat similar to that of  $H_2O$  which shows an enhancement in the fraction of  $OT_1$  species in hydrous silicate melts (Mookherjee et al., 2008; Bajgain et al., 2015; Bajgain et al., 2019). Carbon bearing melts have up to ~10%  $OT_0$  atoms which were nearly absent in volatile free jadeite melt and less than  $\sim 2\%$  in hydrous jadeite melt (Bajgain et al., 2019).

In the jadeite melt with ~10 wt.% carbon dioxide, carbon is mainly present in the form of molecular carbon dioxide  $(CO_2)$  and carbonate  $(CO_3)$  ions throughout the pressure and temperature range of this study (Fig. 2, Supplementary Fig. S7). At 4000 K and 0 GPa, average C—O coordination number  $(CO_X)$  is 2.4, i.e., with nearly equal fraction of



Fig. 2. Plots showing the fraction of (a)  $CO_X$  as a function of pressure at 4000 K (Thick lines), 3000 K (Dashed lines) and 2500 K (Thin lines). Dashed lines with open diamond symbols represent the results for  $CO_X$  fraction from the larger simulation cell at 3000 K. Circles with cross inside connected by dotted lines show the results from simulation with  $2 \times 2 \times 2$  k-points mesh. Panel (b) shows the plot of ratio of  $CO_2/(CO_2 + CO_3)$  as a function of pressure. Results from previous FPMD study for MgSiO<sub>3</sub> melt with 17 wt.%  $CO_2$  (Ghosh et al., 2017), pyrolite with 5 and 10 wt.%  $CO_2$  (Solomatova et al., 2020) are also shown for comparison.

molecular carbon dioxide  $(CO_2)$  and carbonate  $(CO_3)$  and <5% CO. At lower isotherms- 3000–2500 K,  $CO_X$  is  $\sim$ 2.7, i.e., ~60%  $CO_3$  and ~40% molecular  $CO_2$ . Fraction of  $CO_2$ decreases with increasing compression which is compensated by the increasing amount of CO3 ions. Upon compression till ~8-10 GPa, fraction of CO3 reduces which is compensated by an increase in 4-fold coordinated CO<sub>4</sub> species. At ~25 GPa and 4000 K, carbon bearing melt consists of  $\sim 13\%$  CO<sub>4</sub> species (Fig. 2). Tetrahedrally coordinated carbon species are also found in crystalline carbonates but occurs at deep lower mantle pressures, i.e., >80 GPa for MgCO<sub>3</sub> (Oganov et al., 2008; Boulard et al., 2011), >105 GPa for CaCO<sub>3</sub> (Oganov et al., 2006; Arapan et al., 2007) and >50 GPa for FeCO<sub>3</sub> (Liu et al., 2015). The four-fold coordinated carbon species are also reported in carbonate melts in the deep Earth but the transition from 3-fold to 4-fold begins at lower pressure compared to their crystalline counterpart (Zhang and Liu, 2015; Sanloup et al., 2019). Recent Raman spectroscopy study at room temperature revealed the presence of 4-fold carbon species which are in fact carbonate groups  $(CO_3)$  with one oxygen attached, i.e.,  $CO_{3+1}$  coordination of carbon in crystalline dolomite (Vennari and Williams, 2018). This  $CO_{3+1}$  species does not have a regular tetrahedral shape and is characterized by one of the C-O bond length being longer than the rest of the other three C–O bond lengths. Similar  $CO_{3+1}$ coordination environment of carbon was detected in previous molecular dynamics simulation of carbonate melts and also confirmed by Raman studies (Wilding et al., 2019).

Our results on carbon speciation at low pressure agrees well with previous studies (Fig. 2, inset). Experiments showed that predominant carbon species in polymerized (e.g., rhvolite) and depolymerized melt (e.g., kimberlite, diopside) compositions are  $CO_2$  and  $CO_3$ , respectively, but aluminosilicate melts contain both  $CO_2$  and  $CO_3$  as major carbon species at temperature 1773-1923 K and pressures up to 2.5 GPa (Fine and Stolper, 1985; Brooker et al., 1999; Nowak et al., 2003; Moussallam et al., 2016; Xue et al., 2018). Experiments on several  $CO_2$  bearing melts along the NaAlO<sub>2</sub>-SiO<sub>2</sub> join indicate that the relative abundance of molecular CO2 decreases with decreasing Si/(Na + Al) ratio or increasing  $Na_2O$  (Brooker et al., 1999). Based on our study, we find the relative proportion of  $CO_2$  in polymerized aluminosilicate melt is similar to the previous FPMD studies of depolymerized melt compositions including Mg<sub>2</sub>SiO<sub>4</sub>, MgSiO<sub>3</sub>, and multi-component pyrolytic melts (Ghosh et al., 2017; Solomatova et al., 2019; Solomatova et al., 2020). In another classical MD simulation, a larger fraction of molecular  $CO_2$  was reported in carbon bearing mid-oceanic ridge basalt (MORB) melts (Guillot and Sator, 2011).

The partial molar volume of  $CO_2 (V_{CO_2})$  for silicate melts is influenced by several factors including pressures, temperature, and composition (e.g., silica content, carbon content) & atomistic scale structure (e.g., degree of polymerization) of the silicate melt. Our results show that  $\bar{V}_{CO_2}$  decreases asymptotically with pressure. At pressures <5 GPa,  $\bar{V}_{CO_2}$ decreases rapidly. At pressures >5 GPa, the reduction in  $\bar{V}_{CO_2}$  is more gradual (Supplementary Fig. S11). We find that  $\overline{V}_{CO_2}$  for aluminosilicate melt with 10 wt.%  $CO_2$  is  $35.32 \pm 4.68$  cm<sup>3</sup> mol<sup>-1</sup> at 0 GPa and 2500 K. We find that the  $\overline{V}_{CO_2}$  also increases with increasing temperature (Supplementary Table S2). At ~0 GPa and 2000 K, V<sub>CO2</sub> for aluminosilicate melt is  $\sim 30.35$  cm<sup>3</sup> mol<sup>-1</sup> which is smaller than the  $\overline{V}_{CO_2}$  for peridotite melt with 2.3 wt.%  $CO_2$ , i.e., 34.78 cm<sup>3</sup> mol<sup>-1</sup> (Sakamaki et al., 2011). We find that the  $\overline{V}_{CO_2}$  for carbon bearing polymerized aluminosilicate melts are generally lower than the  $V_{CO_2}$  for more depolymerized melt compositions including komatiite, basalt, peridotite, and carbonate (Ghosh et al., 2007; Duncan and Agee, 2011; Sakamaki et al., 2011; Vuilleumier et al., 2015). Larger  $V_{CO_2}$  in depolymerized/mafic melts is likely to be related with the higher concentration of  $CO_3$  species in those melts (e.g., Blank, 1994; Ni and Keppler, 2013). However, the role of degree of polymerization and melt structure on  $V_{CO_2}$  is not clear at this point because the available limited density experiments are performed with a range of carbon content (~2-20 wt.%) and melt compositions (Supplementary Fig. S11).

## 3.3. Transport properties

Upon compression, carbon bearing aluminosilicate melts exhibit anomalous reduction in viscosity and enhancement in diffusivity for network former cations. The trend is more pronounced at lower temperatures i.e., 2500–3000 K (Figs. 3–5). At higher temperature, 4000 K, the transport properties exhibit normal behavior, i.e., diffusivity of Al, Si, and O atoms decreases, and viscosity of the melt increases upon compression (Figs. 3–5). Both the diffusion and viscosity data at explored *P*, *T* range (~0–25 GPa, 2500–4000 K) cannot be explained using simple Arrhenius model with constant activation energy and activation volume. To adequately describe the pressure and temperature dependent anomalous transport properties, we use the general formalism:

$$A = A_0 exp\left(-\frac{E_a + PV_a + \Delta E_a \times S}{RT}\right)$$
(10)

where, A refers to either of (a) diffusivity of ionic species  $(D_x)$ , (b) the electrical conductivity  $(\sigma_x)$ , (c) viscosity  $(\eta)$  of aluminosilicate melt;  $x = Na, Al, Si, O, C, A_0$  is the preexponential factor,  $E_a$  is the activation energy, R is the gas constant,  $V_a$  is the activation volume, and S is given by:

$$S = S_0 exp\left(\frac{\Delta E - P\Delta V}{RT}\right) \tag{11}$$

*S* varies as a function of *P*, *T* so that activation energy varies both as a function of *P* and *T*. Here  $S_0$  is pre-exponential factor, *R* is the gas constant, the  $\Delta E$  and  $\Delta V$  are the differences in energy and volume between the melt structure at low pressures (related to anomalous behavior) and high pressures (related to transport behaviors); an additional activation energy term,  $\Delta E_a$  in Eq. (10) refers to the energy difference between the normal and anomalous domains of the melt. Note that for the expression of viscosity ( $\eta$ ), the



Fig. 3. Pressure and temperature variation of self-diffusion coefficient for (a) Na, (b) O, (c) Al, (d) Si, and (e) C along 4000 K (filled red circles), 3000 K (filled green circles), and 2500 K (filled purple circles). Open diamond symbols show the self-diffusion results from larger simulation cell with 184 atoms. Solid lines represent the fitted results (Eqs. (10) and (11)) with fit parameter listed in Supplementary Table S3. Long and short dashed lines are the results for self-diffusion coefficients of respective ions for volatile free and hydrous jadeite melt, respectively (Bajgain et al., 2019). In panel (b), blue stars (P97) and black pluses (TL01) indicate the oxygen diffusion from previous experiments for volatile free albite melt and dry dacite melt, respectively (Poe et al., 1997; Tinker and Lesher, 2001). Panel (f) shows the comparison of self-diffusion coefficient between various ions along 4000 K and 2500 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Pressure and temperature variation of electrical conductivity ( $\sigma$ ) for (a) volatile free jadeite melt, (b) jadeite melt with ~10 wt.% CO<sub>2</sub>, and (c) jadeite melt with ~4 wt.% H<sub>2</sub>O along 4000 K (filled red circles), 3000 K (filled green circles), and 2500 K (filled purple circles). Solid lines represent the fitted results (Eqs. (10) and (11)) with parameters listed in Supplementary Table S3. Previous results of  $\sigma$  for other silicate melts are D18: Komatiite, Peridotite melts, and K18: mid-oceanic ridge melt (Dufils et al., 2018; Karki et al., 2018). In panel (b), long and short dashed lines indicate results for  $\sigma$  for volatile free and hydrous jadeite melt, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

negative sign within the parenthesis of Eq. (10) is dropped since in normal viscosity behavior of silicate melts, viscosity increases with increasing pressure.

#### 3.3.1. Diffusion

Results from the FPMD simulations show that the selfdiffusion of sodium is the fastest in both carbon bearing and volatile free aluminosilicate melt (Fig. 3). The selfdiffusivity of the ions exhibits the following relation:  $D_{Na} > D_C > D_O > D_{Al} > D_{Si}$ , with the alkali ions being the fastest and aluminum/silicon being the most sluggish. At 4000 K, self-diffusivity of all ionic species continuously decreases with increasing pressure. At T < 3000 K, selfdiffusivity of Na and C shows normal pressure dependence of self-diffusion, i.e., diffusivity decreases with increasing pressure. However, the diffusivity of network former cations (Al/Si) and oxygen first increases with increasing pressures up to ~8 GPa. Upon further compression, the self-diffusion coefficients follow normal pressure behavior (Fig. 3). This anomalous pressure dependent self-diffusion behavior has been observed in albitic melts and polymerized natural silicate melts (Poe et al., 1997; Zhang and Ni, 2010; Zhang et al., 2010). Our diffusivity results show that the difference between the diffusivity of most mobile ion, Na and least mobile ion, Si are small at high temperature, i.e., 4000 K. The discrepancy in mobility between Na and Si increases at lower temperatures of 3000 K and 2500 K. At 2500 K and 0 GPa,  $D_{Na}$  is nearly two orders of magnitude higher than  $D_{Si}$  (Fig. 3). However,  $D_{Na} \approx 8 \times D_{Si}$  at ambient pressure and 4000 K. Increasing pressure also have the similar effect which means the difference in mobility between different species is reduced at high pressures. For instance, at 2500 K and ~17 GPa,  $D_{Na} \approx 2 \times D_{Si}$  whereas at the same temperature condition and ~0 GPa,  $D_{Na} \approx 100 \times D_{Si}$ . The Na diffusivity is mostly insensitive to the carbon content on the melt. In carbon bearing melt,

the diffusivity of Al, Si, and O ions are slightly enhanced at lower pressures and temperature (Fig. 3). Results from classical and FPMD simulation on basalt and kimberlite melt with ~20 wt.%  $CO_2$  shows that the diffusion of individual species remain largely unaffected by addition of volatile species i.e., carbon (Vuilleumier et al., 2015). Our findings at 4000 K are similar to pyrolytic melt which shows that the diffusion of individual species are unaffected for a range of CO and  $CO_2$  concentration (Solomatova et al., 2019). In contrast to the effect of carbon, hydrogen enhances diffusion of all ions at all explored pressures (Fig. 3).

# 3.3.2. Electrical conductivity

Greater mobility and diffusion of charged ions in silicate melt may produce high electrical conductance ( $\sigma$ ) (Kelbert et al., 2009; Naif et al., 2013). In contrast to silicate melts, crystalline silicate minerals in crust and mantle are insulators and enhanced electrical conductivities are associated with changes in oxygen fugacity and or the extrinsic defects such as protons (Wang et al., 2006). The electrical conductivity can also be related to the diffusivity of charge carrier ions via Nernst-Einstein relation

$$\sigma_{NE} = \frac{1}{k_B T H_R} \sum_{i=1}^{N_s} \rho_i z_i^2 D_i \tag{12}$$

where  $\rho_i$ ,  $z_i$  and  $D_i$  are the number density, the electric charge and self-diffusion coefficient of species *i*.  $k_B$  is the Boltzmann constant and the  $H_R$  (Haven ratio). When  $H_R = 1$ , the ion correlations are ignored and the  $z_i$  is considered to be same as formal charges i.e.,  $Z_{Na} = +1e$ ,  $Z_{Al} = +3e$ ,  $Z_{Si} = +4e$ ,  $Z_O = -2e$ ,  $Z_C = +4e$ , and  $Z_H = +1e$ . It is well known that the bonding crystalline silicates have partial ionic characters and could be extended to aluminosilicate melts. Thus, the interatomic interactions cannot be ignored, and the ionic charges are smaller than the formal charges. Our results show that  $\sigma_{NE}$  calculated using



Fig. 5. Plots of pressure and temperature dependent of viscosity for NaAlSi<sub>2</sub>O<sub>6</sub> melt with 10 wt.% CO<sub>2</sub> at 4000 K (filled red circles), 3000 K (filled green circles), and 2500 K (filled purple circles). Open diamond symbols represent the viscosity of carbon bearing jadeite melt for the simulation with 184 atoms. Solid lines show the fitted results (Eqs. (10) and (11)) for viscosity with parameters listed in Supplementary Table S3. Long and short dashed lines show the viscosity for volatile free and hydrous jadeite melt, respectively (Bajgain et al., 2019). Viscosity results from previous experiments are for SU11: volatile free jadeite melt (Suzuki et al., 2011); SU18: jadeite melt with 0.5 wt.% CO<sub>2</sub> (Suzuki, 2018); S20: melilititic melt with 1.4 and 1.6 wt.% CO<sub>2</sub> (Stagno et al., 2020b); S20A: carbonate–silicate melt with 22.5 wt.% CO<sub>2</sub> (Stagno et al., 2020a); K14 carbonate melts (Kono et al., 2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

formal charges is larger than  $\sigma$  calculated using the effective charges estimated from Bader analysis (Henkelman et al., 2006; Tang et al., 2009). For the *P*, *T* range of this study, we find that  $\frac{\sigma_{NE}}{\sigma} = \sim 1.8$  for volatile free and volatile bearing jadeite melts (Supplementary Fig. 12). Previous MD simulation also reported the larger Haven ratio, i.e.,  $H_R > 1$  is required in Nernst-Einstein relation to estimate the electrical conductivity for silicate melt (Ghosh and Karki, 2017; Dufils et al., 2018).

Our results of aluminosilicate melts show that the electrical conductivity increases with increasing pressure upon initial compression. However, there is a negative correlation of  $\sigma$  with pressures at higher pressures (Fig. 4). The change of positive pressure correlation of  $\sigma$  from lower pressure to negative pressure correlation of  $\sigma$  at higher pressure is comparable to the pressure dependent trend of self-diffusion coefficient of Al, Si and O (Figs. 3, 4). Recent classical molecular dynamics simulation of several melt compositions reported that  $\sigma$  increases with increasing pressure at temperature above 2073 K whereas  $\sigma$  reduces with increasing pressure at lower temperature, i.e., 1673 K (Dufils et al., 2017; Dufils et al., 2018). Based on experimental studies on dry and hydrous albitic melt, it is also inferred that  $\sigma$  may be positively correlated with pressure at temperatures, i.e., >2200 K (Ni et al., 2011b). A trend that is likely due to the anomalous mobility of network forming ions. However, at lower temperatures i.e., <2200 K, the network forming ions are sluggish and the iconic conductivity is dominated by alkali cation or volatile species exhibiting normal behavior, thus electrical conductivity decreases upon compression (Ni et al., 2011b). Our results indicate that electrical conductivity for carbon bearing melt is greater than that of volatile free melts at lower pressures up to ~6 GPa. However,  $\sigma$  is unaffected by carbon in melt at pressures >6 GPa (Fig. 4). In contrast to the effect of carbon, the electrical conductivity of hydrous melts is greater than that of volatile free melts at all explored pressures and temperatures (Fig. 4). Our results are consistent with the previous experiments on hydrous carbonated basaltic melt that indicated an increase in  $\sigma$  with increasing water and carbon dioxide at ~3 GPa and 1173–1773 K (Sifré et al., 2014).

#### 3.3.3. Viscosity

The pressure dependence of melt viscosity  $(\eta)$  for carbon bearing aluminosilicate melt exhibits the distinct behavior for the low (2500–3000 K) and high temperature isotherms (4000 K). At 4000 K,  $\eta$  exhibits normal behavior, i.e., continuously increases with increasing pressure. In contrast, for lower isotherms,  $\eta$  exhibits anomalous behavior. At 3000 K, we find that upon compression  $\eta$  decreases up to ~6 GPa and at pressures  $\geq 6$  GPa,  $\eta$  exhibits normal behavior. At 2500 K, the transition from anomalous to normal behavior transition happens at ~8 GPa (Fig. 5). At ambient pressure and 2500-3000 K, we find that ~10 wt.% CO2 in aluminosilicate melt reduces the melt viscosity. At high pressures, the viscosity is less sensitive to the carbon content (Fig. 5). Our results on the effect of carbon on the viscosity of melt at low pressure agrees with earlier experimental results where  $CO_2$ reduces the melt viscosity by 1-2 order of magnitude (Brearley and Montana, 1989; White and Montana, 1990; Suzuki, 2018). However,  $CO_2$  have little effect on the viscosity of sodium melilite liquid (NaCaAlSi<sub>2</sub>O<sub>7</sub> with ~2 wt.%  $CO_2$ ) (Brearley and Montana, 1989).

Based on this study and earlier FPMD results on aluminosilicate melts, we find that both carbon and hydrogen affect the viscosity along lower temperature isotherms, i.e., 2500–3000 K (Bajgain et al., 2019). At 4000 K, the viscosity of jadeite melt remains unaffected by the presence of volatiles such as  $CO_2$  and  $H_2O$  (Fig. 5). At low pressures and low temperature isotherms, reduction of melt viscosity due to  $H_2O$  is more pronounced compared to the reduction due to  $CO_2$ . At low temperature isotherms and the pressure conditions where minima in viscosity is observed, viscosity of volatile free and volatile bearing melts are very similar (Fig. 5). Recent experimental work on the viscosity of volatile bearing melilititic melts (~39 wt.% SiO<sub>2</sub>, 1.42–1.6 wt.% CO<sub>2</sub>, 1.0–5.7 wt.%  $H_2O$ ) shows that the viscosity of melt composition with higher volatile content is lower than that of silicate melt with lower volatile content (Stagno et al., 2020b). Viscosity of transitional melt with lower silica and higher carbon content (~18 wt.%  $SiO_2$ , 22.5 wt.%  $CO_2$ ) are found to be lower than that of melilititic melts but orders of magnitude higher when viscosity is compared with the carbonate melts (Kono et al., 2014; Stagno et al., 2020a).

# 4. DISCUSSION

Densification in silicate melt is accommodated by pressure induced structural changes. The initial compression is often accommodated by changes in the inter-tetrahedral (T-O-T) bond angle, and when the void spaces in between the tetrahedral spaces diminishes, further compression is accommodated by changes in coordination polyhedral. Average Na-O, C-O and O-O coordination number increases sharply upon compression at lower pressure region and transitions into a gradual increase at high pressures (Supplementary Fig. S7). This is followed by a rather gradual increase at high pressure (Supplementary Figs. S6-7). Thermodynamic parameters such as the coefficient of thermal expansivity,  $\alpha$  also decreases sharply in low pressure regime along all isotherms (Supplementary Fig. S5). Pressure dependent trend of Na-O and C-O coordination can be correlated with the self-diffusion coefficient of Na and C which shows large decrease at lower pressures followed by more gradual decrease at higher pressures (Fig. 3). Effect of  $CO_2$  on the self-diffusion coefficient of Al, Si and O species are also prominent in the lowpressure regime. At higher pressures, diffusivity of Al, Si, O in volatile free and  $CO_2$  bearing melts are indistinguishable (Fig. 3). Similar to the Al, Si and O diffusivity,  $CO_2$ bearing melt have order of magnitude lower viscosity compared to volatile free melt at ambient pressure and lower temperatures (Fig. 5). However, effect of  $CO_2$  in lowering the melt viscosity diminishes substantially at high pressures (Fig. 5).  $CO_2$  in the silicate melt has depolymerizing effect at lower pressure with large portion of carbon species being CO and  $CO_2$  (Supplementary Fig. S13). As pressure increases, carbon speciation changes from isolated CO and  $CO_2$  to  $CO_3$  and  $CO_4$  (Supplementary Fig. S13). The depolymerizing nature of carbon at low pressures could explain the increase in self-diffusion and reduction in melt viscosity. However, the polymerizing nature of carbon at high pressure is likely to explain the fact that carbon has no effect on transport properties at these conditions. Similar pressure dependent changes in speciation of carbon have been observed in carbon bearing pyrolite melt (Solomatova et al., 2019).

There is difference in pressure dependent self-diffusion coefficient trend of network former cations at high (4000 K) and low (2500-3000 K) temperatures (Fig. 3). Similarly, the melt viscosity is also distinct for the high and low temperature isotherms (Fig. 5). This is likely due to the pressure induced coordination change in Al-O and the lifetime of these bonds. Transport properties of polymerized melts are significantly influenced by the structural changes in the network former cations Al/Si i.e., the changes in the degree of polymerizations (Poe et al., 1997). With increasing pressure, the abundance of  $AlO_5$ species increases and reaches its maximum at ~8 GPa. At higher pressures, abundance of AlO<sub>6</sub> species also increases followed by the reduction in the AlO<sub>5</sub> species (Supplementary Fig. S9). The AlO<sub>5</sub> species is a transient species and has a relatively shorter lifetime. There are frequent snapping of bonds as the coordination transitions from 4-fold to 5-fold to 6-fold (Bajgain et al., 2019; Bajgain and Mookherjee, 2020). These snapping of bonds are likely to mobilize the oxygen atoms that could enhance the self-diffusion coefficient of Al, Si and O atoms in polymerized melt. At higher pressures, the abundance of AlO<sub>5</sub> species reduces at the expense of a 6-fold coordinated Al/Si, which is relatively stable, i.e., the lifetime of the Al–O bonds in  $AlO_6$  are greater than that of AlO<sub>5</sub>. This could result into reduction of self-diffusion coefficient of Al, Si and O atoms at high pressures (Fig. 3). In contrast to network former cations, network modifier cations, i.e., Na is weakly bonded with oxygen atoms and the effect of pressure is stronger than the pressure induced local structural rearrangement. So, the self-diffusion coefficient of Na shows normal pressure behavior even at lower temperatures, i.e., decrease in diffusion with increasing pressure (Fig. 3).

Temperature also affects the degree of polymerization. For instance, at low pressures along low temperature isotherms (2500-3000 K), while the network formers such as Na exhibits normal behavior, the network modifiers exhibit anomalous transport properties owing to coordination changes. In contrast, at high temperatures, melts are more depolymerized and both network formers and modifiers exhibit normal behavior thus explaining the temperature effect of the anomalous behavior (Figs. 3, 5). In contrast to the polymerized melts, the transport properties of depolymerized melts may not show the anomalous transport behaviors or shows weak anomalous behavior (e.g., Wang et al., 2014). At constant temperature, the anomalous pressure behavior of transport properties become weaker with the increasing degree of silicate melt depolymerization, i.e., increasing amount of network modifier atoms. Increasing temperature plays a similar role as increasing content of network modifiers. For example, carbon bearing jadeite melt contain ~18% of  $OT_1$  (NBO) and ~10%  $OT_0$  (free oxygens) species at ~0 GPa and 4000 K. However, there are ~14% NBOs at 3000 K and ~6% NBOs at 2500 K. Since the jadeite melt at 4000 K is more depolymerized compared to that at lower temperatures (3000-2500 K), melt at 4000 K shows normal transport behavior or weaker anomalous behavior of pressure dependent transport properties (Figs. 3, 5). However, jadeite melt at lower temperatures show stronger anomalous trend which increases with decreasing temperature (Figs. 3, 5).

The energetics of pressure and temperature induced changes in the atomistic scale structure including changes in coordination and speciation of the silicate melt can be expressed in terms of the equilibrium constant (K)-

$$\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta E^* - T\Delta S^* + P\Delta V^*}{RT}$$
(13)

where,  $\Delta G$  is the Gibbs energy associated with the change in coordination/speciation.  $\Delta G$  is related to energy ( $\Delta E^*$ ), entropy  $(\Delta S^*)$ , volume  $(\Delta V^*)$  changes of the speciation. We use the relative abundances of the different coordination species from our FPMD simulation at various pressures and temperatures and evaluate the equilibrium constants for speciation reaction (Eq. (13)). Coordination of network former cations T (Al/Si) with oxygen  $(TO_X)$ increases with increasing pressure from 4-fold coordination at ambient pressure to larger than 5 at ~25 GPa (Supplementary Fig. S6). The changes in coordination of Al/Si are facilitated by  $OT_1 + TO_4 = TO_5$  or  $OT_2 + TO_4 = TO_5$ reactions. Experimental study on Na aluminosilicate glass also indicated the formation of  $TO_5$  in above mentioned speciation reactions (Lee et al., 2004). Concomitant with the transformation of  $TO_4 \rightarrow TO_5$  via the speciation reaction  $OT_1 + TO_4 = TO_5$ , the  $OT_1$  itself transforms to  $OT_2$ . Similarly, concomitant with the transformation of  $TO_4 \rightarrow TO_5$  via the speciation reaction  $OT_2 + TO_4 = TO_5$  and  $OT_2$  transforms to  $OT_3$ . The equilibrium constant of these speciation reactions can be expressed as-

$$K1 = -\frac{[X_{TO_5}]}{[X_{TO_4}] \cdot [X_{OT_1}]}$$
(14)

$$K2 = -\frac{[X_{TO_5}]}{[X_{TO_4}] \cdot [X_{OT_2}]}$$
(15)

Here,  $X_{TO_5}$ ,  $X_{TO_4}$ ,  $X_{OT_1}$  and  $X_{OT_2}$  are amount of Si/Al in  $TO_5$ ,  $TO_4$ , non-bridging oxygen (*NBO*), and bridging oxygen (*BO*), respectively. The speciation reaction:  $OT_1 + TO_4 = TO_5$  is favorable up to P ~ 10 GPa, beyond which it ceases to operate since all the non-bridging oxygens are used up (Supplementary Table S4, Supplementary Fig. S14). At pressures >10 GPa, T—O coordination change will follow reactions involving bridging oxygens, i.e.,  $OT_2 + TO_4 = TO_5$ .

Our FPMD simulation shows that oxygen atoms that interact with molecular  $CO_2$  to form carbonate groups, i.e.,  $CO_3$  (Supplementary Fig. S14). Experimental studies have also shown that the coordination changes in C—O species is mainly via the speciation reaction:  $CO_2 + O = CO_3$ (Brooker et al., 2001; Ni and Keppler, 2013). The equilibrium constants of these speciation reactions can be expressed in terms of the type of oxygens that  $CO_2$  bonds with to form  $CO_3$ -

$$K3 = -\frac{[X_{CO_2}]}{[X_{CO_3}] \cdot [X_{OT_0}]}$$
(16)

$$K4 = -\frac{[X_{CO_2}]}{[X_{CO_3}] \cdot [X_{OT_1}]}$$
(17)

$$K5 = -\frac{[X_{CO_2}]}{[X_{CO_3}] \cdot [X_{OT_2}]}$$
(18)

Here,  $X_{CO_2}$  and  $X_{CO_3}$  are the faction of  $CO_2$  and  $CO_3$ , respectively. Amount of oxygen atoms that form the carbonate group  $CO_3$ , could be  $X_{OT_0}$  (oxygen atoms coordinated only with Na, i.e., O<sub>ONa</sub>), X<sub>OT1</sub> (non-bridging oxygens), and  $X_{OT_2}$  (bridging oxygens) (Supplementary Fig. S14). Energetics of reaction: $CO_2 + O_{ONa} = CO_3$  are  $\Delta E^* = -70,047$  J/mol,  $\Delta V^* = -7.4$  cm<sup>3</sup>/mol, and  $\Delta S^* =$ 0.7 J/mol/K. This reaction has lower  $\Delta E^*$  compared to the reaction involving NBOs and BOs. Energetics of the reaction clearly indicate that the formation of  $CO_3$  is thermodynamically more favorable when  $CO_2$  reacts with oxygen which is only attached to network modifier cation, i.e., Na in the case of carbon bearing jadeite melt (Supplementary Table S4). This may explain the observations in previous experiments that  $CO_3$  being dominant species in depolymerized melts whereas  $CO_2$  is major carbon species in polymerized melts (e.g., Blank, 1994; Brooker et al., 1999; Morizet et al., 2013; Ni and Keppler, 2013; Moussallam et al., 2016; Muth et al., 2020).

The residence times of silicate melt at depth depends on the mobility of the silicate melt (Bargen and Waff, 1986; Connolly et al., 2009). The mobility of partial melt within the solid matrix can be estimated using the Darcy's law. The ascent velocity  $(w_0)$  for a melt fraction  $(\emptyset)$ , is related to the density difference between the melt and the surrounding  $(\Delta \rho)$  and viscosity  $(\eta)$  can be expressed as-

$$\emptyset w_0 = \frac{kg\Delta\rho}{\eta} \tag{19}$$

where k is the permeability and g is the acceleration due to gravity. Permeability (k) can be further evaluated using-

$$k = \frac{a^2 \emptyset^n}{C} \tag{20}$$

where a represents the dimensions (diameter) of the grain constituting the matrix, n and C are constants that reflect spatial information. Matrix grain size of a = 5-15 mm has been proposed for asthenosphere depth (Solomatov and Reese, 2008; Behn et al., 2009). We assume the melt to be interconnected along grain edges so that it will be able to extract from the source rock. So we use n = 2 based on previous studies (Bargen and Waff, 1986; Connolly et al., 2009). Similarly, we adopted constant parameter C = 3000 from prior estimates (Bargen and Waff, 1986; Connolly et al., 2009). We estimate the ascent velocity of aluminosilicate melt by using the melt density and viscosity form this study. First, we extrapolate the viscosity and density of melt along a realistic geotherm (Supplementary Text S1, Supplementary Fig. S15). For a fixed permeability of magmatic system, mobility of silicate melt is proportional to  $\frac{\Delta\rho}{\eta}$  (Eq. (19)). The predicted melt mobility,  $\frac{\Delta\rho}{\eta}$  for volatile free aluminosilicate melt is orders of magnitude smaller than that of basaltic melt (Sakamaki et al., 2013). It is well known that LDA pseudopotential tends to predict volumes that are slightly lower than that of the experimental volume, in contrast, GGA tends to predict volumes that are slightly larger than that of the experimental volume. Thus,  $\Delta \rho$  predicted in our study is likely to be different if we were to use the density obtained using GGA calculations. However, the effect of pseudopotential on melt viscosity is negligible (Fig. 5). We have calculated the melt properties using GGA along the 3000 K isotherm and using the density difference between LDA and GGA calculations, we have estimated the melt mobility along adiabatic geothermal gradient (Supplementary Fig. S15). Volatile free basaltic melts have mobility similar to that of hydrous aluminosilicate melt but they are less mobile compared to carbonate melts (Kono et al., 2014) (Supplementary Fig. S15).

We find that volatile plays a significant role in the enhancing the mobility of aluminosilicate melts (Fig. 6). For instance, the ascent velocity ( $w_0$ ) for volatile free aluminosilicate melt at 90 km depth (~3 GPa) and present-day mantle temperature (1573 K) for a fixed melt fraction of 1% is  $16 \times 10^{-5}$  km/year whereas  $w_0$  for carbon bearing and hydrous melts are 0.01 km/year and 0.23 km/year, respectively. Since the predicted densities using GGA are smaller than that of LDA, the ascent velocity based on GGA calculations are  $4.3 \times 10^{-5}$ , 0.0023, 0.09 km/year for volatile free, carbon bearing, and hydrous melts, respectively. Because of the small ascent velocity, the residence time for volatile free aluminosilicate melt is expected to be much longer compared to the melt composition with volatile and/or lower silica content. Previous work

on melilititic melts with <40 wt.% SiO<sub>2</sub>,  $\sim 2$  wt.% CO<sub>2</sub> estimated an ascent velocity of  $\sim 1.9$  km/year at lithospheric asthenosphere boundary (LAB) depth of  $\sim 90$  km and 1573 K (Stagno et al., 2020b).

Electromagnetic data is crucial for detecting partial melt in the Earth's interior, particularly in deep crustal and upper mantle settings (Evans et al., 2005; Toffelmier and Tyburczy, 2007). Bulk electrical conductivity of solid mantle and partial melt mixture can be used to understand the melt interconnectivity (Gaillard et al., 2019; Zhang et al., 2021). In fact, various tectonic settings including midocean ridges, subduction zone and volcanic provinces often indicate existence of high electrical conductivity (EC) anomalies (Brasse et al., 2002; Evans et al., 2005; Naif et al., 2013). High EC is also associated with major seismic discontinuities including the lithosphere-asthenosphere boundary (LAB), top of the mantle transition zone, and the core-mantle boundary (Song et al., 2004; Toffelmier and Tyburczy, 2007; McNamara et al., 2010; Tauzin et al., 2010; Schmerr, 2012). Mantle metasomatism, i.e., fluid or melt induced alteration of mantle may also explain some of these anomalous geophysical observation (Pilet et al., 2008; Aulbach et al., 2017). Nominally anhydrous minerals including the major mantle phases such as olivine also are likely to have proton defect induced high electrical conductivity (Karato, 1990; Wang et al., 2006; Yoshino et al., 2006). Volatile such as H<sub>2</sub>O and CO<sub>2</sub> induced partial melting could also explain anomalously high EC in the mantle (e.g., Naif et al., 2013; Tauzin et al., 2010). Significant efforts have been made to relate the melt fraction and chemistry of the melt including the volatile content (Gaillard et al., 2008; Sifré et al., 2014; Gaillard et al., 2019). However, natural mantle melts have diverse chemistries, and the transport properties are sensitive to a combination of pressure, temperature, and volatile chemistry. Thus, electrical conductivity of volatile bearing silicate melts and the effect of volatile on the EC at depth is required to explain anomalous geophysical observations (Yoshino et al., 2010; Ni et al., 2011a; Sifré et al., 2014; Laumonier et al., 2015) and this also helps to interpret the chemistry of volatiles.

To model the electrical conductivity of two-phase aggregate consisting of melt and a solid matrix, we use the Hashin-Shtrikman (HS<sup>+</sup>) to estimate the bulk electrical conductivity of the mantle. The expression of the bulk electrical conductivity ( $\sigma_{bulk}$ ), is given as:

$$\sigma_{bulk} = \sigma_{melt} + \frac{(1+\varphi)}{\left(\frac{1}{\sigma_{solid} - \sigma_{melt}} + \frac{\varphi}{3\sigma_{melt}}\right)}$$
(21)

Where,  $\varphi$  is the melt volume fraction,  $\sigma_{melt}$ , and  $\sigma_{solid}$  are the electrical conductivity of melt and the solid matrix, respectively. For  $\sigma_{solid}$ , we use prior results of the EC of dry olivine (Yoshino et al., 2009) and nominally anhydrous olivine (Wang et al., 2006). The EC of melt,  $\sigma_{melt}$  is estimated from this study by extrapolating our EC results to temperatures relevant for the mantle. The HS + model provides the upper bound of the bulk electrical conductivity of melt/solid mixture since the model assumes that the silicate melt completely wets the matrix grain with wetting angle  $\theta = 0^{\circ}$ . For larger wetting angles i.e.,  $0^{\circ} < \theta < 60^{\circ}$  melts



Fig. 6. Bulk electrical conductivity (EC) of aluminosilicate melt intermixed with olivine mixture at 1773 K and 3 GPa (90 km depth) for volatile free aluminosilicate melt: B19 (purple lines) (Bajgain et al., 2019) and CO<sub>2</sub> bearing aluminosilicate melt (grey lines). Solid and dashed lines represent bulk EC calculated using Hashin-Shtrikman (HS<sup>+</sup>) model (Eq. (21)) tubular veins model (Eq. (22)), respectively. Cyan lines: G19 represent the bulk EC for carbonate melts (Gaillard et al., 2019) Light green: N13 and red: B10, E5, K13, P10 shaded area show the high EC anomalies of  $10^{-0.5}$  Sm<sup>-1</sup> in the subduction zone (Naif et al., 2013) and  $10^{-1}$  Sm<sup>-1</sup> in the upper mantle (Evans et al., 2005; Baba et al., 2010; Pinto et al., 2010; Key et al., 2013), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

could be interconnected via tubular veins along grain edges. The expression of the bulk electrical conductivity ( $\sigma_{bulk}$ ), where the melts are interconnected via tubes is expressed as-

$$\sigma_{bulk} = \frac{1}{3} \varphi \sigma_{melt} + (1 - \varphi) \sigma_{solid}$$
<sup>(22)</sup>

We find that for both volatile bearing and dry aluminosilicate melts, bulk EC remains low for small melt faction (<0.1 vol.%). For melt faction >0.1 vol.%, bulk EC sharply increases with increasing melt fraction. Our results indicate that the observed high electrical conductivities anomalies at upper mantle, i.e.,  $10^{-1}$  Sm<sup>-1</sup> (Evans et al., 2005; Baba et al., 2010; Pinto et al., 2010; Key et al., 2013) can be matched with ~2–5 vol.% dry aluminosilicate melt whereas similar electrical conductance can be generated by ~0.5–1.5 vol.% volatile bearing melt (Fig. 6). Similarly, greater than 10 vol.% dry aluminosilicate melt may require for satisfying the geophysical anomaly, i.e., electrical conductance of  $10^{-0.5}$  Sm<sup>-1</sup> in the subduction zone (Naif et al., 2013). In contrast, less than 1 vol.% carbonate melts is sufficient to explain the high EC at subduction zone and upper mantle (Gaillard et al., 2019). This clearly shows how electrical conductivity increases from a carbon free silicate melts to carbon bearing silicate melts and is the highest for carbonate melts and conversely, the required melt fraction to explain geophysical anomalies are reversed (Fig. 6).

### 5. CONCLUSION

We conducted *first principles* molecular dynamics simulations to study the effect of pressure, temperature and volatile on the structure and properties of aluminosilicate melts. We find the strongest effect of volatile, i.e.,  $CO_2$ ,  $H_2O$  on melt density and compressibility at ambient pressures i.e.,

~0 GPa. With increasing pressures, the effect of volatile becomes weaker. Thus, the density difference between volatile free and volatile bearing melts increases for upward moving magma providing added buoyancy for the magma with volatile as it reaches the surface. Even though density is affected by the presence of volatiles in aluminosilicate melts, its effect on average cation-oxygen coordination, i.e., NaO<sub>x</sub>, AlO<sub>x</sub>, and SiO<sub>x</sub> are small. However, average oxygen-cation coordination for CO<sub>2</sub> and H<sub>2</sub>O bearing melts are lower than that of volatile free melts that suggest the depolymerization of melt. Comparison of CO<sub>2</sub> and H<sub>2</sub>O bearing melts with volatile free melt shows that the effect of volatile on structural depolymerization are dependent on the number of added oxygens in the system.

Our results are in good agreement with available experimental results at lower pressures. The pressure dependent anomalous viscosity behavior weakens at higher temperatures and in the presence of volatile. Our results show that the effect of volatile is more dominant at lower pressures. Our results on electrical conductivity of volatile bearing aluminosilicate melts, indicate that the melt fraction required to explain anomalous geophysical observations are 3-7% and 0.7-1.5% respectively for aluminosilicate melts and volatile bearing aluminosilicate melts.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# ACKNOWLEDGEMENT

Authors acknowledge the National Science Foundation grant (EAR1763215 and EAR1753125) for funding this research and thank the Extreme Science and Engineering Discovery (XSEDE) supercomputing facilities (TG-GEO170003) and the Research Computing Center (RCC) at Florida State University (FSU) for computing resources.

#### APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2021.07.039.

## REFERENCES

- Allen M. and Tildesley D. (1987) Computer Simulation of Liquids. Clarendon, Oxford.
- Arapan S., De Almeida J. S. and Ahuja R. (2007) Formation of sp<sup>3</sup> hybridized bonds and stability of CaCO<sub>3</sub> at very high pressure. *Phys. Rev. Lett.* **98** 268501.
- Audétat A. and Keppler H. (2004) Viscosity of fluids in subduction zones. Science 303, 513–516.
- Aulbach S., Massuyeau M. and Gaillard F. (2017) Origins of cratonic mantle discontinuities: a view from petrology, geochemistry and thermodynamic models. *Lithos* 268, 364–382.
- Baba K., Utada H., Goto T.-N., Kasaya T., Shimizu H. and Tada N. (2010) Electrical conductivity imaging of the Philippine Sea upper mantle using seafloor magnetotelluric data. *Phys. Earth Planet. Inter.* 183, 44–62.

- Bajgain S., Ghosh D. B. and Karki B. B. (2015) Structure and density of basaltic melts at mantle conditions from firstprinciples simulations. *Nat. Commun.* 6, 9578.
- Bajgain S. and Mookherjee M. (2020) Structure and properties of albite melt at high pressures. ACS Earth Space Chem. 4, 1–13.
- Bajgain S., Peng Y., Mookherjee M., Jing Z. and Solomon M. (2019) Properties of hydrous aluminosilicate melt at high pressures. ACS Earth Space Chem. 3, 390–402.
- Bargen N. and Waff H. S. (1986) Permeabilities, interfacial areas and curvatures of partially molten systems: results of numerical computations of equilibrium microstructures. J. Geophys. Res.: Solid Earth 91, 9261–9276.
- Behn M. D., Hirth G. and Elsenbeck, II, J. R. (2009) Implications of grain size evolution on the seismic structure of the oceanic upper mantle. *Earth Planet. Sci. Lett.* 282, 178–189.
- Blank J. G. (1994) Experimental studies of carbon dioxide in silicate melts: solubility, speciation and stable isotope behavior. *Rev. Mineral. Geochem.* 30, 157–186.
- Blöchl P. E. (1994) Projector augmented-wave method. *Phys. Rev. B* **50**, 17953.
- Boulard E., Gloter A., Corgne A., Antonangeli D., Auzende A.-L., Perrillat J.-P., Guyot F. and Fiquet G. (2011) New host for carbon in the deep Earth. *PNAS* 108, 5184–5187.
- Bourgue E. and Richet P. (2001) The effects of dissolved CO<sub>2</sub> on the density and viscosity of silicate melts: a preliminary study. *Earth Planet. Sci. Lett.* **193**, 57–68.
- Brasse H., Lezaeta P., Rath V., Schwalenberg K., Soyer W. and Haak V. (2002) The Bolivian altiplano conductivity anomaly. J. Geophys. Res.: Solid Earth 107, EPM 4-1–EPM 4-14.
- Brearley M. and Montana A. (1989) The effect of CO<sub>2</sub> on the viscosity of silicate liquids at high pressure. *Geochim. Cosmochim. Acta* 53, 2609–2616.
- Brooker R., Kohn S., Holloway J. and McMillan P. (2001) Structural controls on the solubility of CO<sub>2</sub> in silicate melts: part I: bulk solubility data. *Chem. Geol.* **174**, 225–239.
- Brooker R., Kohn S., Holloway J., McMillan P. and Carroll M. (1999) Solubility, speciation and dissolution mechanisms for CO<sub>2</sub> in melts on the NaAlO<sub>2</sub>–SiO<sub>2</sub> join. *Geochim. Cosmochim. Acta* 63, 3549–3565.
- Ceperley D. M. and Alder B. (1980) Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.* **45**, 566–569.
- Chen T., Smit B. and Bell A. T. (2009) Are pressure fluctuationbased equilibrium methods really worse than nonequilibrium methods for calculating viscosities? J. Chem. Phys. 131 246101.
- Connolly J. A., Schmidt M. W., Solferino G. and Bagdassarov N. (2009) Permeability of asthenospheric mantle and melt extraction rates at mid-ocean ridges. *Nature* 462, 209–212.
- Dasgupta R. (2013) Ingassing, storage, and outgassing of terrestrial carbon through geologic time. *Rev. Mineral. Geochem.* 75, 183– 229.
- Dasgupta R. and Hirschmann M. M. (2006) Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440, 659– 662.
- Dasgupta R., Mallik A., Tsuno K., Withers A. C., Hirth G. and Hirschmann M. M. (2013) Carbon-dioxide-rich silicate melt in the Earth's upper mantle. *Nature* 493, 211–215.
- Dixon J. E. and Stolper E. M. (1995) An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. J. Petrol. 36, 1633–1646.
- Dufils T., Folliet N., Mantisi B., Sator N. and Guillot B. (2017) Properties of magmatic liquids by molecular dynamics simulation: the example of a MORB melt. *Chem. Geol.* 461, 34–46.
- Dufils T., Sator N. and Guillot B. (2018) Properties of planetary silicate melts by molecular dynamics simulation. *Chem. Geol.* 493, 298–315.

- Dufils T., Sator N. and Guillot B. (2020) A comprehensive molecular dynamics simulation study of hydrous magmatic liquids. *Chem. Geol.* 533 119300.
- Duncan M. S. and Agee C. B. (2011) The partial molar volume of carbon dioxide in peridotite partial melt at high pressure. *Earth Planet. Sci. Lett.* **312**, 429–436.
- Evans R. L., Hirth G., Baba K., Forsyth D., Chave A. and Mackie R. (2005) Geophysical evidence from the MELT area for compositional controls on oceanic plates. *Nature* 437, 249–252.
- Falloon T. J. and Green D. H. (1989) The solidus of carbonated, fertile peridotite. *Earth Planet. Sci. Lett.* **94**, 364–370.
- Fine G. and Stolper E. (1985) The speciation of carbon dioxide in sodium aluminosilicate glasses. *Contrib. Mineral. Petrol.* 91, 105–121.
- Flyvbjerg H. and Petersen H. G. (1989) Error estimates on averages of correlated data. J. Chem. Phys. 91, 461–466.
- Foley S. F. and Pintér Z. (2018) Primary melt compositions in the Earth's mantle. In Magmas Under Pressure. Elsevier, pp. 3–42.
- Funakoshi K.-I., Suzuki A. and Terasaki H. (2002) In situ viscosity measurements of albite melt under high pressure. J. Phys.: Condens. Matter 14, 11343.
- Gaillard F., Malki M., Iacono-Marziano G., Pichavant M. and Scaillet B. (2008) Carbonatite melts and electrical conductivity in the asthenosphere. *Science* 322, 1363–1365.
- Gaillard F., Sator N., Gardés E., Guillot B., Massuyeau M., Sifré D., Hammouda T. and Richard G. (2019) The link between the physical and chemical properties of carbon-bearing melts and their application for geophysical imaging of Earth's Mantle. In *Deep Carbon: Past to Present* (eds. B. Orcutt, I. Daniel and R. Dasgupta). Cambridge University Press, Cambridge, pp. 163– 187.
- Gerlach T. M. (1982) Interpretation of volcanic gas data from tholeiitic and alkaline mafic lavas. *Bull. Volcanologique* **45**, 235–244.
- Ghosh D. B., Bajgain S. K., Mookherjee M. and Karki B. B. (2017) Carbon-bearing silicate melt at deep mantle conditions. *Sci. Rep.* 7, 1–8.
- Ghosh D. B. and Karki B. B. (2017) Transport properties of carbonated silicate melt at high pressure. *Sci. Adv.* **3**, e1701840.
- Ghosh S., Ohtani E., Litasov K., Suzuki A. and Sakamaki T. (2007) Stability of carbonated magmas at the base of the Earth's upper mantle. *Geophys. Res. Lett.* **34**, L22312.
- Giordano D. and Dingwell D. B. (2003) Non-Arrhenian multicomponent melt viscosity: a model. *Earth Planet. Sci. Lett.* 208, 337–349.
- Giordano D., Russell J. K. and Dingwell D. B. (2008) Viscosity of magmatic liquids: a model. *Earth Planet. Sci. Lett.* 271, 123– 134.
- Guillot B. and Sator N. (2011) Carbon dioxide in silicate melts: a molecular dynamics simulation study. *Geochim. Cosmochim. Acta* 75, 1829–1857.
- Henkelman G., Arnaldsson A. and Jónsson H. (2006) A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* 36, 354–360.
- Holloway J. R. (1976) Fluids in the evolution of granitic magmas: consequences of finite CO<sub>2</sub> solubility. *Geol. Soc. Am. Bull.* 87, 1513–1518.
- Karato S.-I. (1990) The role of hydrogen in the electrical conductivity of the upper mantle. *Nature* **347**, 272–273.
- Karki B. B., Bhattarai D. and Stixrude L. (2007) First-principles simulations of liquid silica: structural and dynamical behavior at high pressure. *Phys. Rev. B* 76 104205.
- Karki B. B., Ghosh D. B. and Bajgain S. K. (2018) Simulation of silicate melts under pressure. In *Magmas Under Pressure*. Elsevier, pp. 419–453.

- Karki B. B., Ghosh D. B. and Banjara D. (2020) Mixed incorporation of carbon and hydrogen in silicate melts under varying pressure and redox conditions. *Earth Planet. Sci. Lett.* 549 116520.
- Kelbert A., Schultz A. and Egbert G. (2009) Global electromagnetic induction constraints on transition-zone water content variations. *Nature* 460, 1003–1006.
- Key K., Constable S., Liu L. and Pommier A. (2013) Electrical image of passive mantle upwelling beneath the northern East Pacific Rise. *Nature* 495, 499–502.
- Kono Y., Kenney-Benson C., Hummer D., Ohfuji H., Park C., Shen G., Wang Y., Kavner A. and Manning C. E. (2014) Ultralow viscosity of carbonate melts at high pressures. *Nat. Commun.* 5, 1–8.
- Konschak A. and Keppler H. (2014) The speciation of carbon dioxide in silicate melts. *Contrib. Miner. Petrol.* **167**, 998.
- Kresse G. and Furthmüller J. (1996) Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 54, 11169.
- Kresse G. and Hafner J. (1993) Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 47, 558–561.
- Kushiro I. (1976) Changes in viscosity and structure of melt of NaAlSi<sub>2</sub>O<sub>6</sub> composition at high pressures. J Geophys. Res. 81, 6347–6350.
- Laumonier M., Gaillard F. and Sifré D. (2015) The effect of pressure and water concentration on the electrical conductivity of dacitic melts: implication for magnetotelluric imaging in subduction areas. *Chem. Geol.* 418, 66–76.
- Lee S. K. (2011) Simplicity in melt densification in multicomponent magmatic reservoirs in Earth's interior revealed by multinuclear magnetic resonance. *PNAS* 108, 6847–6852.
- Lee S. K., Cody G. D., Fei Y. and Mysen B. O. (2004) Nature of polymerization and properties of silicate melts and glasses at high pressure. *Geochim. Cosmochim. Acta* **68**, 4189–4200.
- Lee S. K., Mosenfelder J. L., Park S. Y., Lee A. C. and Asimow P. D. (2020) Configurational entropy of basaltic melts in Earth's mantle. *PNAS* 117, 21938–21944.
- Liu J., Lin J.-F. and Prakapenka V. B. (2015) High-pressure orthorhombic ferromagnesite as a potential deep-mantle carbon carrier. Sci. Rep. 5, 1–6.
- Lowenstern J. B. (2001) Carbon dioxide in magmas and implications for hydrothermal systems. *Miner. Deposita* 36, 490–502.
- McNamara A. K., Garnero E. J. and Rost S. (2010) Tracking deep mantle reservoirs with ultra-low velocity zones. *Earth Planet. Sci. Lett.* 299, 1–9.
- Mookherjee M., Stixrude L. and Karki B. (2008) Hydrous silicate melt at high pressure. *Nature* 452, 983–986.
- Morizet Y., Brooker R. and Kohn S. (2002) CO<sub>2</sub> in haplophonolite melt: solubility, speciation and carbonate complexation. *Geochim. Cosmochim. Acta* **66**, 1809–1820.
- Morizet Y., Brooker R. A., Iacono-Marziano G. and Kjarsgaard B. A. (2013) Quantification of dissolved CO<sub>2</sub> in silicate glasses using micro-Raman spectroscopy. *Am. Mineral.* 98, 1788–1802.
- Moussallam Y., Florian P., Corradini D., Morizet Y., Sator N., Vuilleumier R., Guillot B., Iacono-Marziano G., Schmidt B. C. and Gaillard F. (2016) The molecular structure of melts along the carbonatite–kimberlite–basalt compositional joint: CO<sub>2</sub> and polymerisation. *Earth Planet. Sci. Lett.* **434**, 129–140.
- Muth M., Duncan M. S. and Dasgupta R. (2020) The effect of variable Na/K on the CO<sub>2</sub> content of slab-derived rhyolitic melts. *Carbon Earth's Interior*, 195–208.
- Naif S., Key K., Constable S. and Evans R. (2013) Melt-rich channel observed at the lithosphere-asthenosphere boundary. *Nature* 495, 356–359.

- Nesbitt H. W., Bancroft G. and Henderson G. (2020) Nucleophilic substitution reaction mechanisms: an atomic-molecular perspective on chemical speciation and transport properties in silicate melts. *Chem. Geol.* 555 119818.
- Nevins D. and Spera F. (2007) Accurate computation of shear viscosity from equilibrium molecular dynamics simulations. *Mol. Simul.* 33, 1261–1266.
- Ni H. and Keppler H. (2013) Carbon in silicate melts. *Rev. Mineral. Geochem.* **75**, 251–287.
- Ni H., Keppler H. and Behrens H. (2011a) Electrical conductivity of hydrous basaltic melts: implications for partial melting in the upper mantle. *Contrib. Miner. Petrol.* **162**, 637–650.
- Ni H., Keppler H., Manthilake M. and Katsura T. (2011b) Electrical conductivity of dry and hydrous NaAlSi<sub>3</sub>O<sub>8</sub> glasses and liquids at high pressures. *Contrib. Miner. Petrol.* **162**, 501– 513.
- Nosé S. (1984) A unified formulation of the constant temperature molecular dynamics methods. J. Chem. Phys. 81, 511–519.
- Nowak M., Porbatzki D., Spickenbom K. and Diedrich O. (2003) Carbon dioxide speciation in silicate melts: a restart. *Earth Planet. Sci. Lett.* 207, 131–139.
- Oganov A. R., Glass C. W. and Ono S. (2006) High-pressure phases of CaCO<sub>3</sub>: crystal structure prediction and experiment. *Earth Planet. Sci. Lett.* **241**, 95–103.
- Oganov A. R., Ono S., Ma Y., Glass C. W. and Garcia A. (2008) Novel high-pressure structures of MgCO<sub>3</sub>, CaCO<sub>3</sub> and CO<sub>2</sub> and their role in Earth's lower mantle. *Earth Planet. Sci. Lett.* **273**, 38–47.
- Okuno M. and Marumo F. (1982) The structures of anorthite and albite melts. *Mineral. J.* 11, 180–196.
- Pilet S., Baker M. B. and Stolper E. M. (2008) Metasomatized lithosphere and the origin of alkaline lavas. *Science* 320, 916– 919.
- Pinto L. G. R., de Pádua M. B., Ussami N., Vitorello Í., Padilha A. L. and Braitenberg C. (2010) Magnetotelluric deep soundings, gravity and geoid in the south São Francisco craton: geophysical indicators of cratonic lithosphere rejuvenation and crustal underplating. *Earth Planet. Sci. Lett.* 297, 423–434.
- Poe B. T., McMillan P. F., Rubie D. C., Chakraborty S., Yarger J. and Diefenbacher J. (1997) Silicon and oxygen self-diffusivities in silicate liquids measured to 15 gigapascals and 2800 Kelvin. *Science* 276, 1245–1248.
- Sakamaki T., Ohtani E., Urakawa S., Terasaki H. and Katayama Y. (2011) Density of carbonated peridotite magma at high pressure using an X-ray absorption method. *Am. Mineral.* 96, 553–557.
- Sakamaki T., Suzuki A., Ohtani E., Terasaki H., Urakawa S., Katayama Y., Funakoshi K.-I., Wang Y., Hernlund J. W. and Ballmer M. D. (2013) Ponded melt at the boundary between the lithosphere and asthenosphere. *Nat. Geosci.* 6, 1041–1044.
- Sakamaki T., Wang Y., Park C., Yu T. and Shen G. (2012) Structure of jadeite melt at high pressures up to 4.9 GPa. J. Appl. Phys. 111 112623.
- Sanloup C., Hudspeth J. M., Afonina V., Cochain B., Konôpková Z., Lelong G., Cormier L. and Cavallari C. (2019) Polymerized 4-fold coordinated carbonate melts in the deep mantle. *Front. Earth Sci.* 7, 72.
- Schmerr N. (2012) The Gutenberg discontinuity: melt at the lithosphere-asthenosphere boundary. *Science* **335**, 1480–1483.
- Schmidt M. W. (2015) Melting of pelitic sediments at subarc depths: 2. Melt chemistry, viscosities and a parameterization of melt composition. *Chem. Geol.* 404, 168–182.
- Sifré D., Gardés E., Massuyeau M., Hashim L., Hier-Majumder S. and Gaillard F. (2014) Electrical conductivity during incipient melting in the oceanic low-velocity zone. *Nature* 509, 81–85.

- Solomatov V. and Reese C. (2008) Grain size variations in the Earth's mantle and the evolution of primordial chemical heterogeneities. J. Geophys. Res.: Solid Earth 113, B07408.
- Solomatova N., Caracas R. and Cohen R. (2020) Carbon Speciation and Solubility in Silicate Melts. *Carbon Earth's Interior*, 179–194.
- Solomatova N. V. and Caracas R. (2020) Buoyancy and structure of volatile-rich silicate melts. J. Geophys. Res.: Solid Earth 126, e2020JB021045.
- Solomatova N. V., Caracas R. and Manning C. E. (2019) Carbon sequestration during core formation implied by complex carbon polymerization. *Nat. Commun.* 10, 789.
- Song T.-R.-A., Helmberger D. V. and Grand S. P. (2004) Lowvelocity zone atop the 410-km seismic discontinuity in the northwestern United States. *Nature* 427, 530–533.
- Spera F. J. (1984) Carbon dioxide in petrogenesis III: role of volatiles in the ascent of alkaline magma with special reference to xenolith-bearing mafic lavas. *Contrib. Miner. Petrol.* 88, 217– 232.
- Stagno V., Cerantola V., Aulbach S., Lobanov S., McCammon C. A. and Merlini M. (2019) Carbon-bearing phases throughout Earth's Interior. In *Deep Carbon: Past to Present*. Cambridge University Press, pp. 66–88.
- Stagno V., Kono Y., Stopponi V., Masotta M., Scarlato P. and Manning C. E. (2020a) The Viscosity of Carbonate-Silicate Transitional Melts at Earth's Upper Mantle Pressures and Temperatures, Determined by the In Situ Falling-Sphere Technique. *Carbon Earth's Interior*, 223–236.
- Stagno V., Stopponi V., Kono Y., D'Arco A., Lupi S., Romano C., Poe B. T., Foustoukos D. I., Scarlato P. and Manning C. E. (2020b) The viscosity and atomic structure of volatile-bearing melilititic melts at high pressure and temperature and the transport of deep carbon. *Minerals* **10**, 267.
- Stebbins J. F. (2017) "Free" oxide ions in silicate melts: thermodynamic considerations and probable effects of temperature. *Chem. Geol.* 461, 2–12.
- Sun Y., Zhou H., Liu X., Yin K. and Lu X. (2020) Physical state of an early magma ocean constrained by the thermodynamics and viscosity of iron silicate liquid. *Earth Planet. Sci. Lett.* 551 116556.
- Suzuki A. (2018) Effect of carbon dioxide on the viscosity of a melt of jadeite composition at high pressure. J. Mineral. Petrol. Sci. 113, 47–50.
- Suzuki A., Ohtani E., Terasaki H., Nishida K., Hayashi H., Sakamaki T., Shibazaki Y. and Kikegawa T. (2011) Pressure and temperature dependence of the viscosity of a NaAlSi<sub>2</sub>O<sub>6</sub> melt. *Phys. Chem. Miner.* **38**, 59–64.
- Tang W., Sanville E. and Henkelman G. (2009) A grid-based Bader analysis algorithm without lattice bias. J. Phys.: Condens. Matter 21 084204.
- Tauzin B., Debayle E. and Wittlinger G. (2010) Seismic evidence for a global low-velocity layer within the Earth's upper mantle. *Nat. Geosci.* 3, 718–721.
- Tinker D. and Lesher C. E. (2001) Self diffusion of Si and O in dacitic liquid at high pressures. *Am. Mineral.* **86**, 1–13.
- Tinker D., Lesher C. E., Baxter G. M., Uchida T. and Wang Y. (2004) High-pressure viscometry of polymerized silicate melts and limitations of the Eyring equation. *Am. Mineral.* 89, 1701– 1708.
- Toffelmier D. A. and Tyburczy J. A. (2007) Electromagnetic detection of a 410-km-deep melt layer in the southwestern United States. *Nature* 447, 991–994.
- Torquato S., Truskett T. M. and Debenedetti P. G. (2000) Is random close packing of spheres well defined? *Phys. Rev. Lett.* **84**, 2064.

- Tsuno K. and Dasgupta R. (2012) The effect of carbonates on nearsolidus melting of pelite at 3 GPa: relative efficiency of H<sub>2</sub>O and CO<sub>2</sub> subduction. *Earth Planet. Sci. Lett.* **319**, 185–196.
- Vennari C. E. and Williams Q. (2018) A novel carbon bonding environment in deep mantle high-pressure dolomite. Am. Mineral. 103, 171–174.
- Vuilleumier R., Seitsonen A. P., Sator N. and Guillot B. (2015) Carbon dioxide in silicate melts at upper mantle conditions: insights from atomistic simulations. *Chem. Geol.* 418, 77–88.
- Wang D., Mookherjee M., Xu Y. and Karato S.-I. (2006) The effect of water on the electrical conductivity of olivine. *Nature* 443, 977–980.
- Wang Y., Sakamaki T., Skinner L. B., Jing Z., Yu T., Kono Y., Park C., Shen G., Rivers M. L. and Sutton S. R. (2014) Atomistic insight into viscosity and density of silicate melts under pressure. *Nat. Commun.* 5, 3241.
- White B. S. and Montana A. (1990) The effect of H<sub>2</sub>O and CO<sub>2</sub> on the viscosity of sanidine liquid at high pressures. J. Geophys. Res.: Solid Earth 95, 15683–15693.
- Whittington A., Richet P. and Holtz F. (2000) Water and the viscosity of depolymerized aluminosilicate melts. *Geochim. Cosmochim. Acta* 64, 3725–3736.
- Wilding M., Bingham P. A., Wilson M., Kono Y., Drewitt J. W., Brooker R. A. and Parise J. B. (2019) CO<sub>3+1</sub> network formation in ultra-high pressure carbonate liquids. *Sci. Rep.* 9, 1–11.
- Xue X., Kanzaki M., Floury P., Tobase T. and Eguchi J. (2018) Carbonate speciation in depolymerized and polymerized (alumino) silicate glasses: constraints from 13C MAS and static NMR measurements and ab initio calculations. *Chem. Geol.* 479, 151–165.

- Yoshino T., Laumonier M., McIsaac E. and Katsura T. (2010) Electrical conductivity of basaltic and carbonatite melt-bearing peridotites at high pressures: implications for melt distribution and melt fraction in the upper mantle. *Earth Planet. Sci. Lett.* 295, 593–602.
- Yoshino T., Matsuzaki T., Shatskiy A. and Katsura T. (2009) The effect of water on the electrical conductivity of olivine aggregates and its implications for the electrical structure of the upper mantle. *Earth Planet. Sci. Lett.* 288, 291–300.
- Yoshino T., Matsuzaki T., Yamashita S. and Katsura T. (2006) Hydrous olivine unable to account for conductivity anomaly at the top of the asthenosphere. *Nature* 443, 973–976.
- Zhang B.-H., Guo X., Yoshino T. and Xia Q.-K. (2021) Electrical conductivity of melts: implications for conductivity anomalies in the Earth's mantle. *Natl. Sci. Rev.*, nwab064.
- Zhang Y. and Ni H. (2010) Diffusion of H, C, and O components in silicate melts. *Rev. Mineral. Geochem.* 72, 171–225.
- Zhang Y., Ni H. and Chen Y. (2010) Diffusion data in silicate melts. *Rev. Mineral. Geochem.* 72, 311–408.
- Zhang Z. and Liu Z. (2015) High pressure equation of state for molten CaCO<sub>3</sub> from first principles simulations. *Chin. J. Geochem.* 34, 13–20.
- Zhang Z., Stixrude L. and Brodholt J. (2013) Elastic properties of MgSiO<sub>3</sub>-perovskite under lower mantle conditions and the composition of the deep Earth. *Earth Planet. Sci. Lett.* **379**, 1–12.

Associate editor: Xiandong Liu