Experimental determination of the viscosity of Na$_2$CO$_3$ melt between 1.7 and 4.6 GPa at 1200–1700 °C: Implications for the rheology of carbonatite magmas in the Earth's upper mantle

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ABSTRACT

Knowledge of the rheology of molten materials at high pressure and temperature is required to understand magma mobility and ascent rate at conditions of the Earth's interior. We determined the viscosity of nominally anhydrous sodium carbonate (Na$_2$CO$_3$), an analogue and ubiquitous component of natural carbonatitic magmas, by the in situ “falling sphere” technique at 1.7, 2.4 and 4.6 GPa, at 1200 to 1700 °C, using the Paris-Edinburgh press. We find that the viscosity of liquid Na$_2$CO$_3$ is between 0.0028 ± 0.0001 Pas and 0.0073 ± 0.0001 Pas in the investigated pressure-temperature range. Combination of our results with those from recent experimental studies indicate a negligible dependence on pressure from 1 atm to 4.6 GPa, and a small compositional dependence between molten alkali metal-bearing and alkaline earth metal-bearing carbonates. Based on our results, the viscosity of Na$_2$CO$_3$ is consistent with available viscosity data of both molten calcite (determined at high pressure and temperature) and Na$_2$CO$_3$ at ambient pressure. Molten Na$_2$CO$_3$ is a valid experimental analogue for study of the rheology of natural and/or synthetic near-solidus carbonatitic melts. Estimated values of the mobility and ascent velocity of carbonatitic melts at upper conditions are between 70 and 300 g cm$^{-3}$·Pa$^{-1}$·s$^{-1}$ and 330–1450 m·year$^{-1}$, respectively, when using recently proposed densities for carbonatitic melts. The relatively slow migration rate allows magma-rock interaction over time causing seismic anomalies and chemical redox exchange.

1. Introduction

The percolation of CO$_2$-rich magmas has played an important role in modifying the composition of the mantle lithosphere, creating seismic low-velocity zones, and transferring volatiles from Earth’s interior to its atmosphere over time (Chandet et al., 2016; Keller et al., 2017; Stagno et al., 2013). Experimental studies on melting of synthetic carbonated mantle rocks have provided important chemical and mineralogical constraints on the amount of carbon dissolved in the originated melts (Dalton and Wood, 1993; Dalton and Presnall, 1998; Gudfinnsson and Presnall, 2005; Dasgupta and Hirschmann, 2010), element distribution coefficients to determine the melt fractions (Dasgupta et al., 2009), and redox reactions that are essential to explain the origin of diamonds (Stagno and Frost, 2010; Rohrbach and Schmidt, 2011). However, understanding these processes also requires information on the time during which rock and melt can interact, as controlled by the rheology and migration rates of CO$_2$-rich magmas at depth.

Experimental study of the rheology of carbonatite liquids is plagued by problems associated with the choice of appropriate analogue material. The chemical composition of natural mantle carbonatites may be influenced by late-stage processes such as fractional crystallization and wall rock assimilation. It is thus problematic to employ natural carbonatite rock compositions. On the other hand, use of synthetic systems that approach natural compositions in complexity is difficult due to the tendency of the liquids to crystallize and/or lose CO$_2$ upon quench during initial preparation (Genge et al., 1995). Investigations of the rheological properties of carbonatitic melts at mantle conditions have therefore typically employed highly simplified, analogue compositions like pure carbonates. Fig. 1 shows the pressure and temperature conditions of previous studies including those discussed here with viscosity
data ranging from 750 °C up to almost 1800 °C at pressures between 1 atm and 6.2 GPa, and employing simplified compositions such as K$_2$Mg(CO$_3$)$_2$ and K$_2$Ca(CO$_3$)$_2$ (Dobson et al., 1996), and dolomite and calcite (Kono et al., 2014a), as analogue of natural carbonatitic magmas. Viscosity values for molten calcite and dolomite estimated by Kono et al. (2014a)using the falling sphere technique (Maude, 1961; Kanzaki et al., 1987) combined with ultrafast in situ X-ray imaging are between 0.006 and 0.01 Pa·s (Table 1). However, some compositions resulted in higher melting temperatures than expected for near-solidus melts at the P-T conditions relevant for the mantle adiabat (Fig. 1). In contrast, the starting material used by Dobson et al. (1996) allowed performing measurements at lower temperatures representative of Archaean cratons (Fig. 1); their proposed viscosities resulted to be up to one order of magnitude higher but were overestimated due to the low recording time (40 frame per second).

In this study, we used Na$_2$CO$_3$ to investigate the effect of alkali metal compositions on the viscosity of carbonatitic melts. Na$_2$CO$_3$ is an important component of complex natural carbonatitic melts (Woolley and Kjarsgaard, 2008), as testified by natrocarbonatites erupted at Ol Doinyo Lengai (Tanzania), Na-rich carbonate inclusions in kimberlite-hosted mantle xenoliths (Na$_2$O up to 34.3 wt%; Giuliani et al., 2012), and Na-carbonate-bearing inclusions in fibrous diamonds (6.58 wt% Na$_2$O vs. 16.99 wt% CaO, Kopylova et al., 2010, up to 9.5 wt% Na$_2$O vs. 29 wt% CaO, Shiryaev et al., 2005). Recent studies used Na$_2$CO$_3$ to investigate the reactivity of CO$_2$-rich melts by mineral assimilation (Russell et al., 2012), and to determine the viscosity of natrocarbonatites at ambient pressure (Di Genova et al., 2016; Table 1). The Na$_2$CO$_3$ was used in experimental studies on the dissolution of mantle minerals to explain the origin and emplacement of kimberlitic rocks (Kamenetsky and Yaxley, 2015) considering that carbonatites have been proposed to be parental of kimberlitic melts (Kamenetsky et al., 2013, 2014). Importantly, carbonate melts at depths have been experimentally demonstrated to be Ca-, Mg- rich, Fe- rich. However, phase relations explored accurately by adding Na$_2$O like in the CMASFN +CO$_2$ and CMASN+CO$_2$, systems by Litasov and Ohtani (2009a, 2009b, 2010); Litasov et al. (2013, 2014) showed that near solidus melts can contain even up to 18.89 wt% of Na$_2$CO$_3$ component vs. 19.13 wt% CaCO$_3$ within a single produced carbonatitic melt. Recently, Thomson et al. (2016) emphasized the important role of Na$_2$CO$_3$ in lowering the melting temperature of a carbonated subducted slab with formation of Na-rich carbonate melts (up to 15.24 wt% Na$_2$O versus 22.85 wt% CaO in the reported RUN #3) that eventually will limit the subduction of carbon further in the lower mantle. These experimental studies supported by the frequent presence of Na both in melt inclusions and in the mantle adiabat.

Table 1

<table>
<thead>
<tr>
<th>Composition, references</th>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-carbonatite, Wolf (1994)</td>
<td>0.0001</td>
<td>800</td>
<td>0.08</td>
</tr>
<tr>
<td>Natrocarbonatite, Wolf (1994)</td>
<td>0.0001</td>
<td>800</td>
<td>0.008</td>
</tr>
<tr>
<td>K$_2$Mg(CO$_3$)$_2$, Dobson et al. (1996)</td>
<td>3.0</td>
<td>800</td>
<td>0.036 (± 0.019)</td>
</tr>
<tr>
<td>K$_2$Ca(CO$_3$)$_2$, Dobson et al. (1996)</td>
<td>3.0</td>
<td>900</td>
<td>0.022 (± 0.010)</td>
</tr>
<tr>
<td>25 wt% MgCO$_3$-75 wt% K$_2$CO$_3$, Dobson et al. (1996)</td>
<td>4.0</td>
<td>1500</td>
<td>0.023</td>
</tr>
<tr>
<td>K$_2$CO$_3$, Dobson et al. (1996)</td>
<td>3.0</td>
<td>530</td>
<td>0.155 (± 0.065)</td>
</tr>
<tr>
<td>REE-rich carbonatite, Dobson et al. (1996)</td>
<td>0.9</td>
<td>1380</td>
<td>0.0067 (± 0.0006)</td>
</tr>
<tr>
<td>Calcite (CaCO$_3$), Kono et al. (2014a, 2014b)</td>
<td>1.5</td>
<td>1480</td>
<td>0.0062 (± 0.0003)</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>1540</td>
<td>0.0059 (± 0.0004)</td>
</tr>
<tr>
<td></td>
<td>4.8</td>
<td>1779</td>
<td>0.006 (± 0.0003)</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>1790</td>
<td>0.0061 (± 0.0004)</td>
</tr>
<tr>
<td>Dolomite ((Mg$<em>{0.40}$Fe$</em>{0.09}$Ca$_{0.51}$)CO$_3$)$_2$, Kono et al. (2014a, 2014b)</td>
<td>3</td>
<td>1410</td>
<td>0.0099 (± 0.0007)</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>1400</td>
<td>0.0084 (± 0.0008)</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
<td>1510</td>
<td>0.0087 (± 0.0007)</td>
</tr>
<tr>
<td>Double-layered probing sphere measured for dolomite, Kono et al. (2014a, 2014b)</td>
<td>No data</td>
<td>1360</td>
<td>0.0117 (± 0.0007)</td>
</tr>
<tr>
<td>K$_2$CO$_3$, Di Genova et al. (2016)</td>
<td>2.9</td>
<td>1490</td>
<td>0.007 (± 0.0005)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$, Di Genova et al. (2016)</td>
<td>0.0001</td>
<td>910</td>
<td>0.0038</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>930</td>
<td>0.0036</td>
</tr>
<tr>
<td>Li$_2$CO$_3$, Di Genova et al. (2016)</td>
<td>0.0001</td>
<td>880</td>
<td>0.0049</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>900</td>
<td>0.0047</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>880</td>
<td>0.0067</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>740</td>
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<td></td>
<td>0.0001</td>
<td>750</td>
<td>0.0136</td>
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<tr>
<td></td>
<td>0.0001</td>
<td>760</td>
<td>0.0132</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>770</td>
<td>0.0129</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>780</td>
<td>0.0125</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>800</td>
<td>0.0121</td>
</tr>
</tbody>
</table>

Notes: uncertainties written in italics were obtained from Fig. 5 in Dobson et al. (1996). No uncertainties are provided by Di Genova et al. (2016), although it is claimed to be smaller than the symbol size in their Fig. 4 (i.e. < ± 0.001). No uncertainties are available for Wolf (1994) data.
of fibrous diamonds (Kopylova et al., 2010) and in natural carbonatites (Woolley and Kjærgaard, 2008) implies a critical role of alkali metals dissolved into carbonatitic melts in lowering further their viscosity affecting, then, their migration rate. The high concentration of Na2O of these melts is expected to affect their viscosity and, in turn, the kinetics of the reactions between these melts and the surrounding reduced mantle. At mantle conditions, Na2CO3-dominated melts are interconnected in fine-grained rocks at low melt fractions of 0.05 wt% (Minarik and Watson, 1995; Watson et al., 1990), and that these melts can percolate rapidly upward through polycrystalline mineral assemblages over long distances (Hammouda and Lafort, 2000).

To date, no viscosity measurements have been performed on Na2CO3 liquids at pressure and temperature conditions relevant for the Earth’s upper mantle that would allow modeling their ascent rate and provide insights on the effect of alkali on the viscosity of carbonatitic magmas. We determined the viscosity of Na2CO3 liquids in situ at upper mantle pressures and temperatures. By combining our results with previous work, we show that low viscosity leads to elevated carbonate liquid mobility, but that ascent rates are low when appropriate rock parameters are taken into account. The results provide improved understanding of carbonatite liquid migration in the mantle.

2. Experimental methods

The starting material used in this study is anhydrous Na2CO3 (Puratronic®, purity of 99.997%) permanently stored in a desiccator to minimize contamination from moisture. A cylindrical graphite capsule with diameter of 1.2 mm and 2.0 mm of height was filled with the Na2CO3 crystalline powder. Except for the run at 4.6 GPa, we used double-layered probing sphere configuration (Terasaki et al., 2001) using a small cup filled with CaCO3 (calcite, Puratronic®, purity of 99.999%; Fig. 2) powder, which because of its higher melting T, delays the release of the probing sphere. Two small platinum spheres with diameter of 0.038–0.113 mm (Table 2) were placed in the center portion of the capsule and the lid, respectively. The capsule was then enclosed in a cell assembly, surrounded by a boron nitride (BN) outer capsule, graphite heater, MgO sleeve as pressure medium, ZrO2, a rounded boron epoxy gasket as thermal insulator, and a plastic (Lexan) ring. Details on the cell assembly used in this study can be found in Kono et al. (2014b). The in-situ viscosity measurements were performed using the falling sphere technique at 16 BM-B HPCAT beamline of the Advanced Photon Source (Argonne, Illinois, USA) (Kono et al., 2014b) equipped with the Paris-Edinburgh press (Besson et al., 1992; Klotz et al., 2004). The loaded cell was first compressed to the target pressure by a hydraulic system connected to the Paris-Edinburgh press. The pressure was monitored by the equation of state (EOS) of the Pt and MgO (Kono et al., 2010) determined both collecting X-ray diffraction patterns on the metal spheres and cell parts. After compression at 1.7, 2.4 and 4.6 GPa, the sample was heated quickly (~100 °C/s) and the temperature estimated using a power vs. temperature calibration curve reported by Kono et al. (2014b) and the melting temperature of CaCO3 and Na2CO3 (Irving and Wyllie, 1975; Li et al., 2017; Shatskiy et al., 2015; Suito et al., 2001). The temperature uncertainty is ± 50 °C similar to Kono et al. (2014b) due to combination of power vs T calibration and T change during sphere decent.

Experimental measurements of the viscosity were performed using unfocused white X-ray beam with radiographic images captured by a high-speed camera (Photron FASTCAM SA3) with 500 frames per second (f.p.s.) recording time. The radiographic images were collected during heating of the run until the fall of the sphere could be observed. Fig. 2 is a radiographic image showing the initial position of the Pt spheres in the middle part of the Na2CO3 starting sample, and inside the graphite cap at the top of the capsule embedded in CaCO3 powder. Because the melting T of calcite is higher than that of Na2CO3, this technique allows determination of the viscosity of the liquid at two different temperatures. In our run, the fall of the Pt sphere from the middle portion of the capsule never reached terminal velocity, likely owing to the initially slow heating when approaching the Na2CO3 melting temperature. Therefore, our results were obtained using the top Pt sphere. The falling sphere velocity, necessary to determine the viscosity using Stokes equation, was determined from the collected radiographic images with the Tracker plugin in the ImageJ software. The diameter of the Pt spheres was measured by X-ray radiography using a high-resolution camera with a pixel size of 0.945 mm (0.850 mm for the run at 4.6 GPa) per pixel (Kono et al., 2014b). Viscosities were calculated from the falling sphere velocity determined from the radiographic images (500 f.p.s.) and Stokes law,

\[
\eta = \frac{g d^2 (\rho_0 - \rho_l) F}{18u E}
\]

where \( g \) is the gravitational acceleration, \( d \) is the diameter of the sphere determined from radiographic images (pixel resolution of 0.850 and 0.945 μm/pixel), \( Z \) is the total height of the molten sample (i.e. height of the capsule of 2 mm). A fixed value of 2 g cm\(^{-3}\) was chosen for the density of molten Na\(_2\)CO\(_3\) (Liu and Lange, 2003); however, a difference up to ± 1 g cm\(^{-3}\) (an extreme case) would not produce any considerable effect on the calculated viscosity being this < 0.001 Pa s. Importantly, whether the two compositions (starting material and calcite) should mix, this would not interfere with the initial composition of our liquid due to the low fractions involved (< 10 vol%), and the short duration of the experiment (Table 2). However, we cannot exclude that softening/melting of Na\(_2\)CO\(_3\) triggered softening/melting of calcite at lower temperature than expected. For this reason, our viscosity results are strictly applicable to temperatures at which both Na\(_2\)CO\(_3\) and CaCO\(_3\) are molten at the estimated pressure. Finally, experiments were quenched by shutting down the electrical power to the heater.

![Fig. 2. Radiographic image showing the location of the two Pt spheres in the experiment at 1.7 GPa.](image)
Table 2: Parameters for viscosity calculations.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Pt sphere Ø (mm)</th>
<th>Falling Time (s)</th>
<th>Terminal velocity (mm/s)</th>
<th>Viscosity (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>1.7</td>
<td>1200</td>
<td>0.091</td>
<td>0.17</td>
<td>12.71</td>
<td>0.0049 (± 0.0001)</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>1400</td>
<td>0.038</td>
<td>0.22</td>
<td>4.5</td>
<td>0.0028 (± 0.0001)</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>1300</td>
<td>0.113</td>
<td>0.12</td>
<td>13.02</td>
<td>0.0073 (± 0.0001)</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>1700</td>
<td>0.135</td>
<td>0.17</td>
<td>20</td>
<td>0.0045 (± 0.0000)</td>
</tr>
</tbody>
</table>

3. Results

Run conditions and results are summarized in Table 2. Fig. 3 shows radiography images of the falling sphere with elapsed time for the run at 2.4 GPa and 1300 °C. The rapid sphere decent in these experiments narrows the terminal velocity region in the charge, thereby reducing the uncertainty in the determined viscosities to ± 0.0001 Pas (one sigma), which is lower than that of Kono et al. (2014a, 2014b) (Fig. S2, S4 and S8 of Supplementary Materials). With this uncertainty, the determined Na₂CO₃ melt viscosities are 0.0049 Pas at 1200 °C and 1.7 GPa, 0.0073 Pas at 1300 °C and 2.4 GPa, and 0.0045 Pas at 1700 °C and 4.6 GPa. At 1.7 GPa and 1400 °C, we obtained a viscosity of 0.0028 Pas based on the fall of another small sphere attached at the top of capsule at higher temperature of 1400 °C, which confirms that the increase of temperature decreases the viscosity of molten carbonates.

4. Discussion

4.1. Effect of pressure and temperature on the viscosity of molten carbonates

Viscosity data obtained in this study using the in-situ falling sphere technique can be compared with the viscosity determined from previous studies on different carbonate compositions. Table 1 summarizes all the results on viscosity of different molten carbonates available in literature. As illustrated in Fig. 4, our results at 1200–1700 °C and 1.7–4.6 GPa yield viscosities of ~0.003 to ~0.007 Pas, which are comparable to or lower than all previous results obtained at high pressure and temperature. In particular, runs at 1.7 GPa/1200 °C and 2.4 GPa/1300 °C fall within the range of 0.0047–0.0069 Pas measured at ambient pressure on molten Na₂CO₃ by Di Genova et al. (2016) (Fig. 4a) using an improved rheometer capable of performing measurements under controlled CO₂-rich atmosphere. This interval also includes the viscosity data for molten calcite by Kono et al. (2014a) at pressures between 0.9 and 6.2 GPa where almost no pressure dependence was observed, and that of K₂Mg(CO₃)₂ of 0.006 at 5.5 GPa and 1200 °C proposed by Dobson et al. (1996) although likely overestimated. The lowest viscosity of 0.0028 Pas was determined at 1.7 GPa and 1400 °C for Na₂CO₃ liquid, even lower than the viscosity of K₂CO₃ liquid measured at ambient pressure (Di Genova et al., 2016), as well as the viscosity data at 4.6 GPa/1700 °C (0.0045 Pas) that also falls below the viscosity trend at ambient pressure. The high viscosities reported by Dobson et al. (1996) for K₂CO₃, K₂CO₃-MgCO₃ and K₂CO₃-CaCO₃ melts, and by Wolff (1994) Ca-carbonatite, although overestimated, likely still indicate a strong temperature dependence for these compositions (Fig. 4b). The viscosity of K₂CO₃ at 1 atm pressure by Di Genova et al. (2016) is 1 order of magnitude lower (0.004 Pas) at 1 atm and 910–930 °C than that determined by Dobson et al. (1996; 0.023 Pas at 4 GPa and 1500 °C). It is possible that viscosities of Dobson et al. (1996) are up to one order of magnitude higher because of the limitation in the in situ falling sphere velocity measurements using early synchrotron X-ray techniques and slower recording rates (40 f.p.s. versus the latest falling sphere viscosity measurements at 1000 f.p.s.; Kono et al., 2014a, 2014b); however, this conclusion should be tempered by the absence of more recent measurements on the same compositions. Although we decided to show previous data by Dobson et al. (1996) (Fig. 4a–b and Fig. 5), their results are somehow overestimated.
and will not be used for fitting.

Fig. 4b shows the effect of temperature on the viscosity, as determined in this and previous studies. The decrease of the viscosity is a common feature clearly observed in all compositions investigated to date. It is notably difficult to collect isobaric data due to the pressure effect on the melting temperature of solid carbonate, and the effect that heating has on the cell assembly itself, which results in a change of the nominal target pressure. In any case, the viscosity determined at 1.7 GPa decreases from 0.005 to 0.003 Pa·s within about 200 °C. Interestingly, these data along the extrapolated trend of viscosity of both Li$_2$CO$_3$ and Na$_2$CO$_3$ melts reported by Di Genova et al. (2016). A gradual decrease in viscosity is observed from 800 to 1550 °C, regardless of compositional differences. These trends (highlighted in Fig. 4b with the red arrows) are consistent with the negligible role played by the pressure resulting from the relatively constant interatomic distances, as inferred for calcite and dolomite melts (Kono et al., 2014a; Hudspeth et al., 2018).

Fig. 5 compares viscosities from our experiments with data from the literature in terms of the logarithm of viscosity vs. reciprocal absolute temperature, to allow fitting to the Arrhenian relation,  

$$\eta = \eta_0 \exp \left( \frac{E_a + P V_a}{R(T - T_0)} \right)$$  

(4)

where $\eta$ is the viscosity in Pa·s, $E_a$ and $V_a$ are the activation energy (kJ·mol$^{-1}$), and the activation volume (cm$^3$·mol$^{-1}$), $\eta_0$ and $T_0$ the viscosity (Pa·s) and temperature (Kelvin) at reference condition, respectively, and T is the absolute temperature in Kelvin. Our data were fitted along with those for Na$_2$CO$_3$ collected at ambient pressure (Di Genova et al., 2016) by fixing the $E_a$ at 28 kJ·mol$^{-1}$ (i.e. assuming no pressure effect on the activation energy) and setting the other variables unconstrained. We obtained the following parameters $\eta_0 = 0.0065$ Pa·s, $E_a = 28$ kJ·mol$^{-1}$, $V_a = 54.52$ cm$^3$·mol$^{-1}$ and $T_0 = 1496$ K as best fitting with a misfit of less than ± 0.001 Pa·s for runs at 1.7 GPa/1200 °C and 2.4 GPa/1300 °C, ± 0.002 Pasm for runs at 4.6 GPa/1700 °C, and ± 0.003 Pa·s for runs at 1.7 GPa/1400 °C. It can be noted that both activation energy and activation volume are lower than those obtained by Kono et al. (2014a) of 305 kJ·mol$^{-1}$ and 179 cm$^3$·mol$^{-1}$, respectively, likely as result of the different behavior of the liquid alkali carbonates with respect to calcite and dolomite melts as consequence of the effect of the ionic radius on the viscosity of molten carbonates (Di Genova et al., 2016). Finally, when our data are fitted with a pressure-independent equation with A and B fitting parameter of ~ 2.862 and 804, respectively, this still reproduces well the results both at ambient pressure and high pressure within ± 0.0025 Pas.

As shown in Fig. 5, therefore, two main trends of viscosities for molten carbonates can be distinguished, mostly resulting from the different activation energy, one including Na-carbonates, and a second one including calcite, dolomite and K-Ca and K-Mg carbonate solid solutions. In contrast with the common viscosity trend exhibited by silicate liquids (Dingwell, 2006; Giordano et al., 2006), which varies within 3–4 orders of magnitude, Fig. 5 shows variations in viscosity that are smaller than 0.4 log unit for each proposed trend corresponding to a difference of < 0.005 Pa·s, well within the field of ultralow viscosity for carbonatitic melts. Further, our results appear consistent with the low viscosity measured on liquid NaCl and KCl ranging between 0.001 and 0.0027 Pa·s (Kono et al., 2013), and this can be explained as consequence of the ionic nature of carbonate liquids.

4.2. Migration rate of carbonatitic melts from the mantle source rock

The presence of small volumes of carbonatitic melts (< 0.1% in volume; Dasgupta et al., 2013) in the Earth’s upper mantle has been subject of several studies aimed at understanding the origin of seismic anomalies detected beneath mid-ocean ridges. Such studies were based mainly on electrical conductivity experimental models (Gaillard et al., 2008) and geophysical interpretations of the seismic anisotropy near ridge axis (Gu et al., 2005; Dunn et al., 2001; Evans et al., 1999) that show evidence of the possible presence of carbonatitic melts formed by partial melting of a carbonated garnet peridotite (Salters and Hart, 1989) anticipating the formation of large fractions of mid ocean-ridge basalts (MORBs).

Experimental studies in the last decades investigated the origin of CO$_2$-melts both in natural and synthetic simplified systems representative of either carbonated peridotite or eclogite mineral assemblages (Hammouda and Keshav, 2015, and references therein). The composition of quenched near-solidus melts ranged between 35 and 45 wt% CO$_2$ and ~zero (pure dolomitic melts) and 10 wt% SiO$_2$ in a pressure range of 3–27 GPa and temperatures representative of either the mantle adiabat or thermal regimes of various subducting slabs from 800 to 1800 °C. As these small melt fractions form when the local carbonated mantle rock crossed the appropriate mantle adiabat under redox conditions buffered by the surrounding silicate minerals at the carbon-carbonate level (EMOD; Eggler and Baker, 1982; Stagno and Frost, 2010), it is likely that near-solidus melts are stable within a certain depth depending on the availability of diamonds to oxidise to molten carbonate and their rheological properties before evolving towards more silica-rich melts during their ascent (Stagno et al., 2013; Stagno et al., 2015).

Following Kono et al. (2014a, 2014b), we can use our data to model the mobility and migration rate of carbonatitic melts at upper mantle conditions and estimate the difference of the obtained results for both molten carbonate of Na$_2$CO$_3$ and alkali earth metal carbonates (e.g. molten calcite and dolomite). The migration rate was calculated using the equation,  

$$\phi_0 = \frac{k a}{\eta}$$  

(5)

with,  

$$k = \frac{a^2 \phi a}{C}$$  

(6)

where k is the permeability, a is the characteristic grain diameter, $\phi$ is the melt fraction, while n (equal to 2) and C (equal to 1600) are numerical constants, g is the gravitational acceleration constant, and $\phi_0$ is the melt ascent velocity. This leads to an average mobility, $\phi_0$, of carbonatitic melts obtained in this study varying between of ~70 and
confirm Arrhenian behavior, highlighting the important effect of the alkali elements on the rheology of molten carbonates at upper mantle conditions. We find that, molten Na$_2$CO$_3$ provides a valid analogue for investigating the rheology of carbonatitic magmas at high pressure, and can help to better understand the role of alkali on the migration rate of CO$_2$-rich magmas at mantle conditions. The relatively low ascent rate of carbonatitic melts is consistent with the presence of low seismic velocity zones detected beneath mid-ocean ridges, as well as their presence as melt inclusions in lithospheric fibrous diamonds.

Acknowledgments

V.S. gratefully acknowledges financial support from PRIUS program (GRC, Ehime University) and the Deep Carbon Observatory. This work was performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operation is supported by DOE-NNSA under Award No. DE-NA0001974, with partial instrumentation funding by NSF. The Advanced Photon Source is a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Y.K. acknowledges the support of DOE-BES/DMSE under Award DE-FG02-99ER45775 and support by the National Science Foundation under Award No. EAR-1722495. An early version of this manuscript benefited from critical comments by Michele Lustrino. We thank two anonymous reviewers for their constructive comments.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.09.036.

References


300 g·cm$^{-3}$·Pa$^{-1}$·s$^{-1}$ using our P-dependent fitting parameters to Eq. (4) (including the 1-atm data by Di Genova et al., 2016) for alkali carbonatitic melts and assuming $\Delta$ (density of the solid mantle-density of pure carbonatitic melt) equal to 0.3–0.6 g·cm$^{-3}$ at the lithosphere-asthenosphere boundary up and 1.3 g·cm$^{-3}$ in the oceanic lithosphere, respectively (Hudspeth et al., 2018; Li et al., 2017). The calculation using Eq. (5) and Eq. (6) results in the melt ascent velocity between $\sim$330 m/yr and 1450 m/yr using a of 5 mm and melt fraction of 0.01% in volume (Keller et al., 2017) over the investigated density range. These values are higher than those obtained by Kono et al. (2014a, 2014b) of $\sim$80–115 m/yr for CaMg(CO$_3$)$_2$ melts owing to the different calculated mobility (i.e. the lower viscosity) and material parameters.

It has been generally proposed that most of the upper mantle would fall in the stability field of diamond due to the limited amount of oxygen with depth required to stabilize carbonate minerals and melts (Stagno and Frost, 2010; Stagno et al., 2015; Woodland and Koch, 2013). The oxidation of diamonds (C) to carbonate (CO$_2$) with consequent melting can only occur as result of the oxygen provided by the surrounding Fe-bearing garnet peridotite during asthenospheric convection at about 120 km beneath mid-ocean ridges (Stagno et al., 2013). This process of redox melting is summarized in Fig. 6, and it has likely occurred over the last 3.8 Gy of Earth history (Aulbach and Stagno, 2016), even at shallower depths in response of the varying mantle thermal regime. Diamond oxidation therefore plays a major role in modulating the exchange of carbon from the interior to the atmosphere. Our results show that once carbonatic melts are generated in the upper mantle, their stability is strongly controlled by both the local oxygen fugacity and the mobility at the time when the melt is still penetrating the source rock, prior than being in an open conduit. This relatively slow migration rate resulting from the density contrast between the mantle rock source and carbonatitic melts is a precondition that allows linking seismic anomalies with the presence of small degree of partial melts.

5. Conclusions

We determined the viscosity of molten Na$_2$CO$_3$ at 1.7, 2.4 and 4.6 GPa, at temperatures of 1200 °C–1700 °C to be 0.0028 to 0.0073 Pas. Our results agree with data from previous studies of molten calcite and Na$_2$CO$_3$ (Kono et al., 2014a; Di Genova et al., 2016), and

Fig. 6. Artistic representation of the redox melting of a diamond (or graphite) bearing garnet peridotite (photo courtesy of S.D. Jacobsen from the webpage http://sites.northwestern.edu/jacobsen/research-3/garnet/∗∗∗) chosen to represent the upper mantle by which carbonatitic melts can form and migrate upward though the hosting rock.


