Determination of calcium carbonate and sodium carbonate melting curves up to Earth's transition zone pressures with implications for the deep carbon cycle

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ABSTRACT

Melting of carbonated eclogite or peridotite in the mantle influences the Earth's deep volatile cycles and bears on the long-term evolution of the atmosphere. Existing data on the melting curves of calcium carbonate (CaCO_3) and sodium carbonate (Na_2CO_3) are limited to 7 GPa and therefore do not allow a full understanding of carbon storage and cycling in deep Earth. We determined the melting curves of CaCO_3 and Na_2CO_3 to the pressures of Earth's transition zone using a multi-anvil apparatus. Melting was detected *in situ* by monitoring a steep and large increase in ionic conductivity, or inferred from sunken platinum markers in recovered samples. The melting point of CaCO_3 rises from 1870 K at 3 GPa to ~ 2000 K at 6 GPa and then stays within 50 K of 2000 K between 6 and 21 GPa. In contrast, the melting point of Na_2CO_3 increases continuously from ~ 1123 K at 3 GPa to ~ 1950 K at 17 GPa.

A pre-melting peak in the alternating current through solid CaCO_3 is attributed to the transition from aragonite to calcite V. Accordingly the calcite V-aragonite-liquid invariant point is placed at 13 ± 1 GPa and 1970 ± 40 K, with the Clapeyron slope of the calcite V to aragonite transition constrained at ~ 70 K/GPa. The experiments on CaCO_3 suggest a slight decrease in the melting temperature from 8 to 13 GPa, followed by a slight increase from 14 to 21 GPa. The negative melting slope is consistent with the prediction from our *ab initio* simulations that the liquid may be more compressible and become denser than calcite V at sufficiently high pressure. The positive melting slope at higher pressures is supported by the *ab initio* prediction that aragonite is denser than the liquid at pressures up to 30 GPa.

At transition zone pressures the melting points of CaCO_3 are comparable to that of Na_2CO_3 but nearly 400 K and 500 K lower than that of MgCO_3 . The fusible nature of compressed CaCO_3 may be partially responsible for the majority of carbonatitic melts found on Earth's surface being highly calcic. It also provides a plausible explanation for low-degree melts

38 of carbonated silicate rocks being particularly calcic at these depths. The melting curves of
39 CaCO_3 and Na_2CO_3 overlap with the estimated ocean-island geotherm at transition zone
40 pressures, indicating that carbonatitic melt is readily generated from multi-component carbonate
41 systems in the transition zone. The occurrence of such melt between the 410 and 660 km depths
42 may facilitate the formation of ultradeep diamonds, produce low-velocity regions within the
43 transition zone, and create a barrier to carbonate subduction into the lower mantle.

1. Introduction

Carbonates are common rock-forming minerals in the Earth's crust and act as sinks of atmospheric CO₂, which is released from the mantle through volcanism. Subduction of hydrothermally altered oceanic lithosphere returns carbon to the interior, where more than three quarters of Earth's carbon is stored (Dasgupta et al. 2013, Chen et al. 2014). Carbonate melts have distinct physical and chemical properties and therefore play unique roles in mantle processes. The presence of low-degree carbonatitic melt may be responsible for the enhanced electric conductivity of the asthenosphere (Gaillard et al. 2008). Chemically reactive and highly mobile carbonatitic melt or C-H-O fluid may have facilitated the growth of diamonds, including the ultradeep diamonds from the transition zone or lower mantle (Pearson et al. 2014). Carbonate melt is buoyant with respect to the surrounding mantle and therefore melting of carbonates may create a barrier to carbon subduction into the deep Earth (Thomson et al. 2016). Given the profound influences of carbonate melting on mantle properties and dynamics, understanding the melting behavior of carbonated rocks is important for interpreting geophysical observations and elucidating the Earth's geochemical cycles.

Previous studies showed that the majority of carbonatitic melts found at the Earth's surface are highly calcic (e.g., Hammouda 2015), and that low-degree melts of alkali-free carbonated silicate rocks are particularly calcic at transition zone pressures (Keshav and Gudfinnsson 2010, Keshav et al. 2011). The origins of calcium enrichment in these melts are not well understood. Moreover, the reported solidus temperatures of carbonated silicate rocks vary considerably among different studies. For example, the solidus temperature of carbonated eclogite at 15 GPa spans more than 300 K range (Litasov and Ohtani 2010, Keshav and Gudfinnsson 2010, Grassi and Schmidt 2011, Kiseeva et al. 2013). In order to understand

67 complex carbonate systems, it is desirable to seek insights from the melting behavior of pure
68 carbonates.

69 Dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnesium carbonate (MgCO_3) and calcium carbonate
70 (CaCO_3) are dominant ingredients in most carbonatites, kimberlites, and carbonated peridotite or
71 eclogite (Litasov and Ohtani 2010, Keshav et al. 2011). In subducted slabs MgCO_3 and CaCO_3
72 may persist beyond the 300 km depth or 9 GPa because of their high melting points (Dasgupta et
73 al. 2013). The melting point of MgCO_3 has been tightly constrained at 2.7 to 3.6 GPa (Irving and
74 Wyllie 1975) and loosely bracketed at 8 and 15 GPa (Katsura and Ito 1990). Tight constraints on
75 the melting curve of CaCO_3 are limited to 7 GPa (Suito et al. 2001, Spivak et al. 2012, Shatskiy
76 et al. 2015). At elevated pressures and/or temperatures, CaCO_3 undergoes a series of structural
77 transformations. The boundary between calcite V and aragonite has been investigated between 1
78 bar and 6 GPa but remains uncertain at pressures above 2 GPa (Suito et al. 2001, Shatskiy et al.
79 2014, Shatskiy et al. 2015). The pressure and temperature of the invariant point among calcite V,
80 aragonite, and liquid are still controversial (e.g., Shatskiy et al. 2014).

81 Sodium carbonate (Na_2CO_3) dissolves in ambient humidity and hence its natural
82 occurrence is rare. The mineral natrite was found in Lovozero massif of Kola Peninsula in Russia
83 (Semenov 1972). Moreover, Na_2CO_3 represents a major constituent of rare minerals nyerereite
84 ($(\text{Na},\text{K})_2\text{Ca}(\text{CO}_3)_2$) and gregoryite ($(\text{Na},\text{Ca},\text{K})_2\text{CO}_3$), which were found in Oldoinyo Lengai
85 natrocarbonatite (Zaitsev and Keller 2006) and in the natrocarbonatite tephra of Kerimas volcano
86 in Tanzania (Hay 1983). At mantle pressures, sodium carbonate is stable in the subsolidus
87 assemblages of carbonated oceanic lithosphere (e.g., Kiseeva et al. 2013, Thomson et al. 2016).
88 Data on the melting curve of Na_2CO_3 are sparse and limited to pressures between 1 bar and ~0.4
89 GPa (van Groos et al. 1990), and one set of constraints at 6 GPa (Shatskiy et al. 2015).

In this study, *in situ* and quench experiments were conducted to investigate the melting behavior of CaCO_3 and Na_2CO_3 up to transition zone pressures, and to obtain constraints on the phase boundary between calcite V and aragonites. *Ab initio* simulations were performed to investigate the structures and compare the densities as a function of pressure of calcite V, aragonite, and liquid CaCO_3 . The melting behavior of individual carbonates was applied to understanding the occurrence and composition of carbonatitic melts, which bear on the genesis of ultradeep diamond, the origin of low-velocity zone, and the deep carbon cycle.

2. Method

2.1. Experimental Methods

Two types of measurements were performed for melting point determination. With the *in situ* conductivity method, melting was detected on the basis of a steep and large rise in the ionic current through the sample (Li and Li 2015). With the *ex situ* marker method, melting was inferred from sunken dense markers in the recovered experimental product. Marker experiments were carried out at moderate pressures to double-check the results of the *in situ* experiments.

High-pressure experiments were conducted using the multi-anvil apparatus at the University of Michigan, as described in Li and Li (2015). Experiments at pressures up to 10 GPa used Fansteel tungsten carbide (WC) cubes with 8 mm truncation edge length (TEL); Those at pressures up to 21 GPa used Toshiba-Tungaloy F-grade tungsten carbide cubes with 5 mm TEL (Fig. 1). Experiments at ambient pressure used the same octahedral cell assemblies as in the 8-mm multi-anvil experiments except that thermocouple, heater and WC cubes were excluded. The 1-bar cell assembly was placed inside a muffle furnace, with the sample temperature monitored through a type-K thermocouple in the furnace.

Fine powders of CaCO_3 (99.997%, Alfa Aesar 43073) and Na_2CO_3 sample (99.997%, Alfa Aesar 10861) were used as starting materials. The presence of water can significantly reduce the melting points of carbonates (Wyllie and Boettcher 1969). To minimize moisture, the sample was kept in a vacuum oven at less than ~ 3400 Pa, equivalent to 1 inch of mercury (inHg) pressure and 400 K for more than one week before loading into a cell assembly. The entire cell assembly was kept in the vacuum oven for 24 h before the experiment. To assess the influence of moisture, three control experiments were conducted, where the sample was exposed to 70-80% relative humidity for one day before the experiment.

The conductivity experiments used 0.1 VAC, 60 Hz probing voltage. In a typical high-pressure experiment, the sample was compressed to a target pressure and then heated at the rate of 1 K/s until melting was detected. It was subsequently cooled at a rate of 3 K/s or quenched to room temperature. Heating and cooling cycles were repeated up to three times before further compression to the next target pressure. In the experiment at ambient pressure, the furnace was heated at a rate of 0.3 to 1 K/s and cooled at a lower rate by turning off the power. Platinum (Pt) wire electrodes were enclosed in mullite tubing and exited through the observation hole on the furnace door.

In the conductivity experiments at high pressures, accurate determination of the sample temperature requires placing the thermocouple junction and the electrode tips at the same distance from the equator of the cylindrical heater. The recovered experimental products were inspected using a Leica microscope for the final placements of the electrode tips and thermocouple junction. Experiments that approached the ideal symmetric placement within 5% of the total heater length were included in further consideration.

The marker experiments used axial thermocouples and graphite capsules, with two 100 to 150-micron-sized Pt spheres placed near the top of the sample (Fig. 1b). At the target pressure, the sample was heated at a rate of 1 K/s to the target temperature, held for 10 min, and then quenched by shutting off the heating power. The experimental product was ground to reveal the Pt spheres, and inspected using a Leica microscope for the final positions of the spheres.

Selected products from the conductivity experiments on CaCO_3 and Na_2CO_3 and all the recovered samples from the marker experiments were analyzed using a Renishaw confocal Raman microscope to check for significant chemical contamination and identify polymorphic phase transformations.

The sample in a conductivity experiment is in direct contact with a four-bore alumina and the electrodes, and therefore subject to potential chemical contamination. All products from the conductivity experiments on CaCO_3 were examined for chemical contamination using the JOEL 7800FLV field emission scanning electron microscope and the CAMECA SX100 electron microprobe at the Central Campus Electron Microbeam Analysis Laboratory (EMAL) of the University of Michigan. We did not probe the Na_2CO_3 products because they were hygroscopic and turned into mush soon after exposure to ambient humidity.

2.2 Simulation Methods

We performed *ab initio* molecular dynamics simulations based on the density functional theory to study the structures and relative densities of calcite V, aragonite, and liquid CaCO_3 , using the Vienna *ab initio* simulation package (VASP, Kresse and Furthmüller 1996) with the generalized gradient approximation. Standard VASP PAW pseudopotentials were employed, which explicitly treated 10, 4, and 6 electrons for the Ca, C, and O atoms, respectively. The core radii were 2.30, 1.50, and 1.52 Å. The simulations used NVT ensembles and Nosé thermostat.

Large supercells with 48 formula units (240 atoms) were used throughout. The simulations employed a time step of 1.0 fs and lasted between 3 and 9 ps. The wave functions of valence electrons were represented in a plane-wave basis with an energy cutoff of 500 eV. The Brillouin zone was sampled with the Γ point. By performing a test calculation with a 2x2x2 k-point Monkhorst-Pack grid, we found that every element of the resulting stress tensor, and thus the pressure, differed by 0.01% or less from the Γ point results as is expected for large supercells. We thermalized the system using a standard procedure that uses the final positions and velocities of one long simulation of 30 ps to start new simulations at nearby density-temperature conditions. The resulting $P(\rho, T)$ relationships were smooth and showed no indication of a poor thermalization. The same VASP thermostat has been applied to over 10,000 simulations of various materials at high pressure and temperature before. The CaCO_3 system exhibited no unusual behavior, suggesting that the thermostat is functioning properly. To generate liquid configurations, we heated an initially solid configuration to 4000 K with MD simulations. Melting was detected by monitoring root-mean-squared displacements from the initial positions. The liquid simulation was then cooled down from 4000 K and one long simulation of 30 ps was performed for thermalization. No recrystallization occurred during this process. We tracked the diffusion of every atom species and confirmed that the atoms kept diffusing with time as expected for a liquid rather than a glass. Approximate values of the c/a and b/a ratios of the aragonite cells were obtained by relaxing the geometry at a constant cell volume at zero temperature. Similarly, we relaxed the calcite I structure to obtain an initial estimate for the c/a ratios of the calcite V structure. We then performed a number of independent simulations at 2000 K with slightly different c/a ratios and for all further simulations we selected the value that best

represented hydrostatic stress conditions. This increased the c/a ratio by 4% compared to the initial value.

3. Results and Discussion

3.1 Melting curve of CaCO_3 from in situ conductivity experiments

Five experiments yielded constraints on the melting temperatures of CaCO_3 between 3 and 21 GPa (Table 1). In each heating cycle a steep and large increase in the current was observed between 1800 K and 2100 K. The current increased by two orders of magnitude from a few μA to several hundred μA within about 20 K, and the change reversed upon cooling, at a temperature lower by 20 to 30 K (Fig. 2). Attributing the rise to melting and the reversal hysteresis to super-heating and super-cooling, we determined the melting points of CaCO_3 from the data collected during the heating cycles, following the previously established procedure (Li and Li 2015). Repeated heating cycles in a single experiment yielded results that are consistent within ± 5 K, whereas duplicate experiments reproduced the results within ± 40 K. Chemical analyses showed that the recovered samples remained pure CaCO_3 with the totals close to 99.95 wt.% and the Mg, Al, Si, Zr contents below the detection limits of 300, 200, 250, and 700 ppm, respectively.

The melting temperature of CaCO_3 first increases upon compression from ~ 1870 K at 3 GPa to ~ 2000 K near 6 GPa, and then stayed within 50 K of 2000 K between 6 and 21 GPa (Fig. 3). In the three control experiments on wet CaCO_3 a small current rise was observed at temperatures that were 200 to 300 K below the melting point of the dry samples, followed by shorting of the electrodes. By inspecting the recovered samples we found that the shorting occurred because the sample leaked out.

In some conductivity experiments, the positions of the thermocouple junction and electrode tips in the recovered products deviated from ideal symmetric placement by more than 5% of the total heater length. In these experiments, the measured melting temperatures were systematically offset by more than 100 K from the nearly symmetric experiments. The data from these asymmetric experiments were discarded. In several earlier conductivity experiments where tungsten (W)-rhenium (Re) wires were used as the electrodes and the probing voltage was set at 11.6 VAC, CaCO_3 reacted with electrodes to produce sheelite (CaWO_4), and the melting signal deteriorated in repeated heating cycles. In an experiment using Pt electrodes and 11.6 VAC probing voltage, needle-shaped CaAl_2O_4 crystals were found near the wall of the Pt container. The sample in one experiment was accidentally contaminated by ZrO_2 cement placed at the end of heater, producing anomalously low melting temperatures at pressures above 15 GPa. These experiments were excluded.

3.2 Melting points of CaCO_3 from marker experiments

Eleven experiments using Pt sphere markers and axial placement of type C thermocouple provide bounds on the melting temperatures of CaCO_3 at moderate pressures (Fig. 3b). The bracketed melting temperatures are generally 20 to 80 K lower than the results of the conductivity experiments. The offset towards lower values is not surprising because in the marker experiments the thermocouple junction was further away from the heater equator than the sample and therefore measured a lower temperature (Fig. 1b). With the Pt spheres and the thermocouple junction placed about 1.0 mm and 2.0 mm away from the heater equator, respectively, a temperature gradient of -20 to -80 K/mm between the heater equator and thermocouple junction can explain the small difference between the results of conductivity and marker experiments. This temperature gradient agrees well with the estimated values for similar

cell assemblies (Leinenweber et al. 2012). Reducing the separation between the sample and thermocouple junction can diminish such systematic bias. A limiting factor, however, is that the sample must be sufficiently long in order to allow unambiguous inference of melting from the initial and final positions of the Pt spheres.

Marker experiments conducted in the early stage of the study used radial placement of type C thermocouple, either around or through the heater. They gave temperature readings that were hundreds of degrees lower than indicated by the heating power, probably because the W-Re wires reacted with the sample. These experiments were abandoned.

3.3 Comparison with existing data on the melting curve of CaCO_3

Previous studies reported the melting points of CaCO_3 up to about 7 GPa (Fig. 3b). At 1 bar calcite I decomposes at 1173 K before melting (Baker 1962), and a nominal melting temperature of 1583 K is obtained by back-extrapolating the melting curve from higher pressures (Treiman 1995). The melting behavior of compressed CaCO_3 has been investigated up to 3.6 GPa using a piston-cylinder apparatus and by observing the texture of recovered samples (Irving and Wyllie 1975). The phase relations of CaCO_3 were further studied between 1 bar and 9 GPa using a multi-anvil press and combining *in situ* x-ray diffraction with Raman and x-ray diffraction analyses of retrieved samples (Suito et al. 2001). Constraints on the melting behavior of CaCO_3 at 6 GPa have been obtained through electron microprobe and Raman analyses of recovered products from multi-anvil experiments on various binary systems (Shatskiy et al. 2014). More recently, the stability of CaCO_3 melt was examined between 11 and 43 GPa using a diamond-anvil cell and *in situ* x-ray diffraction (Spivak et al. 2012).

Between 0.1 and 0.7 GPa CaCO_3 melts incongruently to produce CO_2 and a CO_2 -depleted liquid (Wyllie and Tuttle 1960). At higher pressures it melts congruently with the melting point

rising rapidly from 1700 K near 0.1 GPa to 1870 K at 3 GPa. The melting curve from this study passes through the tightly constrained melting points up to 3.6 GPa and is consistent with the existing bounds at higher pressures (Fig. 3b). For example, multiple studies agree upon the melting point of CaCO_3 at 6 GPa, which is placed at 2000 ± 40 K (this study), between 1873 and 1973 K (Shatskiy et al. 2014), and between 1903 and 2003 K (Suito et al. 2001). The recovered samples are calcite I and/or aragonite (Fig. 3b), confirming congruent melting between 3 and 21 GPa

3.4 Melting curve of Na_2CO_3

Three *in situ* conductivity experiments yielded constraints on the melting curve of Na_2CO_3 between 1 bar and 17.2 GPa (Table 1). The 1-bar result is in excellent agreement with the literature value at 1124 K (van Groos et al. 1990), and the high-pressure data are consistent with the existing bounds at 6 GPa (Shatskiy et al. 2015). The melting temperature of Na_2CO_3 increases steadily with pressure (Fig. 4). Fitting the melting curve to Simon's equation $(T/T_0)^c = (P - P_0)/A + 1$ yields $A = 0.30 \pm 0.01$ GPa, $c = 7.3 \pm 1.4$, with T_0 held at 1124 K at $P_0 = 0.0001$ GPa. The fitted curve agrees with the existing data between 1 bar and ~ 0.4 GPa (van Groos et al. 1990).

3.5 Phase boundary between calcite *V* and aragonite

In some conductivity experiments on CaCO_3 the current versus temperature profile at a given oil load showed a distinct peak at 100 K to 600 K below melting, where the current increased from a few μA to tens of μA within tens of degrees (Fig. 2). The pre-melting current rise was considerably smaller than that associated with melting, and it was not seen in the conductivity experiments on NaCl (Li and Li 2015) or Na_2CO_3 . As pressure increased, the pre-melting peak shifted to higher temperatures (Fig. 3a). Moreover, the signal was stronger at

intermediate pressures between 5 and 10 GPa, weaker at higher or lower pressures, and absent at pressures above 15 GPa.

The pressure-temperature conditions of the peaks generally coincided with the calcite/aragonite boundary between 5 and 8 GPa proposed by Suito et al. (2001), suggesting that the peak may be associated with the phase transition between calcite and aragonite. This interpretation is plausible given the unusual structure of calcite V, where the oxygen triangle in CO₃ group is not confined to specified lattice position but migrate along an undulated circular orbit about the carbon center, resembling that of a propeller (Ishizawa et al. 2013). This rotational motion introduces an additional degree of freedom into the structure, which may allow oxygen ions in CO₃ group to oscillate under external alternating voltage, or it may increase the mobility of point defects that are generated via thermal vibration, thus giving rise to enhanced conduction. This motion is unique to calcite V, and therefore the pre-melting peak was missing at pressures below 5 GPa, where heating led to direct transition from aragonite to calcite I or calcite IV. The pre-melting peak was absent at higher pressures where aragonite was the only solid phase below the melting point. Between 13 and 15 GPa, the pre-melting peak was less prominent probably because the conduction enhancement across the aragonite to calcite transition was relatively small compared with the thermally induced increase in the ionic conductivity resulting from a growth in the defect population.

Attributing the pre-melting peak to the aragonite to calcite V transition, the triple point of calcite V, aragonite, and liquid is placed at 13 ± 1 GPa and 1970 ± 40 K, and the Clapeyron slope of the calcite V to aragonite boundary is estimated at 70 K/GPa. The trends formed by the data from the 8-mm and 5-mm experiments appear to differ slightly, but they can be brought into agreement when the pressure uncertainties of ± 1 GPa are taken into account (Fig. 3a).

The relatively steep slope of the calcite V/aragonite boundary implies that the temperature of the transition between calcite V and aragonite increases significantly with pressure, which may explain why aragonite was recovered from most experiments above 7 GPa, whereas calcite I was recovered from lower pressures (Fig. 3b). The pressure-dependence of sample recovery suggested that, upon quench, the high-temperature phase (metastable liquid, glass, or calcite V) was able to transform to aragonite if the transition temperature was above 1600 K, but the transition to aragonite was kinetically hindered at temperatures below 1600 K. As a result, the high-temperature phase (glass or calcite V) persisted in its metastable structure at high pressures and 300 K, and eventually transformed to calcite I during decompression. Because no clear correlation was found between the recovered phase and the physical state of the sample before quench, our results do not support the proposal to infer melting from aragonite in the recovered sample, an idea that was derived from experiments at a single pressure of 6 GPa (Suito et al. 2001).

3.6 Density crossovers between solid and liquid CaCO_3

At pressures between 6 and 21 GPa, the melting curve of CaCO_3 is relatively flat and the melting point stayed within 50 K of 2000 K (Fig. 3a). The experiments indicate a slight decrease in the melting temperature from 8 to 13 GPa, followed by a slight increase from 14 to 21 GPa. The downward and upward trends of melting temperature as a function of pressure are better resolved by a series of measurements in each experiment, where the uncertainties in temperature are smaller within a single loading. The Clapeyron slope of the melting curve $dT/dP = \Delta V/\Delta S = T\Delta V/\Delta H$ is governed by the entropy of fusion ($\Delta S = S_{\text{liquid}} - S_{\text{solid}}$) and the volume of fusion ($\Delta V = V_{\text{liquid}} - V_{\text{solid}}$). Because melting of a single component is usually an endothermic process ($\Delta H > 0$), ΔS is positive. The sign of the melting curve slope is therefore determined by the ΔV term: A

positive sign implies that the liquid is less dense than the solid and vice versa. A sign change indicates a density crossover between the liquid and solid.

At 300 K, calcite I (space group R-32) undergoes a series of pressure-induced structural transitions to form aragonite (space group Pmcn), calcite II (space group P2₁/c) and calcite III (space group C2) near 1 bar, 0.4, 1.5 and 2 GPa, respectively (Suito et al. 2001), followed by a transition to post-aragonite (space group P2₁2₁2) at approximately 40 GPa (Ono et al. 2005). When heated at pressures slightly above 1 bar, calcite I transforms to calcite IV (space group R-3c) at 985 K and then to calcite V (space group R-3m) at 1240 K (Redfern and Angel 1999). Between 3 and 21 GPa, calcite V and aragonite are the solid phases involved in melting.

For pressures up to ~7 GPa, the melting curve slope is positive, indicating that the liquid is less dense than the solid. As pressure increases, the slope flattens and appears to turn negative near 8 GPa, indicating that the liquid may be more compressible and it becomes denser than the solid at this pressure. The higher compressibility of the liquid may reflect its structural freedom to gradually access the denser states that are possible in rigid crystal structures.. This interpretation is consistent with our theoretical calculations that predicted a pressure-induced density crossover between liquid and calcite V at 2000 K (Fig. 5). Near 13 GPa the melting curve changed from a slightly downward trend into a slightly upward trend, which likely indicates a transition in the solid to a denser polymorph and is readily explained by the formation of aragonite at the invariant point near 13 GPa (Fig. 5). This interpretation is consistent with the prediction from our *ab initio* simulations and that of Zhang and Liu (2015) that aragonite is denser than the liquid and therefore has a positive volume of fusion.

At 2000 K, the simulations predict a density crossover between calcite V and liquid near 17 GPa (Fig. 5). While it is encouraging the a crossover near 8 GPa is suggested by the

experimental results, the discrepancy in pressure needs to be resolved by future studies. Zhang and Liu (2015) proposed a pressure correction of -4.4 GPa to bring the GGA-based *ab initio* predictions of crystalline materials into better agreement with x-ray diffraction measurements. If one applied the pressure correction equally to both solid and liquid, then the discrepancy between our simulations and experiments would be reduced from 9 GPa to about 5 GPa. We attribute the discrepancy to approximations made in the *ab initio* simulations, which does not capture all exchange-correlation effects. While the statistical uncertainties in our calculated pressure are 0.1 GPa or less, the systematic errors could be as large as 3 to 7 GPa (Zhang and Liu 2015), which are larger than the experimental errors ($\pm 5\%$, or less than ± 1 GPa). Moreover, it is known that *ab initio* simulations can be performed for temperature-pressure conditions where structures are not thermodynamically stable. Structures do not melt or freeze unless one performs simulations way above or below the melting temperature. This means one can readily perform simulations for thermodynamically unstable solids and liquid but cannot detect the melting line in this way.

In contrast, the melting temperature of Na_2CO_3 rises continuously between 3 and 17 GPa along a smooth curve, by nearly 400 K. At pressures up to 9 GPa, Na_2CO_3 occurs in three polymorphs: The monoclinic γ phase at ambient condition transforms into the monoclinic β phase upon compression or heating, and subsequently to the hexagonal α phase at higher temperatures before melting (Shatskiy et al. 2015). The Raman measurements show that the starting material and recovered samples are the γ phase (Meekes et al. 1986). The smooth melting curve is consistent with the expectation that Na_2CO_3 remains in the β structure throughout the experimental pressure range of this study (Fig. 4)

4. Implications

The distinct melting curve of CaCO_3 offers insights into the behavior of carbonated silicate rocks under the deep mantle conditions. At low pressures, the melting points of MgCO_3 (Katsura and Ito 1990) and CaCO_3 are similar and considerably higher than that of Na_2CO_3 (Fig. 6). As pressure increases, the melting curve of CaCO_3 diverges from that of MgCO_3 and approaches that of Na_2CO_3 . Consequently, CaCO_3 becomes significantly less refractory than MgCO_3 and comparably fusible to Na_2CO_3 at transition zone pressures. The increasing separation between the melting points of CaCO_3 and MgCO_3 with depth may be partially responsible for the majority of carbonatitic melt found on Earth's surface being highly calcic (e.g., Hammouda et al. 2015). Furthermore, the fusible nature of CaCO_3 provides a plausible explanation for the particularly high calcic contents in low-degree melts of alkali-free carbonated silicate rocks, at pressures between 15 and 20 GPa for simplified carbonated peridotite compositions (Keshav et al. 2011), and between 12 and 16 GPa for simplified carbonated eclogite compositions (Keshav and Gudfinnsson 2010) (Fig. 6). On the other hand, Na_2CO_3 melts at lower temperatures than both CaCO_3 and MgCO_3 . This is consistent with the observation that sodic carbonate controls the melting temperatures of carbonated eclogite compositions (Litasov et al. 2013, Thomson et al. 2016).

At transition zone pressures, the melting curves of Na_2CO_3 and CaCO_3 overlap with the geotherm beneath ocean islands, suggesting that carbonate-rich melt may be readily generated at these depths. Carbonate systems are known to form either eutectics (e.g., Na-Ca-carbonate system) or minima (near dolomite composition), which are several hundreds of degrees lower than pure calcite, magnesite or Na-carbonate melting curves (Shatskiy et al. 2015). The overlap between the melting curves of Na_2CO_3 and CaCO_3 and the geotherm, therefore, suggest that carbonatitic melt is likely present in the transition zone. Commonly associated with diamond

formation, such melt provides the source materials as well as the mobility that enables rapid transport of diamonds through low-pressure and high temperature conditions where the metastable structure may be destroyed (Stachel and Harris 2009, Harte 2010, and references therein). The presence of carbonatitic melt in the transition zone, therefore, can facilitate the genesis of ultradeep diamonds, as indicated by the occurrence of hydrous ringwoodite inclusions (Pearson et al. 2014).

In addition, carbonatitic melt may offer an alternative mechanism to produce small-scale and sporadic low-velocity zones (LVZ) at the depth of 350 to 600 km, which have been attributed to hydrous melting resulting from reduced water storage capacity in mantle minerals in hotter regions (Vinnik and Farra 2006). If some of the LVZs are caused by carbonate-based melt, then their velocity variations reflect chemical heterogeneity rather than temperature differences. The two competing hypotheses may be resolved by examining the spatial distribution of the LVZs: Hydrous melting is expected to correlate with upwelling mantle plumes whereas carbonate melting may occur in both upwelling (Rohrbach and Schmidt 2011) and downwelling regions (Thomson et al. 2016).

Carbonatitic melt is buoyant in the mantle (Fig. 5) and its return from the transition zone to shallow depth, therefore, hinders further subduction of carbonates to the lower mantle (Grassi and Schmidt 2011, Thomson et al. 2016). The fate of subducted carbon, however, also depends on the redox condition. It has been shown that the stability of siderite FeCO_3 was strongly influenced by the oxidation state of the system (Tao et al. 2013, Kang et al. 2015). Moreover, previous studies suggested at depths greater than 250 km carbonates might be reduced by iron metal to elemental carbon or carbides, which melt at significantly higher temperatures; Conversely, carbon in reduced forms may rise to shallow depths through upwelling plume and

oxidize into carbonates (Rohrbach and Schmidt 2011). The feedback between the redox and melting processes, therefore, holds a key for understanding Earth's deep carbon cycle and evaluating its geochemical and geophysical consequences.

5. Conclusions

The melting curves of CaCO_3 and Na_2CO_3 have been determined through *in situ* conductivity and *ex situ* marker experiments up to 21 and 17 GPa, respectively. The melting point of CaCO_3 rises from 1870 K at 3 GPa to ~2000 K at 6 GPa and then stays within 50 K of 2000 K between 7 and 21 GPa. In contrast, the melting point of Na_2CO_3 increases continuously from ~1123 K at 3 GPa to ~1950 K at 17 GPa. Experimental data from this study place the calcite-aragonite-liquid triple point near 13 GPa and 1970 K. The calcite V/aragonite boundary is found to be linear within experimental uncertainties, with a slope of 70 K/GPa. Our *ab initio* simulations predict a pressure-induced density crossover between calcite V and the liquid, and that aragonite is denser than the liquid between 1 bar and 30 GPa. These predictions may explain the downward trend between 8 and 13 GPa and the upward trend between 13 and 21 GPa in the melting curve of CaCO_3 , as indicated by the experiments. The melting curve of Na_2CO_3 is consistent with the absence of subsolidus phase changes between 3 and 17 GPa.

As pressure increases, the melting point of CaCO_3 diverges from that of MgCO_3 (Katsura and Ito 1990) and becomes similar to that of Na_2CO_3 at Earth's transition zone pressures (Fig. 6). The fusible nature of CaCO_3 at the transition zone pressures may be partially responsible for the majority of carbonatitic melts being highly calcic (Hammouda et al. 2015), and for the particularly calcic composition of low-degree melts of alkali-free carbonated silicates (Keshav and Gudfinnsson 2010, Keshav et al. 2011). The melting curves of CaCO_3 and Na_2CO_3 overlap with the geotherm beneath ocean islands, suggesting that carbonate-rich melt likely occurs in the

transition zone and may facilitate the genesis of ultradeep diamond, cause seismic low-velocity zone, and create a barrier for carbonate subduction.

The melting curves of CaCO_3 and Na_2CO_3 will be useful for constructing a thermodynamic model to predict the melting behavior of complex mantle rocks in a wide pressure-temperature-composition space. New constraints on the compression behavior of liquid CaCO_3 and Na_2CO_3 can be derived through fusion curve analysis, in which the pressure dependent melting point is connected with the enthalpy and volume of fusion, as well as with the equation-of-state and heat capacity of the relevant solid and liquid phases, through thermodynamic relations (Liu et al. 2007). In particular, this study has extended the constraints on the melting curves of CaCO_3 and Na_2CO_3 from the pressures of the upper mantle (6 to 7 GPa) to that of the transition zone (17 to 21 GPa). The wider pressure ranges will allow tighter constraints on the pressure derivatives of the bulk moduli of the liquid carbonates, which are necessary for modeling mantle melting under a broad range of geological settings but difficult to determine by experiments.

In this study, the melting curve slope of CaCO_3 appears to change signs because of the relative compressibility of liquid versus solid and structural phase transitions in solid CaCO_3 . Theoretical calculations predicted diverse landscapes in the evolution of crystalline structure with pressure, some of which are already verified by experiments (Shatskiy et al. 2015). Future measurements of the melting curves of other alkali earth carbonates (MgCO_3 , BaCO_3 , and SrCO_3) and alkali carbonates (K_2CO_3 and Li_2CO_3) can help unravel the key parameters that govern the solid-liquid boundary in these systems. Systematic comparisons of the melting curves of carbonates with different cations may improve our understanding of how the charge and ionic

radius influence the chemical bonding and melting points, which in turn will help us construct more realistic models for the Earth's deep volatile cycles.

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582

Figure captions

Fig. 1 Experimental configuration and images of recovered samples. (a) Schematic configuration of the 5-mm assembly for melting point determination using the conductivity method. (b). Reflected-light optical images of the recovered sample from the 8-mm conductivity experiment M121713_8 showing symmetric placement of the electrode tips and thermocouple junction with respect to the sample (left), and that from the 8-mm marker experiment M121012_8 showing one Pt sphere remaining at the top of the sample (right). At the lower-right corner is a Raman map showing cavities (dark) amid aragonite (red).

Fig. 2 Representative current-temperature data at selected pressures. The data were collected during the heating cycles of the experiments M121713_8 (red), M042414_5 (blue), and M110113_5 (green), and during a cooling cycle of the experiment M110113_5 (black). Melting is located at the point of steep and large increase in the current along each heating path (black arrow). Smaller pre-melting peaks in the magnified traces (inset) were attributed to an increase in conductivity across the aragonite to calcite V transition.

Fig. 3 Melting curve and calcite V/aragonite boundary of CaCO_3 . (a) Data from conductivity experiments. The melting curve (black) is established by connecting the average of the melting points from multiple experiments (open circles) at each pressure. The calcite V to aragonite boundary (gray) is represented by a linear fit to the transition points indicated by the pre-melting peaks (open squares). (b) Data from marker experiments and Raman measurements of recovered samples. The melting curve from the conductivity experiments agrees well with the existing data up to 3.6 GPa (Irving and Wyllie 1975) and is consistent with the existing bounds at higher pressures (not shown are an upper bound at 8 GPa and 2273 K and a lower bound at 9 GPa and up to 1800 K, Suito et al. 2001). The calcite V to aragonite boundary from this study overlaps

with the previous constraint (dashed line, Suito et al. 2001). The bounds from the marker experiments in this study (upward and downward triangles) place the melting points at 20 to 80 K below the melting curve determined by the conductivity experiments, likely because the thermocouple junction is located at a colder position than the Pt marker spheres. The recovered samples from most marker experiments and two quenched conductivity experiments were aragonite (red open squares), with diagnostic Raman peaks at 180 and 209 cm^{-1} (Gillet et al. 1993). Only two molten and one solid samples from 6 GPa turned into calcite I (blue crosses) at ambient conditions, with a diagnostic Raman peak at 281 cm^{-1} (Gillet et al. 1993). Two other samples from 8.5 GPa ended up as mixtures of calcite I and aragonite (green cross-in-squares).

Fig. 4 Melting curve of Na_2CO_3 from *in situ* conductivity experiments. A Simon equation fit (black curve) to the measured melting points from this study agrees with the existing bounds at 6 GPa (Shatskiy et al. 2015). The boundary between the α and β phases (Shatskiy et al. 2015) likely intersects with the melting curve near 3 GPa.

Fig. 5 Simulations results on the density profiles of calcite V, aragonite, liquid CaCO_3 at 2000 K. In the second vertical axis V_0 is the volume of each polymorph (calcite V, aragonite, or liquid) at 1 bar and 2000 K. Five liquid (red open circles) and five calcite V (blue open triangles) simulations predict a pressure-induced density crossover between the two phases (cross).and find that aragonite (black open squares) is denser than the liquid between 1 bar and 30 GPa. Simulation results from Zhang and Liu (2015) are shown for comparison. Liquid CaCO_3 is expected to be buoyant in the mantle because it is less dense than basaltic melt (Sakamaki et al. 2013) and the ambient mantle as represented by the PREM model (Dziewonski and Anderson 1981).

628 **Fig. 6** Melting behavior of carbonates and carbonated silicate rocks in the Earth's mantle. The
629 largest separation between the melting curve of CaCO_3 and that of MgCO_3 (Irving and Wyllie
630 1975, Katsura and Ito 1990) occurs at the transition zone pressures, and roughly coincides with a
631 broad plateau in the $\text{Ca\#}$, defined as $\text{Ca}/(\text{Ca}+\text{Mg})$ in mol.%, of low-degree melts of the Ca-Mg-
632 silicate (CMS) and Ca-Mg-Al-silicate (CMAS) compositions (Keshav and Gudfinnsson 2010,
633 Keshav et al. 2011). The flat segment in the melting curve of CaCO_3 runs parallel to and slightly
634 above the flattened solidus curves of carbonated peridotite (Ghosh et al. 2014) and carbonated
635 eclogite (Kiseeva et al. 2013). The melting curves of CaCO_3 and Na_2CO_3 (this study) are higher
636 than the geotherms of hot slabs and ridges but overlap with that beneath the ocean islands (the
637 geotherms are from Dasgupta et al. 2013).

638

639

Table 1 Experimental results on CaCO₃ and Na₂CO₃

<i>P</i> ¹ , GPa	Melting <i>T</i> ² , K	Premelting, K	<i>P</i> ¹ , GPa	Melting <i>T</i> ² , K
CaCO₃			Na₂CO₃	
3.0	1867		1 bar	1123
4.4	1960		2.8	1544
5.8	2008	1438	4.2	1621
7.1	2023	1580	5.5	1694
7.9	2025	1669	7.0	1729
8.5	2011	1669	8.5	1793
9.0	2013	1782	9.9	1796
9.9	2012	1732	11.2	1854
11.2	1990		12.9	1849
12.9	1979	1893	14.2	1904
13.6	1972		17.2	1981
14.2	1965			
15.2	1979			
16.1	2001			
17.2	2005			
18.2	2002			
19.4	2029			
20.6	2038			
21.1	2068			

¹The pressure uncertainty is <2 GPa

²Average of multiple experiments (Table S1). Uncertainty is ±40 K.

640

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6