



# 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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## ARTICLE INFO

### Article history:

Received 10 May 2016

Received in revised form 1 October 2016

Accepted 15 October 2016

Available online 4 November 2016

Editor: B. Marty

### Keywords:

calcite V  
aragonite  
Clapeyron slope  
density crossover  
carbonatite  
subduction

## 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 ( $\text{CaCO}_3$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) 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  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$  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  $\text{CaCO}_3$  rises from 1870 K at 3 GPa to  $\sim 2000$  K at 6 GPa and then stays within 50 K of 2000 K between 6 and 21 GPa. In contrast, the melting point of  $\text{Na}_2\text{CO}_3$  increases continuously from  $\sim 1123$  K at 3 GPa to  $\sim 1950$  K at 17 GPa.

A pre-melting peak in the alternating current through solid  $\text{CaCO}_3$  is attributed to the transition from aragonite to calcite V. Accordingly the calcite V-aragonite-liquid invariant point is placed at  $13 \pm 1$  GPa and  $1970 \pm 40$  K, with the Clapeyron slope of the calcite V to aragonite transition constrained at  $\sim 70$  K/GPa. The experiments on  $\text{CaCO}_3$  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  $\text{CaCO}_3$  are comparable to that of  $\text{Na}_2\text{CO}_3$  but nearly 400 K and 500 K lower than that of  $\text{MgCO}_3$ . The fusible nature of compressed  $\text{CaCO}_3$  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 of carbonated silicate rocks being particularly calcic at these depths. The melting curves of  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$  overlap with the estimated ocean-island geotherm at transition zone pressures, indicating that carbonatitic melt is readily generated from multi-component carbonate systems in the transition zone. The occurrence of such melt between the 410 and 660 km depths may facilitate the formation of ultradeep diamonds, produce low-velocity regions within the transition zone, and create a barrier to carbonate subduction into the lower mantle.

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## 1. Introduction

Carbonates are common rock-forming minerals in the Earth's crust and act as sinks of atmospheric  $\text{CO}_2$ , 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, 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 car-

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bon 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., Woolley and Kjarsgaard, 2008), 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 complex carbonate systems, it is desirable to seek insights from the melting behavior of pure carbonates.

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

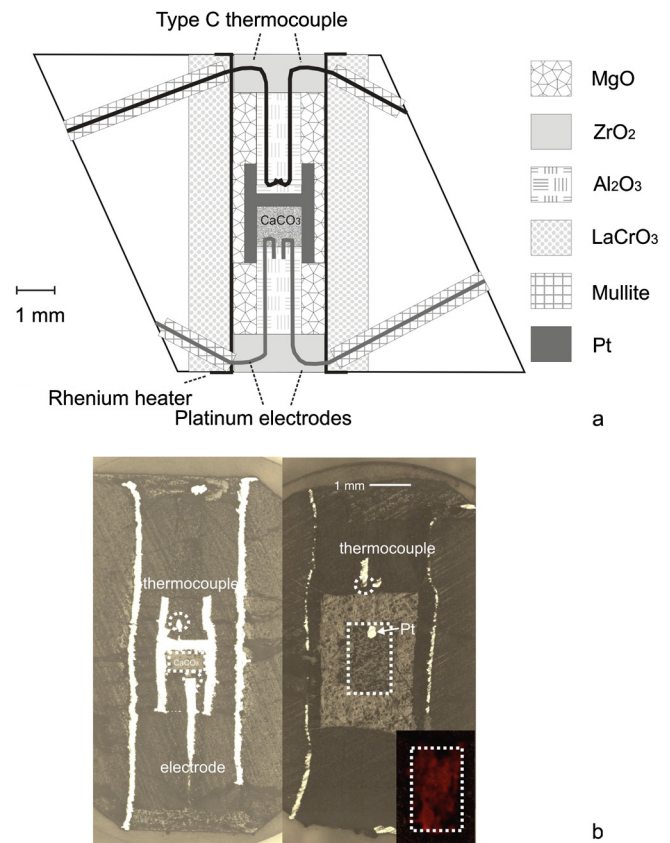
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) dissolves in ambient humidity and hence its natural occurrence is rare. The mineral natrite was found in Lovozero massif of Kola Peninsula in Russia (Semenov, 1972). Moreover,  $\text{Na}_2\text{CO}_3$  represents a major constituent of rare minerals nyerereite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



**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). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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  $\text{CaCO}_3$  (99.997%, Alfa Aesar 43073) and  $\text{Na}_2\text{CO}_3$  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  $\sim 3400$  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

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