The $\text{K}_2\text{CO}_3$ fusion curve revisited: New experiments at pressures up to 12 GPa

Meili Wang*,**, Qiong Liu*,**, Toru Inoue***, Baosheng Li**,†, Samuel Pottish†, Justin Wood†, Cuiping Yang*** and Renbiao Tao*,**

*Key Laboratory of Orogenic Belts and Crustal Evolution, MOE, Peking University, Beijing 100871, China
**School of Earth and Space Sciences, Peking University, Beijing 100871, China
***Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan
†Mineral Physics Institute, State University of New York, Stony Brook, New York 11794, USA

The melting temperatures of $\text{K}_2\text{CO}_3$ were experimentally determined to be $1220 \pm 20 \, ^\circ\text{C} (4.0 \pm 0.5 \, \text{GPa})$, $1290 \pm 10 \, ^\circ\text{C} (9.0 \pm 0.5 \, \text{GPa})$, and $1313 \pm 10 \, ^\circ\text{C} (11.5 \pm 0.5 \, \text{GPa})$ in a 2000 ton split-sphere apparatus and $1195 \pm 15 \, ^\circ\text{C} (5.0 \pm 0.5 \, \text{GPa})$ in a 1000 ton uniaxial split-cylinder apparatus. The fusion curves of $\text{K}_2\text{CO}_3$ were calculated up to ~12.0 GPa for various $K_0'$ (pressure dependence of bulk modulus) values of the liquid, according to the thermodynamic properties for crystalline and liquid $\text{K}_2\text{CO}_3$. On the basis of these experimental results and fusion curves of $\text{K}_2\text{CO}_3$, the $K_0'$ for liquid $\text{K}_2\text{CO}_3$ is constrained to be ~14.4 ± 1.1 at pressures lower than 5.0 GPa in a third-order Birch-Murnaghan equation of state (EOS). However, the results at pressures above 9.0 GPa deviate from this trend, which suggests a possible phase transformation in either the crystalline or liquid phase of $\text{K}_2\text{CO}_3$ between 5.0 and 9.0 GPa. Determination of liquid $K_0'$ allows the density of $\text{K}_2\text{CO}_3$ liquid to be calculated at high pressure. In comparison with other common carbonates, $\text{K}_2\text{CO}_3$ is shown to have the lowest melting temperature.

Keywords: $\text{K}_2\text{CO}_3$, Fusion curve, High pressure, Phase transition

INTRODUCTION

Research on potassium recycling in subduction zones has attracted considerable interest of geologists (e.g., Domnik and Holloway, 1996; Schmidt, 1996; Konzett and Fei, 2000). Mantle carbonatite melts with high-alkali contents have been reported by the studies of inclusions in fibrous diamonds (Navon, 1991; Sobolev et al., 1998; Zedgenizov et al., 2004; Hwang et al., 2006; Tomlinson et al., 2006; Klein-BenDavid et al., 2007). High pressure experiments on the partial melting of lithospheric mantle and subducted rocks indicate that near solidus melts of carbonated peridotite (Ghosh et al., 2009; Brey et al., 2011), carbonated eclogite (Dasgupta et al. 2004; Yaxley and Brey 2004; Litasov and Ohtani, 2010; Kiseeva et al., 2013), and carbonated pelite (Grassi and Schmidt, 2011a, 2011b) show strong alkali enrichment. Chemical analyses of erupted products from Oldoinyo Lengai volcano also show high alkali content at 15–19 wt% and 4–5 wt% for $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$, respectively (Keller et al., 2010).

As the first melt formed from carbonated mantle (Dalton and Presnall, 1998; Dasgupta et al., 2004; Brey et al., 2011; Grassi and Schmidt, 2011a), carbonatite melt is considered as an efficient agent for mantle metasomatism owing to its high reactivity, high mobility, and high concentrations of incompatible trace elements (e.g., Green and Wallace, 1988; Dalton and Wood, 1993; Yaxley et al., 1998). Minor amounts of $\text{K}_2\text{O}$ in the lithospheric mantle and subducted rocks can cause appreciable decreases in their solidus temperatures of 300 °C at 10 GPa for carbonated peridotites (Brey et al., 2011), 50–150 °C at 3–5 GPa for eclogites (Spandler et al., 2008), and 100–300 °C at 8 and 13 GPa for carbonated pelites (Grassi and Schmidt, 2011a). In addition, the high conductivities of carbonate melt containing alkalies in the asthenosphere are suggested to be responsible for the presence of low velocity zones (LVZ) at the top of the 410 km discontinuity (Gaillard et al., 2008; Sifre and Gaillard, 2012). Moreover, alkali carbonates can be used as
a medium for the formation of diamonds in the Earth’s mantle (Paliyano & al., 1999, 2002; Sokol & al., 2000). It is thus essential to understand the behavior of alkali carbonate liquids at mantle conditions, which has been discussed only in recent studies (Dobson & al., 1996; Liu & Lange, 2003; Liu & al., 2007; Litasov & al., 2013; Shatskiy & al., 2013a, 2013b). In the research of Litasov & al. (2013), the true solidi of Na–K-bearing carbonate systems at high pressure were determined, and the possibility of subducting alkaline carbonates melting at the transition zone was reported. Phase relations in simple binary carbonate systems such as K₂CO₃–MgCO₃ and Na₂CO₃–CaCO₃ have been studied by Shatskiy & al. (2013a, 2013b).

In this work, we examine the stability of a single alkali carbonate, K₂CO₃, at high pressure by using fusion curve analysis (Lange, 2003), which is a comparison of phase equilibrium experiments on the melting reaction of a mineral that melts congruently with the calculated melting reaction for that mineral obtained from measured thermodynamic properties. The density and compressibility of potassium carbonate at high temperatures and high pressures can also be obtained from this method. However, controversies remain for the equation of state of carbonate liquids at mantle conditions, which has been measured at pressures lower than 3.2 GPa.

Phase equilibrium experiments

Most of the high pressure melting experiments were performed in a Kawai-type multi-anvil apparatus at GRC, Ehime University, Japan. The experiments at 5.0 GPa were conducted in a 1000-ton uniaxial split-cylinder apparatus (USCA–1000) at MPI, Stony Brook University, USA. For the experiments conducted at GRC, we used a 14/8 cell assembly, including 14 mm octahedron and 8 mm truncated edge lengths of tungsten carbide, with a semi-sintered (Mg,Co)O octahedron as the pressure medium and a cylindrical graphite as the heater. The starting materials were loaded into a Pt can with inner and outer diameters of 1.6 mm and 1.8 mm, respectively, which was capped with a second Pt can of 1.8 mm and 2.0 mm inner and outer diameters, respectively, to create a sample capsule, as adopted in the work of Inoue and Sawamoto (1992). The average capsule length was designed to be 1.5–1.8 mm in length. In most experiments, two sample capsules containing starting materials were placed symmetrically in one cell assembly to directly double-check the position of the Pt bead described below. Temperatures were measured with a W₉₅Re₁₅–W₇₅Re₂₅ thermocouple, in which the hot junction was placed in the center of the furnace between the two capsules to monitor the sample temperatures; the error was ±5 °C over the temperature range of the experiments. For the experiments conducted at Stony Brook University, the cell assembly was quite similar to that used in Ehime University. The major difference was that only one Pt capsule ~ 4 mm in length sealed with an arc welder graphite pencil was used at Stony Brook University, whereas two Pt capsules sealed by high pressure were used at Ehime University.

In all experiments, the pressure was applied first to the target ram loads, and the temperature was then increased to the desired value. The temperature was kept for 30–40 min before the run was quenched by turning off the electric power supply to the graphite furnace.

The method of bracketing the melting temperature of K₂CO₃ at high pressure involves the placement of a small Pt bead on top of tightly packed crystalline K₂CO₃ powder in the Pt capsule (Liu & al., 2007). In addition, a thin layer of K₂CO₃ powder was packed on top of the Pt bead.
to separate the bead from the capsule. The capsule was carefully marked to indicate the up direction. After the high-pressure experiment, the recovered sample was polished longitudinally under dry conditions to identify the position of the Pt bead. As shown in Figure 1, if the sample is melted completely, the Pt bead will drop to the bottom of the capsule owing to the higher density of the Pt bead compared with that of the carbonate liquid and the low viscosity of K$_2$CO$_3$ liquid. The Pt bead will stay on top of the capsule if melting does not occur. The two experimental conditions thus provide a bracket for the melting temperature. Another scenario is that the Pt bead will be in the middle part of the capsule when the sample partially melts and a boundary between the crystal and the liquid phase exists. In such a case, the melting temperature of K$_2$CO$_3$ can be calculated on the basis of the thermocouple readings and the distances between the position of the thermocouple and the liquid/crystal texture boundary of the two experimental runs at a fixed pressure by assuming a constant temperature gradient at the same pressure.

**Pressure calibration and temperature gradient**

For the experiments conducted at GRC, pressure at a high temperature of ~1400 °C was calibrated on the basis of the high-pressure phase transformation of olivine (Akaogi, 2007), where the partitioning of Mg and Fe between olivine and wadsleyite or wadsleyite and ringwoodite were used to estimate the pressure. The compositions of the used pressure markers were (Mg$_{0.91}$Fe$_{0.09}$)$_2$SiO$_4$, (Mg$_{0.8}$Fe$_{0.2}$)$_2$SiO$_4$, or (Mg$_{0.3}$Fe$_{0.7}$)$_2$SiO$_4$ depending on the experimental pressures. In most experiments, the pressure marker was placed between the two capsules. For the experiments conducted at MPI, the pressure was calibrated on the basis of the phase equilibrium of quartz–coesite and coesite–stishovite (Zhang et al., 1993). The error of the pressure was estimated to be ±0.5 GPa.

The thermal gradients across the sample charges were examined by two different heights of boundaries between crystalline and liquid K$_2$CO$_3$ at the same pressure, according to its similar melting temperature at a fixed pressure (Fig. 1). However, this method was simply a rough procedure in which the radial thermal gradient was ignored. The thermal gradients were estimated to be about 47 °C/mm at 9.0 GPa and 64 °C/mm at 11.5 GPa. Moreover, Kyoko N. Matsukage (personal communication) estimated the thermal gradient at 1 bar to be 65 °C/mm by using a two-pyroxene thermometer (Gasparik, 1990) with results similar to those in our study. The thermal gradient was found to increase with increasing pressure. The thermal gradients at 4.0 and 5.0 GPa were not determined because the melting temperature of K$_2$CO$_3$ can be bracketed between 1210–1230 °C and 1190–1200 °C, respectively.

**THERMODYNAMIC CALCULATION OF THE FUSION CURVE**

The equation used to calculate the crystal–liquid equilibrium for K$_2$CO$_3$ as a function of temperature and pressure is

\[
\Delta H_{T_f} + \int_{T_f}^{T} \Delta C_p(T)\,dT - T\left(\Delta S_{T_f} + \int_{T_f}^{T} \frac{\Delta C_p(T)}{T}\,dT\right) = -\int_{P_t}^{P} \Delta V(P)\,dP
\]

where \(T_f\) is the one-bar melting temperature of crystalline K$_2$CO$_3$, \(\Delta H_{T_f}\) and \(\Delta S_{T_f}\) are the enthalpy and entropy differences between liquid and solid K$_2$CO$_3$ at \(T_f\), respectively, \(\Delta C_p(T)\) is the heat capacity of the liquid minus that of the solid, and \(\Delta V(P)\) is the volume of the liquid minus that of the solid (Lange, 2003). The data needed to calculate the fusion curve include: (1) the melting temperature of K$_2$CO$_3$ at 1 bar; (2) the enthalpy and the entropy of fusion at 1 bar; (3) the heat capacity of K$_2$CO$_3$ crystal and liquid; and (4) the volume, thermal expansivity, and compressibility of K$_2$CO$_3$ crystal and liquid. The values or equations for the thermodynamic properties used in Equation 1 which have been summarized by Liu et al. (2007), are listed in Table 1. In addition, the compressibility of the crystalline K$_2$CO$_3$ was obtained from unpublished theoretical data (S.A.T. Redfern, personal communication). An uncertainty of ±10% can lead to an uncertainty in the fusion temperature of ±50 °C or the \(K'_o\) value of ±1.3 at 5 GPa. Among the thermodynamic data required, the only unknown is the pressure dependence of the liquid bulk modulus: \(K'_o\).

For calculations of the fusion curve below 1 GPa, the \(K'_o\) value for the liquid can be neglected. However, in order to obtain accurate fusion curve of K$_2$CO$_3$ at high pressure (>1 GPa), the incorporation of the pressure dependence of the liquid and crystal compressibilities into the liquid and crystal volume expression in Equation 1 are required. In this study, the third-order Birch–Murnaghan equation of state (EOS), a truncated series expansion derived from finite-strain theory (Birch, 1978), was used to model the volume of K$_2$CO$_3$. The third-order form is

\[
P = \frac{3}{2}K_{T,0}\left[R^2 - R^1\right]^2\left[1 - \frac{3}{4}(4 - K'_o)\left(R^2 - 1\right)\right]
\]

where \(R = V_{T,0}/V_{T,0}\), \(V_{T,0}\) is the volume at temperature T.
Figure 1. Microphotographs of cut and polished charges for eight experiments that delineate the melting reaction at 4.0, 5.0, 9.0, and 11.5 GPa. The top four show the temperature of the thermocouple (TC) reading, the distance (average of seven positions) between the boundary and the position of the thermocouple junction, and the calculated melting temperature at a given pressure ($T_m = T_{TC} - \text{thermal gradient} \times \text{distance}$). The thermal gradient was roughly assumed to be linear with the distance. The error of the temperature gradient led to an uncertainty of ±1.0 in the calculated $K_0'$ value of K$_2$CO$_3$ liquid assuming a maximum thermal gradient of 80 °C/mm.
and zero pressure (1 bar), \( V_{TP} \) is the volume at temperature T and pressure P, \( K_{T,0} \) is the bulk modulus \( (K_{T,0} = 1/\beta_{T,0}) \) where \( \beta_{T,0} \) is the isothermal compressibility) at zero pressure, and \( K_0' \) is the pressure dependence of the bulk modulus at zero pressure.

Incorporation of the Birch-Murnaghan relation (Equation 2) into Equation 1 requires an integration that follows the method suggested by P. Asimow (outlined in the Appendix of Ghiorso et al., 2002), the resultant integral is shown by:

\[
\int V_{TP}^0 dP = PV_{TP}^0 - V_{T,0}^0 + \frac{9}{8} K_{T,0} V_{T,0}^0 (R^5 - 1)^2 \\
\times \left[ 1 + \frac{1}{2} (K'_0 - 4) \left( \frac{R^5}{R^5 - 1} \right) \right]
\]

Equation 3 allows the fusion curves of K\(_2\)CO\(_3\) to be calculated at high pressure for the liquid at various \( K_0' \) values.

**RESULTS**

**Experimental results**

All results of the high pressure experiments are summarized in Table 2. Photomicrographs of a selection of polished recovered samples are presented in Figure 1. Some of the recovered products from 9.0 to 11.5 GPa showed a distinct boundary between the crystal and the liquid, from which the melting temperature of K\(_2\)CO\(_3\) was calculated or bracketed according to the method discussed in the preceding section. The results indicate that the melting temperature of K\(_2\)CO\(_3\) was calculated or bracketed according to the method discussed in the preceding section. The results indicate that the melting temperature of K\(_2\)CO\(_3\) is 1220 ± 20 °C at 4.0 ± 0.5 GPa, 1195 ± 15 °C at 5.0 ± 0.5 GPa, 1290 ± 10 °C at 9.0 ± 0.5 GPa, and 1313 ± 10 °C at 11.5 ± 0.5 GPa. Shatskiy et al. (2015) reported that the melting temperature of K\(_2\)CO\(_3\) at 6 GPa is about 1425 °C, which is about 225 °C higher than those at 5 GPa determined in this study. Thus far, the difference has been difficult to explain. One possible reason is that Shatskiy et al. (2015) determined the melting of K\(_2\)CO\(_3\) from an image. In such a case, overestimation of the melting temperature is easy because of the unobvious difference between the separate melt and solid of K\(_2\)CO\(_3\). For the partially molten sample in the present study, the boundary between the crystal and liquid curve near the Pt bead exactly mimics the shape of the thermal gradient curve (e.g., OS2283 and OS2290), which proves the validity of our method of determining the melting temperature.

**Table 1. Summary of thermodynamic data used to calculate the K\(_2\)CO\(_3\) fusion curve**

| Parameter | Value | Reference |
|----------|-------|-----------|
| \( T_f \) | 1170 ± 2 K | Liu et al. (2007) |
| \( \Delta H_f \) | 27.6 ± 0.4 KJ/mol | Rolin and Recapet (1964) |
| \( \Delta S_f \) | 23.23 J/mol.K | Rolin and Recapet (1964) |
| \( C_p \) liquid | 231 J/mol.K | Rolin and Recapet (1964) |
| \( C_p \) crystal | 442.6 - 8914 \( T^{-0.5} \) + 34278267 \( T^{-2} \) - 5240000000 \( T^{-3} \) J/mol.K | Janz et al. (1963) and Liu et al. (2007) |
| \( V(T) \) crystal | 64.248 ± 0.0095 \( (T - 1078) \) cm\(^3\)/mol | Schneider and Levin (1973) |
| \( V(T) \) liquid | 71.50 + 0.01640 \( (T - 1100) \) cm\(^3\)/mol | Liu and Lange (2003) |
| \( \beta_T \) liquid | 14.2 + 0.0059 \( (T - 1100) \) \( 10^{-6} \) bar\(^{-1} \) | Zhu et al. (1991) and Liu and Lange (2003) |
| \( K_0 \) crystal | 45 GPa | Redfern, unpublished data |
| \( K' \) crystal | 4 | Redfern, fixed at 4 when calculating \( K_0' \) of crystal |

**Table 2. Experimental results for K\(_2\)CO\(_3\) melting reaction**

| Run | P (GPa) | \( T \) (°C) | Pt bead position |
|-----|--------|-------------|-----------------|
| OS2309 | 4 | 1130° | Top |
| OS2311 | 4 | 1180° | Top |
| OS2314 | 4 | 1210 | Top |
| OS2318 | 4 | 1220 | Middle |
| OS2316 | 4 | 1230 | Bottom |
| OS2298 | 4 | 1250 | Bottom |
| OS2296 | 4 | 1300 | Bottom |
| OS2295 | 4 | 1350 | Bottom |
| 832 | 5 | 1130 | Top |
| 4 | 5 | 1155° | Top |
| 833 | 5 | 1180° | Top |
| 836 | 5 | 1190 | Top |
| 834 | 5 | 1200 | Bottom |
| 6 | 5 | 1223 | Bottom |
| 5 | 5 | 1249 | Bottom |
| OS2265 | 9 | 1300 | Top |
| OS2283 | 9 | 1335 | Middle |
| OS2281 | 9 | 1350° | Middle |
| OS2259 | 9 | 1400 | Bottom |
| OS2271 | 11.5 | 1300 | Top |
| OS2267 | 11.5 | 1330 | Middle |
| OS2279 | 11.5 | 1340 | Middle |
| OS2290 | 11.5 | 1370 | Middle |
| OS2267 | 11.5 | 1400° | Bottom |

* TC broken.

The temperature is estimated from the relationship of power and resistance. Most of the melting temperature of K\(_2\)CO\(_3\) were determined by the successful experiments.
**$K_0'$ value for K$_2$CO$_3$ liquid at high pressure**

The experimental results that bracket the location of the K$_2$CO$_3$ fusion curve in the $P$-$T$ space are superimposed in Figure 2 on a family of fusion curves for different $K_0'$ values for K$_2$CO$_3$ liquid calculated by using the third-order Birch-Murnaghan EOS. The phase equilibrium experiments in combination with the data of Liu et al. (2007) and Klement and Cohen (1975) constrain the value of liquid $K_0'$ to be about $14.4 \pm 1.1$ at pressures lower than 5.0 GPa. However, the melting temperatures at pressures above 9.0 GPa deviate from this trend, which is related to the possible phase transitions of crystalline or liquid K$_2$CO$_3$ at high pressure and high temperature. Thus, the following discussion involves the validity of the $K_0'$ value only at $<~6$ GPa. Moreover, when the errors in the 1 bar thermodynamic data are considered, which leads to an uncertainty of $\pm51 \degree C$ in the calculated fusion temperature at 5.0 GPa, as mentioned in Liu et al. (2007), the uncertainty in the liquid $K_0'$ value varies by $\pm1.3$ or $\pm1.2$ units. The small difference of $K_0'$ value for K$_2$CO$_3$ liquid between the present study, at 14.4, and that of Liu et al. (2007), at 13.7, could be attributed to systematic error from the different cell assembly.

**DISCUSSION**

**Phase transformations for liquid and crystalline K$_2$CO$_3$**

The structure of liquid K$_2$CO$_3$ at high pressure is fundamental for controlling its macroscopic properties. However, significantly fewer studies have been conducted on this topic in comparison to its structure at ambient pressure (Tissen and Janssen, 1990; Koura et al., 1996; Koishi et al., 2000). Molecular dynamics simulations of molten alkali carbonates reported by Tissen and Janssen (1990) suggest that the calculated coordination of K by oxygen at ambient pressure is between 5.36 and 6.5. With increasing pressure, a transformation in the liquid structure accompanying a change in coordination of K by oxygen is expected rather than an abrupt (first- or second-order) phase transition such as that occurring in minerals. For example, in a molecular dynamics simulations study of CaCO$_3$ melts from 0.01 GPa to 11.5 GPa, Genge et al. (1995) suggested that the coordination number for Ca-O changes from 5.128 at 0.067 GPa to 6.32 at 11.56 GPa; however, no obvious phase transition in liquid CaCO$_3$ was found.

It is widely accepted that as crystalline solids transform to different polymorphs in response to varying pressure and temperature, they undergo large changes in structure and properties. Analogous density- or entrophy-driven phase transitions in the liquid state have been reported, such as those in phosphorus (Katayama et al., 2000) and cerium (Cadieu et al., 2013). If the liquid transition in K$_2$CO$_3$ indeed exists between 5.0 and 9.0 GPa, the thermodynamic properties of the K$_2$CO$_3$ liquid, such as $C_v$ and $C_p$, would be affected, and the deviation of $K_0'$ values for K$_2$CO$_3$ liquid at high pressure shown in Figure 2 can be explained, where the fusion curves were calculated through the thermodynamic data of $\alpha$-K$_2$CO$_3$ phase.

Thus far, little information has been reported on the phase stability of crystalline K$_2$CO$_3$ simultaneously at high pressure and high temperature even though this type of data is also important for fusion curve calculation. Canavecic et al. (2006) used ab initio calculations to determine that ambient $\gamma$-K$_2$CO$_3$ transforms to $\beta$-Na$_2$CO$_3$ at 0.86 GPa, to $\gamma$-Na$_2$CO$_3$ at 2.75 GPa, and then to K$_2$CO$_3$-Type-11 at 48.16 GPa (computed via HF); to $\gamma$-Na$_2$CO$_3$ at 0.84 GPa and then to K$_2$CO$_3$-Type-11 at 37.3 GPa (computed via DFT). The $\alpha$-K$_2$CO$_3$ phase did not appear in their results. Furthermore, Grzecznik et al. (2003) reported that the monoclinic Li$_2$CO$_3$ (C2/c) transformed to a new non-quenchable hexagonal polymorph (P6$_3$/mcm) above 10 GPa, where the carbonate groups are in a staggered configuration along the c-axis. However, the above results indicate that it is still difficult to determine the stable phase of K$_2$CO$_3$ during crystal-liquid equilibrium experiments at the conditions of this study. If the phase transition of crystal K$_2$CO$_3$ occurs between 5.0 and 9.0 GPa at...
high temperatures, the inconsistent trend of the $K'_0$ value shown in Figure 2, which was calculated by using the same phase, can also be explained.

**Density of K$_2$CO$_3$ liquid with pressure**

The density of liquid K$_2$CO$_3$ can be calculated to high pressure by using the third-order Birch–Murnaghan equation of state (EOS) (Eq. 2) with constraints on the $K'_0$ value. The one-bar density and bulk modulus for K$_2$CO$_3$ liquid used in this calculation are from Liu and Lange (2003) and Zhu et al. (1991). As illustrated in Figure 3, the density of liquid K$_2$CO$_3$ at 1500 °C with various liquid $K'_0$ values was calculated as a function of pressure up to 6.0 GPa, in which the density curve with a $K'_0$ value of 14.4 is highlighted. The calculated density of liquid K$_2$CO$_3$ at 1500 °C and 4.0 GPa is 2.16 g/cm$^3$. The density of liquid K$_2$CO$_3$ is still significantly lower than those of silicate liquids, which is consistent with that suggested by Liu et al. (2007). For example, at 5.0 GPa and 1500 °C, the KAlSi$_3$O$_8$ liquid density is 2.65 g/cm$^3$ (Lange, 2007), whereas the calculated density of K$_2$CO$_3$ liquid is 2.16 g/cm$^3$. However, the density of K$_2$CO$_3$ liquid is lower than that of CaCO$_3$ liquid within the pressure range of this study. A molecular dynamics simulation conducted by Gege et al. (1995) suggested that CaCO$_3$ liquid density varies from 2.06 to 2.9 g/cm$^3$ at pressures of 0.01–10.0 GPa, which causes a crossover between CaCO$_3$ liquid density and KAlSi$_3$O$_8$ liquid density at about 7.5 GPa, as shown in Figure 3. This type of crossover has also been observed in a molecular dynamics simulation conducted by Vuilleumier et al. (2014) but at much lower pressure of about 3.0 GPa.

**Compressibility of K$_2$CO$_3$ liquid with pressure**

In addition to calculating the liquid density of K$_2$CO$_3$ at a different pressure, it is also interesting to calculate the change in compressibility of liquid K$_2$CO$_3$ with pressure:

$$
\beta_T(P) = \frac{1}{K'_0} \left( \frac{\partial P}{\partial V} \right)_T
$$

where 

$$
\left( \frac{\partial P}{\partial V} \right)_T = - \frac{1}{V_T} \left[ \frac{\partial^2 P}{\partial V^2} \right]_T
$$

The combination of Equations 4 and 5 allows the compressibility of K$_2$CO$_3$ liquid to be calculated up to 6.0 GPa for various $K'_0$ values. The resultant family of liquid compressibility curves at 1500 °C is shown in Figure 4, along with that for crystalline K$_2$CO$_3$. A pronounced curvature in $\beta_T$ of 14.4–22 is shown for these liquid $K'_0$ values, with $\beta_T$ decreasing rapidly within the pressure range of 0–4.0 GPa followed by a less steep decrease toward the compressibility for the crystalline phase. This result is consistent with the observation reported by Liu et al. (2007). In contrast, the compressibility of crystalline K$_2$CO$_3$ decreases slowly with increasing...
pressure below 6.0 GPa. At ambient pressure at 1500 °C, the compressibility of K₂CO₃ liquid is more than 10 times greater than that for crystalline K₂CO₃; by 6.0 GPa, with a $K_{0}'$ value of 14.4 for the liquid phase, the difference between the liquid and crystal is only 35.5%. These results suggest that at one bar, mechanisms of compression available to liquid K₂CO₃ are not accessible to its crystalline equivalent, as discussed in the work of Liu et al. (2007).

Melting of carbonates at high pressure

The melting of carbonates at high pressure and high temperature is an important issue for understanding the origin and evolution of carbonatites in the mantle. The melting curves of CaCO₃ (Irving and Wyllie, 1975; Suito et al., 2001), MgCO₃ (Irving and Wyllie, 1975), FeCO₃ (Tao et al., 2013, and K₂CO₃ (Shatskiy et al., 2015; this study) combined with typical subduction paths are given in Figure 5. This figure indicates that K₂CO₃ has a relatively low melting temperature compared with other common carbonates and that its melting curve is lower than the mantle geotherm at pressures higher than 9.0 GPa. In previous experiments (Dasgupta and Hirschmann, 2006; Ghosh et al., 2009; Grassi and Schmidt, 2011a, 2011b), mass–balance calculations often produce clear alkali and particularly K deficits in inferred subsolidus runs, although the near–solidus melts of carbonated peridotite and eclogite are enriched in alkalis. The results of this study indicate that K may be concentrated in K₂CO₃–rich liquid, where the melting of K₂CO₃ may occur at depths greater than 270 km.

In a study of the physical properties of molten carbonates, Gaillard et al., (2008) reported that alkali-rich molten carbonates such as (LiNaK)$_2$(CO$_3$)$_3$, (NaK)$_2$(CO$_3$)$_2$, and (NaKCa)(CO$_3$)$_2$ have electrical conductivity three orders of magnitude higher than those of molten silicates and up to five orders of magnitude higher than those of hydrated olivine, which can potentially explain the high asthenosphere conductivities. This observation was corroborated by Sifre et al. (2015) at high temperature and high pressure, in which a weak dependence of electrical conductivity on temperature, pressure, and chemical composition was found. Thus, the molten K₂CO₃ may also have high electrical conductivity, which can also contribute to high mantle conductivity. In addition, analyses of microinclusions in diamond (e.g., Sobolev et al., 1998; Hwang et al., 2006) and diamond-formation experiments (e.g., Pal’yanov et al., 1999, 2007) indicate that the composition of the diamond-forming medium can be roughly considered as ultrapotassic carbonate fluid. Considering the low melting temperature of K₂CO₃, we suggest that the existence of K₂CO₃–rich liquid may contribute to the formation of diamond in the mantle.

Most plutonic, older carbonatite complexes worldwide are dominated by either Ca–(calcite) or Mg–rich (dolomite) carbonate (Woolley and Kjarsgaard, 2008) with
the exception of alkali-rich natrocarbonatite lavas erupted at Oldoinyo Lengai in Tanzania (Dawson, 1962). However, many studies (Dawson, 1993; Zaitsev and Keller, 2006; Le Bas, 2008; Chen et al., 2013) argue that the parental carbonatite liquid is alkali-rich. Such a carbonate component could be easily lost within a few days through replacement by secondary calcite at atmospheric conditions, or the loss of alkalis can occur during melt evolution and crystallization such as that during fenitization of country rocks. Therefore, we suggest that alkali-rich carbonate melt may exist in the mantle and play an important role in the internal structure of the earth.

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