

## Phase relation in $\text{MgCO}_3$ - $\text{SiO}_2$ system up to the lowermost mantle

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Diamond is an evidence for deep carbon in the Earth. Some diamonds are considered to have originated at various depth ranges from the mantle transition zone to the lower mantle (e.g., Brenker et al., 2007; Harte and Richardson, 2012). These diamonds from 'super-deep' regions have been paid attention because they are possible to carry significant information about the interior of the Earth (e.g., Pearson et al., 2014). We have to take account of an unusual environment to form such diamonds when interpreting information from super-deep diamonds. However, we do not have enough clues to speculate processes or environments of super-deep diamond formation.

Subduction has been considered to be related to diamond formation in the lower mantle (e.g., Harte, 2010), and a reaction of  $\text{MgCO}_3$  and  $\text{SiO}_2$  was suggested to form diamond in slabs descending into the lower mantle (Seto et al., 2008; Takafuji et al., 2006). Therefore, we determined the phase relations in an  $\text{MgCO}_3$ - $\text{SiO}_2$  system up to 152 GPa and 3100 K in order to reveal an origin of super-deep diamonds. Seto et al. (2008) suggested that a reaction between  $\text{MgCO}_3$  magnesite and  $\text{SiO}_2$  stishovite could react with each other in the lower mantle in hot slabs and might subduct to the lowermost mantle in cold slabs without any reactions. However, their experimental results were limited to the middle lower mantle conditions up to  $\sim 80$  GPa. We extended the pressure range to the lowermost mantle and estimated their reaction up to the lowermost mantle.

We used a double-sided laser-heated diamond anvil cell (LHDAC) combined with in situ synchrotron X-ray diffraction at beamline BL10XU of Spring-8 in Hyogo, Japan. Starting materials were a natural magnesite and a reagent quartz. They were ground to  $>10 \mu\text{m}$  in diameter and mixed 1:1 by mole fraction using agate mortar. We loaded the powder mixture into a sample chamber in a tungsten gasket which was pre-compressed to 40–80  $\mu\text{m}$  in thickness and drilled a 30–100- $\mu\text{m}$  hole in diameter. Culet diameters of diamond anvils used were between 100 and 350  $\mu\text{m}$ . A size of a sample chamber was decided based on a culet diameter of anvils. Double-sided laser heating was conducted using a fiber laser equipped at BL10XU. We used Pt powder, foil or doughnut as a laser absorber. Experimental pressures were determined using a thermal equation of state of Pt (Fei et al., 2007) and thermal pressures were calculated using Mie-Grüneisen-Debye model (e.g., Fei et al., 1992). XRD patterns were analyzed using IPAnalyzer and PDIndexer software (Seto et al., 2010).

Magnesite reacted with stishovite or  $\text{CaCl}_2$ -type  $\text{SiO}_2$  to form  $\text{MgSiO}_3$  bridgmanite and maybe  $\text{CO}_2$  above  $\sim 2000$  K. These results almost corresponded to Seto et al. (2008) below 80 GPa. The phase relation was drastically changed above 80 GPa: diamond and bridgmanite were observed below 2000 K near 80 GPa and the reaction temperature seemed to gradually increase above 80 GPa.  $\text{MgCO}_3$  was reported to transform from magnesite to a high-pressure polymorph, phase II, above 82 GPa (Oganov et al., 2008). We actually observed  $\text{MgCO}_3$  phase II above 80 GPa and at high temperature, and thus the phase transition of  $\text{MgCO}_3$  might be related to the change of the phase relation.

We speculate a reaction between  $\text{MgCO}_3$  and  $\text{SiO}_2$  in a subduction process based on the present phase diagram.  $\text{MgCO}_3$  and  $\text{SiO}_2$  can react in hot or cold slabs up to 1900-km depth in the middle lower mantle, which forms high-pressure  $\text{CO}_2$  polymorph or diamond. On the other hand,  $\text{MgCO}_3$  and  $\text{SiO}_2$  are possible to subduct up to the lowermost mantle in a very cold slab. Their reaction is expected at the lowermost mantle due to heating from the core in this case. Therefore, their reaction in a cold subduction can explain a formation process of some super-deep diamonds having an especially deep origin (e.g., Harte

and Richardson, 2012; Hayman et al., 2005; Wirth et al., 2014).

Keywords: magnesite, silica minerals, diamond, LHDAC, lower mantle

## High-pressure study of coronene: phase transitions, oligomerization, decomposition and thermal expansion

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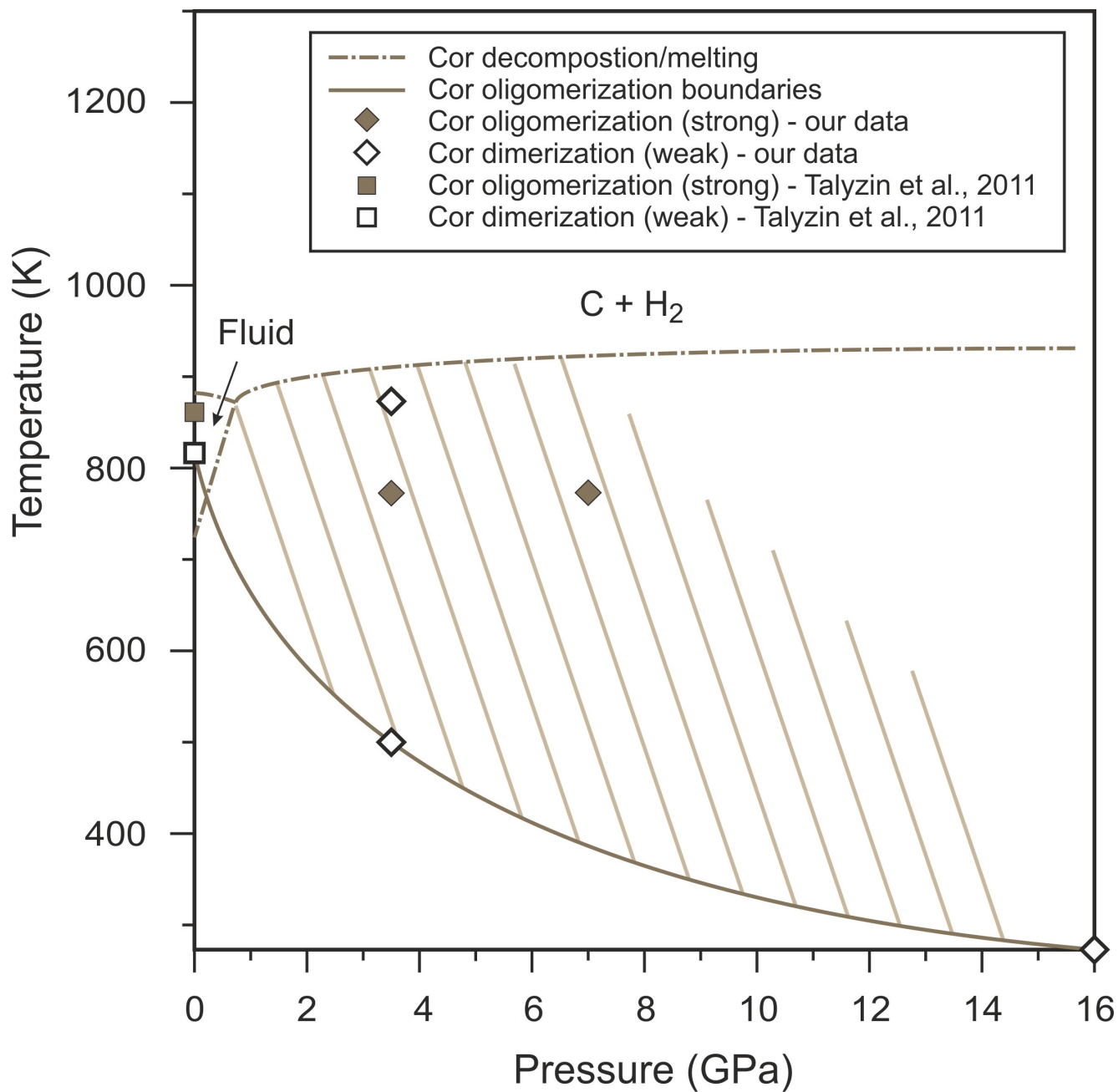
Coronene C<sub>24</sub>H<sub>12</sub> is a polycyclic aromatic hydrocarbon (PAH) consisting of six benzene rings. PAHs are believed to be the most abundant organic molecules in the Universe (Ehrenfreund and Charnley, 2000; Tielens, 2008) possibly due to electron delocalization over their carbon skeleton, which makes them remarkably stable (Ehrenfreund and Charnley, 2000). Coronene was found in hydrothermal (Echigo et al., 2007) and metamorphic rocks (Sawada et al., 2008) as well as in meteorites (e.g. Oro et al., 1971). Moreover, PAHs have been identified as inclusions in garnet, olivine, and diamond from mantle xenoliths in kimberlite pipes (e.g. Garanin et al., 2011; Kulakova et al., 1982). At 300 K and ambient pressure coronene possesses the space group  $P2_1/a$  (Fawcett and Trotter, 1966). Two high-pressure phase transitions of coronene at 1.5 and 12.2 GPa were determined by Jennings et al. (2010). High-pressure phases were identified as monoclinic (1.5  $P$  12.2 GPa) and orthorhombic ( $P$  12.2 GPa) crystal structures with space groups of  $P2/m$  and  $Pmmm$ , respectively (Zhao et al., 2013).

Here we performed high-pressure experiments using multi-anvil apparatus and DAC. We observed phase transition ( $P2_1/a$ - $P2/m$ ) between 0 and 0.9 GPa. Compressibility parameters of coronene phase  $P2/m$  were defined in the pressure range of 0.9-8.1 GPa at 300 K as  $K_0 = 13.0(3)$  GPa,  $K_0' = 7$  at  $V_0 = 795.5 \text{ \AA}^3$  using Vinet EOS (Vinet et al., 1987); the thermal expansion coefficient was found to be low at 2.0-7.5 GPa and 473-873 K (about  $10^{-5} \text{ K}^{-1}$ ). The same low thermal expansion coefficient at  $P > 3$  GPa was defined previously for naphthalene C<sub>10</sub>H<sub>8</sub> (Likhacheva et al., 2014).

Coronene decomposition was determined in the pressure range of 2.0-15.5 GPa between 900-1000 K. Coronene decomposition products consist of nanocrystalline graphite, amorphous carbon and diamond with trans-polyacetylene lying along the grain boundaries. At lower temperatures (500-773 K) we observed significant oligomerization of coronene by MALDI measurements. Coronene oligomer formation occurs via PAH dehydrogenation and successive fusion of the initial hydrocarbon molecules through C-C bond formation. Based on our results and previous experimental study at ambient pressure (Talyzin et al., 2011) we have identified PT diagram of coronene phase transitions, oligomerization and decomposition parameters to 16 GPa and 1000 K (Fig. 1). Defined coronene phase diagram is extremely important for understanding the planet accretion by carbonaceous chondrites.

Figure 1. PT-diagram of coronene with phase transitions, oligomerization and decomposition parameters. Shaded area is a coronene oligomerization field.

Keywords: aromatic hydrocarbons, carbon cycle, planetary interiors



## Pressure-induced phase transitions of vaterite, a metastable phase of $\text{CaCO}_3$

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Calcium carbonate plays an important role in global carbon cycle. Calcium carbonate has three polymorphs, calcite, aragonite and vaterite. Vaterite is a meta stable phase and no systematic experiments on the behavior under high pressure have been conducted so far. In this study, pressure-induced phase transitions of vaterite, a metastable phase of  $\text{CaCO}_3$ , were observed from Raman spectra and X-ray diffraction patterns at high pressure using diamond anvil cells at room temperature. Pressure dependence of Raman peaks assignable to the symmetric stretching vibration modes of carbonate ion indicated the phase transitions of vaterite. At 4.3 GPa, vaterite (vaterite I) transformed to a high-pressure form of vaterite (vaterite II). With increasing pressure, a part of vaterite II gradually transformed to calcite III, and the remainder of vaterite II transformed to another new phase (vaterite III). The phase transition from vaterite II to calcite III was irreversible, and calcite III back-transformed to calcite I during decompression. Moreover, at the pressures higher than 13.1 GPa, several diffraction spots were observed on an imaging plate, indicating another phase transition from vaterite III to a phase having coarse grains (vaterite IV). Our results indicate that vaterite undergoes more complex phase transitions at high pressure than other polymorphs of calcium carbonate, calcite and aragonite. These phase transitions of vaterite will open a window to understanding phase transitions of metastable minerals at high pressure.

Keywords: vaterite, calcium carbonate, high pressure, phase transformation

## Effect of alkalis on the reaction of clinopyroxene with Mg-carbonates at 6 GPa: Implications for partial melting of carbonated lherzolite

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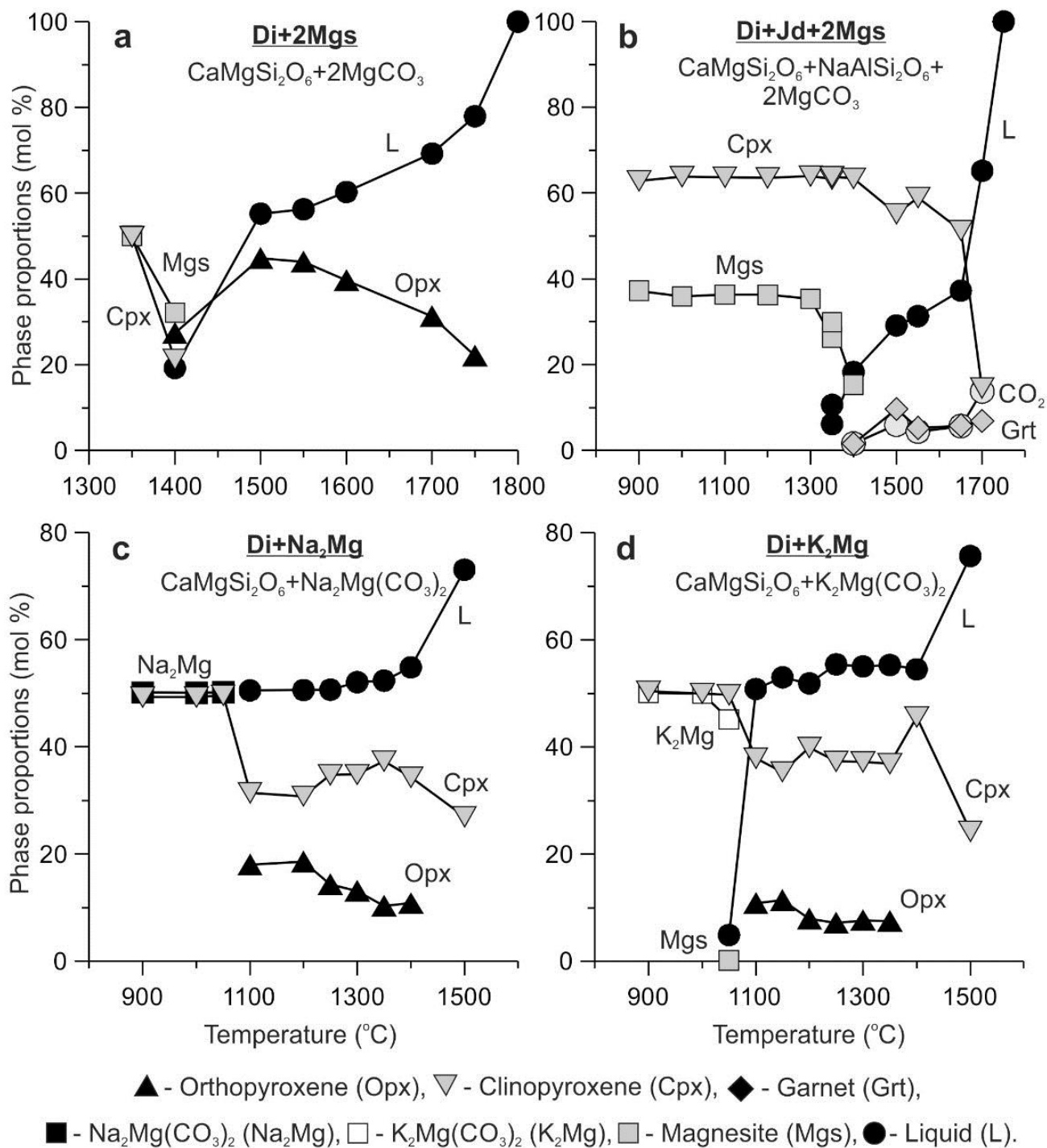
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The reaction between clinopyroxene and Mg-carbonate is supposed to define the solidus of carbonated lherzolite at pressures exceeding 5 GPa. To investigate the effect of alkalis on this reaction, subsolidus and melting phase relations in the systems  $\text{CaMgSi}_2\text{O}_6 + 2\text{MgCO}_3$  (Di + 2Mgs),  $\text{CaMgSi}_2\text{O}_6 + \text{NaAlSi}_2\text{O}_6 + 2\text{MgCO}_3$  (Di + Jd + 2Mgs),  $\text{CaMgSi}_2\text{O}_6 + \text{Na}_2\text{Mg}(\text{CO}_3)_2$  (Di +  $\text{Na}_2\text{Mg}$ ), and  $\text{CaMgSi}_2\text{O}_6 + \text{K}_2\text{Mg}(\text{CO}_3)_2$  (Di +  $\text{K}_2\text{Mg}$ ) have been examined at 6 GPa. The results are summarized in Fig. 1. The Di + 2Mgs system begins to melt at 1400 °C via the approximate reaction  $\text{CaMgSi}_2\text{O}_6$  (clinopyroxene) +  $2\text{MgCO}_3$  (magnesite) =  $\text{CaMg}(\text{CO}_3)_2$  (liquid) +  $\text{Mg}_2\text{Si}_2\text{O}_6$  (orthopyroxene) leading to essentially carbonate liquid (L) with composition of  $\text{Ca}_{0.56}\text{Mg}_{0.44}\text{CO}_3 + 3.5 \text{ mol\% SiO}_2$ . The initial melting in the Di + Jd + 2Mgs system occurs at 1350 °C via the reaction  $2\text{CaMgSi}_2\text{O}_6$  (clinopyroxene) +  $2\text{NaAlSi}_2\text{O}_6$  (clinopyroxene) +  $8\text{MgCO}_3$  (magnesite) =  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (garnet) +  $5\text{MgSiO}_3$  (clinopyroxene) +  $2\text{CaMg}(\text{CO}_3)_2$  (liquid) +  $\text{Na}_2\text{CO}_3$  (liquid) +  $3\text{CO}_2$  (liquid and/or fluid) yielding the carbonate liquid with approximate composition of  $10\text{Na}_2\text{CO}_3 \cdot 90\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3 + 2 \text{ mol\% SiO}_2$ . The systems Di +  $\text{Na}_2\text{Mg}$  and Di +  $\text{K}_2\text{Mg}$  start to melt at 1100 and 1050 °C, respectively, via the reaction  $\text{CaMgSi}_2\text{O}_6$  (clinopyroxene) +  $2(\text{Na or K})_2\text{Mg}(\text{CO}_3)_2$  (solid) =  $\text{Mg}_2\text{Si}_2\text{O}_6$  (orthopyroxene) +  $(\text{Na or K})_4\text{CaMg}(\text{CO}_3)_4$  (liquid). The resulting melts have alkali-rich carbonate compositions of  $\text{Na}_2\text{Ca}_{0.4}\text{Mg}_{0.6}(\text{CO}_3)_2 + 0.4 \text{ mol\% SiO}_2$  and  $43\text{K}_2\text{CO}_3 \cdot 57\text{Ca}_{0.4}\text{Mg}_{0.6}\text{CO}_3 + 0.6 \text{ mol\% SiO}_2$ . These melts do not undergo significant changes as temperature increases to 1400 °C retaining their calcium number, high  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and low  $\text{SiO}_2$ . We suggest that the clinopyroxene–Mg-carbonate reaction controlling the solidus of carbonated lherzolite is very sensitive to the carbonate composition and shifts from 1400 °C to 1050 °C at 6 GPa yielding K-rich carbonate melt if subsolidus assemblage contains  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  compound. Such a decrease in solidus temperature has been observed previously in the K-rich carbonated lherzolite system. Although a presence of eitelite,  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$ , has a similar effect, this mineral cannot be considered as a potential host of Na in carbonated lherzolite as far as whole Na added into the system dissolves as jadeite component in clinopyroxene if bulk Al/Na 1. The presence of jadeite component in clinopyroxene has little impact on the temperature of the solidus reaction decreasing it to 1350 °C at 6 GPa.

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Fig. 1. Modal abundances of phases present as a function of temperature in the systems  $\text{CaMgSi}_2\text{O}_6 + 2\text{MgCO}_3$  (a),  $\text{CaMgSi}_2\text{O}_6 + \text{NaAlSi}_2\text{O}_6 + 2\text{MgCO}_3$  (b),  $\text{CaMgSi}_2\text{O}_6 + \text{Na}_2\text{Mg}(\text{CO}_3)_2$  (c), and  $\text{CaMgSi}_2\text{O}_6 + \text{K}_2\text{Mg}(\text{CO}_3)_2$  (d) at 6.0 GPa. Modes are in mol% were determined from the bulk compositions of starting mixtures and compositions of phases measured by electron microprobe.

Keywords: Alkalis, Clinopyroxene, Mg-carbonates, High pressure and temperature, solidus, phase relations



## Existence of Carbon in the Earth' s inner core

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Carbon is an important candidate for light element in the Earth' s core. There have been contradictory results on the stability of Fe–C compounds, such as  $\text{Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  under the core conditions. We observed  $\text{Fe}_3\text{C}$  melts incongruently to form  $\text{Fe}_7\text{C}_3$  and liquid at 4200 K and 200 GPa. Additionally, it was shown that the C content of the liquid coexisting with  $\text{Fe}_7\text{C}_3$  decreases and the Fe– $\text{Fe}_3\text{C}$  eutectic composition shifts toward the Fe-rich direction with increasing pressure. The present result revealed that  $\text{Fe}_3\text{C}$  and  $\text{Fe}_7\text{C}_3$  are plausible constituents of the inner core, with a possible layering of  $\text{Fe}_7\text{C}_3$  in the central region and  $\text{Fe}_3\text{C}$  in the outer region of the inner core formed during cooling of the core. We also conducted the equation of state and sound velocity measurements at high pressure and temperature by using XRD and IXS measurements at Spring-8. The results indicate that the sound velocity of the mixture of Fe– $\text{Fe}_3\text{C}$  is higher than the PREM inner core under the Earth' s core conditions. Thus, it is difficult to explain that the Earth' s inner core is composed of only a Fe– $\text{Fe}_3\text{C}$  mixture. Since the inner core temperature is very close to the eutectic temperature of the Fe– $\text{Fe}_3\text{C}$  system, pre-melting effect of  $\text{Fe}_3\text{C}$  could be important to account for the sound velocity of the PREM inner core.

Keywords: Carbon,  $\text{Fe}_3\text{C}$ , Melting relation, equation of state, Sound velocity



# Phase relations and liquid immiscibility in $\text{KAlSi}_3\text{O}_8$ - and $\text{CaMg}(\text{CO}_3)_2$ -bearing systems at 6 GPa: Implications for origin of fibrous diamonds

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The reaction between potassium feldspar (Kfs) and dolomite (Dol) could define the solidus of carbonated pelite below 7 GPa under nominally anhydrous conditions (Grassi and Schmidt, 2011). To investigate this reaction subsolidus and melting phase relations in the systems  $\text{KAlSi}_3\text{O}_8 + \text{CaMg}(\text{CO}_3)_2$  (Kfs + Dol),  $\text{KAlSi}_3\text{O}_8 + \text{CaMgSi}_2\text{O}_6 + \text{NaAlSi}_2\text{O}_6 + \text{CaMg}(\text{CO}_3)_2$  (Kfs + Di + Jd + Dol), and  $\text{KAlSi}_3\text{O}_8 + \text{Na}_2\text{CO}_3 + \text{CaMg}(\text{CO}_3)_2$  (Kfs +  $\text{Na}_2$  + Dol) have been examined at 6 GPa and compared with those established in dry carbonated pelite (DG2).

In the system Kfs+Dol at 1000 °C, the subsolidus assemblage consists of Kfs and Dol. Besides, Kfs contains numerous inclusions of  $\text{K}_2\text{Si}_4\text{O}_9$  wadeite (K-wad), kyanite (Ky), coesite (Coe). At lower temperature 900 °C, Kfs and Dol are not stable and the assemblage includes K-wad, Ky, Coe, aragonite (Arg) and magnesite (Mgs). The system begins to melt at 1100 °C via reaction  $6\text{KAlSi}_3\text{O}_8$  (Kfs) +  $6\text{CaMg}(\text{CO}_3)_2$  (Dol) =  $2(\text{Ca}_n\text{Mg}_{1-n/3}\text{Al}_2\text{Si}_3\text{O}_{12}$  (Grt) +  $\text{Al}_2\text{SiO}_5$  (Ky) +  $11\text{SiO}_2$  (Coe) +  $3\text{K}_2(\text{Ca}_{1-n}\text{Mg}_n)_2(\text{CO}_3)_3$  (L) +  $3\text{CO}_2$  (F and/or L), where  $n \sim 0.3-0.4$ , leading to essentially carbonate liquid, L(C), with composition of  $32\text{K}_2\text{CO}_3 \cdot 68(\text{Ca}_{0.63}\text{Mg}_{0.37})\text{CO}_3 + 1-2 \text{ mol\% SiO}_2 + 0.5-1 \text{ mol\% Al}_2\text{O}_3$ . Kfs and Dol completely disappear at 1150 °C. Starting from 1300 °C, immiscible silicate melt, L(S), coexists with L(C). L(S) contains (in mol%): 64  $\text{SiO}_2$ , 9  $\text{Al}_2\text{O}_3$ , 2 MgO, 2 CaO, 11  $\text{K}_2\text{O}$ , and 12  $\text{CO}_2$ . The Grt + Coe + Ky + L(C) + L(S) phase assemblage remains stable up to 1500 °C.

Adding Di-Jd clinopyroxene in the Kfs + Dol system does not affect phase relations. At 1000 °C, the subsolidus assemblage is Kfs + CPx + Dol. Kfs is partially replaced by K-wad + Ky + Coe assemblage. Above the solidus at 1150 °C, Cpx, Grt, Ky, Coe coexist with L(C) [ $34(\text{K}_{0.92}\text{Na}_{0.08})_2\text{CO}_3 \cdot 66(\text{Ca}_{0.62}\text{Mg}_{0.38})\text{CO}_3 + 3 \text{ mol\% SiO}_2 + 1 \text{ mol\% Al}_2\text{O}_3$ ]. L(S) appears at 1250 °C and contains (in mol%): 67  $\text{SiO}_2$ , 7  $\text{Al}_2\text{O}_3$ , 4 MgO, 4 CaO, 1  $\text{Na}_2\text{O}$ , 7  $\text{K}_2\text{O}$ , and 10  $\text{CO}_2$ . The Cpx + Grt + Ky + Coe + L(C) + L(S) phase assemblage was established at 1250 and 1350 °C, whereas at 1500 °C only CPx remains in coexistence with L(C) and L(S). At 900 °C in the Kfs +  $\text{Na}_2$  + Dol system, the subsolidus assemblage consists of Cpx ( $\text{Jd}_{87-90}\text{Di}_{10-13}$ ),  $(\text{Na}_{0.55}\text{K}_{0.45})_2\text{Mg}_{0.90}\text{Ca}_{0.10}(\text{CO}_3)_2$  (NaKMg),  $(\text{Na}_{0.63}\text{K}_{0.37})_2(\text{Ca}_{0.93}\text{Mg}_{0.07})_3(\text{CO}_3)_4$  (NaKCa<sub>3</sub>), Coe, and Mgs. As temperature increases to 1000 °C, NaKMg and NaKCa<sub>3</sub> disappear, while minor amount of Mgs and Coe remains. The sample consists of Cpx ( $\text{Jd}_{78}\text{Di}_{22}$ ) and L(C) [ $44(\text{Na}_{0.51}\text{K}_{0.49})_2\text{CO}_3 \cdot 56\text{Ca}_{0.57}\text{Mg}_{0.43}\text{CO}_3$ ]. Thus, an addition of  $\text{Na}_2\text{CO}_3$  into the Kfs+Dol system yields formation of Cpx, NaKMg and NaKCa<sub>3</sub> at the expense of K-wad, Ky, Mgs, and Arg. Molar abundances of phases and their compositions change slightly with further temperature increase up to 1500 °C. Thus,  $\text{Na}_2\text{CO}_3$  causes redistribution of  $\text{K}_2\text{O}$  into carbonate phases, whereas  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are consumed on jadeite formation:  $\text{Na}_2\text{CO}_3 + \text{KAlSi}_3\text{O}_8$  (Kfs or L(S)) =  $\text{NaAlSi}_2\text{O}_6 + \text{SiO}_2 + \text{NaKCO}_3$  (L(C)). As a result, immiscible L(S) does not appear in this system.

In dry carbonated pelite (DG2), subsolidus assemblage established at 1000 °C is represented by Cpx, Grt, Ky, Coe, Dol, and  $\text{K}_2\text{Ti}_{1-n}\text{Si}_{3+n}\text{O}_9$  wadeite. Two immiscible liquids were established at 1350 and 1500 °C in coexistence with Cpx, Coe, Grt, Ky and  $\text{CO}_2$  fluid. At 1350 °C, L(S) contains (in mol%): 56.6  $\text{SiO}_2$ , 1.8  $\text{TiO}_2$ , 8.3  $\text{Al}_2\text{O}_3$ , 2.9 FeO, 1.3 MgO, 3.2 CaO, 1.4  $\text{Na}_2\text{O}$ , 9.7  $\text{K}_2\text{O}$ , and 15.0  $\text{CO}_2$ , whereas L(C) composition is  $(\text{K}_{0.74}\text{Na}_{0.26})_2(\text{Ca}_{0.58}\text{Mg}_{0.18}\text{Fe}_{0.24})_4\text{CO}_3 + 4.2 \text{ mol\% SiO}_2 + 1.7 \text{ mol\% TiO}_2 + 1.4 \text{ mol\% Al}_2\text{O}_3$ .

The obtained immiscible L(C) and L(S) resemble compositions of melt inclusions in fibrous diamonds worldwide. Thus, the K-aluminosilicate and K-Na-rich carbonatite melts entrapped by fibrous diamonds

could be derived by liquid immiscibility during partial melting of carbonated pelite subducted down to 180 km depth and heated to 1300 °C or higher temperature.

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Keywords: Phase relations, Liquid immiscibility,  $\text{KAlSi}_3\text{O}_8$ ,  $\text{CaMg}(\text{CO}_3)_2$ , fibrous diamonds

