Diamond nucleation barrier and melting relations for Ol-Opx-Cpx-Grt-carbonate system: syngenesis of diamond and silicate minerals

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The solution of the problem of diamond genesis in the Earth mantle should be mostly based on the chemical composition of parental media, which is evident from syngenetic inclusions in diamonds from kimberlites and lamproites. Fragments of parental media as silicate minerals demonstrate their variable paragenetic associations, from olivine-bearing peridotite and pyroxenite to eclogite and grospydite including coesite-bearing varieties (e.g., Meyer, 1987). Numerous studies of crystalline inclusions in diamonds demonstrate that the most of them were formed at depths of 150–250 km, in a temperature range of 900–1300°C (e.g., Taylor, Anand, 2004).

Finds of fluid carbonatite inclusions enriched in H_2O, CO_2, SiO_2, K_2O in diamonds, which have high internal pressure (4–7 GPa) (e.g., Navon, 1991; Schrauder, Navon, 1994), confirm the idea of strongly compressed parental multi-component carbonate-silicate melts with dissolved carbon and variable concentrations of minor (oxides, phosphates, chlorides, sulfides, metals, carbides, etc.) components (Litvin, 2007). In this connection mineralogical data solely does not allow to establish the chemical nature and composition of mantle media, which may provide the diamond formation. Such media may be established exclusively in experiments at high pressures and temperatures using the criteria of their efficiency for *diamond nucleation* and *syngenesis* of diamonds and their inclusions. In this paper we demonstrate diamond-forming efficiency of peridotite-carbonate and eclogite-carbonate melts in experiments at 7.0–8.5 GPa and 1200–1800°C.

Peridotite-carbonate system

We simulated crystallization of diamonds in melts with dissolved carbon (graphite) and variable compositions of model peridotite [60 wt.% olivine (Ol), 16 wt.% orthopyroxene (Opx), 12 wt.% clinopyroxene (Cpx), 12 wt.% garnet (Grt)] with carbonate of dolomite composition ($CaCO_3 \cdot MgCO_3$), K_2CO_3, and also multi-component K-Na-Ca-Mg-Fe-carbonatite [Carb; the composition is taken from (Schrauder, Navon, 1994)]. Carbonate-silicate melts in all experiments performed at PT-conditions of diamond stability are completely soluble. Concentration barriers of diamond nucleation

(CBDN) were estimated at a pressure of 8.5 GPa for variable concentrations of silicate and carbonate components in parental melts: 25, 30, and 30 wt.% of silicate components for $CaCO_3 \cdot MgCO_3$, K_2CO_3, and model carbonatite, respectively (Figs. 1, 2). At higher silicate concentrations in carbonate-silicate melts, diamond grows only on seed being accompanied by thermodynamically metastable graphite phase.
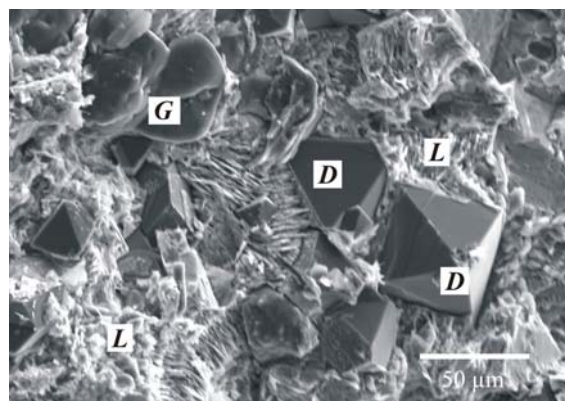

Fig. 1 SEI of diamond and graphite crystals in quenched silicate-carbonate melt at CBNA (30 wt.% peridotite–70 wt.% K-Na-Mg-Ca-Fe carbonate). P=8.5 GPa; T=1770°C; run duration 10 min.

The appearance of silicate minerals syngenetic to diamond in the studied diamond-forming melts was established in special run series at P = 7.0 GPa and T = 1200–1800°C for the composition of peridotite$_{30}$–carbonate$_{70}$ (wt.%), which corresponds to CBDN. Ol is a liquidus phase in the system with ($CaCO_3 \cdot MgCO_3$); at T < 1700°C, an association of Cpx + Ol + carbonate-silicate melt (L) is stable; at 1600°C, Grt is added. The prevalence of Cpx over other silicates was established for this system; none of the runs demonstrated the presence of Opx. It is assumed that in $CaCO_3$-rich systems Opx enters into reaction like $2MgSiO_3 + CaCO_3 \rightarrow CaMgSi_2O_6 + MgCO_3$ and practically is not presented as a proper phase. In the system of peridotite–alkali carbonate (K_2CO_3) the following assemblages are established: Opx(Ol) + L (1800°C); Opx + X phase + L (1500°C); Opx + Ol + carbonate + L (1300°C), Opx + Ol + wadeite + carbonate (1200°C). For the first time iron admixture was established in phase X, which was recently synthesized in some

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experimental studies of amphibole and phlogopite stability at T = 1150–1400°C and P = 9–17 GPa (e.g., Luth, 1997). The composition of X phase may be expressed by the following formula: $(K_{1.31}Na_{0.02}Ca_{0.01})(Mg_{1.50}Fe^{3+}_{0.37}Al_{0.05}Ti_{0.01})[Si_2O_7]H_{0.35}$. Crystallization of melts with model multi-component (K-Na-Ca-Mg-Fe) carbonatite proceeds with the following change of mineral parageneses as the temperature decreases: Ol + L → Ol + Cpx (Grt) + L → Ol + Cpx (Grt) + carbonate (Fig. 3). In principle, the appearance of Opx is possible in this system (shown by dotted line), but only if initial peridotite is enriched in this component and alkali carbonate (K_2CO_3) essentially prevail over $CaCO_3$ among carbonate phases.
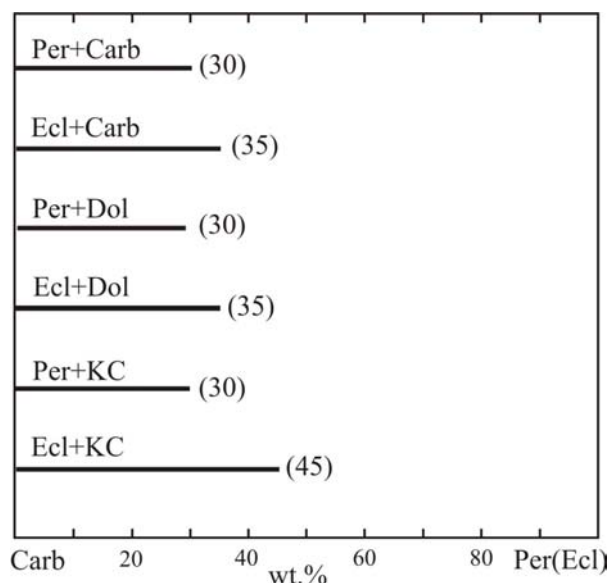

Fig. 2 Concentration barriers of diamond nucleation (CBDN) in the studied silicate-carbonate systems. Per = peridotite; Ecl = eclogite; Carb = multi-component K-Na-Mg-Ca-Fe carbonate (Schrauder, Navon, 1994); Dol = $CaCO_3\cdot MgCO_3$; KC = K_2CO_3.

Eclogite-carbonate system

In this study we simulated crystallization of diamonds in melts with variable compositions of model eclogite [50 wt.% clinopyroxene (Cpx), 50 wt.% garnet (Grt)] with $CaCO_3\cdot MgCO_3$, K_2CO_3, and multi-component K-Na-Ca-Mg-Fe-carbonatite (Schrauder, Navon, 1994). CBDNs estimated at a pressure of 8.5 GPa and 1800°C for variable concentrations of silicate and carbonate components in parental melts were 45 and 35 wt.% of silicate components for K_2CO_3 and model carbonatite, respectively (Fig. 2). As evident from the diagram, CBDNs in the eclogite-carbonate system are closer to silicate components in comparison with the peridotite-carbonate system.
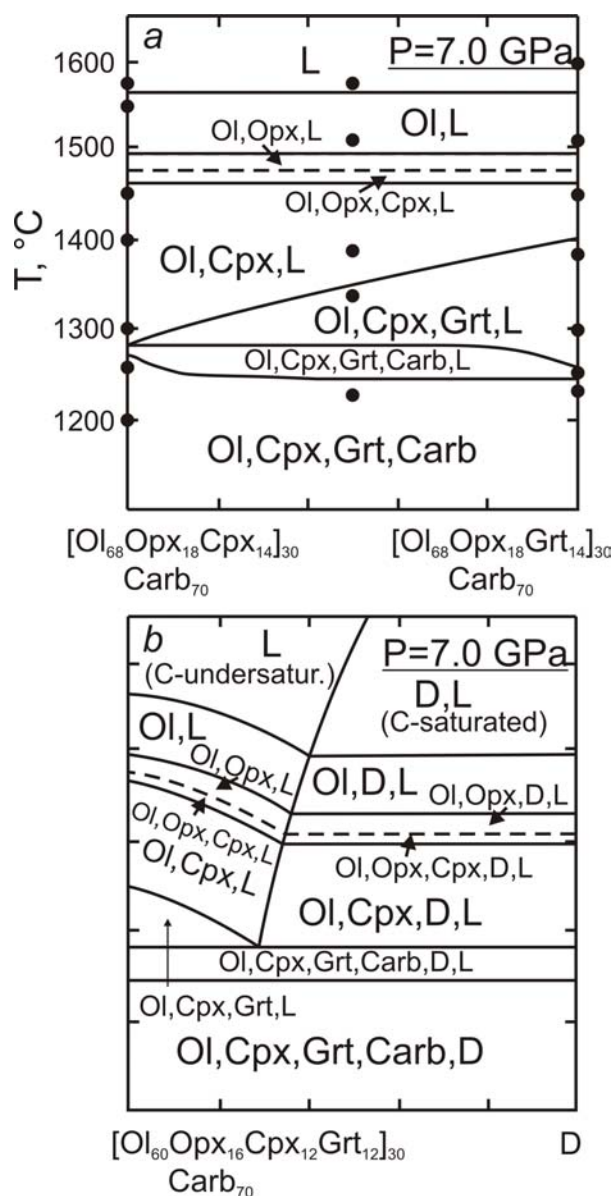

Fig. 3 Scheme of melting relations (*a*) and diagram of syngenesis of diamond (D) and its silicate and carbonate inclusions (*b*) in peridotite-carbonate system at CBDN (30 wt.% peridotite–70 wt.% K-Na-Mg-Ca-Fe carbonate).

Melting relations in the eclogite-carbonate diamond-forming systems were studieded in special run series at P = 7.0 GPa and T = 1200–1800°C for the composition of eclogite$_{35}$ – multi-component carbonate$_{65}$ (wt.%). Fig. 4 demonstrates melting relations in this eclogite–carbonatite system at P = 7.0 GPa. In clinopyroxene-rich part of the system, at a temperature above 1600°C, we obtained fine-grained aggregate of skeletal pyroxene, carbonate and phlogopite crystals, which was interpreted as a quenched carbonate-silicate melt. At 1600°C the first liquidus mineral, Cpx, appears; further increase of temperature (~1380°C) results in addition of Carb. At a temperature of 1200°C and lower we observed an aggregate of subidiomorphic crystals of pyroxene, carbonate and minor garnet, with

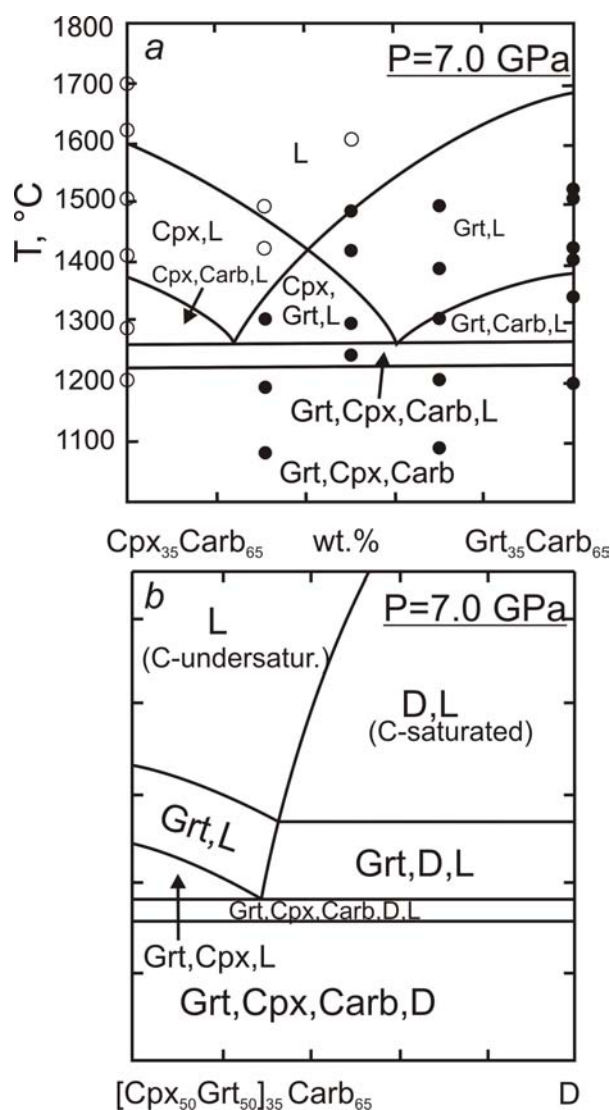no signs of quench textures, that points on the solidus of the system.

Fig. 4 Scheme of melting relations (*a*) and diagram of syngenesis of diamond (D) and its silicate and carbonate inclusions (*b*) in the eclogite-carbonate system at CBDN (35 wt.% eclogite–65 wt.% K-Na-Mg-Ca-Fe carbonate).

The increase of garnet content in the starting materials results in the decrease of the temperature of pyroxene crystallization, so that at 30 wt.% Grt, pyroxene first appears at a temperature of 1420°C. With further increase of garnet concentration, we established a change of liquidus mineral: at 50 wt.% Grt, crystallization of garnet from carbonate-silicate melts was observed. Liquidus field of garnet on the scheme (Fig. 4) is quite wide and spreads over the concentration of garnet in starting materials from ~40 to 100 wt.% Grt, within the temperature range from ~1600 to ~1250°C. As this takes place, garnet concentration in experimental samples increases from 5 to 20–25% with a temperature decrease. In near-solidus area three-phase assemblage of Cpx+Grt+L appears

being replaced with an association of Grt+Carb+L with an increase of garnet content in the system. Finally in one of the runs (1250°C) we established a four-phase assemblage Grt+Cpx+Carb+L that is typical for multi-component system and shown in Fig. 4 as a narrow field. Subsolidus mineral aggregate of Grt+Cpx+Carb was formed below this field in the whole range of starting compositions.

Conclusion

The results obtained prove the carbonatite (carbonate-silicate) model of diamond genesis and point on theoretical possibility of crystallization of peridotitic and eclogitic silicate minerals syngenetically to diamond in silicate-carbonate melts under PT-conditions of diamond stability.

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