

## Diamond crystallization in carbonate-silicate systems: implications for natural diamond genesis

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The abundance of inclusions in diamonds implies that the base of the mantle diamond-forming medium was made up of sulfides, silicates, and oxides. Findings of fluid inclusions in diamonds from kimberlite pipes suggest that a very important feature of the mantle medium of diamond crystallization was its enrichment in potassium and carbonates (Schrauder & Navon 1994). According to experimental data only alkaline carbonate melts and C-O-H fluid can provide the diamond crystallization at the P-T conditions corresponding to the formation of natural diamonds (Pal'yanov et al., 2002). Since the major constituent of the Earth's mantle is silicates, the experimental study of diamond crystallization in potassium bearing carbonate-silicate systems is essential for understanding the natural diamond formation.

Diamond crystallization and character of phase formation in the systems  $K_2CO_3$ -C,  $K_2CO_3$ -SiO<sub>2</sub>-C, and  $K_2CO_3$ -Mg<sub>2</sub>SiO<sub>4</sub>-C were studied at 6.3 GPa and 1650 °C for 40 hours, using a Malinovskiy-type (8-6) multi-anvil apparatus (BARS) installed in the Institute of Geology and Mineralogy at Novosibirsk. The SiO<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> and Mg<sub>2</sub>SiO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub> ratios were chosen as variable parameters. The degree of graphite-to-diamond transformation and rate of diamond growth on seeds have been determined as a function of these ratios.

The character of phase formation as a function of SiO<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub> is schematically shown in Fig. 1a. As SiO<sub>2</sub> increases in the system, the carbonate-silicate melt loses its capacity to initiate diamond nucleation and, in the domain of high concentrations of SiO<sub>2</sub>, provides only recrystallization of metastable graphite and diamond growth on seeds. As the melt becomes richer in silica, first K-wadeite (K<sub>2</sub>SiSi<sub>3</sub>O<sub>9</sub>) and then coesite crystallize.

The character of phase formation and diamond crystallization with different K<sub>2</sub>CO<sub>3</sub>/Mg<sub>2</sub>SiO<sub>4</sub> ratios is shown in Fig. 1b. It is seen that as the Mg<sub>2</sub>SiO<sub>4</sub> content increases, the carbonate-silicate melt ceases to provide spontaneous nucleation of diamond, and in the domain of high concentrations of Mg<sub>2</sub>SiO<sub>4</sub>, only seeded diamond growth and recrystallization of metastable graphite are possible. Simultaneously, the carbonate-

silicate melt becomes oversaturated first with forsterite and then, with forsterite and periclase.

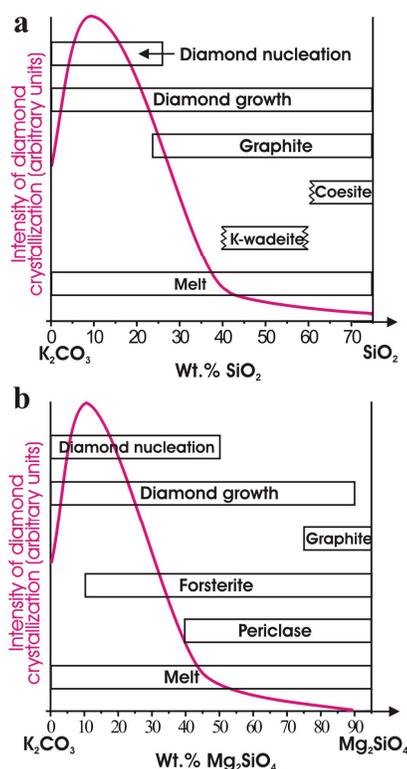


Fig. 1. Character of phase formation and diamond crystallization in the system  $K_2CO_3$ -SiO<sub>2</sub>-C (a) and  $K_2CO_3$ -Mg<sub>2</sub>SiO<sub>4</sub>-C (b) at 6.3 GPa, 1650 °C and run duration of 40 hs.

The geochemical and petrological data available indicate that the crystallization, at least, of some part of diamonds is related to processes of mantle metasomatism and occurred from the carbon-oversaturated carbonate-silicate fluxes. According to experimental data, carbonate melts could have been formed under the conditions of the upper mantle as a result of partial melting of carbonated mantle peridotite near its solidus. An increase in temperature

by 70–100 °C above the solidus could lead to a considerable increase in silicate/carbonate ratio and gradual transition from carbonate to carbonate-silicate melt compositionally close to kimberlite (Dalton & Presnall, 1998).

To estimate the effect of the silicate/carbonate ratio on the diamond formation in the studied systems, we determined the degree of graphite-to-diamond transformation as:  $A = (M_{Dm}/M_{Gr})100\%$ , where  $M_{Dm}$  is the mass of the obtained diamond except of the diamond layers grown on the seed crystals,  $M_{Gr}$  is the mass of the initial graphite. The results show that as the  $\text{SiO}_2$  content in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  increases to 10 wt.%,  $A$  increases by 50% and then, with a further increase in silica concentration, successively decreases to zero (Fig. 2). The dependence of the degree of graphite-to-diamond transformation on the  $\text{Mg}_2\text{SiO}_4$  content in the system  $\text{K}_2\text{CO}_3\text{-Mg}_2\text{SiO}_4\text{-C}$  is similar to the  $A$  dependence of  $\text{SiO}_2$  concentration in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  (Fig. 2). In the domain of high concentrations of silica and forsterite, the intensity of diamond formation was estimated from the rate of diamond seeded growth. The results of measurements given in Fig. 3 indicate a gradual decrease in diamond growth rate on the faces {100} and {111} of seed crystals with increasing content of silica in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  and forsterite in the system  $\text{K}_2\text{CO}_3\text{-Mg}_2\text{SiO}_4\text{-C}$  (Fig. 3). Thus, the general tendency is that the catalytic potential of the studied systems relative to diamond varies with an increase in silicate/carbonate ratio, increasing in the domain of low concentrations of silicate and decreasing in the domain of its high concentrations (Fig. 1).

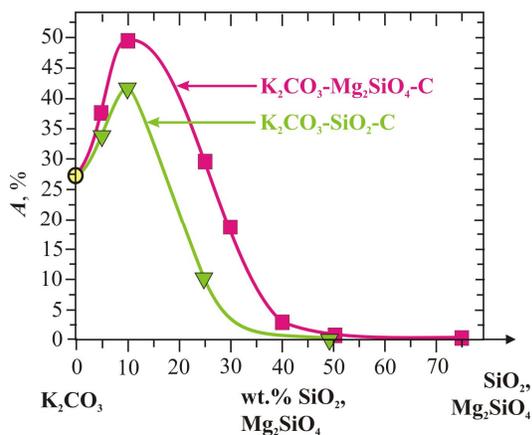


Fig. 2. Degree of graphite-to-diamond transformation ( $A$ ) as a function of  $\text{SiO}_2$  concentration in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  and  $\text{Mg}_2\text{SiO}_4$  in the system  $\text{K}_2\text{CO}_3\text{-Mg}_2\text{SiO}_4\text{-C}$ .

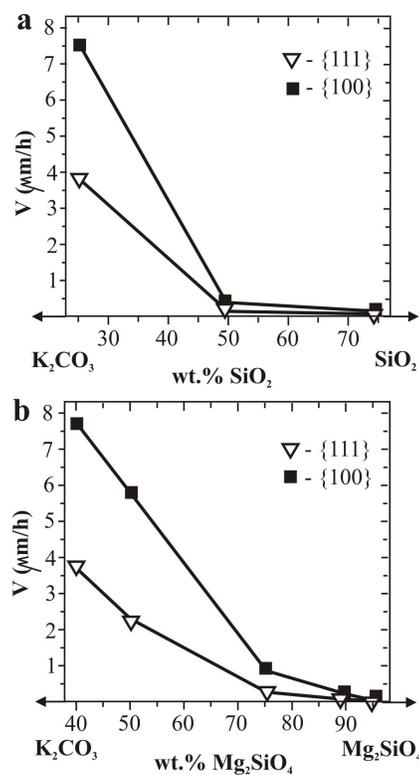


Fig. 3. Rate of diamond crystal growth on the seed versus  $\text{SiO}_2$  and  $\text{Mg}_2\text{SiO}_4$  content in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  (a) and  $\text{K}_2\text{CO}_3\text{-Mg}_2\text{SiO}_4\text{-C}$  (b), respectively.

In the range of compositions from 5 to 25 wt.%  $\text{SiO}_2$  in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$ , silica was completely dissolved in the carbonate melt (Fig. 1). Therefore, an increase in  $\text{SiO}_2$  concentration in the system was accompanied with the same increase in its concentration in the melt. At 50 wt.%  $\text{SiO}_2$ , the system becomes oversaturated with K-wadeite, and at 75 wt.%, with coesite (Fig. 1). On the basis of these data, the solubility of  $\text{SiO}_2$  in the  $\text{K}_2\text{CO}_3$  melt at 6.3 GPa and 1650 °C is estimated at  $\geq 25$  wt.%. The principal structural differences of the carbonate and silicate melt suggest that the  $\text{SiO}_2$  dissolution in the carbonate melt should be accompanied by an increased degree of its polymerization and viscosity (Treiman & Schedl 1983). Given these estimates and experimental data, the change in intensity of diamond formation in the system  $\text{K}_2\text{CO}_3\text{-SiO}_2\text{-C}$  is most likely due to considerable changes in the structure and properties of carbonate-silicate melt with increasing concentration of  $\text{SiO}_2$  dissolved in it. Since the dependence of the catalytic potential on  $\text{SiO}_2/\text{K}_2\text{CO}_3$  and  $\text{Mg}_2\text{SiO}_4/\text{K}_2\text{CO}_3$  in the system are similar, the change in intensity of diamond crystallization with an increased content of  $\text{Mg}_2\text{SiO}_4$  in the system  $\text{K}_2\text{CO}_3\text{-Mg}_2\text{SiO}_4\text{-C}$  is possibly related to the increased silica-to-carbonate ratio in the melt.

The crystallization of metastable graphite (Fig. 4) as well as termination of diamond crystallization in the domain of high concentrations of  $\text{SiO}_2$  or  $\text{Mg}_2\text{SiO}_4$  (Fig. 1) are probably related to the fundamental

changes of structural properties of the carbonate-silicate melt, which favor the crystallization of carbon in  $sp^2$  and  $sp^3$  forms at high and low silicate concentration, respectively.

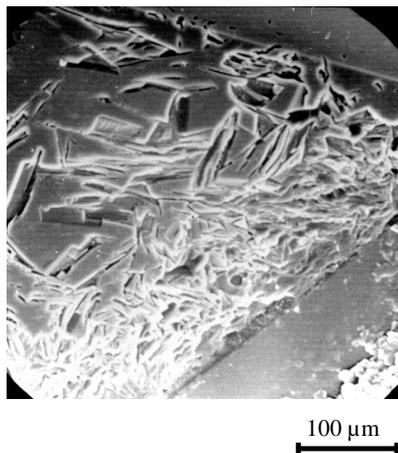


Fig. 4. Prints of joint diamond-graphite growth on the {111} face of the seed at 75 wt%  $Mg_2SiO_4$  in the system  $K_2CO_3-Mg_2SiO_4-C$ .

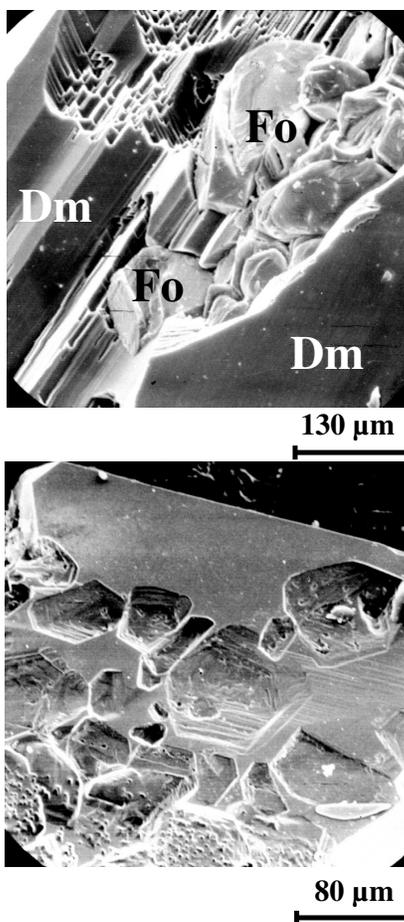


Fig. 5. Illustration of cocrystallization of diamond and forsterite: a) fragment of diamond seed crystal with in-grown forsterite crystals at 40 wt%  $Mg_2SiO_4$ ; b)

induction surfaces of diamond-forsterite cocrystallization on {111} face of seed crystal at 30 wt%  $Mg_2SiO_4$ .

In solving many problems related to diamond genesis, of special importance is the study of the effect of physicochemical conditions of growth on crystal morphology. It has been established in (Pal'yanov et al. 1999) that in the alkaline carbonate-carbon systems at 7.0 GPa and 1700–1750 °C the diamond morphology is well determined by the cationic composition of carbonates and gradually changes from cuboctahedron to octahedron in the series  $Li_2CO_3-Na_2CO_3-K_2CO_3-Cs_2CO_3$ . The results of our studies show that under the constant cationic composition of alkaline carbonate, the introduction of silica or forsterite into the system  $K_2CO_3-C$  does not change the diamond morphology (Shatskii et al. 2002). It is probable that in alkaline carbonate and carbonate-silicate systems the carbonate composition is one of the main factors controlling the diamond morphology.

The cooccurrence of ultrapotassic fluxes and minerals of the main mantle-derived parageneses in inclusions in natural diamonds implies that these melts played an important role in crystallization of diamonds of eclogitic and peridotitic mantle parageneses. In the present work, we succeeded in reproducing the conditions under which diamond was crystallized from a potassium carbonate-silicate melt including the main components of mantle ultrapotassic fluxes, together with coesite (mineral of eclogite paragenesis) in the  $K_2CO_3-SiO_2-C$  system and with forsterite (mineral of peridotite paragenesis) in the system  $K_2CO_3-Mg_2SiO_4-C$  (Fig. 5).

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