



DIAMOND-FORMING EFFICIENCY OF CHLORIDE-SILICATE-CARBONATE MELTS: THE ROLE OF CHLORIDES

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INTRODUCTION

According to the carbonatite model of the diamond formation (Litvin, 2007) based on the large volume of mineralogical and physicochemical experimental information, carbon-silicate-carbonate (carbonatitic) melts with widely variable compositions are the growth medium for most mantle diamonds and inclusions in them. In addition to the major completely miscible carbonate and silicate components (minerals of peridotite and eclogite assemblages), such melts contain minor soluble components (oxides, phosphates, chlorides, C-O-H-N fluids, and others), as well as minor completely immiscible and insoluble solid and melt phases (sulfides, metals). The diamond-forming efficiency of silicate-carbonate melts clearly corresponds to the important criterion of syngensis of diamond with its silicate and carbonate inclusions. High-pressure experimental associations not only include the whole set of minerals typical for inclusions in diamonds of peridotitic (olivine, garnet, clino-, and orthopyroxenes) and eclogitic (garnet and clinopyroxene) type, but demonstrate the characteristic features of minerals of diamond paragenesis. These comprise significant admixtures of Na in garnets and K in clinopyroxenes, which are the reliable indicators of crystallization of these minerals from alkaline silicate-carbonate melts.

Experimental investigations of multicomponent *peridotite*-carbonatite and *eclogite*-carbonatite systems at a standardized pressure of 8.5 GPa within the narrow temperature range of 1760-1820°C demonstrated that the diamond-forming efficiency of their carbon-bearing melts had concentration limitations (Bobrov and Litvin, 2009). The compositions effective for the diamond nucleation are related to only significantly carbonatite parts of the systems and are limited by the concentration barriers of diamond nucleation (CBDN) in the cases of K-Na-Ca-Mg-Fe-carbonatite, Ca-Mg-, and K-carbonate compositions (at the concentrations of 30, 25, and 30 wt % of peridotite components and 35, 30, and 45 wt % of eclogite component, respectively). This means that the inhibitory influence of peridotite and eclogite components dissolved in carbon-bearing carbonatite melts on diamond nucleation is observed only at their relatively low concentrations.

Diamond nucleation and growth were observed in experiments with *chloride components*. Yu.A. Litvin (2007) carried out successful diamond synthesis in the KCl-C melts at pressures of 7.0-8.0 GPa and temperatures up to 1700°C. The efficiency of diamond formation in carbonate-chloride (K₂CO₃-KCl) melts with dissolved carbon was established at 7.7 GPa and 1050-1420°C (Tomlinson et al., 2004). Yu.N. Pal'yanov et al. (2007) studied diamond



crystallization in the fluid-bearing system $\text{KCl}^*\text{K}_2\text{CO}_3\text{H}_2\text{O}^*\text{C}$ at 7.5 GPa and 1400–1800°C. The concentration of chloride components in some fluid/melt inclusions in diamonds is quite significant (Izraeli et al., 2001; Klein-BenDavid et al., 2004). Their influence on the diamond formation (and mainly on CBDN position) in multicomponent silicate-carbonate melts is not clear and requires experimental investigation.

EXPERIMENTAL TECHNIQUES

In this study we performed testing of the diamond-forming efficiency of chloride-silicate-carbonate melts with dissolved carbon, the components of which are widely abundant in crystal and fluid/melt inclusions in natural diamonds. The silicate component is represented by the model compositions of bimineral eclogite; the carbonate component, by multicomponent K-Mg-Ca-carbonatite; chloride component, by mixture of KCl and NaCl taken in equal weight proportions. 40 wt % of chemically pure graphite was added to the prepared chloride-silicate-carbonate mixtures.

Our investigations were performed on a high-pressure toroidal “anvil-with-hole” apparatus using special cells with tubular graphite heaters [Bobrov and Litvin, 2009] at standardized PT-parameters (8.5 GPa, 1800°C) in the Institute of Experimental Mineralogy, Russian Academy of Sciences. We performed two series of experiments.

RESULTS AND DISCUSSION

The first series of experiments allowed us to observe the formation of graphite (the area of metastable oversaturation) or diamond (the area of labile solutions) depending on relationships between silicates and carbonates. In the first case small segregations of graphite as scales or round globules were obtained. As this took place, the growth of diamond was registered on (100) and

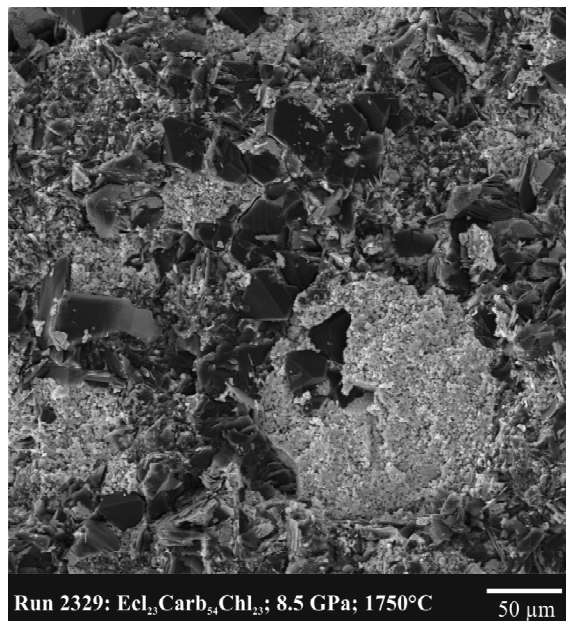


Fig. 1. Effect of immiscibility between chloride and silicate-carbonate melts in the experimental sample after quenching. Diamond crystals occur in fine-granular silicate-carbonate groundmass. Secondary electron image.

(111) seed faces. In the second case we obtained diamond as octahedral and twins (spinel law). We calculated the density of diamond nucleation, which characterizes the number of embryos in the volume unit of experimental samples and, accordingly, may be the quantitative characteristic of the diamond-forming efficiency. The values obtained (from $4.1 \cdot 10^4$ to $6.7 \cdot 10^4$ grains/mm³) are quite high being typical for diamond synthesis in carbonate melts. Spontaneous diamond nucleation was obtained for the compositions $(\text{Ecl}_{20}\text{Carb}_{80})_{60}\text{C}_{40}$ and $(\text{Ecl}_{30}\text{Carb}_{70})_{60}\text{C}_{40}$. The latter composition was accepted as the CBDN position; because of this, it was applied in the second experimental series.

In the second experimental series performed with participation of chloride components, the formation of diamond was registered only for two starting compositions $([\text{Ecl}_{21}\text{Carb}_{49}\text{Chl}_{30}]_{60}\text{C}_{40})$ and $([\text{Ecl}_{15}\text{Carb}_{62}\text{Chl}_{23}]_{60}\text{C}_{40})$, the density of nucleation decreased ($2.2 \cdot 10^4$ grains/mm³), whereas average crystal sizes increased. Note that



the relationships between carbonate and silicate components in the first composition correspond to the CBDN of chloride-free carbonate-silicate melts obtained in the first series. Increase of chloride concentration in comparison with this composition $[(\text{Ecl}_{20}\text{Carb}_{47})\text{Chl}_{33}]_{60}\text{C}_{40}]$ results in termination of diamond spontaneous nucleation. Some runs performed at long durations demonstrated the samples with clear signs of liquid immiscibility (Safonov et al., 2007): globules of essentially chloride composition (SiO_2 1.13; Al_2O_3 0.43; FeO 1.87; MgO 7.58; CaO 9.64; Na_2O 13.58; K_2O 30.36; Cl 32.98 wt %) are located in the silicate-carbonate groundmass (SiO_2 4.31; Al_2O_3 0.77; FeO 0.85; MgO 41.69; CaO 18.84; Na_2O 2.46; K_2O 2.23; Cl 2.57 wt %). The formation of diamond occurred only in silicate-carbonate (carbonatite) melt (Fig. 1). It should also be noted that liquid immiscibility was not detected for compositions with less than 30 wt % of silicates even in long (>2 h) experiments, and an increase in the concentration of chloride component diminished the diamond-forming efficiency of the melts up to the complete cessation of diamond nucleation at a chloride content of >30 wt %.

As was shown by O.G. Safonov et al. (2007), the behavior of chloride-carbonate-silicate systems is characterized by the following features: (1) the wide area of liquid immiscibility, which controls the existence of two trends of the evolution of the composition of fluid inclusions in diamonds (silicate-carbonate and chloride-carbonate) and the absence of transitional silicate-chloride compositions; (2) the wide field of silicate crystallization near the liquidus; and (3) the direction of cotectic lines toward carbonates in the pseudo-ternary system. The main process in the evolution of such melts is the liquidus crystallization of silicate phases, which will result in melt depletion in silicate components, hence, stimulating better miscibility in the residual melts. With decreasing temperature, the high-temperature carbonate-silicate melt coexisting

with chloride-carbonate liquid may evolve into a homogeneous chloride-carbonate-silicate melt in equilibrium with silicate minerals.

CONCLUSION

Thus, the chloride components of diamond-forming melts should also be considered as typical *minor* constituents. Moreover, the preliminary experimental results suggest that they probably play an inhibitory role in the process of diamond formation. The wide occurrence of chlorides in the composition of high-density melt/fluid inclusions in diamonds is explained by the processes of immiscibility in parental diamond-forming systems with separation of chloride-carbonate melts with variable contents of chloride components.

Accounting for the influence of minor components on diamond formation allows us to develop the concept of carbonate-silicate (carbonatite) growth media for the majority of natural diamonds. The proposed concept is well consistent with the mineralogical database on the chemical compositions of materials captured by diamonds in situ from the parental melts and the results of experimental physicochemical investigations based on the syngensis of diamond and inclusions in it. This provides a basis for development of a genetic classification of growth inclusions of minerals, melts, and fluids in natural mantle-derived diamonds (Litvin, 2009). Such a classification reveals physicochemical relations of the materials of growth inclusions with the components of carbonatitic growth melts and the physical parameters of the formation of particular inclusions.

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