

### Diamond-forming efficiency of chloride-silicate-carbonate melts

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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 comprise 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.

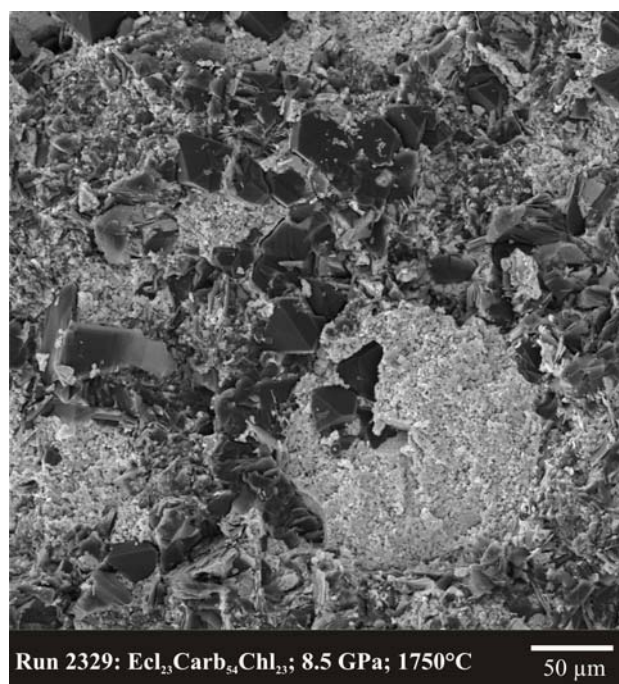
Experimental investigations of multicomponent peridotite-carbonatite and eclogite-carbonatite systems at a standardized pressure of 8.5 GPa within the narrow pressure range of 1760–1820°C demonstrated that the diamond-forming efficiency of their carbon-bearing melts had concentration limitations [Bobrov and Litvin, 2009]. The compositions effective for the diamond nucleation comprise 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.

We established the diamond-forming efficiency of chloride [Litvin, 2003] and chloride-carbonate [Tomlinson *et al.*, 2004] melts with dissolved carbon. The concentration of chloride components in some fluid/melt inclusions in diamonds is quite significant [Izraeli *et al.*, 2001; Klein-BenDavid *et al.*, 2004]. As this takes place, their influence on the diamond formation (and mainly on CBDN position) in multicomponent silicate-carbonate melts is not clear and requires experimental investigation. 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 biminerall 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. The first series was carried out in the carbonate-silicate system in order to determine the compositional range (the relationships between silicate and carbonate components, CBDN), in which spontaneous nucleation occurs during the first minutes of the

experiment; the run duration did not exceed 10 min. The second experimental series was aimed on the study of the influence of chloride components on diamond crystallization in multicomponent melts.

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 (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/mm<sup>3</sup>) are quite high being typical for diamond synthesis in carbonate melts. Spontaneous diamond nucleation was obtained for the compositions (Ecl<sub>20</sub>Carb<sub>80</sub>)<sub>60</sub>C<sub>40</sub> and (Ecl<sub>30</sub>Carb<sub>70</sub>)<sub>60</sub>C<sub>40</sub>. The latter composition was accepted as the CBDN position; because of this, it was applied in the second experimental series.



**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.

In the second experimental series performed with participation of chloride components, the formation of diamond was registered only for two starting compositions ([Ecl<sub>21</sub>Carb<sub>49</sub>Chl<sub>30</sub>]<sub>60</sub>C<sub>40</sub> and [(Ecl<sub>15</sub>Carb<sub>62</sub>)Chl<sub>23</sub>]<sub>60</sub>C<sub>40</sub>), the density of nucleation decreased ( $2.2 \cdot 10^4$  grains/mm<sup>3</sup>), 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 [(Ecl<sub>20</sub>Carb<sub>47</sub>)Chl<sub>33</sub>]<sub>60</sub>C<sub>40</sub> 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<sub>2</sub> 1.13; Al<sub>2</sub>O<sub>3</sub> 0.43; FeO 1.87; MgO 7.58; CaO 9.64; Na<sub>2</sub>O 13.58; K<sub>2</sub>O 30.36; Cl 32.98 wt %) are located in the silicate-carbonate groundmass (SiO<sub>2</sub> 4.31; Al<sub>2</sub>O<sub>3</sub> 0.77; FeO 0.85; MgO 41.69; CaO 18.84; Na<sub>2</sub>O 2.46; K<sub>2</sub>O 2.23; Cl 2.57 wt %). As this took place, the formation of diamond occurred only in silicate-carbonate (carbonatite) melt. In our opinion, this observation, as well as termination of spontaneous diamond nucleation with increase of chloride concentration provides evidence for the negative influence of chloride components on the diamond formation, at least in the cases of their high concentrations.

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