

DIAMOND SYNTHESSES FROM SILICATE-CARBONATE-CARBON MELTS AT 6-8.5 GPa: LIMITS OF DIAMOND FORMATION AND FORMS OF DISSOLVED CARBON

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Syngenetic fluid and mineral inclusions in diamonds are the fragments of parental environment from which diamonds have crystallized. Inclusion compositions are indicative of the complexity and variability of natural diamond parental environment. Fluid inclusions are characterized by complex chemical compositions [1, 2]. It is established that at room temperature they contain silicates, carbonates, phosphates, oxides, chlorides, and other solid phases together with water and carbon dioxide. Primary solid inclusions contain minerals of both peridotitic and eclogitic parageneses [3].

Experimental attempts of diamond synthesis in silicate systems in wide ranges of pressures and temperatures proved these systems to be ineffective as parental despite their statistical domination in primary diamond inclusions. Experiments on diamond crystallization in carbonate systems of different compositions similar to those of primary inclusions showed that carbonates are very effective as parental diamond environment [4, 5, 6]. Nevertheless, silicates and carbonates dominate among the components of the parental diamond environment in terms of concentrational contribution [7]. Thus, the problem of physico-chemical role of silicate components in natural processes of diamond formation in carbonate-silicate-carbon parental melts steps out.

There are experimental data [8, 9] on diamond synthesis in simple carbonate-silicate-carbon systems: $K_2CO_3 - SiO_2 - C$ and $K_2CO_3 - Mg_2SiO_4 - C$ when simplified technique was used – starting materials were mechanical mixtures of components, where the thresholds of spontaneous diamond nucleation were established at silicate component concentration of 25 and 50 wt.% respectively.

There are several reasons why the problem of diamond crystallization in natural carbonate-silicate-carbon melts is of interest. Among those are questions regarding the origin and evolution of melts parental to diamonds, physico-chemical conditions of syngeneses of diamonds and silicate minerals of peridotitic and eclogitic parageneses, forms of carbon dissolution in carbonate-silicate melts, etc.

Experiments in this study started in carbonate-silicate systems of model compositions that to some extent are close to the natural environment of diamond genesis. Silicate is represented by a model eclogite of the following composition: $(Di_{50}Jd_{50})_{50}(Grs_{60}Pyr_{40})_{50}$ and does not contain any iron - an element with a variable valence (it's done to avoid possible influence of variable red-ox states on dissolved forms of carbon in melts).

Carbonates are represented by alkali carbonate K_2CO_3 and dolomite $CaMg(CO_3)_2$ on this stage of the research. In the future it is planned to approach our model carbonate compositions to those multi component carbonate compositions representative of natural diamonds parental environment. Essential innovation in experimental approach is the use of homogeneous carbonate-silicate glasses as starting materials. These glasses when melted produce only one interface with starting graphite where the dissolution of carbon into the homogeneous carbonate-silicate melt occurs. In the mechanical mixture of silicate and carbonate components on the other hand there are three interfaces: carbonate – graphite, silicate – graphite and carbonate – silicate. The carbonate – silicate melt and graphite interface does form with time but at this moment because of high speed of spontaneous nucleation of diamond on the carbonate – graphite interface it is already possible to have diamonds in the system. Such scenario of experiment might result in incorrect estimate of diamond genesis limits in carbonate-silicate systems.

Experiments were carried out on the “anvil with hole” high-pressure apparatus [10] at pressures 6 – 8.5 GPa and temperatures 1200 – 1800°C. Starting carbonate-silicate glasses were prepared in a high pressure gas apparatus at 1 kbar and 1350°C in the presence of argon in open platinum capsules. Homogeneity of glasses is confirmed by microscope inspection and by microprobe analyses. Crushed glasses were mixed with graphite of high purity (99.95%) in the 60:40 proportion and then placed in graphite capsules of 5 mm diameter (wall thickness - 1 mm). These graphite capsule were also serving as heaters. Such assembly allows us to assume oxygen fugacity limited by $C/CO_2(CO_2^{2-})$ buffer pair and limited within 1-2 logarithmic units below FMQ buffer. Experiments carried out earlier on the same experimental assembly showed the stability of oxygen fugacity during experiments [11].

The goal of our experiments is to establish maximum content of silicate component that allows effective diamond nucleation and crystallization in carbonate – silicate system. The criterion of efficiency estimate is the fact of spontaneous nucleation of diamond in experiments.

Experimental study was started from model systems eclogite $[(\text{Di}_{50}\text{Jd}_{50})_{50}(\text{Grs}_{60}\text{Pyr}_{40})_{50}]_{50} - [\text{K}_2\text{CO}_3]_{50}$ or dolomite $\text{CaMg}(\text{CO}_3)_2$ and eclogite $[(\text{Di}_{50}\text{Jd}_{50})_{50}(\text{Grs}_{60}\text{Pyr}_{40})_{50}]_{70} - [\text{K}_2\text{CO}_3]_{30}$ or dolomite $\text{CaMg}(\text{CO}_3)_2$.

The formation of labile melts oversaturated in respect to diamond and intense spontaneous nucleation of diamond was registered in the model system $\text{eclogite}_{50}[\text{K}_2\text{CO}_3]_{50}$ at 7.5 – 8.5 GPa - at least $3 - 5 \cdot 10^3$ of “survived” nucleuses in 1 mm^3 in areas of high temperature gradients, temperature was lower than 1700°C (Fig. 1-3, run conditions are in parentheses). Spontaneous nucleation and formation of metastable single crystals of graphite was observed in the central zone of sample at conditions of low temperature gradients (around 1700°C ; Fig. 4).

Carbon phase is represented by well-crystallized graphite grains in experimental products of $\text{eclogite}_{70}[\text{K}_2\text{CO}_3]_{30}$ system (Fig. 5), which are metastable at experimental conditions.

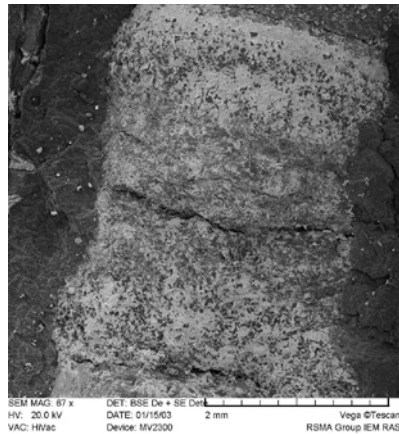


Fig. 1. Spontaneous nucleation of diamond in $\text{eclogite}_{50}(\text{K}_2\text{CO}_3)_{50}$ system. Diamonds are concentrated in the zones of high temperature gradients – on the periphery of the sample (general view of sample 965, 7.5 GPa, 1700°C , 40 minutes).

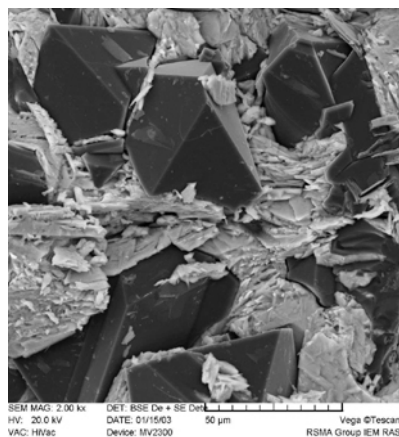


Fig. 2. Mass crystallization of diamond in carbonate-silicate melt (quenches in homogeneous carbonate-silicate glass; sample 965, 7.5 GPa, 1700°C , 40 minutes).

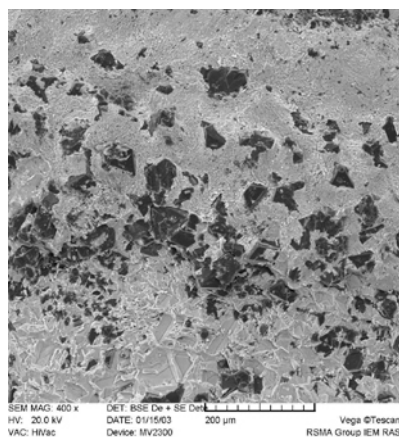


Fig. 3. Diamond crystals in the place of formation in carbonate-silicate melt with carbon (after experiment – quenched glass; sample 965, 7.5 GPa, 1700°C , 40 minutes).

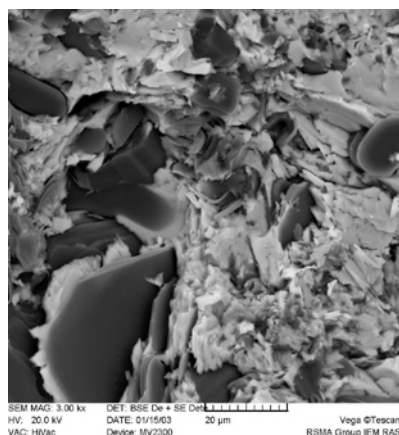


Fig. 4. Single crystals of graphite forming as metastable phase in the diamond stability field in eclogite₅₀-(K₂CO₃)₅₀ system (sample 965, 7.5 GPa, 1700°C, 40 minutes).

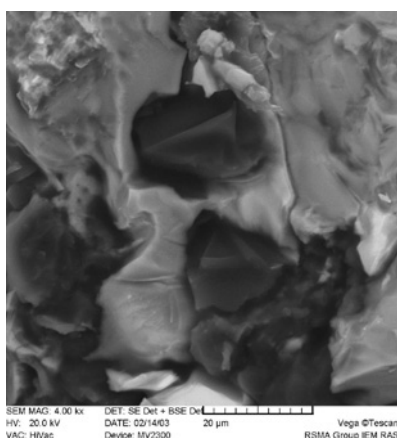


Fig. 5. Single crystals of graphite forming as metastable phase in the diamond stability field in eclogite₇₀-(K₂CO₃)₃₀ system (sample 1000, 8.5 GPa, 1700°C, 40 minutes).

Despite the absence of diamonds of spontaneous nucleation in experimental products, the growth of seed crystal faces was still registered in the system of mentioned composition as well as in our model systems with the content of eclogite component up to 70 wt.%. This fact shows that there are kinetic difficulties in spontaneous nucleation of diamond in the field of its stability from carbonate-silicate-carbon melts in the area of silicate-rich rich compositions. Based on experimental data received for model system eclogite - K₂CO₃, the limit of diamond spontaneous nucleation lies in the interval of compositions eclogite₆₀ – eclogite₅₀. Higher content of silicate component in the system suppresses formation of solutions that characterized by labile oversaturation in respect to diamond.

Growth of seed crystal faces was also noticed in experiments on eclogite – dolomite system. However spontaneous nucleation and further crystallization of diamonds was not registered in the whole range of pressures (6.5 – 8.5 GPa), temperatures (1200 – 1800°C) and compositions investigated (carbonate/silicate ratios from 70/30 to 30/70). In all experiments conducted carbon phase was represented by thermodynamically unstable graphite (Fig. 6). Such results allow us to suggest that kinetic threshold for this system was not reached (i.e. the boundary of solutions that have labile oversaturation to diamonds is situated at higher pressures). Another interesting fact has been experimentally established – it is clear from experimental products that strong convective mixing took place in our experiments in carbonate-silicate-carbon systems of different compositions (alike processes might be taking place at Earth's mantle conditions, example of convective mixing is shown in Fig. 7). This suggests that together with diffusive mechanism of mass – transfer of carbon during formation of diamonds and metastable graphite, convective mass – transfer of carbon dissolved in carbonate-silicate melts might also be very important process.

Investigation of forms of dissolved carbon and its compounds has also been started in this work. IR and RAMAN spectroscopy are being used for this purpose. It is also interesting to investigate possible dependence between diamond spontaneous nucleation and oxygen fugacity.

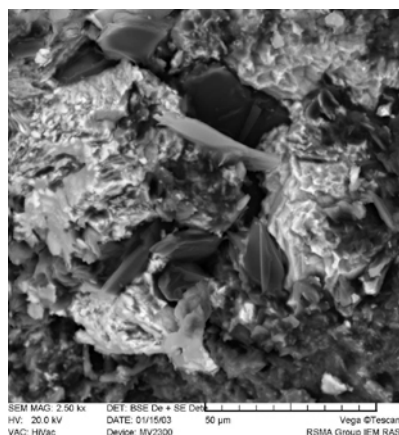


Fig. 6. Single crystals of graphite forming as metastable phase in the diamond stability field in eclogite₅₀-dolomite₅₀ system (sample 964, 7.5 GPa, 1700°C, 40 minutes).

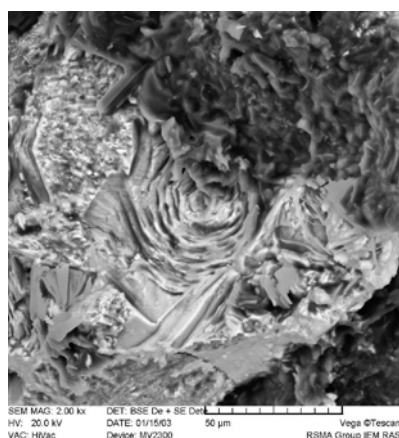


Fig. 7. Convectional forms of "tornado" type in carbonate-silicate-carbon melt of eclogite₅₀-dolomite₅₀ system (sample 967, 7 GPa, 1700°C, 40 minutes).

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