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An experimental demonstration of diamond formation in the dolomite-carbon and dolomite-fluid-carbon systems

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Abstract: The results of a study of diamond crystallisation in dry and fluid-rich dolomite-carbon systems are presented. For the dry system an induction period preceding spontaneous diamond nucleation was found of about 4 h at 7 GPa, 1700 °C. No diamonds were observed after 42 h of reaction at 5.7 GPa, 1420 °C. Adding H_2O and H_2O-CO_2 fluids to the dolomite-carbon system resulted in spontaneous diamond nucleation at 1420 °C, and growth of diamond on seed crystals at 1300-1420 °C. In the presence of H_2O or H_2O-CO_2 fluids, dolomite decomposes to dolomite solid solution + brucite + aragonite. Results of the experiments indicate that dolomitic melts in the mantle, enriched in H_2O and CO_2, promote the formation of natural diamond.

Key-words: diamond crystallisation, dolomite, carbon, fluid, HP/HT experiments.

Introduction

The origin of natural diamond has been debated for many decades. Recent models for diamond formation are based on a combination of mineralogical, geochemical and petrological data (Sobolev, 1977; Meyer, 1987; Sobolev & Shatsky, 1990; Harris, 1992; Schrauder & Navon, 1994; Haggerty, 1999). Traditionally, the main directions of investigation in this area are the reconstruction of diamond crystallisation parameters, estimation of its age and connection with certain deep-seated parageneses as well as the determination of a probable carbon source. The basic assumption of such models is a proposition that the conditions of diamond thermodynamic stability are sufficient for the realisation of its crystallisation in the mantle.

The first calculation of the diamond thermodynamical stability region (Leipunsky, 1939) and the idea about the interconnection of natural diamond genesis problems with the problems of its laboratory synthesis (Sobolev, 1960) served as important supports for the beginning of experimental investigations in this area. Until recently, experimental modelling of mantle diamond formation has encountered a problem with the impossibility of diamond synthesis in the petrologically important systems. Historically first was a study of Wentorf (1974). Based on the results of short-term experiments in the region of diamond thermodynamic stability, he recognised graphite- and diamond-producing systems. On the basis of obtained data, silicate, sulphide and carbonate systems were related to the group of graphite-producing carbon solvents. The experimental data on catalytic properties of carbonates and some other non-metallic compounds in connection with diamond synthesis (Akaishi *et al.*, 1990; Taniguchi *et al.*, 1996; Litvin, 1998; Pal'yanov *et al.*, 1998a and b; Sato *et al.*, 1999) have changed the situation in this direction. Their experimental works were carried out with a specificity at P ≥ 7 GPa and T ≥ 1600 °C, in other words, at parameters essentially exceeding the conventional PT conditions of natural diamond forma-

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Table 1. Experimental results.

Run No	Initial composition	P, (GPa)	T, (°C)	Time, (h)	Seeds sink	Final phases (X-ray)	Diamond	
							Nucleation	Growth on seeds
D1	Do+Gr	7.0	1700	2	+	Do+Gr	–	+
D2	Do+Gr	7.0	1700	4	+	Do+Do$_{ss}$+Gr	+	+
D3	Do+Gr	7.0	1700	16	+	Do+Do$_{ss}$+Ar+Gr	+	+
D4	Do+Gr	7.0	1700	18.5	+	Do+Do$_{ss}$+Ar+Gr+Dm	+	+
D5	Do+Gr	7.0	1700	42	+	Do+Do$_{ss}$+Ar+Gr+Dm	+	+
D6	Do+Gr	5.7	1420	42	–	Do+Gr	–	–
DF1	Do+Gr+H_2O	5.7	1420	42	+	Do$_{ss}$+Br+Ar+Gr	+	+
DF2	Do+Gr+$H_2C_2O_4$x$2H_2O$	5.7	1420	42	+	Do$_{ss}$+Br+Ar+Gr+Mc$_{ss}$	+	+
DF3	Do+Gr+$Ag_2C_2O_4$	5.7	1420	42	–	Do+Do$_{ss}$+Gr	–	+
DF4	Do+Gr+$H_2C_2O_4$x$2H_2O$	5.7	1300	42	–	Mc$_{ss}$+Do$_{ss}$+Ar+Gr	–	+
DF5	Do+Gr+$Na_2C_2O_4$	5.7	1300	42	–	Et+Do$_{ss}$+Gr	–	+

Do - dolomite; Gr - graphite; Do$_{ss}$ - dolomite solid solutions; Ar - aragonite; Dm - diamond; Mc$_{ss}$ - magnesite solid solution; Et - eitelite, Br - brucite.

tion (Sobolev, 1977; Meyer, 1987; Harris, 1992). The studies on diamond formation kinetics in carbonate-carbon systems at 7 GPa and 1700 °C (Pal'yanov *et al.,* 1998a, 1999a) substantiated the possibility of decreasing temperature and pressure of diamond synthesis by increasing the experiments' duration. Another important factor leading to the decrease of diamond crystallisation parameters may be the presence of fluid in growth systems. Investigations of this factor for non-metallic systems are only in the beginning stages (Pal'yanov *et al.,* 1999b; Sokol *et al.,* 2000; Akaishi & Yamaoka, 2000). Pal'yanov *et al.* (1999b) clearly demonstrated the role of fluids in decreasing the parameters of spontaneous diamond nucleation in alkaline carbonate–carbon systems. It is especially important, because contemporary diamond formation concepts assume an essential role of the C-O-H fluids in carbon transport, diamond nucleation and crystallisation (Schrauder & Navon, 1994; Haggerty, 1999).

We investigated diamond crystallisation in the $CaMg(CO_3)_2$–C, $CaMg(CO_3)_2$–CO_2–C, $CaMg(CO_3)_2$–H_2O–C, $CaMg(CO_3)_2$–H_2O–CO_2–C and $CaMg(CO_3)_2$–$Na_2C_2O_4$–C systems at PT parameters corresponding to the ones of natural diamond formation. The selection of the dolomite–carbon system as the basic system was caused by the following factors. During the last decade alkaline-earth carbonates have been found as inclusions in natural diamonds, with their primary origin being corroborated by the presence of intergrowths of carbonates and silicates (Bulanova, 1995; Wang *et al.,* 1996; Sobolev *et al.,* 1997). Participation of carbonated mantle rocks in the formation of kimberlite magmas was experimentally shown in a number of works (Girnis *et al.*, 1995; Canil & Scarfe, 1990; Wyllie & Lee, 1998; Dalton & Presnall, 1998a and b). The abundance of dolomite, magnesite and calcite in diamond-bearing metamorphic rocks was established by Sobolev & Shatsky (1990) and Shatsky *et al.* (1995). The fluid composition we used for the experimental modelling was chosen in accordance with the conventional opinion that H_2O–CO_2 fluids dominate in the upper mantle (Wood *et al.,* 1990; Ballhaus, 1993).

Experimental procedures

The experiments were performed using the "BARS" multi-anvil apparatus (Pal'yanov *et al.,* 1997). A detailed description of the high-pressure cell (18.4x18.4x21.8 mm) and the general methodical approach has been given by Pal'yanov *et al.* (1998a). The pressure was calibrated at room temperature by measuring the variation in conductivity of Bi and PbSe as a function of pressure (2.55, 4.0, and 6.8 GPa respectively). The temperature inside the graphite heater (ø 9 mm and height 15 mm) was monitored during each experiment using a 0.2 mm diameter $PtRh_6/PtRh_{30}$ thermocouple. The thermocouple was calibrated at 7.0 GPa according to the melting of nickel, and at 5.7 GPa to the melting of Ag and Au. Additional P and T corrections were made based on the results of diamond synthesis in the Ni–C system.

In all experiments, graphite with a purity not less than 99.99 % and natural dolomite (Table 1) from the Satka deposit (Chelyabinsk region, Rus-

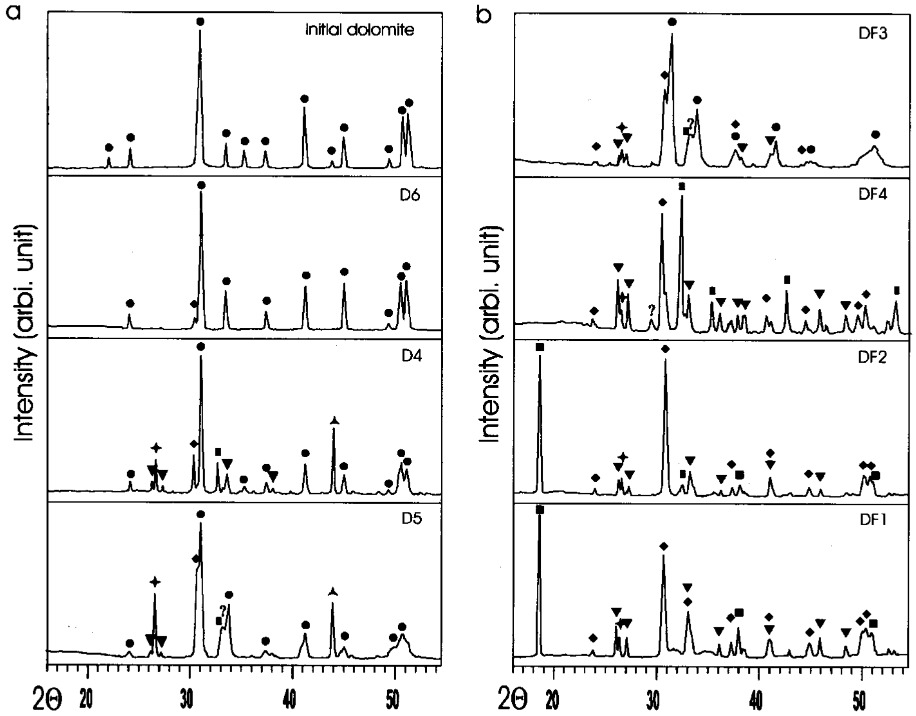

Fig. 1. X-ray diffraction analyses of run products (Cu*K*α-radiation): a – dolomite-carbon system; b – dolomite-fluid-carbon systems; • – dolomite; ◆ – dolomite solid solution; ▼ – aragonite; ✦ – graphite; ★ – diamond; ▮ – magnesite solid solutions; ■ – brucite.

sia) were used. Dolomite was heat treated at 300 °C for 5 hours prior to experimental use. Pt ampoules with an inner diameter of 5.6 mm were used for the experiments. A graphite tablet weighing 15 mg, 77 mg of carbonate, three seeds of synthetic diamond (cuboctahedron) and two seeds of natural diamond (flat-faced octahedron) up to 0.5 mm in size were loaded into the ampoules. For the generation of C-O-H fluids 15 wt. % of distilled H_2O, or 15 wt.% of $H_2C_2O_4 \times 2H_2O$, or 38 wt. % of $Ag_2C_2O_4$, or 22 wt. % $Na_2C_2O_4$ were added into the Pt ampoule. The ampoules were sealed by arc-welding. The melting of dolomite was defined according to the sinking of diamond seeds to the ampoule bottom. Phase and chemical compositions of run products were determined by X-ray diffraction (DRON-3, Cu*K*α radiation) and microprobe ("Camebax-Micro"), respectively. Diamond morphology was studied with optical microscopes and a JSM-35 scanning electron microscope. Tiny spontaneously grown diamond crystals were identified by Raman spectroscopy (OMARS 89).

Results and discussion

The first series of experiments (D1-D6, Table 1) was carried out in the dolomite-C system without fluid. For runs D1-D5, sinking of the seed crystals to the bottom of the Pt ampoule was established, unequivocally pointing to the melting of dolomite, while in experiment D6 seed crystals did not change their position in the ampoule. According to the X-ray (Fig. 1) and microprobe analyses (Table 2), samples D1-D5 consist of dolomite, dolomite solid solution and small quantities of newly formed graphite. An increase in the duration of the experiments resulted in an increase of the dolomite solid solution content along with the appearance of aragonite, diamond and magnesite solid solution. It should be noted that this increase was also accompanied with a broadening of the closely located (018), (116) and (009) peaks of dolomite and a decrease in their intensity. In the D6 sample, no alteration of dolomite was established (Fig. 1).

In experiments D2 and D3, individual newly formed diamond crystals (Fig. 2a) were found at

Table 2. Composition of initial dolomite and carbonates in run products.

				D4			D5			D5		
wt. %	Initial Dolomite			Dolomite solid solution			Dolomite solid solution			Aragonite		
CaO	30.12	30.04	30.24	37.12	37.23	39.29	40.66	40.85	41.68	58.49	58.97	59.16
MgO	21.37	21.64	21.44	18.73	21.13	19.69	16.66	16.77	15.51	0.21	0.06	0.08
Total*	51.49	51.68	51.68	55.85	58.36	58.98	57.32	57.51	57.19	58.70	59.03	59.24
	DF3			DF4			DF4			DF2		
	Dolomite solid solution			Dolomite solid solution			Magnesite solid solution			Dolomite solid solution		
CaO	27.58	27.98	28.65	38.96	38.02	36.13	2.20	2.34	2.50	37.37	40.87	
MgO	29.75	30.11	30.50	16.34	17.00	18.32	45.39	45.37	45.09	16.91	15.13	
Total	57.33	58.09	59.15	55.30	55.02	54.45	47.59	47.71	47.59	54.28	56.00	
	DF5			DF5								
	Dolomite solid solution			Eitelite								
CaO	43.17	44.65		1.93	2.09							
MgO	19.25	14.12		33.76	35.75							
Na_2O	0.57	0.23		21.39	20.29							
Total	62.99	59.00		57.08	58.13							

*- CO_2 cannot be detected.

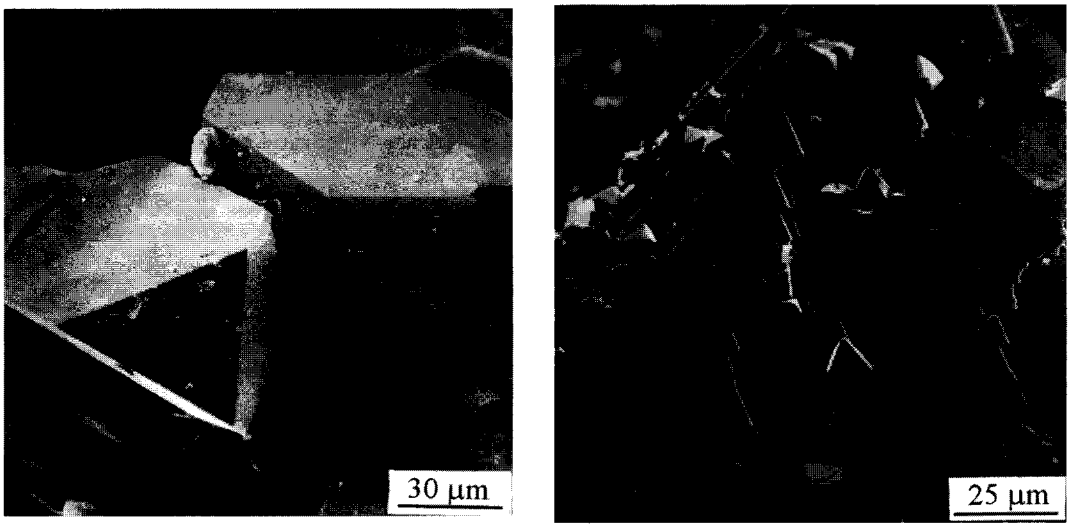

Fig. 2. Scanning electron micrographs: a – spontaneous diamonds synthesised in the $CaMg(CO_3)_2$–C system at 7.0 GPa and 1700 °C; b – growth layers and spontaneous octahedral diamond crystals obtained on the surface of a seed crystal in the $CaMg(CO_3)_2$–H_2O–CO_2–C system at 5.7 GPa and 1420 °C.

the contact of carbonate and graphite. Thus, an inductive period of spontaneous diamond nucleation in the dolomite-carbon system at 7.0 GPa and 1700 °C without fluid lasted about 4 h. In each case, diamond crystals are separated from graphite by thin (30-50 µm) carbonate films. Newly formed diamonds from samples D3-D5 are colourless and reach 200-450 µm. In the D6 experiment, performed at 5.7 GPa and 1420 °C, neither spontaneous crystallisation, nor growth of diamond on seed crystals was established.

In the second series of experiments at 5.7 GPa in the dolomite-fluid-carbon systems, the sinking of diamond seed crystals was established only in experiments DF1 and DF2. In all other cases, the definite determination of their movement failed. The phase compositions of the samples of the first and second series differ essentially (Table 1, Fig. 1).

Only in the dolomite–CO_2–C system (DF3) the degree of dolomite decomposition is relatively small and close to that in D5. In other experiments, the phase composition of the systems experienced significant changes. In DF4, after an experiment at 1300 °C, intense peaks of magnesite solid solution appeared in X-ray patterns (Fig. 1), along with the reflections of dolomite solid solution and aragonite. With increasing temperature in the dolomite–H_2O–C (DF1) and dolomite–CO_2–C (DF2) systems, magnesite solid solution disappears, while dolomite solid solution and brucite become the dominant phases. Among the products of the DF5 experiment, the appearance of eitelite, $Na_2Mg(CO_3)_2$, and dolomite solid solution was established (Table 2). In all the samples of the second series, the presence of newly formed graphite was observed.

Spontaneous octahedral diamond crystals, up to 15 and 8 μm, were found on the surface of seed crystals only in DF1 and DF2 (Fig. 2b). Diagnostics of these spontaneous diamond crystals were confirmed by the Raman spectroscopy. Diamond growth on seed crystals was observed in all experiments of this series. On the {111} faces the maximum thickness of the grown diamond layers was 15 μm in DF1 and 10 μm in DF2. In most cases, the growth occurred as flat layers of triangular shape (Fig. 2b). Growth rates on the {100} faces of seed crystals were essentially higher than on the {111} faces. For example, in DF3 the thickness of the grown layer was 55 μm and in DF1, DF2 and DF5 varied within the range of 15-25 μm. The minimal growth rate on the {100} faces of seed crystals was observed in DF4.

The obtained experimental data on the kinetics and intermediate stages of dolomite decomposition are of interest in the context of the widely discussed problem of carbonate stability at mantle PT parameters (Goldsmith, 1980; Biellmann *et al.*, 1993; Martinez *et al.*, 1996). Dolomite decomposition at the parameters of our experiments begins with the process of cation disordering, manifesting itself in intensity decrease of superstructural reflexes in X-ray patterns (Goldsmith, 1980). Then the formation of dolomite solid solution, aragonite and magnesite solid solution takes place. The process of dolomite decomposition in the dolomite–carbon system proceeds essentially slower than in the systems with fluid. Water and water-carbonic acid, in contrast to the carbonic acid, accelerate dolomite decomposition and provide conditions for the reaction: $MgCO_3 + H_2O = Mg(OH)_2 + CO_2$.

Dolomite decomposition in the dolomite–H_2O–C and dolomite-H_2O–CO_2–C systems at the parameters of the experiments probably can be illustrated by the following scheme: dolomite → disordered dolomite → dolomite solid solution + magnesite solid solution + aragonite → dolomite solid solution + brucite + aragonite. These results are consistent with the curve of dolomite decomposition by Martinez *et al.* (1996), extrapolated into the field of higher temperatures. Apparently, brucite was precipitated during the quench of hydrous dolomite melt.

The characteristic feature of diamond synthesis in the carbonate–carbon systems is the prolonged induction period preceding spontaneous diamond nucleation. The main factors, determining its duration, are the composition of system and PT parameters. Spontaneous diamond nucleation is the most intensive in melts of alkaline carbonates (Akaishi *et al.*, 1990; Pal'yanov *et al.*, 1998a, 1999a). Among alkaline-earth carbonates, dolomite is characterised by the maximum catalytic activity (Pal'yanov *et al.*, 1998a). The decrease of PT parameters apparently leads to an essential increase of the induction period preceding diamond nucleation. By just this circumstance it is possible to explain the absence of diamond synthesis in the first studies of carbonate–carbon systems, for example by Wentorf (1974). In our experiments no diamonds were observed after 42 h of reaction at 5.7 GPa, 1420 °C.

The second series of experiments demonstrates the great significance which fluid components have for diamond synthesis and growth in the carbonate–carbon systems at the PT parameters of natural diamond formation. The presence of H_2O and H_2O-CO_2 fluids, the decrease in the melting temperature of dolomite, as well as a probable decrease in the period of induction preceding diamond nucleation were observed. The combined effect of these factors, in our opinion, created conditions for spontaneous diamond crystallisation in the dolomite–H_2O–CO_2–C system at 5.7 GPa and 1420 °C. As shown by Pal'yanov *et al.* (1999b), the temperature of spontaneous diamond nucleation in the alkaline carbonate–fluid–carbon systems can be reduced to 1150 °C at an experiment durations of 120 h. It follows that in fluid-saturated alkali-bearing dolomite melts, with process durations exceeding 100 h, spontaneous nucleation can occur at temperatures lower than 1400 °C. Diamond growth on seed crystals, in contrast to its nucleation in dolomite–carbon and dolomite–fluid–carbon systems, is probably characterised by a smaller inductive period, just as in the case of alkaline carbonate–carbon systems, and may possibly be realised in a broader range of PTt parameters.

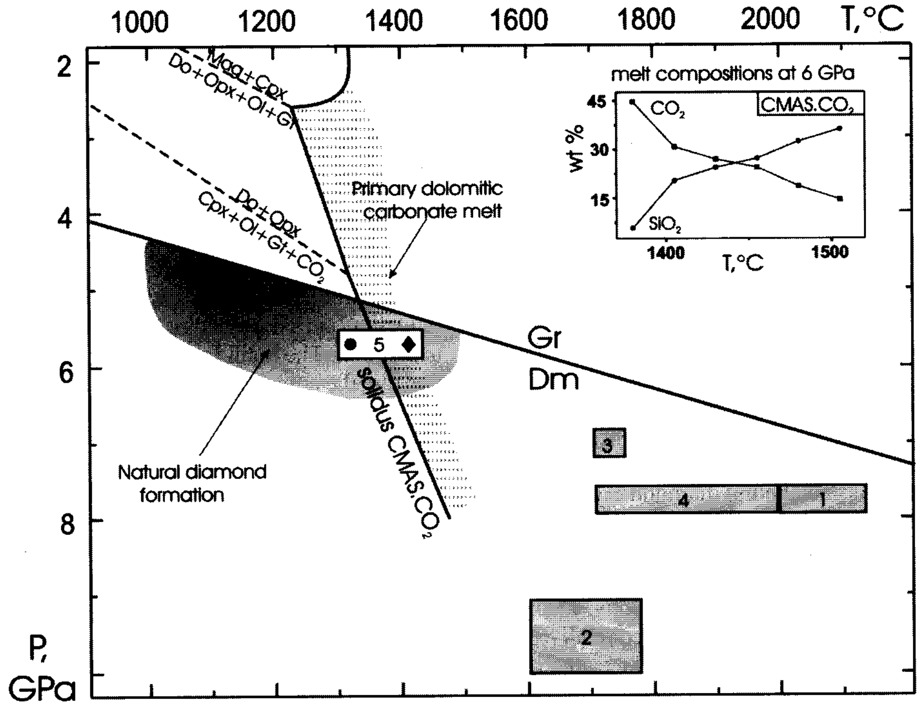

Fig. 3. PT parameters of synthesis and growth of diamond in the alkaline–earth carbonate–carbon systems: 1 – $MgCO_3$–C, $CaCO_3$–C (Akaishi *et al.*, 1990); 2 – $MgCO_3$–C, $K_2Mg(CO_3)_2$–C (Taniguchi *et al.*, 1996); 3 – $CaMg(CO_3)_2$–C (this work) and $CaCO_3$–C, $CaMg(CO_3)_2$–C, $MgCO_3$–C (Pal'yanov *et al.*, 1998a; 1998b); 4 – $CaCO_3$–$MgCO_3$–C (Sato *et al.*, 1999); 5 – $CaMg(CO_3)_2$–CO_2–C, $CaMg(CO_3)_2$–H_2O–C, $CaMg(CO_3)_2$–H_2O–CO_2–C (this work; ◆ – spontaneous diamond nucleation, ● – growth of diamond on seed crystals); PT conditions of natural diamond formation (Sobolev, 1977; Meyer, 1987; Harris, 1992); Solidus curve for model carbonated lherzolite (Ol+Opx+Cpx+Gr+carbonate) in the system CaO–MgO–Al_2O_3–SiO_2–CO_2 (CMAS.CO_2), composition and conditions formation of primary dolomitic carbonate melts according to Dalton & Presnall, 1998a and b; Gr – graphite; Dm – diamond.

The significance of the obtained experimental data is illustrated in Fig. 3. Parameters of diamond crystallisation in the second series of our experiments correspond to PT conditions of natural diamond formation. Experimental data indicate that carbonate-rich melts may be generated by partial melting of carbonated peridotite (Wyllie & Lee, 1998) and carbonated lherzolite (Dalton & Presnall, 1998a and b). According to these data, carbonate melts of dolomite composition are formed at 3-7 GPa and at temperatures slightly exceeding the solidus ones (Wyllie & Lee, 1998; Dalton & Presnall, 1998a). With a degree of partial melting of carbonated lherzolite up to 1 % (6 GPa, CO_2 – 0.15 wt. %) there is a regular change of composition in the generated melt from practically pure carbonate (SiO_2 ~ 5 wt. %) at the subsolidus temperature through intermediate compositions to kimberlite (SiO_2 > 25 wt. %) at 70-100 °C higher than the solidus temperature (Dalton & Presnall, 1998b). According to various data, the solidus temperatures at the pressures of natural diamond formation can vary from about 1200 °C for peridotite in the presence of H_2O-CO_2 fluid (Canil & Scarfe, 1990) to up to 1350 °C for lherzolite in the presence of carbonic acid fluid (Dalton & Presnall, 1998a and b). Therefore, the formation temperatures of initial mantle dolomite melts at 5-6 GPa can vary within the range of 1200-1400 °C. These experimental results indicate that diamond-forming carbonate-rich melts may be generated in the upper mantle.

Conclusions

The process of diamond crystallisation in dolomite-carbon systems at P = 7 GPa and T = 1700 °C is characterised by an inductive period of spontaneous nucleation lasting about 4 h. At the same time, in experiments lasting for 42 h at P = 5.7 GPa and T = 1420 °C, at conditions at which dolomite does not melt, neither diamond synthesis nor growth on seed crystals was observed.

Adding of carbonic acid, water or water-carbonic acid to the dolomite-carbon system at P = 5.7 GPa and T=1420 °C creates conditions for diamond growth on seed crystals. In the presence of water and water-carbonic acid, growth on the {111} faces proceeds in the form of flat triangular or hexagonal layers, which is common for natural crystals. In dolomite melt, saturated with water and water-carbonic acid, the formation of spontaneous diamond crystals was established at T = 1420 °C. The existing data allow to suppose that the process of diamond growth on seed crystals, in contrast to its nucleation in the dolomite–carbon and dolomite–fluid–carbon systems, can be accomplished in a wider range of PTt parameters.

The data, obtained from the process of diamond formation in dolomite–fluid–carbon systems, allow us to conclude that some natural diamond crystals can crystallise in initial mantle dolomite melts. Fluid is the controlling factor in this process; from one side, it provides the generation of carbonate melts in the mantle, and from the other side, apparently promotes shortening the duration of the induction period preceding spontaneous diamond nucleation.

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References

Akaishi, M., Kanda, H., Yamaoka, S. (1990): Synthesis of diamond from graphite-carbonate systems under very high temperature and pressure. *J. Cryst. Growth*, **104**, 578-581.

Akaishi, M. & Yamaoka, S. (2000): Crystallization of diamond from C-O-H fluids under high-pressure and high-temperature conditions. *J. Cryst. Growth*, **209**, 999-1003.

Ballhaus, C. (1993): Redox states of lithospheric and asthenospheric upper mantle. *Contrib. Mineral. Petrol.*, **114**, 331-348.

Biellmann, C., Gillet, P., Guyot, F., Peyronneau, J., Reynard, B. (1993): Experimental evidence for carbonate stability in the Earth's lower mantle. *Earth Planet. Sci. Lett.*, **118**, 31-41.

Bulanova, G.P. (1995): Formation of diamond. *J. Geochem. Explor.*, **53**, 1-23.

Canil, D. & Scarfe, C.M. (1990): Phase relations in peridotite+CO_2 systems to 12 GPa: implications for the origin of kimberlite and carbonate stability in the Earth's upper mantle. *J. Geophys. Res.*, **95**, 15805-15816.

Dalton, J.A. & Presnall, D.C. (1998a): Carbonatitic melts along the solidus of model lherzolite in the system CaO-MgO-Al_2O_3-SiO_2-CO_2 from 3 to 7 GPa. *Contrib. Mineral. Petrol.*, **131**, 123-135.

–,– (1998b): The continuum of primary carbonatitic-kimberlitic melt composition in equilibrium with lherzolite: data from the system CaO-MgO-Al_2O_3-SiO_2-CO_2 at 6 GPa. *J. Petrol.*, **39**, 1953-1964.

Girnis, A.V., Brey, G.P., Ryabchikov, I.D. (1995): Origin of group 1A kimberlites: fluid-saturated melting experiments at 45-55 kbar. *Earth Planet. Sci. Lett.*, **134**, 283-296.

Goldsmith, J.R. (1980): Thermal stability of dolomite at high temperatures and pressures. *J. Geophys. Res.*, **85**, 6949-6954.

Haggerty, S.E. (1999): A diamond trilogy: Superplumes, Supercontinents, and Supernovae. *Science*, **285**, 851-860.

Harris, J.W. (1992): The properties of natural and synthetic diamond. *in* "Diamond geology", J.E. Field, ed., Academic Press, London, 345-393.

Leipunsky, O.I. (1939): On manmade diamonds. *Uspekhi khimii*, **8**, 1519-1528 (in Russian).

Litvin, Yu.A. (1998): Hot spots of mantle and experiment to 10 GPa: alkaline reactions, lithosphere carbonatization, and new diamond-generating systems. *Geologiya i Geofizika*, **39**, 1772-1779 (in Russian). English Translation: *Russian Geology and Geophysics*, **39**, 1760-1768.

Martinez, I., Zhang, J., Reeder, R.J. (1996): In situ X-ray diffraction of aragonite and dolomite at high pressure and high temperature: Evidence for dolomite breakdown to aragonite and magnesite. *Am. Mineral.*, **81**, 611-624.

Meyer, H.O.A. (1987): Inclusions in diamond. *in* "Mantle xenoliths", H.P. Nixon, ed., John Wiley and Sons, New York, 501-523.

Pal'yanov, Yu.N., Khokhryakov, A.F., Borzdov, Yu.M., Sokol, A.G., Gusev, V.A., Rylov, G.M., Sobolev, N.V. (1997): Growth conditions and real structure of synthetic diamond crystals. *Geologiya i Geofizika*, **38**, 882-918 (in Russian). English translation: *Russian Geology and Geophysics*, **38**, 920-945.

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Khokhryakov, A.F., Shatsky, A.F., Sobolev, N.V. (1999a): The diamond growth from Li_2CO_3, Na_2CO_3, K_2CO_3 and Cs_2CO_3 solvent-catalysts at P=7 GPa and T=1700-1750 °C. *Diamond. Relat. Mater.*, **8**, 1118-1124.

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Khokhryakov, A.F., Sobolev, N.V. (1998b): Crystallization of diamond in the $CaCO_3$-C, $MgCO_3$-C and $CaMg(CO_3)_2$-C systems. *Doklady Earth Sciences*, **363**, 1156-1159.

–,–,–,–,– (1999b): Diamond formation from mantle carbonate fluids. *Nature*, **400**, 417-418.

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Sobolev, N.V. (1998a): Experimental study of diamond crystallization in carbonate-carbon systems in connection with the problem of diamond genesis in magmatic and metamorphic rocks. *Geologiya i Geofizika*, **39**, 1780-1792 (in Russian). English translation: *Russian Geology and Geophysics*, **39**, 1768-1779.

Sato, K., Akaishi, M., Yamaoka, S. (1999): Spontaneous nucleation of diamond in the system $MgCO_3$-$CaCO_3$-C at 7.7 GPa. *Diamond Relat. Mater.*, **8**, 1900-1905.

Schrauder, M. & Navon, O. (1994): Hydrous and carbonatitic mantle fluids in fibrous diamond from Jwaneng, Botswana. *Geochim. Cosmochim. Acta*, **58**, 761-771.

Shatsky, V.S., Sobolev, N.V., Vavilov, M.A. (1995): Diamond-bearing metamorphic rocks of the Kokchetav Massif (Northern Kazakhstan). *in* "Ultrahigh Pressure Metamorphism", R. G. Coleman & X. Wang, eds., University Press, Cambridge, 427-455.

Sobolev, N.V. (1977): The deep-seated inclusions in kimberlites and the problem of the composition of the upper mantle. American Geophysics Union, Washington, 304 p.

Sobolev, N.V., Kaminsky, F.V., Griffin, W.L., Yefimova, E.S., Win, T.T., Ryan, C.G., Botkunov, A.I. (1997): Mineral inclusions in diamonds from the Sputnik kimberlite pipe, Yakutia. *Lithos*, **39**, 135-157.

Sobolev, N.V. & Shatsky, V.S. (1990): Diamond inclusions in garnets from metamorphic rocks: A new environment for diamond formation. *Nature*, **343**, 742-746.

Sobolev, V.S. (1960): Formation conditions of diamond deposits. *Geologiya i Geofizika*, **1**, 7-22 (in Russian).

Sokol, A.G., Tomilenko, A.A., Pal'yanov, Yu.N., Borzdov, Yu.M., Pal'yanova, G.A. Khokhryakov, A.F. (2000): Fluid regime of diamond crystallisation in carbonate-carbon systems. *Eur. J. Mineral.*, **12**, 367-375.

Taniguchi, T., Dobson, D., Jones, A.P., Rabe, R., Milledge, H.J. (1996): Synthesis of cubic diamond in the graphite-magnesium carbonate and graphite-$K_2Mg(CO_3)_2$ systems at high pressure of 9-10 GPa region. *J. Mater. Res.*, **11**, 2622-2632.

Wang, A., Pasteris, J.D., Meyer, H.O.A., Dele-Duboi, M.L. (1996): Magnesite-bearing inclusion assemblage in natural diamond. *Earth Planet. Sci. Lett.*, **141**, 293-306.

Wentorf, R.H. (1974): Diamond formation at high pressures. *Advance in High-Pressure Research*, **4**, 249-281.

Wood, B.J., Bryndzia, T., Johnson, K.E. (1990): Mantle oxidation state and its relationship to tectonic environment and fluid speciation. *Science*, **248**, 337-345.

Wyllie, P.J. & Lee, W.-J. (1998): Model system controls on conditions for formation of magnesiocarbonatite and calciocarbonatite magmas from the mantle. *J. Petrol.*, **39**, 1885-1893.

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