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Fluid-bearing alkaline carbonate melts as the medium for the formation of diamonds in the Earth's mantle: an experimental study

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Abstract

We have experimentally studied the formation of diamonds in alkaline carbonate–carbon and carbonate–fluid–carbon systems at 5.7–7.0 GPa and 1150–1700 °C, using a split-sphere multi-anvil apparatus (BARS). The starting carbonate and fluid-generating materials were placed into Pt and Au ampoules. The main specific feature of the studied systems is a long period of induction, which precedes the nucleation and growth of diamonds. The period of induction considerably increases with decreasing P and T, but decreases when adding a C–O–H fluid to the system. In the range of P and T corresponding to the formation of diamonds in nature, this period lasts for tens of hours. The reactivity of the studied systems with respect to the diamond nucleation and growth decreases in this sequence: $Na_2CO_3–H_2C_2O_4\cdot2H_2O–C > K_2CO_3–H_2C_2O_4\cdot2H_2O–C >> Na_2CO_3–C > K_2CO_3–C$. The diamond morphology is independent of P and T, and is mainly governed by the composition of the crystallization medium. The stable growth form is a cubo-octahedron in the Na_2CO_3 melt, and an octahedron in the K_2CO_3 melt. Regardless of the composition of the carbonate melt, only octahedral diamond crystals formed in the presence of the C–O–H fluid. The growth rates of diamond varied in the range from 1.7 μm/h at 1420 °C to 0.1–0.01 μm/h at 1150 °C, and were used to estimate, for the first time, the possible duration of the crystallization of natural diamonds. From the analysis of the experimental results and the petrological evidence for the formation of diamonds in nature, we suggest that fluid-bearing alkaline carbonate melts are, most likely, the medium for the nucleation and growth of diamonds in the Earth's upper mantle. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In petrology, diamond is viewed, first of all, as an indicator of high pressures and temperatures in deep-level magmatic and metamorphic processes (Sobolev, 1977; Haggerty, 1999; Dobretsov and Kirdyashkin, 1998). The data from geothermobarometry of mineral inclusions in diamonds indicate that most diamonds formed at 5–6 GPa and 900–1500 °C (Sobolev, 1977; Meyer, 1987; Harris, 1992). The P–T conditions of the diamond formation in metamorphic complexes are also close to the above pressures and temperatures (Sobolev and Shatsky, 1990; Dobretsov and Kirdyashkin, 1998). Current models for the formation of diamonds in nature are based mainly on the synthesis of the information obtained from mineralogical, petrological, and geochemical observations (Sobolev, 1977; Meyer, 1987; Harris, 1992; Galimov,

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1991). However, the state and the composition of the crystallization medium, the sources of carbon, the mechanisms of the diamond growth, the typical time durations of the diamond-forming processes, and the redox conditions are issues still open to debate.

Most of the information about the diamond-forming medium has been obtained from the studies of inclusions in diamonds. It has been established that the most common minerals trapped during the diamond growth are sulphides, silicates, and oxides (Sobolev, 1977; Meyer, 1987; Harris, 1992; Bulanova, 1995). The most important source of information about the diamond-forming medium are the fluid- and brine-inclusion studies on some varieties of diamonds (Navon et al., 1988; Navon, 1991; Izraeli et al., 2001). Findings of carbonate inclusions in natural diamonds (Bulanova, 1995; Wang et al., 1996; Sobolev et al., 1997; Stachel et al., 1998) are, undoubtedly, also of great importance. Recently reported occurrences of mineral inclusions of majoritic garnet, ferropericlase, and $CaSiO_3$ perovskite in diamonds from São Luiz (Brazil) and Guinea (West Africa) provide evidence in favor of the lower-mantle origin for some diamonds (Harte et al., 1999; Joswing et al., 1999; Gasparik and Hutchison, 2000). These observations form the basis for hypotheses about the possible range of the $P-T$ conditions and the environment suitable for the formation of diamonds in nature. The most commonly assumed medium for the crystallization of natural diamonds is the silicate (Robinson, 1978; Sunagawa, 1994) or sulphide (Bulanova et al., 1998) melt. Many models suggest an active participation of fluid in the crystallization of diamonds (Haggerty, 1986; Sobolev and Shatsky, 1990; Galimov, 1991; Schrauder and Navon, 1994; Navon, 1999; Dobrzhinetskaya et al., 2001). It is also worth pointing out that the $P-T$ conditions in the thermodynamic stability field of the diamond are viewed by many as quite sufficient for diamonds to nucleate and grow, but the evidence from experiments on the synthesis and growth of diamonds suggests this to be a necessary but not always a sufficient condition.

Successful synthesis of diamond by experiments at high pressures and temperatures was achieved at the end of the 1950s in metal–carbon systems. At 5–6 GPa and 1400–1600 °C, diamond started to crystallize after several minutes at a graphite-melt interface (Wentorf, 1974). The relatively high solubility of carbon in the melts of such metals as Fe, Ni, Co, Mn, and the very high rate of the graphite to diamond transformation in these systems, formed the basis of the approach used in the experimental studies on the diamond synthesis before the 1990s. These procedures for the diamond synthesis were automatically extended to other chemical systems. On the basis of a great number of short experiments, whole classes of substances, including carbides, carbonates, chlorides, sulphides, oxides, and various silicates (serpentine, muscovite, biotite, etc.) were identified as the so-called graphite-producing solvents of carbon (Wentorf, 1974). At the $P-T$ conditions typical for the formation of natural diamonds (5–6 GPa and 900–1500 °C), diamond was synthesized in laboratories only in metal–carbon systems and only at the highest values of P and T of the above range. On the basis of these experimental data, a hypothesis was proposed that the transition-metal melts played the key role in the formation of natural diamonds (Wentorf and Bovenkerk, 1961). A great body of petrological, mineralogical, and geological information obtained from the diamondiferous assemblages, the compositions of mineral and fluid inclusions, and geothermobarometry, were in a serious conflict with the experimental data on the synthesis of diamonds. Consequently, most petrologists lost interest in using experimental data to explain the formation of diamonds in nature.

At the beginning of the 1990s, the first report appeared about the synthesis of diamond in carbonate–carbon systems at 7.7 GPa pressure and 2000 °C or higher temperatures (Akaishi et al., 1990). Further systematic investigations revealed the specific features of the diamond crystallization in a kimberlitic melt (Arima et al., 1993) and in alkaline and alkaline-earth carbonate melts of different compositions (Kanda et al., 1990; Taniguchi et al., 1996; Litvin, 1998; Pal'yanov et al., 1998a,b; Litvin et al., 1999; Sato et al., 1999; Litvin and Zharikov, 2000). Most experiments were short (typically 20–30 min) and were carried out at fairly high $P-T$ conditions: $P \geq 7$ GPa and $T > 1600–1700$ °C. When the duration of the experiments was increased to several hours, diamond grew on seed in the Na_2CO_3 melt at 1650 °C (Kanda et al., 1990). In experiments lasting for about 20 h at 7 GPa and 1700–1750 °C, and using alkaline and alkaline-earth carbonates, Pal'yanov et al. (1998a,b,

1999a) grew diamond crystals of up to 400–700 μm in size, and showed that the nucleation of diamond is significantly affected by time. Recently, Pal'yanov et al. (1999b) experimentally confirmed that diamond can crystallize in alkaline carbonate and carbonate-fluid systems at the $P-T$ conditions corresponding to the formation of natural diamonds.

The purpose of this study was to experimentally constrain the important factors controlling the crystallization of diamond in model alkaline carbonate and carbonate-fluid systems at the $P-T$ conditions corresponding to the formation of natural diamonds, and to suggest the compositions of the most appropriate medium for the crystallization of diamonds in nature.

2. Experimental procedure

Experiments were carried out using a "split-sphere" multi-anvil apparatus with a 300-mm outer diameter of the multi-anvil sphere (Pal'yanov et al., 1997). The sphere consists of eight steel anvils enclosing an octahedral cavity. An inner set of six tungsten carbide anvils is located in the octahedral cavity, and encloses a cubic cavity holding the cell assembly. In this work, we used cells developed for the growth of large diamond crystals. This type of cells have a shape of a tetragonal prism $19 \times 19 \times 22$ mm, and use a graphite heater, 9 mm in diameter and 15.8 mm in length. Pressure was calibrated at room temperature by the change in the resistance of Bi at 2.55 GPa, and of PbSe at 4.0 and 6.8 GPa, and at high temperatures by the graphite-diamond equilibrium (Kennedy and Kennedy, 1976). Temperature was measured in each experiment with a Pt6%Rh/Pt30%Rh thermocouple whose junction was placed inside the heater. The thermocouple was calibrated at 7 GPa by the melting of Ni, and at 5.7 GPa by the melting of Ag, Au, and Al (Pal'yanov et al., 1997, 1998b). In some experiments, control ampoules were used for reference, in addition to the sample ampoule, for the crystallization of diamond in the well-studied Ni–C system (A ampoule) and/or for substances with known melting temperatures (B ampoule), as shown in Fig. 1. The melting of metals (Ag, Au, and Al) was detected from the change in the position of natural diamond crystals, which were initially placed in the
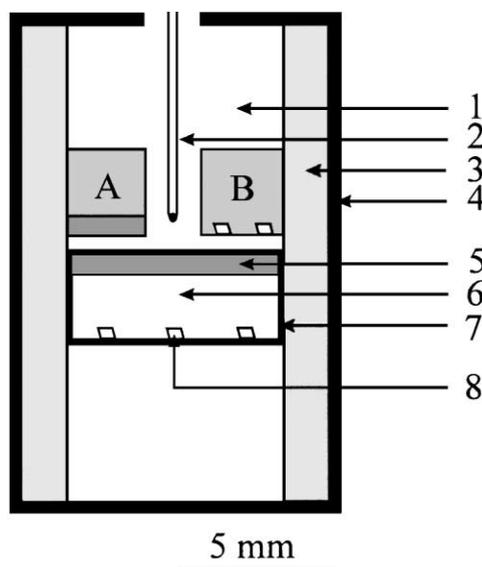

Fig. 1. The sample assembly used in this study: (1) $ZrO_2 + 20\%$ NaCl pressure medium; (2) thermocouple; (3) MgO + 20% NaCl pressure medium; (4) graphite heater; (5) graphite sample; (6) carbonate sample; (7) Pt or Au ampoule; (8) seed crystal. A = control ampoule for diamond growth in Ni–C; B = control ampoule for temperature calibration by melting Au, Ag, or Al.

center of a metal sample. When the melting of a metal occurred, diamonds floated in the Ag and Au melts and sank in the Al melt. The use of the control and sample ampoules, which were symmetrically located with respect to the hot spot of the cell assembly, made it possible for a direct comparison of the $P-T$ conditions of the diamond synthesis in carbonate–carbon systems with the well-calibrated data on the diamond synthesis in the system Ni–C (Table 1). Based on the previously published data (Borzdov and Popkov, 1983; Pal'yanov et al., 1997, 1998b) and the results of the present work (Table 1), we estimated the accuracy of the pressure and temperature measurements to be at the level of ± 0.1 GPa and ± 20 °C, respectively, at 5.7 GPa and 1150–1420 °C. For experiments at 7 GPa and 1700 °C, the accuracy was estimated to be ± 0.2 GPa and ± 40 °C. In a series of systematic experiments that were previously carried out to measure thermal gradients with two thermocouples (Borzdov and Popkov, 1983; Pal'yanov et al., 1997), we established that there was a symmetric "low-gradient" zone with the diameter of about 7 mm and the height of about 7 mm, located at

Table 1
Results from the calibration experiments

Run number	P (GPa)	T_1 (°C)	T_2 (°C)	Time (h)	Control ampoule	Results	
						Synthesis of diamond	Melting
X-1	5.7	1500	1600	20	NiC	no[a]	yes
X-2	6.0	1500	1600	20	NiC	yes	yes
X-3	5.5	1350	1420	20	NiC	yes	yes
					Au	–	yes
N-1	5.7	1350	1420	20	NiC	yes	yes
					Au	–	yes
N-2	5.7	1350	1420	30	NiC	yes	yes
N-3	5.7	1350	1420	40	NiC	yes	yes
					Au	–	yes
N-4	5.7	1300	1360	40	NiC	no	no
					Au	–	yes
N-5	5.7	1250	1300	40	Au	–	no
					Ag	–	yes
N-6	5.7	1200	1250	40	Ag	–	no
					Al	–	yes
NF-4	5.7	1100	1150	120	Ag	–	no
					Al	–	yes
X-4	5.7	990	1030	20	Al	–	no

T_1—temperature according to the emf of the thermocouple; T_2—temperature corrected according to the data on the melting of metals.

[a] Newly crystallized graphite was observed.

the center of the heater. Within this zone, the temperature gradient did not exceed 10 °C/mm at 6 GPa and 1400 °C. The sample and the control ampoules were symmetrically placed in this zone with respect to the hot spot. It should be noted that we have used these cells for a long time for growing large high-quality diamonds by the temperature gradient method (Pal'yanov et al., 1997). This provided an aditional proof of the low thermal gradients in our cells, based on the well-known experimental fact that the temperature difference between the dissolution zone and the growth zone for the growth of diamonds must be approximately 30 °C, which is less than 10 °C/mm (Burns and Davies, 1992). Otherwise, large high-quality single crystals of diamond cannot be grown.

For the starting materials, we used Na_2CO_3 and K_2CO_3 of purity no less than 99.9%, and graphite of purity no less than 99.99%. Carbonates were annealed at 500 °C for 2 h. After the preparation, the starting materials were kept at 90 °C. In each experiment, three seeds of synthetic diamond (cubo-octahedra) and three seeds of natural diamond (flat-faced octahedra), approximately measuring 0.5 mm, were used. The starting materials were placed into Pt ampoules and sealed

Table 2
Experimental results on the crystallization of diamond in the Na_2CO_3–C and K_2CO_3–C systems

Run number	Initial composition	Ampoule	P (GPa)	T (°C)	Time (h)	Diamond nucleation			Diamond growth		
						N	Size (μm)	Morphology	G	$h(100)$	$h(111)$
C-110	Na_2CO_3-Gr	Gr	7	1700	0.3	–	–	–	–	–	–
C-115	Na_2CO_3-Gr	Gr	7	1700	2	+	100–300	111>100	+	20	30
C-113	Na_2CO_3-Gr	Pt	7	1700	16.5	+	300–600	111>100	+	260	450
N-10	Na_2CO_3-Gr	Pt	5.7	1420	10	–	–	–	–	–	–
N-1	Na_2CO_3-Gr	Pt	5.7	1420	20	–	–	–	+	4	3
N-2	Na_2CO_3-Gr	Pt	5.7	1420	30	+	5	111>100	+	18	20
N-3	Na_2CO_3-Gr	Pt	5.7	1420	40	+	40	111+100	+	40	35
N-4	Na_2CO_3-Gr	Pt	5.7	1360	40	–	–	–	+	20	6
N-5	Na_2CO_3-Gr	Pt	5.7	1300	40	–	–	–	+	12	10
N-6	Na_2CO_3-Gr	Pt	5.7	1250	40	–	–	–	–	–	–
C-120	K_2CO_3-Gr	Gr	7	1700	0.3	–	–	–	–	–	–
C-125	K_2CO_3-Gr	Gr	7	1700	2	+	90–180	111	+	4.5	20
C-124	K_2CO_3-Gr	Pt	7	1700	7	+	200–350	111	+	16	75
K-1	K_2CO_3-Gr	Pt	5.7	1420	30	–	–	–	+	10	1
K-2	K_2CO_3-Gr	Pt	5.7	1420	40	–	–	–	+	15	3
K-3	K_2CO_3-Gr	Pt	5.7	1300	40	–	–	–	+	8	2
K-4	K_2CO_3-Gr	Pt	5.7	1250	40	–	–	–	–	–	–
K-5	K_2CO_3-Gr	Au	5.7	1250	84	–	–	–	+	~ 2	1

N (+)—nucleation of diamond was observed, (–)—not observed; G (+)—growth of diamond on seeds was observed, (–)—not observed; $h(100)$ and $h(111)$—thickness of the diamond layer on seeds (μm).

Table 3
Experimental results on the crystallization of diamond in the alkaline carbonate−carbon systems with C−O−H fluid

Run number	Initial composition	Ampoules	P (GPa)	T (°C)	Time (h)	Diamond nucleation			Diamond growth		
						N	Size (μm)	Morphology	G	$h(100)$	$h(111)$
NF-8	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1420	5	−	−	−	−	−	−
NF-5	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1420	10	−	−	−	+	3	<2
NF-1	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1420	20	+	13	111	+	20	14
NF-2	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1360	40	+	65	111	+	60	45
NF-3	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1250	40	−	−	−	+	10	8
NF-6	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Au	5.7	1200	136	+	3	111	+	4	2
NF-4	$Na_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1150	120	+	4	111	+	3	1.5
KF-5	$K_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1420	10	−	−	−	−	−	−
KF-1	$K_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1420	20	−	−	−	+	~1	~1
KF-2	$K_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1250	40	−	−	−	+	25	4
KF-3	$K_2CO_3-H_2C_2O_4\cdot2H_2O$-Gr	Pt	5.7	1150	120	+	2	111	+	1.5	1
NW-1	$Na_2CO_3-H_2O$-Gr	Pt	5.7	1420	40	+	4−7	111	+	18	8
KW-1	$K_2CO_3-H_2O$-Gr	Pt	5.7	1420	40	+	10	111	+	15	6
NA-1	$Na_2CO_3-Ag_2C_2O_4$-Gr	Pt	5.7	1420	40	+	100	111	+	120	8−10
KA-1	$K_2CO_3-Ag_2C_2O_4$-Gr	Pt	5.7	1420	40	+	70	111	+	100	10

N (+)—nucleation of diamond was observed, (−)—not observed; G (+)—growth of diamond on seeds was observed, (−)—not observed; $h(100)$ and $h(111)$—thickness of the diamond layer on seeds (μm).

by arc welding. For generating the C−O−H fluid, we added to the samples, just before sealing, either oxalic acid dihydrate ($H_2C_2O_4\cdot2H_2O$) or distilled water (H_2O), or silver oxalate ($Ag_2C_2O_4$) in quantities of 20, 20, and 40 wt.%, respectively.

The experimental results are shown in Tables 2 and 3. In all runs in which diamond grew on seed crystals, the grown layer had minute black inclusions, and in some cases, transparent inclusions of carbonate melt, which made it easier to identify the grown layer. To verify the obtained results, control experiments were carried out in graphite containers and gold ampoules. In all the experiments with fluid, the weight of the sealed samples was measured before and after the runs. Only those experiments in which the ampoules remained hermetically sealed are reported in Tables 2 and 3. In this case, intense release of vapor occurred during the opening, resulting in the corresponding weight loss. An exception were the runs with $Ag_2C_2O_4$, in which case, due to the formation of metallic Ag and its interaction with platinum, no hermetically sealed ampoules were preserved. The experimental products were studied by X-ray analysis. Formation of small diamond crystals was confirmed by Raman spectroscopy using an OMARS 89 device. Graphite and diamond were also studied using optical microscopes and an electron scanning microscope (JSM-35).

3. Results and discussion

3.1. Diamond crystallization in the fluid-free systems Na_2CO_3-C and K_2CO_3-C

At 7 GPa and 1700 °C, 20 min were insufficient for the nucleation of diamond in the systems Na_2CO_3-C and K_2CO_3-C (Table 2). For the runs that lasted for 2 h, the synthesis of diamond was detected at the graphite−carbonate interface by both X-ray diffraction and optical microscopy. A complete transformation of graphite into diamond at these conditions required about 11 h. It is worth noting that the reactivity of the Na_2CO_3 melt for the diamond synthesis was better than that of the K_2CO_3 melt. Moreover, in the Na_2CO_3 melt, diamond was crystallized as cubo-octahedra, whereas in the K_2CO_3 melt, only octahedra was formed. Additional data from kinetic studies of diamond nucleation and growth were reported earlier (Pal'yanov et al., 1998b, 1999a).

In the Na_2CO_3-C system at 5.7 GPa and 1420 °C, a 10-h period was not sufficient either for the growth or the nucleation of diamond. In a 20-h run, only the initial stage of the diamond growth was observed. In a 40-h run, the number of formed crystals was 500−600, with their sizes reaching 40 μm. Spontaneously nucleated crystals were cubo-octahedra (Fig. 2d).
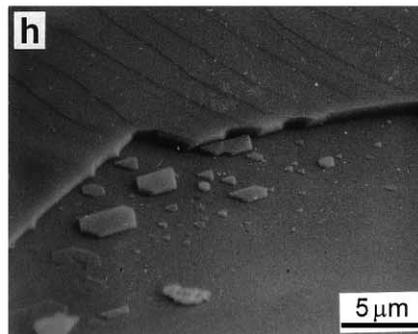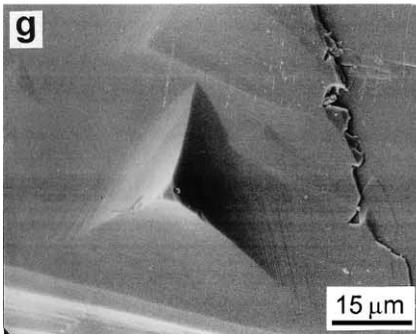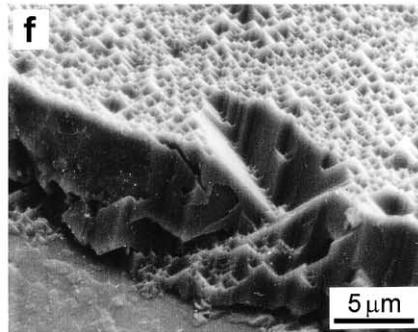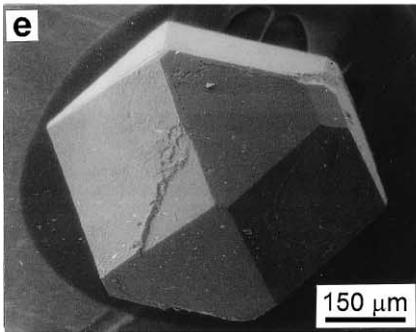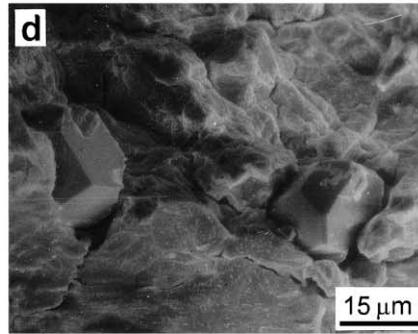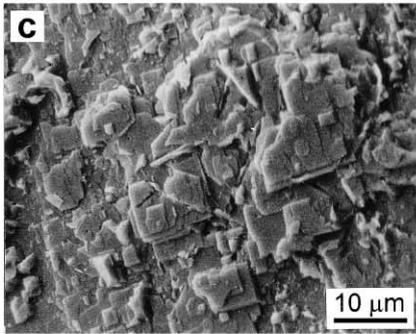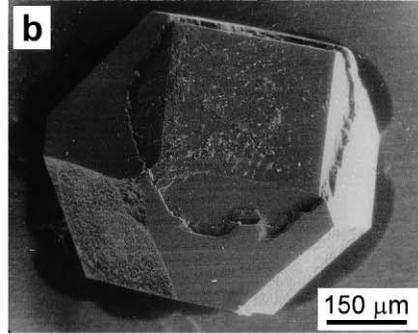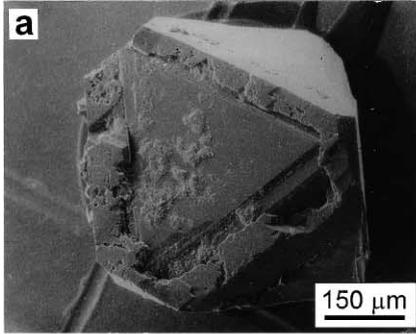
They were transparent, of light yellowish tint, and located within carbonate at a distance of no less than 100–200 μm from graphite. The zone in the vicinity of the graphite did not contain newly crystallized diamond. Diamond growth on seed crystals took place on the {111} and {100} faces (Fig. 2a–c). No growth occurred on the seed crystals which were located in graphite and had no contact with the carbonate melt. This allowed us to estimate, by comparison, the thickness of the grown layer. The thickness regularly decreased with decreasing temperature (see Table 2). At 5.7 GPa and 1420 °C, the induction period of the diamond nucleation in the Na_2CO_3 melt was about 30 h, while the induction period preceding the diamond growth was about 20 h. A decrease in temperature in the 40-h experiments caused a regular decrease in the thickness of the grown layer on both the {100} and {111} faces. At temperatures below 1420 °C, a 40-h period was insufficient for the nucleation of diamond.

In the K_2CO_3–C system, spontaneously nucleated diamond crystals were not observed at 5.7 GPa. Diamond growth on seed crystals took place at 1300 °C and higher temperatures. The main characteristics of the diamond growth on seeds in the K_2CO_3–C system were, in general, similar to those described above for the Na_2CO_3–C system. The {100} faces had rough surfaces formed by tetragonal pyramids with octahedral faceting (Fig. 2e and f). In all cases, the mirror-smooth octahedral faces exhibited triangular vicinal forms and growth layers (Fig. 2g and h). The seed-grown diamond layers were considerably thinner than in the Na_2CO_3–C system, but otherwise the same.

The obtained results confirmed the earlier observed differences in the *reactivity* of these systems at 7 GPa and 1700° (Pal'yanov et al., 1999a). The differences in the morphology of the diamonds, grown spontaneously at 1700 °C, were the same as those for the diamonds grown on seeds in these systems at 1300–1420 °C. These were evaluated from the change in the ratio of the grown layer thicknesses $h(100)/h(111)$, which reflects the ratio of the growth rates of a cube and an octahedron $v(100)/v(111)$.

3.2. Diamond crystallization in the Na_2CO_3–C and K_2CO_3–C systems with fluid

In the Na_2CO_3–$H_2C_2O_4 \cdot 2H_2O$–C system, the diamond formation was enhanced in comparison with the fluid-free system (Tables 2 and 3). For example, in the fluid-free Na_2CO_3–C system, diamond nucleation did not occur in the melt at 1360 °C. In contrast, several thousand crystallization centers were observed in the same carbonate in the presence of H_2O–CO_2 fluid. Diamonds were irregularly distributed in the carbonate melt, and in some places, the number of the crystallization centers reached only a few tens per square millimeter. No diamonds formed in graphite. In addition to the newly crystallized diamond, the carbonate melt contained minute graphite crystals or their aggregates. Spontaneously nucleated diamond crystals were transparent, had a yellow tint, and were represented by octahedra, their intergrowths, and twins (Fig. 3c). Diamond growth on seeds took place on both the {111} and the {100} faces. In some cases, spontaneously nucleated diamond crystals that were intergrown with seed crystals were present in numbers reaching a few tens on a single crystal face (Fig. 3a and b). The most active nucleation and intense growth of diamond took place in the run NF-2 at 1360 °C. Spontaneous nucleation of octahedral diamond crystals measuring 1–4 μm, and growth of diamond crystals on the {111} and {100} faces, occurred in experiments lasting 120 h at 1150 °C (Fig. 3d).

In the K_2CO_3–$H_2C_2O_4 \cdot 2H_2O$–C system, 20–40-h experiments at 1250–1420 °C did not nucleate diamond, but diamond grew on the {100} and {111} faces of the seed crystals (Fig. 3e–g). Only in the run KF-3 at 1150 °C and 120 h, both the spontaneous nucleation and the diamond growth on seed crystals occurred (Fig. 3h). In the runs with oxalic acid dihydrate, newly crystallized graphite was observed in the form of dispersed particles and small crystals, which grew on the original graphite, the seed crystals, and the walls of the Pt ampoules.

Fig. 2. Scanning electron micrographs of diamonds synthesized in the systems Na_2CO_3–C (a–d) and K_2CO_3–C (e–h): a general view of seed crystals with overgrowth (a—run N-3; b—run N-2; e—run K-1); growth patterns on the (100) face of seed crystals (c—run N-2; f—run K-1); spontaneously nucleated cubo-octahedral diamonds in carbonate melt (d—run N-3); growth patterns on the (111) face of seed crystals (g, h—run K-2).
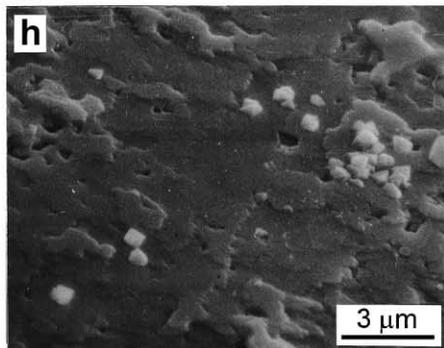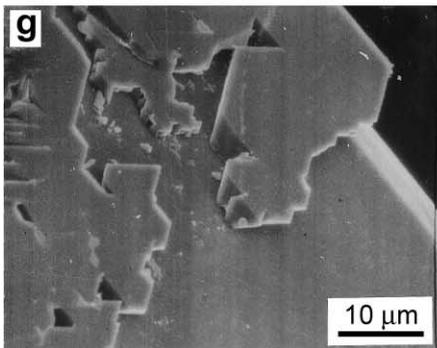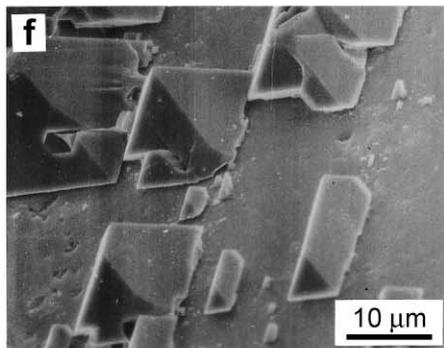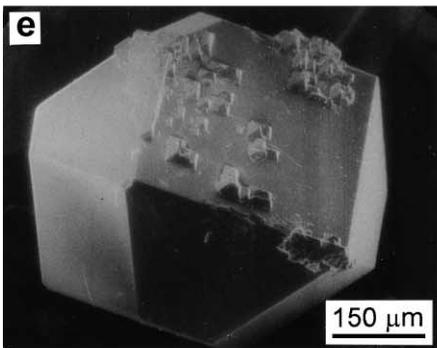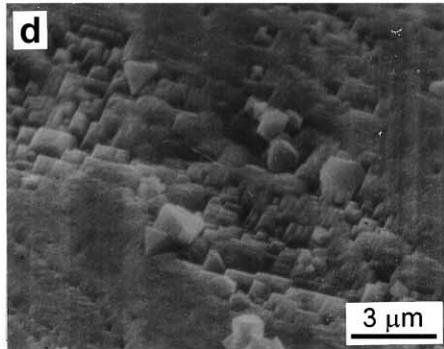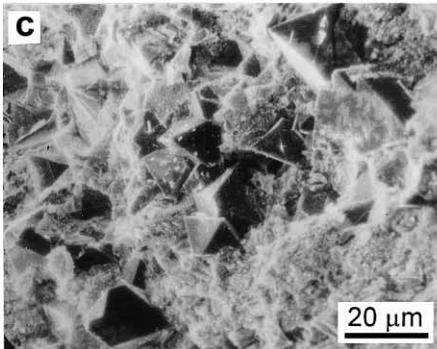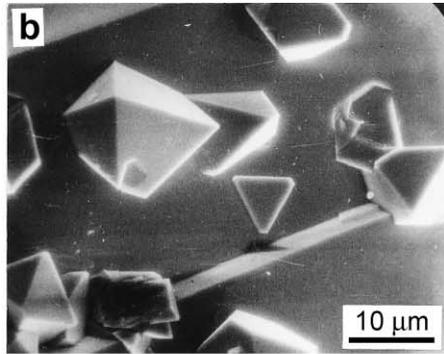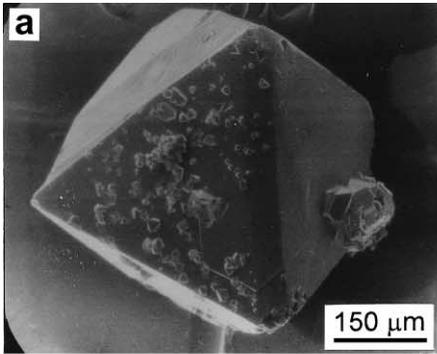
Experiments of the series NF and KF (Table 3) can be viewed as conducted in the presence of H_2O-CO_2 fluid, because oxalic acid dihydrate decomposes under experimental conditions to H_2O and CO_2. Some preliminary experiments on the effect of the fluid composition on the diamond formation in alkaline carbonate systems were carried out with water or silver oxalate ($Ag_2C_2O_4$), the latter decomposes under experimental conditions to Ag and CO_2 (Table 3). Runs with H_2O (NW-1 and KW-1) produced octahedral diamond crystals, 10 μm in size. In the runs with $Ag_2C_2O_4$ (NA-1, KA-1) carried out at the same conditions, we observed the growth of polycrystalline aggregates of larger (up to 100 μm) octahedral diamond crystals. The resulting crystal size and the thickness of the diamond layers grown on seed crystals (Table 3) indicate that the formation of diamond in the carbonate–carbon system is much more enhanced with the addition of $Ag_2C_2O_4$ than with the addition of H_2O. These experimental results suggest a potentially significant influence of the fluid composition on the diamond nucleation and growth in the carbonate melt, but additional studies would be needed to address this in detail.

3.3. Induction period of the diamond crystallization

The new experimental results and the data from previous studies (Pal'yanov et al., 1998a,b, 1999a,b; Sato et al., 1999) suggest that the crystallization of diamond in carbonate–carbon systems is characterized by a relatively long induction period preceding the nucleation of diamond. This can be demonstrated by the example of a rather well-studied Na_2CO_3-C system. According to the data of Akaishi et al. (1990), a complete transformation of graphite to diamond occurred in 20 min at 7.7 GPa and 2200 °C. At 7 GPa and 1700 °C, no growth was observed in the 10- and 20-min runs, but in the runs at the same conditions lasting for 2 h and more, the synthesis of diamond did occur (Pal'yanov et al., 1999a). The

induction period of the diamond nucleation at these conditions is about 1 h. The data from Table 2 indicate that at 5.7 GPa and 1420 °C, the first crystallization centers of diamond appeared in no less than 30 h. The dependence of the duration of the induction period of the diamond nucleation on the $P-T$ parameters is shown in Fig. 4. Hence, the main specific feature of the diamond crystallization in the carbonate–carbon systems is the dependence of the induction period of the reaction: graphite → solution of carbon in carbonate melt → diamond, on temperature and pressure. This is fundamentally different from the metal–carbon systems in which diamond crystallizes in a few minutes. In our opinion, this is the reason why diamond was not previously obtained in the carbonate–carbon systems (Wentorf, 1974), and the carbonate melts were initially classified as the graphite-producing type of carbon solvents. Recent experimental results on the crystallization of diamond in C–O–H fluid at 5.7–7.7 GPa and 1300–2000 °C also indicate the existence of a prolonged induction period that preceeds the nucleation of diamond (Hong et al., 1999; Akaishi and Yamaoka, 2000; Pal'yanov et al., 2000).

Considering the kinetic character of the diamond-formation reactions in the carbonate–carbon systems, the lowest temperature of 1420 °C, at which the spontaneous nucleation of diamond took place, cannot be viewed as minimal for the Na_2CO_3-C system. This is because diamond growth on seed crystals proceeded even at 1300 °C in the 40-h experiments. Hence, at 1300 °C, the induction period preceding the nucleation of diamond is probably longer than 40 h.

A comparative analysis of the results in Tables 2 and 3 shows that the alkaline carbonate melts containing C–O–H fluid are more reactive than the fluid-free alkaline carbonate melts with respect to both the nucleation and the growth of diamond. Addition of H_2O-CO_2 fluid to the K_2CO_3-C and Na_2CO_3-C systems allowed to decrease the temperature of the diamond nucleation and growth to 1150 °C, which is

Fig. 3. Scanning electron micrographs of diamonds synthesized in the systems $Na_2CO_3-H_2C_2O_4\cdot2H_2O-C$ (a–d) and $K_2CO_3-H_2C_2O_4\cdot2H_2O-C$ (e–h): spontaneously nucleated octahedral diamonds on the (111) face of seed crystals (a, b) and in carbonate melt (c) (run NF-2); spontaneously nucleated octahedral diamonds and growth patterns on the (100) face of seed crystals (d—run NF-4); a seed crystal (e) and growth patterns on the (100) face (f) and (111) face (g) (run KF-2); growth layers and spontaneously nucleated diamonds on the (111) face of a seed crystal (h—run KF-3).
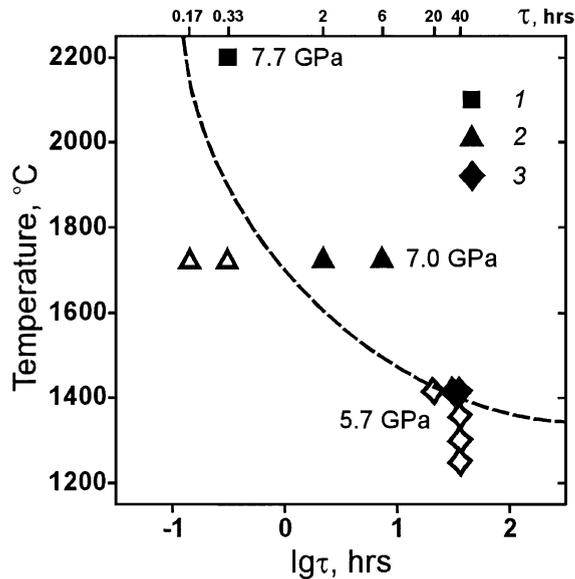
Fig. 4. Dependence of the induction period preceding diamond nucleation on temperature for the Na_2CO_3–C system, according to the data of: (1)—Akaishi et al. (1990); (2)—Pal'yanov et al. (1999a); (3)—this work. τ is the run duration. Symbols show if the spontaneous nucleation of diamond was observed (solid) or not (open).

considerably lower than the minimal temperature of the diamond synthesis in the metal–carbon systems. The results showed that the reactivity in the studied compositions decreases in the following sequence:

$$Na_2CO_3 - H_2C_2O_4 \cdot 2H_2O - C$$
$$> K_2CO_3 - H_2C_2O_4 \cdot 2H_2O - C$$
$$\gg Na_2CO_3 - C > K_2CO_3 - C.$$
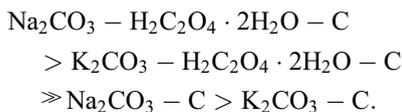
As seen from Tables 2 and 3, most experiments were performed in Pt ampoules. At this stage of the investigation, it is rather difficult to evaluate the possible role of platinum in the diamond synthesis. However, the results from the control runs C-115 and C-125, performed in graphite ampoules, and the K-5 and NF-6 runs in gold ampoules, do not significantly differ from the data obtained with Pt ampoules.

3.4. Diamond growth rate

At the P–T conditions of the diamond formation in nature, the specific features of the diamond growth were studied only in the metal–carbon systems. Two major features were recognized: rather high rates of

the diamond synthesis and the dependence of the diamond morphology on the P–T conditions (Wentorf, 1974; Burns and Davies, 1992). In this process of the diamond synthesis from graphite in the presence of transition-metal melts, linear growth rates are the highest and vary in the range from about 500 to 10 000 μm/h. When diamond is grown on seeds by the temperature gradient method in the same systems, the growth rate of high-quality single crystals is approximately 30 μm/h.

The data reported in Tables 2 and 3 allow a qualitative evaluation of the main trends of change in the diamond growth rates in alkaline carbonate–carbon systems with and without fluid, and in some cases, exact values for the growth rates can be obtained. On the basis of the available data, it is possible to estimate the change in the rates of the diamond growth in a rather wide range of temperatures from 2200 to 1150 °C. From the data of Akaishi et al. (1990), the linear growth rates in the Na_2CO_3–C system at 7.7 GPa and 2200 °C vary from 100 to 1000 μm/h. According to our data (Pal'yanov et al., 1999a) at 7 GPa and 1700–1750 °C, the growth rate of the spontaneously nucleated diamond crystals could reach 150 μm/h, whereas that of the crystals grown on seeds is about 10–25 μm/h. More accurate data for the growth rate estimates were obtained by Pal'yanov et al. (1999b) at 5.7 GPa and 1420 °C (Fig. 5). The growth rates determined from the slopes of the curves for the spontaneously nucleated crystals and the seed-grown crystals were the same and corresponded to 1.7 μm/h. For alkaline carbonate–carbon systems with H_2O–CO_2 fluid, the induction period at 1150 °C can be estimated by extrapolation. Diamond growth rates in this case are 0.1–0.01 μm/h. Apparently, as the temperature decreases from 2200 to 1150 °C, the growth rates decrease by four to five orders. A simple estimate shows that in the range of 1420–1150 °C, the growth time for the growth of a 1-carat diamond varies from 100 days to a few tens of years. Taking the complicated growth history of natural diamonds into account, including discontinuous growth, these rates should be considered minimal. In comparison, the growth of a diamond weighing 1 carat in the metal–carbon systems requires about 100 h.

3.5. Diamond morphology

Pal'yanov et al. (1998b, 1999a) reported that the diamond morphology depended on the composition of
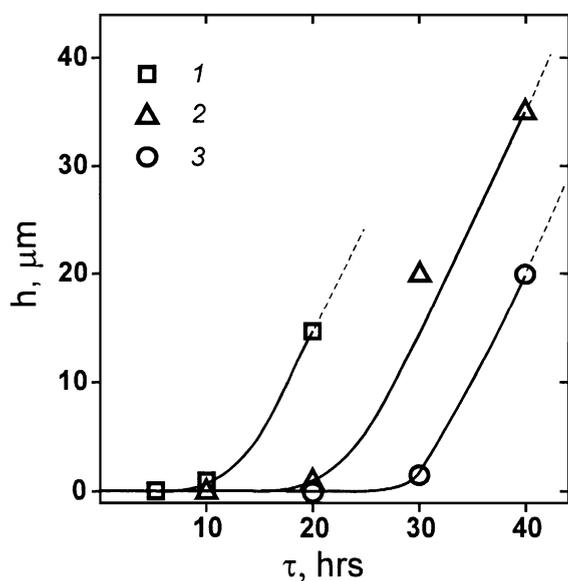
Fig. 5. Dependence of the thickness of the diamond growth layers on the (111) faces on the run duration at 1420 °C and 5.7 GPa: (1) growth on seeds in the system $Na_2CO_3 - H_2C_2O_4 \cdot 2H_2O - C$; (2) growth on seeds in the $Na_2CO_3 - C$ system; (3) average half-thickness of diamond crystals spontaneously nucleated in the $Na_2CO_3 - C$ system.

the alkaline carbonate medium. At 7 GPa and 1700 °C, diamond crystallized as cubo-octahedra in the $Na_2CO_3 - C$ system, and predominantly as octahedra in the $K_2CO_3 - C$ system. Table 2 shows that cubo-octahedra formed in the $Na_2CO_3 - C$ system also at 5.7 GPa and 1420 °C. If diamond grows on seeds, the ratio $h(100)/h(111)$ remains proportional to $v(100)/v(111)$ in this system up to 1300 °C, and corresponds to the $v(100)/v(111)$ ratio typical for cubo-octahedra. For the runs of the "K" series in Table 2, spontaneously nucleated crystals were not found at 1300–1420 °C, but in the runs with crystals grown on seeds, the ratios $h(100)/h(111)$ and $v(100)/v(111)$, corresponded to an octahedron. Thus, for the fluid-free alkaline carbonate systems, diamond morphology mainly depends on the composition of the crystallization medium. In the range of 1300–1750 °C, the stable growth formed in the sodium carbonate melt is a cubo-octahedron, but is an octahedron in the potassium carbonate melt. In the presence of $H_2O - CO_2$ fluid, diamond forms only octahedra at 1150–1420 °C, regardless of the composition of the carbonate melt. In the runs NW-1 and KW-1 (Table 3), in which alkaline carbonates were used with

H_2O, and in the presence of CO_2 fluid (runs NA-1 and KA-1), diamond also crystallized as octahedra. Hence, the diamond morphology in the studied systems is mainly governed by the crystallization medium, and does not depend on the $P-T$ conditions in the investigated range.

4. The medium for the formation of diamonds in the mantle

Analyses of mineral and fluid inclusions in natural diamonds suggest a multi-component crystallization medium with wide variations in compositions, but the problem is how to identify which particular components of the natural system are responsible for the dissolution and transport of carbon that ultimately favor the nucleation and growth of diamonds in the mantle. As previously mentioned, the most common inclusions in diamonds are sulphides, silicates, and oxides. However, there are no reliable experimental data suggesting the possibility of the diamond nucleation and growth in the sulphide–carbon, silicate–carbon, or oxide–carbon systems at the $P-T$ conditions corresponding to the formation of natural diamonds. The issue is also complicated by the fact that the bulk composition of the inclusions does not always adequately reflect the crystallization medium, because of the possible effect of selective entrapment of the inclusions during the diamond growth in heterogenous multi-component systems (Pal'yanov et al., 1997).

The available experimental data on the diamond nucleation and growth summarized in Fig. 6 provide the evidence suggesting that the fluid-bearing alkaline carbonate melts are the medium responsible for the formation of diamonds in the mantle. The formation of diamonds is possible under the mantle conditions from alkali-enriched $H_2O - CO_2$ fluids, as shown by this and other experimental studies (Pal'yanov et al., 1999b). Spontaneous nucleation of octahedral diamond crystals, 1–4 μm in size, and the growth of diamonds on the {111} and {100} faces of seed crystals took place in 120-h runs at 1150 °C. Since the kinetics significantly affect the formation of diamonds in carbonate–carbon systems, diamond nucleation should be possible at lower temperatures in longer experiments.

It is generally agreed that the redox state of the lithospheric and asthenospheric mantle corresponds to
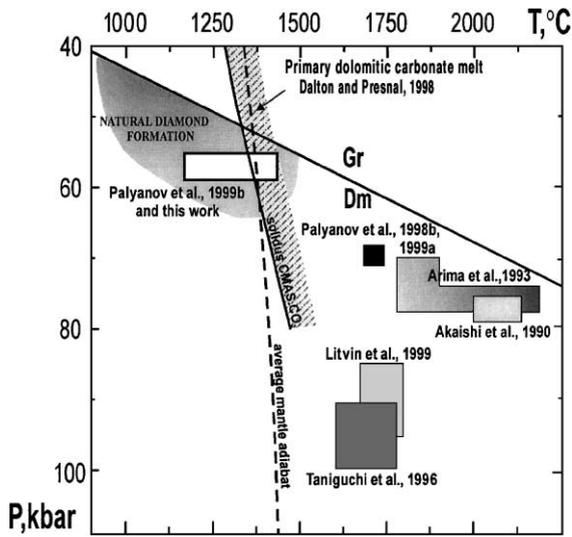
Fig. 6. The $P-T$ conditions of formation of natural diamonds and the experimental conditions resulting in the crystallization of diamond in carbonate–carbon systems. Data from Akaishi et al., 1990; Arima et al., 1993; Dalton and Presnall, 1998; Litvin et al., 1999; Pal'yanov et al., 1998b, 1999a, 1999b, this work; Taniguchi et al., 1996.

the stability field of carbonates. The oxygen fugacity of the upper mantle varies with increasing depth from FMQ + 1 to FMQ-3, and in some cases, up to FMQ-5 log units (Wood et al., 1990; Ballhaus, 1993). The main fluid components in the upper mantle are H_2O and CO_2 (Wood et al., 1990; Navon, 1991; Ballhaus, 1993; Wyllie and Ryabchikov, 2000). A direct evidence for the presence of a fluid with a composition similar to the proposed diamond-forming medium is provided by the data on alkali-enriched hydrous and carbonatic mantle fluids in fibrous diamonds from Jwaneng (Schrauder and Navon, 1994) and brine inclusions in diamonds from Koffiefontein (Izraeli et al., 2001). Fluids of this composition could form by partial melting of the aphanitic group II kimberlite (Yamashita et al., 1998). An experimentally studied melt-fluid system at 900 °C was composed of 31.79% CO_2, 28.09% K_2O, 9.21% H_2O, and 3.34% SiO_2. According to the data obtained by Ryabchikov and Boettcher (1980) at 3.0 GPa and 1100 °C, the concentration of potassium in H_2O fluid equilibrated with phlogopite could reach 25 wt.%. Nowadays, a concept is evolving that the influence of the carbonate melts/fluids is the cause of the metasomatic reworking of mantle rocks (Green and Wallace, 1998; Haggerty, 1999). The temperature range of these

processes seems to be rather wide, and the compositions of the metasomatic melts/fluids could vary with increasing temperature from alkali-enriched $H_2O–CO_2$ fluids (Ryabchikov and Boettcher, 1980; Perchuk and Lindsley, 1982; Perchuk and Yapaskurt, 1998; Schrauder and Navon, 1994) to dolomitic melts (Green and Wallace, 1998; Ryabchikov et al., 1989; Kogarko et al., 1995).

However, some measurements of the oxygen fugacity in natural diamonds indicate that the ancient lithospheric mantle had the oxygen fugacity sufficiently low for iron to be present as metal (Kadik, 1997). Thus, at early stages of the Earth's formation, native Fe–Ni melts could have been the diamond-forming medium. Experimental data on the diamond crystallization obtained during the studies of the metal–carbon systems indicate highly reducing conditions during the synthesis and growth of diamond. Studies of the fluid inclusions in synthetic diamonds revealed that they essentially had a hydrocarbon composition (Tomilenko et al., 1998). Minor amounts of hydrogen–methane fluid were found after experiments on the diamond growth in the Fe–Ni–C system, carried out with platinum ampoules (Sokol et al., 2000). Hence, the fluid regimes of the diamond crystallization in metal–carbon and carbonate–carbon systems fundamentally differ (Sokol et al., 2000). Important characteristics of the diamond formation in metal–carbon systems are the strongly reducing character and the low concentration of the fluid phase. It was experimentally shown that the addition of even minute amounts of H_2O to the metal–carbon systems completely inhibits the formation of diamond and leads to a metastable growth of graphite crystals in the thermodynamic stability field of diamond (Pal'yanov et al., 1997).

Thus, the available experimental results and the information obtained from petrological and mineralogical observations of natural samples are not in conflict. We think that the nucleation and growth of diamonds in nature result from processes that supply carbon to the crystallization medium or cause a decrease of the carbon solubility in it. A source of carbon for the diamond crystallization could be redox reactions between the components of fluid, fluid and carbonate, carbonate and silicates (Brey et al., 1983; Yaxley and Green, 1994; Wyllie, 1995; Haggerty, 1999). Changes in the $P-T$ conditions or the oxygen

fugacity could be the driving forces for the diamond-forming reactions. Experimental studies of these diamond-forming reactions have just started and will most likely yield new interesting results.

5. Conclusions

We showed that the crystallization of diamond in alkaline carbonate–carbon systems is characterized, first of all, by an induction period preceding nucleation and growth. The duration of the induction period depends to a great extent on the $P-T$ conditions and strongly increases with decreasing P and T. At the $P-T$ conditions corresponding to the formation of diamonds in nature, the duration of the induction period is tens of hours. The duration preceding the nucleation and growth can be reduced by adding a C–O–H-fluid to the system. In general, the nucleation and growth of diamonds are more active in the fluid-bearing alkaline carbonate systems than in the fluid-free systems. The reactivity of the studied systems with respect to the nucleation and growth of diamond decreases in the following sequence: $Na_2CO_3-H_2C_2O_4 \cdot 2H_2O-C > K_2CO_3-H_2C_2O_4 \cdot 2H_2O-C \gg Na_2CO_3-C > K_2CO_3-C$.

The growth rates of diamonds in the studied systems heavily depend on the temperature, and decrease approximately by four orders from 2200 to 1150 °C. At the $P-T$ conditions corresponding to the formation of diamonds in nature, the diamond growth rates change from 1.7 μm/h at 1420 °C to 0.1–0.01 μm/h at 1150 °C, suggesting that the possible growth rates for diamond in natural processes could vary from hundreds of days to a few tens of years.

Contrary to the existing concepts about the predominant dependence of the diamond morphology on the $P-T$ conditions of crystallization, based mainly on the experiments in metal–carbon systems, the diamond morphology in alkaline carbonate–carbon systems is independent of the $P-T$ conditions in the investigated range. The main factor controlling the ratio of the growth rates of different diamond faces in the studied systems is the composition of the crystallization medium (the composition of the carbonate melt and the presence of the C–O–H fluid). The stable crystal form in the sodium carbonate melt is a cubo-octahedron, and an octahedron in the potassium car-bonate melt. Only octahedral diamond grows in the presence of the C–O–H fluid.

The observed occurrence of carbonate minerals in the diamondiferous rocks of the magmatic and metamorphic origin, elevated contents of alkalies (mainly K and Na) in deep-level diamondiferous assemblages, essentially alkaline and H_2O-CO_2 compositions of mantle fluids, in combination with the obtained experimental data, suggest that fluid-bearing alkaline carbonate and carbonate–silicate melts are the most probable medium for the formation of diamonds in nature. These melts/fluids are able to dissolve carbon, transport it, and serve as the medium for the nucleation and growth of diamonds at the $P-T$ conditions corresponding to the formation of natural diamonds.

Acknowledgements

References

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.

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.

Arima, M., Nakayama, K., Akaishi, M., Yamaoka, S., Kanda, H., 1993. Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiment. Geology 21, 968–970.

Ballhaus, C., 1993. Redox states of lithospheric and asthenospheric upper mantle. Contrib. Mineral. Petrol. 114, 331–348.

Borzdov, Yu.M, Popkov, A.D., 1983. Distribution of temperatures in the cell of multi-anvil apparatus (in Russian). Experimental Study of Diamond Crystallization in Metallic Systems. Institute of Geology and Geophysics, Novosibirsk, pp. 71–77.

Brey, G., Brice, W.R., Ellis, D.J., Green, D.H., Harris, K.L., Ryabchikov, I.D., 1983. Pyroxene–carbonate reactions in the upper mantle. Earth Planet. Sci. Lett. 62, 63–74.

Bulanova, G.P., 1995. Formation of diamond. J. Geochem. Explor. 53, 1–23.

Bulanova, G.P., Griffin, W.L., Ryan, C.G., 1998. Nucleation envi-

ronment of diamonds from Yakutian kimberlites. Mineral. Mag. 62 (3), 409–419.

Burns, R.C., Davies, G.J., 1992. Growth of synthetic diamond. In: Field, J.E. (Ed.), The Properties of Natural and Synthetic Diamonds. Academic Press, London, pp. 395–423.

Dalton, J.A., Presnall, D.C., 1998. 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.

Dobretsov, N.L., Kirdyashkin, A.G., 1998. Deep-Level Geodynamics. Edited by A.A. Balkema, Brookfield, Rotterdam, 328 pp.

Dobrzhinetskaya, L.F., Green, H.W., Mitchell, T.E., Dickerson, R.M., 2001. Metamorphic diamonds: mechanism of growth and inclusion of oxides. Geology 29, 263–266.

Galimov, E.M., 1991. Isotope fractionation related to kimberlite magmatism and diamond formation. Geochim. Cosmochim. Acta 55, 1697–1708.

Gasparik, T., Hutchison, M.T., 2000. Experimental evidence for the origin of two kinds of inclusions in diamonds from the deep mantle. Earth Planet. Sci. Lett. 181, 103–114.

Green, D.H., Wallace, M.E., 1988. Mantle metasomatism by ephemeral carbonatite melts. Nature 336, 459–461.

Haggerty, S.E., 1986. Diamond genesis in a multiply constrained model. Nature 320, 34–38.

Haggerty, S.E., 1999. A diamond trilogy: superplumes, supercontinents, and supernovae. Nature 285, 851–859.

Harris, J.W., 1992. Diamond geology. In: Field, J.E. (Ed.), The Properties of Natural and Synthetic Diamond. Academic Press, London, pp. 345–393.

Harte, B., Harris, J.W., Hutchison, M.T., Watt, M.C., Wilding, M.C., 1999. Lower mantle mineral association in diamonds from Sao Luiz, Brazil. In: Fei, Y., Bertka, C.M., Mysen, B.O. (Eds.), Mantle Petrology: Field Observations and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd. Geochemical Society, Special Publication, vol. 6, pp. 125–153.

Hong, S.M., Akaishi, M., Yamaoka, S., 1999. Nucleation of diamond in the system of carbon and water under very high pressure and temperature. J. Cryst. Growth 200, 326–328.

Izraeli, E.S., Harris, J.W., Navon, O., 2001. Brine inclusions in diamonds: a new upper mantle fluid. Earth Planet. Sci. Lett. 5807, 1–10.

Joswing, W., Stachel, T., Harris, J.W., Baur, W.H., Brey, G.P., 1999. New Ca-silicate inclusions in diamonds—tracers from the lower mantle. Earth Planet. Sci. Lett. 173, 1–6.

Kadik, A.A., 1997. Evolution of Earth's redox state during upwelling of carbon-bearing mantle. Phys. Earth Planet. Inter. 100, 157–166.

Kanda, H., Akaishi, M., Yamaoka, S., 1990. Morphology of synthetic diamonds grown from Na_2CO_3 solvent-catalyst. J. Cryst. Growth 106, 471–475.

Kennedy, C.J., Kennedy, G.C., 1976. The equilibrium boundary between graphite and diamond. J. Geophys. Res. 81, 2467–2470.

Kogarko, L.N., Henderson, C.M.B., Pacheco, H., 1995. Primary Ca-rich carbonatite magma and carbonate–silicate–sulphide liquid immiscibility in the upper mantle. Contrib. Mineral. Petrol. 121, 267–274.

Litvin, Yu.A., 1998. Hot spots of mantle and experiment to 10 GPa: alkaline reactions, lithosphere carbonatization, and new diamond-generating systems. Geol. Geofiz. 39, 1772–1779 (in Russian). English Translation: Russ. Geol. Geophys. 39, 1760–1768.

Litvin, Yu.A., Zharikov, V.A., 2000. Experimental modeling of diamond genesis: diamond crystallization in multicomponent carbonate–silicate melts at 5–7 GPa and 1200–1570 °C. Dokl. Earth Sci. 373, 867–871.

Litvin, Yu.A., Aldushin, K.A., Zharikov, V.A., 1999. Synthesis of diamond at 8.5–9.5 GPa in the system $K_2Ca(CO_3)_2-Na_2Ca(CO_3)_2-C$ corresponding to the composition of fluid-carbonatitic inclusions diamond from kimberlites. Dokl. Earth Sci. 367, 529–532.

Meyer, H.O.A., 1987. Inclusions in diamond. In: Nixon, H.P. (Ed.), Mantle Xenoliths. Wiley, New York, pp. 501–523.

Navon, O., 1991. Infrared determination of high internal pressures in diamond fluid inclusions. Nature 353, 746–748.

Navon, O., 1999. Diamond formation in the Earth's mantle. In: Gurney, J.J., Gurney, J.L., Pascoe, M.D., Richadson, S.H. (Eds.), VII International Kimberlite Conference 2, Red Roof Design, Cape Town, 584–604.

Navon, O., Hutcheon, I.D., Rossman, G.R., Wasserburg, G.J., 1988. Mantle-derived fluids in diamond micro-inclusions. Nature 335, 784–789.

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. Geol. Geofiz. 38, 882–918 (in Russian). English translation: Russ. Geol. Geophys. 38, 920–945.

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

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Sobolev, N.V., 1998b. Experimental study of diamond crystallization in carbonate–carbon systems in connection with the problem of diamond genesis in magmatic and metamorphic rocks. Geol. Geofiz. 39, 1780–1792 (in Russian). English translation: Russ. Geol. Geophys. 39, 1768–1779.

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., 1999b. Diamond formation from mantle carbonate fluids. Nature 400, 417–418.

Pal'yanov, Yu.N., Sokol, A.G., Khokhryakov, A.F., Pal'yanova, G.A., Borzdov, Yu.M., Sobolev, N.V., 2000. Diamond and graphite crystallization in C–O–H fluid at PT parameters of the natural diamond formation. Dokl. Earth Sci. 375A, 1395–1399.

Perchuk, L.L., Lindsley, D.H., 1982. Fluid–magma interaction at high pressure-temperature conditions. In: Akimoto, S., Manghnani, M.N. (Eds.), High-Pressure Research in Geophysics. Center for Academic Publications Japan, Tokyo, pp. 251–259.

Perchuk, L.L., Yapaskurt, O.V. 1998. Deep-seated ultrapotassic liquids. Geol. Geofiz. 39, 1772–1779 (in Russian). English translation: Russ. Geol. Geophys., 1756–1766.

Robinson, D.N., 1978. The characteristics of natural diamond and their interpretation. Miner. Sci. Eng. 10, 55–72.

Ryabchikov, I.D., Boettcher, A.L., 1980. Experimental evidence at high pressure for potassic metasomatism in the mantle of the Earth. Am. Mineral. 65, 915–919.

Ryabchikov, I.D., Brey, G., Kogarko, L.N., Bulatov, V.K., 1989. Partial melting of carbonated peridotite at 50 kbar. Geochemistry 1, 3–9 (in Russian).

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.

Sobolev, N.V., 1977. The Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle. American Geophysics Union, Washington, p. 304.

Sobolev, N.V., Shatsky, V.S., 1990. Diamond inclusions in garnets from metamorphic rocks. Nature 343, 742–746.

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.

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 crystallization in carbonate–carbon systems. Eur. J. Mineral. 12, 367–375.

Stachel, T., Harris, J.W., Brey, G.P., 1998. Rare and unusual mineral inclusions in diamonds from Mwadui, Tanzania. Contrib. Mineral. Petrol. 132, 34–47.

Sunagawa, I., 1994. Investigation of crystal growth in the Earth and planetary sciences. In: Hurle, D.T.J. (Ed.), Handbook of Crystal Growth. Elsevier, Amsterdam, pp. 3–50, Chap. 1.

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.

Tomilenko, A.A., Chepurov, A.I., Pal'yanov, Yu.N., Shebanin, A.P., Sobolev, N.V., 1998. Hydrocarbon inclusions in synthetic diamonds. Eur. J. Mineral. 10, 1135–1141.

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. Adv. High Pressure Res. 4, 249–281.

Wentorf, R.H., Bovenkerk, H.P., 1961. The origin of natural diamonds. Astrophys. J. 134, 995–1005.

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., 1995. Experimental petrology of upper mantle materials, process and products. J. Geodyn. 20, 429–468.

Wyllie, P.J., Ryabchikov, I.D., 2000. Volatile components, magmas, and critical fluids in upwelling mantle. J. Petrol. 41, 1195–1206.

Yamashita, H., Arima, M., Ohtani, E., 1998. Melting experiments of kimberlite composition up to 9 GPa: determination of melt composition using aggregates of diamond grains. Ext. Abstr. 7th Int. Kimberlite Conf., Cape Town, 977–979.

Yaxley, G.M., Green, D.H., 1994. Experimental demonstration of refractory carbonate-bearing eclogite and siliceous melt in the subduction regime. Earth Planet. Sci. Lett. 128, 313–325.