Diamond Crystallization in Fluid and Carbonate–Fluid Systems under Mantle *P–T* Conditions: 2. An Analytical Review of Experimental Data

A. G. Sokol and Yu. N. Pal'yanov

Institute of Mineralogy and Petrography, Siberian Division, Russian Academy of Sciences, pr. Akademika Koptyuga 3, Novosibirsk, 630090 Russia
e-mail: SokolA@uiggm.nsc.ru
Received October 31, 2002

Abstract—This paper discusses recent experimental data on diamond crystallization in fluid (CO_2–C, H_2O–CO_2–C, H_2O–C, CH_4–H_2O–C, and CH_4–H_2–C) and carbonate–fluid (K_2CO_3–H_2O–CO_2–C, Na_2CO_3–H_2O–CO_2–C, and $CaMg(CO_3)_2$–H_2O–CO_2–C) systems under the thermodynamic conditions of diamond stability. The intensity of diamond crystallization under 5.7–7.7 GPa and 1150–2000°C is a function of the temperature, the composition, and probably the pressure of the system. Spontaneous diamond nucleation and growth on seed crystals is preceded by an inductive period, whose duration increases from several minutes to hundreds of hours as the temperature decreases from 2000 to 1150°C. The stable habit of the crystallizing diamond is octahedral. In terms of the experimental intensity of diamond crystallization, these fluid and fluid–carbonate systems are set in the following order: $K_2CO_3(Na_2CO_3)$–H_2O–CO_2–C > CO_2–C ≈ H_2O–CO_2–C ≈ H_2O–C ≈ $CaMg(CO_3)_2$–H_2O–CO_2–C ≫ CH_4–H_2O–C ≫ CH_4–H_2–C. Metastable graphite can crystallize in them under 5.7 GPa and 1150–1420°C and under 7.7 GPa and 1400–1600°C. Our data show that, under upper mantle *P–T* conditions, C–O–H fluids and fluids with a more complex composition (with alkali and alkali-earth carbonates) can serve both as a carbon source and as a natural medium of diamond crystallization.

INTRODUCTION

Primary inclusions in natural diamond provide important information on its crystallization medium. The principal characteristics of the fluid regime in which this mineral crystallizes were obtained by direct *in situ* analyses. For example, inclusion compositions in rims of the cubic diamonds from the Zhvaneng kimberlite pipe show that the fluid contained oxidized gases (CO_2 and H_2O) and varying amounts of silicic acid and alkali and alkali-earth carbonates [1, 2]. Cloud-like zones in diamonds from the Koffienfontein kimberlite pipe host silicic, carbonate, and brine inclusions. The latter consist of water, K and Na chlorides, alkali-earth carbonates, and silicic acid [3]. Fluid inclusions with elevated carbonate, water, SiO_2, and alkali concentrations were also found in metamorphic diamonds and diamond-bearing garnets [4, 5]. Newly obtained facts point to a more considerable compositional variability of mantle-derived fluids and suggest their genetic relations to both mantle metasomatism [2, 3] and natural diamond formation [2, 3, 6, 7].

Diamond crystallization in carbonate–carbon systems under the thermodynamic conditions of diamond stability has been studied since the early 1990s [8–11]. Spontaneous diamond nucleation and growth on seed crystals were studied in melts of alkali and alkali-earth carbonates under $P ≥ 7$ GPa and $T ≥ 1600–1700$°C.

Diamond growth on seed crystals in the H_2O–C experimental system under 7.7 GPa and 2000–2200°C was first reported in 1992 [12]. Spontaneous diamond nucleation and growth on seed crystals in a C–O–H fluid was studied over the past two–three years [13–20]. According to these experimental data, diamond can crystallize in fluid and carbonate–fluid systems at 5.7 GPa and 1150–1420°C, i.e., under the *P–T* conditions of diamond formation in the upper mantle [14, 19, 21–23].

Thus, new petrologic and experimental data are prerequisites for a deeper understanding of diamond crystallization in the mantle. However, experimental data on diamond crystallization in fluid systems are mostly published in international materials-science journals and remain unsystematic. Most of these data seem to remain out of sight of researchers interested in the formation of mantle diamond. Because of this, we formulated the goal of this research as analyzing available experimental data on diamond crystallization in fluid and carbonate–fluid systems under the thermodynamic conditions of diamond stability and, on this basis, searching for regularities important for understanding the genesis of diamond. The experimental data were taken from the publications listed in the table.

Experimental conditions of diamond crystallization in fluid and fluid-containing systems

No.	System composition	P, GPa	T, °C	τ, h	Author, reference
1	H_2O–C	7.7	1800–2200	0.3–2	Yamaoka et al., 1991 [12]
2	H_2O–C	7.7	1700–2100	0.5–4	Hong et al., 1999 [13]
3	Na_2CO_3–H_2O–CO_2–C	5.7	1150–1420	20–136	Pal'yanov et al., 1999 [21]
	K_2CO_3–H_2O–CO_2–C				
4	$CaMgSi_2O_6$–H_2O–CO_2–C	7.0	1700–1750	4	Sokol et al., 1999 [21]
	$NaAlSi_2O_6$–H_2O–CO_2–C				
5	CO_2–C	7.7	1500–2000	0.5–27	Sun et al., 2000 [15]
6	H_2O–C	7.7	1200–1500	24	Yamaoka et al., 2000 [25]
		5.5	1200–1500	24	
7	H_2O–CO_2–C	7.7	1400–2000	0.5–360	Akaishi and Yamaoka, 2000 [16]
8	H_2O–CO_2–C	7.7	1300–1500	24–240	Kumar et al., 2000 [17]
9	H_2O–C	5.7	1300	84	Pal'yanov et al., 2000 [14]
	H_2O–CO_2–C				
	CO_2–C				
	CH_4–H_2–C				
10	H_2O–CO_2–C	7.7	1600	0–24	Akaishi et al., 2000 [18]
11	H_2O–CO_2–C	7.7	1500	24	Kumar et al., 2001 [26]
12	H_2O–CO_2–C	7.7	1500–1600	0–48	Akaishi et al., 2001 [27]
	H_2O–C				
	H_2O–CH_4–C				
13	$CaMg(CO_3)_2$–H_2O–CO_2–C	5.7	1300–1400	42	Sokol et al., 2001 [22]
	$CaMg(CO_3)_2$–H_2O–C				
	$CaMg(CO_3)_2$–CO_2–C				
14	H_2O–C	5.7	1200–1420	42–136	Sokol et al., 2001 [19]
	H_2O–CO_2–C				
	CO_2–C				
	CH_4–H_2–C				
15	Na_2CO_3–H_2O–CO_2–C	5.7	1150–1420	20–136	Pal'yanov et al., 2002 [23]
	Na_2CO_3–H_2O–C				
	Na_2CO_3–CO_2–C				
	K_2CO_3–H_2O–CO_2–C				
	K_2CO_3–H_2O–C				
	K_2CO_3–CO_2–C				
16	H_2O–C	7.7	1500	1–33	Yamaoka et al., 2002 [20]
17	CO_2–C	7.7	1500	1–24	Yamaoka et al., 2002 [28]

EXPERIMENTAL

Preparatory to analyzing the experimental data, it is expedient to touch upon some features of experiments conducted at elevated P–T parameters. The experiments listed in the table were carried out by two research teams: on a modified Belt apparatus with a working diameter of 32 mm at the Advanced Materials Laboratory of the National Institute for Materials Science (before 2001, NIRIM), Japan, and on a "split sphere" multi-anvil apparatus with a high-pressure cell of 19 vs. 19 vs. 22 mm at the Laboratory of Crystallization and Mineralogy of Diamond of the Institute of Mineralogy and Petrology, Siberian Division, Russian Academy of Sciences, Russia. Each of the laboratories used a procedure adapted for their high-pressure equipment. In the modified Belt experiments, pressure was calibrated against Bi, Te, and Ba phase transitions. The samples were heated on the basis of calibration curves approximating the correlation between the power consumption of the heater and the electromotive force of
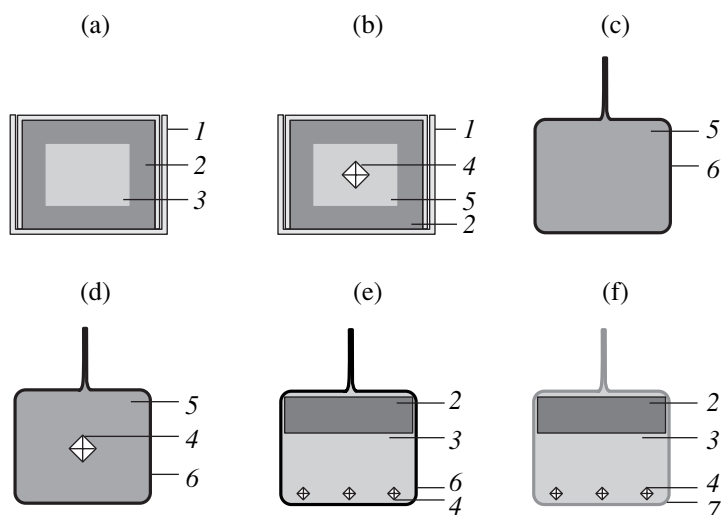
Fig. 1. Capsules and charging schemes used for the experimental diamond crystallization in fluid and carbonate–fluid systems: (a) graphite-lined molybdenum capsule charged with fluid-generating matter [15, 16]; (b) graphite-lined molybdenum capsule charged with a mixture of graphite powder, fluid-generating matter, and a seed crystal [12, 13]; (c) platinum capsule charged with a mixture of graphite powder and fluid-generating matter [17, 18, 26–28] or charged only with fluid-generating matter [20]; (d) platinum capsule charged with a mixture of graphite powder and fluid-generating matter and with a seed crystal [25]; (e) platinum capsule charged with a graphite pellet, fluid-generating matter, and seed crystals [14, 19], or charged with a graphite pellet, fluid-generating matter with carbonate or silicate admixture, and seed crystals [21–24]; (f) gold capsule charged with a graphite pellet, fluid-generating matter, and seed crystals [14], or charged with a graphite pellet, fluid-generating matter with a carbonate admixture, and seed crystals [23]. *1*—molybdenum capsule; *2*—graphite; *3*—fluid-generating matter; *4*—seed diamond crystal; *5*—a mixture of graphite and fluid-generating matter powders; *6*—platinum capsule; *7*—gold capsule.

the W5%Re/W26%Re [13] or Pt6%Rh/Pt30%Rh [17] thermocouples. In the multi-anvil apparatus experiments, the calibration was made against Bi and PbSe. The temperature was determined by a Pt6%Rh/Pt30%Rh thermocouple mounted in each cell [23, 29]. Then, the thermocouple values were corrected using the calibration curves constructed on the basis of Al, Ag, Au, and Ni melting and the results of diamond synthesis in the Ni–C system [23].

Diamond crystallization was performed in capsules (Fig. 1) from molybdenum [13], platinum [18, 21], and gold [19, 23]. The experimental fluids were generated by silver oxalate ($Ag_2C_2O_4$) and oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) or anhydrous oxalic acid ($H_2C_2O_4$), water (H_2O), glucose ($C_6H_{12}O_6$), and anthracene ($C_{14}H_{10}$). Note that silver oxalate used for the experimental generation of a CO_2 fluid was thermally decomposed to give metallic silver. During long experiments, silver penetrates into the walls of the platinum capsules, which results in the failure of the capsule [19]. According to the recent report [28], PtO_2 can be used as a source of oxygen for graphite oxidation and the generation of a CO_2 fluid. The capsules were charged by a fluid generator mixed with graphite powder and, sometimes, seed diamond crystals [13]. In other experiments, a two-layer infilling of capsules was used [14]. Carbon was generated by high-purity graphite. The experiments were terminated by switching off the power supply, after which the temperature decreased with a rate of 3.3°C /s in experiments on the Belt equipment [13] and with a rate of 150°C /s in experiments on the multi-anvil apparatus [30].

DIAMOND CRYSTALLIZATION

Spontaneous Crystallization

Spontaneous diamond crystallization was examined in experiments with a C–O–H fluid under 5.7–7.7 GPa and 1200–2200°C (table). The synthesized diamonds were colorless, gray, or pale yellow octahedral crystals (Figs. 2a and 2b). Their size strongly depended on the experimental temperature, duration, and fluid composition. For example, 2-h experiments in the H_2O–C system at 1900–2000°C gave crystals up to 200 μm in size, while similar experiments at 1700°C yielded 10- to 20-μm crystals [13]. Relatively large elongated crystals (up to 700 μm) were synthesized in 2-h experiments in the CO_2–C system at 1800°C [15]. A decrease in the experimental temperature resulted in a decrease in the average size of diamond crystals. Crystals synthesized in the 42-h experiment in the H_2O–C system under 1420°C measured up to 100–300 μm. Diamonds that crystallized under the same experimental conditions in CO_2–C and CO_2–H_2O–C systems did not exceed 100 μm, while those obtained in the 136-h run in the CO_2–H_2O–C system at 1200°C were only 3–4 μm in size [19]. The crystals synthesized in the 120-h experiments with alkaline carbonate–fluid–carbon systems at

1500°C attained 2–4 µm [21, 23]. Octahedral diamond crystals (Fig. 2c) and dendritic aggregates up to 400 µm in size (Fig. 3) were formed on the walls of the platinum capsules during experiments with CO_2–C, CO_2–H_2O–C, and H_2O–C systems under 7.7 GPa and 1500°C [20] and 5.7 GPa and 1200–1420°C [14, 19].

Diamond Nucleation

Upon attaining the experimental P–T conditions in the ampoules with fluid, metastable graphite contained in them started to dissolve, creating the supersaturation necessary for the onset of spontaneous diamond nucleation. Differing from the fluid in density, spontaneous diamond crystals newly formed in the fluid volume should sink. Hence, we can discuss the experimental data only in terms of heterogeneous diamond nucleation. Experiments in graphite capsules (Fig. 1a) under 7.7 GPa and 1400–2000°C resulted in heterogeneous diamond nucleation on the capsule walls [15, 16]. Under the same P–T conditions, experiments in capsules charged by a mixture of graphitic powder with fluid-generating matter (Figs. 1b–1d) resulted in diamond nucleation over the whole charge volume [12, 13, 17, 18, 25–28]. Heterogeneous nucleation was also revealed on seed diamond crystals [13]. In experiments with layered charges (Figs. 1e and 1f) under 5.7 GPa and 1150–1420°C, heterogeneous diamond nucleation occurred on seed crystals (Fig. 2b) [14, 19, 21–23]. The distribution of spontaneous crystals in the experimental products suggests that some of them probably nucleated in the fluid volume. However, no spontaneous diamond crystals were found on the graphite surface after experiments under 5.7 GPa and 1150–1420°C.

In analyzing data on spontaneous diamond nucleation, it is necessary to discuss the effect of capsule composition on spontaneous diamond nucleation in fluid systems. Although the effect of molybdenum capsules was not specially studied, it was shown in [31] that diamond nucleation in the alkaline-earth carbonate system with a molybdenum foil begins at a lower (by 200°C) temperature than in the alkaline carbonate–carbon system. In graphite-lined molybdenum capsules, the fluid-generating substance is not in direct contact with molybdenum. Nevertheless, owing to its high mobility, the fluid can contact the molybdenum capsule walls, which is indirectly confirmed by the presence of MoO_2-containing products in some experiments [16]. Platinum capsule walls can also affect heterogeneous diamond nucleation, as is evident from the distribution of spontaneous crystals and dendritic diamond aggregates on the walls after experiments under 5.7 and 7.7 GPa (Figs. 2c and 3) [14, 19, 20]. After experiments in gold capsules under the same P–T conditions, spontaneous crystals were found on seed crystals but not on the capsule walls [19, 23]. In general, this problem is to be additionally studied.
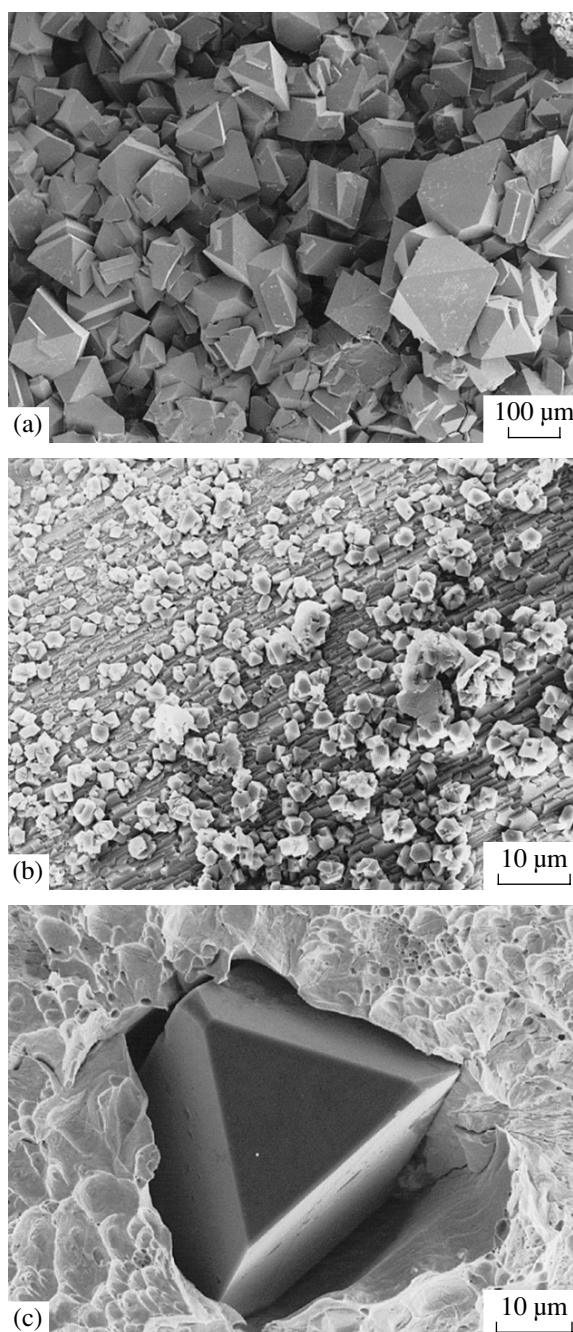

Fig. 2. Spontaneous diamond crystals: (a) complete graphite–diamond transition (40-h experiment with CO_2–H_2O–C system under P = 7.0 GPa and T = 1600°C); (b) on the surface of a seed crystal (135-h experiment in the CO_2–H_2O–C system under P = 5.7 GPa and T = 1200°C in a gold capsule); (c) on the surface of the platinum capsule (42-h experiment in the CO_2–C system under P = 5.7 GPa and T = 1420°C).

Inductive Period

Under the thermodynamic conditions of diamond stability, its spontaneous nucleation is preceded by a time period, which was first revealed in experiments
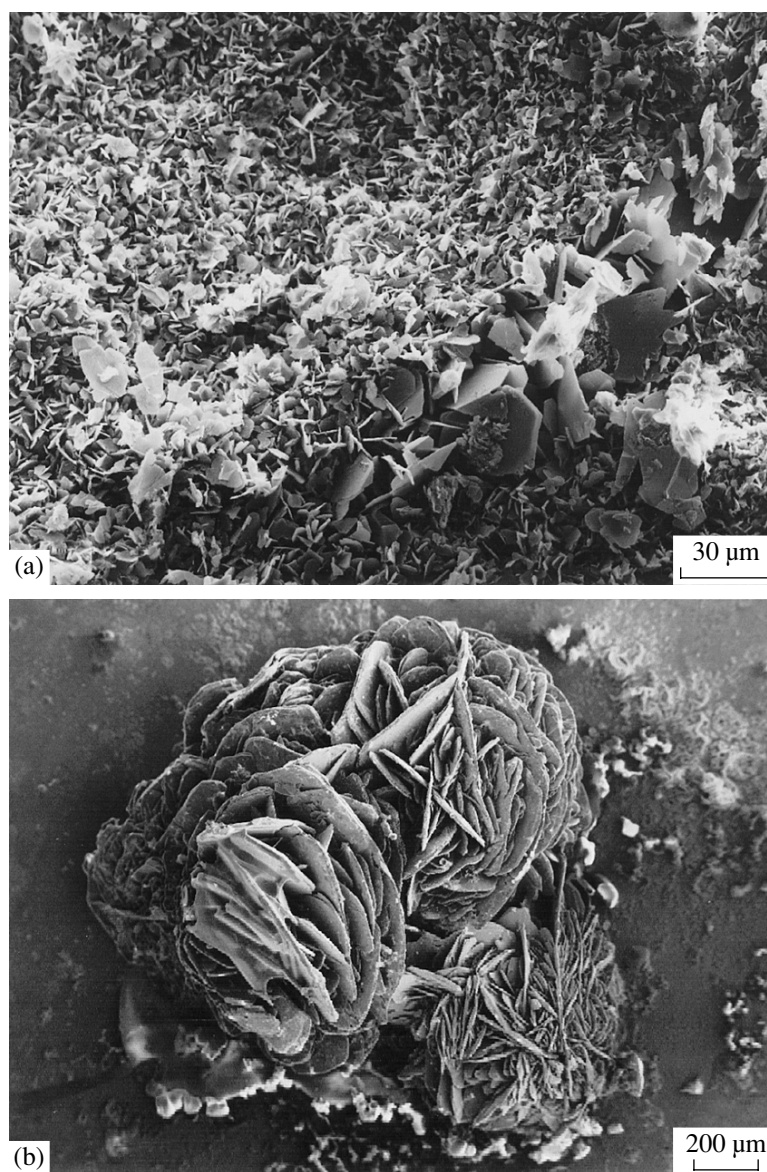
Fig. 7. Metastable graphite in capsules after (a) an 84-h experiment in the CO_2–H_2O–C system under P = 5.7 GPa and T = 1300°C and (b) an 84-h experiment in the H_2O–C system at P = 5.7 GPa and T = 1300°C.

Some of the fluid-generating substances (oxalic acid, glucose, and anthracene) decomposed, releasing excess amorphous carbon [16, 19, 20]. The latter recrystallized into graphite during the first hour, with this process completed by the beginning of diamond crystallization [20]. The decomposition of other fluid-generating substances is not accompanied by carbon release. In these experiments, graphite recrystallization begins with the saturation of the system with carbon owing to the dissolving of the initial graphite. Graphite continues to crystallize after the beginning of diamond growth on seed crystals. These experimental data show that diamond can grow together with metastable graphite on seed crystals in the CO_2–C, CO_2–H_2O–C, and H_2O–C systems under 5.7 GPa. Optical and electron

microscopic studies of the seed crystals after the experiments revealed compromise boundaries between these carbon phases (Fig. 8) [14, 19]. Nevertheless, it remains uncertain as to whether graphite crystallization continued after the beginning of spontaneous diamond nucleation. The recrystallized graphite showed evidence of dissolution only in experimental products with a considerable grade of carbon–diamond transition [20]. Otherwise, the recrystallized graphite was not subjected to dissolution [14, 19].

Let us discuss the inductive period preceding diamond nucleation in terms of the simultaneous crystallization of stable and metastable carbon phases. It is demonstrated in [20] that the duration of the inductive
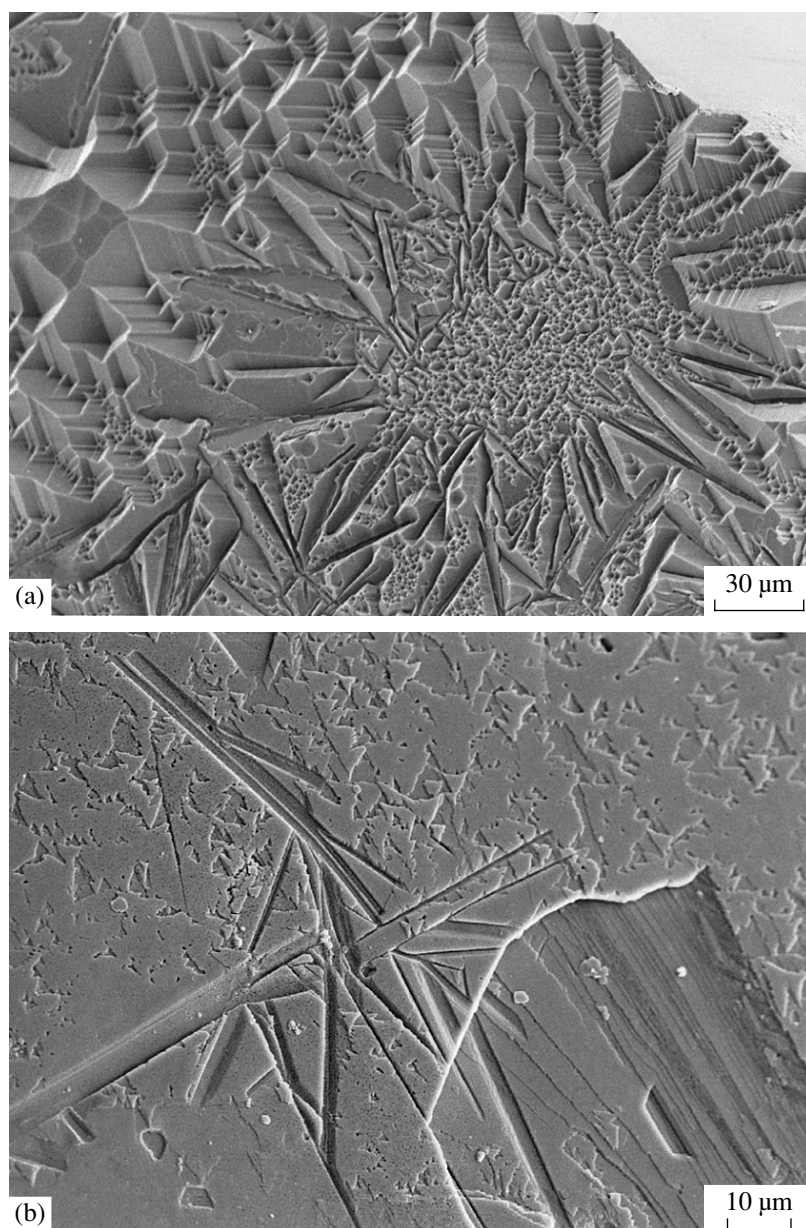
Fig. 8. Compromise boundaries between diamond and metastable graphite on seed crystals: (a) on an {100} crystal face after a 42-h experiment in the CO_2–C system at $P = 5.7$ GPa and $T = 1420°C$, and (b) on a {111} crystal face after a 135-h experiment in the CO_2–H_2O–C system at $P = 5.7$ GPa and $T = 1200°C$.

period does not depend on the presence of excess atomic carbon in experimental systems, which is very important for discussing changes in the carbon concentration in fluids during the inductive period. According to Yamaoki *et al.* [20], the carbon concentration in fluids increases during the inductive period. Sokol *et al.* [19] suggested that spontaneous graphite crystallization is preceded by the saturation of the system with carbon, and that this inductive period is shorter than the inductive period before diamond crystallization. This viewpoint is supported by thermodynamic data in [34, 35], according to which the solubility of carbon

phases in a fluid decreases as follows: amorphous carbon ⟶ graphite ⟶ diamond. Therefore, as compared with diamond, amorphous carbon and graphite should crystallize in fluid systems with essentially higher carbon concentrations. Hence, fluid systems become carbon-oversaturated with respect to diamond long before the termination of the inductive period preceding spontaneous diamond nucleation. Although there are still insufficient data on the effect of pressure on metastable graphite crystallization, graphite absence from fluid systems under 7.7 GPa and temperatures
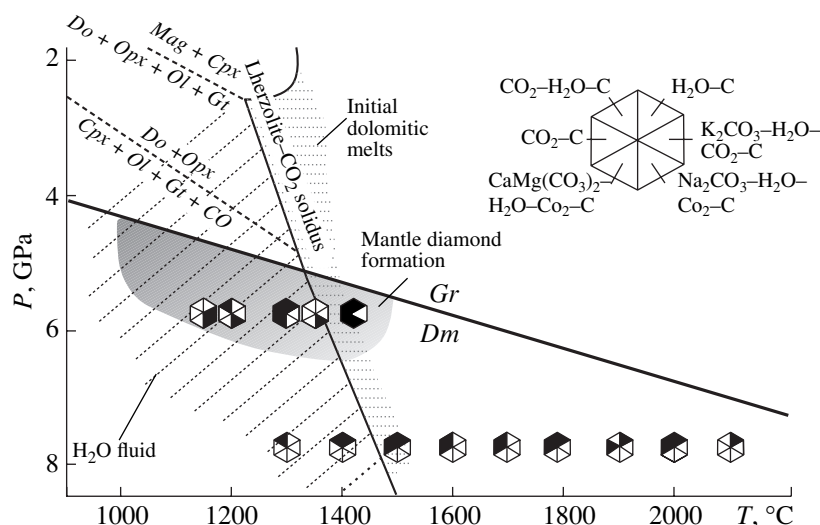
Fig. 9. *P–T* characteristics of diamond growth in fluid and carbonate–fluid systems (the shaded field shows the composition of the system in which diamond formation was experimentally studied). The conditions of natural diamond formation are plotted according to [60–62]; the solidus curve of carbonatized lherzolite (CMAS. CO_2) and the formation conditions of initial dolomitic melts are according to [58, 59]; the subsolidus fluid zone is shown after [7]. *Gr*—graphite, *Dm*—diamond.

over 1600°C allows us to suggest that pressure affects metastable graphite crystallization.

SOME ASPECTS OF DIAMOND FORMATION IN THE UPPER MANTLE

The analysis of experimental data is a new approach to many problems of mantle diamond formation. Based on these data, the discussion of natural diamond crystallization can be extended from the postulation of common regularities to the analysis of probable mechanisms and kinetics. Subsequent experimental studies of diamond crystallization in fluid and carbonate–fluid systems and additional petrological data are necessary to develop a theory for diamond formation in the mantle.

During the Earth's evolution, mantle fluids have played a very important role in the generation of asthenospheric and lithospheric magmas and in the formation of the atmosphere. The modes of occurrence and concentration of volatile components in the mantle are the matter of heated discussions [36–41]. The H_2O content in the primitive mantle is estimated at 1160 ppm [42]; and the CO_2 content is thought to be 230 to 550 ppm [43]. The average carbon concentration in the mantle is estimated at 80 to 400 ppm, reaching several hundred thousand ppm in some zones, as is evident from unique finds of diamond-containing kimberlites [39, 40]. Fluid components can accumulate in mantle magmas. The H_2O concentration of the primitive mantle melts can vary over the interval of 1 to 2.9 wt % and can reach 4–8 wt % owing to fractional crystallization [44]. Oxygen fugacity is a major factor controlling the fluid composition in the C–O–H system. Petrological and geochemical data suggest that oxygen fugacity varies in the upper mantle over the interval

from FMQ – 3 to FMQ + 1, occasionally to FMQ – 5 logarithmic units [45, 46]. Major components of fluids with these oxygen fugacities must be H_2O and CO_2. The oxidizing nature of mantle fluid is confirmed by multiple data on inclusion compositions in deep-seated minerals [47–49] and by finds of CO_2 inclusions in diamonds [1, 50, 51].

The hypothesis by V. S. Sobolev [52] that fluid is an important source of carbon during diamond formation in the mantle is currently adopted practically universally [53–56]. However, only a few modern models for diamond formation consider H_2O- and CO_2-saturated carbonate-containing melts–fluids to be a medium of diamond crystallization [2, 6, 57]. In this context, it is interesting to compare the experimental results with petrologic data on the probable medium in which diamond crystallizes in the mantle. Available experimental data on diamond crystallization in fluid and carbonate–fluid systems are plotted in Fig. 9, along with the probable zones of an initial dolomite melt [58, 59] and an H_2O fluid [7] separated on the lherzolite–CO_2 solidus [58]. It is worth noting that the solidus temperatures of the systems under the pressure of natural diamond formation can vary over the interval from about 1200°C (peridotite in the presence of H_2O–CO_2 fluid) [63] to 1350°C (lherzolite in the presence of CO_2 fluid) [59]. According to [7], the lherzolite–H_2O–CO_2 system under $P > 7$ Gpa reaches the second critical point, and the solidus disappears in this zone, i.e., the difference between the subsolidus fluid and the melt must disappear. The H_2O fluid zone in the mantle at low temperatures is bounded by the stability fields of hydrous phases [38, 41]. At temperatures exceeding the zone of

initial dolomitic melts, kimberlite-like magmas must be molten from the mantle [59].

According to Wyllie and Ryabchikov [7], the zones depicted in Fig. 9 correspond to two types of fluid inclusions in cubic diamond crystals with a rim. These inclusions vary in composition from carbonatite to water-rich with high K_2O and SiO_2 concentrations [2]. Similar carbonatite and brine inclusions were also revealed in the cloudlike zones of octahedral diamond crystals from the Koffifontane kimberlite pipe [3]. Note that cubic diamonds with a rim belong to the eclogite mineral assemblage [2], whereas brine inclusions were revealed in diamonds with inclusions of both eclogite and peridotite mineral assemblages [3]. The presence of the polyphase assemblages and their composition suggest that all mineral phases from the fluid inclusions were completely dissolved in the fluid under mantle conditions [2]. Diamonds crystallized in mantle fluids with a high K content, as is evident from K-pyroxene inclusions in diamonds from kimberlites [64] and diamond-bearing metamorphic rocks [55, 65].

Experimental data show that fluids with a high K content can be generated in the mantle. The solubility of silicates in the H_2O fluid depends on the silicate compositions and the P–T conditions [66–70]. The SiO_2 concentration in the fluid in equilibrium with solid SiO_2 can be 35 wt % at 3 GPa and 1100°C [66]. Under similar conditions, the olivine solubility is much lower [67]. According to the experimental data by Stalder et $al.$ [68], at 6–9 GPa and 1100–1200°C an H_2O fluid in equilibrium with enstatite and forsterite can contain 20–40% silicate. The K_2O concentration in an aqueous fluid in equilibrium with phlogopite under 3 GPa and 1100°C can reach 25 wt % [69]. Experimental data on the K partition between melt and pyroxene [71, 72] definitely indicate that the K_2O concentration in the region of K-pyroxene crystallization could reach 30 wt % [72]. In turn, carbonate-rich melts can be products of the partial melting of carbonatized peridotites [7] and carbonatized lherzolites [58, 59]. According to these data, carbonate melts of dolomite composition are formed under 3–7 GPa and temperatures slightly exceeding the solidus [7, 58]. When the degree of carbonatized lherzolite melting is below 1% (6 GPa, 0.15 wt % CO_2), the melt composition changes from almost carbonate (5 wt % SiO_2) at subsolidus temperature to kimberlite (>25 wt % SiO_2) at 70–100°C above the solidus [59].

The analysis of experimental data from [60–62] in Fig. 9 suggests that diamonds can crystallize from fluids under the P–T conditions of upper mantle ultrabasites and eclogites, i.e., under 5–6 GPa and 900–1500°C. The spontaneous nucleation and growth of diamond in CO_2, CO_2–H_2O, and H_2O fluids was experimentally studied under 5.7 GPa and 1200–1420°C [14, 19] and under 7.7 GPa and 1400–2000°C [13, 15–18, 25–27]. Thermodynamic calculations show that diamond crystallization is possible over a wide Eh inter-

val, spanning >4 logarithmic units of oxygen fugacity (from the CCO buffer to reducing conditions stronger than the IW buffer) [73]. Moreover, diamond formation was experimentally studied in alkaline carbonate–H_2O–CO_2–C [21, 23] and dolomite–CO_2–H_2O–C [22] systems modeling the compositions of diamond-hosted inclusions in the rims. These studies revealed that the addition of alkalis to the fluid systems causes diamond nucleation and growth at 5.7 GPa and 1150°C [21, 23]. The kinetic relations identified in the diamond-forming processes suggest that diamond nucleation is also possible at lower temperatures, if the duration of this process is longer [21]. Based on experimental data for the alkaline carbonate–H_2O–CO_2–C system under 1150–1420°C, the growth period of a 1-karat diamond crystal in the mantle is estimated as ranging from 100 days to one year [23]. Diamond formation in kimberlite-like magmas under higher P–T conditions can be experimentally modeled by diamond crystallization in the $CaMgSi_2O_6$–H_2O–CO_2–C and $NaAlSi_2O_6$–H_2O–CO_2–C systems under 7 GPa and 1700–1750°C [24]. An important role of the fluid phase in diamond crystallization under ultrahigh-pressure metamorphism was demonstrated using the examples of pyroxene–carbonate and garnet–pyroxene diamond-containing rocks of the Kokchetav massif [74]. In experiments under 5.7–7.0 GPa and 1420–1700°C, only the pyroxene–carbonate rock with a considerable content of H_2O–CO_2 fluid showed partial melting and provided conditions necessary for spontaneous diamond nucleation and growth.

Octahedron is the stable growth habit of diamond in all experimentally studied fluid and carbonate–fluid systems. At the same time, the habit of diamond crystallizing in dry carbonate systems is mostly controlled by the composition of the carbonate. In the Na_2CO_3–C system under 5.7 GPa and 1420°C and 7.7 GPa and 1700°C, diamond crystallized in the form of cuboctahedrons, whereas, under similar P–T conditions, octahedral diamond crystals are formed in the K_2CO_3–C system [23]. In the alkaline earth carbonate–carbon system, the habit of synthesized diamonds is a combination of octahedron, cube, and trapezohedron [11]. Natural diamonds usually have an octahedral habit, which suggests that their crystallization medium contained much fluid. Nevertheless, natural diamonds are also found in other habits, which is probably explained by the fact that their crystallization medium was locally fluid-poor, and that the composition of its carbonate–silicate component could significantly vary.

Graphite inclusions are often found in natural diamonds and diamond-containing xenoliths [60, 62]. The crystallization characteristics of these diamonds and the origin of their graphite inclusions have been actively discussed. Experimental data show that the presence of graphite cannot serve as a criterion of the P–T conditions thermodynamically different from the field of diamond stability, and metastable graphite with

or without diamond can crystallize from fluids in the thermodynamic field of diamond stability [4, 16, 19, 21, 27].

According to the isotopic data [18, 27], carbon transport to diamond crystals growing in a fluid can be mediated by redox reactions involving CO_2, CH_4, and graphite. Carbon isotopic fractionation between graphite and CO_2 is explained by the isotopic reaction $^{13}C + ^{12}CO_2 = ^{12}C + ^{13}CO_2$ [18]. These are the first experimental data to show that the fluid plays an important role in carbon transport to growing natural diamonds.

Data on diamond formation during carbonate–silicate interaction [75] and carbonate reduction by silicon or silicon carbide [76] are important for studying the probable carbon sources and fluid role. It is shown in [75] that magnesite reacts with coesite and enstatite under 6–7 GPa and 1350–1800°C in the presence of hydrogen diffusing into the platinum capsule. The experimentally produced assemblages were magnesite + enstatite + diamond + fluid ± coesite and magnesite +forsterite+ diamond + fluid ± enstatite, and the isotopic composition of the synthesized diamond ($\delta^{13}C = -1.27‰$) is comparable with the isotopic composition of the initial magnesite ($\delta^{13}C = -0.2‰$). Diamond also crystallized from carbon generated by dolomite reacting with metallic silicon or silicon carbide under 7.7 GPa and 1500–1800°C [76].

Hence, experimental data constrain the principal physicochemical characteristics of diamond crystallization in fluid and carbonate–fluid systems under upper mantle conditions. It is very important that experimental data obtained at different laboratories in different high-pressure equipment under widely varying $P–T$ conditions correlate with one another. Analysis of these data allowed us to find the most general relations characterizing diamond crystallization, which are interesting for petrologists studying the mantle.

CONCLUSIONS

(1) The intensity of diamond crystallization in the thermodynamic field of its stability is a function of temperature, composition, and probably pressure. Spontaneous diamond nucleation and growth on seed crystals under 5.7–7.7 GPa and 1150–2000°C is preceded by an inductive period. The duration of this period increases nearly exponentially from several minutes to hundreds of hours as temperature decreases from 2000 to 1150°C. In terms of the intensity of diamond crystallization, the fluid and fluid–carbonate systems can be arranged in the following sequence: $K_2CO_3(Na_2CO_3)–H_2O–CO_2–C > CO_2–C \approx H_2O–CO_2–C \approx H_2O–C \approx CaMg(CO_3)_2–H_2O–CO_2–C > CH_4–H_2O–C \gg CH_4–H_2–C$.

(2) Octahedron is the stable habit of crystallizing diamond in fluid and carbonate–fluid systems under widely varying pressure (5.7–7.7 GPa) and temperature (1150–2000°C). Under these experimental conditions, diamond crystals grow according to the tangential mechanism.

(3) In fluid and carbonate–fluid systems, metastable graphite crystallizes together with diamond in the thermodynamic field of diamond stability, under 5.7 GPa and 1150–1420°C and under 7.7 GPa and 1400–1600°C. Diamond and metastable graphite simultaneously grow on seed crystals in $CO_2–C$, $H_2O–CO_2–C$, and $H_2O–C$ systems under 5.7 GPa.

(4) Diamond can crystallize in fluid and fluid-containing systems under the $P–T$ conditions of the upper mantle. For mantle rocks, H_2O or $H_2O–CO_2$ alkali-saturated fluid is likely to play an important role in the nucleation and growth of natural diamond under subsolidus temperatures, whereas a fluid-containing dolomite melt plays an important role under above-solidus temperatures.

REFERENCES

1. O. Navon, I. D. Hutcheon, G. R. Rossman, and G. J. Wasserburg, "Mantle-Derived Fluids in Diamond Micro-Inclusions," Nature **335**, 784–789 (1988).

2. M. Schrauder and O. Navon, "Hydrous and Carbonatitic Mantle Fluids in Fibrous Diamonds from Jwaneng, Bostwana," Geochim. Cosmochim. Acta **58** (2), 761–771 (1994).

3. E. S. Izraeli, J. W. Harris, and O. Navon, "Brine Inclusions in Diamonds: A New Upper Mantle Fluid," Mar. Geol. **187** (3–4), 323–332 (2001).

4. K. De Corte, P. Cartigny, V. S. Shatsky, et al., "First Evidence of Inclusions in Metamorphic Microdiamonds from the Kokchetav Massif, Northern Kazakhstan," Geochim. Cosmochim. Acta **62**, 3763–3765 (1998).

5. B. Stockhert, J. Duyster, C. Trepmann, and H. J. Massonne, "Microdiamond Daughter Crystals Precipitated from Supercritical COH Plus Silicate Fluids Included in Garnet, Erzgebirge, Germany," Geology **29**, 391–394 (2001).

6. O. Navon, "Diamond Formation in the Earth's Mantle," in VII International Kimberlite Conference 2, Ed. by J. J. Gurney, J. L. Gurney, M. D. Pascoe, and S. H. Richadson (Red Roof Design, Cape Town, 1999), pp. 584–604.

7. P. Wyllie and I. Ryabchikov, "Volatile Components, Magmas, and Critical Fluids in Upwelling Mantle," J. Petrol. **41**, 1195–1206 (2000).

8. M. Akaishi, H. Kanda, and S. Yamaoka, "Synthesis of Diamond from Graphite–Carbonate Systems under Very High Temperature and Pressure," J. Cryst. Growth **104**, 578–581 (1990).

9. T. Taniguchi, D. Dobson, A. P. Jones, *et al.*, "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 (1996).

10. Yu. A. Litvin, L. T. Chudinovskikh, and V. A. Zharikov, "Experimental Crystallization of Diamond and Graphite from Alkali–Carbonate Melts at 7–11 GPa," Dokl. Akad. Nauk **355** (5), 669–672 (1997) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **355A** (5), 908–911 (1997)].

11. Yu. N. Pal'yanov, A. G. Sokol, Yu. M. Borzdov, *et al.*, "Diamond Crystallization in the Systems $CaCO_3$–C, $MgCO_3$–C, and $CaMg(CO_3)_2$–C," Dokl. Akad. Nauk **363** (2), 230–233 (1998) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **363** (8), 1156–1159 (1998)].

12. S. Yamaoka, M. Akaishi, H. Kanda, and T. Osawa, "Crystal Growth of Diamond in the System of Carbon and Water under Very High Pressure and Temperature," J. Cryst. Growth **125**, 375–377 (1992).

13. S. M. Hong, M. Akaishi, and S. Yamaoka, "Nucleation of Diamond in the System of Carbon and Water under Very High Pressure and Temperature," J. Cryst. Growth **200**, 326–328 (1999).

14. Yu. N. Pal'yanov, A. G. Sokol, A. F. Khokhryakov, *et al.*, "Diamond and Graphite Crystallization in COH Fluid under the *P–T* Parameters of Natural Diamond Formation," Dokl. Akad. Nauk **375** (3), 384–388 (2000) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **375A** (9), 1395–1398 (2000)].

15. L. Sun, M. Akaishi, and S. Yamaoka, "Formation of Diamond in the System of Ag_2CO_3 and Graphite at High Pressure and High Temperatures," J. Cryst. Growth **213**, 411–414 (2000).

16. M. Akaishi and S. Yamaoka, "Crystallization of Diamond from C–O–H Fluids under High-Pressure and High-Temperature Conditions," J. Cryst. Growth **213**, 999–1003 (2000).

17. M. S. D. Kumar, M. Akaishi, and S. Yamaoka, "Formation of Diamond from Supercritical H_2O–CO_2 Fluid at High Pressure and High Temperature," J. Cryst. Growth **213**, 203–206 (2000).

18. M. Akaishi, M. S. D. Kumar, H. Kanda, and S. Yamaoka, "Formation Process of Diamond from Supercritical H_2O–CO_2 Fluid under High Pressure and High Temperature Conditions," Diamond Relat. Mater. **9**, 1945–1950 (2000).

19. A. G. Sokol, Yu. N. Pal'yanov, G. A. Pal'yanova, *et al.*, "Diamond and Graphite Crystallization from C–O–H Fluids," Diamond Relat. Mater. **10**, 2131–2136 (2001).

20. S. Yamaoka, M. S. D. Kumar, H. Kanda, and M. Akaishi, "Thermal Decomposition of Glucose and Diamond Formation under Diamond-Stable High Pressure–High Temperature Conditions," Diamond Relat. Mater. **11**, 118–124 (2002).

21. Yu. N. Pal'yanov, A. G. Sokol, Yu. M. Borzdov, *et al.*, "Diamond Formation from Mantle Carbonate Fluids," Nature **400**, 417–418 (1999).

22. A. G. Sokol, Yu. M. Borzdov, Yu. N. Pal'yanov, *et al.*, "An Experimental Demonstration of Diamond Formation in the Dolomite–Carbon and Dolomite–Fluid–Carbon Systems," Eur. J. Mineral. **13**, 893–900 (2001).

23. Yu. N. Pal'yanov, A. G. Sokol, Yu. M. Borzdov, and A. F. Khokhryakov, "Alkaline Carbonate-Fluid Melts as the Medium for the Formation of Diamonds in the Earth's Mantle: An Experimental Study," Lithos **60** (3–4), 145–159 (2002).

24. A. G. Sokol, Yu. M. Borzdov, A. F. Khokhryakov, *et al.*, "Diamond Crystallization in Silicate–Fluid Systems at *P* = 7.0 GPa and *T* = 1700–1750°C," Dokl. Akad. Nauk **368** (1), 99–102 (1999) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **368** (7), 954–957 (1999)].

25. S. Yamaoka, M. S. D. Kumar, M. Akaishi, and H. Kanda, "Reaction between Carbon and Water under Diamond-Stable High-Pressure and High Temperature Conditions," Diamond Relat. Mater. **10**, 1480–1486 (2000).

26. M. S. D. Kumar, M. Akaishi, and S. Yamaoka, "Effect of Fluid Concentration on the Formation of Diamond in the CO_2–H_2O–Graphite System under HP–HT Conditions," J. Cryst. Growth **222**, 9–13 (2001).

27. M. Akaishi, M. S. D. Kumar, H. Kanda, and S. Yamaoka, "Formation of Diamond from C–O–H Fluids under HP–HT Conditions," in *International Symposium on Advanced Materials* (2001), pp. 43–44.

28. S. Yamaoka, M. S. D. Kumar, H. Kanda, and M. Akaishi, "Crystallization of Diamond from CO_2 Fluid at High Pressure and High Temperature," J. Crystal. Growth **234**, 5–8 (2002).

29. Yu. N. Pal'yanov, A. F. Khokhryakov, Yu. M. Borzdov, *et al.*, "The Growth Conditions and Actual Structure of Synthetic Diamond," Geol. Geofiz. **38** (5), 54–78 (1997).

30. A. G. Sokol, A. A. Tomilenko, Yu. N. Pal'yanov, *et al.*, "Fluid Regime of Diamond Crystallization in Carbonate–Carbon Systems," Eur. J. Mineral. **12**, 367–375 (2000).

31. K. Sato, "Drastic Effect of Mo on Diamond Nucleation in System of $MgCO_3$–$CaCO_3$–Graphite at 7.7 GPa," J. Crystal. Growth **210**, 623–628 (2000).

32. Yu. N. Pal'yanov, A. G. Sokol, Yu. M. Borzdov, *et al.*, "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 (1999).

33. K. Sato, M. Akaishi, and S. Yamaoka, "Spontaneous Nucleation of Diamond in the System $MgCO_3$–$CaCO_3$–C at 7.7 GPa," Diamond Relat. Mater. **8**, 1900–1905 (1999).

34. R. H. Wentorf, "Some Studies of Diamond Growth Rates," J. Phys. Chem. **75** (12), 1833–1837 (1971).

35. M. I. Samoilovich and N. G. Sanzharlinskii, "Thermodynamics of Direct Graphite–Diamond Transition and Diamond Crystallization from a Carbon-Supersaturated Solution," in *Synthesis of Minerals* (Nedra, Moscow, 1987), pp. 301–317.

36. A. A. Kadik and O. A. Lukanin, *Degassing of the Upper Mantle during Melting* (Nauka, Moscow, 1986) [in Russian].

37. E. M. Galimov, "Isotope Fractionation Related to Kimberlite Magmatism and Diamond Formation," Geochim. Cosmochim. Acta **55**, 1697–1708 (1991).

38. A. B. Thompson, "Water in the Earth's Upper Mantle," Nature **358**, 295–302 (1992).

39. M. Javoy, "The Major Volatile Elements of the Earth: Their Origin, Behavior, and Fate," Geophys. Res. Lett. **24** (2), 177–180 (1997).

40. R. W. Luth, "Carbon and Carbonates in the Mantle," in *The Geochemical Society, Special Publication,* No. 6: *Mantle Petrology: Field Observation and High Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd,* Ed. by Y. Fei, C. M. Bertka, and B. O. Mysen (1999), pp. 297–316.

41. K. D. Litasov, E. Otani, and N. L. Dobretsov, "Stability of Hydrous Phases in the Earth's Mantle," Dokl. Akad. Nauk **378** (2), 238–241 (2001) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **378** (4), 456–459 (2001)].

42. H. St. C. O' Neil and H. Palme, "Composition of Silicate Earth: Implications for Accretion and Core Formation," in *The Earth's Mantle: Composition, Structure, and Evolution,* Ed. by I. Jackson (Cambridge Univ. Press, Cambridge, 1998), pp. 3–126.

43. Y. Zhang and A. Zindler, "Distribution and Evolution of Carbon and Nitrogen in Earth," Earth Planet. Sci. Lett. **117**, 331–345 (1993).

44. A. V. Sobolev, Doctoral Dissertation in Geology and Mineralogy (GEOKhI, Moscow, 1997).

45. B. J. Wood, T. Bryndzia, and K. E. Johnson, "Mantle Oxidation State and Its Relationship to Tectonic Environment and Fluid Speciation," Science **248**, 337–345 (1990).

46. C. Ballhaus, "Redox States of Lithospheric and Asthenospheric Upper Mantle," Contrib. Mineral. Petrol. **114**, 331–348 (1993).

47. S. C. Bergman and J. Dubessy, "CO_2–CO Fluid Inclusions in a Composite Peridotite Xenolith: Implications for Upper Mantle Oxygen Fugacity," Contrib. Mineral. Petrol. **85**, 1–13 (1984).

48. T. Andersen and E. R. Neumann, "Fluid Inclusions in the Mantle Xenoliths," Lithos **55**, 301–320 (2001).

49. M. Scambelluri and P. Philippot, "Deep Fluids in Subduction Zones," Lithos **55**, 213–227 (2000).

50. A. A. Tomilenko, A. I. Chepurov, Yu. N. Pal'yanov, *et al.*, "Volatiles in the Upper Mantle," Geol. Geofiz. **38** (1), 276–285 (1997).

51. A. A. Tomilenko, A. L. Ragozin, V. S. Shatsky, and A. P. Shebanin, "Variation in the Fluid Phase Composition in the Process of Natural Diamond Crystallization," Dokl. Akad. Nauk **378** (6), 802–805 (2001) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **379** (5), 571–574 (2001)].

52. V. S. Sobolev, "Formation Conditions of Diamond Deposits," Geol. Geofiz., No. 1, 7–22 (1960).

53. F. A. Letnikov, "Diamond Formation in Deep Tectonic Zones," Dokl. Akad. Nauk SSSR **271** (2), 433–435 (1983).

54. S. E. Haggerty, "Diamond Genesis in a Multiply Constrained Model," Nature **320**, 34–38 (1986).

55. N. V. Sobolev and V. S. Shatsky, "Diamond Inclusions in Garnets from Metamorphic Rocks," Nature **343**, 742–746 (1990).

56. S. E. A. Haggerty, "Diamond Trilogy: Superplumes, Supercontinents, and Supernovae," Nature **285**, 851–859 (1999).

57. S. R. Boyd, F. Pineau, and M. Yavoy, "Modeling the Growth of Natural Diamonds," Chem. Geol. **116**, 29–42 (1994).

58. J. A. Dalton and D. C. Presnall, "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 (1998a).

59. J. A. Dalton and D. C. Presnall, "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 (1998b).

60. N. V. Sobolev, *The Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle* (Am. Geophys. Union, Washington, 1977).

61. H. O. A. Meyer, "Inclusions in Diamond," in *Mantle Xenoliths*, Ed. by H. P. Nixon (Wiley, New York, 1987), pp. 501–523.

62. J. W. Harris, "Diamond Geology," in *The Properties of Natural and Synthetic Diamond*, Ed. by J. E. Field (Academic, London, 1992), pp. 345–393.

63. D. Canil and C. M. Scarfe, "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 (1990).

64. N. V. Sobolev, I. T. Bakumenko, E. S. Efimova, and N. P. Pokhilenko, "Microdiamond Morphology, Sodium Concentration in Granites, and Potassium Concentration in Pyroxenes from Two Eclogite Xenoliths from the Udachnaya Kimberlite Pipe, Yakutia," Dokl. Akad. Nauk SSSR **321** (3), 585–592 (1991).

65. V. S. Shatsky, N. V. Sobolev, and M. A. Vavilov, "Diamond-Bearing Metamorphic Rocks of the Kokchetav Massif, Northern Kazakhstan," in *Ultrahigh Pressure Metamorphism*, Ed. by R. G. Coleman and X. Wang (Cambridge Univ. Press, Cambridge, 1995), pp. 427–455.

66. Y. Nakamura and J. Kushiro, "Composition of Gas Phase $Mg_2SiO_4–SiO_2–H_2O$ at 15 Kbar," Carnegie Inst. Washington, *Yearbook 73*, 255–258 (1974).

67. I. D. Ryabchikov, W. Schreyer, and K. Abraham, "Composition of Aqueous Fluids in Equilibrium with Pyroxenes and Olivines at Mantle Pressures and Temperatures," Contrib. Mineral. Petrol. **79**, 80–84 (1982).

68. R. Stalder, P. Ulmer, A. B. Thompson, and D. Gunther, "High Pressure Fluid in the System $MgO–SiO_2–H_2O$ under Upper Mantle Conditions," Contrib. Mineral. Petrol. **140**, 607–618 (2001).

69. I. D. Ryabchikov and A. L. Boettcher, "Experimental Evidence at High Pressure for Potassic Metasomatism in the Mantle of the Earth," Am. Mineral. **65**, 915–919 (1980).

70. B. O. Mysen and M. Acton, "Water in H_2O-Saturated Magma–Fluid Systems: Solubility Behavior in K_2O–Al_2O_3–SiO_2–H_2O to 2.0 GPa and 1300°C," Geochim. Cosmochim. Acta **63**, 3799–3815 (1999).

71. G. E. Harlow, "K in Clinopyroxene at High Pressure and Temperature: An Experimental Study," Am. Mineral. **82**, 259–269 (1997).

72. L. L. Perchuk, O. G. Safonov, V. O. Yapaskurt, and J. M. Barton, Jr., "Crystal–Melt Equilibria Involving Potassium-Bearing Clinopyroxene as Indicator of Mantle-Derived Ultrahigh-Potassic Liquids: An Analytical Review," Lithos **60**, 89–111 (2002).

73. A. G. Sokol, Yu. N. Pal'yanov, G. A. Pal'yanova, and A. A. Tomilenko, "Diamond Crystallization in Fluid and Carbonate-Fluid Systems under Mantle P–T Conditions: I. Fluid Composition," Geochem. Intern. **42** (9), 830–838 (2004).

74. Yu. N. Pal'yanov, V. S. Shatskii, A. G. Sokol, *et al.*, "Crystallization of Metamorphic Diamond: An Experimental Modeling," Dokl. Akad. Nauk **380** (5), 671–675 (2001) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **381** (8), 935–938 (2001)].

75. Yu. N. Pal'yanov and Yu. M. Borzdov, *et al.*, "Diamond Formation through Carbonate–Silicate Interaction," Am. Mineral. **87**, 1009–1013 (2002).

76. M. Arima, Yu. Kozai, and M. Akaishi, "Diamond Nucleation and Growth by Reduction of Carbonate Melts under High-Pressure and High-Temperature Conditions," Geology **30**, 691–694 (2002).
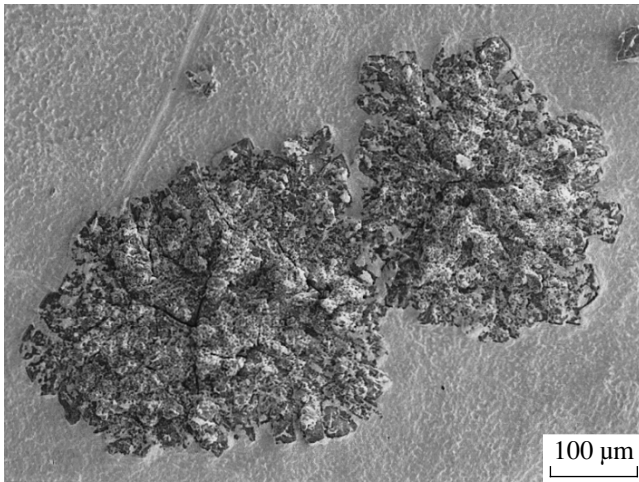
Fig. 3. Dendritic diamond aggregate on the surface of the platinum capsule (42-h experiment in the CO_2–C system at $P = 5.7$ GPa and $T = 1420$°C).
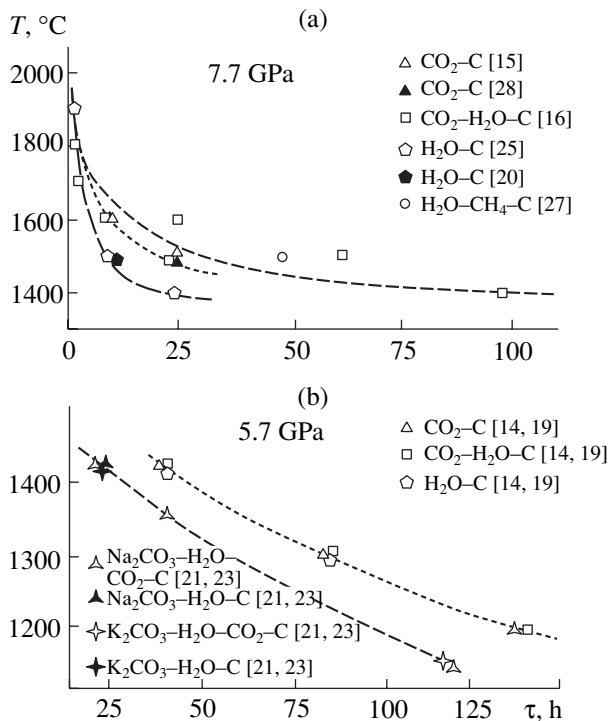

Fig. 4. Onset of diamond nucleation as a function of temperature in fluid and fluid-carbonate systems at (a) 7.7 GPa and (b) 5.7 GPa.

with the carbonate–carbon system [11, 32, 33]. A similar phenomenon was also studied in the alkaline carbonate–fluid–carbon [21] and fluid [16, 18–20] systems. As is evident from Figs. 4a and 4b, the inductive period of fluid and carbonate–fluid systems under 7.7 and 5.7 GPa increases almost exponentially with decreasing temperature. The graphite–diamond conversion as a function of the experiment duration was stud-

ied in detail by Akaishi *et al.* [18] in fluid systems under 7.7 GPa and 1600°C and by Yamaoka *et al.* [20] in fluid systems under 1500°C (Fig. 5a). Spontaneous diamond nucleation in H_2O–CO_2 and H_2O fluids under these experimental *P–T* conditions was preceded by an 8- to 10-h inductive period, after which the degree of the graphite–diamond transition (α) drastically increased. The fluid and carbonate–carbon systems are similar in the α dependence on time (Figs. 5a and 5b), which suggests a common nature of their inductive periods. Nevertheless, carbonate–carbon systems with an introduced fluid show a shorter inductive period. For example, the inductive period in the Na_2CO_3–C system under 5.7 GPa and 1420°C is 1.5 times longer than in the Na_2CO_3–H_2O–CO_2–C system under the same experimental conditions [23]. Moreover, the introduction of H_2O or H_2O–CO_2 fluid into the $CaMg(CO_3)_2$–C system that produces no diamond under 5.7 GPa and 1420°C causes melting and spontaneous diamond nucleation in the 42-h experiments [22]. In addition, the duration of the inductive period decreases with a change in the initial ratio of the fluid-generating matter to graphite. An increase of the $C_2H_2O_4$/graphite mole ratio from 0.1 to 1% results in an increase of the graphite–diamond conversion from 20 to 90% [26].

Because different schemes were used in charging capsules for the experiments under 5.7 and 7.7 GPa, we cannot draw an unambiguous conclusion about the dependence of the inductive period on pressure. However, some facts allow us to suggest the existence of this dependence. For example, a weak diamond peak was revealed in the X-ray spectrum of a sample synthesized in a 24-h experiment in the H_2O–C system under 7.7 GPa and 1400°C, and no diamond crystallized in a similarly charged capsule under similar experimental conditions, except a pressure of 5.5 GPa [25]. However, spontaneous diamond nucleation occurred in the H_2O–C system under 5.7 GPa and 1420 and 1300°C in 42- and 84-h experiments, respectively [19]. Based on these data, we suppose that the duration of the inductive period of spontaneous diamond nucleation in the fluid systems increases with decreasing pressure.

According to Akaishi and Yamaoka [16], a long inductive period can be explained by the fact that diamond-generating systems have to pass through three preliminary stages, including (1) the generation of a C–O–H fluid by the decomposition of the fluid-producing reactant, (2) graphite dissolution in the fluid, and (3) the formation of a carbon-supersaturated fluid. Excess atomic carbon is released by some fluid-generating substances (for example, glucose) under the experimental *P–T* conditions, and the generated fluid should be carbon-supersaturated. However, experimental data show that complete graphite conversion under 7.7 GPa and 1500°C in the presence of glucose ($C_6H_{12}O_6$, which decomposes into water and atomic carbon) and water is characterized by similar time intervals [20, 25, 27]. These data allow us to suggest
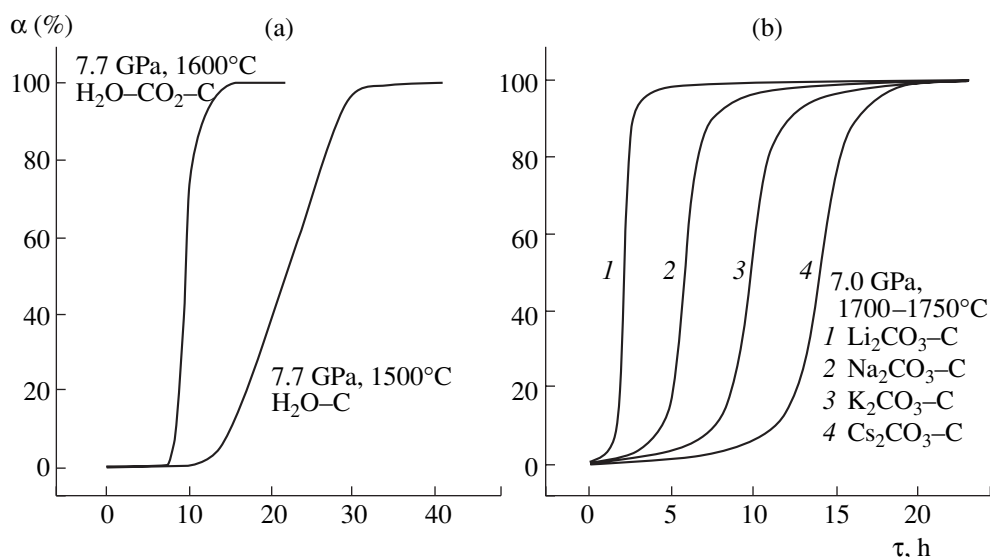
Fig. 5. Degree of the graphite–diamond transition (α) as a function of the experiment duration in systems (a) H_2O–CO_2–C [18] and H_2O–C [20] and (b) alkaline carbonate–carbon [32].

that fluid saturation with respect to carbon is not a limitative stage determining the duration of the inductive period.

Fluid Composition

The composition of the generated fluid can notably affect the rate of diamond formation. Graphite was completely converted to diamond in the 17-h experiment with a H_2O–CO_2 fluid under 7.7 GPa and 1600°C and in the 33-h experiment with a H_2O fluid at 1500°C, whereas only single diamond crystals were formed in the 48-h experiment with a H_2O–CH_4 fluid at 1500°C [27]. Analysis of the experimental data on diamond formation at 5.7 GPa and 1300°C [14] and at 1200°C and 1420°C [19] revealed that the intensity of this process changes with the following fluid composition order: H_2O–C $\approx$ H_2O–CO_2–C $\approx$ CO_2–C $\gg$ CH_4 + H_2–C. Note also that those experimental studies did not find any essential difference between the intensities of spontaneous diamond nucleation and diamond growth on seed crystals in CO_2, CO_2 + H_2O, and H_2O fluids. Conversely, the intensity of diamond formation in a CH_4–H_2 fluid was very low. No spontaneous diamond nucleation occurred in this fluid at 1200–1420°C for 136 h, and growth layers on seed crystals with a thickness less than 1 μm were formed only at 1300–1420°C [19].

Na_2CO_3- or K_2CO_3-containing fluid systems under 5.7 GPa are characterized by the shortest inductive period and the highest intensity of diamond formation (Fig. 4b) [21, 23]. Systems with dolomite and H_2O–CO_2 or H_2O fluid showed an activity comparable to the activity of compositionally similar C–O–H fluid [22]. Thus, the intensity of diamond formation in fluid and carbonate–fluid systems under close to natural *P*–*T* conditions changes in the following order of fluid composition: $K_2CO_3(Na_2CO_3)$–H_2O–CO_2–C > CO_2–C $\approx$ H_2O–CO_2–C $\approx$ H_2O–C $\approx$ $CaMg(CO_3)_2$–H_2O–CO_2–C > CH_4–H_2O–C $\gg$ CH_4–H_2–C.

Diamond Growth on Seed Crystals

Diamond growth on seed crystals in the H_2O–C system was first studied in 1992 [12]. The experiments were conducted under 7.7 GPa and 2000–2200°C for tens of minutes, and the weight increase of the seed crystals was as great as 70%. The growth layers on the seed crystals contained multiple graphite inclusions. Comprehensive experimental studies of fluid systems under 5.7 GPa and 1150–1420°C revealed that the rate of diamond growth in oxidized fluids (CO_2, CO_2 + H_2O, and H_2O) was higher than in reduced fluids (H_2O + CH_4 and CH_4 + H_2), provided that their experimental temperatures were identical. For example, the rate of diamond growth in the H_2O–C system at 1420°C is tens of times higher than in the CH_4–H_2–C system [19]. The experimentally grown diamonds are colorless or gray with a slight yellowish tint. Their micromorphology indicates the tangential mechanism of crystal growth in the fluid systems (Fig. 6) [14]. The persistent habit of the crystallizing diamond is octahedral [14, 19]. The {100} faces of the cuboctahedral seed crystals are unstable under these conditions, which results in their regeneration to faces {111} and the formation of octahedral apexes on cubic faces (Fig. 6b). A comparative analysis of the data obtained in experiments under 5.5 and 7.7 GPa and 1300–1500°C [14, 19, 25] revealed that the diamond morphology did not depend on temperature. The octahedral habit of the crystallizing dia-
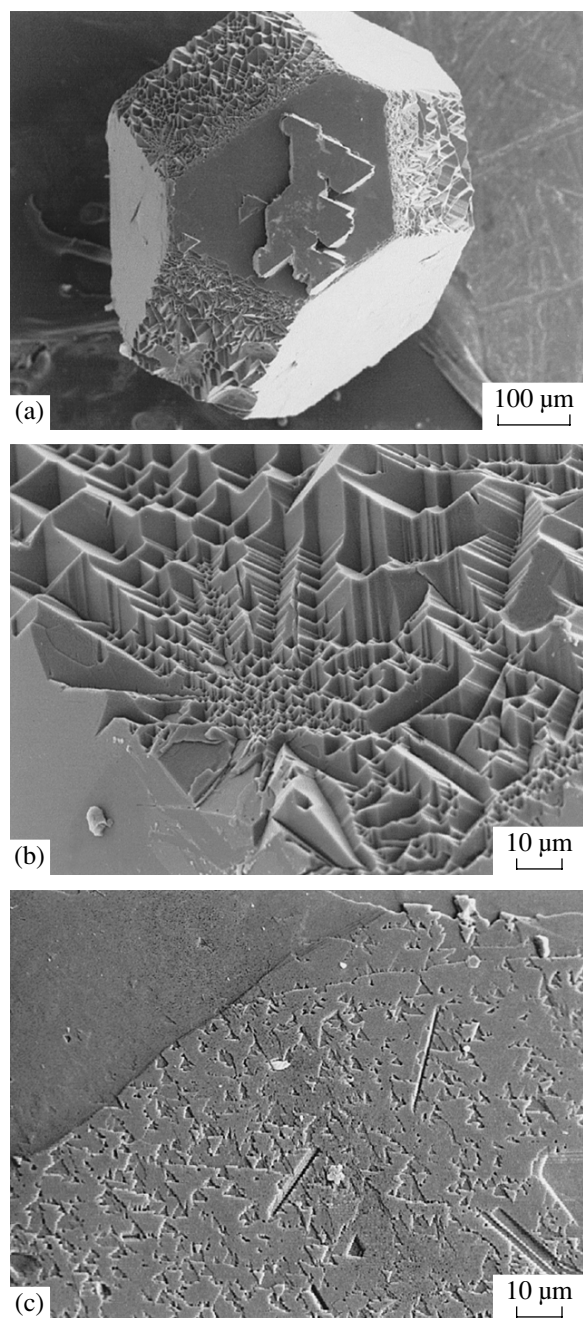
Fig. 6. Growth surface microtopography of seed diamond crystals: (a) an image of a seed crystal after a 42-h experiment in the CO_2–C system under $P = 5.7$ GPa and $T = 1420°C$; (b) regeneration of a {100} crystal face after a 42-h experiment in the CO_2–C system at $P = 5.7$ GPa and $T = 1420°C$; (c) growth layers on a {111} crystal face after a 135-h experiment in the H_2O–C system at $P = 5.7$ GPa and $T = 1200°C$.

mond is most likely stable under widely varying pressure, temperature, and composition of C–O–H fluid [19]. However, in the CH_4–H_2–C system, the thickness of growth layers on seed crystals did not exceed 1 μm, and, hence, the habit of the crystallizing diamond is

unlikely to be stable in this system. Moreover, as was mentioned above, capsules with a CO_2 fluid generated by $Ag_2C_2O_4$ were probably depressurized in the course of long-lasting experiments. Unfortunately, diamond growth on seed crystals was not studied in experiments with PtO_2 as the fluid-generating substance [28].

The stable habit of crystallizing diamond in alkaline carbonate–fluid–carbon systems under 5.7 GPa and 1150–1420°C is octahedral, regardless of the carbonate and fluid compositions [21–23]. According to [23], the rate of diamond growth in these systems decreases from 0.1 to 0.01 μm/h with decreasing temperature from 1420 to 1150°C. Diamond layers overgrowing seed crystals at 1150°C for 120 h had a thickness of up to several micrometers [21]. In the 42-h experiments in the dolomite–H_2O–CO_2–C system under 5.7 GPa and 1300–1420°C, diamond growth on seed crystals was 10–15 μm on {111} faces and up to 55 μm on {100} faces [22]. Note that the thickness of a growth layer is understood as the overall thickness of the diamond layer formed on a seed crystal during the whole experiment.

Our data show that diamond growth on seed crystals is preceded by an inductive period, whose duration probably also depends on the temperature, pressure, and composition of the system. Nevertheless, this inductive period is briefer than the inductive period of spontaneous diamond nucleation, i.e., the diamond formation in fluid and fluid–carbonate systems begins with diamond growth on seed crystals and is then accompanied by spontaneous diamond formation [19–23, 25]. According to Yamaoki *et al.* [25], no spontaneous diamond nucleation occurred in 24-h experiments in the H_2O–C system under 5.5 GPa and 1300–1500°C, while the diamond growth on seed crystals took place. Nevertheless, spontaneous diamond nucleation was revealed in 24-h experiments at 7.7 GPa and 1400°C, whereas diamond growth on seed crystals also occurred at 1300°C. In 42-h experiments in the dolomite–H_2O–CO_2–C system under 5.7 GPa, spontaneous diamond nucleation was identified only at 1420°C, whereas diamond growth on seed crystals occurred at 1420 and 1300°C [22].

Crystallization of Metastable Graphite

In the thermodynamic field of diamond stability, metastable graphite crystallization from a C–O–H fluid occurs over a wide interval of compositions, pressure, and temperature. Graphite nucleation and subsequent growth in different forms (fine flakes, aggregates up to 100–200 μm, and tabular crystals up to 50 μm) were noted in all experiments under 5.5 and 5.7 GPa and 1150–1420°C (Fig. 7) [14, 19, 21, 23, 25]. However, graphite flakes up to 10 μm crystallized in the CO_2–H_2O–C and H_2O–C systems under 7.7 GPa only at temperatures not exceeding ≤1600°C [16, 18, 20].