PHASE FORMATION AND DIAMOND CRYSTALLIZATION IN CARBON-BEARING ULTRAPOTASSIC CARBONATE-SILICATE SYSTEMS

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Diamond crystallization and character of phase formation in the systems K_2CO_3–C, K_2CO_3–SiO_2–C, and K_2CO_3–Mg_2SiO_4–C were studied at 6.3 GPa and 1650 °C for 40 hours using the multianvil split-sphere equipment. The SiO_2/K_2CO_3 and Mg_2SiO_4/K_2CO_3 ratios were chosen as variable parameters. The degree of graphite-to-diamond transformation and rate of diamond growth on seeds have been determined as a function of these ratios. Composition domains have been revealed in which spontaneous diamond nucleation and seeded growth occur. As the concentrations of silica and forsterite in the systems K_2CO_3–SiO_2–C and K_2CO_3–Mg_2SiO_4–C, respectively, increase to 10 wt.%, the diamond formation becomes more intense. Given a further increase in contents of SiO_2 or Mg_2SiO_4, this intensity gradually decreases until the complete termination of spontaneous nucleation and seeded diamond growth. The conditions were created under which diamond was crystallized from a potassium carbonate-silicate melt, including the main components of mantle-derived ultrapotassic fluxes, together with coesite in the system K_2CO_3–SiO_2–C and with forsterite in the system K_2CO_3–Mg_2SiO_4–C.
Diamond, high pressure, crystallization, carbonate-silicate systems

INTRODUCTION

Combined petrological and experimental information indicates that the carbonates are stable under *P-T* conditions of the upper and lower mantle [1, 2]. According to the existing points of view, carbonate melts played an important role in processes of mantle metasomatism [3, 4] and could form under partial melting of carbonatized mantle rocks [3, 5]. The main information on the composition of the medium from which diamond crystallizes can be obtained from inclusions in natural diamonds. The abundance of inclusions in diamonds implies that the base of the mantle diamond-forming medium was made up of sulfides, silicates, and oxides [6–8]. Findings of carbonate inclusions in diamonds from kimberlite pipes [9–13] and in metamorphogenic diamonds [14, 15] suggest that carbonates were also present in the medium of diamond crystallization. Moreover, impurities in some diamonds from Zaire and Botswana are ultrapotassic fluxes with high contents of carbonates, K_2O, CaO, FeO, and MgO [11, 12]. There are also data [3] that the composition of these inclusions is close to the mantle metasomatic fluid [11, 12]. Experimental data on the conditions under which potassium enters the pyroxene structure [16] permit some authors [17] to hypothesize that pyroxenes from inclusions in diamonds with more than 1 wt.% K [18, 19] were crystallized from ultrapotassic carbonate-silicate melts. Thus, a very important feature of the mantle medium of diamond crystallization was its enrichment in potassium and carbonates.

Analysis of published data on experimental modeling of processes of diamond formation shows that carbonates are able to provide diamond crystallization in a very wide range of temperatures (1300–2150 °C) and pressures (5.7–11.0 GPa) [20–26]. The main feature of carbonate-carbon systems at 5.7–7.0 GPa and 1300–1750 °C is a very long period before the spontaneous nucleation of diamond, which depends heavily on the carbonate composition and becomes longer as *P* and *T* decrease [23–29]. The available data on diamond crystallization in

carbonate and carbonate-bearing melts [20–29] permit a systematic study of more complicated systems in order to adequately simulate processes of natural diamond formation. In this context, of great interest are potassium-bearing carbonate-silicate-carbon systems. The possibility of diamond crystallization in a medium containing silicates and carbonate was first demonstrated in the kimberlite–carbon system at 7.0–7.7 GPa and 1800–2200 °C [27]. Because of a great diversity of phases in products of experiments (olivine, clinopyroxene, carbonate, magnetite, and apatite) we cannot unambiguously estimate the effect of each component of this rather complicated system on the process of diamond formation. The results of experiments in silicate-carbon systems indicate that a "dry" silicate melt does not provide diamond formation even at 7.0 GPa and 1700–1750 °C [28]. On the other hand, spontaneous nucleation and diamond growth on seed crystals have been recorded in the carbonate-silicate-carbon system at the same *P* and *T*, and conditions have been created for cocrystallization of diamond with silicates and oxides [28]. According to experimental data [29], spontaneous nucleation and seeded diamond growth in the carbonate-silicate melts compositionally close to some inclusions in natural diamonds can proceed even at lower *P-T* (5.0–7.0 GPa and 1200–1570 °C).

Therefore, the present work was aimed at experimental study of the character of phase formation and diamond crystallization in ultrapotassic carbonate-silicate systems with carbon.

METHODS

Experimental crystallization of diamond has been carried out in the systems K_2CO_3–C, K_2CO_3–SiO_2–C, and K_2CO_3–Mg_2SiO_4–C for 40 h at 6.3 GPa and 1650 °C, using the "split-sphere" high-pressure apparatus (BARS) [30]. The high-pressure cell in the form of tetragonal prism ($20.4 \times 20.4 \times 25.2$ mm) was made of a mixture of refractory oxides not subjected to phase transitions at the parameters of the experiments. The cell is schematically shown in Fig. 1. The pressure was measured at room temperature from a change in electric resistances of Bi and PbSe. A correction for the change of pressure on heating the cell was obtained from comparison of results of diamond crystallization in the Ni-C system at 1650 °C and *P-T* values corresponding to the graphite-diamond equilibrium line [31]. In each experiment, the temperature was controlled with the help of the $Pt_{94}Rh_6 / Pt_{70}Rh_{30}$ thermocouple 0.2 mm in diameter, whose joint was inside the heater above the ampoule (see Fig. 1). The thermocouple was precalibrated at 6.3 GPa from melting of Au wire ($T_{melt} = 1402\pm2$ °C [32]) in the $NaNO_3$ melt
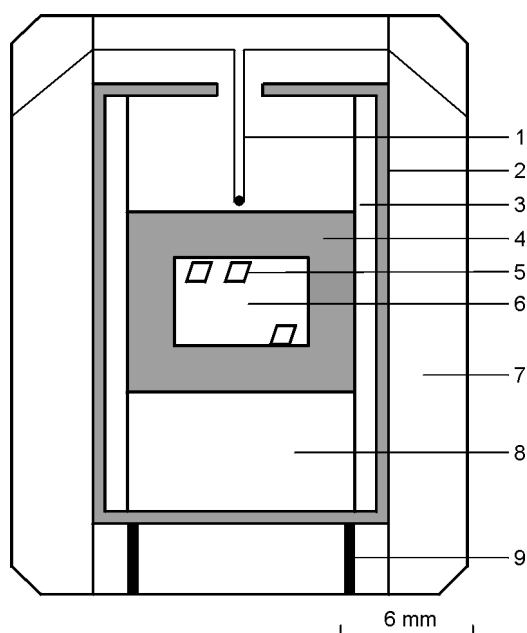

Fig. 1. A schematic high-pressure cell for exploration of phase formation and diamond crystallization in carbonate, carbonate-oxide, and carbonate-silicate systems. 1 — thermocouple, 2 — graphite heater, 3 — insulating MgO plug, 4 — graphite ampoule, 5 — diamond seeds, 6 — K_2CO_3 or mixture of K_2CO_3 with SiO_2 or forsterite, 7 — housing, 8 — ZrO_2, 9 — power supply.

(T_{melt} = 650 °C [33]) and of Ni wire (T_{melt} = 1620±20 °C [34]) in the melt of NaCl (T_{melt} = 1544 °C [35]). The time of melting was marked by a drastic increase in electric resistance resulting from the rupture of wire on melting of the reference metal. The experiments were carried out to follow the scheme: creation of external pressure, heating of the cell at a rate of 1 °C/s, 40-hour-long exposure under fixed P and T, cooling of the cell at a rate of 150 °C/s, and decrease in external pressure to atmospheric one.

The initial materials were: graphite (99.99%), K_2CO_3 and SiO_2 (with the purity no less than 99.9%), as well as synthetic forsterite with 56.97 wt.% MgO and 42.93 wt.% SiO_2. Before the experiment, the carbonate was dried for 2 hours at 300 °C, and powders of forsterite and SiO_2, for 1 h at 1000 °C. Reagents and mounted cells were stored at 100 °C. The seed crystals were cuboctahedra of synthetic diamond 0.5 mm in size. Powders of carbonate, forsterite, or silica were mixed in the proportions given in Table 1 and placed into graphite ampoules (see Fig. 1). In each experiment, some of the diamond seeds were placed in the upper part of the ampoules so that their dropping could indicate the melting of carbonate or carbonate-silicate material [23].

The experimental products were visually studied under the microscopes MBS-9 and MBI-15. The phase composition of specimens was analyzed on the DRON-3 diffractometer (CuK_α emission). The chemical composition is determined on the *X*-ray Camebax-Micro probe. The photomicrographs were obtained with the use of the JSM-35 electron scanning microscope.

RESULTS

K_2CO_3–C system. The behavior of diamond during its synthesis in this system at 7 GPa and 1700–1750 °C has been analyzed by us earlier [23, 24]. A decrease in P and T to 6.3 GPa and 1650 °C did not principally change the picture. An aggregate of cuboctahedral crystals of diamond formed on the inner surface of graphite ampoules (Fig. 2, *a*). The crystals vary in size from 10 to 400 μm. The diamond crystals are separated from graphite by a thin layer of carbonate. The color of crystals varies from pale-yellow to black depending on concentration of black disperse inclusions, which were identified as graphite [22]. Diamond growth on seeds is characterized by triangular layers on the {111} faces and pyramidal relief on the {100} faces. The melting of carbonate is recorded in all experiments, unambiguously marked by the drop of diamond seeds onto the bottom of the ampoules (see Fig. 2, *a*).

K_2CO_3–SiO_2–C system. Results of the experiments in which, under constant P, T, and t, we changed only SiO_2 concentration from 5 to 75 wt.% are reported in Table 1.

In the domain of low concentrations of silica (from 5 to 25 wt.%) a drop of diamond seeds was recorded, indicative of melting. The ampoules were filled with an aggregate of dendrite crystals of carbonate and potassium silicate ($K_2SiSi_3O_9$) with the hexagonal wadeite-type structure (Fig. 3, *a*). Diamond has been found at the contact between graphite and carbonate-silicate melt. In all cases, diamond crystals are separated from graphite by a film of carbonate-silicate material. The diamonds have the cuboctahedral habit and form a great number of intergrowths and twins, including polysynthetic and cyclic ones (Fig. 4, *a*). The maximum size of spontaneous crystals of diamond is 500 μm. The obtained crystals are yellow and, unlike the diamonds synthesized in the K_2CO_3–C system, have little, if any, black inclusions.

With SiO_2 concentration increasing to 50 wt.%, no diamond nucleation has been found. Only crystals of metastable graphite up to 70 μm in size were observed on the inner surface of graphite ampoules. Diamond growth on seed crystals has been recorded, though the grown layers were considerably thinner than they were in the experiments with low SiO_2 (see Table 1). X-ray data indicate the presence of potassium wadeite in the products of experiment (see Fig. 3, *b*). It forms colorless prismatic crystals up to 500 μm in size, whose composition is given in Table 2. Newly formed diamond has been established in the study system, at 75 wt.% SiO_2, either and the size of graphite crystals increased to 200 μm. An aggregate of colorless isometric crystals of coesite up to 300 μm in size has been formed inside the ampoules (see Fig. 3, *c*, Table 2). In both cases, the material of intergranular space is an aggregate of chilling dendrites of potassium carbonate and potassium wadeite (see Table 1).

Seeded diamond growth has been recorded throughout the range of investigated compositions. Distinct layers are on octahedral faces, whereas the faces of cube contain octahedrons and induction surfaces of cogrowth of diamond with K-wadeite and coesite. The maximum thickness of diamond layer grown over the {100} faces of seed crystals was 300 μm, and on the {111} faces, 150 μm (see Table 1). In all cases, the diamond growth rate on the cube faces is 2–2.5 times as high as that on the octahedron faces.

The character of phase formation as a function of SiO_2/K_2CO_3 is schematically shown in Fig. 5. As SiO_2 increases in the system, the carbonate-silicate melt loses its capacity to initiate diamond nucleation and, in the domain of high concentrations of SiO_2, provides only recrystallization of graphite and diamond growth on seeds. As the melt becomes richer in silica, first K-wadeite and then coesite crystallize.

K_2CO_3–Mg_2SiO_4–C system. Characteristics of phase formation and diamond crystallization with the
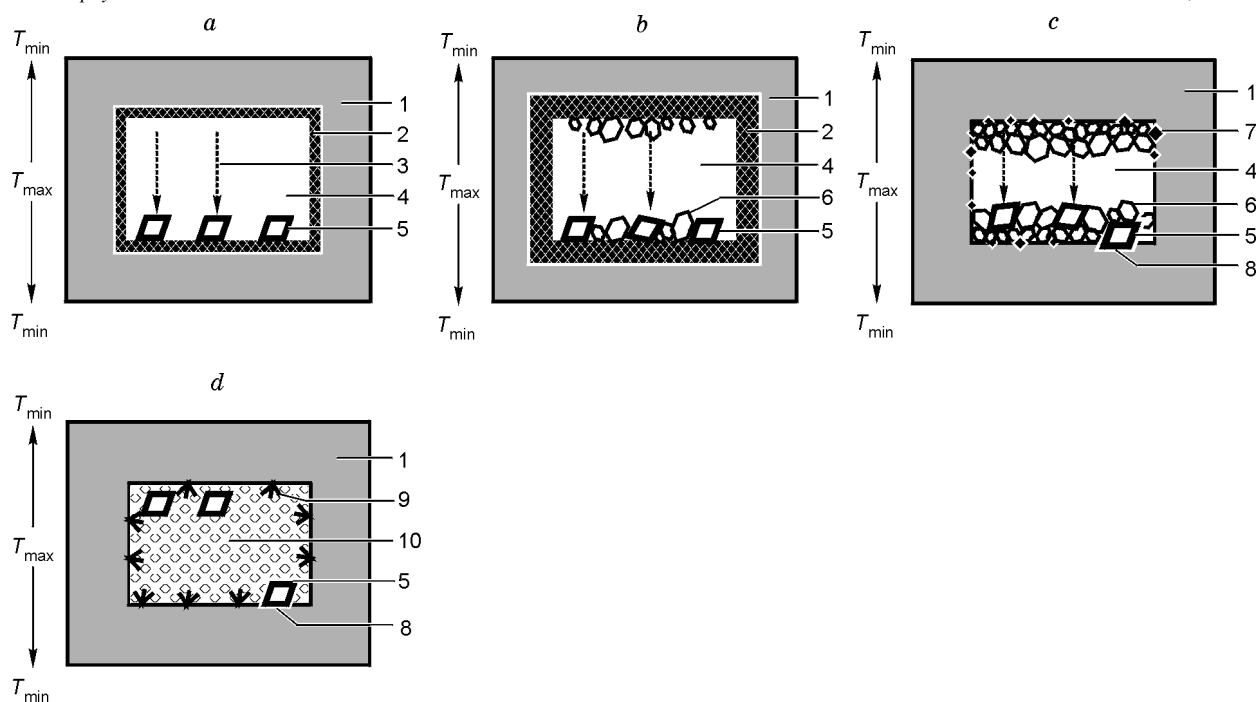
Fig. 2. Schematic crystallization in systems K_2CO_3–C and K_2CO_3D–Mg_2SiO_4–C. *a* — System K_2CO_3–C, *b–d* — system K_2CO_3–Mg_2SiO_4–C at forsterite concentration of 10, 50, and 75 wt.%, respectively. 1 — graphite ampoule, 2 — diamond-carbonate aggregate, 3 — direction of seed drop, 4 — carbonate or carbonate-silicate melt, 5 — seed crystals overgrown with diamond, 6 — forsterite crystals, 7 — diamond crystals, 8 — melt film, 9 — graphite crystals, 10 — aggregate of forsterite and carbonate crystals.

concentration of Mg_2SiO_4 in the system varying from 5 to 95 wt.% in experiments, under constant P, T, and t, are given in Table 1.

In the domain of low concentrations of Mg_2SiO_4, from 5 to 50 wt.%, the drop of diamond seeds is indicative of melting (see Fig. 2, *b*, *c*). At the melt-graphite boundary, an aggregate of diamond crystals up to 600 μm in size formed. Morphologically, they are similar to crystals obtained in the systems K_2CO_3–C and K_2CO_3–SiO_2–C (see Fig. 4, *b*). The diamonds contain abundant black disperse inclusions. In the range of compositions from 10 to 50 wt.% Mg_2SiO_4, an aggregate of forsterite crystals formed in the cool zone of ampoule (see Figs. 2, *b*, *c* and 6, *a*). Their composition is given in Table 2. Forsterite forms colorless transparent prismatic crystals whose maximum size reaches 800 μm.

At Mg_2SiO_4 concentration higher than 50 wt.%, no spontaneous diamond crystals have been established, and platy crystals of graphite up to 250 μm in size have been found on the inner surface of the ampoules (see Fig. 2, *d*). Seeded diamond growth is also observed at much higher concentrations of forsterite, up to 90 wt.%. The thickness of the overgrown layer of diamond considerably decreased with increasing Mg_2SiO_4. Thus, at 40 wt.% forsterite it was 320 μm on the {100} faces and 150 μm on the {111} faces, whereas at 90 wt.% forsterite its thickness decreased to 8 and 4 μm, respectively. At 95 wt.% Mg_2SiO_4, diamond growth has not been established. According to X-ray data, in the range of compositions from 40 to 95 wt.% Mg_2SiO_4, forsterite and periclase have been recorded in the products (see Fig. 6, *b*). After experiments, the specimens are represented by an aggregate made up chiefly of crystals of forsterite and scarce octahedral crystals of periclase. The interstices are filled with carbonate. The microrelief of diamond layers grown on the seeds is similar to the microrelief established in the systems K_2CO_3–C and K_2CO_3–SiO_2–C (Fig. 7). Moreover, numerous crystals of forsterite occur on faces of the seeds (Fig. 8) as well as induction surfaces of diamond and forsterite cogrowth (Fig. 9). As a rule, the diamond layer on the cube faces is 2–2.5 times as thick as the layers grown on the octahedron faces.

The character of phase formation and diamond crystallization with different K_2CO_3/Mg_2SiO_4 ratios is shown in Fig. 10. It is seen that as the Mg_2SiO_4 content increases, the carbonate-silicate melt ceases to provide spontaneous nucleation of diamond, and in the domain of high concentrations of Mg_2SiO_4, only seeded diamond growth and recrystallization of metastable graphite are possible. Simultaneously, the carbonate-silicate melt becomes oversaturated first with forsterite and then, with forsterite and periclase.

Table 1

**Experimental Results of Diamond Crystallization in Systems K_2CO_3–C, K_2CO_3–SiO_3–C,
and K_2CO_3–Mg_2SiO_4–C at 6.3 GPa and 1650 °C for 40 h**

Run no.	Initial composition	C, wt.%	Resulting phases	Diamond crystallization		
				A, %	Seeded growth rate, μm/h	
					{100}	{111}
1	K_2CO_3 + Gr	0	Dm + Q(KC)	25	*	*
2	K_2CO_3 + Gr	0	Dm + Q(KC)	29	*	*
3	K_2CO_3 + Gr	0	Dm + Q(KC)	29	*	*
4	K_2CO_3 + SiO_2 + Gr	5	Dm + Q(KC + K-wad)	33	*	*
5	K_2CO_3 + SiO_2 + Gr	10	Dm + Q(KC + K-wad)	41	*	*
6	K_2CO_3 + SiO_2 + Gr	25	Dm + Gr + Q(KC + K-wad)	9	7.5	3.8
7	K_2CO_3 + SiO_2 + Gr	50	K-wad + Dm + Gr + Q(KC + K-wad)	0	0.4	0.2
8	K_2CO_3 + SiO_2 + Gr	75	Co + Dm + Gr + Q(KC + K-wad)	0	0.2	<0.1
9	K_2CO_3 + Fo + Gr	5	Dm + Q(KC)	37	*	*
10	K_2CO_3 + Fo + Gr	10	Fo + Dm + Q(KC)	49	*	*
11	K_2CO_3 + Fo + Gr	10	Fo + Dm + Q(KC)	49	*	*
12	K_2CO_3 + Fo + Gr	25	Fo + Dm + Q(KC)	33	*	*
13	K_2CO_3 + Fo + Gr	25	Fo + Dm + Q(KC)	25	*	*
14	K_2CO_3 + Fo + Gr	30	Fo + Dm + Q(KC)	18	*	*
15	K_2CO_3 + Fo + Gr	40	Fo + Pc + Dm + Q(KC)	3	7.5	3.5
16	K_2CO_3 + Fo + Gr	40	Fo + Pc + Dm + Q(KC)	2	8.0	3.8
17	K_2CO_3 + Fo + Gr	50	Fo + Pc + Dm + Q(KC)	<0.1	5.0	2.3
18	K_2CO_3 + Fo + Gr	50	Fo + Pc + Dm + Q(KC)	<0.1	6.5	2.5
19	K_2CO_3 + Fo + Gr	75	Fo + Pc + Dm + Gr + Q(KC)	0	1.0	0.4
20	K_2CO_3 + Fo + Gr	75	Fo + Pc + Dm + Gr + Q(KC)	0	1.5	0.6
21	K_2CO_3 + Fo + Gr	75	Fo + Pc + Dm + Gr + Q(KC)	0	0.5	0.2
22	K_2CO_3 + Fo + Gr	75	Fo + Pc + Dm + Gr + Q(KC)	0	0.5	0.2
23	K_2CO_3 + Fo + Gr	90	Fo + Pc + Dm + Gr + Q(KC)	0	0.2	<0.1
24	K_2CO_3 + Fo + Gr	90	Fo + Pc + Dm + Gr + Q(KC)	0	0.2	<0.1
25	K_2CO_3 + Fo + Gr	95	Fo + Pc + Gr + Q(KC)	0	0	0
26	K_2CO_3 + Fo + Gr	95	Fo + Pc + Gr + Q(KC)	0	0	0

Note. C — Initial concentration of SiO_2 or forsterite in systems, Fo — forsterite, Pc — periclase, Co — coesite, K-wad — potassium wadeite ($K_2SiSi_3O_9$), KC — potassium carbonate, Dm — diamond, Gr — graphite, Q — quenching phases. $A = (M_{Dm}/M_{Gr})100\%$ (M_{Dm} is the mass of produced diamond, without seeds, M_{Gr} — the mass of initial graphite).
* Not determined.

DISCUSSION

The geochemical and petrological data available indicate that the crystallization, at least, of some part of diamonds is related to processes of mantle metasomatism and occurred from the carbon-oversaturated carbonate-silicate fluxes [11, 12], actively changing the composition of mantle rocks [3, 4]. According to experimental data, carbonate melts could have been formed under the conditions of the upper mantle as a result of partial melting of carbonatized mantle peridotite near its solidus [3, 5]. An increase in temperature by 70–100 °C above the solidus could led to a considerable increase in silicate/carbonate ratio and gradual transition from carbonate to carbonate-silicate melt compositionally close to kimberlite [5].

To estimate the effect of the silicate/carbonate ratio on the diamond formation in the studied systems, we determined the degree of graphite-to-diamond transformation as: $A = (M_{Dm}/M_{Gr}) \cdot 100$, where M_{Dm} is the mass of
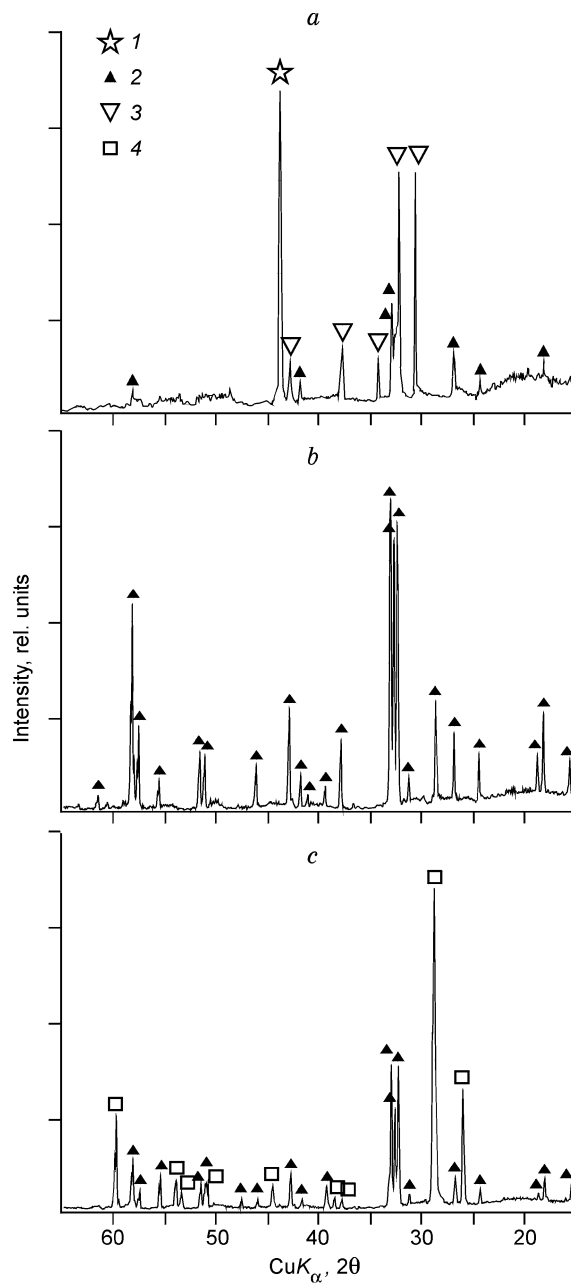
Fig. 3. Results of X-ray analyses of specimens after experiments in the system K_2CO_3–SiO_2–C. *a*, *b*, and *c* — at initial concentrations of SiO_2 of 10, 50, and 75 wt.%, respectivelly. *1* — diamond, *2* — potassium wadeite, *3* — K_2CO_3, *4* — coesite.

the obtained diamond except of the diamond layers grown on the seed crystals, M_{Gr} is the mass of the initial graphite. The results show that as the SiO_2 content in the system K_2CO_3–SiO_2–C increases to 10 wt.%, *A* increases by 50% and then, with a further increase in silica concentration, successively decreases to zero (Fig. 11). The dependence of the degree of graphite-to-diamond transformation on the Mg_2SiO_4 content in the system K_2CO_3–Mg_2SiO_4–C is similar to the *A* dependence of SiO_2 concentration in the system K_2CO_3–SiO_2–C (see Fig. 11). In the domain of high concentrations of silica and forsterite, the intensity of diamond formation was estimated from the rate of diamond seeded growth. The results of measurements given in Table 1 indicate a gradual decrease in diamond growth rate on the faces {100} and {111} of seed crystals with increasing content of silica in the system K_2CO_3–SiO_2–C and forsterite in the system K_2CO_3–Mg_2SiO_4–C (see Table 1). Thus, the general

Table 2

**Results of Microprobe Analysis of Mineral Phases Cocrystallized with Diamond
from Carbonate-Silicate Melt (wt. %)**

Run no.	Phase	SiO_2	MgO	K_2O	Total
System K_2CO_3–SiO_2–C					
7	K-wad	67.2	0.02	24.8	92.02
7	K-wad	68.3	0.00	26.3	94.6
7	K-wad	70.3	0.00	25.1	95.4
8	Co	98.4	0.00	0.02	98.42
8	Co	95.7	0.00	0.03	95.73
System K_2CO_3–Mg_2SiO_4–C					
10	Fo	42.7	56.9	0.00	99.6
10	Fo	42.6	56.5	0.01	99.11
13	Fo	42.6	57.3	0.08	99.98
15	Fo	41.0	56.3	0.00	97.3
15	Pc	0.00	97.1	0.01	97.11
17	Fo	42.9	57.0	0.01	99.91
22	Fo	41.7	56.9	0.01	98.61
22	Pc	0.00	95.9	0.01	95.91
23	Fo	43.0	56.8	0.03	99.83
24	Fo	42.7	56.4	0.05	99.15
24	Fo	43.5	57.6	0.08	101.18
25	Fo	43.5	57.6	0.07	101.17
26	Fo	42.7	56.7	0.02	99.42

Note. Fo — forsterite, Pc — periclase, K-wad — potassium wadeite ($K_2SiSi_3O_9$), Co — coesite.

tendency is that the catalytic potential of the studied systems relative to diamond varies with an increase in silicate/carbonate ratio, increasing in the domain of low concentrations of silicate and decreasing in the domain of its high concentrations.

In the range of compositions from 5 to 25 wt.% SiO_2 in the system K_2CO_3–SiO_2–C, silica was completely dissolved in the carbonate melt (see Table 1). Therefore, an increase in SiO_2 concentration in the system was accompanied with the same increase in its concentration in the melt. At 50 wt.% SiO_2, the system becomes oversaturated with K-wadeite, and at 75 wt.%, with coesite (see Fig. 5). On the basis of these data, the solubility of SiO_2 in the K_2CO_3 melt at 6.3 GPa and 1650 °C is estimated at ≥25 wt.%. The principal structural differences of the carbonate and silicate melt suggest that the SiO_2 dissolution in the carbonate melt should be accompanied by an increased degree of its polymerization and viscosity [36]. Given these estimates and experimental data, the change in intensity of diamond formation in the system K_2CO_3–SiO_2–C is most likely due to considerable changes in the structure and properties of carbonate-silicate melt with increasing concentration of SiO_2 dissolved in it. Since the dependence of the catalytic potential on SiO_2/K_2CO_3 and Mg_2SiO_4/K_2CO_3 in the system are similar, the change in intensity of diamond crystallization with an increased content of Mg_2SiO_4 in the system K_2CO_3–Mg_2SiO_4–C is possibly related to the increased silica-to-carbonate ratio in the melt.

The termination of spontaneous nucleation and diamond growth in the domain of high concentrations of silicate (see Fig. 5, 10) can be explained by data [23–26, 37] on the existence on an induction period preceding spontaneous nucleation and growth of diamond. It has been experimentally established that in the alkaline carbonate-carbon systems the duration of the induction period depends on the composition of crystallization medium. We can suppose on this basis that the increase in concentration of silica or forsterite in the studied systems was accompanied by an increase in the induction period of nucleation and growth of diamond. It is possible that at a greater duration of experiments the nucleation and growth of diamond in the systems K_2CO_3–SiO_2–C and K_2CO_3–Mg_2SiO_4–C can proceed in a wider range of concentrations of silica and forsterite. It is necessary to note that the termination of spontaneous nucleation of diamond in the studied systems coincides with the beginning
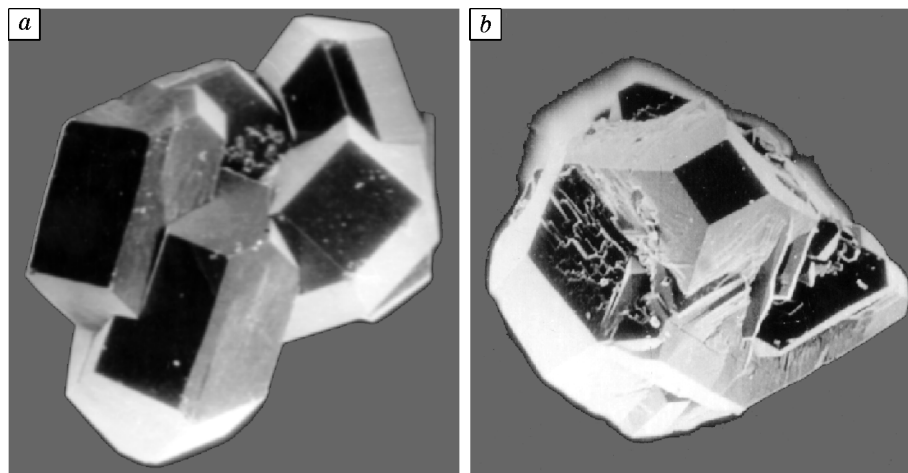
Fig. 4. Morphology of spontaneous diamond crystals. *a* — **Irregular inter-growth of cuboctahedral crystals (system K_2CO_3–SiO_2–C, run no. 6), × 150;** *b* — **twinned intergrowth of cuboctahedra with distinct growth layers on the faces {111} (system K_2CO_3–Mg_2SiO_4–C, run no. 16), × 150.**
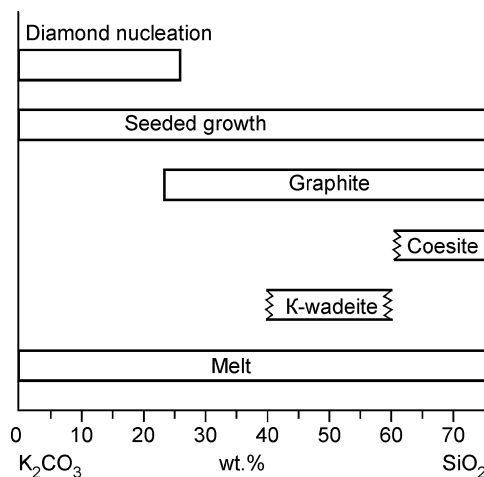

Fig. 5. A schematic diagram illustrating the character of phase formation and diamond crystallization in the system K_2CO_3–SiO_2–C at 6.3 GPa and 1650 °C.

of crystallization of metastable graphite (see Fig. 5, 10). Cocrystallization of metastable graphite and stable diamond was earlier recorded in the C–O–H fluid and in the alkaline carbonate-fluid-carbon systems and was possibly due to kinetic features of diamond and graphite formation processes [25, 37]. Hence, we suppose that the crystallization of metastable graphite in our experiments is related to an increase in the induction period of diamond nucleation in the domain of high concentrations of SiO_2 or Mg_2SiO_4.

In solving many problems related to diamond genesis, of special importance is the study of the effect of physicochemical conditions of growth on crystal morphology. It has been established in [23, 24] that in the alkaline carbonate-carbon systems at 7.0 GPa and 1700–1750 °C the diamond morphology is well determined by the cationic composition of carbonates and gradually changes from cuboctahedron to octahedron in the series Li_2CO_3—Na_2CO_3—K_2CO_3—Cs_2CO_3. The results of our studies show that under the constant cationic composition of alkaline carbonate, the introduction of silica or forsterite into the system K_2CO_3–C does not change the diamond morphology (see Fig. 4). It is probable that in alkaline carbonate and carbonate-silicate systems the carbonate composition is one of the main factors controlling the diamond morphology.
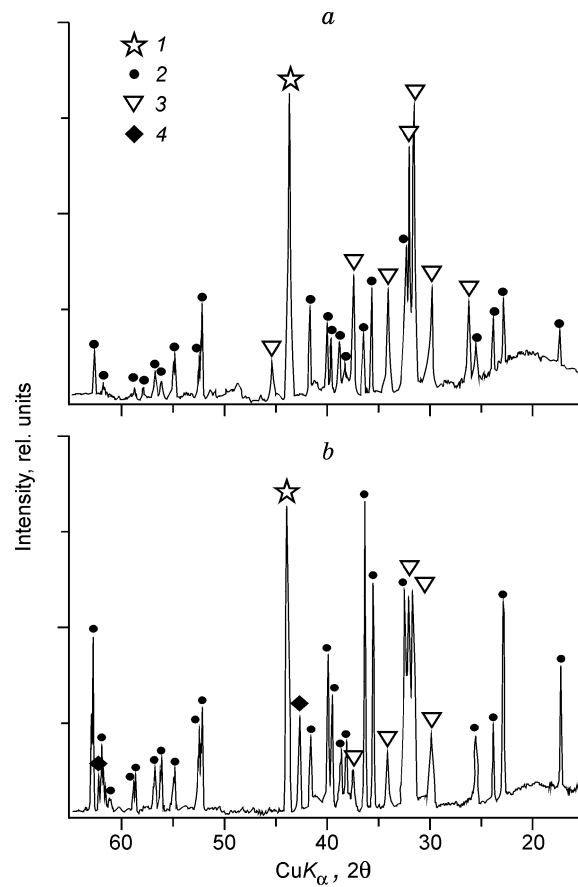
Fig. 6. Results of X-ray analysis of specimens after experiments in the system K_2CO_3–Mg_2SiO_4–C. *a* and *b* — at initial concentration of forsterite of 30 and 75 wt.%, respectively. *1* — diamond, *2* — forsterite, *3* — K_2CO_3, *4* — periclase.
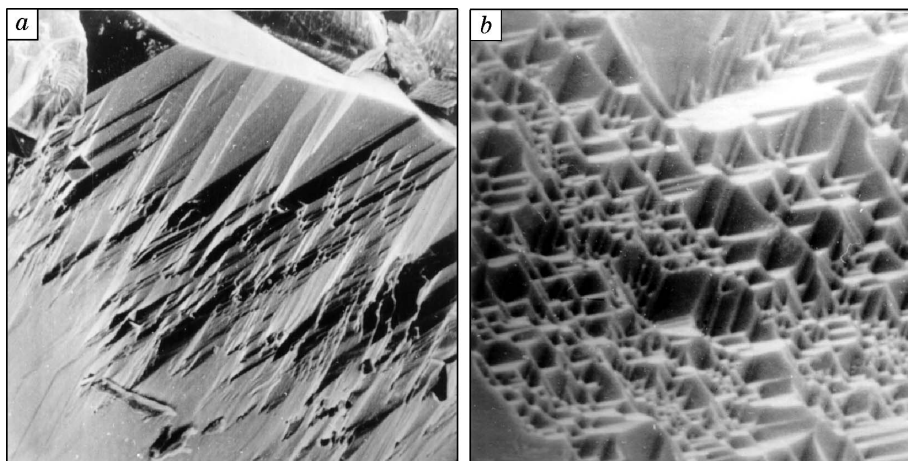

Fig. 7. Microrelief of diamond overgrown seed crystals (system K_2CO_3–Mg_2SiO_4–C, run no. 15). *a* — Triangular layers of growth on {111} face, × 350; *b* — octahedra on {100} face, × 1100.

**Fig. 8. Forsterite crystals on diamond surface (system
K_2CO_3–Mg_2SiO_4–C, run no. 15), $\times$ 440.**

**Fig. 9. Induction susrfaces of diamond and forsterite cogrowth on {111} face of seed crystal
(K_2CO_3–Mg_2SiO_4–C system, run no. 14), $\times$ 220.**

The cooccurrence of ultrapotassic fluxes and minerals of the main mantle-derived parageneses in inclusions in natural diamonds implies that these melts played an important role in crystallization of diamonds of eclogitic and peridotitic mantle parageneses [13]. In the present work, we succeeded in reproducing the conditions under which diamond was crystallized from a potassium carbonate-silicate melt including the main components of mantle ultrapotassic fluxes, together with coesite (mineral of eclogite paragenesis) in the K_2CO_3–SiO_2–C system and with forsterite (mineral of peridotite paragenesis) in the system K_2CO_3–Mg_2SiO_4–C (see Figs. 8 and 9). Crystallization of diamond, forsterite, and periclase has been established in the range from 40 to 90 wt.% Mg_2SiO_4 in the system K_2CO_3–Mg_2SiO_4–C (see Fig. 10). Simultaneous formation of forsterite and periclase in the compositionally close system $K_2Mg_2Si_2O_7$–K_2CO_3 at 3.7 GPa and 1300–1650 °C was mentioned earlier [38]. There are two possible versions of periclase origin in the mantle medium of diamond crystallization. One of them implies that periclase in association with MgSi-perovskite formed during the olivine decomposition under conditions of lower mantle [39]. According to the other version, periclase could have been formed as a result of magnesite decomposition in carbonatized dunite with a decrease in partial pressure of CO_2 [40]. Our experimental data suggest yet another version, according to which periclase could have been produced by the metasomatic effect of high-potassium mantle fluxes on ultrabasic rocks.
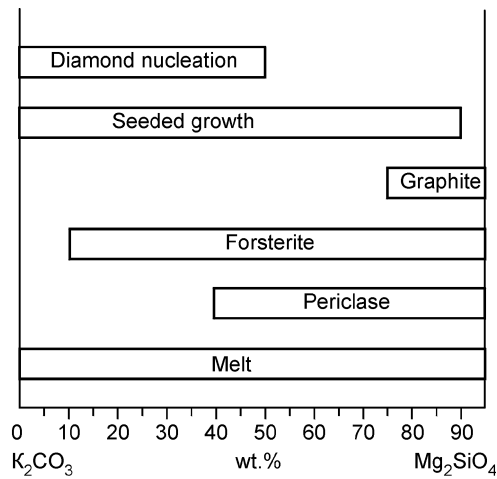
Fig. 10. A schematic diagram illustrating the features of phase formation and diamond crystallization in the system K_2CO_3–Mg_2SiO_4–C at 6.3 GPa and 1650 °C.
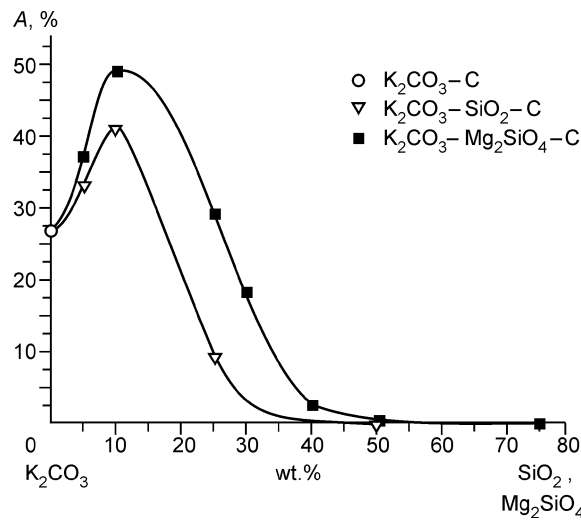

Fig. 11. Degree of graphite-to-diamond transformation (A) as a function of SiO_2 concentration in the system K_2CO_3–SiO_2–C and Mg_2SiO_4 in the system K_2CO_3–Mg_2SiO_4–C.

CONCLUSIONS

It has been experimentally shown that the spontaneous diamond nucleation in the system K_2CO_3–SiO_2–C at 6.3 GPa, 1650 °C for 40 h proceeds in the range of compositions from 0 to 25 wt.% SiO_2 and the diamond growth on seeds continues up to 75 wt.% SiO_2. As the silica concentration increases, the degree of graphite-to-diamond transformation (A) first increases and then drops to zero. The rate of diamond growth on seeds also decreases as SiO_2 content increases in the system in the domain of high concentrations of silica. It is possible that the change in catalytic potential of the system K_2CO_3–SiO_2–C during diamond formation with an increase in SiO_2 content is due to an increase in the SiO_2/K_2CO_3 ratio in the melt.

In the system K_2CO_3–Mg_2SiO_4–C, the spontaneous diamond nucleation is realized at a concentration of Mg_2SiO_4 of 0 to 50 wt.%, and the diamond growth on seeds, of 0 to 90 wt.%. The dependence of A and diamond growth rate on forsterite content in the system K_2CO_3–Mg_2SiO_4–C is like to the dependence of these quantities on SiO_2 concentration in the system K_2CO_3–SiO_2–C. The similar character of these dependences suggests that the

change in the diamond formation intensity in the system K_2CO_3–$MgSiO_4$–C is also related to the increased SiO_2/K_2CO_3 in the melt.

Our experimental results show that the introduction of silica or forsterite into the system K_2CO_3–C does not change the diamond morphology. At the same time, in the alkaline carbonate-carbon systems, the diamond morphology essentially depends on the cationic composition of carbonates. It is likely that in the alkaline carbonate and carbonate-silicate systems the cationic composition of carbonate is one of the main factors governing the diamond morphology.

We were first to create the conditions under which diamond was crystallized from a potassium carbonate-silicate melt including the main components of mantle-derived ultrapotassic fluxes, together with coesite in the system K_2CO_3–SiO_2–C and with forsterite in the system K_2CO_3–Mg_2SiO_4–C. The obtained results experimentally confirm an important role of potassic carbonate-silicate melts in the diamond formation of both eclogite and peridotite parageneses.

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