Doklady Earth Sciences, Vol. 389A, No. 3, 2003, pp. 388–391. Translated from Doklady Akademii Nauk, Vol. 389, No. 3, 2003, pp. 382–386.

GEOCHEMISTRY

Alkaline-Chloride Components in Processes of Diamond Growth in the Mantle and High-Pressure Experimental Conditions

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Presented by Academician V.A. Zharikov November 10, 2002

Received November 14, 2002

Judging from the primary fluid microinclusions [1–3], parent media of diamond formation under mantle conditions represent partial or complete multicomponent carbonate–silicate melts containing dissolved chloride, phosphate, and other components, as well as water. Their efficiency for the diamond formation was demonstrated by direct experiments at high pressures [4, 5]. These experiments revealed important aspects of diamond genesis, namely, the chemical nature and physicochemical mechanisms of diamond formation in the mantle. According to numerous thermobarometric estimates, natural diamonds are most often crystallized at 4.5–7.5 GPa and 950–1350°C [6], which corresponds to the *PT* region of thermodynamic stability of diamond on the phase diagram of carbon [7].

Investigations of the parent media entrapped by diamonds suggest substantial variations in their chemical compositions. Thus, highly concentrated alkaline-chloride aqueous solutions (brines) were found in cloudy primary fluid microinclusions in diamonds of the Koffiefontein diatreme, South Africa [8]. Average compositions of the brines are expressed as $(K,Na)_8(Ca,Fe,Mg)_4SiO(CO_3)Cl_{10}(H_2O)_{28–44}$, which corresponds to 30–42 wt % H_2O, 19–22 wt % Cl, 14–17 wt % (K + Na), 22–25 wt % Fe–Ca–Mg carbonates, and 3–4 wt % SiO_2. At room temperature (and pressures of about 1.5–2.0 GPa [9]), alkaline-chloride and carbonate components of the brines in the inclusions are associated with syngenetic silicate minerals of both peridotite and eclogite parageneses. It must be noted that the general component composition of the inclusions containing the alkaline-chloride brines is analogous to that of more common fluid inclusions with low chloride contents [1–3]. All the carbonate, silicate, alkaline-chloride, and other substances associated in the primary inclusions are melt products formed during cooling under pressure. In connection with the find of alkaline-chloride aqueous brines in the inclusions, the problems of diamond crystallization in the KCl–C and KCl–H_2O–C systems acquire a particular significance, since they make it possible to estimate the diamond formation capacity of the parent media during their chemical evolution with noticeable variations in the concentration ratio of the components.

In the present work, we experimentally studied the possibility of spontaneous nucleation and crystallization of diamond, as well as its growth on monocrystal seeds in melts of the key (potassium chloride–carbon) system at high pressures.

Haloid melt-solutions of carbon were previously used for the diamond synthesis in mixtures of carbon (graphite) with LiCl, NaCl, KCl, RbCl, CsCl, NaF, NaBr, and NaI at 6 GPa and 1620°C [10]. However, all these attempts failed to realize a spontaneous diamond nucleation, although they yielded overgrowths on diamond seeds. In this case, KCl, RbCl, and CsCl were in the solid state, as opposed to other halogenides that melted under experimental conditions of diamond synthesis. The observed effects of diamond growth on the seeds were explained by the presence of oxygen admixtures in the salts, synthesis of carbon oxide, its subsequent decomposition, and precipitation of elemental carbon on the seed surface. This version does not admit direct chemical participation of alkaline-chloride substance in diamond synthesis.

In order to achieve the purpose formulated above, we conducted the experiments in KCl–graphite mixtures (weight ratio 3 : 2) at 7–8 GPa and 1200–1700°C. We used homogeneous mixtures of dried powders of spectrally pure KCl and graphite as starting substances. The experiments were conducted according to the procedure described in [4, 5, 11] using a graphite heater as an ampule (diameter 3–4 mm, wall thickness 0.5 mm) and a high-pressure anvil-with-hole apparatus with a lithographic limestone cell. The starting mixture was fed either directly into the graphite heater ampule or into a 0.05-mm-thick tungsten foil ampule that was insulated from the graphite heater by magnesia-based

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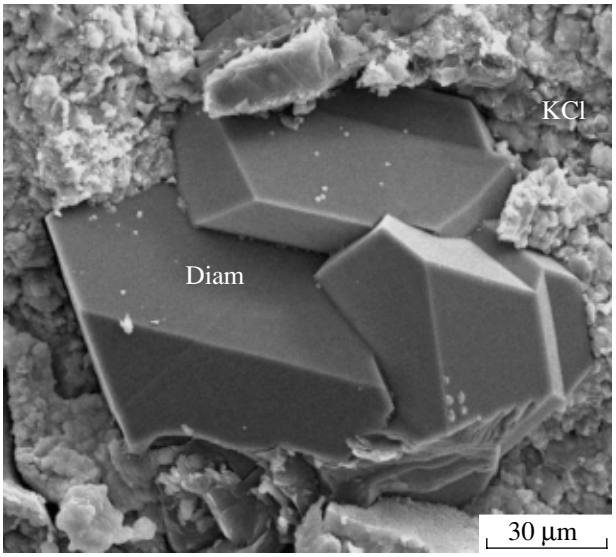

Fig. 1. Intergrowth of diamond crystals formed under conditions of spontaneous crystallization at a fracture in the sample after experiment (Sample 876; 8 GPa; 1550°C; run duration 40 min).

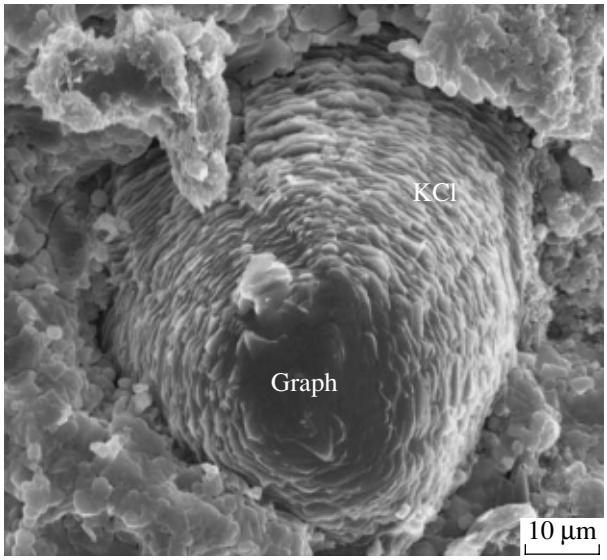

Fig. 2. Graphite spherule within a basket-shaped shell of solidified KCl melts (here and in Figs 3 and 4: Sample 877; 7.5 GPa; 1550°C; run duration 40 min).

ceramics. This difference exerted no substantial influence upon experimental results. A diamond monocrystal about 0.6 mm in size was placed in the central zone with the KCl–graphite mixture for testing the experimental conditions (effects of growth, dissolution, or "no changes"). The accuracy of pressure and temperature determination was ±0.01 GPa and ±15–20°C, respectively (based on the calibration curve for the temperature depending on current power to the heater). Samples obtained in the experiments were studied by scanning electron microscopy and electron probe microanalysis on a CamScan microscope at the Department of Petrology, Moscow State University (E.V. Guseva, analyst).

Spontaneous crystallization and growth of diamond on monocrystal "metal-synthetic" diamond seeds in melts of the KCl–C system was observed at 7–8 GPa and 1500–1700°C. The density of the diamond nucleation and mass crystallization is high at 8 GPa and markedly falls with decreasing the pressure to 7 GPa. It should be noted that the spontaneous crystallization rate is very high: diamond monocrystals up to 0.1 mm in size formed during the first 10 s from the onset of crystallization. In most cases, however, the experimental conditions were maintained over 40–60 min to provide the time sufficient for revealing effects of the growth of diamond on seeds. Examples of diamond crystallization from carbon solutions in alkaline-chloride (KCl) melts at high pressures are presented in Figs. 1, 3, and 4. These are the first documentary photomicrographs of diamonds crystallized from carbon solutions in KCl melts under conditions of spontaneous crystallization and growth on a seed. Diamond overgrowths on seeds in the NaCl–C system were documented in [10].

Diamond monocrystals forming in the course of the spontaneous diamond crystallization in the alkaline-chloride (KCl) melt solutions of carbon are up to 0.1 mm in size. They have an octahedral habit and (111) plane faces and are observed as individual crystals or their intergrowths (Fig. 1). (100) plane faces are not developed. Hollows with an appearance of "negative semioctahedrons" can sometimes be observed in place of the cubic faces. Spinel-type twinning along the octahedron plane is common. Diamond crystals can be observed in fractures that are developed in the solidified alkaline-chloride solvent within the experimental samples (Fig. 1). The KCl melt is predominantly solidified as a fine-grained spherulitic mass. One can also observe rhythmic basket-shaped solidified KCl segregations (Fig. 2) around spherules of recrystallized metastable graphite. The spherules are formed in association with diamonds under conditions approaching the graphite–diamond equilibrium boundary from the diamond domain. Microprobe investigations of the solidified substance in the contact zone with both diamond monocrystals and graphite spherules yield the stoichiometric KCl composition. All these facts indicate that both diamond and metastable graphite were crystallized from alkaline-chloride (KCl) melts with dissolved carbon.

Effects of the growth on the monocrystal seeds were detected for the major (octahedral and cubic) faces. Plane-faced cuboctahedral monocrystals (±0.6 mm) of metal-synthetic diamonds synthesized in melts of the Ni–Mn–C system at high pressures were used as seeds. On the octahedron face (Fig. 3), the chloride-synthetic diamond growth was observed as layers with the (111) planes oriented parallel to the eponymous seed face.

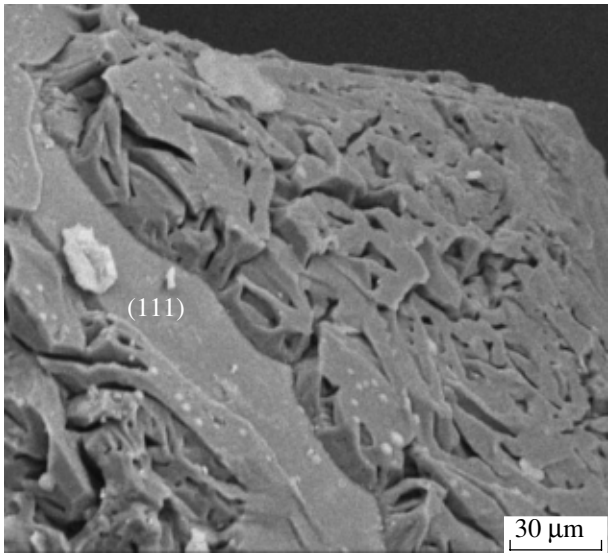

Fig. 3. Details of growth on the (111) face of a monocrystal seed.

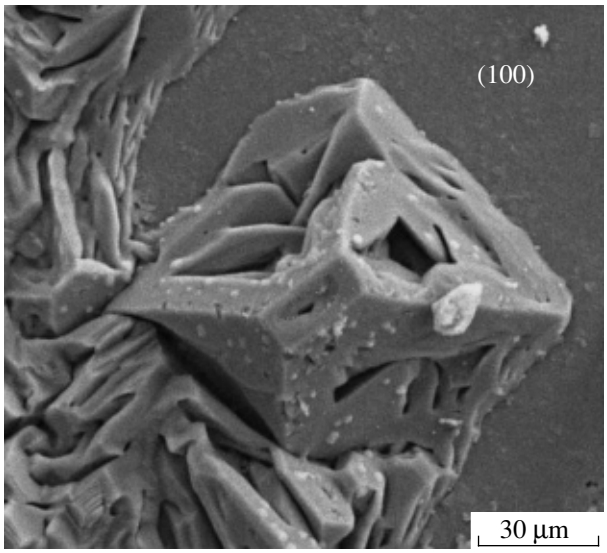

Fig. 4. Details of growth on the (100) face of a monocrystal seed.

The growth rate was probably sufficiently high, which led to the formation of a skeleton-shaped diamond layer with characteristic growth defects. On the cube face, the growth was realized as layers composed of tight accretions of octahedral microcrystals or, sometimes, as relatively larger semioctahedron-shaped growth pyramids (Fig. 4). The skeletal appearance of the overgrowths testifies to high crystallization rates. It is interesting that plane cubic faces are also absent on the seed overgrowths, and signs of the origination of negative semioctahedrons can be found instead.

The experimental data obtained suggest the following conclusion on physicochemical conditions of the spontaneous crystallization and growth of diamond crystals on seeds in the KCl–C system. At parameters of the thermodynamic stability of diamond, the starting graphite mixed with KCl is preserved as a metastable phase. At temperatures above those of eutectic melting of the KCl–C system, the metastable graphite is dissolved in the KCl melt to form alkaline-chloride melt solutions of carbon. As a thermodynamically metastable phase, graphite has a higher solubility in the alkaline-chloride melt than diamond under similar physical conditions. Therefore, dissolution of graphite leads to formation of carbon melt solutions, which are automatically supersaturated relative to diamond. The facts of the spontaneous diamond nucleation in the alkaline-chloride carbon melt-solutions suggest that they have reached labile levels of the supersaturated state of carbon. It should be noted that under actual high-pressure experimental conditions, the thermodynamic stimulus of diamond formation at the expense of the graphite source owing to the difference in solubilities is supplemented by the existence of apparatus-related stimulus in the reaction zone, namely, temperature gradients that also govern the carbon concentration level in the alkaline-chloride melt solution. For the diamond growth on the seed, lower (metastable, according to the terminology accepted) supersaturations are sufficient. However, under conditions of labile supersaturations, the growth on the seed proceeds concurrently with the competitive processes of spontaneous diamond crystallization and is characterized by elevated growth rates and formation of the skeletal morphology. In terms of crystal morphology, the growth of diamond crystals in KCl melts with dissolved carbon is analogous to their growth in carbonate, carbonate–silicate, and sulfide systems [4, 5, 11–13].

Any modern concept of the chemical composition of parent diamond-forming media must take into consideration the major role played by multicomponent carbonate–silicate melts. It is expedient to distinguish the main and trace components in their composition. These melts efficiently dissolve carbon from mantle sources (the idea of “asthenospheric” carbon seems to be preferable [3]). Spontaneous diamond nucleation is provided by labile supersaturations of carbon in the melt-solutions. The labile supersaturations do not appear in silicate melts, because their carbon solubility is insignificant. In contrast, the carbon solubility is high and responsible for labile supersaturations in carbonate–silicate melts. This unambiguously suggests the crucial role of the carbonate constituent. Nevertheless, both the carbonate and silicate components are the major contributors in natural parent carbonate–silicate melts.

Elucidation of the possibility and peculiarities of diamond crystallization in individualized carbon–trace component systems is essential for estimation of their role and influence upon natural diamond formation and

mineralogical properties of diamonds. The trace components are diverse (oxides, phosphates, sulfides, haloids, carbon dioxide, water, and others). Direct experiments have already demonstrated that the carbon solubility in sulfide melts under high pressures is sufficiently high to reach labile carbon supersaturations and spontaneous diamond crystallization [13]. Researchers have reported spontaneous diamond crystallization in water–carbon [14] and water–carbon dioxide–carbon systems. In the latter case, models with an individual system [14] and addition of carbonates (Na_2CO_3 and K_2CO_3) [15] were investigated.

Mineralogical data indicate that concentrations of trace components may substantially increase in local zones and become major components along with carbonate and silicate ones. The most prominent example is local high concentrations of sulfide inclusions, suggesting the appearance of an additional sulfide-related type of diamond formation under mantle conditions [13]. The appearance of strongly concentrated alkaline-chloride aqueous solutions is also related to local concentrations of trace elements in the parent melts.

Variation in the chemical composition of the parent carbonate–silicate medium during the growth of natural diamonds can be explained by processes of the fractional crystallization of silicate and carbonate minerals and the consequent accumulation of incompatible components in the residual melts, including chlorides of the alkali metals K and Na, as well as water. The generalized diagram for the fluid inclusion compositions (Fig. 5 in [8]) revealed compositional variation trends for parent media during the predominant fractionation of silicate and carbonate minerals with the accumulation of alkaline-chloride components and water. Reality of the fractionation of carbonate–silicate melts is confirmed by experiments on joint crystallization of diamonds and syngenetic minerals in carbonate–silicate melts of the Chagatai Complex in Uzbekisan [14].

Thus, our experimental investigations at high pressures and temperatures have revealed that processes of spontaneous nucleation and crystallization of diamond are efficiently realized in melts of the KCl–C system. This is an essential aspect of the problem of alkaline-chloride brines in natural diamond-hosted cloudlike microinclusions. Since the diamond growth at high pressures proceeded in the H_2O–C system [12], efficiency of melt solutions of carbon in the KCl–H_2O–C system (the basic system of brines in fluid microinclusions) for diamond formation is undoubted. Hence, the growth of natural diamonds will not cease during local high concentrations of components of alkaline-chloride aqueous solutions in the parent carbonate–silicate melts, although their influence upon the growth kinetics and defect structure of diamonds (fluid microinclusions and morphological defects of crystal growth) can be expected.

ACKNOWLEDGMENTS

I am grateful to O. Navon and E. Izraeli for the discussion during my visit to the Jerusalem University in February 2002, as well as to the Israel Academy of Science and the Russian Academy of Science for funding the visit.

This work was supported by the Russian Foundation for Basic Research, project no. 02-05-64684.

REFERENCES

1. Schrauder, M. and Navon, O., *Geochim. Cosmochim. Acta*, 1994, vol. 58, no. 2, pp. 761–771.
2. Izraeli, E., Schrauder, M., and Navon, O., *Int. VII. Kimberlite Conf. Extended Abstr.*, Cape Town, 1998, pp. 352–354.
3. Navon, O., *Proc. VII Int. Kimberlite Conf.*, Cape Town, 1999, vol. 2, pp. 584–604.
4. Litvin, Yu.A. and Zharikov, V.A., *Dokl. Akad. Nauk*, 1999, vol. 367, no. 3, pp. 397–401.
5. Litvin, Yu.A. and Zharikov, V.A., *Dokl. Akad. Nauk*, 2000, vol. 372, no. 6, pp. 808–811.
6. Harris, J.W., *The Properties of Natural and Synthetic Diamonds*, London: Academic Press, 1992, vol. 345–393.
7. Kennedy, C.S. and Kennedy, G.C., *J. Geophys. Res.*, 1976, vol. 8, no. 14, pp. 2467–2470.
8. Izraeli, E.S., Harris, J.M., and Navon, O., *Earth Planet. Sci. Lett.*, 2001, vol. 187, pp. 323–332.
9. Navon, O., *Nature* (London), 1991, vol. 353, pp. 746–748.
10. Wang, Y. and Kanda, H., *Diamond Relat. Mater.*, 1998, vol. 7, pp. 57–63.
11. Litvin, Yu.A., Chudinovskikh, L.T., Saparin, G.V., *et al.*, *Diamond Relat. Mater.*, 1999, vol. 8, pp. 267–272.
12. Litvin, Yu.A., Jones, A.P., Beard, A.D., *et al.*, *Dokl. Akad. Nauk*, 2001, vol. 381, no. 4, pp. 528–531.
13. Litvin, Yu.A., Butvina, V.G., Bobrov, A.V., and Zharikov, V.A., *Dokl.Akad. Nauk*, 2002, vol. 382, no. 1, pp. 106–109.
14. Akaishi, M. and Yamaoka, S., *J. Cryst. Growth*, 2000, vol. 209, pp. 999–1003.
15. Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., *et al.*, *Nature* (London), 1999, vol. 400, pp. 417–418.