

## Mineral Microinclusions in Cubic Diamonds from the Yakutian Deposits Based on Analytical Electron Microscopy Data

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A great number of publications are devoted to inclusions in natural diamonds, because these data allow us to reconstruct the crystallization conditions of diamonds at a great depth and to obtain unique information on deep geologic processes as a whole. The main attention of researchers has been focused on perfect octahedral diamond crystals, whereas inclusions of diamond crystals of cubic habit (hereafter, cubic diamonds) remained poorly studied for many years. This was caused by a low transparency of most cubic crystals, their micrometer size, and the presence of heterogeneous inclusions. These attributes substantially complicate the traditional study with an electron microprobe [1]. Recent investigations of cubic diamond crystals from various deposits all over the world have shown that they contain many unusual melt or fluid microinclusions of complex carbonatite composition [1–4]. Melt sulfide microinclusions were revealed in cubic diamond crystals from the Yakutian deposits [3]. However, the published information on the composition of specific mineral phases contained in cubic diamond crystals as inclusions remains scanty.

Analytical electron microscopy is a very efficient method of studying microinclusions incorporated into translucent crystals. This method is a combination of transmission and scanning electron microscopy with energy-dispersive analysis. We used this method to study mineral inclusions in imperfect translucent diamond crystals of various types [5 and references therein]. In particular, the inclusions in a few cubic crystals from deposits in northern China were investi-

gated with this method [6, 7]. The aim of this study was to use analytical electron microscopy for the examination the mineral microinclusions in cubic diamond crystals from deposits in the Siberian Craton.

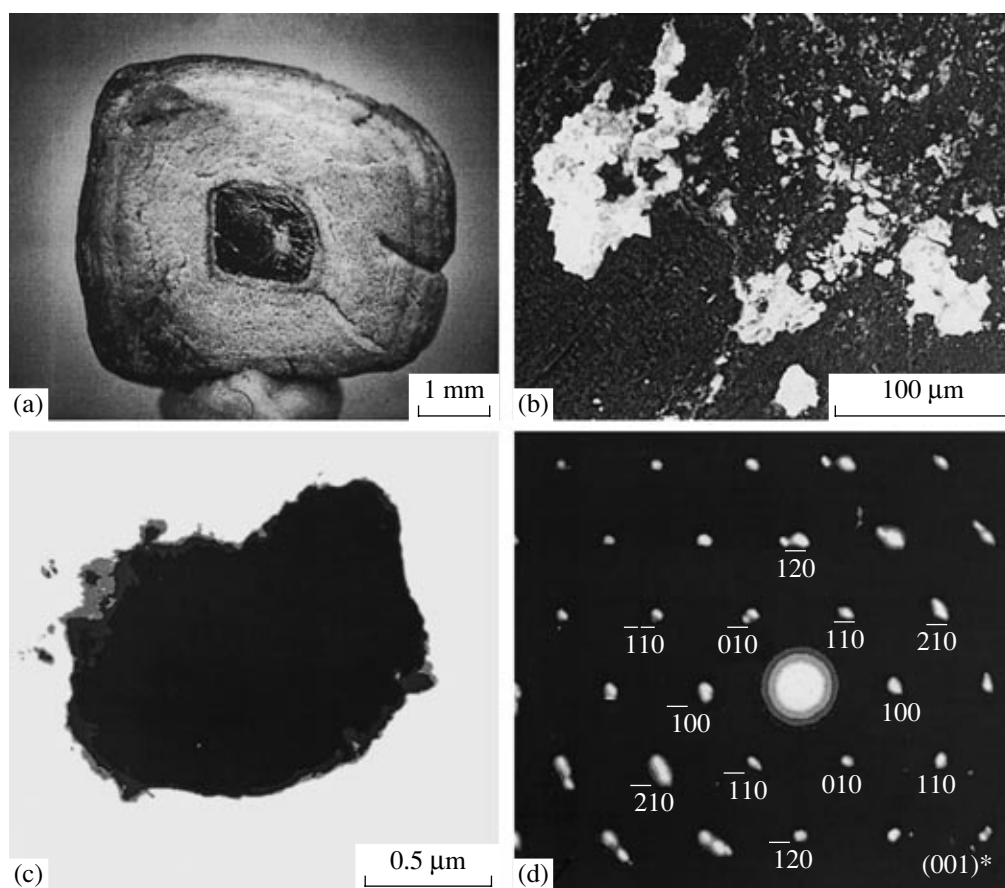
In the course of this study, we examined whitish gray crystals from the Yubileynaya kimberlite pipe (samples 1 and 2), gray and greenish yellow crystals from the Aikhal pipe (samples 3 and 4), black crystals from the Udachnaya pipe (sample 5), and orange-brown and brown-gray crystals from the Anabar placer (samples 5 and 6). All crystals were virtually opaque owing to the presence of numerous microinclusions and defects.

Before the study, each diamond crystal was broken in a small anvil, with precautions taken against the incorporation of metallic particles into the specimen. For this purpose, the diamond sample was wrapped in several sheets of dense paper. Then the fresh chips of relatively large fragments were sputtered with carbon to allow charge flow and were studied in detail on a JSM-5300 SEM (Jeol, Japan) equipped with a Link-ISIS energy-dispersive spectrometer (Oxford, England), which can determine the contents of chemical elements from Be to U, including oxygen.

The fine (dusty) fraction left after crushing the samples was placed into a test tube with distilled water and additionally crushed for 7–10 min using both a mechanical method and a UZDN-A ultrasonic dispersant. Afterwards, a few drops of the suspension were placed on a special coal-shadowed copper grid. After drying, the obtained specimens were examined with a JEM-100C TEM (Jeol, Japan) equipped with a Kevex-5100 energy-dispersive analyzer (United States) capable of qualitatively determining chemical elements from Na to U. The compositions of inclusions and their structure were determined by energy-dispersive spectra and electron diffraction patterns, respectively. This technique made it possible to obtain the most comprehensive information on micrometer- and submicrome-

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**Fig. 1.** (a) Internal structure of a cubic diamond crystal with numerous carbonate inclusions, (b) back-scattered electron image, (c) transmitted electron image, and (d) electron diffraction pattern of calcite microinclusions in cubic diamond.

ter-sized inclusions in diamonds. Some of these inclusions were retained on fracture surfaces, while others passed into suspension specimens.

In sample 1, the microinclusions of native Fe, Fe–Cr intermetallide, polydymite,  $\text{CaCO}_3$  phase, and apatite were identified with the analytical SEM method; in sample 2, microinclusions of native Cu and Fe, Fe–Cr intermetallide, Fe and Ni sulfides, chalcocite,  $\text{CaCO}_3$  phase, anhydrite, and chrysotile; in sample 3, microinclusions of native Fe, Cr, and Cu and Cu–Zn intermetallide; in sample 4, native Fe and Cu, Cu–Zn intermetallide, Zn sulfide, and Ce, Nd, La, and Pr oxides; in sample 5, native Fe, Fe–Cr intermetallide, magnetite,  $\text{SiO}_2$  phase, halite–sylvite solid solution, barite, intergrowths of dolomite and apatite, dolomite, and Na and Ba phosphates; in sample 6, native Fe, Fe–Cr intermetallide,  $\text{CaCO}_3$  and  $\text{SiO}_2$  phases; and in sample 7, native Fe, Fe–Cr intermetallide, magnetite,  $\text{SiO}_2$  phase, and barite.

Based on the composition and structural parameters determined by the analytical TEM method, Fe–Cr and Fe–Cr–Ni intermetallides and clinochrysotile were identified in diamond sample 1; in sample 2, native Cu and Fe, chalcocite, rutile, calcite, and clinochrysotile;

in sample 3, native Fe and Cr, ilmenite, and metamict (amorphous) zircon; in sample 4, native Fe and Cr and fluorite; in sample 5, native Fe, Fe–Cr intermetallide, ilmenite, rutile, apatite, and barite; in sample 6, native Fe, Fe–Cr intermetallide, pyrrhotite, and ilmenite; and in sample 7, native Fe, Fe–Cr intermetallide, calcite, and dolomite.

This study has shown that microinclusions of native metals (largely, native Fe) and Fe–Cr intermetallides are abundant in the imperfect diamond crystals of cubic habit. Similar inclusions of native metals were detected previously with the same technique in cubic diamonds from kimberlites [6] and placers [7] in northern China, as well as from polycrystalline aggregates and imperfect octahedral diamond crystals from various deposits [5 and references therein]. At the same time, the cubic diamond crystals contained much more carbonate microinclusions in comparison with other diamond varieties. Carbonate inclusions were especially abundant in cubic crystals from kimberlite of the Yubileynaya pipe, where the diamond crystals acquire a characteristic milky gray color. The wide growth zones with rounded boundaries are typical of cubic diamond crystals. A small, more perfect core almost devoid of inclusions is seen in the center of the crystal shown in

Fig. 1a. As can be seen from the BSE image (Fig. 1b), the round crystals are merely overfilled with calcium carbonate microinclusions 1–100  $\mu\text{m}$  in size. The electron diffraction pattern (Fig. 1d) indicates that these inclusions fit calcite in structure. The darker zones of these crystals are enriched in microinclusions of sulfides and native metals. It should be noted that sporadic  $\text{CaCO}_3$  microinclusions in the imperfect octahedral diamond crystals detected by the same method also fit calcite in structure [5]. Previously, carbonate inclusions in cubic diamond crystals were reported from the Yakutian deposits [3, 8], Botswana and Zaire [2], Brazil [4], and elsewhere on the basis of IR spectra. Separate inclusions of  $\text{CaCO}_3$  phases were also identified with microprobe and analytical electron microscopy in cubic diamonds from kimberlites of Botswana [2] and northern China [7].

In earlier publications, calcite microinclusions in natural diamonds were regarded as epigenetic formations. However, recent studies of isolated inclusions of calcite and other carbonates in perfect octahedral crystals have confirmed that these inclusions may be syngenetic with diamond [9, 10]. As was established in experiment, the disordered structural modification of calcite exists in the field of thermodynamic stability of diamond [11]. At the same time, the electron diffraction patterns of  $\text{CaCO}_3$  phase inclusions in the diamond crystals under study correspond to the common rhombohedral modification of calcite, probably because the earlier generations of carbonate (high-temperature aragonite or calcite) were transformed into the rhombohedral calcite at lower temperatures.

We detected a black diamond crystal of cubic habit with numerous magnetite microinclusions (sample 5). As was established previously, precisely magnetite is responsible for the black color of some coarse-grained diamond aggregates from the Yakutian deposits [12]. The physicochemical formation conditions of this crystal apparently differed from those of other cubic diamond crystals.

Thus, the cubic diamond crystals under study contain microinclusions of native metals, carbonates (calcite, dolomite), sulfides (pyrrhotite, polydymite), oxides (magnetite, ilmenite), phosphates, and some other minerals. The formation of such nonequilibrium mineral assemblage may be explained in terms of the hypothesis of [13], according to which diamond is crystallized in the process of injection of reduced fluids into more oxidized mantle rocks. Precisely these fluids might be a source of native metal microinclusions in diamonds.

The recent experimental studies have shown that diamonds can crystallize directly from carbonate [14] and silicate–carbonate melts. They can also be produced by the interaction of carbonates with silicates in

the presence of C–H–O fluids. The wide abundance of carbonate inclusions in cubic diamond crystals probably indicates their formation at a great depth with the participation of carbonate melts, in particular, in the course of injection of C–H–O fluids into the mantle rocks and the consequent carbonation of the mantle. Some of the studied cubic diamond crystals overfilled with carbonate microinclusions could be formed at that stage of interaction when a sufficient amount of carbonate melt has already been produced or in the carbonate-saturated zone of the fluid system.

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#### REFERENCES

1. G. P. Bulanova, Yu. P. Barashkov, S. B. Tal'nikova, and G. B. Smelova, *Natural Diamond: Genetic Aspects* (Nauka, Novosibirsk, 1993) [in Russian].
2. M. Schrauder and O. Navon, *Geochim. Cosmochim. Acta* **58**, 761 (1994).
3. A. M. Longvinova, O.K. BenDavid, E. S. Izraeli, et al., in *Extended Abstracts of VIII Int. Kimberlite Conference* (Victoria, 2003), CD-ROM.
4. A. A. Shiryayev, E. S. Izraeli, E. G. Haury, et al., *Geol. Geofiz.* **46**, 1207 (2005).
5. S. V. Titkov, A. I. Gorshkov, N. G. Zudin, et al., *Geochem. Int.* (in press) [*Geokhimiya* (in press)].
6. S. F. Vinokurov, A. I. Gorshkov, Yan Nan Bao, et al., *Geochem. Int.* **36**, 676 (1998) [*Geokhimiya* **36**, 759 (1998)].
7. A. I. Gorshkov, S. V. Titkov, S. F. Vinokurov, et al., *Geochem. Int.* **40**, 299 (2002) [*Geokhimiya* **40**, 340 (2002)].
8. Yu. L. Orlov, Yu. A. Dudenkov, and Yu. P. Solodova, in *New Data on Minerals* (Moscow, 1978), No. 27, pp. 109–112 [in Russian].
9. P. McDade and J. W. Harris, in *Proceedings of VII Int. Kimberlite Conference* (Cape Town, 1999), Vol. 2, pp. 557–565.
10. I. Leost, T. Stachel, G.P. Brey, et al., *Contrib. Mineral. Petrol.* **145**, 15 (2003).
11. K. Suito, J. Namba, T. Horikawa, et al., *Am. Mineral.* **86**, 997 (2001).
12. S. V. Titkov, N. G. Zudin, A. I. Gorshkov, et al., *Gems Gemol.* **39**, 200 (2003).
13. W. R. Taylor and D. H. Green, *Geol. Soc. Australia Spec. Publ.*, No. 14, 592 (1988).
14. Yu. A. Litvin and A. V. Spivak, *Materialovedenie*, No. 3 (84), 27 (2004).
15. Yu. N. Pal'yanov, A. G. Sokol, and N. V. Sobolev, *Geol. Geofiz.* **46**, 1290 (2005).