

GEOCHEMISTRY

Evidence for Evolution of Diamond Crystallization Medium in Eclogite Xenolith from the Udachnaya Kimberlite Pipe, Yakutia

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The recently obtained data on the superimposed character of diamonds in eclogite xenoliths have compelled us to consider the problem of diamond formation in the upper mantle from a new standpoint [1]. In [2], we reported the first results of the study of a unique diamond-bearing xenolith (length 18 cm, weight 6900 g) from the Udachnaya kimberlite pipe (Yakutia). The results testify to the superimposed character of diamonds (particularly, the chemistry of minerals) and suggest that diamond crystallized as a product of interaction between the high-K and C-bearing fluid with the ultramafic substrate [2]. The study of diamond-hosted inclusions from xenoliths and the comparison of their chemical composition with minerals of the xenolith groundmass would be of special interest for reconstructing conditions of formation, composition, and evolution of diamond. In this communication, we present results of the study of inclusions along with defects, impurities, and the internal structure of diamond from this xenolith.

We selected from the xenolith 44 diamond crystals 1–5 mm in size. The crystals with crystalline inclusions were polished along axes (110) and (100) until the exposure of inclusions. These inclusions were examined with a Camebax-micro electron microprobe. The internal structure of diamond crystals was investigated with cathode luminescence on a LEO 1430VP scanning electron microscope. The IR absorption spectra were recorded with a Bruker VERTEX 70 IR Fourier spectrometer to study the impurities and to estimate concentration of structural defects in diamonds from this xenolith.

The diamonds in xenoliths occur largely in the intergranular space and as inclusions in pyroxene and mica. They have the shape of differently distorted octahedra. Cathode luminescent images distinctly show two zones (core and shell). As a rule, the core is characterized by a weak luminescence, while the shell reveals a more intense luminescence (Fig. 1). The nonuniform zoning and distorted growth layers confirm the previous conclusion on the growth of the xenolith-hosted diamonds in a confined space.

According to the results of IR Fourier spectroscopy, diamonds from this xenoliths pertain to the IaA/B type, widespread among natural diamonds; i.e., they contain impurity centers A (a pair of nitrogen atoms that isomorphically replace carbon), B1 (four nitrogen atoms around a vacancy), and in some cases B2 (sheetlike defects oriented parallel to (001)) with linear dimensions varying from a few nanometers to a few micrometers [3]. The total content of nitrogen admixture in the crystals ranges from 40 to 800 ppm. Besides the absorption bands related to the main nitrogen impurity centers, additional lines 3310, 3237, 3150, 3107, 1405,

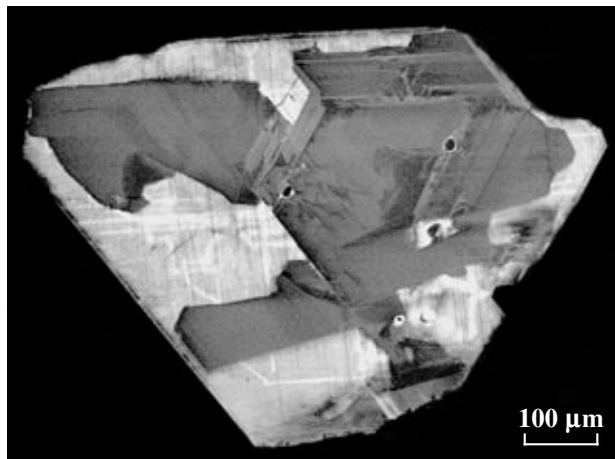


Fig. 1. Internal structure of diamond crystal from xenolith

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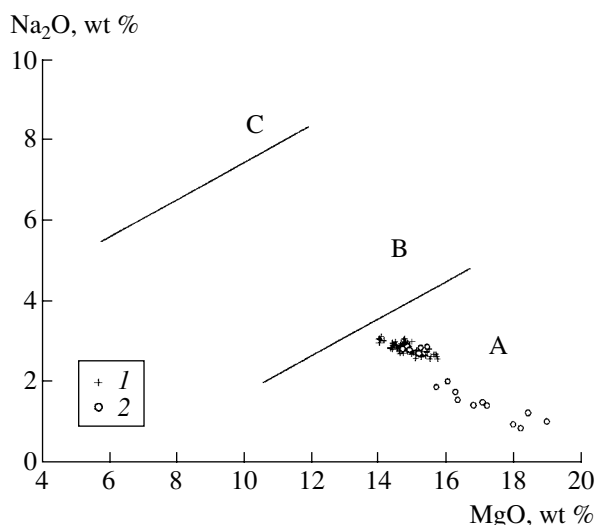


Fig. 2. Chemical composition of clinopyroxene from (1) inclusions in diamonds and (2) groundmass of xenolith.

and 1430 cm^{-1} related to the hydrogen admixture in the diamond crystals were recorded [4, 5].

The method of sequential polishing was used to open 60 inclusions in 35 crystals. Inclusions of clinopyroxene, garnet, sulfide, and phases of SiO_2 and CaCO_3 were identified by their chemical compositions. An olivine inclusion was also detected in one diamond crystal.

The sulfide inclusions in xenolith-hosted diamonds are composed of monosulfide solid solution based on pyrrhotite, which is typical of sulfide inclusions of eclogitic assemblage. The inclusions contain Fe (45.3–48.3 wt %), Ni (3.5–3.7 wt %), and Co (0.08–0.11 wt %). We previously described exsolution structures (pentlandite lamellae in the pyrrhotite matrix) in sulfides from the eclogite groundmass. The occurrence of pyrite in the groundmass and at boundaries between large pyrrhotite crystals is unusual for an eclogitic assemblage and probably indicates exsolution of the monosulfide solid solution (or melt).

The clinopyroxene inclusions are characterized by high Mg# value ($\text{MgO}/(\text{MgO} + \text{FeO}) = 0.82\text{--}0.83$) and relatively low Na_2O content. The content of Eskola Ca molecule reaches 10%. According to the geochemical classification proposed in [6], these inclusions correspond to the minerals from eclogites of group A. This fact had been established previously for clinopyroxene from the eclogite groundmass (Fig. 2). Pyroxenes from inclusions fall into the same compositional field as pyroxene from the groundmass. The main difference consists in the higher K_2O content (0.7–0.8 wt %) in clinopyroxene from inclusions in comparison with clinopyroxene from the matrix (<0.45 wt %). It should be noted that pyroxenes from the matrix contain phlogopite lamellae. This gives grounds to suggest that pyroxene from the matrix contained more potassium before the exsolution caused by pressure release.

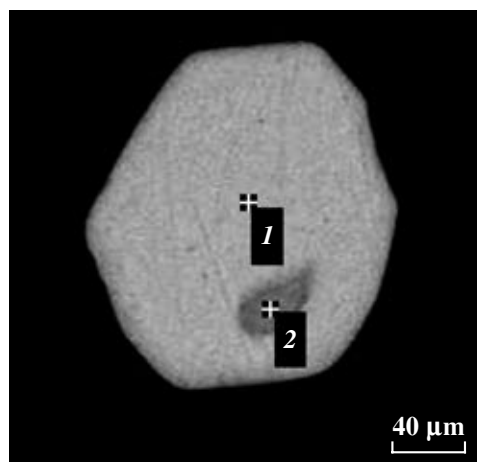


Fig. 3. Two-phase inclusion in diamond from xenolith (inclusion size $35\text{ }\mu\text{m}$). BSE image: (1) clinopyroxene, (2) coesite.

Two garnet inclusions found in diamonds also correspond to minerals of eclogite group A and are close in composition to the garnet from the groundmass. The inclusions are characterized by high Mg# and relatively low Cr_2O_3 content (table).

Among four inclusions of SiO_2 phase established in diamonds, two inclusions are represented by intergrowths with clinopyroxene (Fig. 3). By characteristic blue luminescence under the influence of microprobe beam, these phases are identified as coesite.

Numerous small (up to $5\text{ }\mu\text{m}$) oblong inclusions oriented parallel to the octahedron faces are detected in the cores of most diamonds (Fig. 4). Five such inclusions were exposed by polishing the plates, and the composition of solid phases in the inclusions was studied using the SEM equipped with an energy-dispersive X-ray spectrometer. As follows from the analytical data, the microinclusions are composed of CaCO_3 . The BSE images indicate the homogeneous composition of these phases.

An elongated olivine inclusion was found in the outer zone of one diamond crystal. The analysis of olivine (table) shows the high contents of Fo ($\sim 93\text{ mol}\%$), NiO (0.32 wt %), and Cr_2O_3 (0.03 wt %) that are typical of olivine in diamond-hosted inclusions [7].

It should be noted that neither olivine, nor quartz, nor coesite have been detected in matrix. The coexistence of SiO_2 phase (eclogite-type assemblage) with olivine (peridotitic assemblage) as inclusions in diamonds from one xenolith may reflect different stages of diamond growth and related change of chemical conditions in the crystallization medium. The mixed assemblage of mineral inclusions in diamond has only been described in rare cases [8–11].

Thus, we have found inclusions reflecting the mixing of peridotitic and eclogitic assemblages in diamond

Representative chemical compositions (wt %) of silicate minerals from inclusions in diamonds and from the groundmass of the eclogite xenolith

Oxide	Cpx-1 incl.	Cpx-2 incl.	Grt incl.	Ol incl.	Cpx gr.	Grt gr.
SiO ₂	55.94	56.27	41.87	41.48	56.70	42.80
TiO ₂	0.35	0.33	0.31	n.a.	0.22	0.11
Al ₂ O ₃	5.44	4.84	22.86	n.a.	4.98	23.40
Cr ₂ O ₃	0.06	0.07	0.06	0.03	0.06	0.06
MnO	0.09	0.11	0.41	0.12	0.11	0.47
FeO	2.84	3.17	8.89	7.16	2.57	9.34
MgO	14.65	15.30	20.90	51.14	14.70	20.70
CaO	16.60	16.42	3.42	0.02	17.50	3.17
Na ₂ O	2.76	2.61	0.08	n.a.	2.81	0.07
K ₂ O	0.78	0.54	n.a.	n.a.	0.44	n.a.
NiO	n.a.	n.a.	n.a.	0.33	n.a.	n.a.
Total	99.52	99.65	98.80	100.28	100.09	100.12

Note: (Cpx-1 incl.) Cpx-1 inclusion in diamond; (Cpx-2 incl.) Cpx-2 inclusion in diamond; (Grt incl.) Grt inclusion in diamond; (Ol incl.) Ol inclusion in diamond; (Cpx gr.) Cpx groundmass of xenolith; (Gr gr.) Grt groundmass of xenolith; (n.a.) not analyzed.

crystals from one xenolith. This finding may testify to the existence of specific mantle processes. In [11], the coexistence of peridotitic and eclogitic assemblages in diamond crystals from one xenolith is explained in the following way. According to phase diagrams, the liquidus temperature of eclogite is lower than the solidus temperature of peridotite up to a pressure of 12 GPa. Therefore, during the ascent of the mantle plume with diamond-bearing eclogite, diamond crystals may be detached from the initial eclogite substrate and transported to the peridotite substrate due to the selective

melting of eclogite and high density of diamond. However, this mechanism implies the transition from the eclogitic to peridotitic assemblage and is hardly applicable to the case when olivine and coesite inclusions occur in diamonds from the eclogite-hosted xenolith. According to the model [12], eclogites of group A are formed as a result of the reaction of peridotites of the mantle wedge with carbonatite and tonalite-trondhjemite melts of the subducted oceanic crust. The data obtained confirm the proposed model to a certain extent. The presence of K-clinopyroxene and CaCO₃

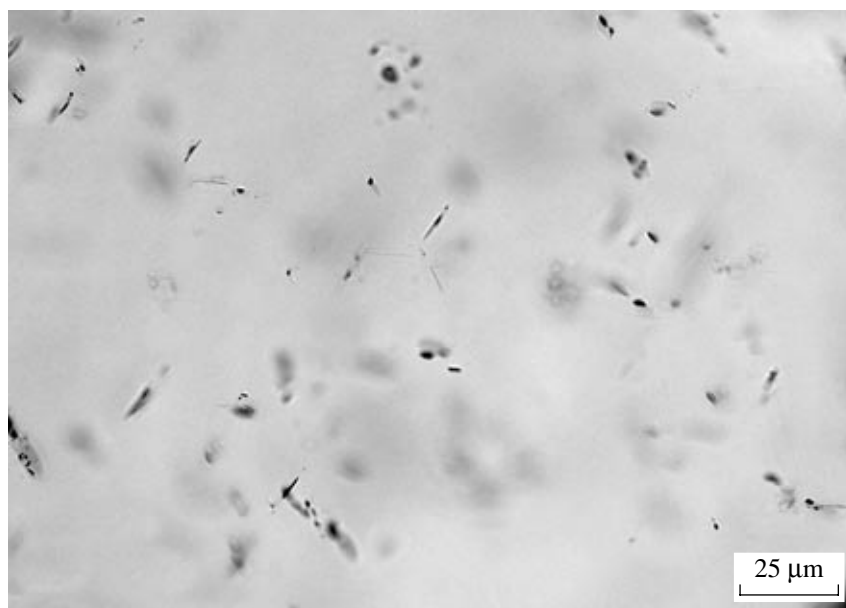


Fig. 4. Oblong inclusions in the central zone of diamond crystal (in transmitted light).

inclusions in diamond, phlogopite grains in the matrix, phlogopite lamellae in clinopyroxene of the eclogite groundmass, the arrangement of diamond crystals in the intergranular space and their morphology, and the development of glass and its replacement products around diamond crystals allow us to suggest that the diamonds crystallized during interaction of high-K carbonate-bearing fluid with ultramafic substrate [13, 14]. The CO₂ necessary for such metasomatic process could be derived from metasomatic carbonate-rich veins or subducted crustal carbonates. The enrichment of the xenolith-hosted diamonds in light oxygen isotope also supports participation of the subducted material in diamond formation. We believe that this mechanism of metasomatic reworking of peridotites could produce the eclogite assemblage. Thus, the olivine-bearing diamond crystal found in an eclogite xenolith is a relict material that was formed before the metasomatic transformation of the substrate or at the early stage of this process.

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