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The Nature of the Elongated Form of Diamond Crystals From Urals Placers

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The article presents the results of a study of the internal structure of highly elongated diamond crystals from placers in the Krasnovishersky district of the Urals. Very elongated crystals are found within diamond-bearing placer with unrevealed primary sources. Determining the conditions of such crystals formation can help one to determine the primary deposits type. There are three hypotheses for the formation of the elongated shape of such crystals: 1) crystals initially elongated along the <100> (strongly distorted octahedra); 2) individual crystals of columnar aggregates; 3) elongated crystals fragments. To study the internal structure, we selected three most elongated individuals of the 155 crystals samples. The study of the internal structure of selected crystals with the usage of photoluminescent (PL) tomography, cathodoluminescence (CL), and optical microscopy has shown that these samples are fragments of larger single crystals. CL imaging allowed to determine slip lines within the crystal's volume. The recorded PL spectra show the 912, 946, and 986 nm peaks, which are characteristic of crystals with plastic deformation. The revealed features are indicators of plastic deformation accompanying the destruction of the crystals. The significant dissolution following the destruction of the crystals led to the rounding of the vertices and edges of their fragments. Apparently, most of the very elongated crystals from placers with unknown sources are also highly dissolved isometric crystal fragments. The obtained results have shown that the deformation and dissolution of diamond crystals are related events characteristic of diamonds from hitherto undetected, but highly productive primary deposits.

***Key words*:** diamond; crystal deformation; cathodoluminescence; photoluminescence; Ural; placers

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Introduction. Perfect octahedron as a natural diamond crystal form does not occur in nature [9]. Natural crystals are asymmetric to varying degrees and are altered by post-growth dissolution, leaching, and deformation. Dissolution experiments [11] and analysis of the morphological diversity of natural crystals [8] show that the limiting form of the dissolution of diamond crystals is a curved rhombic dodecahedron – tetrahexaedroid (according to A.A.Kuharenko [6]). Sometimes very elongated drop-like crystals are found among natural ones [1, 6, 10]. Such individuals bear traces of strong dissolution and are found only in placers with the large amount of dissolved crystals of the Ural type. Such elongated crystals are described in deposits of the Urals Brazil, and Kalimantan [6, 10, 16] with still undetected primary sources. Therefore, the determination of the formation conditions of the elongated diamond crystals can help one to determine the primary deposits type of Ural-type crystals.

Three hypotheses of the formation of the initial elongated form of such crystals can be suggested: 1) crystals initially elongated along the <100> (strongly distorted octahedra); 2) individual crystals of columnar aggregates; 3) elongated crystals fragments [4]. Destruction by cleavage leads to the formation of fragments with elongation along <110>. To determine the nature of elongated crystals, it is necessary to study their internal structure. Cathodoluminescence (CL) imaging is the best tool for revealing the internal structure of diamond crystals [17]. Under the electron-beam excitation, luminescence occurs in the surface layer with a thickness of several µm and, therefore, CL is the most contrasting method for revealing the internal heterogeneities of diamond crystals. Under electron-beam excitation, there are various active luminescence centres: intrinsic and impurity defects, impurity–vacancy complexes [18]. CL imaging allows one to obtaining high contrast images of both growth inhomogeneities and the results of such superimposed processes as irradiation and plastic deformation. The internal structure can also be visualized by optical microscopy using anomalous birefringence and photoluminescence (PL) [14]. The best results can be obtained using the whole set of methods: optical microscopy, CL, and PL.

To determine the nature of the elongated form of dissolved crystals, it is necessary to study their internal inhomogeneities, as well as visualize their internal structure by CL and PL imaging. Sample preparation for such a study requires crystals polishing, providing a plane section for CL imaging and an optical window, which allows studying the PL inhomogeneities and optical anisotropy.

Samples and analytical techniques The diamond crystals for study were mined in modern alluvial sediments of the Krasnovishersky district, Urals. After a preliminary study of 155 crystals, the three most elongated samples were selected for further research (Fig.1). To reveal the internal structure, the crystals were polished on one side. Images in PL, reflected and transmitted light (in crossed polarizers, too) were obtained with a Leica M205 optical microscope. We got CL and surface topography images in secondary electrons (SEI) using CamScan MX2500 S scanning electron microscope. The PL spectra were recorded on a Renishaw inVia spectrometer at 785 nm laser excitation under 77 K. Internal inhomogeneities were also revealed by PL excited by 405 and 450 nm lasers, with 450 and 500 nm edge filters, respectively.

Results and discussion. Fig.1, *a* shows images of the studied crystals in reflected light. All three crystals are strongly distorted dodecahedroids (according to the Ural type). The crystal edges are highly smoothed, with signs of natural mechanical polishing [7]. CL images (Fig.1, *b*) of crystals 1 and 2 show that zoning is directed along the elongation. There are no closed zone contours, that could indicate that elongation formed during the crystal growth. Also, there is no transverse zoning typical for the crystals being the part of columnar aggregates. In the CL image of crystal 3 no growth zoning is observed. All features of sample 3 visible in the CL images are typical of diamond crystals with post-growth deformation [12, 17]. In anomalous birefringence, crystals 1 and 2 are characterized by a high level of residual stresses that do not allow visualization of their internal structure. In crystal 3, severe plastic deformation led to the appearance of a very contrasting zonal optical anisotropy along the {111} planes. Five systems of parallel lines (three light and two dark) are distinguished in the CL image of this crystal. There are three systems of slip planes {111}, caused by plastic deformation in diamond and marked by the luminescence of nitrogen-vacancy centres H3 [12, 13, 17]. Dark lines could be polishing defects. An additional indicator of internal stresses is the crystal destruction into three fragments during polishing.

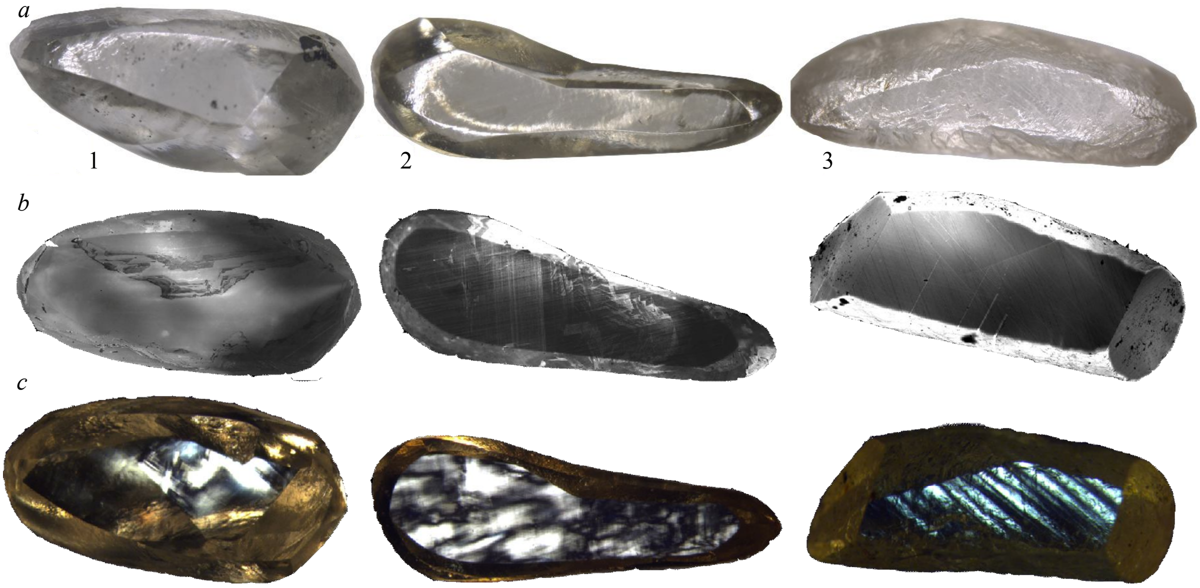

Fig.1. Images of the crystals under study: *a* – in reflected light; *b* – in cathodoluminescence; *c* – in transmitted light in crossed polarizers

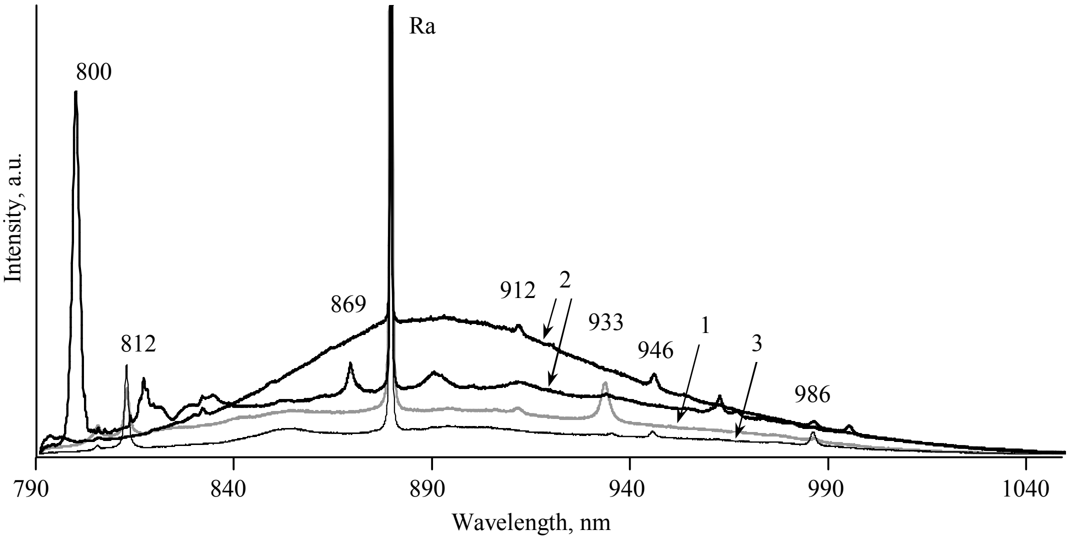

Fig.2. The PL spectra of the studied crystals under excitation of 787 nm laser (at 76 K).
Ra – Raman line

The undersurface layers of crystal 3 have bright luminescence due to nitrogen-vacancy centers of radiation nature [3]. Such luminescence is observed in individual parts of crystal 2 and only in one zone of crystal 1.

A sensitive indicator of the plastic deformation in diamonds is PL in the range of 8000-1050 nm. Upon excitation of 785 nm in the spectra of crystals with signs of plastic deformation it could be recorded doublets of 890 and 900.3 nm; 918 and 930 nm; 946.5 and 961.5 nm; 981 and 994 nm or a set of 921, 946, 961.5, 986, 1020 nm lines [2]. The relative line intensities in these systems can vary widely [2].

Recorded spectra (Fig.2) show 912, 946, and 986 nm peaks characteristic of crystals with signs of plastic deformation [2]. These lines are an additional indicator of plastic deformation accompanying the crystals destruction. Also, set of luminescence lines 800, 812, and 869 nm are distinguished on the spectra. The nature of these luminescence systems has not yet been studied [13, 18]. We previously observed these luminescence bands in the spectra of cubic habit crystals with <100> growth pyramids. They are probably due to Ni-containing centers. Apparently, sample 2 is a fragment of a crystal with a complex internal structure.

Let us consider three hypotheses of the initial elongated shape of crystals in relation to the obtained results. The first formation hypothesis, consisting in the distortion octahedra does not match the obtained results. In the internal structure of the studied crystals, growth zones for such single crystals were not revealed. The second hypothesis suggests that elongated crystals are parts of columnar aggregates [4]. Polycrystalline structure is not uncommon for diamonds. So, diamonds of the VII and VIII varieties according to the classification of Yu.L.Orlov are widespread in placers in the North of Yakutia. Such diamonds are precisely aggregates of disoriented crystals. Such crystals are apparently formed due to split resulting from the high concentration of nitrogen isomorphic impurities or high content of inclusions. Elongated individuals can be formed by the destruction of crystals with split growth. Also in some deposits, there are intergrowths with elongation of individual crystals. When they are destroyed, elongated crystals can be formed. A third possible hypothesis suggests that elongated diamonds are fragments or large crystals. By all indications, the studied samples correspond to fragments of larger single crystals. Apparently, the primary destruction of single crystals, accompanied by plastic deformation, and the subsequent dissolution of fragments is the main pathway for elongated crystals formation.

Among diamonds from placers with unrevealed primary deposits of the Urals, Anabar-Olenek interfluve, and Kalimantan [16], the majority of crystals have signs of strong dissolution, and there are also many crystals with signs of plastic deformation. Such signs may be a brown, pink or purple colour, especially in the PL and CL spectra, as well as characteristic striae on their faces, which appears upon dissolution. Deformation and dissolution of crystals are presumably related events that indicate the formation features of their primary deposits.

This relation also appears in some diamonds from primary deposits. So, in the kimberlites of the M.V.Lomonosov deposit within the Arkhangelsk diamondiferous province, there are three groups of crystals formed under different conditions: 1) relatively high-temperature slightly dissolved crystals; 2) crystals with strong dissolution and an average value of the model temperature; 3) low-temperature crystals of cubic habit, frequently without traces of dissolution. The polygenic nature of diamonds from the M.V. Lomonosov deposit is confirmed by the results of a xenoliths study [15]. In the deposits of the Mirny kimberlite field, there are very few dissolved crystals, as well as crystals with signs of plastic deformation [5]. The Zapolyarnaya kimberlite pipe contains a high proportion of diamonds with signs of plastic deformation, dissolution, and corrosion [5]. Apparently, the presence of diamond in consolidated peridotites and eclogites under deformation precedes the dissolution of crystals. It can be assumed that deposits of the Mirny kimberlite field are characterized by rapid removal of crystals without significant deformation and melting of diamondiferous rocks. A long stage of deformation and fluid saturation of diamond-bearing rocks is, on the contrary, characteristic for primary diamond deposits of unknown genesis, which are the source of Ural diamond placers.

Conclusions. We revealed signs of high mechanical stresses in the elongated crystals. We did not find any signs of growth nature of elongation. Signs of high stress are: 1) optical anisotropy; 2) bright lines of slip planes detected in CL images and crossing the entire crystal; 3) PL bands in the range of 900-1020 nm, characteristic of diamonds with plastic deformation. Thus, according to the internal structure study, it can be argued that the studied crystals are fragments of larger deformed diamond crystals, and their final shape is the result of strong dissolution. Apparently, most of the very elongated crystals from placers with unknown sources are also highly dissolved fragments of larger crystal. The obtained results show that deformation and dissolution of crystals are presumably related events that indicate the formation features of their still unrevealed primary deposits.

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