The study of the ontogenesis of crystals of the Ural type diamonds by the method of IR-spectrometry

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Abstract. The collection of the Ural, Anabar and Brazilian diamonds conducted research by infrared spectrometry method. It was found that a diamond with a low degree of aggregation of nitrogen defects composing the crystals of the later generation from mantle eclogite xenoliths and outer zones of the greater part of the crystals from deposits of kimberlite-lamproite type is missing or is poorly developed in the crystals of the Ural type. Conclusions about the thermal conditions of the Ural diamonds formation and their possible affinity to the specific and type of original sources.

1. Introduction

The Ural type diamonds, combining rounded crystals of this mineral, for which flat-cut forms of the most diamonds from the deposits of kimberlite-lamproite type are not characteristic, attracted attention by specific morphological features and high yield of jewelry differences. The most important characteristic of the Ural type diamond deposits is the lack of a reliable set of the original sources of placers, despite the fact that many of them are being developed more than 100 years. A range of assumptions about the possible types of original sources of these placers is rather great: from ancient completely eroded kimberlite bodies to the modern diamondiferous tuffisites. In the absence of reliable information of original sources and the rarity of finds of minerals-satellites in these placers, the diamonds can be the most important sources of information about the genetic characteristics of potential original sources. Therefore, studies based on the analysis of the crystal-chemical characteristics of this mineral can contribute to the understanding of the formation processes and question decision of possible indigenous sources of the Ural type diamonds.

One of the most important crystal-chemical diamond characteristics is the presence of structural impurities of nitrogen. To identify the concentration and location of nitrogen in diamond crystals the method of IR-spectroscopy has been successfully used. Scientists have made a great contribution to the development of spectroscopic methods of the study of diamond crystals: Kaminskii F V, Sobolev E V, Klyuev Y A, Boyd S R, Taylor W R, Woods G S. A significant amount of research of diamond crystals using the methods of IR-spectroscopy was made by Bogush I N, Vasiliev E A, Kopchikov M B, Palazhchenko O V, Petrovsky V A, Khachatryan G K, Laiginhas F and others, but the Ural type diamonds were insufficiently studied by this method. Therefore, the method of IR-spectroscopy was chosen as the primary method in this study because it allows to identify patterns of occurrence of nitrogen defects in diamond crystals without destroying mineral individuals quantitatively and with a high enough productivity to determine the concentration of nitrogen in the diamond, its shapes in the
form of A and B1 defects. In the present work under the patterns of the nitrogen defects in diamond crystals refers to the quantitative determination of the nitrogen concentration in diamond, in various forms of its presence, zone identification of their placement within the crystals, the setting of statistical regularities of allocation of diamond crystals in their content of various nitrogen defects.

Conducted research of extensive and representative collection of the Ural type diamonds from the different regions have allowed to reveal regularities of occurrence of the nitrogen defects in the studied crystals and to give them the correct genetic interpretation. These results are the basis for a more balanced approach to the analysis of the possible genetic types of indigenous sources of placers of the Ural type diamonds, which will contribute the choice of optimal search methods or make a reasonable decision about inexpediency of identifying the indigenous sources as potential industrial fields.

The work purpose is to identify regularities of occurrence of nitrogen defects in the crystals of the Ural type diamonds from the various regions.

2. Research techniques

The materials were obtained in the course of studying of the diamond collections of Mining Museum, Department of Mineralogy of St. Petersburg University, Komi Research center of the Ural branch of RAS, the research materials of the Ural diamonds collection of All-Russian scientific research geological Institute and information from published sources. On the basis of the spectroscopy laboratory of St. Petersburg Mining University has been studied the collections of the Ural diamond crystals - 173 pcs., Anabar-Olenek interfluves - 164 pcs., Brazil - 179 pcs.

The determination of the type and content of nitrogen defects in diamond crystals was carried out by infrared spectroscopy using a FTIR Vertex 70 with IR-microscope Hyperion 1000. The photo luminescence spectra were recorded on a modular Fluorolog 3 spectrophotometer by Horiba – Jobin Ivon, equipped with Olympus microscope. Study with the method of optical spectroscopy was carried out on two-beam spectrophotometer UV-2550PC Shimadzu. Processing the results of the analyses the statistical methods have been used (Microsoft Excel, Statistica 7.0). Processing and interpretation of the spectra was carried out with "Spector Examination".

In diamond, the absorption in the range of 1500-3500 cm\(^{-1}\) can be used as an internal standard in the study of crystals of small sizes or irregular shapes for the purpose of calculating their thickness and considering the reflection. Spectra of optical density have been normalized at its own two-phonon absorption. The absorption coefficients were taken as internal standard at frequencies of 1973 cm\(^{-1}\) and 2500 cm\(^{-1}\), accordingly \(k_{1973} = 12.5 \text{ cm}^{-1}\), \(k_{2500} = 4.9 \text{ cm}^{-1}\)[2]. Please note that the method of spectra normalization at the optical density in two-phonon absorption now is common and does not require preliminary thickness measurement of the studied sample, which significantly reduces and simplifies the measurement procedure.

The concentration of nitrogen was calculated with the program of visual selection on the standard spectra absorption A, B1 and C, according to the certain coefficients of proportionality [3], [4]. The relative errors of determination of A and B1 defects concentration do not exceed 10% [5], depending on the shape, thickness, presence of inclusions, surface quality of the sample.

3. Research techniques

Ontogenic studies of BeskrovanoV V, who for the first time systematically studied their internal structure on a large and diverse sample of naturally oriented polished plates cut from diamond crystals, allowed us to consider the history of diamond formation within the ontogenic cycle – a set of mineralogical events, including the origin, growth and subsequent changes in crystals [6]. In the diamond crystals, he identified three main ontogenetic areas: central, intermediate and peripheral, which had specific constitutional and anatomical features. BeskrovanoV found that for diamonds formed at the intermediate stage, a characteristic feature of anatomy was the appearance of zoning often with sequence of dissolution and regeneration zones. As the most important features of the diamonds of the Ural placers, he considered the curved forms of crystals and the intensive B2
system in IR absorption and assumed that the internal morphology (anatomy) of the Ural diamonds probably does not contain a peripheral region.

The analysis of the literature data on the peculiarities of the appearance of nitrogen defects in diamond, composing the peripheral ontogenic region, indicates the predominance of A-defects in it with a decrease of the nitrogen content in the form of B1 defects to 10–20%. The late generation crystals from eclogitic mantle xenoliths, which are also characterized by a low degree of aggregation of nitrogen defects [9][8], can be considered as a standard of diamond that is typical for this region [8]. IR spectroscopic studies of crystals belonging to different generations from eclogitic xenoliths of the Udachnaya pipe revealed their significant differences in the peculiarities of nitrogen defects (figure 1).

![Figure 1](image_url)

**Figure 1.** The ratio of nitrogen content and the degree of aggregation of nitrogen: ○ – for the first, × – for the second diamond generation according to table 1 from the work of Spetsius, et al. 2012 (a); from eclogitic xenolith UD 111/02 of the Udachnaya pipe according to Stepanov et al. 2007 (b).

The results obtained by us on the peculiarities of the appearance of nitrogen defects in diamond crystals of the Ural type revealed for internal (figure 2, a) and external (figure 2, b) crystal zones from the deposits of the Urals, Brazil and the Anabar-Olenek interfluve [1] were compared with the results of the determination of these parameters in crystals of two generations from eclogitic xenoliths of the Udachnaya pipe, the late generation of which is considered as a standard for diamond composing the peripheral ontogenic region (figure 2). From the analysis of these diagrams it becomes obvious that the fundamental difference of the whole set of crystals of the Ural type is the absence of crystals or separate zones in it composed by a diamond corresponding to the parameters of nitrogen defects of the peripheral ontogenic region. Consequently, this area was either not presented at all, or it was substantially dissolved at the final stage of their ontogenesis.

The parameters of nitrogen defects in the crystals of the first generation of eclogites fall into the region typical for diamonds of the Ural type (figure 2), which confirms the assumption made by Beskrovanny about the predominance of the intermediate ontogenic region in the internal structure of the Ural diamonds.
Figure 2. Comparison of parameters of nitrogen defects in diamonds of the 1st (●) and 2nd (●) generations from mantle eclogite xenolith (according to Stepanov et al. 2007) and diamonds of the studied placers: ● - the Urals; ○ - Brazil ○ - Anabar-Olenek interfluve.

Comparison of diamonds of the Ural type with crystals from kimberlite bodies for which the peripheral zone is typical (figure 3), allows assuming that this zone nevertheless was shown in diamonds of the Ural type, but at the final stage of their formation was dissolved. The repeated appearance of dissolution and regeneration process of these diamonds is clearly reflected in their anatomy [6] and morphology [7].

The conducted researches of various material of the Ural type diamonds covering placer deposits of the Urals, Brazil and Anabar-Olenek interfluve confirmed the assumption made earlier about crystal prevalence among them in which the peripheral octahedral zone is absent or poorly shown, but which is the main on a number of fields in kimberlites where composes the most high-quality part of crystals of diamond.

Figure 3. Comparison of the appearance parameters of nitrogen defects of diamonds from different regions: ● – the Urals; ○ – Brazil; ○ – Anabar-Olenek interfluve and indigenous sources: brown dotted line – the Arkhangelsk province; yellow dotted line – Malo-Botuobinsky district; green dotted line – Daldyn-Alakit district; red dotted line – diamonds of the first generation; red line – diamonds of the second generation of the eclogite xenolith [9]; blue dotted line – diamonds of the first generation; blue line - diamonds of the second generation of the eclogite xenolith [8].
4. Conclusions
The comparative analysis of morphological features of diamonds of the Urals, Anabar-Olenek interfluve and Brazil allows to carry them to the same Ural type. They are also united by a wide range of the degree of aggregation of nitrogen defects with a predominance of diamonds with a close ratio of A and B1 defects. The Ural diamonds have a certain specificity, in which there are practically no crystals with a low (less than 500 ppm) nitrogen content; Brazilian diamonds, including crystals containing no A-defects and diamonds of Anabar-Olenek interfluve, some of them have abnormally high (2600 ppm) nitrogen content. Among the Brazilian and Anabar diamonds there are crystals that do not contain B2-defects, which is associated with their destruction at the highest temperature annealing, which is not observed for the Ural diamonds.

A comparison of various indigenous diamond deposits indicates a broad general range as their nitrogen content and degree of aggregation of nitrogen defects, but for the specific indigenous diamondiferous objects the values of these parameters vary over a much smaller range. Therefore, a very wide range of the degree of aggregation of nitrogen defects (0-100%) for crystals of the Ural type does not allow to tie placers containing them with individual indigenous sources of kimberlite-lamproite type. It is necessary to consider the possibility of feeding these placers from many sources, which can be both intermediate reservoirs and various indigenous objects of kimberlite-lamproite type. However, it is difficult to assume the presence in a particular specific and limited area of the alluvial region of the entire spectrum of kimberlite-lamproite bodies, which can provide a wide range of content and degree of aggregation of nitrogen defects typical for diamonds of the considered deposits, and, therefore, it is impossible to exclude the presence of a specific and yet undetected type of indigenous sources, diamonds of which have a very wide range of content and degree of aggregation of nitrogen defects. It is revealed that the principal difference of the whole set of crystals of the Ural type is the absence of crystals or separate zones in them, composed by diamond, corresponding to the parameters of nitrogen defects of the peripheral ontogenic region allocated by Beskrovanov. Consequently, this area was either not presented at all, or it was substantially dissolved at the final stage of ontogenesis. This feature should be taken into account in the development of geological and genetic models of the formation of the Ural type diamonds.

References
[1] Vasiliev E A, Kozlov A V, Nefedov Y V 2013 A comparative analysis of Anabar, Brazil and the Urals diamonds by method of infrared spectroscopy (The notes of the Mining Institute) T 200 pp 167-171
[2] Klyuev Y A 1971 The Intensity of stripes in the IR spectrum of absorption of natural diamonds (Diamonds) vol 6 pp 9-12
[3] Boyd S R, Kiflawi I, Woods G S 1995 Infrared absorption by the B nitrogen aggregate in diamond (Phil Mag B) vol 72 pp 351-361
[4] Boyd S R, Kiflawi I, Woods G S 1994 The relationship between infrared absorption and the A defect concentration in diamond (Phil Mag B) vol 69 pp 1149-1153
[5] Khachatryan G K 2003 An improved method of estimating concentrations of nitrogen in diamond and its application (Geological aspects of the mineral resource base of "ALROSA". Modern state and prospects of solution) pp 319-322
[6] Lavrenko S A, Korolev I A 2018 Analysis of Cambrian clay cutting during Saint-Petersburg subway construction (Gornyi Zhurnal) vol 2 pp 53 – 58
[7] Rakin V I 2013 Morphology of the Ural type diamonds (Ekaterinburg) p 396
[8] Spetsius Z V, Kovalchuck O E, Bogush I N 2012 Properties of diamonds in xenoliths from kimberlites of Yakutia: implication to their origin and exploration (Materials of 10th International Kimberlite Conference Bangalore) p 5
[9] Stepanov A S, Shatsky V S, Zedgenizov D A, Sobolev N V 2007 The causes of diversity of morphology and impurities of diamonds from eclogites of the Udachnaya pipe (Geology and Geophysics) vol 48 № 9 pp 974-988