Methodological Aspects of Diamond Diagnostics for Solving of Geological Interpretation Problems

V A Pakhomova¹, V A Solyanik¹, V B Tishkina¹

¹Far Eastern Geological Institute FEB RAS
159, Prospekt 100-letiya, Vladivostok 690022, Russia

E-mail: pakhomova@fegi.ru

Abstract. The article reveals the results of the long-term studies for diamond crystals found on the territory of Primorye in placer samples. The crystals’ optical and gemological characteristics, morphology, and the composition of micro inclusions were examined with the microprobe method. Special attention was paid to the study of the photoluminescence spectra of the diamonds, since it is one of the relatively new methods which enables to determine the origin of the diamonds. The rapid development of technologies for the synthetic technical-grade diamonds production has expanded the usage of rough diamonds, including the field of geological exploration. It is widely known that the natural diamonds of technical quality were initially used for making diamond crowns (the end of the XIX century and the beginning of the XX century). Synthetic diamonds are also used to produce crown bits, since the volume of their production is several times higher than the volume of the natural diamonds extraction. The synthetic diamonds properties are similar to those of the natural ones; synthetic diamonds are equal to natural diamonds in abrasive qualities, and the most important thing is that they have a lower processing cost. During the long-term exploitation of drilling crowns, diamond grains may fall out of their seats and be lost. This creates a real risk of natural objects contamination while searching new indigenous diamond deposits. The paper gives an algorithm of research conduction that allows to distinguish between natural and synthetic diamonds, prevent incorrect conclusions and to increase the validity of natural diamond findings in placer deposits.

1. Introduction
The questions of diamonds origin, which have always attracted the attention of both industrial geologists and scientific researchers have always been and will continue to be a priority. Since the fine diamonds (700 microns - 2 mm) are being found on the vast territory of the Primorsky region with increasing frequency, this topic has been relevant for several decades. The models suggesting that diamond deposits originated not only from the kimberlitic complexes but from the ones bearing ultrabasites, eclogite-ultrabasites, ultrabasic volcanic formations, metamorphites, carbonatites, and tuffizite facies of mantle kimberlite-lamproites have acquired a special significance among the theories in the scientific literature devoted to the corresponding subject [2, 3, 4, 5, 6, 7, 8, 9, 10]. In spite of the fact that these studies are undoubtedly important and necessity for developing one of the fundamental problems of mineral formation, it is not possible to compare the results of published data, since the researchers use different methodological approaches and methods of posing questions in accordance with their personal preferences and selective research methods to answer these questions.
2. Research and results
The objective of this work is to justify the new approaches to the search of diamond deposits, typification and identification of the exploration prospects, and also to improve the methods of diamond deposit prospecting by means of applying stricter attitude to the diagnostics of diamonds.

The authors of the article also found fine diamonds in gem washings of various regions in Primorye (ballas, cabonado, yellow cuboctahedrons) during the field work. The studies of the collection (shown in Figures 1 and 2), were conducted to exclude the technogenic origin of these finds.

Diamonds in the collection are divided at least into three types: cubo-octahedrons, which make up a clear percentage majority in the terms of volume, dark gray almost opaque polycrystalline carbonados (variety X, according to the classification of Yu. L. Orlov), black, light-gray, greenish semi-transparent dodecahedrons (variety VI according to Yu. L. Orlov, Ballas). The morphology of yellow synthetic diamond crystals is simpler than the morphology of those contained in natural diamonds [11, 12], which is caused by the short history of their formation. The variety of crystals grown by means of HTHP methods and CVD technologies is known to be limited by a combination of several simple forms, they are as follows: octahedron, rhombododecahedron, cube, and rarely tetragontrioctahedron [13].

Figure 1. Morphology of typical diamonds from Primorye region.

Minerals and microinclusions contained in them were studied in the Analytical Center of the FEGI FEB RAS. Standard Gemological instruments were used for this purpose: the NIKON ECLIPSE LV100POL optical polarizing microscope; the JXA-8100 four-channel microanalyzer manufactured by Jeol Co Ltd; and the LabRamHR 800 Raman-scattering spectrometer.

The first results of the collection materials study led to the following conclusions: 1) crystals and their fragments belong to the same grain-size class: the prevailing size is from 500 microns to 2.0 mm; 2) there is similarity of the crystal habit: yellow cuboctahedrons predominate. Dark gray almost opaque polycrystalline carbonados, black, light-gray, greenish semi-transparent dodecahedrons (ballas) are less common; 3) stones become bright green or yellowish-green in ultraviolet rays (365 nm); 4) films of copper, inclusions of nickel and cobalt were found in diamonds during the microprobe analysis [14]. The research of the collection samples is complemented by studying of photoluminescence (PhL) in this work.

Photoluminescence is a traditional method of studying carbon materials. The importance of this research method is due to the fact that the scientific community is greatly interested in the study of optical properties of materials with diamond lattice, in the problem of diagnostics of the diamond origin, as well as in engineering color centers in diamonds.

We have conducted the research of carbonado and yellow cuboctahedrons from the gem washings collection with J-Screen Device Developed by MAGILABS HRD Antwerpen (EXA)™. The luminescence spectrometry unit in this instrument is joined with the Raman scattering spectrometer purposed for detecting natural diamonds. Device (EXA)™ is for samples with weight not less than 0.005 carats, but there is no upper size limit.

Hence in this work we used three methods of analysis: Raman scattering, photoluminescence and spectroscopy in visible band. The apparatus allows to determine both the origin and the method of
synthesis or of diamond treatment. There is no discussion of data referring to such determination diamonds between natural and synthetic in literature sources available, except for the works [15, 16].

Figure 1a shows the PhL spectrum characteristic for the largest diamond grains of the greatest size (50-1000 nm). The spectral curve is bell-shaped. An intense broad band is observed with its maximum in the wavelength range of 515 - 550 nm. The bandwidth marker is an important parameter of the spectrum (that is width of the spectrum measured at its half-height). These features of the spectrum mentioned are typical both for growth pyramids and diamonds grown by the HPHT-synthesis [17].

![Figure 1A. Typical photoluminescence spectrum of the yellow cube-octahedron.](image)

A less intense peak of the spectrum (wave number is equal to about 870 nm) can be associated with the distribution inhomogeneity of impurity defects of nickel or nickel-nitrogen complexes of variable structure according to data from the list [18], which is consistent with the detection of nickel in diamond by means of usage microprobe analysis in our case.

![Figure 2. Carbonado crystal.](image)

The photoluminescence spectrum of natural carbonado from the collection is shown for comparison (Figure 2, 2A). The spectrum contains principally different excitation bands: narrow background-free lines observed in the spectrum at values of 415, 425, 455, and 480 nm and a number of oscillating repetitions. A significant difference in the luminescence intensity of the compared spectra (figures 1A and 2A) deserves a special attention, and according to the data [15] this indicates that this sample may be classified as natural along with the prospectivity of the method and about necessity of collecting of data about the properties of natural and synthetic diamonds.
3. Conclusion

The paper considers the problem of the risk of the concentrate samples contamination with synthetic diamonds and suggests criteria allowing to avoid mistakes in the process of apparent detection of natural diamonds sources due to the possibility of man-made contamination.

The study of the diamonds collection which embraces concentrates from various regions of Primorye showed that most of the samples belong to synthetic diamonds grown by the HPHT method. The synthetic origin of the collection samples is proved by morphology of their crystals, uniformity of the grain-size class, gemological characteristics, composition of inclusions, and the nature of photoluminescence (FL). We believe that the method of the diamond deposits search must be improved with stricter attitude to the diamonds diagnosis. It should be noted that the HPHT method is the earliest among the main mass production methods of the technical diamonds (high-pressure high-temperature synthesis in molten metals (HPHT), chemical vapor deposition (CVD) and detonation synthesis of nanodiamonds (DND). In 1954 G.T.Hall from the General Electric company first successfully crystallized diamond at high pressures, using an efficient high-pressure device which he developed himself and called the "belt". Ni, Co, and Fe [19], which are still the most popular, were used as solvent metals by the General Electric Company. The size of HPHT diamonds usually ranges from fractions to several millimeters, which is determined by the size of the cell itself and its ability to maintain the stable conditions of pressure and temperature. The existing variety of natural and man-made diamonds requires taking the new reports about new diamond bearing sites, especially those presented as new genetic types [20], seriously. At the current level of development of diamond synthesis technologies, they can be considered to be reliably detected after comparison with all well-known types of synthetic diamonds and demonstration of appropriate proofs of difference. Diamond finds in non-conventional natural sites should be checked for their authenticity including reproducibility by independent diamond experts, since the absence of these studies may lead to groundless conclusions.

4. References

[1] Bulanova G P, Barashkov Yu P, Talnikov S B and Smelova G B 1993 Natural diamond: genetic types Responsible editor academician N V Sobolev Novosibirsk: Science p 168 (in Russian)
[2] Biryukov V M, Gornov P Yu, Ivanov G I and Kosygin Yu A 1989 First diamond discovery in deep xenoliths of the eastern outskirts of the Siberian Platform J. Doklady Academii Nauk SSSR [Doklady Academy of Sciences USSR] 305 5 pp 1190–93 (in Russian)

[3] Biryukov V M, Kosygin Yu A 1989 About the discovery of accessory diamonds in drusite-eclogites of some banded complexes of the Baikal region J. Doklady Academii Nauk SSSR [Doklady Academy of Sciences USSR] 306 5 pp 1204-09

[4] Gurulev Yu T, Matyunin A P, Sakhno V G, Dmitruk S I and Zimin S S 1995 Kimberlite-like diamondiferous rocks of the northern part of the Khankaisk massif (Primorye) J. Tikhookeanskaya Geologiya [Pacific Geology] 14 5 pp 103–08 (in Russian)

[5] Dobretsov N L, Tenissen K and Smirnova L V 1998 Structural and geodynamic evolution of diamond-containing metamorphic rocks of the Kokchetav massif (Kazakhstan) J. Geologiya i Geofizika [Geology and Geophysics] 39 12 pp 1645–66 (in Russian)

[6] Izosov L A, Konovalov Yu I, Vrublevsky A A and Emelyanova T A 2000 Prospects for the diamond potential of East of Asia and the marginal seas J. Tikhookeanskaya Geologiya [Pacific Geology] 19 3 pp 78–96 (in Russian)

[7] Malyshev Yu F, Karsakov L P and Nosyrev M Yu 1995 Deep structure of diamondiferous regions of East Asia and prospects of the Amur region J. Tikhookeanskaya Geologiya [Pacific Geology] 14 6 pp 53–73 (in Russian)

[8] Sakhno V G, Matyunin A P and Zimin S S 1997 Kurkhan diamondiferous diatreme of the northern part of the Khankaisk massif: structure and composition of rocks J. Tikhookeanskaya Geologiya [Pacific Geology] 16 5 pp 6–59 (in Russian)

[9] Silaev V I, Karpov G A, Rakin V I, Anikin L P et al 2015 Diamonds in the products of the fissure Tolbachinsky eruption of 2012–13 Kamchatka Bulletin' Permskogo universiteta [Perm University Bulletin] 1 26 pp 6–27 (in Russian)

[10] Rybalchenko A Ya, Rybalchenko T M and Silaev V I 2011 Theoretical foundations of forecasting and prospecting for primary diamond deposits of tuffisite type Izvestia of the Komi Scientific Center Ural. branch of the Russian Academy of Sciences 1 5 pp 54–66 (in Russian)

[11] Afanasyev V P, Efimova E S, Zinchuk N N and Koptil V I 2000 Atlas of Russia diamonds morphology Ed. Soboleva N V Scientific publication "Reterburg" typeface p 300

[12] Kvasnitsa V N, Zinchuk N N and Koptil V I 1999 Typomorphism of diamond microcrystals M: Nedra p 296

[13] Rakin V I and Piskunova N N 2012 The morphology of artificial diamonds Izv. Komi Scientific Center URO RAS Sykytvyr 3 11 pp 61-67

[14] Pakhomonova V A, Fedoseyev D G, Tishkina V B and Buravleva S Yu 2015 A new “genetic type” of Primorye diamond deposits: man-made diamonds from drill cuttings VII Sci. Conf. «Gemology» Responsible editor S I Konovalenko ed. A A Peshkov, L A Zyrryanova (Tomsk) pp 113-123 (In Russian)

[15] Zienko S I and Slabkovsky D S 2019 Comparative analysis of the luminescence spectra of diamonds Optics and spectroscopy 127 3 pp 507-13

[16] Mudryi A V, Larionova T P, Shakin I A, Gusakov G A, Dubrov G A and Tikhonov V V 2004 Optical properties of synthetic diamond single crystals Physics and technology of semiconductors 38 5 pp 538–42

[17] Zaitsev A M 2001 Optical Properties of Diamond A Data Handbook Berlin: Springer p 502

[18] Eliseev A, Babich Yu, Nadolinnik V, Fisher D and Feigelson B 2002 Spectroscopic study of HPHT synthetic diamonds, as grown at 1500°C Diamond Relat. Mater 11 23 pp 22 - 37

[19] Bovenkerk H P, Bundy F P, Hall H T, Strong H M and Wentorf R 1959 Preparation of Diamond Nature 184 pp 1094-98

[20] Shumilova T G 2018 Typomorphic indications of synthetic diamonds and possible ways of technogenic contamination of natural objects International scientific-research journal 11 77 pp 104-08