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The Informational Significance of Studies of Diamond Accessory Minerals

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Abstract—The history of the diamond field discoveries in Russia was briefly overviewed, and the leading role of the mineralogical prospecting methods was emphasized. Recent advances in studies of diamond accessory minerals were discussed, with the focus placed on the most important among them, the discovery of syngenetic metal films on the diamond surface. Based on the presence of these films, the mechanism of diamond growth in nature was interpreted as consisting in a growth from solution in a metal melt.

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INTRODUCTION

The discovery of kimberlite pipes of the Siberian platform, the primary sources of diamonds in Russia, dates back to over 50 years ago, and its history is now a matter of common knowledge [1, 2]. The first kimberlite pipe Zarnitsa in Siberia was found in August 1954 by geologist L.A. Popugaeva with the use of the “pyrope track” technique underlain by dispersion in the recent alluvium (river sediments) of a diamond accessory mineral chrome garnet, blood-red, cherry, lilac color pyrope. This mineral is well-diagnosed visually in the field directly, and coarsening and increase in the number of its grains in the heavy fraction of the primary concentrates specify the direction of further prospecting for the primary source of diamond, a kimberlite pipe. Guided by increases in the size and number of pyrope and picroilmenite grains, Popugaeva moved upstream small rivers and creeks in the impassable Siberian taiga and washed river sand until finally succeeded in discovery of the first kimberlite pipe, the first primary source of diamonds in the former USSR-Russia, in the basin of the Daldyn river (within the area enclosed by Zagadochnyi creek and Shestopalovka river). This discovery was made possible by in-depth scientific pre-analysis combined with intimate knowledge of the subject of research, which resulted in development of a new mineralogical prospecting method. The pioneering work on development of this method was conducted by reputed Soviet-Russian scientists N.N. Sarsadskikh and A.A. Kukharenko.

The importance of the discovery of the first kimberlite pipe in Siberia can hardly be overestimated. It was demonstrated that the diamonds are not carried over distances of thousands of kilometers by water streams; their primary deposits are somewhere nearby, and one needs only to know how to search them. Naturally, the best way is to carry out mineral prospecting over the area of spread of the mineral itself (carrier of useful component). For example, prospecting activities over the areas of dispersion of not only pyrope but also of diamond itself have culminated in the epoch-making discovery of the first commercial diamondiferous kimberlite pipe Mir as early as in the year that followed (1955). The washing of river sand and gravel on sand banks has resulted in finding octahedral diamond crystals directly in the cradle, so that a rich recent diamond placer was discovered in the vicinity of the Mir kimberlite pipe, and later on, the pipe itself. The discoverers sent a well-known coded message through the airwaves: “We have smoked the pipe of peace, this is a great snuff.”

Since then, the mineralogical method of prospecting for kimberlite pipes has enjoyed high popularity and demand; it was put into use by many geologists not only in Russia. Other kimberlite pipes

(Udachnaya, Sytykanskaya) were found in Siberia with the use of this method. Today, the results obtained through mineralogical prospecting for diamonds on all the continents complement the information retrieved with the use of geophysical remote sensing by magnetic prospecting, gravity prospecting, and other techniques. The contribution made by Russian geologists into the prospecting activities toward diamond deposits in Africa, North and South America, etc. is highly estimated [3, 4]. Along with chrome pyrope, efficient prospecting indicator minerals can be found in picroilmenite, olivine, diopside, enstatite, high-chromium chromospinelide, pyrope-almandine, zircon, and some other diamond accessory minerals. They all are brought up by kimberlite or lamproite magma from the Earth's depths (150–650 km), where, together with diamond, they form upper-mantle rocks, peridotites and eclogites. The composition of the upper mantle and parent rocks of diamond can be estimated from the chemical and mineral composition of xenoliths, deep-seated inclusions (fragments of the underlying mantle rocks) that were rounded and quenched during their ascent and incorporation into the Earth's crust by a special volcanic rock that performs a transporting function [5]. Recent studies showed that, along with kimberlites and lamproites which are known to transport diamond, there exist other weakly diamondiferous rocks that can perform this function (volcanic varieties) or act as parental materials (generating diamond under ultrametamorphic and high-stress conditions): alpine-type ultramafites, eclogites, alkali basalts, lamprophyres (minettes), picrites, and some other ores [6].

Under surface conditions, silicate- and oxide-based indicator minerals exhibit different resistances to abrasion; they are rounded in water streams, and the extent of their preservation is essential for estimation of the distance by which they were transported and, thereby, the distance separating them from their primary source [7].

Diamonds themselves, as well as their crystallographic forms, facet surface relief, physical properties, isotopic composition of carbon, inclusions of minerals inside the crystals, and mineral adhesions on the surface are very informative about the condi-tions of formation and transportation of diamond crystals. Based on inclusions of accessory minerals in diamond it is possible to identify the substrate in which it was formed and even estimate the depth from which it was brought to the surface [8]. Suitable indicators of extremely deep-lying levels of diamond formation in the mantle at ~650-km depths can be found in inclusions of garnet with a high pyrope-majorite component. The occurrence in diamond of microinclusions represented by olivine, enstatite, chromospinellide, pyrope, picroilmenite, iron-nickel sulfides, and other grains is indicative of formation of crystals in the peridotite mantle, and microinclusions of coesite, omphacites, pyrope- almandine, pyrrhotite, and some other minerals suggest the diamond formation in the eclogite mantle. Similar information can be derived from the isotopic composition of carbon in diamond: Diamonds from the peridotitic substrate are typically characterized by a heavier carbon isotopic composition ($-4\pm4‰\ \delta^{13}C$), and eclogitic substrate, by a lighter composition ($-20\pm10‰\ \delta^{13}C$) [9]. Based on the content of CaO and Cr_2O_3 in pyrope garnet, a diamond accessory mineral, is possible to identify, with the use of the well-known diagram, the petrographic types of mantle peridotites (highly diamondiferous pyrope-bearing dunites, harzburgites, lherzolites, wehrlites, etc.) and sometimes to forecast the diamond potential of kimberlite pipes [2, 10].

The De Beers Geology Division reported that over 5000 kimberlite pipes are known to currently exist in the world; among them, diamonds occur in 800 pipes, of which only 50 are commercially diamondiferous ones.

One of the most interesting reviews among those currently available on the status of contemporary studies on diamond and lonsdaleite, its closest polymorph, is that provided by V.K. Garanin and G.P. Kudryavtseva, based on a rich material collected by those researchers [11].

The origination of diamond with its diversified crystal morphology, the correlations between the spectroscopic and other physical properties of diamonds, on the one hand, and the specific features of its faceting and formation conditions, on the other, as well as valuable genetic information provided by studies of diamond accessory minerals (indicators), belong to the scope of the most fascinating domains of mineralogy of diamond, which swayed the minds of many scientists [12–17]. Recent years have witnessed a snowballing growth of the number of relevant publications. Many aspects concerning the diamond age, genesis, and delivery, as well as the origination of its curved-face crystals, still remain debatable.

Let us dwell upon some of the above-mentioned aspects.

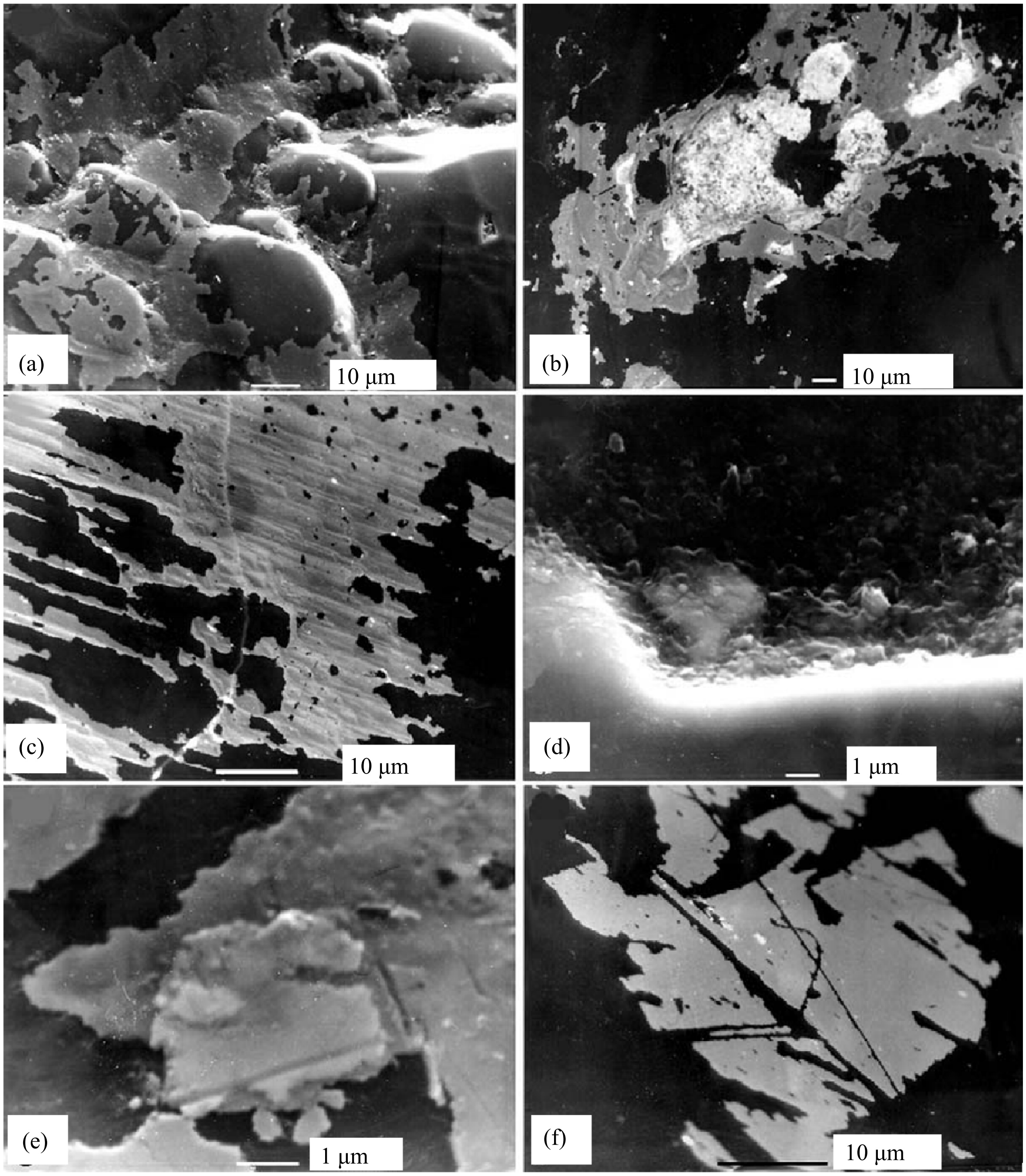

Fig. 1. Fragments of thin gold-palladium metal films on the surface of curved-face diamond crystals from Ichet'yu occurrence, Middle Timan: (a) vicinal surfaces of curved-face diamond crystal no. 27 coated with a thin Au-Pd alloy film; (b) binary film on diamond no. 29 crystal: (bottom) Au_2Pd_3 natural intermetallic (gray segments) and (top) florencite (white segments); (c) fragment of blurred Au-Pd films on diamond no. 43; (d) Au-Pd film scales in a cavity on diamond no. 45; (e) concertina-folded multilayer Au-Pd film on diamond no. 62; and (f) Au-Pd film on diamond no. 84, scratched during the crystal transportation.

The Discovery of Metal Films on Diamonds

The first observation of thin metal films comprised of a gold-palladium alloy in which the content of palladium was uncommonly high, >40% (Fig. 1), was made in 1998 in studies of a collection of thirteen diamond crystals from the Yuzhnyi and Zolotokamennyi plots of Ichet'yu occurrence (Vol'sk-Vym Range, Middle Timan) and modern alluvium of the Kos'yu river (Chetlas Rock) [18]. On the surface of all those

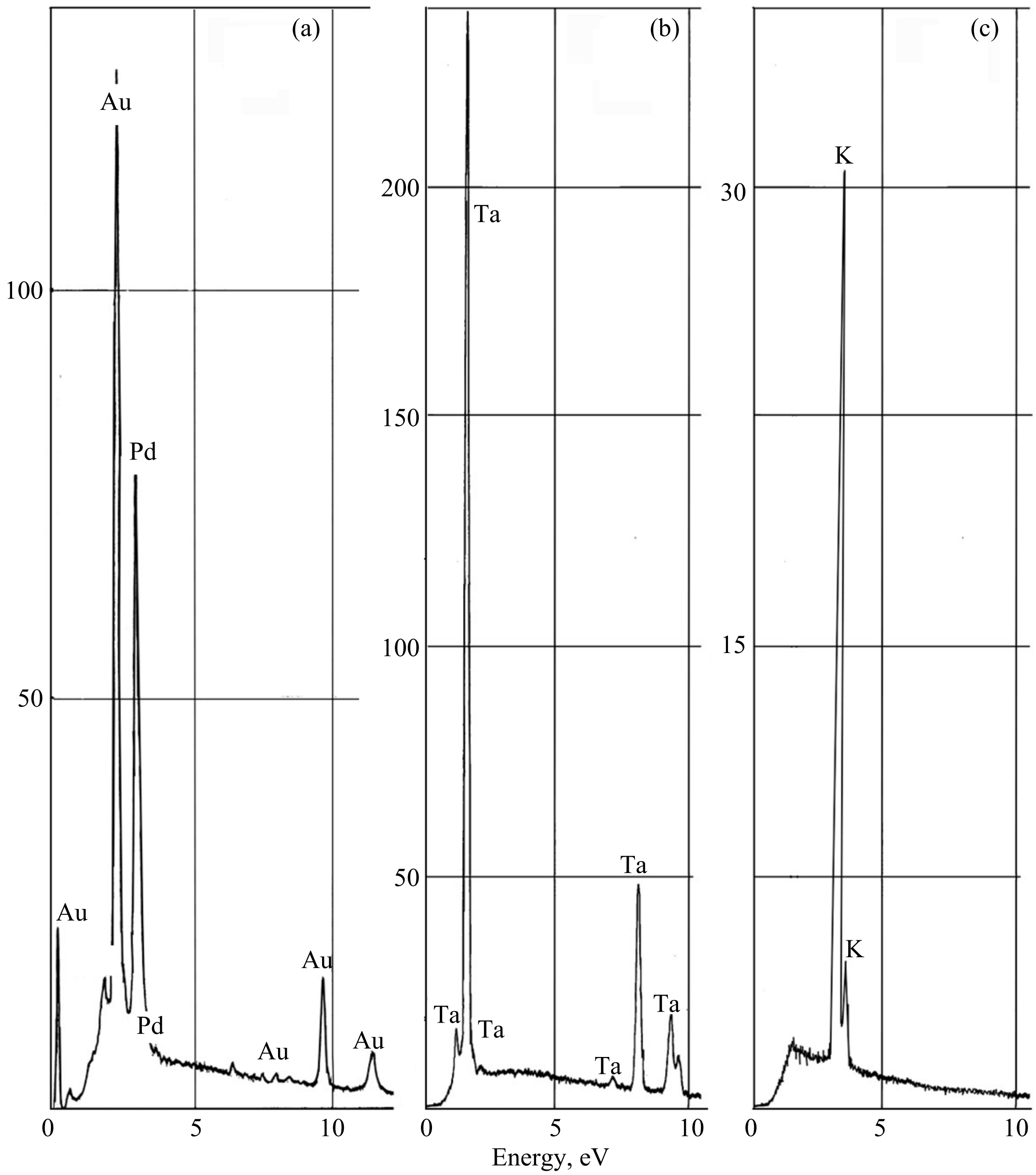

Fig. 2. Energy-dispersive spectra of (a) Au_2Pd_3 gold-palladium film on diamond no. 78 crystal, (b) tantalum film on crystal no. 7, Middle Timan, and (c) native potassium from inclusion in diamond no. 570 [XXIII Party Congress kimberlite pipe, Republic of Sakha (Yakut Republic)].

crystals the alloy forms a stable intermetallic sesqui compound (Au_2Pd_3), which previously covered the entire crystal with a 0.1-μm-thick film, as confirmed by nearly forty microprobe analyses and measurements (Fig. 2a). The content of the components in the intermetallic compounds exhibits narrow variations within 52.48–60.42% for gold and 37.57–47.36% for palladium; a significant contribution is made by isomorphic impurities: Ni (0.04–2.94%), Cu (tr.– to 3.44%), Hg (tr.– to 1.03%), and Fe (tr.– to 0.58%). As of the time of the experiments, the gold-palladium film was represented by islands and spots rather than by a continuous coating (Figs. 1a and 1b), which is well-preserved on 3–70% of the surface area, mainly in the negative relief forms. The film is very thin for the most part, ca. 0.1 μm, and only certain islands (on the electron microscopic images taken in the COMPO mode, their brighter spots stand out of the pack) are characterized by increased film thicknesses of 0.5–1.0 μm. The above-mentioned brighter spots may result from recrystallization and contraction of the intermetallide in local sites, as well as from mechanical

Types of metal films on the surface of diamonds from various deposits and accessory native minerals of ultramafic and other rocks

Deposits, rocks	Types of metal films and inclusions	Number of types
Metal film on the diamond surface		
Southern section of Ichet'yu occurrence (56 crystals)	Ag, Au, Au_7Ag, AuCuAg, Cu_5Au_3Ag, AuCuHgPd, Au_2Pd_3, Cu_3Sn, Cu_3Zn_2, Pb, Sn, Bi, Ta, Fe, Fe_7Cr, Fe_7Cr_2Ni, Ti, W–Mo	18
Zolotokamennyi plot of Ichet'yu occurrence (26 crystals)	Au_2Pd_3, Cu_5Au_3Ag, Cu , Zn, Cu-Zn, Zn–Cd(S), Pb, Sn, Pb–Sn, Pb–Sn–Cu(Au), Fe, Ni, Ni–Fe, Ti, Ti–Fe	15
Sidorovskii plot of Ichet'yu occurrence (8 crystals)	Ag, Pb–Sn, Fe, Ti, W(Mo)	5
Lomonosov kimberlite pipe (16 crystals)	Ag (Ag_2S), Cu (CuS), Cu_3Zn_2, Cu–Sn–Pb, Pb (PbS), Pb–Sn, Sn–Pb, Zn, Fe, Fe–Cr, Cr, Fe–Ni, Ni, Ni–Fe, Ti	15
XXIII Party Congress kimberlite pipe (10 crystals)	Ag (Ag_2S), Cu_5Au_3Ag, Cu, Cu–Zn, Fe, Fe–Cr, Fe–Ni, Ni, Fe–Sn, Ti, Zn, Zn–Mg, Zn–Cr–Mg, W–Ni(Mo)	14
Krasnovishersk raion, Perm oblast (14 crystals)	Cu(CuS), Cu_2Zn, Sn-Cu-Pb(Au), Zn, Pb(PbS), Sn, Pb–Sn, Fe, Fe–Cr	9
Tou Dou Gou kimberlite pipe, China (100 crystals)	Fe, Fe_7Cr, Ni, Ni–Fe	4
Films on Brazilian diamonds from Juina kimberlite field (25 crystals)	Au–Ag–Cu, Ag(Cl), Fe, Ni, Ti, Fe–Cr, Fe–Cr–Mo, Fe–Zn, Ni–Fe, Fe (Cd), Fe–Zn–Mg–Mn, Sn–Fe, Fe–Ni–Cu, Cr–Fe–Ni, Fe–Cu, Fe(Ni,Pt), Zn, Pb, Al, Cu, Cu_2Zn, Cu_3Zn_2, Cu–Zn–Sn, $(Ce,La,Nd,Al,Ca)_2O_3$, Zr–Yb, $(Ce,Nd,La,Y)_2O_3$	26
Inclusions in diamonds and carbonados		
Inclusions in diamonds and carbonados (according to Gorshkov et al. [19])	Au, Ag, Cu, Fe, Ni, Cr, Fe–Cr, Fe–Ni, Ti, Ta	10
Collection (10 samples) of Brazilian carbonados, State of Bahia (according to Makeev et al. [21])	Films on the surface: Au, Au–Ag, Sn, Bi, Pb–Cr, Fe, Ni, W, Fe_7Cr, Fe–Ni–Cr, Fe–Sn . Inclusions: Au, Ag, Fe, Ti, Ni, Fe–Ni, Ni(Fe,Co), Fe–Cr, Fe–Ni–Cr, Ni–Cr, Sn–Cu, W(Fe,Cr,V)	11 12
Inclusions in rock-forming minerals and rocks		
Native metals in halos of Arkhangelsk kimberlite pipes (according to Makeev et al. [22])	Au, Ag(S), Fe, Ni, W, Fe–Cr, Fe–Ni, Fe–Ni–Cu, Fe–Ni–Cr, Ni–Cr–Fe–W–Mo, Fe–Mn–Si, Ni–Sn(Fe), Cu–Ni, Cu–Zn–Ni, Cu–Cu–Sn, Cu–Zn, Cu–Zn–Sn, Cu–Al, Cu, Sn, Zn, Pb, Pb–Sb, Pb–Cu–Zn	24
Polar-Urals alpine-type ultramafites [20]	Ag, $AgIn_2$, Cu-Au, Pt–Ir, Ru–Os–Ir, Os–Ir, Cu, Cu–Ag, Cu_2Zn, Bi, Pb, Bi–Pb, Al, Fe.	14
Siberian kimberlites (according to Oleinikov [24, 25])	Au, Cu, Zn, Sn, Pb, Al, Cu–Zn, Cu–Zn–Sn, Cu_2Sb, Cu_6Sb_5, SnSb, Fe, Cr, SiC	14
Kamchatka concentrically-zoned ultramafites (According to Makeev et al. [23])	Ag, Au, Pt_3Fe, Cu_2Zn, Pb, Sn, Bi, Pb–Bi	8

stripping and concertina-folding of film segments (Figs. 1c and 1f).

Even the first examination of the collection of 90 curved-face diamonds from Ichet'yu occurrence (Middle Timan) under a JSM-6400 scanning electron microscope equipped with a Link IsIs-300 energy-dispersive accessory showed that some of these diamonds (40 to 100% in different sections of the occurrence) were coated with very thin metal films of diversified compositions [15, 18]. Most of these metals and intermetallic compounds are naturally occurring in native form in different parageneses (ultramafites, kimberlites, meteorites, and hydrothermal ores) [19–25]. The fact of their being preserved for a long time in thin films carved in the negative relief forms on

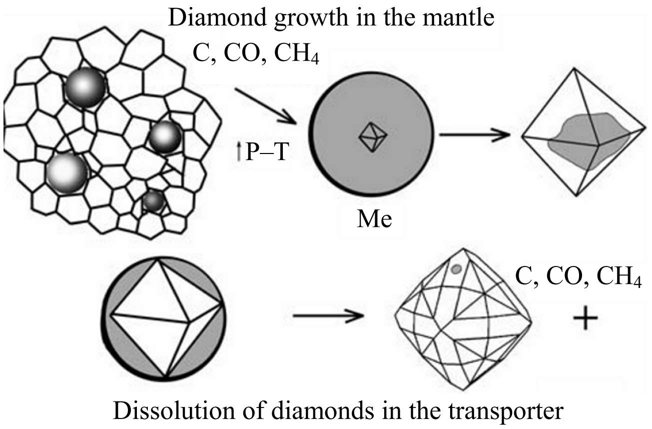

Fig. 3. A model of diamond crystallization and dissolution in the metal membrane.

diamond crystals raises no questions. Several phases, e.g., Ta (Fig. 2b) and some other phases, were detected for the first time. Maybe, all of them are insufficiently explored new mineral (Au_2Pd_3, Cu_3Sn, Zn–Mg, Zn–Cr–Mg, Ta, Ti, etc.).

So late a discovery of metal films on diamonds (at the very end of XX century) can be attributed to the fact that it was made possible by the development of more sophisticated analytical instrumentation combining an electron microscope with an energy-dispersive electron probe (Link). These techniques avoid special pretreatment and allow examination of bulk crystals rather than of plane-parallel polished samples. Also, diamond crystals were not subjected to acid treatment [obligatory for diamonds to be accepted by Gokhran (Russia's State Repository for Precious Metals and Gemstones) for evaluation and storage], which procedure would have inevitably destroyed most of the films.

Further prospecting activities for metal films were undertaken with diamonds from other deposits. To this end, three collections of diamond crystals were provided by the Central Geological Research Institute of Nonferrous and Precious Metals: from Lomonosov kimberlite pipe in Arkhangelsk oblast, from alluvial deposits of Krasnovishersk raion, Perm oblast, and from the XXIII Party Congress kimberlite pipe, Republic of Sakha. A.B. Makeev examined a collection of 25 diamonds from the Juina kimberlite area (State of Mato Grosso, Brazil) jointly with V. Ivanukh, as well as a collection of 100 small diamond crystals from the Tou Dou Gou deposit (Liaoning Province, China) jointly with Mon Fanzhong and a collection of 20 crystals from one kimberlite pipe from south-western Angola jointly with E.F. Roman'ko. Those studies considerably expanded the list of metal films discovered, which is comprised today of 46 items (see table). Some of those films had a composition identical to that of the films revealed on the surface of the Middle-Timan diamonds, and some species were discovered for the first time.

The above-said allows hypothesizing about the mechanism of diamond growth in the mantle with participation of native molten metals. Presumably, diamond crystals are nucleated inside the molten metal droplets (Fig. 3). The diamond nucleus gets overgrown by carbon displaying an excellent solubility in many metals. Carbon from the external side of a liquid metal membrane may be admitted both via dissolution of solid graphite and absorption of the carbon-containing fluid (CO, CH_4, etc.) from the medium. It should be noted that palladium is a unique solvent for hydrogen (up to 1200 volumes). Moreover, the available reference data suggest that up to 10% carbon can be dissolved in palladium. Therefore, a liquid gold-palladium alloy participating in diamond synthesis performs simultaneously several functions, namely, those of a solvent for hydrogen and carbon, a catalyst for chemical reactions, a permeable membrane, an electrical conductor, etc.

If diamond, presumably, owes its origination in the mantle to a graphite → diamond solid-state reaction at the stability boundary of graphite and diamond and at a certain pressure, this could have occurred as a single event which was roughly simultaneous with formation of the Earth planet itself. If this were the case, diamond should have been regarded as one of the oldest minerals on the Earth. The graphite contained in the protoplanetary matter should have been entirely converted to diamond at a certain time as a result of a phase reaction, so that there should have been no graphite, only diamond, in the Earth's mantle at depths in excess of 120–150 km.

The situation will be different if we accept the hypothesis of a diamond growth through a metal membrane, in which carbon can be dissolved, both in the solid form and in the form of various gases of mantle fluids. Considering the known fact of continuous degassing of hydrogen-hydrocarbon fluid from the lower mantle and the Earth's core, diamond may have very different ages; it can even be formed in the mantle even right now. Hydrogen-hydrocarbon fluid is able of reducing metals from silicates to molten

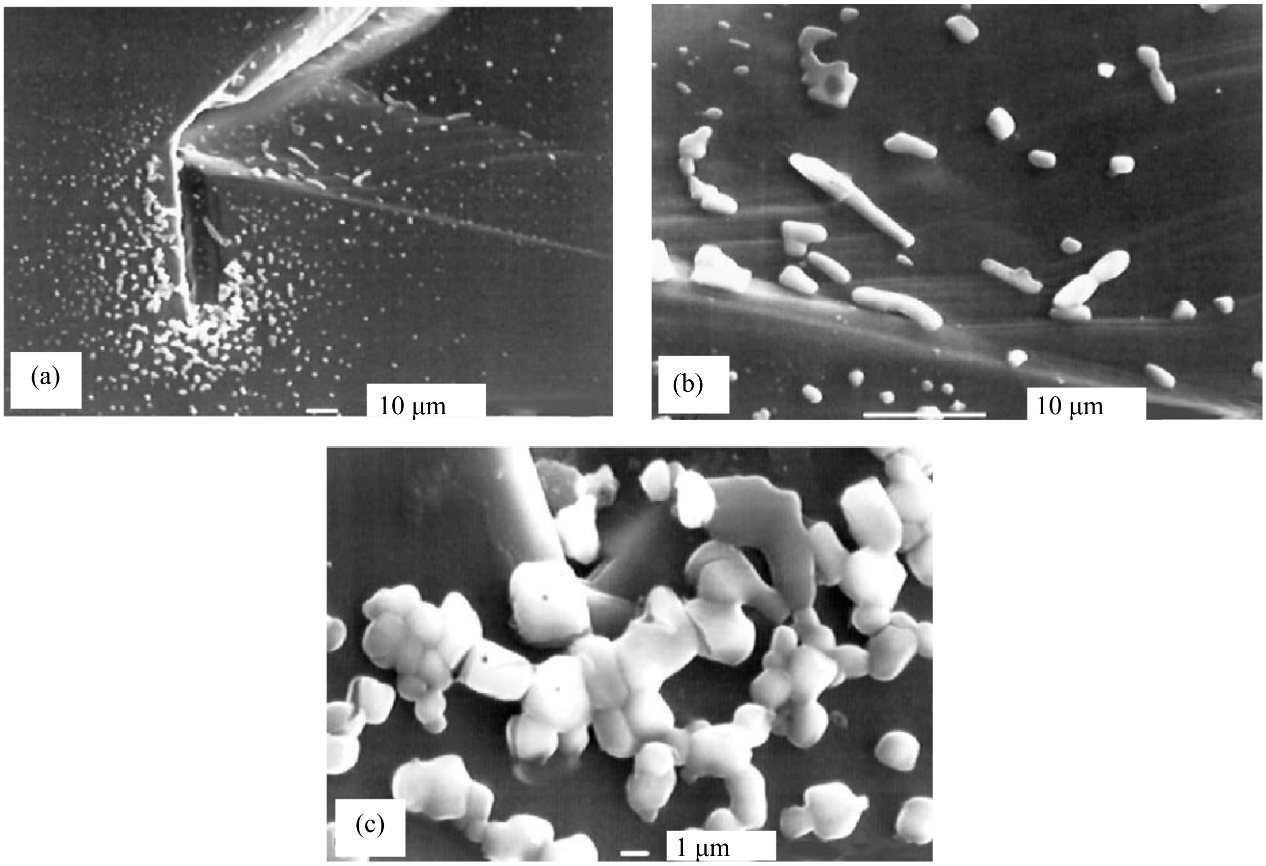

Fig. 4. Electron image of native potassium lamellae ejections. Electron microscope; successive magnifications from the exposed inclusion in diamond no. 570 (XXIII Party Congress kimberlite pipe).

droplets (iron, chromium, nickel, calcium, magnesium, and any other), in which, in turn, carboniferous gas can be dissolved. Carbon dissolved in a metal droplet acts as a building material for the growing diamond. The fluid nitrogen exhibit different solubilities in different metals; its getting into the crystallization medium in a pulsed manner is responsible for concentric zoning in diamonds as suggested by cathodoluminescence images.

Diamond crystals have predominantly minor inclusions of diamond in diamond [11], which fact is indicative of a discrete and plural nature of the diamond crystallization process. Most likely, diamond crystals grow until the metal film is thinned to a certain limit, presumably to 0.1 μm in the case of a gold-palladium alloy, and possibly to 1 μm in the case or films of iron-group transition metals and other. This may result in film discontinuity (or in a sharp decrease in the solubility of carbon therein), which will preclude further growth of a diamond crystal. In this context, let us calculate the diameter of the alloy droplet that could underlay the growth of, e.g., a 2-carat diamond crystal. For the final film thickness of 0.1 and 1.0 μm, the diameter of a molten gold-palladium alloy droplet will be 0.28 and 0.58 mm, respectively. In a similar way it is possible to calculate the dimensions of other droplets needed for the growth of crystals of any size [15]. For example, the growth of a diamond equal to the Cullinan diamond (3106 carats) will require a gold-palladium alloy droplet ranging from 2 to 4 mm in diameter, whose weight does not exceed 0.5 g.

If diamonds were nucleated in the mantle inside relatively large metal droplets (>5 mm in diameter) and were subjected to long-term quenching below the graphite-diamond stability boundary or under slow ascent during the kimberlite process, they would be unstable. For example, during ascent of ultramafic massifs from the mantle into the crust, diamonds in a metal envelope may undergo complete dissolution in the metal and, thereby, conversion to carbides and other carboniferous compounds, in particular, gases. In this case, there could simply be no traces of the original occurrence of diamond in the ultramafic rock.

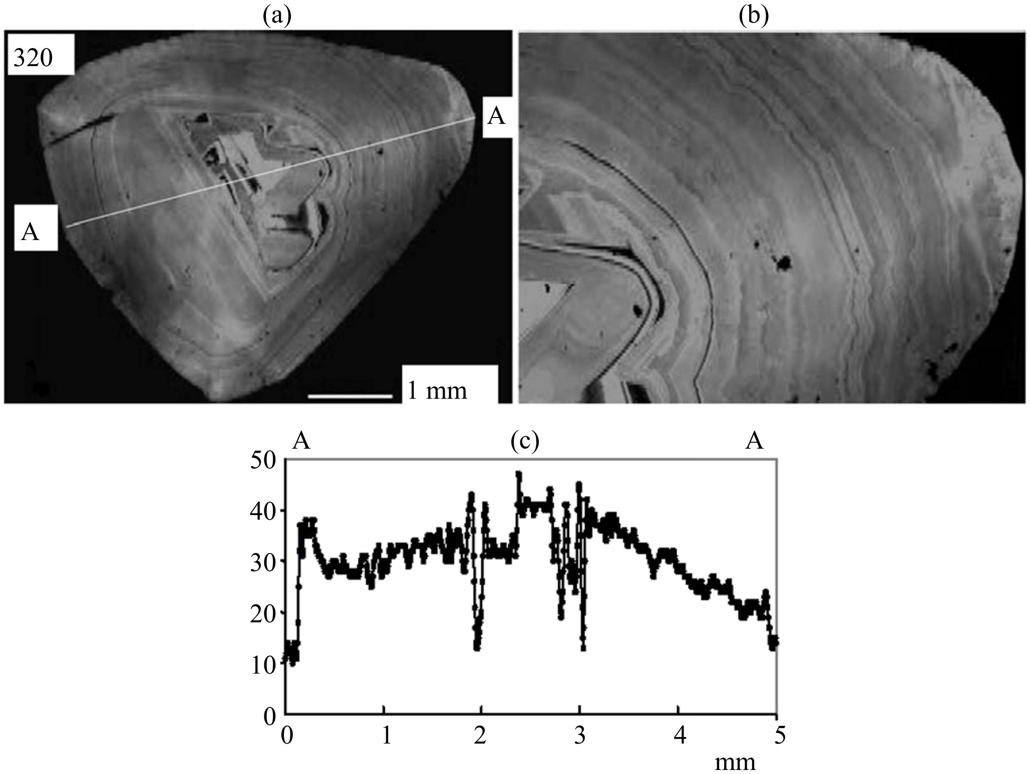

Fig. 5. The cathodoluminescence image for a cut surface of curved-face diamond no. 320. Rassol'ninskoe deposit, Perm oblast: (a, b) visible curved-face growth zones and (c) cathodoluminescence intensity (concentration of isomorphous nitrogen) based on the photometric results for the images along the A–A profile.

Thus, the size of the mantle droplets of native metals and their alloys, best suited to diamond nucleation and synthesis, ranges from 50 μm to 3 mm. A prerequisite to diamond preservation is the fast delivery from the mantle to the crust, which can be achieved only via transportation by kimberlites or lamproites in diatremes.

Diamond Inclusions as Repositories of Information about Diamond Formation Conditions and Medium

The occurrence of solid inclusions of mineral phases in diamond crystals is an ordinary phenomenon. High-magnification examinations visualize solid inclusions in faceted diamond crystals (cut diamonds) which, according to jewelers' opinion, do not deteriorate the diamond quality until they reach a certain size. The highest frequency of occurrence is characteristic for black octahedral chromite inclusions in diamonds, with chromite enriched in chromium at the most (to 62–66% Cr_2O_3). Specifically this chromite from diamond inclusions represents one of the major prospecting indicators among diamond accessory minerals. Other minerals (arranged in accordance with their respective frequencies of occurrence) include red high-chromium pyrope garnet or orange pyrope-almandine, green chrome diopside, clear or pale-green olivine, brown enstatite, etc. The specific association and composition of mineral inclusions are indicative of the diamond growth medium and depth.

Every natural scientist (whether geologist, chemist, or physicist) is aware of the fact that extreme activity of alkali metals (Li, Na, K, etc.) prevents their natural occurrence in native form; in air they would certainly have been oxidized and hydrated. Nevertheless, M.I. Novgorodova found native sodium in geological objects (which fact was appropriately evidenced), and A.B. Makeev happened to observe native potassium.

On one occasion native potassium was discovered on the surface of a plane-face octahedral diamond no. 570 from Yakut collection (Figs. 2c and 4); it appeared as numerous lenticular ejections from the inclusion whose emergence is due to a loss of containment during vacuum treatment. As part of the vacuum treatment procedure, the diamond crystal was immediately subjected to carbon deposition and transferred into an electron microscope for examination, and the carbon

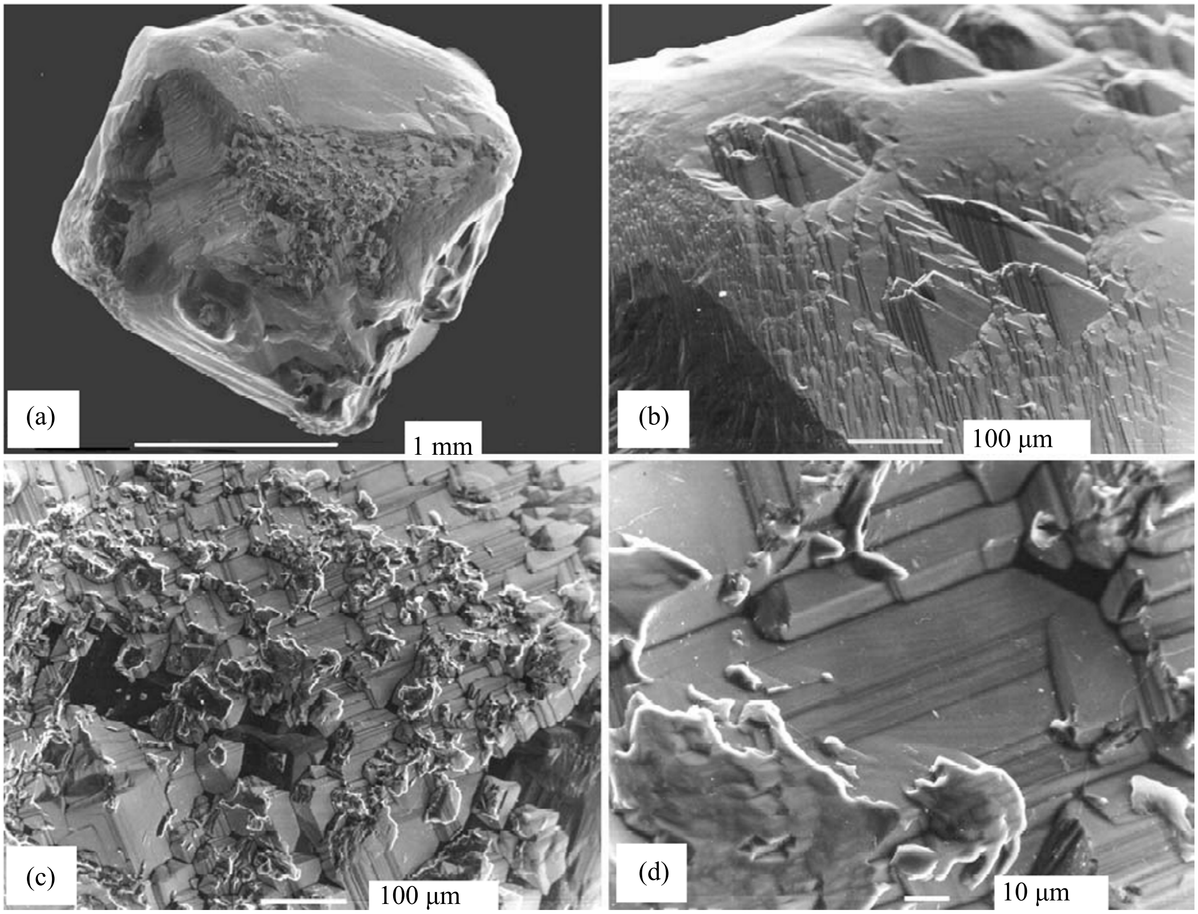

Fig. 6. Electron image of diamond J_{9-2}, a curved-face octahedroid. The diamond is available from a kimberlite pipe of Juina diamondiferous field (State of Mato Grosso, Brazil): (a) general view, (b–d) successive magnifications of the images of faces: (b) multiple-headed vertex of a plane-face octahedron overgrown by a curved-face octahedroid, (c, d) faces of plane-face octahedron overgrown by a second-generation curved-face diamond form.

film prevented metallic potassium from oxidation. The energy-dispersive pattern, obtained for these ejections (Fig. 2c), does not suggest the presence of other elements; quantitative analysis revealed 100% potassium. That was the first case of detection of a new mineral, metallic potassium in native form. Unfortunately, the ejections were small in size and the metal could not be preserved in the native form for prolonged time, which prevented further examinations of the properties and structure of this phase, essential for the discovery of a new mineral.

It should be noted that, overall, potassium significantly contributes to the composition of diamond accessory minerals. Phlogopite, leucite, djerfisherite (all – rock-forming minerals of lamproites) are enriched in potassium which account for a significant proportion of (K, Na)Cl and other salt microinclusions in diamond [15].

Considering their formation conditions, diamond and oil might seem to be difficult to combine objects, which makes all the more surprising the fact that numerous diamonds were found in the Ebelyakh river placers (extreme north of the East Siberian Platform). Those were round zoned diamonds with a transparent core and a dark rim. Abundant minor multiphase hydrocarbon inclusions were revealed in the rims of the diamond crystals. All this creates an impression of diamond crystals undergoing further growth in kimberlite pipes when moving from the mantle in the hydrocarbon stream, in which process small oil droplets were caught up and preserved by them in their interior. Those facts, in turn, prove the inorganic origin

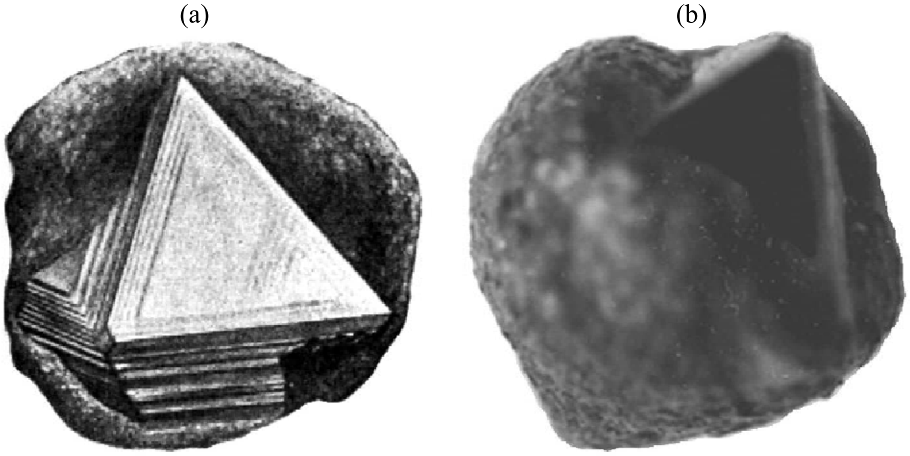

Fig. 7. Diamond octahedrons intergrown with a fine-grained diamond aggregate, carbonado: (a) picture of diamond no. 87 (taken form the monograph by A.E. Fersman [17]) and (b) photographic image (made by V. Ivanukh) of a similar sample available from the University of São Paulo (Brazil) museum; diamond octahedron edge size ~1 cm.

of oil (at least of that from a small part of oil occurrences).

Curved-Face Diamond Crystals

There is no consensus among luminaries in crystallography (O.M. Ansheles, V.M. Gol'dshmidt, A.A. Kukharenko, Yu.L. Orlov, A.E. Fersman, I.I. Shafranovskii, and many others) on whether curved-face diamond crystals are growth or dissolution forms, but most crystallographers tend towards the latter interpretation. Today, we have new interesting results obtained with the use of advanced high-resolution electron microscopes suitable for examination of color cathodoluminescence. Direct observation of zonal and sectorial patterns in the structure of crystals, specifically, the discovery of the fact of intersection of the growth layers by the crystal faces, allows precisely determining whether the crystal faceting results from diamond growth or from diamond dissolution.

Recent observations on curved-face crystals available from Ural and Brazilian deposit revealed and photographically recorded the following fact: Plane faces of diamond are overgrown by the subsequent generation of diamond with curved-face habit. Previously, this phenomenon was visualized for diamond sections (Fig. 5) by the cathodoluminescence technique [15, 16]. The previously studied Brazilian collection of diamonds from Juina field (State of Mato Grosso) contains several crystals whose surface exhibits consistent overgrowth of the octahedron face by a seemingly "amorphous" phase lacking distinct crystallographic surfaces (Fig. 6). In other crystals the plane-face imprints from cuboctahedrons were overgrown by curved-face habit forms: tetrahexahedroid (065) and octahedroid (365).

In a similar way it is possible to continue the evolutionary series of diamond habit forms, in which at even lower mantle parameters the plane-face growth forms are overgrown by curved-face ones: (111) → (111 +100) → (065, 365). This constitutes a new documentary evidence of the fact that curved-face habit forms (065, 365) can represent convergent features and growth forms rather than dissolution forms solely. Analysis of the spread of curved-face diamonds showed that they are confined to the edge parts of the platforms, which can be the sites of natural diamond synthesis in a special reciprocating (regenerative) mode.

Carbonado

The genesis of carbonado (a fine-grained cryptocrystalline form of diamond) remains a subject of a dispute in which two opinions are prevailing. One opinion is based on the fact of detection of carbonado in placer deposits occurring mainly in the southern hemisphere (Australia, Africa, and South America) and postulates formation of carbonado in astroblems owing to meteoritic impacts at the Earth's surface. The alternative opinion associates the genesis of carbonado with that of diamond in view of the existence of their joint finds in kimberlite pipes.

In this respect, a version proposed by A.I. Gorshkov et al. from the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry

[19] seems to be the most attractive. It presumes formation of a fine-grained diamond aggregate, carbonado, at lower P–T parameters compared to those in the case of diamond, though during eruption of the kimberlite fluidizate. This opinion is strongly supported by a zonal cathodoluminescence image obtained from carbonado, which is indicative of a coarse-grained diamond being overgrown by a fine-grained aggregate with intermediate metal film residues between them [21]. In the case of interest Makeev et al. observed a discontinuous spotty TiO_2 film resulted from conversion (oxidation) of titanium metal through a porous carbonado aggregate. The discovery of a thin (0.3-μm) TiO_2 film, which was sealed via overgrowing by a fine-grained diamond aggregate (carbonado) and thereby preserved on the plane of the diamond octahedron face, further validates the diamond growth in the mantle through metal membranes, and also proves the formation of carbonado in the kimberlite process rather than in astroblems or other processes.

Carbonado does not contain appreciable amounts of lonsdaleite which serves as an indicator of formation of carboniferous phases during the catastrophic phenomena of shock metamorphism, and this constitutes one of the major proves of the formation of carbonado in the kimberlite process. The most compelling support to a common origin of diamond and carbonado comes from association of their crystals (Fig. 7).

Current State of the Diamond Industry in Russia

The Yakut, Urals (Perm oblast, Krasnovishersk raion), and Arkhangelsk provinces are the three diamondiferous provinces existing in Russia. The two first-named mining areas have an age of over half a century. In the last-named, Arkhangelsk, province which was put into commercial operation in the XXI century only, the first million carats of diamond crystals was recently mined from Lomonosov deposit (Karpinskii pipe). The pit in this deposit has sunk by nearly 50 m already. It might seem that things are going really well, but for the need in certain adjustments to be made in order to respond to the recent crisis. As was not once the case in a world ruled by capital [1], the mining company owners do not wish to sell rough diamonds for a pittance, which necessitated certain changes, including production and staff reductions, closure of pits, and optimization of costs, to be introduced into the activity of diamond mining enterprises. For example, in South Africa the diamond mining operations are now under way in only one, Finsch, kimberlite pipe.

In Russia, closure of operations at many diamond pits during the crisis was inevitable, but this situation has some positive aspects: In response to the need in reduction of production during the crisis, modernization of the diamond mining enterprises was initiated in Yakut Republic. For example, underground mines are being constructed with a view to diamond extraction in several kimberlite pipes where open-pit mining is already impossible (the pits have sunk in excess of 0.5 km).

The geological prospecting activities for diamonds should undergo modernization as well. There exist new, mineralogical and geophysical, diamond prospecting techniques, and the time has come to test them in operation.

CONCLUSIONS

Both diamond itself, with all its rarity and mysteriousness, and the brilliance of cut diamonds are fascinating to many researchers. New information about diamonds and diamond deposits has become immeasurably wider and more easily accessible for scientists since recently. There exists vast relevant literature, and many of the data are no more confidential, which all attracts the attention of the scientific community. It seems like that not before long all the barriers will be removed and all the mysteries surrounding the origin of diamonds will be unraveled, so that diamond of desired quality could be synthesized in needed quantities.

A great attractive power is inherent in the concept that emphasizes a strong similarity between the mechanisms of natural and artificial syntheses of diamond, involving metals. In both cases, a metal acts as a catalyst, a solvent for carbon, and a liquid medium for synthesis. The natural and artificial diamond crystals bear traces of diamond–metal interaction appearing as metal film residues. Metal films are true genetic mineral accessories of diamond, with which they were involved in a single formation process.

The proportion of metallic films in the entire surface area of natural diamond crystals ranges from traces to 70%. The films are preserved only in negative forms of the face relief on diamond crystals (in prints, composition planes, and small pits, as well as between the vicinal surfaces). Along with native metals appearing as films and adhesions, diamonds have some silicates, aluminosulfophosphates, sulfides, and oxides on their surface. It is very likely that those are former metal films that were altered by oxidation. There is a need to elucidate how widespread this phenomenon is, whether there exist metal films on the surface of diamonds from other placer and primary deposits, and which of the revealed films are syngenetic and which are epigenetic, so that certain genetic inferences could be made on this basis.

Over the past few years, studies of natural diamonds were continued with other collections around the world. This concerns the Lomonosov kimberlite pipe in Arkhangelsk oblast; Krasnovishersk placer deposits in Perm oblast; the XXIII Party Congress kimberlite pipe, Republic of Sakha (Yakut Republic); Juina kimberlite field (State of Mato Grosso, Brazil), Brazilian carbonado (States of Bahia and Minas Gerais); Tou Dou Gou pipe (Liaoning Province, China); and kimberlite pipe from the South West of Angola (Africa). Those studies significantly expanded the geography of findings and proved that films on the diamond surface rather exist already in kimberlite pipes than are formed in deposits. Metal films appearing as inclusions were found in carbonado; a titanium (TiO_2) film was buried and preserved by the fine-grained carbonado aggregate that overgrows the diamond surface [21].

Those studies have demonstrated that the discovery of metal films on the diamond surface is general in its nature; to date, films were found on diamonds available from four continents (Europe, Asia, South America, and Africa). So late a discovery of metal films was made possible at the turn of XX–XXI centuries by recent technical advancements combined with studies on diamond crystals that were not subjected to natural or artificial treatment with acids and alkalis, which inevitably would have destroyed most of them.

The discovery of native metal films on the natural diamond surface allows the following essential genetic inferences.

(1) The presence on the surface of plane- and curved-face natural diamonds of metal films (46 types) [15, 16, 18] whose morphology is identical and composition, in some cases, close to those of the metal films on artificial diamond crystals, Fe-Ni-Mn and Cu-Zn, discloses the natural diamond formation mechanism as consisting in a growth from solution in a metal melt: carbon (C, C_nH_{2n+2}, CO, CO_2) → Me → diamond.

(2) The fact of preservation of metal films on the diamond surface in the negative forms of relief (cavities etc.) suggests that, under changed equilibrium P–T conditions, the dissolution of diamond also proceeds via metallic membranes: diamond → Me → carbon (C, C_nH_{2n+2}, CO, CO_2).

(3) Native metals, along with their alloys and intermetallic compounds, represent a new class of true syngenetic accessory minerals of diamond.

(4) A micron-fraction thickness of the metal film is sufficient for the natural synthesis of carbon-diamond to occur.

(5) Synthesis of diamonds in nature proceeds in a reducing medium.

(6) The occurrence of a discontinuous coating, as well as of traces of conversion of metal films to other mineral forms, suggests that diamonds are transported from their origination site in the mantle to the Earth's surface in an aggressive medium (Cl, S, O, P, etc.). This may be responsible for destruction of some of the films, especially of those on plane-face crystals.

(7) Curved-face diamond crystals of the Urals and Brazilian type, represented by tetrahexahedroids and octahedroids, are growth forms rather than simply dissolution forms: They contain films residues on flat surfaces and bear an impress of curved-face forms overgrown onto plane-face ones (color cathodoluminescence images of cut or cleaved diamond samples).

(8) The size of diamond crystals depends on the size of the original metal droplets in the mantle. The growth of Cullinan diamond, the largest known diamond crystal on the planet, would require a metal droplet as small as having the diameter of 2–4 mm.

(9) The habit forms of diamond crystals for each specific deposit depend on the type of metal films from which the diamond grew. Chemically unstable (alkali and alkaline-earth) metal membranes are rapidly oxidized and converted into other mineral forms during transportation of the crystals from the mantle. Having lost the dissolution power with respect to diamond, such natural membranes are promotive to preservation of the high-temperature octahedral habit of diamonds. Under decreased P–T parameters, oxidation-resistant metals (in the form of molten liquid films) will interact with diamond so that the latter will

be dissolved in its transporting rock. In this case, partial dissolution of diamonds will lead to accumulation of curved-face forms, cuboids (hexahedroids), combined forms, and octahedroids.

(10) The diamond content of kimberlite or lamproite diatremes depends not only on the initial content of diamonds in the fluid but also on the rate of incorporation of the transporting fluid. Fast incurporation of fluid will lead to preservation of diamonds, and slow ascent of the mantle fluid, to dissolution of most of the diamonds via the same metal membranes.

(11) The natural occurrence of various inclusions of native metals in mantle-originated rocks (ultramafites, kimberlites, lamproites, etc.) suggests the import role they play in the mantle mineral formation.

(12) The discovery of metal films on the surface of natural diamonds, that are similar to those observed on artificial crystals, is proof that the natural and artificial growth and dissolution of diamonds follow the same mechanism. Hence, new formulations of mixtures to be used for synthesis of artificial diamonds, including large ones, can be developed on the basis of the chemical composition of natural metal membranes.

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