ISSN 0869-5911, Petrology, 2006, Vol. 14, No. 3, pp. 299–317. © Pleiades Publishing, Inc., 2006.
Original Russian Text © S.A. Shcheka, A.V. Ignat'ev, V. P. Nechaev, V.P. Zvereva, 2006, published in Petrologiya, 2006, Vol. 14, No. 3, pp. 319–336.

First Diamonds from Placers in Primorie

S. A. Shcheka, A. V. Ignat'ev, V. P. Nechaev, and V. P. Zvereva

Far East Geological Institute, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia
e-mail: sashcheka@fegi.ru

Received October 18, 2004

Abstract—The paper reports the results obtained by the detailed studying of carbonado (the first find in a gold placer in Primorie) and a collection of diamonds that was confiscated in 1937 from a poaching small digger and was kept safe at the Nezametnyi mine (near the village of Vostretsovo), which had developed this placer deposit. In the concentrate from the placer, carbonado is associated with green corundum, various ilmenite, zircon titanian amphiboles and pyroxenes, rutile, anatase, and fragments of subvolcanic biotite picrites. All of these minerals, native aluminum, and tin occur as inclusions in the diamonds. The carbonado from Primorie was determined to be practically identical to this mineral from Brazil, has a porous structure, is characterized by orange luminescence, contains inclusions of Y, Ce, La, Ba, and Sr phosphates, and has an isotopically light composition of its carbon (^{13}C from –25 to –32‰). Pores of the carbonado aggregates contain clusters of diamond crystals. The collection of diamonds from an unknown source included six gem-quality transparent crystals, one rounded ballas, two cuboctahedral crystals (one of greenish and the other of silver-gray color, both with outer coats), and one black carbonado grain. The data obtained on the mineralogy of the diamonds have demonstrated that they are completely identical to this mineral from kimberlites and lamproites but bear traces of intense dissolution, fragmentation, multiple recrystallization, and graphitization at defects, which are the most widespread in the ballas. One of the crystals was determined to contain inclusions: aggregates of potassic omphacite (0.50 wt % K_2O) and corundum. Ilmenite (containing up to 8 wt % MgO), titanaugite, kaersutite (4 wt % TiO_2, 0.8 wt % K_2O), and churchite (aqueous phosphate) were obtained from the core of the ballas. The titanaugite, kaersutite, and ilmenite were proven to be compositionally analogous to these minerals from picrites occurring near the placer. The carbon isotopic composition δ^{13}C of the cores of the single diamond crystals varies from –6 to –11‰. The margins of the grains were proved to be enriched in the light carbon isotope (δ^{13}C from –19 to –21‰). The gem-quality transparent diamond crystals are characterized by blue luminescence, and the color of luminescence in the carbonado varies from orange red in the bulk of the aggregate to yellowish green in its core. The aforementioned transformations of diamonds were likely caused by their transportation in pipes of micaceous picrites of the Jurassic meymechite complex. The carbonado are thought to correspond to the final stage of the metastable recrystallization (in pores, within the temperature range of the rutile–anatase transition) of the original isotopically heavy diamonds under the effect of various oxidizers (H_2O, CO_2, F, and others) and in the presence of catalytically acting REE, Ti, and P. The primary diamond source (kimberlite or lamproite) can be older and more distant from the study area. The complete geological analogy between the study area in Primorie, Kalimantan Island in Indonesia, and West Australia (where no sources of the placers are known) led us to consider the territory of Primorie as promising for exploration for diamondiferous placers.

DOI: 10.1134/S0869591106030064

INTRODUCTION

A collection of diamonds was confiscated in the 1930s from a small digger poaching in Primorie. This collection was left kept safe at the old Nezametnyi gold mine in a remote taiga territory. The source of the diamond remained unknown. In 1953–1954, G.M. Gapeeva and A.I. Zhivotovskaya attempted searches for diamonds in the Neogene–Quaternary basalts with ultrabasic nodules. Later, alkaline rocks of the meymechite–picrite series with lamproite diatremes were discovered in Primorie (Shcheka, 1977). Our exploration operations for diamonds at these two complexes, with samples reaching 10 t in mass, did not yield positive results, and it was no earlier than 1978 that carbonado (the first one found in the Soviet Union) was detected at a gold placer not far from the Nezametnyi mine (Shcheka, 1994; Kaminsky et al., 1978). The mineralogy, geochemistry, and isotopic composition of diamonds from the collection were examined in much detail to identify the primary sources and to clarify the genesis of the diamonds.

It is worth mentioning recent sensational reports about diamond and pyrope finds in Primorie (Izosov et al., 1990; Gurulev et al., 1995; Sakhno et al., 1997). The rocks examined by these researchers (the Dmitrievka and Kurkhan zones) are typical melange of the Middle Cambrian and Devonian ophiolites (Shcheka et al., 2001), a fact that is convincingly proved, along with geological and geophysical evidence, by the compositions of the rocks and minerals and the petrographic and isotopic geochemical characteristics of the rocks. Single pyrope grains and diamond dust particles (0.1–0.7 mm across) were found only in concentrates obtained at diamond-producing enterprises (in Arkhangelsk and Tula), at which contamination with diamond is quite usual, as was emphasized by the executors of this work.

METHODS

In addition to geologic and optical methods traditionally used in such research, we employed some techniques specific to diamond. In studying photoluminescence, we used PRK-2 Hg generators with an UFS-3 filter ($\lambda \sim 3650$ Å). Cathodoluminescence was observed on a JXA-5A microprobe at a current of 5 nA and an accelerating voltage of 20 kV. Luminescence in the X-ray range was obtained on a SPARK-2 XRF spectrometer (40 kV, Mo Lα, $\lambda \sim 5.4$ Å). The IR spectra were obtained from small fragments on a Perkin Elmer-325 spectrometer, and the visible part of the spectra was obtained on a KSVU-5 setup at the Monokristall Design Engineering Center in Novosibirsk. The X-ray diffraction research was conducted at an ARS-2 (URS-60) setup with RKD (57.3 mm) and Gandolfi cameras. The latter enabled taking Debye X-ray diffraction patterns of small (0.2–0.3 mm) single crystals.

Our research involved the first local analysis (within spots 10–25 μm in diameter) of diamond for trace elements, which was carried out by the emission technique with laser excitation. The analyses were conducted by Yu.G. Kosovets, the chief designer of the equipment, whose paper (Kosovets and Stavrov, 1983) expounds the technicalities of the method. The chemical composition, morphology, and structural state of inclusions in the diamonds were examined on a JXA-5A (Japan) X-ray microprobe, a JEM-100C transmitting electron microscope equipped with a KEVEX-5100 EDS analytical set, and a JSM U-3 scanning electron microscope.

Several analyses of the carbon isotopic composition were carried out on a modernized and automated MI-1201V mass spectrometer (Ignatyev and Borovik, 1989), following the conventional method (Galimov, 1973) with the oxidation of diamond powder (1–2 mg) to CO_2 in the presence of excess O_2. The precision of the ordinary analyses was ±0.2‰. We also attempted to oxidize the diamond layer by layer in order to estimate its isotopic zoning. Of course, this is coupled with the complicated processes of kinetic and thermodynamic fractionation in the C–CO–CO_2 system, but the results thus obtained allowed us to draw certain conclusions concerning the isotopic zoning of the diamond. The analyses were conducted using undisturbed carbonado grains and single crystals. To preclude surface contamination and get rid of gas–liquid inclusions, the grains were boiled in a KNO_3 solution or annealed for 10–15 min at a temperature of 300°C with pumping out to high vacuum. Analyses of the untreated diamonds and those treated according to this procedure were completely identical, which testified that the contribution of foreign admixtures was negligibly small. After this, oxygen was admitted into the reactor in amount sufficient for the oxidation of 1 mg of diamond to CO_2. The reaction was conducted at 800°C and with the continuous freezing of CO_2. The completion of the reaction was identified using a vacuum gauge ($P = n \times 10^{-2}$ mm Hg) and usually took 30–35 min. Practically all gas portion had equal volumes.

GEOLOGICAL OVERVIEW

The geology of the area is determined by its proximity to an intersection zone of large regional faults (Fig. 1), which bound a wedge of a block of the Khanka Massif in the Sikhote Alin Mesozoic zone. The area is the only one in Primorie where the products of Jurassic alkaline–ultramafic magmatism are most proximal to Precambrian blocks of the “Khanka” basement and cut across Paleozoic rocks. The basin of the Kedrovka River is made up of sandy and clayey deposits, which are deformed into northeast-trending folds. The structures in the margin of the Khanka Massif trend there nearly meridionally and are separated from the Mesozoic zone by melange of a Middle Paleozoic ophiolite complex. The junction zones are complicated by numerous overthrusts of Mesozoic and Upper Permian rocks onto the margin of the Khanka Massif. The Upper Permian rocks of the Mesozoic zone (Khvorostyanka Formation) have lithological and facies compositions distinct from those of the Permian rocks that compose the margin of the Khanka Massif (Pospelovo Formation). The latter are black shales and acid volcanics. At the same time, the Upper Permian sandstones and siltstones along the Kedrovka River are notably enriched in siliceous material, i.e., were most probably produced at the expense of the basement of the Khanka Massif, a fact that can be considered a favorable guide for exploration for economic diamond deposits.

The magmatic rocks in the area are conformable dikes and other bodies of Late Jurassic (152–158 Ma) biotite picrites, ilmenite gabbro, Late Cretaceous granites, and flows and volcanic edifices of Pliocene–Quaternary alkaline basalts. Close to the area described in this paper, the Jurassic rocks include meymechites and a diatreme of micaceous picrites, which are melanocratic lamproites (Shcheka, 1977; Shcheglov et al., 1984; Shcheka et al., 2003). The Pliocene–Quaternary basalts bear scarce nodules of lherzolites and large (up to 20 mm) megacrysts of titanaugite, kaersutite, titanbiotite, zircon, ilmenite, spinel, sanidine, and titanomagnetite (Shcheka, 1983), as well as recently found megacrysts of garnet and sapphire (Vysotskii et al., 2002a). Practically identical mineral associations are typical of the rocks of the Jurassic complex, but all of them are strongly altered, and the chemistries of the minerals differ from those in the Pliocene–Quaternary basalts (see below). Judging from observations in rock expo-

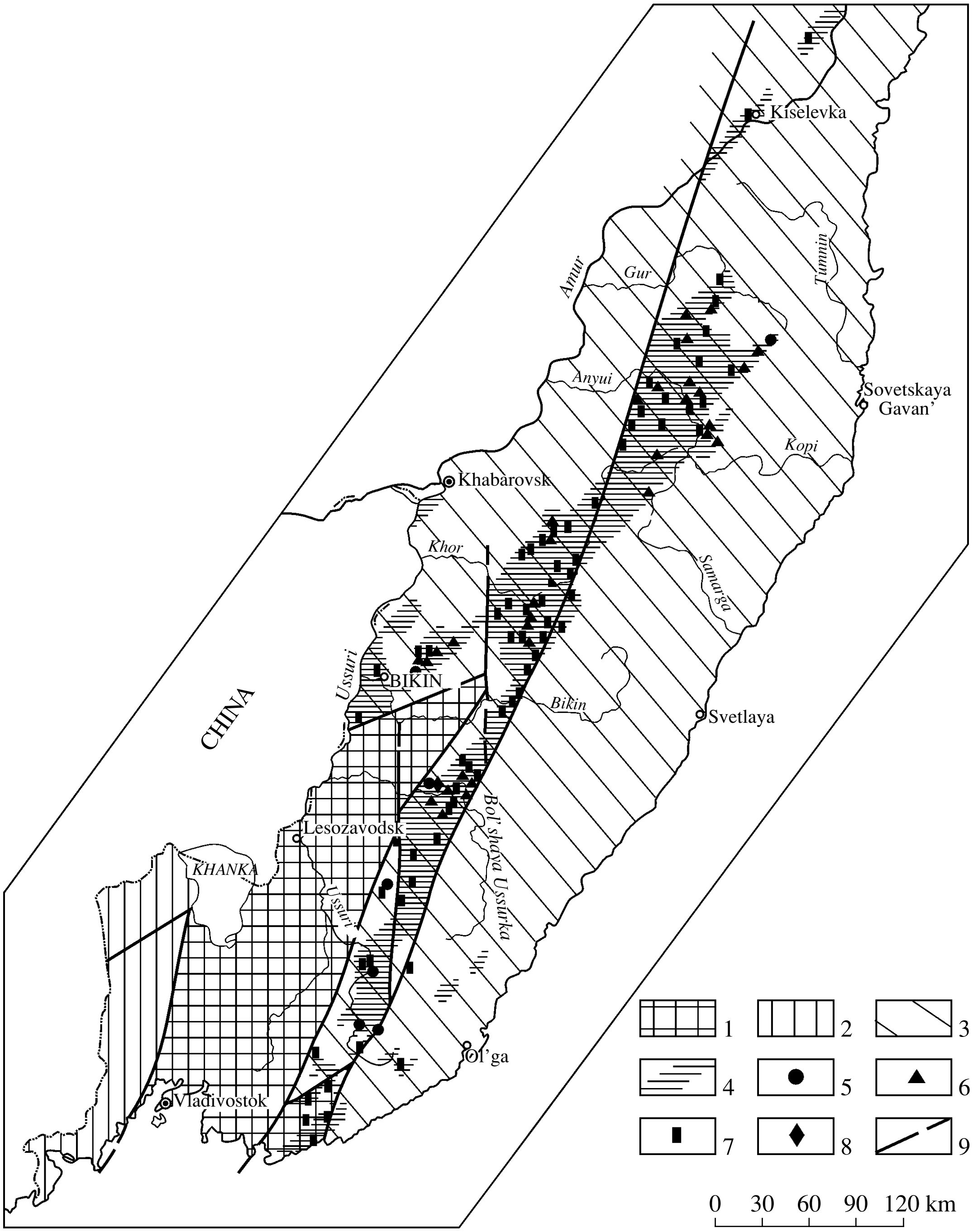

Fig. 1. Schematic map for the setting of the meymechite–picrite complex in Primorie (prepared by A.A. Vrzhosek).
(1) Khanka Massif; (2) Late Paleozoic folded area; (3) Mesozoic folded area; (4–8) Late Jurassic alkaline–ultrabasic complex (4—fields, 5–8 single exposures): (5) diatremes, (6) subvolcanic meymechite bodies, (7) dunite–pyroxenite ring intrusions, (8) carbonado finds in a placer; (9) major faults.

sures and from magnetic anomalies, the rocks of both complexes occur in the bedrock of the Kedrovka River.

Starting in the 19th century, the alluvium of this river was mined as a gold-bearing placer, and hence, the composition of the heavy fraction can be examined where sluice boxes were mounted and where remnants of the heavy fraction remain occasionally preserved. According to the results of pan sampling, the heavy fraction can be subdivided into two mineralogical associations: gold-bearing and basite–ultrabasic. The former consists of quartz, pyrite, arsenopyrite, cinnabar, cassiterite, scheelite, Mn–Fe garnet, and gold; and the latter comprises pyroxenes, amphiboles, olivine, Mg garnet, zircon spinel, ilmenite, rutile, anatase, feld-

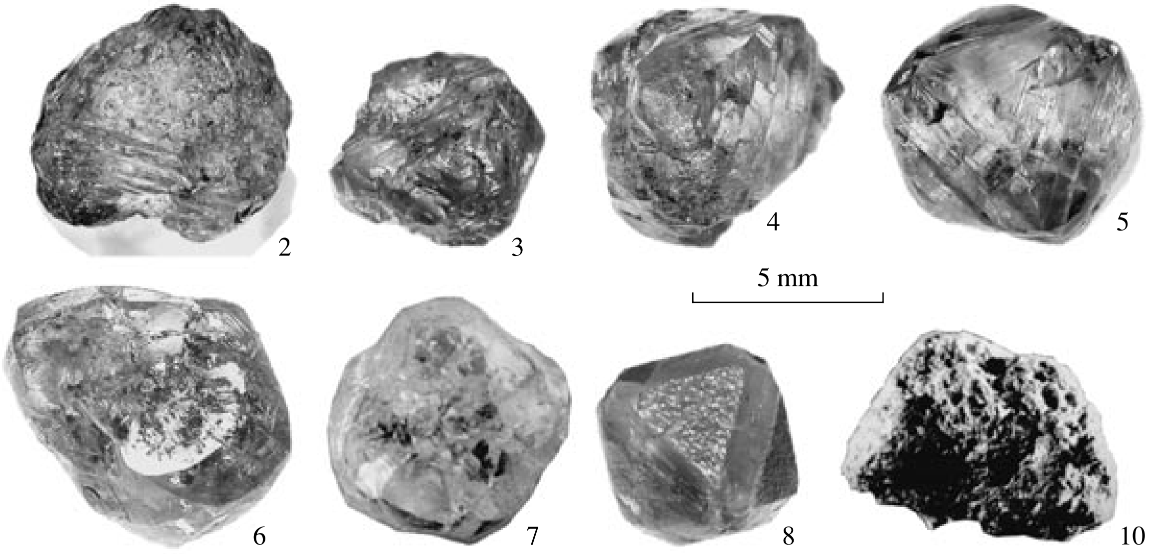

Fig. 2. Morphology of the diamond crystals. See Table 1 for the descriptions of the grains.

spars, magnetite, xenotime, monazite, Os–Ir PGE (Vysotskii et al., 2002b), and corundum, whose color can vary from black to green and blue. All minerals of the second association occur as large (usually >5 mm) rounded grains devoid of traces of mechanical wearing, which resemble megacrysts and the minerals of nodules in the rocks of the Jurassic and Pliocene–Quaternary complexes. In one dump near a trench in the riverbed of the Kedrovka River, S.A. Shcheka found four carbonado grains and green corundum with zircon inclusions. Judging by the occurrence of angular fragments of biotite picrites in the dump, the bed consists of these rocks. Furthermore, rounded boulders of fresh nepheline basalts were also found there. It should be mentioned that analogous associations of diamonds, including ballas and carbonado, are typical of placers in East Australia (Davies et al., 1999) and Kalimantan Island, Indonesia, where diamond is mined starting in the year 600 of our era (Spenser et al., 1988). No primary diamond sources are known in any of these areas as of yet, and corundum findings are considered there to be the main prospecting guide for diamonds.

MINERALOGY OF DIAMONDS

Crystal Morphology and Structure

In addition to the carbonado found by the authors, we also examined a collection of diamonds from an unknown source that was kept safe at the Vostretsovo mine, which is located near the carbonado finding site. The collection included six transparent and two dull colored diamond crystals, one ballas grain, and one grain of carbonado. The carbonado was completely identical to its analogues from the placer. This carbonado was briefly described in our earlier paper (Kaminsky et al., 1978).

The principal crystal morphologic characteristics of the diamonds are summarized in Table 1 and Fig. 2. All single crystals are rounded–angular distorted octahedroids grading into dodecahedroids and cuboctahedrons, which was caused not by the mechanical wearing of the crystals but their active chemical dissolution and recrystallization. This follows from the numerous dissolution features, which are dominated by negative trigonal pyramids or tetrahedrons (Fig. 3a) and commonly develop on (111) faces, whereas rhombododecahedrons of the (110) belt with lengthwise striation develop along edges (Fig. 3b). The shapes of the crystals become thereby significantly distorted, with the development of block structures, as well as phantoms in octahedrons and twins. All of these phenomena were repeatedly reproduced experimentally by the dissolution of diamond in various oxidants and silicate melts (Skvortsova et al., 1983; Khokhryakov and Pal'yanov, 1990; and others).

When broken up, one of the grains (grain no. 7) of rounded morphology revealed a radiating inner structure with concentric features (Fig. 4) and contained a large black inclusion in the core (Fig. 5). These features suggest that the grain is ballas, although it shows some morphological features of an octahedron, and the structure of its surface differs from that of typical ballas. The outermost coat of this grain (0.7–1 mm thick) consists of spongy, poorly polishable diamond.

A somewhat different morphology is typical of opaque crystals nos. 8 and 9. In addition to octahedron faces with trigonal dissolution features and dodecahedron faces with lengthwise striation, they show well developed cube faces with round dissolution knolls.

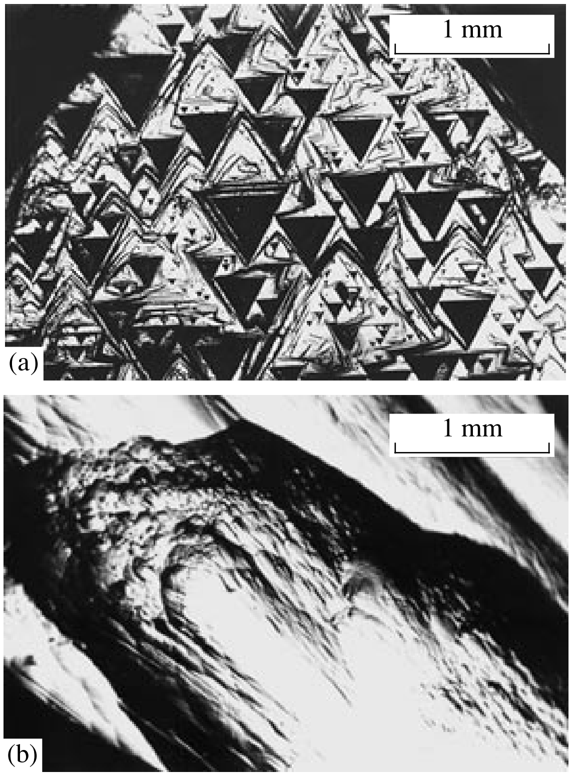

Fig. 3. Dissolution features of diamonds: (a) on (111) faces, grain no. 8; (b) belt (110) of a rhombododecahedron, grain no. 4.

Such crystals usually contain external coats that differ in structure from their cores. Indeed, upon its breakup, one of the grains (no. 9) was found out to contain a dull greenish outer coat (0.7–1.5 mm thick) with a radiating structure and a transparent octahedral core. Furthermore, the outer coat was determined to include a few ellipsoidal pores 1.1 × 0.47 mm, which began at cracks at the surface of the crystal and continued inward the coat (Fig. 6). Near the outer coat, the transparent octahedral core abounds in TiO_2 dust. The microcavernous walls of the pores are covered with small (<20 μm) diamond crystals of steel gray color, which resemble the carbonado aggregate. A seemingly analogous cavity in a diamond crystal was described by Galimov (1984).

The carbonado consisted of large angular grains, with the morphologies of some of them remotely resembling those of some single crystals. The surface of all grains is covered by a glaze-like brownish black film, which also covers the walls of the pores to depths of 1–2 mm from the surface. In fresh fractures, the grains are silvery gray with violet pinkish tints. The pores are sometimes filled with a white or bright green powdery or tabular mineral. The inner crystal morphology of the carbonado (from both the placer and the collection) is analogous to those of its Brazilian analogues (Fig. 2, no. 10). This is a porous aggregate of “imbricated” transparent crystallites (Fig. 7a), whose sizes vary from 1 to 50 μm. This aggregate contains occasional large (up to 3 mm) dull hexagonal prisms of diamond, whose shapes are analogous to those of corundum. The fine-grained aggregate abounds in small (100–150 μm) cavities with flattened and cubic diamond crystals that occur in free space (Fig. 7b). SEM images indicate that the pores are interconnected via numerous tubular pathways.

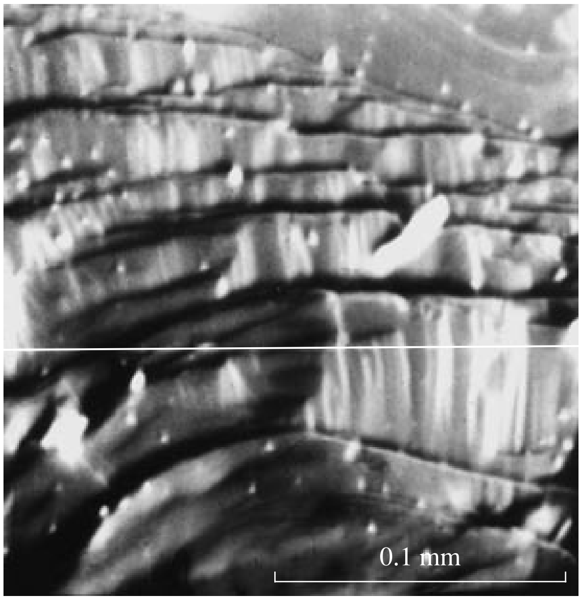

Fig. 4. Radiating with concentric features structure of ballas. Grain no. 7, JXA-5a. SE image.

The powder X-ray diffraction patterns and the X-ray diffraction patterns of both single crystals and carbonado display the characteristic lines of diamond with *d*/*n* 2.05, 1.25, and 1.07. We do not agree with Seliverstov (1996) in that the powder X-ray diffraction patterns of the carbonado show lines of lonsdaleite, and the carbonado itself is analogous to yakutite, a diamond variety recently discovered by F.V. Kaminsky. The latter researcher (Shibata et al., 1993) has convincingly demonstrated that yakutite is a typical impact phase, whose cubic crystal lattice is partly modified into a hexagonal one under the effect of shock pressures. According to the mechanism responsible for the origin of carbonado (see below), lonsdaleite cannot appear in carbonado, as was demonstrated in (Kaminsky et al., 1978). The reflections observed in the electron diffraction patterns were most probably caused by the imperfectness of the structures of twin and crystallite boundaries.

Luminescence

In studying the conditions under which diamonds are produced, much attention is devoted to the luminescence of this mineral under the effect of radiation of variable energy. The luminescence of diamond is known to be caused by defects in its crystal lattice that are related to nitrogen accommodation in it. According

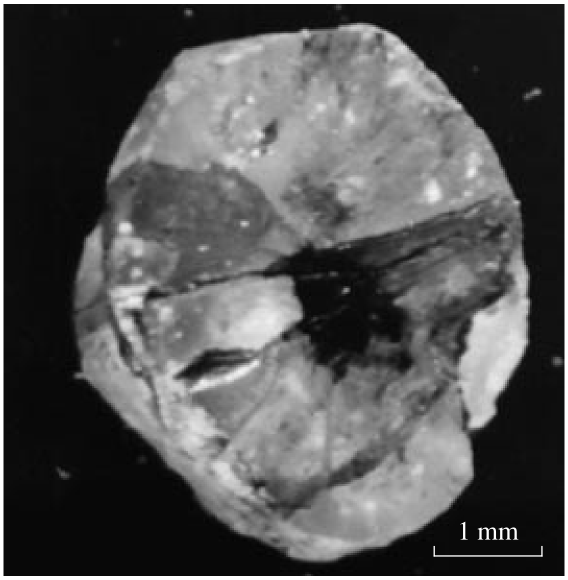

Fig. 5. Inclusion of kaersutite, titanaugite, titanomagnetite, and ilmenite in the core of ballas grain no. 7.

to the systematics proposed by Orlov (1973), our single crystals of diamond belong to variety I, which implies that they should be enriched in nitrogen. Indeed, the IR spectra obtained for one of the transparent crystals (Fig. 8) shows, in addition to lattice oscillation at 1800–2600 cm^{-1}, a few clearly pronounced peaks (at 1010 and 1430 cm^{-1}) indicating that the mineral contains nitrogen at various crystal chemical sites.

According to modern concepts (Bokii et al., 1986), peaks at 1100 and 1282 cm^{-1} are attributed to defects A, which result from the replacement of carbon atoms by two nitrogen atoms in the diamond structure. The calculated nitrogen concentrations in these defects N_A = 3.3 × 10^{19} cm^{-1}. The frequencies of 1010, 1100, 1175, and 1332 cm^{-1} characterize the B1 defect, which is caused by platy aggregates of nitrogen atoms along the (111) plane. The nitrogen concentration (calculated with the use of various equations) in these defects is (5.9–6.5) × 10^{19} cm^{-3}. The defect C (1135 and 1345 cm^{-1}) is absent from the spectrum.

In addition to the aforementioned major defects, the spectrum shows a peak at 1430 cm^{-1}, which is correlated with the defect B2. This defect is caused by the oscillations of platy aggregates of nitrogen atoms in the (100) plane. The appearance of a band at 415 nm in the visible region of the spectrum (Fig. 8, inset) characterizes the defect N3V, which results from the origin of vacancies in the diamond structure due to the entering of nitrogen atoms. The aforesaid led us to attribute this diamond crystal to mixed type III + Ia. The minima at 1630 and 2350 cm^{-1} testify that the structure contains neither H_2O nor CO_2, and the peaks at 2850–2925 and 3107 cm^{-1} suggest the presence of CH_2 and CH bonds.

Blue photoluminescence, cathodoluminescence, and X-ray luminescence is typical of all of the transparent single crystals (Table 1). The opaque greenish and gray “single” crystals and carbonado do no luminesce in the photo and X-ray regions. Upon annealing in oxygen for determining the carbon isotopic composition (see below), the gray crystal showed weak pale blue luminescence. It is interesting to observe the cathodoluminescence of the grain in a cross section under an electron beam. The microcrystalline material luminesces in orange–red, while the inner parts of the grain contain domains with yellowish green luminescence, perhaps, due to the presence of relics of primary nitrogen-bearing diamond. Analogous luminescence is sometimes observed in the marginal parts of grains and along cracks in ballas. Similar phenomena were described by many researchers (Gnevushev et al., 1963;

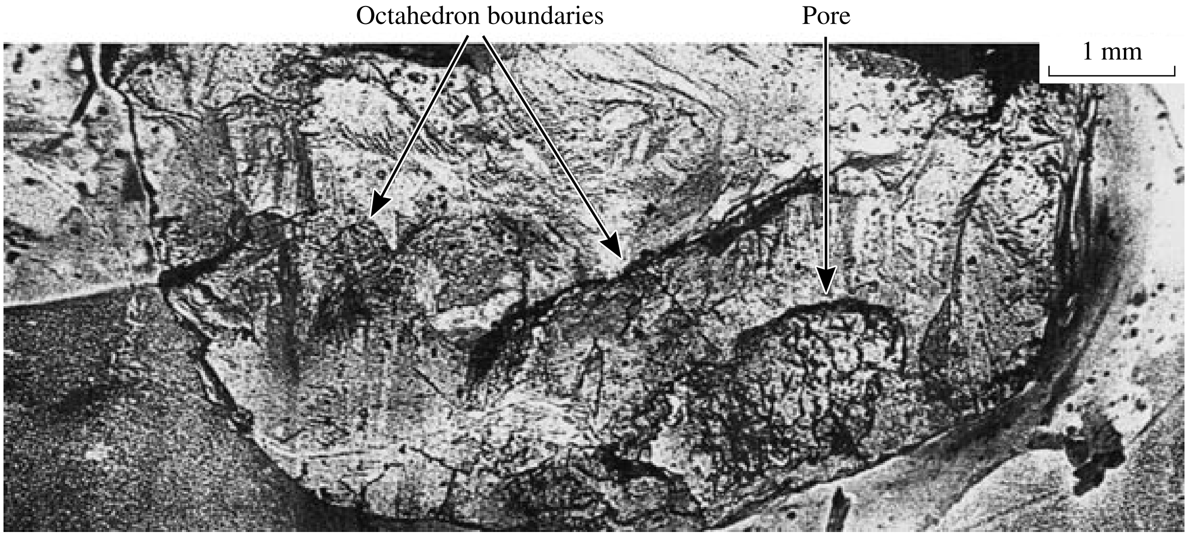

Fig. 6. Outer coat with pores around an octahedron. Grain no. 9.

Argunov et al., 1985; Zinchuk et al., 1993) in recrystallized diamonds from kimberlite pipes. Makeev et al. (2003) found a diamond octahedron with blue luminescence in the core of Brazilian carbonado with orange luminescence. We failed to obtain IR spectrum of small chips and powder of carbonado: intense absorption was observed throughout the whole range of frequencies.

Trace Elements in Diamonds

We analyzed both parts of pure diamond and macroscopically discernible inclusions in it, with two to four analyses in each grain. The analyses indicate (Table 2) that transparent grains (no. 5) are the poorest in trace elements. They contain Ti, Mn, Y, Zr, and, at a few analytical spots, also Ca, Mg, and Si. The latter two elements and Na seem to be contained in silicate inclusions. The list of minor elements is more diverse, and their concentrations are higher in the ballas and colored opaque crystals, which contain, in addition to the aforementioned elements, also Sr, Ba, and Ni, and the concentrations of Y reach 0.007 wt %. It is also pertinent to mention that the greenish crystal (no. 8) is anomalously high in Al, which can be ascribed, based on the stoichiometric proportions with other elements, to possible inclusions of silicates. The carbonado (grains K-1 and K-2) contain the same spectrum of elements but their concentrations are much higher, as high as a few percents. The mineral contains La and P, with the latter element contained in stoichiometric proportions with Y typical of phosphates. This was later corroborated by the identification of Y, La, Sr, and Ba phosphates. The diamonds are characterized by enrichment in Ti in the absence of Cr, or, if the latter is present, it is correlated with “unusual” elements: Zr, Y, Sr, and Ba. The review of trace and minor elements contained in diamonds indicates that the probable deep-seated assemblage of their inclusion minerals most likely corresponds to lamproites and eclogites but not kimberlites and peridotites, and the parental magma was enriched in Ti ad P. The increase in the concentration of Y and other lithophile elements in the carbonado compared with the single crystals argues that these elements were introduced into them by the same process.

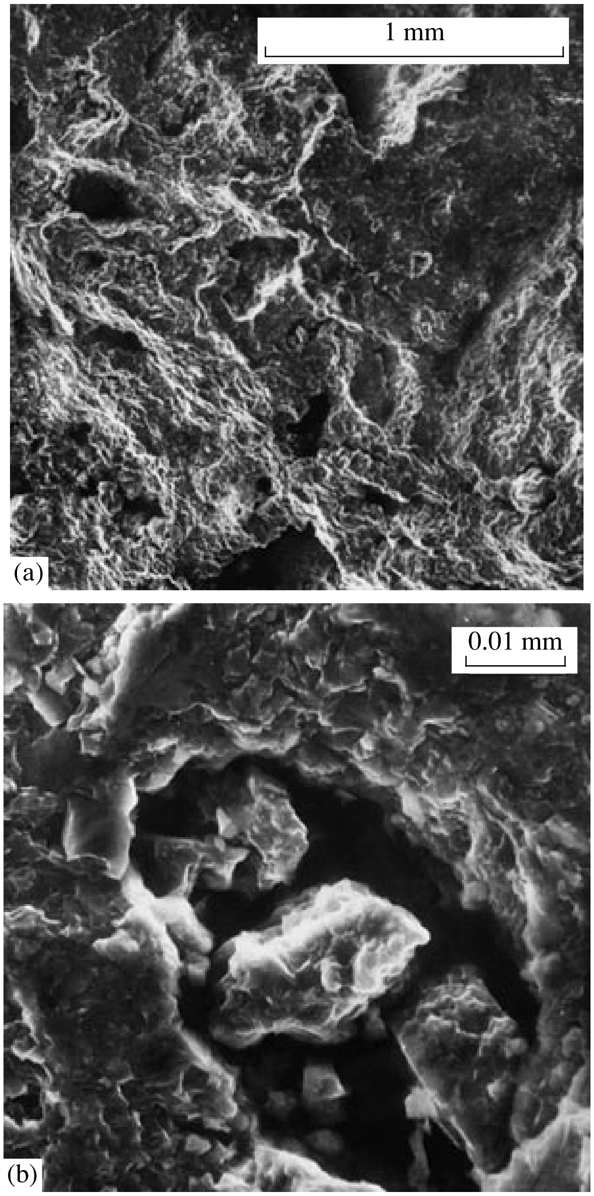

Fig. 7. Surface structure of carbonado. Grain no. 10.
(a) general view; (b) cavity with diamond crystals. JSM U-3. SE image.

Mineral Inclusions in Diamonds

The data obtained on mineral inclusions in diamonds from Primorie provide valuable genetic information. These diamonds were the first determined to contain native Al (Gorshkov et al., 1996) and Sn, along with some REE phosphates (Shcheka, 1994; Seliverstov et al., 1996), which highlights the analogous character of carbonado from Primorie and Brazil.

The obviously secondary inclusions in monocrystalline diamonds are dominated by graphite, whose concentration increases in the most strongly distorted rounded grains. This mineral occurs as intricately shaped radiating aggregates or platelets on crystal faces and in flat cracks directed from the surface of the crystals inward. In some grains, trigonal dissolution cavities are filled with a yellowish white powdery mineral and brown platelets. According to the powder X-ray diffraction pattern (Table 3), this is a mixture of a Ca zeolite (mordenite) and lepidocrocite. In spite of the complete coincidence of the lines of both minerals, the intense reflections at 2.08 and 1.937 allowed us to reliably identify lepidocrocite (to confirm the visual identification). In addition to the aforementioned minerals, the diamonds contain small (1–3 μm) inclusions whose K, Al, and Si proportions correspond to those in muscovite. It should be mentioned that these are the youngest

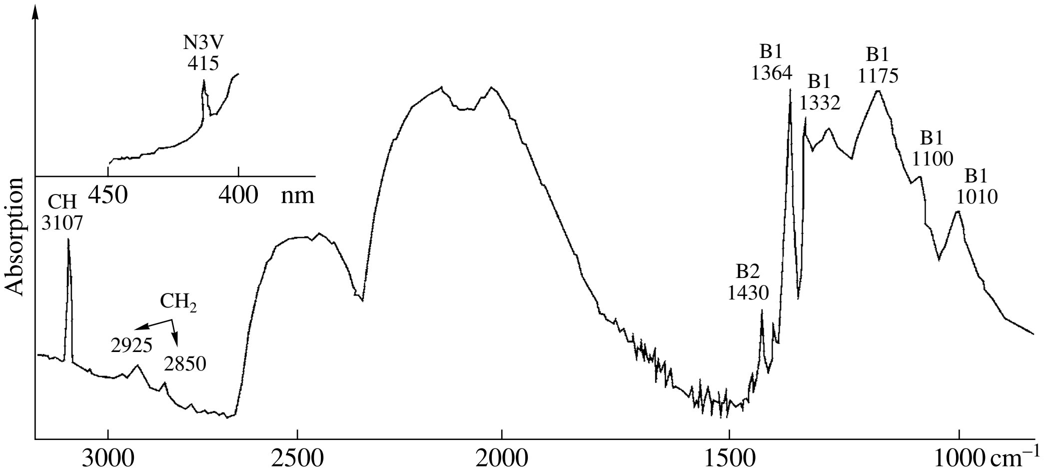

Fig. 8. Absorption spectra of diamond grain no. 5. Perkin Elmer, KSVU-5.

inclusions, which crystallized after diamond dissolution.

The powder X-ray diffraction pattern (Table 3) of the powder extracted from ballas (no. 7) upon its breakup shows lines of churchite (Y hydrophosphate) and rutile, which is consistent with the elevated Y contents in all of our diamonds and with the occurrence of xenotime in them (Shcheka, 1994; Seliverstov et al., 1996). The outer coat of grain no. 9 contained small inclusions of Fe, Mn, Ca, Al phosphate, which was identified on a microprobe.

The spectrum of primary inclusions in the single crystals of diamond is also diverse. Small (20–60 μm) rounded inclusions of K-omphacite, a fairly rare mineral, were identified in a cross section of grain no. 6 (Table 4). The omphacite usually occurs in aggregates with rutile and corundum, a fact that definitely points to an eclogite, deep-seated mineral assemblage of the inclusions. According to Sobolev (1991), pyroxene of this composition is characteristic of diamond from lamproites, but Pinz et al. (1975) have also found them in African diamonds from kimberlites (the mineral contained up to 0.87 wt % K_2O). All of the K-pyroxenes were found in the eclogite mineral assemblage, in association with titanian amphiboles, magnetite, and rutile. According to our microprobe data, the corundum and rutile in our diamonds contain no admixtures.

The black inclusion in the ballas (see above and Fig. 5) was proved to be polymineralic and included identified titanaugite, kaersutite, ilmenite, rutile, and magnetite (Table 4), i.e., high-Ti minerals. We failed to determine the exact relationships between them, but they occur in intricate intergrowths with fine-grained diamond, and the inclusion itself is intersected by cracks along which the diamond is recrystallized into a fine-grained aggregate. This grain contains no graphite. Judging by the highly calcic composition of the pyroxene and the predominantly tetrahedral coordination of Al in this pyroxene and kaersutite, this is a relatively shallow-depth and low-temperature association. The ilmenite has a remarkable composition: the inclusion contains both high-Mg oxidized and high-Fe reduced, Mn-rich varieties. The latter is typical of syngenetic inclusions in Brazilian diamonds (Meyer and Svisero, 1975). The scanning of each of the grains by an electron beam indicates that the grains are homogeneous and have no chemical zoning. The magnetite separated from the same inclusion is rich in Ti, Al, and Cr, a typical feature of high-temperature magmatic magnetite from alkaline–ultrabasic rocks (Shcheka et al., 1980).

Our analyses of inclusions in diamond grain no. 7 indicate that the titanaugite notably differs from deep K-omphacite and likely corresponded to the lower pressure crystallization of the melt. At the same time, all of the aforementioned inclusion minerals are usual components of the Jurassic alkaline picrites and Neogene–Quaternary basalts, as well as of the placer in the area of the Kedrovka River. Table 5 presents analyses of the respective minerals and the host rocks of these complexes. Their comparison with the mineral inclusions in the diamonds demonstrates that their chemical compositions are identical, although ilmenite from the Jurassic rocks is more oxidized, a fact that is readily explainable by the shallow-sitting character of the picrites. The titanaugite and kaersutite inclusions in diamond display much compositional differences from their analogues from the Neogene–Quaternary basalts: the titanaugite in diamond is lower in Al, Fe, and Na, and the kaersutite is poorer in Fe and K. The relatively low Ca concentration and high Al(VI) fraction in pyroxene from the alkaline basalts suggest that these rocks could have crystallized at higher temperatures and pressures.

In a fresh fracture of the ballas (no. 7), we identified native Sn, which is the first find of this phase in diamonds. It should be emphasized that soft minerals can be found in diamonds only in a fracture surface because otherwise they are worn out during polishing. Tin was found in the filling of a trigonal cavity (8–10 μm

Table 1. Main characteristics of the diamonds

Grain no.	Type, according to Orlov (1973)	Morphology	Color	Mass, g	Size, mm	Cathodoluminescence color	Note
1	I	Dodecahedroid, twins	Colorless	0.265	5 × 6	Blue	Numerous cracks with graphite fringes
2	I	Flattened octahedron	″	0.246	4.5 × 6.5	″	Cellular (tetrahedrons) surface
3	I	Rounded octahedron, twins	Bluish	0.282	5 × 6.5	″	Rounded surfaces with abundant dust inclusions
4	I	Distorted octahedron	Colorless	0.239	4.5 × 5.5	″	
5	I	Dodecahedroid with octahedron relics	Pink	0.221	4 × 6	″	Milk-white along cracks
6	I	Flattened and distorted octahedron	Colorless	0.243	4 × 7	″	Graphite inclusions, limonite stains
7	I → VI	Rounded, radiating in fracture	Greenish semitransparent	0.230	4.5 × 5.5	Pale blue	The core contains a large (2 mm) black inclusion
8	I → VI	Combination of rhombododecahedron, octahedron, and cube	Greenish dull	0.124	4 × 4.5	Weak, pale orange	Tetrahedral etching pits on (111) faces, dull outer coat
9	I → VI	Dodecahedroid	Silver gray, opaque	0.121	4 × 4.5	Absent and pale blue after annealing in oxygen	″
10	X	Porous, rounded–angular grains	Brownish black, violet gray after annealing in oxygen	0.117	4 × 7, crystallites 1–50 µm	Red colors, up to yellowish green in single crystallites inside the grain	Inclusions of powdery minerals in pores
K-1	X	″	Brownish gray, pinkish in fresh fracture	0.152	4 × 6, crystallites 1–50 µm	″	″
K-2	X	″	Brownish gray, silvery gray in fresh fracture	0.110	4 × 6, crystallites 1–20 µm, single crystallites 0.5–1.3 mm	″	″
K-3	X	″	Yellowish brown, silvery gray in fresh fracture	0.118	4 × 5, crystallites 1–50 µm	″	″
K-4	X	″	Soot black, violet gray in fresh fracture	0.090	4 × 4, crystallites 1–20 µm	″	″

Table 2. Minor and trace elements in the diamonds

Grain no./analytical spot no.	Si (10)*	Al (1)	Ca (1)	Mg (3)	Fe (3)	Ti (3)	Sr (1)	Ba (30)	Na (0.1)	Mn (1)	Ni (1)	Y (1)	La (10)	Zr (1)	Cr (5)	P (100)	Co (5)
K-1/1	10	10	–	–	–	300	10	–	3	1	–	0.3%	30	5	–	100	–
K-1/2	10	–	–	–	–	0.5%	–	–	1	50	–	5%	50	100	30	2%	30
K-1/3	10	700	–	30	10	50	5	–	3	1	–	100	0.3%	10	5	–	–
K-1/4	70	30	30	50	10	10	10	–	5	–	–	50	100	–	–	–	–
K-2/1	5%	3%	10	–	1%	0.1%	0.1%	100	5	1	–	0.1%	0.3%	70	100	500	–
K-2/2	10	10	10	–	–	100	100	–	3	10	–	1	10	50	30	–	–
5/1	–	–	–	–	–	10	–	–	–	3	–	10	–	–	–	–	–
5/2	–	–	30	10	–	10	–	–	–	3	–	10	–	10	–	–	–
5/3	–	–	–	–	–	–	–	–	–	3	–	–	–	–	–	–	–
5/4	30	–	30	10	–	30	–	–	5	3	1	–	–	10	–	–	–
7/1	10	10	10	–	–	10	30	–	0.1	1	–	50	–	–	–	–	–
7/2	10	10	10	–	–	10	30	30	0.1	1	–	30	–	–	–	–	–
7/3	10	10	10	–	–	10	50	30	0.1	1	70	30	–	–	–	–	–
7/4	10	10	10	–	–	10	–	–	0.1	1	–	70	–	–	–	–	–
8/1	50	500	30	30	–	30	–	–	1	–	1	3	–	–	–	–	–
8/2	30	–	–	10	–	10	–	–	1	–	1	–	–	–	–	–	–
9/1	50	50	30	5	3	10	1	30	n.a.	3	1	–	–	–	–	–	–
9/2	30	30	30	5	3	30	1	–	n.a.	5	3	–	–	–	–	–	–
9/3	40	30	30	3	3	10	1	30	n.a.	3	3	–	–	3	–	–	–

Note: K-1 and K-2 are carbonado from the placer, **5–8** are single crystals from the collection. Analyses were conducted by the semiquantitative laser spectral technique (analyst Yu.G. Kosovets). All elements (except those given in %) are in $n \times 10^{-4}\%$, n.a. means not analyzed.

* Detection limit.

across) in the diamond. The quantitative analysis of this phase indicates that it is 99.9 wt % Sn, with the concentrations of Pb, Bi, Sb, Ag, and In below the detection limit. The same diamond grain was found out to contain an admixture-free apatite (3–5 μm).

In conclusion, it should be mentioned that our single crystals of diamond bear small (1–3 μm) rounded inclusions that contain only K. We provisionally identified these inclusions as consisting of a fluid and salt. They do not contain either S or Cl and are likely K nitrates or carbonates, which lends an argument in support of the potassic composition of the melt. The mineral occasionally contains analogous inclusions with Ca, Na, Cl, and S, i.e., consisting of Ca and Na chlorides and sulfates. Finally, microprobe analyses have also revealed small (0.5–5 μm) inclusions enriched in K and containing Fe, Mg, Ca, Si, Na, Cl, and S. Conceivably, these are relics of the residual melt (Navon et al., 1988). We failed to analyze them by microprobe because of the small sizes of these inclusions and their active evaporation.

According to (Orlov, 1973; Trueb and Wys, 1969; Shibata et al., 1993; and others), carbonado typically contains the maximum amount (up to 20%) of various foreign inclusions, which occur as parallel strips. The inclusions are dominated by Ti-bearing minerals, REE, Sr, Y, and Ba phosphates and bear strongly subordinate amounts of minerals of Mg, Cr, and Ni, which are characteristic of the peridotite assemblage of inclusions contained in single diamond crystals from kimberlites. The same minerals accompany carbonado in placers (Trofimov, 1980). The carbonado from Primorie is no exception. The powder X-ray diffraction pattern of the chips (Table 6, no. 1) shows, in addition to lines belonging to diamond, also lines of anatase and rutile (the latter is predominant). Rutile was also separated in the form of small (no larger than 1 mm) red grains (Table 6, no. 2). According to electron microscopic data (Seliverstov et al., 1996), both minerals occur as aggregates with diamond microcrystals, with anatase (whose grains do not exceed a few fractions of a micrometer) composing the outer coats of the pores. The residue after burning of the chip in oxygen at a temperature of 800°C consists of cellular bluish gray aggregate containing definitely identifiable (Table 3, no. 3) anatase, and α-tridymite, which seem to have be produced by the thermal decomposition of the hydromicas. The latter was identified in the light fraction of the carbonado (Table 6, no. 4), which also shows strong lines at 2.85 and 2.60. These lines usually correspond to phosphates but were not reliably identified for our samples because of the complexity of the composition of the mixture. According to electron microscopic data (Seliverstov et al., 1996), the phosphates include xenotime and monazite, along with REE-, Ba-, and Sr-rich florencite and gorceixite. The hydrous phosphates occur as typical reniform aggregates (Fig. 9). The occurrence of these phosphates is also confirmed by the richness of the carbonado in the aforementioned elements (Table 2). Magnetic magnetite with low concentrations of admixtures [0.21 wt % TiO_2, 0.04 wt % Al_2O_3, 0.14 wt % Cr_2O_3, 68.09 wt % (calculated) Fe_2O_3, 31.00 wt % FeO, 0.15 wt % MnO, 0.00 wt % MgO, total = 99.63 wt %] was separated from a powder of the carbonado. Other inclusions are zircon, corundum, and native Al, all of them containing no admixtures (Gorshkov et al., 1996).

Table 3. Powder X-ray diffraction patterns of secondary inclusions in the diamond crystals

Sample 4			Sample 7		
d/n	I	mineral	d/n	I	mineral
3.77	3	*M*	3.27	4	*Rt*
3.33	10	*M*, *L*	3.06	10	*C*
3.17	3	*M*	2.83	8	*C*
2.80	2	*M*	2.69	3	*C*
2.65	3	*M*	2.47	5	*C*, *Rt*
2.44	3	*M*, *L*	2.15	2	*C*, *Rt*
2.28	2	*M*, *L*	2.06	5	*C*, *Rt*
2.08	10	*M*, *L*	1.871	4	*C*
2.02	4	*M*	1.808	3	?
1.937	10	*M*, *L*	1.709	1	?
1.792	4	*M*	1.532	1	*C*
1.680	3	*M*	1.487	2	*Rt*
1.654	1	*M*	1.447	2	*C*, *Rt*
1.539	1	*M*, *L*	1.343	1	*C*, *Rt*
1.481	1	*M*	1.322	1	*C*
1.424	1	*M*, *L*	1.145	1	*C*
1.356	1	*M*			
1.330	1	?			
1.308	1	*M*, *L*			
1.271	1	*M*			
1.248	1	*M*, *L*			
1.209	1	*M*, *L*			
1.198	1	*M*, *L*			
1.137	3	*M*			
1.114	1	*M*			
1.086	1	?			
1.056	1	*L*			
1.049	1	*L*			

Note: Minerals: *M*—mordenite, *L*—lepidocrocite, *C*—churchite, *Rt*—rutile.

Judging by literature data, Brazilian carbonado contains analogous inclusions. Only carbonado from the Ubangi placer (Trueb and Wys, 1971; Shibata et al., 1993) is enriched in Cr_2O_3 and contains inclusions of chromite, olivine, melilite, and perovskite, along with Ti-bearing minerals and REE phosphates. This association is typical of alkaline–ultrabasic rocks, including

Table 4. Chemical composition (wt %) of syngenetic mineral inclusions in single diamond crystals

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	54.64	51.21	41.84	–	–	–	–	–	–	–
TiO_2	0.59	1.64	4.73	54.89	51.29	51.00	53.45	53.49	53.37	11.53
Al_2O_3	10.83	3.61	11.32	0.01	0.03	–	0.02	–	0.3	3.50
Fe_2O_3	n.a.	n.a.	n.a.	1.92	8.80	7.67	0.88	0.40	–	44.01
FeO	4.90	7.14	11.02	36.07	33.72	35.93	43.54	46.06	45.64	36.16
MnO	0.07	0.08	0.07	0.31	0.38	0.39	0.76	1.09	1.30	0.46
MgO	8.14	14.98	13.61	7.28	6.80	5.37	2.05	0.14	0.11	3.77
CaO	11.98	21.21	11.15	–	–	–	–	–	–	–
Na_2O	6.69	0.22	2.34	–	–	–	–	–	–	–
K_2O	0.52	–	0.80	–	–	–	–	–	–	–
Cr_2O_3	–	–	–	0.06	0.06	0.06	0.04	–	–	0.40
Total	98.38	100.10	96.88	100.54	100.93	100.42	100.73	101.18	100.44	99.84
f	25.3	21.1	31.2	74.5	77.5	81.9	92.5	99.5	99.6	91.9
f^{III}				4.5	19.0	16.1	1.8	0.8	0	52.4

Note: (**1**) Grain no. 6; (**2**–**10**) grain no. 7; (**1**, **2**) pyroxenes, (**3**) kaersutite, (**4**–**9**) ilmenite; (**10**) magnetite. JXA-5a, analyst V.I. Sapin. Here and in Table 5, FeO and Fe_2O_3 in ilmenite and magnetite were calculated based on stoichiometric considerations, $f = Fe/(Fe + Mg)$, at %, $f^{III} = Fe^{3+}/\Sigma Fe$, at %.

Table 5. Chemical composition (wt %) of rocks and minerals from the Jurassic alkaline–ultrabasic complex and the Neogene–Quaternary alkaline basaltic complex at the Kedrovka River

Component	1	2	3	4	5	6	7	8	9	10	11(15)
SiO_2	48.82	40.28	38.37	43.58	–	–	–	46.90	39.81	42.00	45.48
TiO_2	2.18	4.93	5.74	3.57	46.01	46.64	52.43	1.58	6.16	3.32	2.54
Al_2O_3	4.15	11.97	13.77	9.27	0.21	0.18	0.20	11.94	13.97	8.90	13.80
Fe_2O_3	n.a.	n.a.	n.a.	n.a.	12.30	10.78	2.48	5.69	5.86	6.30	4.52
FeO	7.54	9.95	11.44	11.55	39.45	40.09	41.24	4.25	7.48	7.80	6.32
MnO	0.18	0.17	0.19	0.20	1.88	1.83	0.59	0.15	0.11	0.26	0.25
MgO	14.64	14.02	12.72	14.71	–	–	2.94	8.73	9.77	14.50	10.81
CaO	22.04	11.96	11.98	11.26	–	–	–	18.66	10.22	10.50	8.23
Na_2O	0.40	3.07	2.98	3.06	–	–	–	1.62	2.82	1.8	3.40
K_2O	–	0.74	0.94	0.93	–	–	–	0.03	1.68	0.8	2.42
Cr_2O_3	0.03	0.05	0.04	0.16	0.29	0.36	0.04	n.a.	–	n.a.	n.a.
Total	99.98	97.15	98.17	98.29	100.14	99.88	99.93	99.55	97.22	99.53	99.77
f	22.4	28.50	33.50	30.60	100.00	100.00	89.20	37.50	42.20	34.20	35.1
f^{III}					21.80	19.5	5.10	54.70	41.20	42.20	39.4

Note: (**1**–**9**) Minerals: (**1**, **8**) titanaugite, (**2**–**4**, **9**) kaersutite, (**5**–**7**) ilmenite. (**10**, **11**) Rocks: (**10**) biotite picrite; (**11**) average composition of the basalts. (**1**–**3**, **5**) From picrite fragments at the carbonado find site; (**4**, **6**) same, from a primary exposure (no. 10); (**7**) from placer; (**8**, **9**) megacrysts in basalts. Additional determinations: for (**10**), $P_2O_5 = 0.35$ wt %. LOI = 3.0 wt %; for (**11**), $P_2O_5 = 0.78$ wt %. LOI = 2.0 wt %.

Table 6. Powder X-ray diffraction patterns of inclusions in carbonado (no. K-1)

Sample		1	2			3			4		
d/n	I	Mineral	d/n	I	Mineral	d/n	I	Mineral	d/n	I	Mineral
3.49	10	*An*	3.21	10	*Rt*	4.41	7	α*Tr*	3.37	1	*Hm*
3.23	2	*Rt*	2.46	7	*Rt*	4.12	7	α*Tr*, *P*	3.03	2	*Hm*
2.35	2	*An*, *Rt*	2.34	2	*Rt*	3.87	3	α*Tr*, *P*	2.85	2	*Hm*, *P*
2.059	10	*D*, *Rt*	2.18	3	*Rt*	3.51	10	*An*, α*Tr*, *P*	2.61	10	*Hm*, *P*
1.888	7	*An*	1.871	5	*Rt* (?)	3.23	10	*Rt*, α*Tr*	2.54	1	*Hm*
1.693	6	*An*, *Rt*	1.679	6	*Rt*	3.11	8	*P*	2.26	2	*Hm*
1.666	6	*An*	1.602	2	?	2.72	2	α*Tr*	2.21	2	*Hm*
1.481	3	*An*, *Rt*	1.500	2	?	2.51	1	α*Tr*	2.06	10	*D*, *Hm*
1.364	5	*An*, *Rt*	1.438	2	?	2.44	1	α*Tr*	1.988	1	*Hm*
1.336	5	*An*	1.369	3	*Rt*	2.36	2	α*Tr*, *An*	1.888	1	*An*
1.261	10	*D*, *An*	1.348	3	*Rt*	2.10	3	α*Tr*	1.739	1	*P*
1.166	4	*An*, *Rt*	1.230	2	?	1.878	4	*An*, α*Tr*	1.592	1	*Hm*
1.076	10	*D*, *Rt*	1.164	2	*Rt*	1.679	10	*Rt*, α*Tr*	1.476	1	*An*
			1.088	1	*Rt*	1.613	1	α*Tr*	1.380	1	*Hm*
						1.475	7	*An*, α*Tr*	1.328	1	*Hm*
						1.358	1	α*Tr*, *An*	1.297	1	*Hm*
						1.345	1	α*Tr*, *Rt*	1.262	9	*D*, *An*
						1.258	1	*An*	1.239	1	*Hm*
						1.244	1	α*Tr*, *An*	1.160	1	*Hm*, *An*
						1.216	1	*Rt*	1.076	9	*D*, *Hm*
						1.201	1	α*Tr*			
						1.101	1	α*Tr*, *Rt*			
						1.092	1	α*Tr*, *Rt*			
						1.040	1	α*Tr*, *Rt*			

Note: Inclusion **1** was analyzed in chips (Gandolfi camera), others were analyzed in powder (in rubber ball); inclusion **3** was analyzed after the grain was burnt in oxygen. Minerals: *D*—diamond, *An*—anatase, *Rt*—rutile, α*Tr*—α-tridymite, *Hm*—hydromuscovite, *P*—phosphate.

kimberlites. The presence of chromite and olivine definitely points to the peridotitic assemblage of the inclusions in the African carbonado.

In conclusion of this review of inclusions in carbonado, it is pertinent to mention that they can be subdivided into two associations: high-temperature (magmatic) and hydrothermal–supergene (hydromicas, hydrophosphates, chlorites, pyrophyllite, kaolinite, zeolites, and quartz).

Carbon Isotopic Composition

E.M. Galimov was the first to determine the ^{13}C/^{12}C ratio of carbonado from Primorie (Kaminsky et al., 1978), with many of these analyses conducted at the Far East Geological Institute, Far East Division, Russian Academy of Sciences (Table 7, Fig. 10). The results obtained at the two laboratories turned out to be identical. As at other deposits, the carbonado from Primorie is isotopically light (δ^{13}C from –24.4 to –31.9‰), whereas the transparent single crystals are isotopically heavy (δ^{13}C from –5.6 to –6.4‰), and the colored single crystals with coats have an intermediate composition (δ^{13}C from –10.3 to –11.3‰), as was repeatedly stressed by Galimov (1984) and other researchers. These determinations were accomplished using 0.2- to 2-mg samples of diamond powder, with the results of the replicate determinations scattered within the accuracy of ordinary analyses (Table 7).

Because of the unusual character of the diamonds from Primorie (abundant dissolution and recrystallization traces, outer coats, low-temperature mineral inclusions, and zonal luminescence), we determined their isotopic zoning. Analyses of this type are commonly conducted by cutting the crystals into a succession of blocks 0.5 × 0.7 × 1 mm in size that are systematically

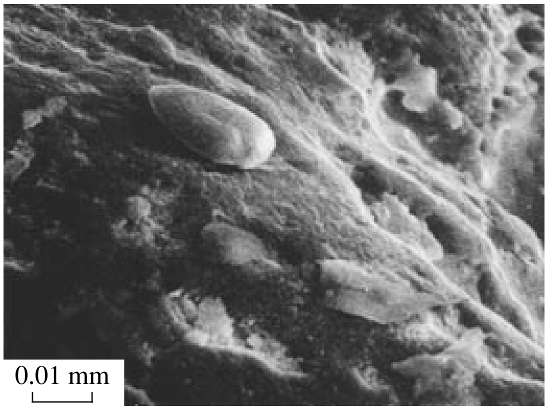

Fig. 9. Reniform aggregates of REE phosphates in carbonado. JSM U-3. SE image. Magnification 1200×.

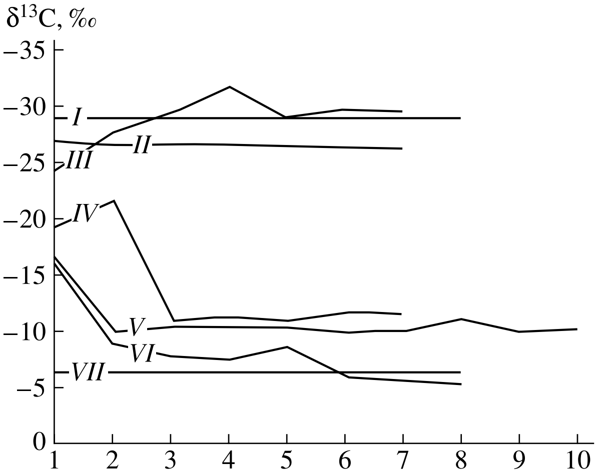

Fig. 10. Isotopic zoning of the diamonds from (1) grain cores to (2–10) margins.

I, *II*, *VII*—bulk compositions in powder, *III*–*VI*—layer-by-layer analyses of grains. *I*—sample K-1, *II*—sample K-3, *III*—no. 10, *IV*—no. 8, *V*—no. 9; *VI*—no. 4, *VII*—no. 7.

arranged in the cross section of the crystal from its core to margin (Boyd et al., 1987; Galimov, 1984; and others). The results thus obtained indicate that the zoning of the grains in terms of $\delta^{13}C$ usually spans a range of no more than 2‰ at this size of the blocks, with the possible presence of both isotopically light and isotopically heavy cores. At anomalously light ($\delta^{13}C$ from –18 to –21‰) cores, the outer coats are usually enriched in the heavy carbon isotope ($\delta^{13}C$ from –5 to –6‰), and the isotopically heavy cores ($\delta^{13}C$ from –2 to –3‰) are surrounded by isotopically light ($\delta^{13}C$ from –5 to –6‰) coats (Swart et al., 1983; Boyd et al., 1987). We believe that the usually insignificant isotopic heterogeneity even of optically zonal diamond grains are caused by the large (>1000 μm) sizes of the blocks cut of the crystal.

We conducted the layer-by-layer oxidation of undisturbed natural grains from their margins inward. We anticipate objections that we should have constantly (i.e., until complete oxidation) extracted the "light" portion of CO due to excess carbon, because the effects of equilibrium isotopic exchange ($\ln \alpha\, 10^3$) for the C_{dia}–CO, C_{dia}–CO_2, and CO–CO_2 pairs are at 800°C, respectively, +4, –6, and +10‰ (Deines, 1980). However, our results appeared to be somewhat different. First, CO was not identified by the mass spectrometer in each portion of the gas in spite of the briefness (30–35 min) of the experiments. Second, effects of different signs were obtained from discrete individual grains: the margins were isotopically heavier in the carbonado and lighter in the single crystals, and the values of $\Delta^{13}C$ from the core–margin pairs exceed the calculated values (up to 11‰). After the analysis of the first gas portions, the spectrum reaches a plateau, whose $\delta^{13}C$ values corresponded to the bulk analysis of an individual sample. Two grains (Table 7, nos. 4 and 9) were broken up after four–five experiments, and $\delta^{13}C$ values obtained for the powder (–5.6 and –10.3‰, respectively) were identical to this parameter for the plateau ($\delta^{13}C$ from –5.4 to –6.2 and from –10 to –11‰, respectively), but this did not modify the general situation. The different isotopic compositions of the marginal zones also follow from the gradual disappearance of the

Table 7. Carbon isotopic composition ($\delta^{13}C$ PDB, ‰) of the diamonds

Grain no.	Analysis no.										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	Average
K-1 (analysis by E.M. Galimov)											–29.0*
K-3 (powder)	–26.9	–26.5	–26.7	–26.6	–26.5	–26.4					–26.5
10 (from margin to core)	–24.4	–27.7	–29.4	–31.9	–29.0	–29.6	–29.6				–29.4 (5–7)
7 (powder)	–6.4	–6.3	–6.6	–6.4							–6.4
4 (from margin to core)	–15.9	–8.9	–7.9	–7.6	–8.7	–6.2	–5.9	–5.4	–5.6*		
8 (from margin to core)	–19.3	–21.7	–11.1	–11.3	–10.8	–11.7	–11.5				–11.3 (4–7)
9 (from margin to core)	–16.7	–10.1	–10.6	–10.4	–10.4	–10.0	–10.1	–11.0	–10.1	–10.3*	–10.3 (2–10)

Note: Analyses **5–8** in grain no. 4 were conducted after its breakup into two fragments; * from a separate powder charge (2 mg).

black outer coat from the carbonado grain (after which the spectrum reached a plateau), and nonluminescent (which is typical of isotopically light diamond) grains nos. 8 and 9 acquired white–blue luminescence after the experiments. Inasmuch as the experiments were carried out discretely (with the unsealing of the ampoule and a temperature decrease to room temperature), we believe that no thermodynamic isotopic equilibrium was reached, and the application of catalysts, high temperature, excess oxidizer, and the brief duration of the process caused an insignificant kinetic effect of fractionation, which is hard to quantify. In other words, not denying the possibility of the of kinetic effects of isotopic exchange in our experiments, we think that the diamonds have isotopic zoning of different signs, which was caused by the later genetic history of these diamonds. The calculated mass losses after each experiment indicate that the outer zones were a few micrometers thick.

DISCUSSION

Our research had two tasks: to identify the source of the diamonds from the unknown collection and to clarify the mechanism that produced the carbonado. The solution of the first problem seems to be simple enough. As was demonstrated above, the collection included single diamond crystals, a carbonado grain, and magnetite poor in admixtures. The composition and characteristics of the carbonado, including its carbon isotopic composition, were proved to be identical to those of its analogues from the placer at the Kedrovka River. The association of diamond with variably colored gem-quality corundum, rutile, anatase, ilmenite, and zircon is typical of placers in Australia and Indonesia (Trofimov, 1980; Spencer et al., 1988; Davies et al., 1999). The Australian and Indonesian placers, as those in Primorie, are spatially restricted to fields of Neogene–Quaternary alkaline basalts that contain gem-quality corundum (sapphire and ruby). Both New South Wales, Australia, and Indonesia have no known primary diamond deposits, but their Upper Cretaceous (older than the basalts) conglomerates were determined to contain diamonds (Trofimov, 1980). Although microdiamonds were detected in alkaline basalts with peridotite nodules in Mongolia (Kaminsky, 1984), analogous nodules in Primorie belong to the spinel facies and contain no diamonds. Hence, corundum, diamond, and gold in all of these areas were supplied from various primary sources, and the simultaneous occurrence of these minerals in the placers was caused by hydrodynamic and gravitational processes.

Minerals found as inclusions in diamonds from Primorie (Table 4, Fig. 11) have a composition identical to those of minerals from subvolcanic potassic picrites of the Jurassic alkaline–ultramafic complex (including the body near the finding site of the carbonado) and notably differ from the analogous minerals of the Neogene–Quaternary basalts. Jurassic picrites near the Kedrovka River are massive rocks that compose dikes and stocks, although diatremes that are rich in kaersutite, Ti-biotite, ilmenite, magmatic carbonates and contain large (up to 0.5 m) spinel peridotite nodules are known in nearby areas (Shcheka, 1977; Shcheka et al., 2003). As follows from the diagram in Fig. 11, the bulk-rock composition of the picrites is close to that of kaersutite, but the rocks are always enriched in K_2O, which makes them similar to the rocks of the lamproite series. Within the field of the Jurassic complex, diamonds were found in placers in adjacent territories of China (Tan Chengren, 1994) and Sakhalin (Bekhtol'd and Semenov, 1990). It should be stressed that, although inclusions of titanaugite, kaersutite, ilmenite, rutile, and high-Ti magnetite occur in the core of the diamond crystal, these are low-pressure phases, and the titanaugite composition remarkably differs from that of high-pressure omphacite. The diamond is recrystallized (see the description of grain no. 7 above) to ballas. This likely suggests that the picrites are intermediate transporters of the diamonds from other, although genetically related, explosion source rocks.

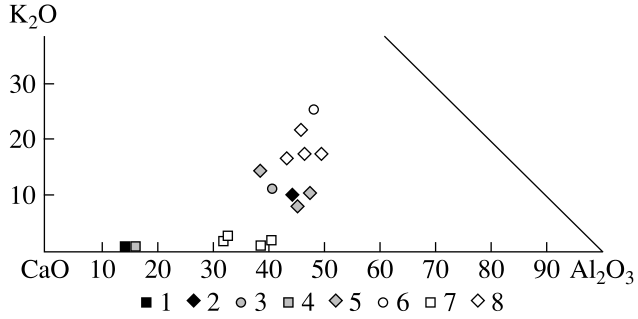

Fig. 11. Composition (at %) of (1, 2) mineral inclusions in diamond grain no. 7 and rocks and minerals of (3–5) the Jurassic alkaline–ultrabasic and (6–8) Neogene–Quaternary alkaline basaltic complexes.

(1, 4, 7)Titanaugite; (2, 5, 8) kaersutite; (3, 6) rocks.

Hence, the occurrence of omphacite, corundum, and high-Ti minerals inclusions in the diamonds and the absence of Cr and Ni point at the eclogite assemblage of these diamonds and their preferable relation to a high-K lamproite magma. The aforesaid leaves no doubt that the diamonds from the unknown collection originated from Primorie, because it is hard to imagine that they were brought to the remote taiga village from Indonesia or Australia.

The problem of the genesis of the carbonado is more complicated. First of all, it is pertinent to recall that the term carbonado was recently applied to a great diversity of diamond aggregates, from small grains of impact diamond (yakutite) to aggregates of diamond grains from kimberlite pipes (types VII–IX, according to Orlov). Both yakutite and metamorphic diamond inherit the carbon isotopic composition of the parental rocks, and the carbon isotopic composition of diamond aggregates from kimberlites is analogous to that of single diamond crystals from the same rocks. We believe that a reference sample of carbonado should be that of Brazilian porous microcrystalline aggregates with an isotopically light carbon composition ($\delta^{13}C < -25‰$) and with inclusions of diverse REE phosphates. Difficulties in the reproduction of the genesis of carbonado are related to the fact that these minerals were found only in placers, although the latter are always spatially associated with kimberlites containing monocrystalline diamond. It is commonly thought that their primary sources are so-called Brazilian phyllites, which occur as veins, dikes, and tabular bodies composed of sericite, talc, and kaolin with Fe–Mn and phosphate nodules and fragments of the host rocks and, occasionally, eclogites. The bodies of these phyllites are broken by numerous quartz veins and, sometimes, granite and pegmatite dikes. Some phyllite bodies contain diamond monocrystals, monazite, xenotime, ilmenite, perovskite, rutile, and zircon. Some researchers believe (Trofimov, 1980) that these phyllites are hydrothermally reworked kimberlites. Analogous rocks seem to be Uralian tuffizites (Shurubor, 1998) and Canadian "minettes" (Kaminsky and Sablukov, 2002). In addition to the presence of diamond, the existence of genetic relations between carbonado and kimberlites also follows from occasional finds of carbonado in diamond concentrates from kimberlites (Argunov et al., 1985) and from the presence of deep nodules with eclogite (omphacite, rutile, and corundum) and peridotite (olivine and chromite) assemblages in carbonado grains (Shcheka, 1994; Trueb and Wys, 1971). The same was repeatedly pointed out by Gorshkov et al. (1996, 1998) based on similarities in the REE patterns of kimberlites and carbonado. An analogous conclusion was definitely drawn by Argunov et al. (1985), who have also demonstrated that the intensification of dissolution and recrystallization traces of single diamond crystals are associated with the gradual transformation of these crystals into ballas and carbonado. The luminescence color is changing thereby from pale blue through yellow–green to orange. All of these features were repeatedly documented for diamonds from Primorie. Trueb and Wys (1971), who examined in much detail the microstructure and composition of Brazilian and African carbonado, conclude that these diamonds suffered the influence of younger volcanic activity (fumaroles etc.) during at least part of their evolutionary history. Analogous phenomena were described in the Udachnaya pipe (Zinchuk et al., 1993), with rocks in its upper part (0–150 m) being extensively altered and the percentage of fine-grained diamonds reaching 60%, although their affiliation with carbonado has not been proved by the carbon isotopic composition.

As was mentioned above, all diamonds from Primorie display traces of significant alterations: the extensive dissolution of the single crystals, the development of outer coats with large dissolution pores, fracturing, radial and concentric block structures, and the high porosity of carbonado. The fine-crystalline (1–50 μm) mass of the carbonado contains large (0.5 × 3 mm) newly formed hexagonal diamond "porphyroblasts." Pores in the carbonado are always filled with low-temperature hydrothermal minerals: phosphates, hydromicas, zeolites, goethite, and chalcedony.

These alterations are associated with changes in the carbon isotopic composition, which were related to the effect of the redox conditions. It is known (Galimov, 1973) that reduction in the succession $CO_2 \longrightarrow CO \longrightarrow CH_4 \longrightarrow C_2H_6 \longrightarrow C_3H_8\ldots$ is accompanied by enrichment in ^{12}C. The equilibrium oxidation of diamond at $T = 700°C$ yields CO_2 that is isotopically heavier than the C_{diam} by 11‰, with this value significantly increasing with decreasing temperature (Deines, 1980) and with the residual diamond becoming enriched in ^{12}C. Numerous experiments (Skvortsova et al., 1983; Khokhryakov and Pal'yanov, 1990; and others) indicate that the dissolution (oxidation) rate of diamond in solutions and melts is much higher than that of graphite, particularly in the presence of catalysts (REE, Cr, Ti, Ni, P, and others). Because of this, we believe that fine-grained porous carbonado can be produced by the oxidation and recrystallization of isotopically heavy kimberlite (lamproite) diamonds under the effect of low-temperature hydrothermal solutions, as was suggested in (Marakushev et al., 1995). The most plausible reaction is

$$2\,^{12-13}C_{diam} + 2\,H_2O \longrightarrow {}^{12}C_{diam} + {}^{13}CO_2 + 2H_2\,(-\Delta V), \quad \text{(I)}$$

which proceeds from left to right with decreasing pressure. The possible oxidants can be metal oxides, CO_2, P_2O_5, Cl, and F. The hydrogen released during reaction (I) should facilitate the metallization of oxides, a process typical of carbonado (which contains native Fe, Al, Cr, Ni, Si, Ta, Sn, etc.). The persistent occurrence of Sr, Ba, Y, and REE phosphates in carbonado is readily explainable in light of the enrichment of kimberlites and lamproites in these elements. The incomplete oxidation of diamond

$$2\,^{12-13}C_{diam} + H_2O \longrightarrow {}^{13}C_{diam} + {}^{12}CO + H_2 \qquad \text{(II)}$$

should result in the development of isotopically heavy outer coats on isotopically light cores, as is often the case with natural diamonds.

Obviously, these diamond transformations were metastable, as is evident from their crystallization in cavities in the form of crystal clusters (Fig. 7b). The simultaneous occurrence of primary rutile and obviously newly formed anatase in the carbonado also suggests that the recrystallization temperature of this diamond was lower than the temperature of the rutile–anatase transition (<730°C).

In conclusion, it should be mentioned that pipes with fresh kimberlites and associated placers contain practically no typical carbonado (with anomalously isotopically light carbon, a porous structure, and inclusions of REE, Ba, Sr, and Y hydrous phosphates). They show traces only of initial alterations of octahedral diamond crystals: their enrichment in the light carbon isotope, newly formed phosphates, and modified crystal morphology of diamonds. Carbonado are known only in Brazilian and Central African placers, in which these minerals are associated with ancient (>2 Ga) kimberlite bodies that were completely transformed into hydrothermally altered rocks during their long-lasting history. Not considering here the recrystallization mechanisms of diamond, we just like to mention that REE, Sr, Y, Ba, P, and F should have undoubtedly acted as catalysts, as also follows from experimental data (Kulakova et al., 1980; and others).

The following should be said concerning the outlooks for the discovery of economic diamond concentrations in Primorie. It is well known that primary (in kimberlites and lamproites) deposits of diamonds occur in ancient cratons. The territory of Primorie is a Paleozoic–Mesozoic folded area of the Sino–Korean Shield, whose margins are known to host large diamond deposits in kimberlites. It is thus unrealistic to expect that kimberlites can be found in Primorie. At the same time, there are two areas in which diamonds have long been mined from gold–sapphire placers: these are Kalimantan Island and West Australia. It is pertinent to recall that diamonds were found in Primorie also in a gold–sapphire placer. The geologic settings of the aforementioned three areas are very closely similar, and no primary sources of diamonds are known in any of them, although these sources should be undoubtedly kimberlitic. The occurrence of small diamonds in the Jurassic meymechite–picrite complex of Primorie, northeastern China (Tan Chengren, 1994), and Sakhalin (Bekhtol'd and Semenov, 1990) is beyond doubt. Judging from published data (Trofimov, 1980; Soesoo et al., 1999), diamonds in Australia and Indonesia are also likely related to analogous complexes. However, the significant percentage of altered diamonds and the presence of carbonado in these territories, the extensive recrystallization of diamonds from Primorie (which contain inclusions of minerals from meymechite–picrite pipes) suggest that these rocks served merely as transporters of diamond from deeper seated sources. It is known (Trofimov, 1980; Ilupin et al., 1990; Marakushev, 1995) that all diamondiferous provinces around the world are characterized by multiphase (occurring over time spans of 2000–40 m.y.) magmatic activity with variable diamond-bearing mineralization. It is thus reasonable to think that diamonds of different ages are in these areas partly metamorphosed and transported far away from their primary sources. The latter could be fragments of ancient diamondiferous plumes, which can be preserved at deeper levels of the cratons. It is pertinent to mention that the pair of Jurassic and Cenozoic alkaline complexes is typical of all continents (Trofimov, 1980; and others) and seems to manifest some universal global relationships. Diamonds were found in both of the complexes. The inherited character of the Cenozoic sources (from Jurassic ones) is highlighted by the similar values of the measured (for the Jurassic rocks) and initial (for the Cenozoic ones) ^{87}Sr/^{86}Sr ratios in Primorie (Shcheka et al., 2000).

In light of the facts and considerations presented above, exploration operations in Primorie should be centered on searches for secondary collectors and placers in clastic sediments of post-Devonian age (by analogy with nearby territories of China).

ACKNOWLEDGMENTS

The authors thank Yu.N. Pal'yanov (United Institute of Geology, Geophysics, and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk), A.V. Varshavskii (Institute of the Geology of Diamonds and Precious Metals, Yakutian Division, Siberian Branch, Russian Academy of Sciences, Yakutsk) for assistance with the study of the diamonds, and V.N. Rybalko (Far East Geological Institute, Far East Division of the Russian Academy of Sciences) for help in studying the morphology of diamonds. G.G. Prishchepov (Rossiya Prospecting Crew, Vladivostok) is thanked for attracting the authors' attention of the problem of the diamondiferous potential of Primorie in 1976. The final part of this research was financially supported by the Far East Division of the Russian Academy of Sciences (Grant 04-3-A-08-069) in 2004.

REFERENCES

1. K. P. Argunov, N. N. Zinchuk, V. V. Zuev, et al., "Carbonado and Defect Crystals among Fine Diamonds from Kimberlites," Mineral. Zh. **7** (2), 95–98 (1985).
2. A. F. Bekhtol'd and D. F. Semenov, "Metabasic and Ultramafic Rocks of the Susunai Range, Sakhalin Island," Tikhookean. Geol., No. 1, 121–126 (1990).
3. T. B. Bokii, G. N. Bezrukov, Yu. A. Klyuev, et al., *Natural–Synthetic Diamonds* (Nauka, Moscow, 1986) [in Russian].
4. S. R. Boyd, D. P. Mattey, C. T. Pilinger, et al., "Multiple Growth Events During Diamond Genesis: an Integrated Study of Carbon and Nitrogen Aggregation State in Coated Stones," Earth Planet. Sci. Lett. **86**, 341–353 (1987).
5. M. R. Davies, S. I. O'Reilly, and W. L. Griffin, "Diamonds from Wellington, NSW: Insights into the Origin of Eastern Australia Diamonds," Mineral. Mag. **63** (4), 447–471 (1999).
6. P. Deines, "The Carbon Isotopic Composition of Diamond: Relationship to Diamond Shape, Color, Occurrence and Vapor Composition," Geochim. Cosmochim. Acta. **44**, 943–961 (1980).
7. E. M. Galimov, "Variations in Diamond Isotope Composition and Their Relation with the Diamond Formation Conditions," Geokhimiya, No. 8, 1091–1117 (1984).
8. E. M. Galimov, *Carbon Isotopes in Oil and Gas Geology* (Nedra, Moscow, 1973) [in Russian].
9. M. A. Gnevushev, G. O. Gomon, and S. I. Futergendler, "On Relation of Diamond Luminescence with Some Other Properties" Mineral. Sb. L'vovsk. Univ., No. 17, 82–89 (1963).

10. A. I. Gorshkov, F. S. Vinokurov, D. I. Solodov, et al., "Polycrystalline Diamond from the Udachnaya Pipe, Yakutia: Mineralogical, Geochemical, and Genetic Characteristics," Litol. Polezn. Iskop. **33** (6), 588–603 (1998) [Lithol. Miner. Resour. **33** (6), 525 (1998)].
11. A. I. Gorshkov, V. A. Seliverstov, S. A. Shcheka, et al., "The First Discovery of Native Aluminum in Carbonado," Geol. Rudn. Mestorozhd. **38** (4), 381–383 (1996) [Geol. Ore Dep. **38** (4), 341 (1996)].
12. Yu. T. Gurulev, A. P. Matyunin, V. G. Sakhno, et al., "Kimberlite-like Diamondiferous Rocks in the Northern Part of the Khanka Massif, Primorie," Tikhookean. Geol. **14** (5), 103–108 (1995).
13. A. V. Ignatyev and L. V. Borovik, "Automated Equipment for Determining C, N, O, S Isotopic Composition and Techniques of Sample Preparation," in *Proceedings of 5th Working Meeting on Isotopes in Nature, Leipzig, Germany, 1989* (Leipzig, 1989).
14. I. P. Ilupin, V. I. Vaganov, and B. I. Prokopchuk, *Kimberlites* (Nedra, Moscow, 1990) [in Russian].
15. L. A. Izosov, I. V. Mishkina, N. M. Pavlichenko, et al., "On Copper Mineralization in the Maloklyuchevskaya Rift Zone, Primorie," Tikhookean. Geol., No. 4, 105–109 (1990).
16. F. V. Kaminsky and S. M. Sablukov, "Unusual Diamond Deposits", Nauka Rossii, No. 1, 4–12 (2002).
17. F. V. Kaminsky, *Diamond Potential of Non-Kimberlitic Magmatic Rocks* (Nedra, Moscow, 1984) [in Russian].
18. F. V. Kaminsky, Yu. A. Klyuev, S. A. Shcheka, et al., "First Findings of Carbonado and New Finding of Ballas in the Soviet Union," Dokl. Akad. Nauk SSSR **242** (3), 687–689 (1978).
19. A. F. Khokhryakov and Yu. N. Pal'yanov, "Morphology of Diamond Crystals Dissolved in Water-Bearing Silicate Melts," Mineral. Zh., No. 1, 14–23 (1990).
20. Yu. G. Kosovets and O. D. Stavrov, *Local Spectral Laser Analysis in Geology* (Nauka, Moscow, 1983) [in Russian].
21. I. K. Kulakova, A. N. Pushkin, A. P. Rudenko, and V. A. Shturman, "Study of Catalytic Oxidation of Diamonds in the Context of Problems of their Growth and Dissolution in Nature," Tr. TsNIGRI, No. 153, 57–64 (1980).
22. A. B. Makeev, V. Ivanukh, S. K. Obydyan, et al., "Relationships of Diamond and Carbonado: Evidence from Investigations of Brazilian and Middle Timan Collections," Dokl. Akad. Nauk **393** (3), 393–397 (2003).
23. A. A. Marakushev, N. N. Pertsev, I. A. Zotov, et al., "Some Petrologic Aspects of Diamond Genesis" Geol. Rudn. Mestorozhd. **37** (2), 105–121 (1995).
24. H. O. A. Meyer and D. P. Svisero, "Mineral Inclusions in Brazilian Diamonds," in *Physics and Chemistry of the Earth* (Pergamon, Oxford, 1975), vol. 9, pp. 785–796.
25. O. Navon, I. D. Hatcheon, G. R. Rossman, et al., "Mantle Derived Fluids in Diamond Microinclusions," Nature **335**, 784–789 (1988).
26. Yu. L. Orlov, *Mineralogy of Diamond* (Nauka, Moscow, 1973) [in Russian].
27. M. Prinz, D. V. Manson, P. F. Hlava, et al., "Inclusions in Diamond: Garnet Lherzolite and Eclogite Assemblages," *Physics and Chemistry of the Earth* (Pergamon, Oxford, 1975), vol. 9, pp. 797–816.
28. V. G. Sakhno, A. P. Matyunin, and S. S. Zimin, "Kurkhansk Diamondiferous Diatreme in the Northern Part of the Khanka Massif: Structure and Rock Composition," Tikhookean. Geol. **16** (5), 46–59 (1997).
29. V. A. Seliverstov, A. I. Gorshkov, S. A. Shcheka, et al., "Diamonds and Carbonado in Primorskii Krai: Mineralogy, Crystal Chemistry, and Genesis," Geol. Rudn. Mestorozhd. **38** (6), 485–499 (1996) [Geol. Ore Dep. **38** (6), 429 (1996)].
30. A. D. Shcheglov, S. A. Shcheka, I. Z. Bur'yanova, et al., *Volcanic Belts in East Asia* (Nauka, Moscow, 1984) [in Russian].
31. S. A. Shcheka, A. Ishiwatari, and A. A. Vrzhosek, "Geology and Petrology of the Cambrian Khanka Ophiolite in Primorye (Far East Russia) with Notes on Its Manganese-Rich Chromian Spinel," Earth Sci. (Jap.) **55** (5), 265–274 (2001).
32. S. A. Shcheka, A. A. Vrzhosek, and S. V. Vysotskiy "Jurassic Meymechite–Picrite Complexes of Primorye, Russia: Comparative Study with Komatiite and Japanese Picrite Suites, in *Plumes and Problem of Deep Sources of Alkaline Magmatism* (Khabarovsk, 2003), pp. 184–200.
33. S. A. Shcheka, "Diamonds of Primorie—Myths and Reality," Vestnik DVO RAN, No. 4, 53–61 (1994).
34. S. A. Shcheka, "Meymechite–Picritic Complexes of the Sikhote-Alin," Dokl. Akad. Nauk SSSR **234** (2), 444–447 (1977).
35. S. A. Shcheka, *Mafic–Ultramafic Intrusions and Inclusions in the Volcanic Rocks of the Russian Far East* (Nauka, Moscow, 1983) [in Russian].
36. S. A. Shcheka, A. A. Vrzhosek, A. V. Grebennikov, and I. Savada, "Notes on Liquid Immiscibility in Silicate Melts," in *Geodynamics and Metallogeny* (Dal'nauka, Vladivostok, 1999), pp. 81–92 [in Russian].
37. S. A. Shcheka, A. G. Pyatkov, A. A. Vrzhosek, et al., *Trace Element Parageneses of Magnetite* (Nauka, Moscow, 1980) [in Russian].
38. K. Shibata, H. Kamioka, F.V. Kaminsky, et al., "Rare Earth Element Patterns of Carbonado and Yakutite: Evidence for their Crustal Origin," Mineral. Mag. **57**, 607–611 (1993).
39. Yu. V. Shurubor, "Initiative Expert Examination of Communications on Discoveries of Magmatic Sources of Diamonds in Urals," Otech. Geol., No. 2, 42–45 (1998).
40. V. P. Skvortsova, I. I. Kulakova, V. P. Zhikhareva, et al., "Morphology of Diamond Crystals "Oxidized" Under Different Conditions," Mineral. Zh. **5** (6), 77–81 (1983).
41. N. V. Sobolev, I. T. Bakumenko, E. S. Efimova, et al., "Morphological Features of Microdiamonds, Contents of Trace Sodium in Garnets and Potassium in Pyroxenes from Two Eclogite Xenoliths from Kimberlites of the Udachnaya Pipe (Yakutiya)," Dokl. Akad. Nauk SSSR **321** (3), 585–590 (1991).
42. A. Soesoo, P. D. Bons, and M. A. Elburg, "Freestone Dykes an Alkali-Rich Jurassic Dyke Population in Eastern Victoria," Aust. J. Earth Sci. **46** (1), 1 (1999).
43. L. K. Spencer, S. D. Dikinis, P. C. Keller, R. E. Kane, "The Diamond Deposits of Kalimantan (Borneo)," Gems Gemology **24** (2), 67–80 (1988).

44. F. L. Sutherland, "Regional Controls in Eastern Australian Volcanism," Publ. Geol. Soc. Australia, New South Wales **1**, 13–32 (1985).

45. P. K. Swart, C. T. Pilinger, H. J. Milledge, et al., "Carbon Isotopic Variations within Individual Diamonds," Nature **303**, 793–795 (1983).

46. Tan Chengren, "Analysis of the Metallogenic Conditions of Diamond on the Jiamusi Massif," Heilongiang Geol. **5** (2), 1–9 (1994).

47. V. S. Trofimov, *Geology of Natural Diamond Deposits* (Nedra, Moscow, 1980) [in Russian].

48. L. F. Trueb and E. C. Wys, "Carbon from Ubangi—A Microstructural Study," Am. Mineral. **56** (7–8), 1252–1268 (1971).

49. L. F. Trueb and W. C. Butterman, "Carbonado: A Microstructural Study," Am. Mineral. **54**, 412–425 (1969).

50. S. V. Vysotskii, S. A. Shcheka, V. P. Nechaev, et al., "First Finding of Sapphire from Cenozoic Alkali-Basaltic Volcanoes in the Primor'e Region," Dokl. Akad. Nauk **387** (6), 806–810 (2002a) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **387** (9), 1100 (2002a)].

51. S. V. Vysotskii, G. G. Shcheka, and B. Lehmann, "First Finding of Platinum-Group Minerals in the Gold- and Sapphire-Bearing Placer of the Kedrovka River (Bol'shaya Ussurka River Basin, Primorie Region)," Dokl. Akad. Nauk **387** (1), 80–84 (2002b) [Trans. Russ. Acad. Sci., Earth Sci. Sec. **387** (8), 890 (2002b)].

52. I. N. Zinchuk, Z. V. Spetsius, V. V. Zuenko, and V. M. Zuev, *Udachnaya Kimberlite Pipe* (Novosibirsk. Univ., Novosibirsk, 1993) [in Russian].