

Interrelation of Diamond and Carbonado (Based on the Study of Collections from Brazil and Middle Timan)

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We investigated a collection of 14 samples of the Brazilian carbonado from Bahja (Andarai area) and Minas Gerais Plateau (Makubas River area), 1 sample of the Middle Timan carbonado, and 3 diamond crystals from the Ichet'yū deposit [1, 6–8, 10, 11]. Study with the help of a JSM-6400 scanning electron microscope equipped with Link ISIS-300 device made it possible to reveal the presence of fragments of 11 metallic film species on the carbonado surface (Au, Au–Ag, Sn, Bi, Pb–Cr, Fe, Ni, W, Fe–Cr, Fe–Ni–Cr, and Fe–Sn) and 12 inclusion species within the carbonado grain (Au, Ag, Fe, Ti, Ni, Fe–Ni, Fe–Cr, Fe–Ni–Cr, Ni(Fe,Co), Ni–Cr, Sn–Cu, and W(Fe,Cr,V). Taking into account repetitions in the list presented above, the total number of metals, intermetallides, and natural alloys is reduced to 18 species [6]. The studied carbonado samples have color cathodoluminescence (CCL) of two types. Cathodoluminescence of the first type (CCL 1) characterized by the zonal color distribution was observed on the chip of a large carbonado grain. It is characterized by red luminescence at the center, green luminescence in the middle zone, and yellowish green luminescence at the edge [6, 7]. Subsequently, the same zonal CCL 1 was observed as blue patches (luminescence of diamond grains 0.1–0.3 mm in size) in a green matrix (luminescence of carbonado) on the surface of another carbonado sample from Bahja, Brazil (K-3). Cathodoluminescence of the second type (CCL 2) characterized by a patchy rather than zonal pattern is typical of all other samples.

We recorded the overgrowth of a relatively large (3 mm) flat-faced octahedral diamond crystal by the fine-grained carbonado aggregate (Fig. 1). This unique observation testifies to the close genetic nature of carbonado and diamond. The carbonado sample chip with the zonal CCL revealed an octahedral face covered with a thin (0.3 μm), nearly continuous coating of titanium oxide (rutile). The coating developed as a result of the oxidation of metallic titanium film and subsequently buried under the carbonado overgrowth. Therefore, the coating is well preserved and provides an additional piece of evidence in favor of diamond crystal growth across metallic membranes [6–11]. This hypothesis is also supported by the preservation of fine native metal inclusions in the microcrystalline diamond aggregate from the Brazilian carbonado sample [6, 7].

According to some researchers, carbonado is confined to the Southern Hemisphere (placer deposits in South America, South Africa, and Australia). They believe that carbonado formed as a result of catastrophic impacts that took place hundreds of millions of years ago on the ancient Gondwana continent, which subsequently broke up into three southern continents. Results of our experiments refute the above hypothesis. In particular, this statement is based on the finding of carbonado associated with diamond in kimberlite pipes and placers of the Northern Hemisphere. In [1, 8], we presented SEM images of a reliable finding of black carbonado fragment (size 3 × 4 mm, weight 74 mg) in the Ichet'yū deposit (Middle Timan). We present the isotope evidence in this paper. The carbonado sample surface contained a coating of titanium oxide (probably rutile), ilmenite, and amphibolite (tremolite). Mineralogical features of carbonado from kimberlite pipes in eastern Siberia are described in [4, 5]. Thus, findings of carbonado in the Ichet'yū diamond deposit and Yakutian kimberlite province dispel the concept of strict confinement of carbonado to the Southern Hemisphere.

Carbon isotopy provides essential genetic information. The issue of $\delta^{13}\text{C}$ isotopy of diamond and carbonado is discussed in numerous publications devoted to

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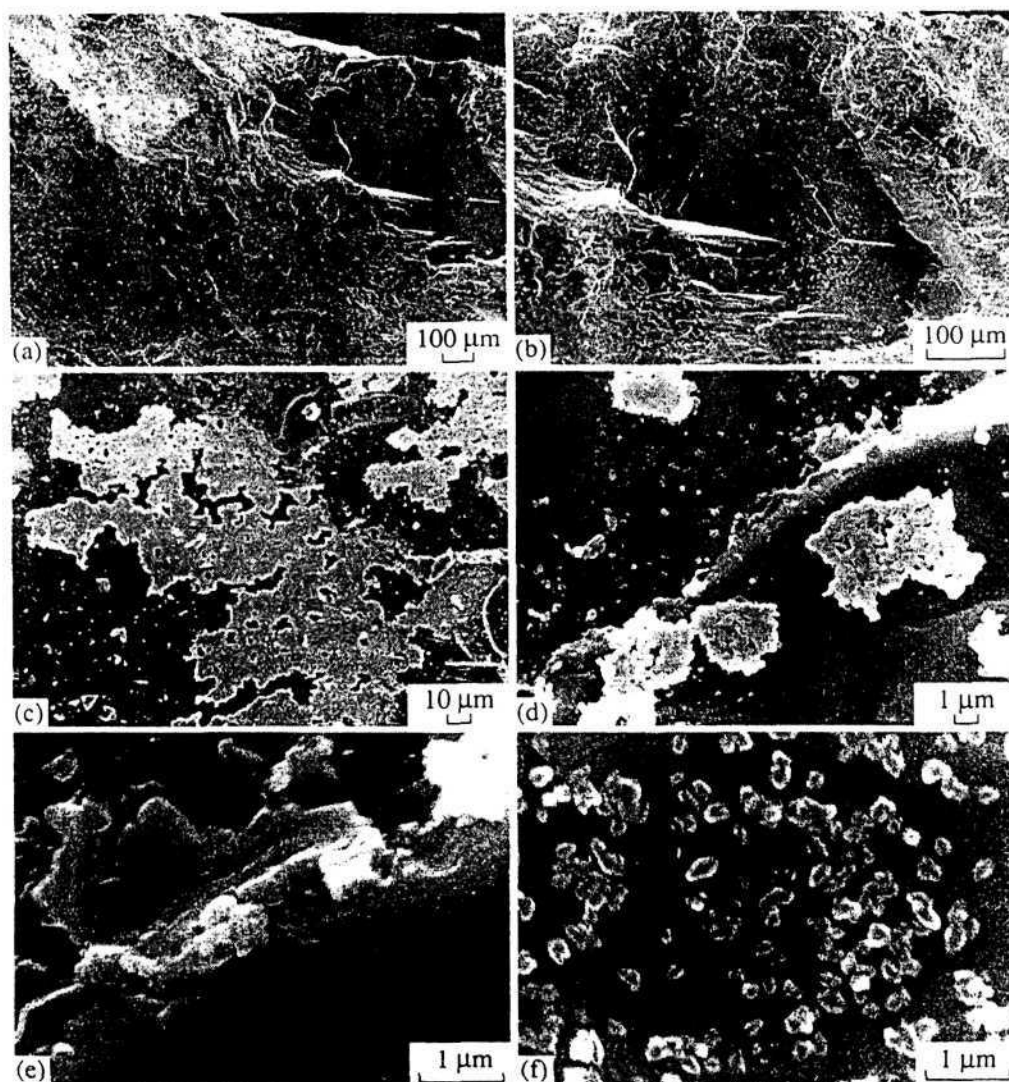


Fig. 1. SEM images of the carbonado sample chip. (a, b) Octahedral diamond crystal inside carbonado; (c, d) octahedron face with remains of titanium film oxidized to TiO_2 ; (e) closeup of the coating (thickness 0.3 μm); (f) individual TiO_2 crystallites.

isotopic relationships in carbonaceous materials [2, 3, 12, and others]. For example, diamond crystals formed in the mantle ultrabasic substrate have the lightest isotopic composition and a narrow $\delta^{13}\text{C}$ variation range of approximately -5‰ (Fig. 2). Diamond from the mantle eclogite paragenesis has a slightly heavier isotopic composition and a wider $\delta^{13}\text{C}$ variation range with two modes approaching -6 and $-(12-13)\text{‰}$, respectively. Carbonado samples from the eclogite paragenesis have an even heavier isotopic composition with the $\delta^{13}\text{C}$ value ranging from -10 to -30‰ and the maximum at approximately -27‰ .

We studied the carbon isotopic composition of the Brazilian carbonado in the Laboratory of Isotope Geochemistry at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Moscow (L.P. Nosik, analyst). The analysis was performed according to the routine procedure of diamond oxidation and carbon conversion into the gaseous dioxide

(CO_2) with the help of copper oxide. The results are presented in the table and Fig. 2. Values of the carbon isotopic composition for the studied carbonado collection do not fit the standard $\delta^{13}\text{C}$ interval for the Brazilian carbonado [12]. Moreover, samples from Minas Gerais have a slightly lighter isotopic composition relative to carbonado samples from placers of Bahja. It is interesting that two carbonado samples (nos. 5 and 10) have a lighter isotopic composition than the other samples (the difference is as much as 4–7 units). The composition of these two samples approaches that of carbon in diamond from eclogites.

As was mentioned above, the color cathodoluminescence analysis revealed that the core of Sample 10 (carbonado collection from Bahja) includes a small (3 mm) diamond crystal overgrown with fine-grained diamond aggregate (carbonado). The crystal shows a bright blue luminescence related to nitrogen luminescence of the N3 center. Probably, mixing of light carbon from dia-

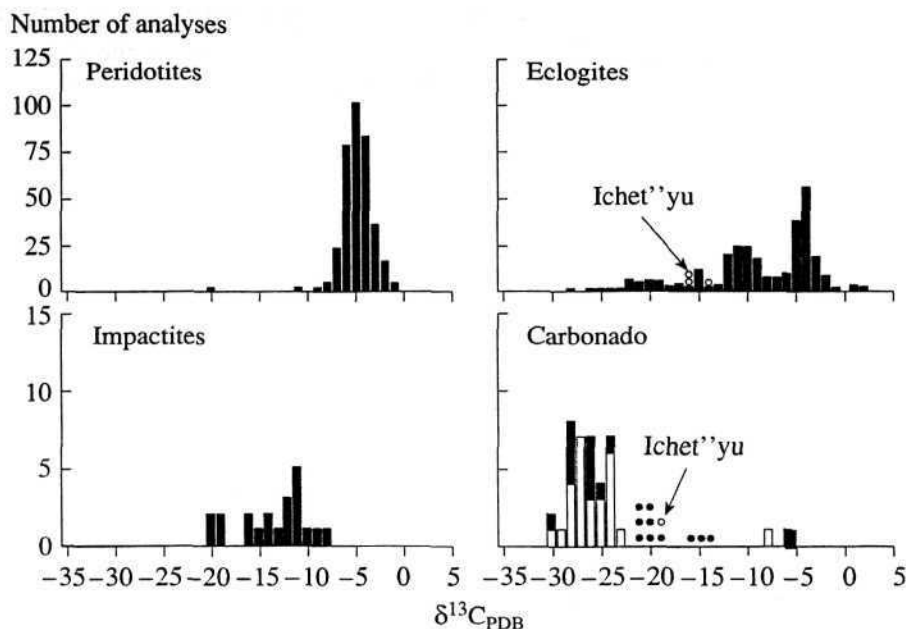


Fig. 2. Histograms of the carbon isotopic composition of diamond, carbonado, and carbonaceous phases of impactites [12]. Filled boxes indicate samples from central Africa; open boxes, samples from Brazil; open circles, diamond and carbonado samples from the Ichet'yū deposit.

mond and heavier carbon from carbonado strongly influenced the isotopic composition of this sample. The coexistence of diamond and carbonado is also supported by the superposition of X-ray luminescence spectra of both diamond and carbonado in a single sample (Fig. 3).

We were the first to determine the carbon isotopic composition of diamond and carbonado from the Ichet'yū deposit (Middle Timan). The results showed that the Ichet'yū carbonado is very similar to the Brazilian counterpart [12] with the $\delta^{13}\text{C}$ value (-20.25‰) approximately corresponding to the mean value for the carbonado sample collection (table, Fig. 2). The carbon isotopic composition of the Ichet'yū diamond appeared to be slightly lighter, with the $\delta^{13}\text{C}$ value ranging from -13.62 to -16.31‰ (average $-15.24 \pm 1.43\text{‰}$). These data can be compared with the carbon isotopic composition of diamond from the Arkhangelsk diamond province [2]. The results suggest the following important conclusion: diamond from the Ichet'yū deposit (Middle Timan) was presumably crystallized in the mantle eclogite substrate.

This conclusion is consistent with data on coatings and inclusions of indicator minerals in diamond crystals from Middle Timan [1, 8, 10]. Previously, we detected inclusions of SiO_2 (probably coesite), garnet (pyrope-almandine series), and ilmenite in the Middle Timan diamond. Additionally, coatings of florencite, native metals (29 species), and other minerals were found on crystal faces [1, 8]. The presence of indicator minerals also indicate diamond crystallization in the Ichet'yū deposit from the mantle eclogite substrate.

Mantle eclogite fragments are the most widespread xenolith type in the Umba, Srednyaya, and Vodorazdel'naya kimberlite pipes of Middle Timan [8].

The information presented above is very important for the refinement of the diamond prospecting strategy in Middle Timan. The application of pyrope survey as a mineralogical prospecting method turned out to be inefficient in Middle Timan. The mistake was related to

Isotopic Composition of carbonado and diamond from different deposits

Sample	$\delta^{13}\text{C}$, ‰	$x \pm \sigma$	Phase	Location
1	-18.68	-18.02 ± 2.24	Carbonado	Makaubas River area, Minas Gerais, Brazil
2	-20.59		"	
3	-19.85		"	
4	-16.48		"	
5	-14.50		"	
1	-21.34	-19.01 ± 3.09	Carbonado	Andorai area, Bahja, Brazil
2	-18.68		"	
3	-19.85		"	
4	-21.32		"	
5	-13.85		"	
O-1	-20.25		Carbonado	Ichet'yū deposit, Middle Timan, Russia
129	-16.31	-15.24 ± 1.43	Diamond	
137	-13.62		"	
152	-15.79		"	

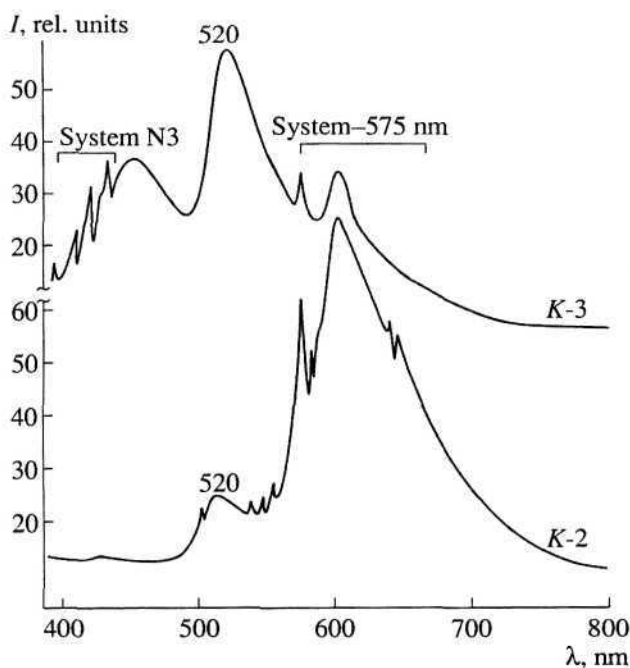


Fig. 3. X-ray luminescence spectra of carbonado and diamond intergrowths (Sample K-3) and carbonado grain (Sample K-2). Nitrogen luminescence in diamond (N3 type, blue region) and carbonado ($\lambda = 575$ nm, yellow-green region).

the fact that researchers prospected for diamond based on pyrope (high-Cr garnet with the knorringite end member) associated with diamond of the mantle ultrabasic paragenesis. However, pyrope is rare in Middle Timan. We should have prospected for diamond based on another garnet, namely, pyrope-almandine (Fe-Mg garnet from mantle eclogites), which is widespread in Middle Timan, in particular, within the Ichet'y deposit area.

Thus, our results dispel one more popular concept suggesting that minerals associated with diamond are

absent in the Middle Devonian diamondiferous breccia-conglomerate, because the latter lacks pyrope with knorringite. According to this concept, the Ichet'y deposit is an intermediate collector located in a distal zone (relative to the source). Actually, the heavy concentrate of the Ichet'y deposit contains abundant diamond-associated minerals, such as pyrope-almandine, ilmenite, and Al_2O_3 -rich Cr-spinel (alumochromite), that are accessory minerals of diamondiferous mantle eclogites. Hence, the Ichet'y deposit may be a proximal body. This assumption is also supported by our recent detection of fine (0.3–0.4 mm) flat-faced octahedral diamond crystals (Fig. 4a) in the heavy concentrate of the productive horizon. These crystals contain the florencite coating typical of the curviplanar diamond face from the Ichet'y deposit. Microprobe analysis revealed an interesting feature of the fine flat-faced diamond. It contains specific segregations of sulfide-iodates ($\text{Cu}_2\text{S} \cdot \text{CuI}$) associated with salt (Na,KCl) formed as a result of the exposure of near-surface inclusions in the diamond and the instantaneous crystallization of salts from brines (Fig. 4b).

Previously, tiny diamond crystals were skipped during the preliminary prospecting, because washout aggregates of dressing plants were equipped with sieves with a mesh size of 2 mm.

Our data show that the studied diamond grains have a bimodal size distribution, indicating the absence of sorting in the productive horizon of the Ichet'y deposit. The grain size distribution appears to be more similar to that in native diamond deposits confined to kimberlite pipes in the Arkhangelsk diamond province [2]. Hence, the native diamond source is located within a few kilometers of the Ichet'y deposit.

The rare finding of carbonado in the Northern Hemisphere is related to the difficulty of its detection (relative to diamond) rather than its scarcity. Carbonado fragments are probably skipped during the industrial-scale separation in dressing plants, because the automatic equipment is tuned to the blue X-ray lumines-

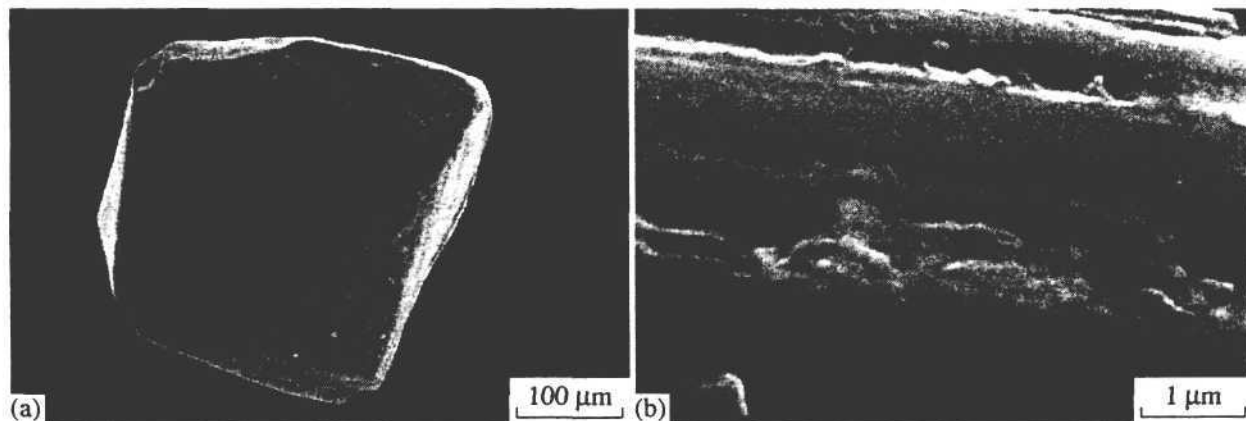


Fig. 4. (a) Tiny flat-faced diamond octahedron from breccia-conglomerate in the Ichet'y deposit (Quarry K-100). (b) Segregations of $\text{Cu}_2\text{S} \cdot \text{CuI}$ in microinclusions on the crystal face.

cence of diamond rather than the yellow-green luminescence of carbonado. Under laboratory conditions, carbonado may be skipped due to the absence of skill for its identification. Moreover, carbonado fragments may be coated with iron or titanium oxides that do not respond to luminescence light. In placers of southern continents, carbonado is generally detected by skilled prospectors of this mineral. The cathodoluminescence method appears to be the most effective and reliable technique for the identification of carbonado. Its patchy dark orange luminescence [6, 7] resembling leopard skin cannot be confused with any other mineral.

The coexistence and intergrowth of carbonado and diamond crystals indicate their common genesis. Under nonequilibrium conditions of diamond transportation from the mantle to the Earth's crust, carbonado could crystallize in the kimberlite fluid and overgrow the diamond crystals.

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