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# "SHELLS" (IMPRINTS) OF DIAMOND IN KIMBERLITE

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A study of the specific way diamond crystals are embedded in kimberlites is extremely important for understanding the genesis of the diamond. It can shed light on the mechanism of diamond preservation in a kimberlite pipe. However, the information on the nature of the direct contact between diamond crystals and the surrounding kimberlite rock is very limited.

A diamond crystal which is embedded in a kimberlite, is known to be separated from the kimberlite host rock by mineral layer (a shell, a rim). So the diamond crystal contact kimberlite rock through such an intermediate coating. When diamond crystals are separated from the kimberlite, these layers are left attached to the kimberlite host rock. The shape of a crystal is imprinted on such a shell, so these layered shells are called sometimes "imprints" of the diamond crystals.

Some investigation of those shells started in the seventies. For example, it was shown on individual samples that the layers between kimberlite and diamond crystals are carbonate, sometimes mixed with serpentine (Nikishov, Bulanova, 1975) or with iron oxides (Rovsha et al., 1979). It has been suggested that there is a genetic link between the carbonate shell and the diamond. The later study of a representative collection (220 samples) showed a wider variety of the shell's mineral composition. With the predominance of monomineral shells of carbonate or serpentine type, also multimineral shells represented by combination of such components as serpentine, calcite, dolomite, pyrite, pyrrhotite, magnetite were detected (Ponomarenko, Spetsius, 1981). It was found a tight connection between a certain composition of shells around the diamond and the particular stage of hydrothermal mineralization of kimberlites. The major conclusion of this study related to the genesis of diamond, was that diamonds are xenocrysts and are brought from different horizons of the upper mantle. However, the question of the interaction of diamond with the surrounding rock has been left open in that study.

Somewhat different perspective on the role of carbonate and serpentine layers around the diamond was developed by Rudenko (Rudenko, Kulakova, 1989; Rudenko et al., 1993). Based on the study of the nature of contact between the diamond crystals and kimberlite rock, the authors suggest that some additional growth as well as the oxidative dissolution of diamond under changing conditions could occur in the kimberlites themselves. According to the degree of manifestation of growth characteristics, diamond imprints were divided into 3 groups: with distinct growth characteristics and allochemical changes in the surrounding rock; with mild growth symptoms and with a complete lack of growth characteristics (i.e., diamond - a typical xenocrysts).

We have recently resumed the study of samples of kimberlite with diamond imprints from the collection compiled by Rudenko (about 150 samples), using mostly non-destructive methods. In the study we have used the methods of optical and scanning electron microscopy

Kimberlite samples we are studying, have been specially selected in the process of enrichment of kimberlite from "Mir" and "Udachnaya" pipes (Yakutiya). In the first stage the diamond imprints of all those samples were thoroughly examined under an optical microscope (AxioPlan 2 imaging, CarlZeiss) and some of them – on SEM (LEO -14 30 vp CarlZeiss). Raman spectra of shells and of diamond were measured with a spectrometer U1000 of JOBIN YVON using Ar (green) laser 514nm. FT-IR of diamond recorded on the instrument Nicolette 380 of Thermo Nicolette. The chemical composition of the fragments of imprints is defined in the electron-probe microanalyzer Camebax SX 50.

Imrint sizes range from 3 to 5 mm. Imprints in the kimberlites of pipe "Mir" reflect predominantly octahedral shape of the extracted crystals , while the imprints from the pipe " Udachnaya" are of transitional form, of dodecahedral shape, or reflect a polycrystal structure of diamonds. We paid a particular attention to finding signs of growth and condition for preservation of crystals in the coatings. Typical channels that connect the shells with the surrounding kimberlite rock were carefully examined.

It was noticed that the majority of shells of diamond in kimberlite of pipe "Mir" contain sulfides (pyrite-pentlandite). Monosulfide layers with thickness up to 50μ are less common. Polymineralic multi-layers with combination of carbonate-silicate-sulfide components with thicknesses of 10--20μ and with the apparent heterogeneity are widespread (Fig. 1). We observe, that those layers can appear in various order, their total thickness varies from 10 to 100μ, a block structure can often be noticed. Carbonate is present as calcite and dolomite; together with calcite, magnetite is often found. Silicate layers adjacent to the carbonate layers are not homogeneous and are presented in the form of serpentine, antigorite, chrysotile, silica, and always contain inclusions of carbonates. The sulfides are represented by pyrite, pyrrhotite, pentlandite. Such a layered structure might give evidence to existence of several phases of formation of those shells and indicate that the formation of shells is a secondary process in relation to the one of diamond.

Much rarer one can meet very thick, up to 300μ, carbonate-silicate shells with clear imprints of faces and edges of the crystal (Fig. 2). Carbonate shells are completely retain the shape of faces of diamond crystals. After removal of the carbonate layer, on silicate layer, imprints of diamond surface are also observed, and more distinct than on the carbonate layer. We can conclude that initially in a direct contact with a crystal of diamond was the silicate layer, which was then pressed back by the carbonate one. Shells of this type could be a good environment not only to preserve the diamond but also, perhaps, for an additional diamond growth at certain stages in the formation of kimberlite pipes.

In some areas of serpentine layers admixture of transition metals (Fe, Cr, Ni, Ti) were detected. Their presence may explain the relics of resorption on the diamond surface imprinted on the shells (Fig. 3), as they are known to be the catalysts for the oxidation of diamonds by water vapor and carbon dioxide (Skvortsova et al. 1975). Obviously, the formation of shells is related to processes of metamorphism of diamond-containing rocks. On the other hand, one can speak of the influence of the diamond itself on metasomatic processes. The study of collection of diamond imprints on kimberlite samples from both “Mir” and ”Udachnaya” pipes reveals the relationship between the composition of shells and the development of a certain particular stage of hydrothermal mineralization of kimberlites, what is consistent with the paper (Ponomarenko, Spetsius, 1981). Of course, the imprints that characterize the diamond as xenocrysts, are the most

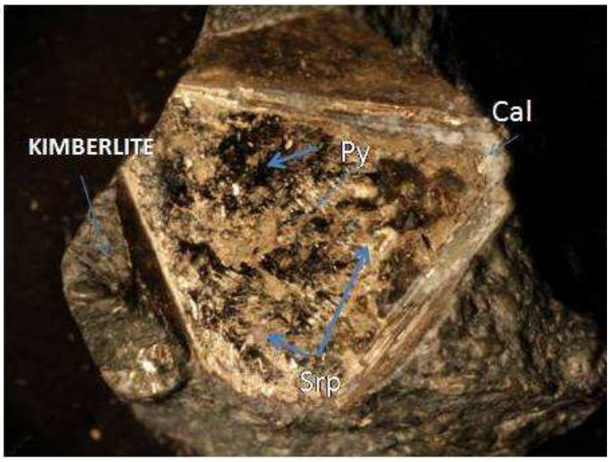


Figure 1. Carbonate, silicate and sulfide fragments in different shell layers of diamond (pipe “Mir”)

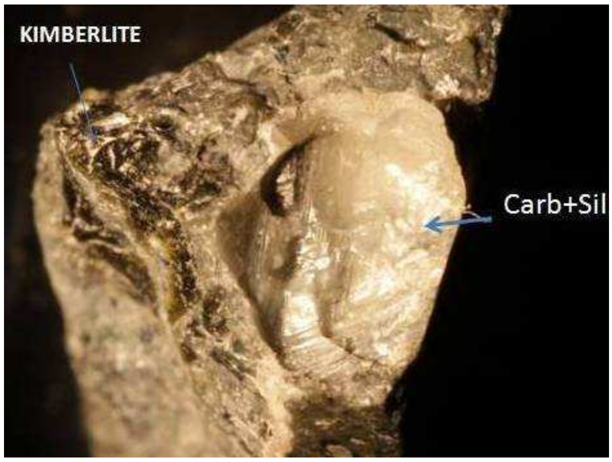


Figure 2. Thick carbonate-silicate shell of diamond (pipe “Mir”)

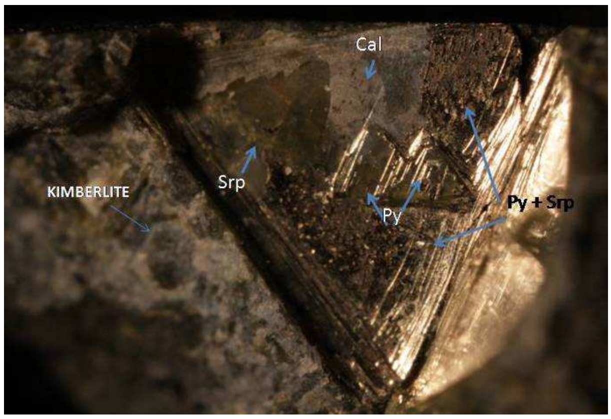


Figure 3. Relics of the resorbed surface of the diamond seen on the imprint (pipe “Mir”)

common. It were this, that led the authors of the above mentioned paper to conclude that the diamonds in kimberlites are xenocrysts.

The study of kimberlite samples from "Udachnaya" pipe reveals a certain type of imprints of diamond polycrystals, united by common coatings of carbonate-silicate composition (Fig. 4, 5, 6). In some samples remaining

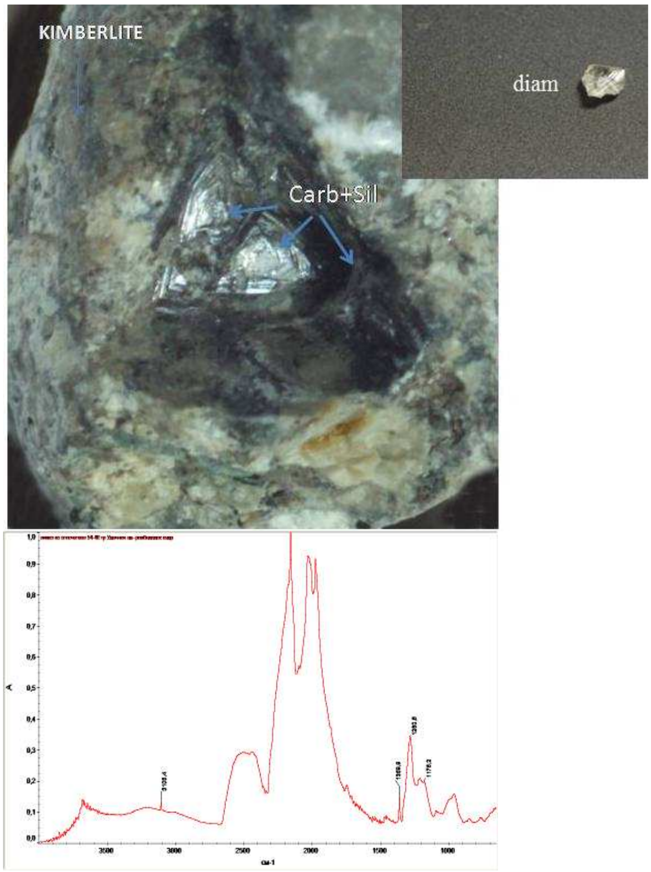


Figure 4. Carbonate-silicate shell of polycrystal of diamond, fragment of diamond, and IR-spectrum of this fragment (pipe "Udachnaya")

fragments of the diamond were found . They were studied by IR and Raman spectroscopy. Note that the IR spectrum of diamond (Fig. 4) is typical for the pipe "Udachnaya". Raman spectra of crystal fragments indicated significant difference in the amount of impurities. (compare Fig 5 and 6). Raman spectra of carbonate-silicate shells were also studied. It was shown that the shells are amorphous. We also carefully studied the characteristic channels and calcite veins connecting the shells with the surrounding kimberlite. It was noted that in a calcite vein it was recorded presence of small diamond crystals (Fig, 7)

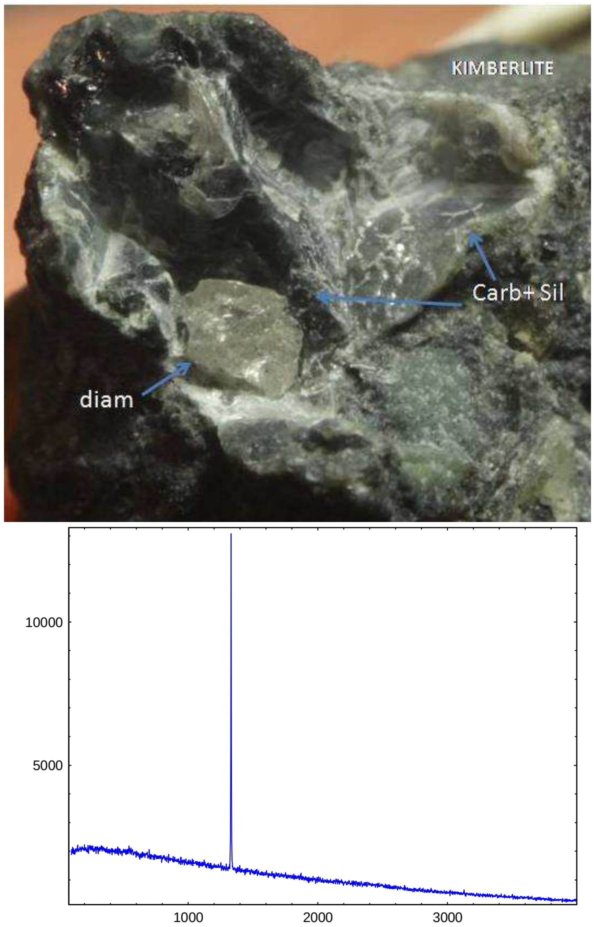


Figure 5. Shell, Raman spectrum of fragment of diamond (pipe "Udachnaya")

It should be remarked that also in (Ponomarenko, Spetsius, 1981) a single diamond crystal was founds not in the shell but in the calcite vein.

A direct contact of the diamond crystal with the shell (Fig 8a) was investigated through scanning electron microscope, without using carbon deposition. Figure 8c shows an image with an increase in 5500. Analysis of the qualitative composition (Fig. 8b) indicates the presence of dolomite in carbonate shell. We have detected in the cleavage planes of diamond a unique scattering of small crystals (size < 200 nm) of pyramidal shape (Fig. 8d with an increase in 20000). Study of the nature of those pyramids is not yet completed. The most daring hypothesis would be that they are pentamantanes, i.e., the simplest centrosymmetric hydrocarbon which has the (111) face of diamond (Schwertfeger et al. 2008). This is a kind of so-called diamondoids. They were found in the petroleum products. It was suggested that they could be found in kimberlites, but the question still remains open.

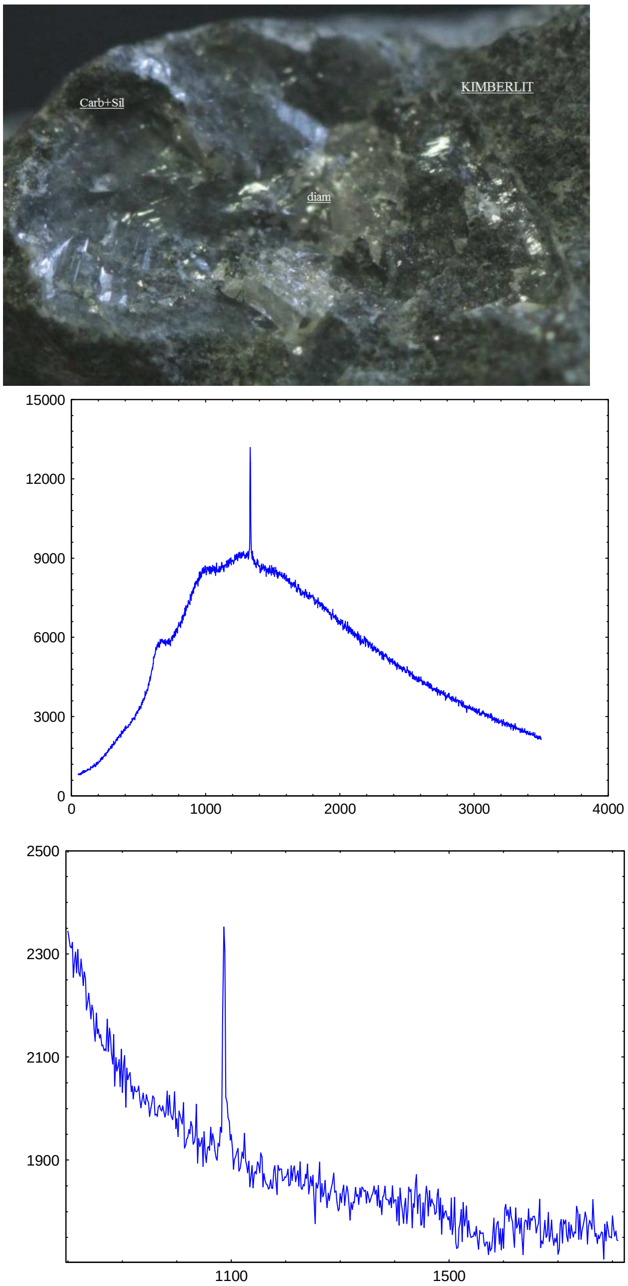


Figure 6. Shell of polycrystal of diamond, Raman spectrum of fragment of diamond and Raman spectrum of shell (pipe “Udachnaya”)

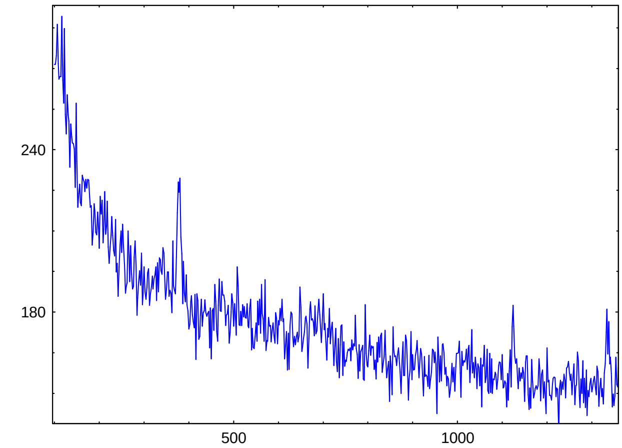

Figure 7. Raman spectrum of calcite vein with peak 1332 of diamond.

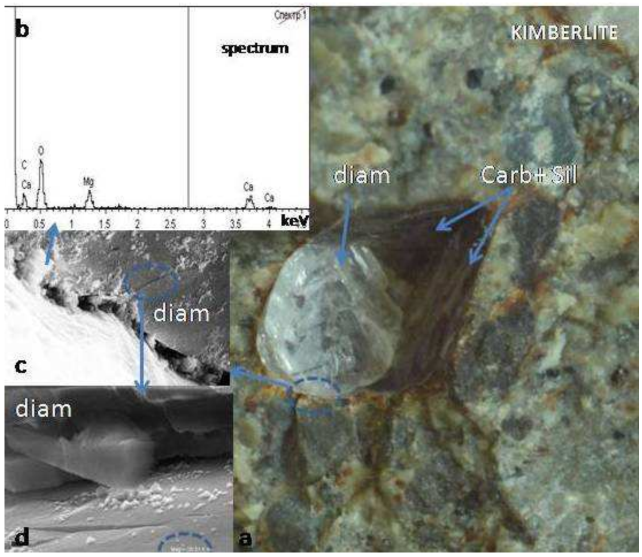


Figure 8. Shell of diamond (a); qualitative composition of contact (b); image in SEM (c); and scattering of small crystals of pyramidal shape (d)

As it was mentioned in the introduction, there are different points of view on the role of shells of diamond. If in the paper (Ponomarenko, Spetsius, 1981), the authors believe that the shell appeared at the final stages of formation of kimberlite rocks, then in (Nikishev, Bulanova, 1975) it was suggested that at the final stages of formation of diamond, in some cases conditions could be favorable for the formation of the coated diamonds, while in other cases -- for the formation of carbonate layers. On the basis of the theory of open catalytic systems, Rudenko (Rudenko, Kulakova, 1989; Rudenko et al., 1993) proposed a model of formation of diamond in kimberlites from simple carbon-containing substances. We are trying to look at the possible compatibility of these points of view on the origin of shells in the light of the modern approach taking into account the role of HDF’s in the processes of formation of diamond during the evolution of magmas ( Navon et al., 2008; Weiss et al., 2009). For the understanding of the role of the shells in the diamond-forming processes we are planning to use also a model based on the potential energy surface and percolation theory (Petrovsky et al., 2004). All this requires further, more detailed research.

## REFERENCES

Navon, O., Klein-BenDavid, O., Weiss,Y (2008): Diamond-forming Fluids: their origin and evolution; 9IKC, Extended Abstract No.9IKC-A-00121.

Nikishov, KN, Bulanova, GP (1975): Nature of the contact of diamond . crystals with kimberlite rocks; in Proc. Mmagmatic formations in North- East of the Siberian Platform, Yakutsk: 218-222.

Petrovsky, VA,/ Troshev, SA,. Sukharev, AE (2004): A mechanism of diamond formation in the presence of metals-catalysts; Doklady Earth Sciences, 397 (2) :703-706

Ponomarenko, AI, Spetsius, ZV. (1982): Mineral rims on diamonds from kimberlites, International Geology Review, 24: 829-834.

Rovsha, VS, Futergendler, OI, Charkov, AD, Zacharova, VR (1979): The relationship of a diamond - carbonate and possible genetic links; in Proc."Materialy po geologii I poleznym iskopaemym Yakutskoi ASSR", Yakutsk.

Rudenko, AP., Kulakova, II (1989): The conditions of formation of kimberlite diamonds and problem of diamond formation in terms of the theory of open catalytic systems; Geokhimiya, 7: 961-972.

Rudenko, AP., Kulakova, II., Skvortsova, VL (1993): The chemical synthesis of diamond. Aspects of the general theory; Russian Chemistry Review, 62 (2): 87–104.

Schwertfeger H, Fokin AA, Schreiner PR (2008): Diamonds are a chemist's best friend: diamondoid chemistry beyond adamantine; Angew Chem Int Ed Engl., 47: 1022-1036.

Skvortsova (Shturman), VL, Kulakova, II, Rudenko, AP (1975): The catalytic effect of the elements that make up the kimberlites, of diamond on the oxidation of water vapor and carbon dioxide; Vest. MGU, Chimiya, 16(3): 347-352.

Weiss, Y, Kessel, R, Griffin, W L, Kiflawi, I, Klein-BenDavid, O, Bell, DR, Harris, JW, Navon, O (2008): A New model for the evolution of diamond-forming fluids: evidence from microinclusion-bearing diamonds from Kankan, Guinea; Lithos.,112, Supp.2: 660-674.

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