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ISOTOPIC COMPOSITION OF CARBON IN POLYCRYSTALLINE AGGREGATES OF DIAMOND WITH INCLUSIONS OF GARNET AND RUTILE FROM THE MIR PIPE

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Polycrystalline aggregates of bort-type diamond with inclusions of garnet and rutile from the Mir pipe have $\delta^{13}\text{C}$ of -3.7 to -22.9% PDB. The bort of variety VIII (Yu. L. Orlov's classification) differs from the bort of variety IX in having a narrower range of $\delta^{13}\text{C}$ (-3.7 to -9.4 and -3.8 to -22.9% , respectively). The isotopically heavy diamond aggregates ($\delta^{13}\text{C} \geq 10\%$) with cubic individuals make a greater contribution of ^{12}C than the aggregates having individuals of other morphological types. Within the Mir pipe, the *E*-type bort is statistically enriched in ^{13}C relative to single crystals of diamond of the same paragenesis. *Carbon isotopes, diamond, polycrystalline aggregates, eclogite inclusions*

INTRODUCTION

To study the carbon isotopic composition of the diamond with mineral inclusions of eclogite paragenesis (*E*-type) is of great interest because diamonds of this type demonstrate the maximum range of variations in $\delta^{13}\text{C}$, from $+2.5$ to -34.4% PDB [1]. Recall that the eclogite type of paragenesis covers diamond-hosted inclusions of the Cr-free minerals, e.g., Mg-Fe-garnet with a variable increased impurity of Ca, omphacite, coesite (quartz), kyanite, and rutile, whereas the ultrabasic type is characterized by inclusions of such minerals as Cr-enriched garnet (pyrope), olivine, chromite, and diopside [2]. Polycrystalline aggregates of the bort-type diamond (varieties VIII and IX according to Orlov's classification [3]) remain to be explored. This is especially important because abnormally low carbon isotope ratios ($\delta^{13}\text{C} = -34.4\%$ PDB) were recorded when studying bort [1].

According to the results obtained by Smelova [4] from a representative collection of polycrystalline aggregates and diamond intergrowths from the Yakutian kimberlite pipes, the mineral inclusions in diamond aggregates are generally similar in composition to inclusions in single crystals, which is fair corroboration of our earlier generalizations [2].

To gain a deeper insight into the isotopic composition of bort carbon and to compare aggregates and single crystals of *E*-type diamond for this parameter, we determined values of $\delta^{13}\text{C}$ for 17 polycrystalline aggregates of diamond from the Mir pipe with inclusions of garnet and rutile.

METHODOLOGICAL

Carbon isotopic composition of diamonds was determined on a Finnigan-MAT Delta spectrometer at the United Institute of Geology, Geophysics and Mineralogy, Novosibirsk. The accuracy of isotope ratio measurement was within 0.02% . The procedure of diamond preparation to mass spectrometric studies has been described in detail elsewhere [5]. The isotope data are compared with the international PDB standard.

Composition of mineral inclusions in polycrystalline aggregates of diamond was determined on a Camebax-Micro probe at the Institute of Mineralogy and Petrography, Novosibirsk.

Table 1

Results of Isotope Analysis of Carbon of Diamond Polycrystalline Aggregates from Mir Kimberlite Pipe with Inclusions of Garnet and Rutile

Specimen	Color	Shape	Inclusions	$\delta^{13}\text{C}$, ‰ PDB	Variety	
MR-553	Colorless	Octahedron-to-rhombododecahedron transitional	Rutile	-4.6	VIII	
MR-555	»		The same	-4.5		
MR-556	»		»	-4.4		
MR-580	Black		Garnet	-4.3		
MR-561	Lilac	Rhombododecahedron	Rutile	-3.74		
	Gray		»	-3.77		
MR-563	Colorless		»	-4.0		
MR-568	»		Garnet	-4.7		
MR-577	»		»	-3.9		
MR-581	Gray		»	-4.0		
MR-832	Black	Cube	»	-6.85	IX	
MR-833	Gray		»	-8.2		
MR-570	Gray	Uncertain	»	-3.8		
MR-571	Black		»	-4.9		
MR-578	»		»	-5.2		
MR-579	»		»	-22.9		
MR-834	Gray		»	-5.5		
MR-573	Colorless	Transitional	Rutile, garnet	-9.4		VIII
	Black	Uncertain		-17.2		IX

RESULTS

Seven specimens from the studied collection were referred to as variety IX diamonds [3]. They are black or dark-gray minute grains. Some authors consider them framesite [6]. The size of individuals does not exceed 300 μm . In specimens MR-832 and MR-833, individuals are of cuboctahedral and cubic habit, respectively. The other aggregates of this variety are composed of grains having no crystallographic shape.

Ten specimens are variety VIII diamonds [3]. These are aggregates of small (to 1 mm) faceted crystals whose heads are, as a rule, light and transparent. Some specimens contain individuals of rhombododecahedral and transitional (octahedron-rhombododecahedron) habit. The inner zone of the aggregates is usually denser and darker. The core of specimen MR-573 is variety IX bort of black color.

Mineral inclusions. The studied polycrystalline aggregates of diamond contain inclusions of yellow-orange garnet of pyrope-almandine series (11 specimens) and rutile (5 specimens). Specimen MR-573 contains inclusions of both minerals (see Table 1). Two groups can be distinguished among the studied garnets: (1) magnesian garnets (containing 47 to 79% pyrope) with a lower content of Ca component (7.96 to 15.4%); (2) garnets with a constant high content of iron (50.3 to 63.2%) and a variable content of Ca component (14.2 to 32.0%). On the triangular diagram of component composition with the fields of *U*- and *E*-type garnet compositions plotted after Meyer [7], the inclusions we have studied form a rather continuous series of compositions within which two branches, corresponding to the described groups, are recognizable (Fig. 1). One of them is subparallel to the contents of Ca end-member (group of magnesian garnets), and the other is parallel to the contents of Fe end-member (group of high-Fe garnets). Interestingly, the magnesian garnets are predominant among the variety IX aggregates (six of seven specimens). Garnet inclusions from separate parts of specimen MR-573 are connected by a line. The garnet from the diamond's interior (extracted by burning the diamond in a platinum crucible) contains less Mg and more Ca as compared with the garnet from

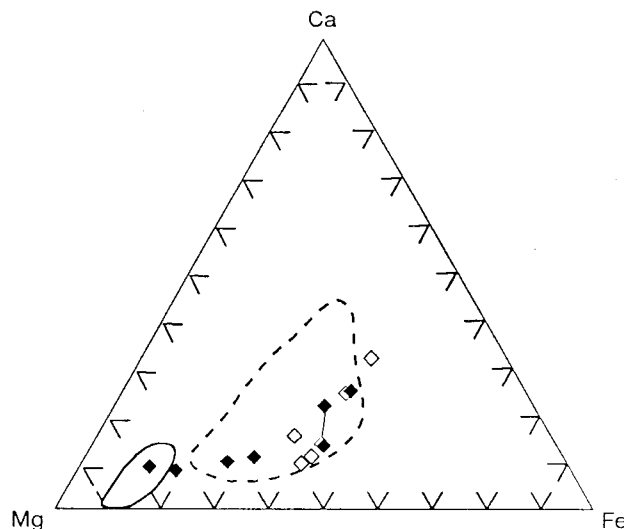


Fig. 1. Diagram of component composition of garnet inclusions in polycrystalline diamond aggregates from the Mir pipe. Line connects inclusions from sp. MR-573 (see text). Fields correspond to distributions of compositions of 95% of inclusions of U-type (solid line) and E-type (dashed) garnets after [7]. Black squares, aggregates of variety IX; open squares, aggregates of variety VIII.

the outer portion of the aggregate (extracted by crushing the specimen), with nearly the same content of iron (51.2 and 50.3%). The Mg-richer garnets with constant CaO can be referred to websterite paragenesis [8]. Orthopyroxene can be present in association with such garnets. Even with omphacite containing up to 5% Na₂O, this paragenesis is important for the stability field of diamond [9, 10].

Rutile intergrown with polycrystalline aggregates of diamond was encountered only in variety VIII (see Table 1). Study of the composition of these rutiles has shown that they have impurities of Al₂O₃ (0.1–0.54 wt.%) and Fe₂O₃ (0.31–1.4 wt.%). The contents of these impurities are variable even within one grain of rutile, testifying to its inhomogeneity, which probably is connected with solid exsolution [11]. The same phenomenon seems to be responsible for the fact that a phase with a lower content of TiO₂ (down to 63.1 wt.%) and higher contents of MgO (up to 25.5 wt.%) and FeO (up to 10.5 wt.%) occurs in some specimens (MR-553, MR-561, and MR-563). In composition, these phases are close to picroilmenite, approaching the end-member – geikielite, with the content of geikielite reaching 80%. As a rule, TiO₂ in rutiles varies from 90.9 to 99.9 wt.%, which is typical of rutile inclusions in diamond [11]. Low contents of Cr₂O₃ (no more than 0.22 wt.%) corroborate the eclogite paragenesis of rutiles [12]. Worthy of note is that the rutiles associated with the studied diamonds typically contain minor amounts of Nb₂O₅ (0.05–1.02 wt.%) and ZrO₂ (0.05–0.3 wt.%).

Isotopic composition of diamonds. Results of analysis of carbon isotopic composition for each specimen are reported in Table 1. The analytical error of determination of $\delta^{13}\text{C}$ values, including the diamond-to-CO₂ transformation, does not exceed $\pm 0.1\text{‰}$. The values of $\delta^{13}\text{C}$ of the studied diamond aggregates ranged from -3.7 to -22.9‰ PDB.

Variety VIII bort. The studied aggregates of variety VIII belong to heavy-isotope diamonds [13] with $\delta^{13}\text{C}$ values ranging from -3.7 to -9.4‰ (Fig. 2). They have faceted heads of individuals and contain inclusions of both garnet and rutile. The aggregates with individuals of octahedron-to-rhombododecahedron transitional form (four specimens) have a carbon isotopic composition averaging -4.45‰ . The values of $\delta^{13}\text{C}$ ranged from -4.3 to -4.6‰ . The value $\delta^{13}\text{C}_{\text{av}}$ of bort with rhombododecahedral individuals (5 specimens) was -4.06‰ (from -3.7 to -4.7‰) (see Table 1).

Variety IX bort. Both heavy- and light-isotope diamonds occur among the variety IX aggregates [13]. The $\delta^{13}\text{C}$ values range from -3.8 to -22.9‰ (see Fig. 2). The inclusions are garnets only. With the exception of two specimens, the individuals have no crystallographic shape. The carbon isotopic composition of the aggregates with cubic-faced individuals was -6.8 and -8.2‰ (see Table 1).

Differently colored individuals have been analyzed in specimen MR-561. The data obtained (see Table 1)

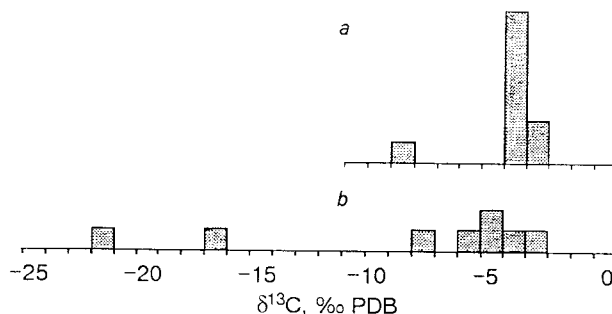


Fig. 2. Carbon isotopic composition of polycrystalline aggregates of diamond of varieties VIII (a) and IX (b) from the Mir pipe with inclusions of garnet and rutile.

show that within a separate aggregate the individuals of varying color have the same isotopic composition of carbon.

Specimen MR-573 has a clear zonal structure and is worthy to be examined in detail. The inner zone is a black fine-grained (with grains about 200–250 μm in size) aggregate (variety IX). The outer zone is made up of larger (~ 0.5 mm) colorless diamonds (variety VIII). The heads of individuals have an octahedron-to-rhombododecahedron transitional habit. The values of $\delta^{13}\text{C}$ for the inner and outer zones of the aggregate were -17.2 and -9.4‰ , respectively (see Table 1). As noted above, this specimen contains garnet inclusions with different compositions. Unfortunately, the uncertain origin of the garnet inclusions precludes correlating the data on inclusions with the morphology of aggregate zones and $\delta^{13}\text{C}$ values.

DISCUSSION

Thus, the compositions of garnets and rutiles extracted from diamond aggregates do not differ from analogous prisoner minerals in single crystals of diamond [2, 4]. It is remarkable that on the diagram of garnet composition, the inclusions from the variety IX aggregates form a branch of magnesian garnets with a constant content of Ca (up to websterite association) (see Fig. 1). The other branch (see Fig. 1, high-Fe garnets) is formed by the variety VIII aggregates. According to isotope data, the variety VIII diamonds are characterized by a narrower range of $\delta^{13}\text{C}$ values as compared with the variety IX bort (see Fig. 2).

Aggregates with individuals of cubic morphology are enriched in a light isotope of carbon relative to the rest of the studied diamonds (Fig. 3). The earlier observed [5] tendency toward the change of $\delta^{13}\text{C}$ in the octahedron-rhombododecahedron habit series of individuals for the bort from the Mir pipe with *U*-type inclusions does not hold in the case of aggregates of *E*-type diamond. On the contrary, the obtained data indicate that the bort with rhombododecahedral individuals is relatively enriched in ^{13}C isotope as compared with the diamond aggregates having individuals of transitional shape (see Fig. 3). Such situation seems to be due to the scarcity of data on polycrystalline aggregates of *E*-type diamond and requires additional research.

The existing notions [14, 15] suppose that the change of diamond crystal habit is a complex function of temperature, C-oversaturation, and composition and concentration of impurities. Since the coefficient of fractionation of carbon isotopes in a medium of diamond formation is governed by the same parameters [13], the diamonds of varying morphology should have different compositions of carbon.

Figure 4 shows histograms of distribution of $\delta^{13}\text{C}$ values of diamond aggregates with inclusions of ultrabasic [5] and eclogitic types from the Mir pipe. It is evident that the *E*-type diamond aggregates have a wider range of $\delta^{13}\text{C}$ values as compared with the *U*-type bort.

Since the light-isotope diamonds with *E*-type inclusions, likely, have a source of carbon different from that for heavy-isotope diamonds [16], it is reasonable to consider them separately. Scarce data (one single crystal [17] and six aggregates [1, 18]) do not presently permit comparison of carbon isotopic composition of light-isotope aggregates and diamond single crystals from the Mir pipe.

With the published data [1, 13, 19] taken into account, the value of $\delta^{13}\text{C}_{\text{av}}$ for heavy-isotope aggregates of *E*-type diamond from the Mir pipe was -5.18‰ ($\sigma = 1.30$; disp. = 1.70; $n = 19$).

Comparative analysis of the $\delta^{13}\text{C}$ values of *E*-type heavy-isotope single crystals ($\delta^{13}\text{C}_{\text{av}} = -6.13\text{‰}$;

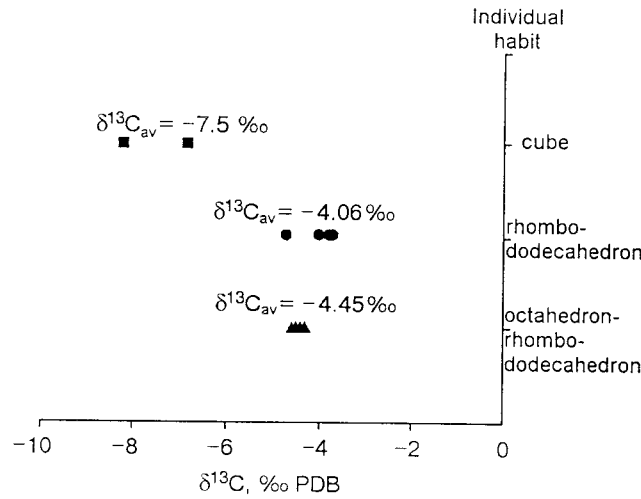


Fig. 3. Carbon isotopic composition of polycrystalline diamond aggregates with inclusions of garnet and rutile, formed by individuals of varying habit.

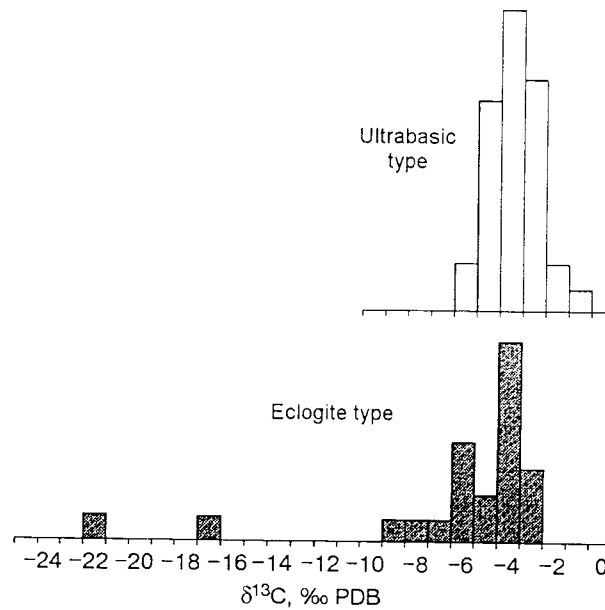


Fig. 4. Carbon isotopic composition of diamond polycrystalline aggregates from the Mir pipe containing mineral inclusions of different paragenetic associations. With the use of data from [1, 5, 13, 17–19].

$\sigma = 1.15$; disp. = 1.33; $n = 23$) [13] and polycrystalline diamond aggregates by means of f - and t -tests has shown that these two groups are not parts of the same distribution. The f -test, revealing similarity of dispersions of two data arrays, gave 0.58. The t -test, analyzing the possibility for the samples to be parts of a general distribution with a common mean, gave 0.018. Figure 5 shows distributions of $\delta^{13}\text{C}$ values of heavy-isotope aggregates and single crystals of the Mir diamond with inclusions of eclogite paragenesis.

According to data by Smelova [4] and general ideas about crystallization of mono- and polycrystalline mineral varieties [14, 20], the diamond aggregates can form under conditions of a relatively more viscous medium of crystallization as compared with single crystals. This difference in characteristics of the crystallization medium must have an effect on parameters of migration of carbon and fractionation of its isotopes. In this connection, the enrichment of the crystallization medium with ^{13}C can be caused by isotope

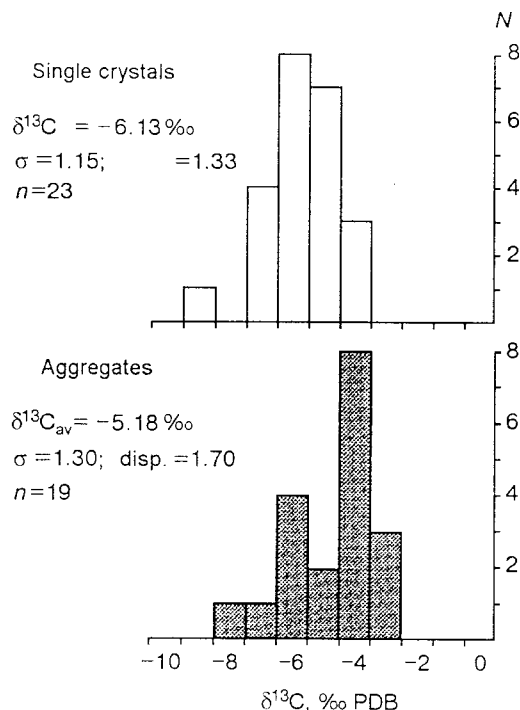


Fig. 5. Carbon isotopic composition of heavy-isotope diamonds from the Mir pipe with inclusions of eclogite paragenesis. With the use of data from [1, 13, 19].

separation at diffusion level. Relatively high migration ability of the light isotope of carbon leads to its primary removal from the region of diamond crystallization.

CONCLUSIONS

The obtained isotope characteristics of carbon of polycrystalline aggregates of diamond from the Mir pipe with inclusions of eclogite paragenesis permit the following conclusions: (1) The variety IX diamond aggregates have a wider range of $\delta^{13}\text{C}$ values relative to the variety VIII bort. (2) The heavy-isotope polycrystalline aggregates of diamond with a cubic habit of individuals make the maximum contribution of ^{12}C as compared with aggregates having different morphological characteristics of individuals. (3) Bort with *E*-type inclusions has a wider range of $\delta^{13}\text{C}$ values relative to bort with *U*-type inclusions. (4) Polycrystalline diamond aggregates from the Mir kimberlite pipe containing inclusions of eclogite paragenesis are enriched in ^{13}C relative to *E*-type single crystals from the same deposit at a statistically significant level, which can be due to different viscosity parameters of the substrate from which they are crystallized.

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