

Chromatographic Study of Diamond Etching in Kimberlitic Melts in the Context of Diamond Natural Stability

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Abstract—The morphology of diamond crystals during resorption in the silicate melt at high *PT* parameters depends on a fluid presence in the system. This is related to the fact that refraction in the $\langle 110 \rangle$ direction of a rounded surface of etching, which, to a first approximation, corresponds to the form $\{110\}$ and appears at the site of octahedron edges, depends on the ratio $H_2O/(CO_2 + CO)$. At a high value of this ratio, the diamond resorption proceeds through ditrigonal etching layers, giving rise to a face suture on surfaces $\{110\}$. Values of the ratio $H_2O/(CO_2 + CO)$ in kimberlite samples, which were established by chromatographic analysis, approach after the experiment the conditions under which octahedral diamond crystals resorb through trigonal layers. The correlation of experimental results with the natural material suggests that diamonds from kimberlites and lamproites experienced resorption and the process was so intense that it affected not only the morphology of crystals but also the diamond potential of kimberlites in general. It was water that acted as the main reagent to resorb diamonds. As its concentration increased, so did the intensity of the process. The increase in the carbon dioxide content assisted not only a change in the type of diamond morphogenesis upon resorption but also a decrease in the depth of the process itself.

INTRODUCTION

Although the problems of the genesis of rounded crystals and establishment of the conditions of diamond preservation in nature are of current interest, the process of diamond etching in the kimberlitic melt has not been adequately studied. The diamond resorption in the kimberlitic melt is known at present to depend on temperature, time, carbon content, and redox conditions determining the fluid regime of the etching medium (Arima, 1996; Yamaoka *et al.*, 1980). The diamond etching was found to proceed prior to kimberlite melting by fluid segregated on its heating (Harris and Vance, 1974). However, in the experimental works listed, morphological features of diamond crystals were not studied in detail or compared to natural crystals.

It was established (Sonin *et al.*, 2002₁) that the etching of diamond crystals in the kimberlitic melt at high pressure and temperature (3.0 GPa, 1300°C) is accompanied by the formation of morphological features identical to those typical of natural diamonds; in this case, the final form of resorption is octahedroid with a face suture on rounded surfaces (an octahedron made up of ditrigonal layers, according to terminology suggested by Bartoshinskii and Kvasnitsa (1991)). The assumption was made that this final form of resorption was determined by the fluid phase composition in the natural kimberlite sample.

In this work, we present data on the chromatographic study of diamond etching in the kimberlitic

melt at high temperature and pressure to establish the fluid effect on the process.

METHODS

The experiments were performed with a high-pressure multiple-punch unit of the slit sphere type at 3.0 ± 0.25 GPa and $1300 \pm 20^\circ\text{C}$ by the methods described in (Sonin *et al.*, 2002₁). For etching, we used micaceous kimberlite from the Udachnaya–Vostochnaya pipe (UV–72–93), which comprised (wt %) 29.98 SiO₂; 1.92 Al₂O₃; 7.9 Fe₂O₃ (total); 0.20 P₂O₅; 0.73 TiO₂; 7.71 CaO; 34.15 MgO; 0.14 MnO; 0.12 Na₂O; 0.90 K₂O; 0.43 H₂O; 15.4 LOI (6.6 CO₂); total 99.22. The diamond etching was carried out in sealed platinum ampoules. The ampoules were sealed by electric arc welding in a special unit which was cooled with liquid nitrogen. In some experiments, distilled water was added to the ampoules with samples. We used for our studies table octahedron crystals without visible inclusions and defects. Preference was given to synthetic crystals because of a lesser amount of dislocations in sectors of the octahedron growth as compared to natural diamonds. The crystals had secondary faces of a cube. One diamond crystal was used in each experiment. The synthetic diamond crystals were grown by the temperature gradient method in the system Fe–Ni–C at high temperature and pressure (Chepurov *et al.*, 1997).

After experiments, the ampoules with samples were put into the special unit connected with the chromatographic system, in which they were heated to 150°C

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Table 1. Conditions and results of experiments ($P = 3.0$ GPa; $T = 1300^{\circ}\text{C}$; $t = 30$ min)

Experiment no.	Crystal weight, mg	Diamond origin	Kimberlite weight, mg	Water weight, mg	Crystal weight after experiment, mg	Weight loss, mg
7-7	4.39	Synthetic	99.0	7.4	3.31	1.08*
7-12	4.42	"	103.5	10.1	4.22	0.20
7-19	2.24	"	102.1	5.4	2.03	0.21
7-25	11.86	Natural	109.6	d.a.	11.74	0.12
7-32	26.80	Synthetic	100.0	5.0	25.15	1.65*

* Crystal was split when disclosing the ampoule (the weight loss is overstated).

and punched by a firing pin, and discharged gases were analyzed. Then, the weighed portion of kimberlite was put into a silica tube connected with the chromatographic system. The content of volatile components in kimberlite was determined by the chromatographic analysis of the gas phase liberated during serial calcination (over 10 minutes) of the weighed portion at the temperatures 200, 600, and 800°C in helium atmosphere. The methods allow analyzing the content of H_2O , CO_2 , CO , H_2 , N_2 , CH_4 , C_2H_n , C_3H_n , and C_4H_n , as well as heavy hydrocarbons, H_2S , and SO_2 (Osorgin *et al.*, 1995).

The morphology of diamond crystals was studied with MBC-10 and MBI-15 light microscopes and a JSM-35 scanning electron microscope. Conditions of the experiments are given in Table 1.

RESULTS

Morphology of Diamond Crystals

Due to slight etching in the experiments (Table 1), the habit of diamond crystals did not change, whereas

the micromorphology of faces underwent transformations. Etching cavities appeared on edges $\{111\}$ and $\{100\}$. The cavities on octahedron edges are flat-bottom or, more rarely, tapered with a truncated bottom, and of a triangular configuration with contours oriented transverse to contours of edges $\{111\}$ (so-called negative trigons) (Fig. 1). Tapered trigons occurred only on the natural crystal. Etching cavities on cubic edges were tapered or, more rarely, with a truncated bottom, and of a rectangular form with sides parallel to the direction $\langle 110 \rangle$ (Fig. 2).

Crystal edges underwent more intense resorption compared to faces because etching layers formed and appeared as a striation on crystals. In the place of edges, rounded surfaces appeared, which corresponded in position to surfaces $\{110\}$. On slight resorption of the octahedron face, contours of layers had visible ditrigonal outlines (Fig. 3). In cases of more intense resorption of a face, layer contours approximated its contours (Fig. 4); i.e., the layer contours could be diagnosed as trigonal. Fig. 5 is a schematic of ditrigonal and trigonal layers on the octahedron face of diamond.



Fig. 1. Negative trigons on the face $\{111\}$ of a diamond crystal etched in the kimberlitic melt.

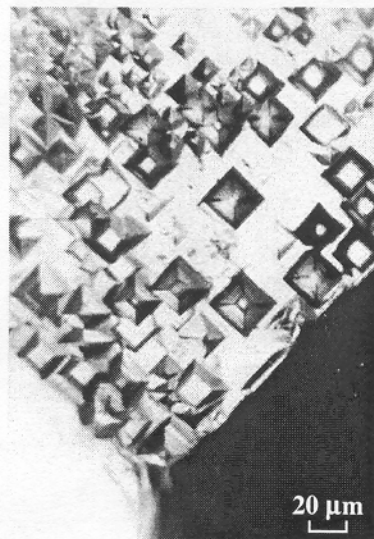


Fig. 2. Square etching cavities of the face $\{100\}$ of a diamond crystal etched in the kimberlitic melt.

Chromatography of Samples

The results of the chromatographic analysis demonstrate that, on disclosing the ampoules with samples at 150°C, the main fluid component is H₂O (Table 2). CO₂ and hydrocarbons are represented in lesser amounts. The ratio H/(O + H) corresponds to nearly pure water (0.664–0.666). On heating of weighed portions of kimberlite, starting from 200°C, CO₂, CO, and H₂ have been established in the discharging gas phase. Other gases (N₂, H₂S, etc.) are present at the level of background values. At 800°C, the discharge of CO₂ and CO is especially intense due to decomposition of the carbonate material. Judging from the total gases escaped from heated samples, the ratio H/(O + H) varies within 0.157–0.204.

DISCUSSION

The study carried out allows the following conclusion. The etching at high temperature and pressure of diamonds of the octahedral habit in kimberlite rich in volatile components results in the formation of etching forms similar to those on naturally occurring diamond crystals. The chromatographic study also allows us to account for the results of diamond etching in the kimberlitic melt presented in (Sonin *et al.*, 2002₁), in which the final form of resorption of the octahedroid type was obtained. This seems to be due to accumulation of carbon oxides during oxidation of diamonds by H₂O under conditions of a closed system, as well as due to a high initial content of carbon dioxide in kimberlite samples.

Table 3 gives ratios of components in fluids from experiments on etching diamonds in the kimberlitic melt as compared to data on etching diamonds in the alkaline basalt melt at high pressure (Sonin *et al.*, 1997, 2001). Relative amounts of components in the fluid were calculated from data on the total gas escape from samples, i.e., from chromatographic analyses made at 200°C and higher (Table 2), which corresponds to the procedure used in the works mentioned.

The ratio H₂O/(CO₂ + CO) in the fluid liberated from the initial kimberlite weighed portion was 1.60. After the experiments, the ratio varied within 0.078–0.117. The evolution of the fluid composition in the experiments proceeded towards decreasing content of H₂O and increasing contents of CO₂ and CO. The fluid composition at the beginning of the experiments corresponded to the area of generation of ditrigonal layers, although, at final stages of the experiments, it evolved towards the area of generation of trigonal layers, which showed up in etching in the silicate melt–fluid system with relatively low values of the ratio H₂O/(CO₂ + CO) (Sonin *et al.*, 1997, 2001). As was mentioned above, the evolution of the fluid regime in experiments with kimberlite was determined by the fact that they were carried out under closed conditions—in sealed platinum ampoules. Experiment 7-32 is noteworthy here, in which a higher value, as compared to experiments 7-19

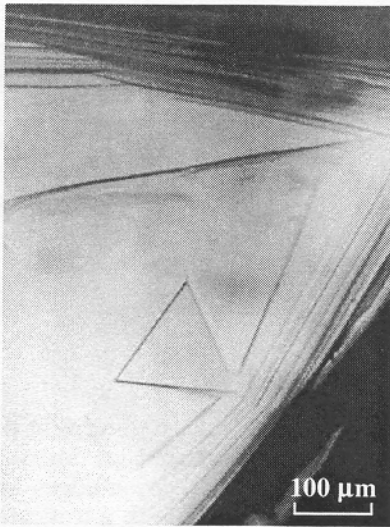


Fig. 3. Ditrigonal striation on a diamond crystal etched in the kimberlitic melt.

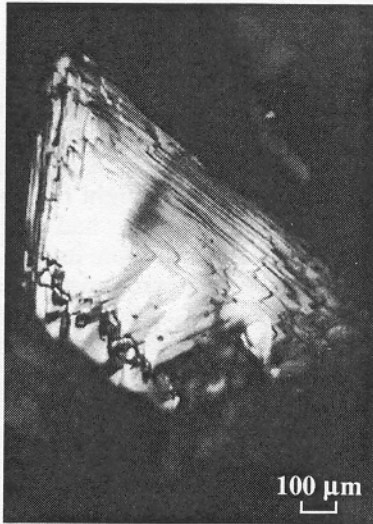


Fig. 4. Trigonal striation on a diamond crystal etched in the kimberlitic melt.

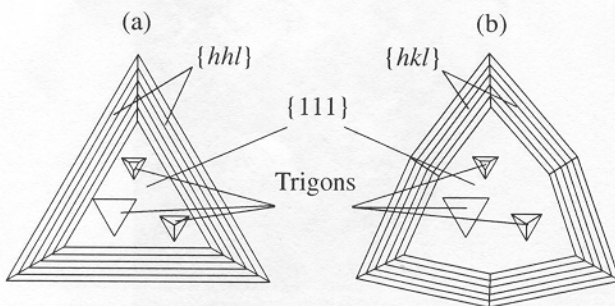


Fig. 5. Scheme of trigonal (a) and ditrigonal (b) layers of etching on faces {111} of diamond crystals.

Table 2. Results of the chromatographic analysis of samples

Material (experiment no.)	Gasification T, °C	Discharged gas, mg/kg											Ratio
		H ₂ O	CO ₂	CO	H ₂	CH ₄	C ₂ H ₂	C ₂ H _{4,6}	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	H/(O + H)
Kimberlite (before ex- periment)	200 + 600	47400	12380	60	20	18	4	1	5	9	7	0.0	0.623
	800	28400	33000	200	3	0.8	0.0	0.0	0.0	13	0.0	0.0	0.505
	1000	4300	4300	40	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.522
	Sum*	80100	49680	300	23	18.8	4	1	5	22	7	0.0	0.570
Kimberlite (7-7)	200 + 600	2180	10130	170	40	20	10	3	10	8	7	2	0.33
	800	2700	34800	1700	20	2	1	0.0	0.3	0.0	0.0	0.0	0.151
	Sum*	4880	44930	1870	60	22	11	3	10.3	8	7	2	0.204
Kimberlite (7-12)	200 + 600	1820	7430	60	20	8	6	2	5	4	3	0.5	0.339
	800	2000	39000	1400	10	1	1	0.0	0.5	0.0	0.0	0.0	0.107
	Sum*	3820	46430	1460	30	9	7	2	5.5	4	3	0.5	0.162
Ampoule	150	300	5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.663
Kimberlite (7-19)	200 + 600	2260	8630	60	30	9	6	2	6	4	4	2	0.354
	800	2800	33300	1200	20	0.6	0.7	0.0	0.2	0.2	0.0	0.0	0.162
	Sum*	5060	41930	1260	50	9.6	6.7	2	6.2	4.2	4	2	0.216
Ampoule	150	120	2	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.664
Kimberlite (7-25)	200 + 600	1640	11020	110	6	8	7	2	5	5	3	1	0.244
	800	2700	34000	1300	7	2	0.9	0.0	0.0	0.0	0.0	0.0	0.150
	Sum*	4340	45020	1410	13	10	7.9	2	5	5	3	1	0.176
Ampoule	150	19000	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.4	0.6	0.666
Kimberlite (7-32)	200 + 600	1710	7110	30	20	6	3	0.6	3	2	2	0.9	0.336
	800	2600	47000	1100	10	1	0.6	0.0	0.0	0.0	0.0	0.0	0.114
	Sum*	4310	54110	1130	30	7	3.6	0.6	3	2	2	0.9	0.157

* Total gas discharged from kimberlite.

Table 3. Ratio of components discharged from samples

Experiment no.	H ₂ O/(CO ₂ + CO)	CO/CO ₂	Configuration of layers	Trigon orientation
Before experiment	1.60	0.006		
7-7	0.104	0.042	Ditrigonal, evolving into trigonal	Negative
7-12	0.08	0.031	—	—
7-19	0.117	0.03	—	—
7-25	0.093	0.031	—	—
7-32	0.078	0.021	—	—
Experiments with water-bearing basalt (Sonin <i>et al.</i> , 1997)				
1	1.312	0.034	Ditrigonal	Negative
3	2.327	0.038	—	—
4	0.86	0.055	—	—
Experiments with "dry" basalt (Sonin <i>et al.</i> , 2001)				
1	0.323	0.126	Trigonal	Negative
2	0.544	0.106	—	—
3	0.413	0.097	—	Hexagons
4	0.294	0.066	Absent	Positive
5	0.454	0.086	—	—

and 7-25, of gas discharge of H₂O was registered directly upon disclosing of the ampoule. This is likely to be accounted for by the fact that this weighed portion initially had an elevated amount of the hydrated phase—phlogopite. However, the calculation method used disregards the gas escape directly from the ampoule. Nevertheless, even taking into account H₂O discharged from the ampoule in the given experiment, the ratio H₂O/(CO₂ + CO) is equal to 0.25, which also corresponds to the area of generation of trigonal layers, as in other experiments.

Values of the ratio CO/CO₂ obtained in the kimberlite–fluid system fall within the interval of 0.021–0.042, which corresponds to experiments in the hydrated basalt–fluid system (0.034–0.055), in which negative trigons were also obtained on crystal faces {111} (Table 3). In a system with an initially low content of H₂O, oxidation by carbon dioxide has a pronounced effect on etching of diamonds; therefore, negative trigons appear at a relatively high CO content. On etching of diamonds in the melt of “dry” basalt, negative trigons are registered in experiments with the ratio CO/CO₂ > 0.1. At lower values of the ratio, positive trigons form.

Sculptures grown on crystals due to etching determine the morphogenesis of diamonds and serve as indicators of the etching process. In using the etching of octahedral diamonds in the model system alkaline basalt–fluid at high pressure, three types of morphogenesis were established depending on the fluid composition (Sonin *et al.*, 2001). It should be noted that these studies were performed with other parameters that could affect the process of etching being fixed: temperature, general pressure, and the silicate melt composition. The existence of three evolutionary types of diamond crystal morphology was confirmed by Khokhryakov *et al.* (2002). The types of morphogenesis distinguished experimentally correspond to the evolutionary morphological series of natural diamonds, which were established by mutual occurrence of different surface sculptures on crystals (Sonin *et al.*, 2002). Characteristic of diamonds from kimberlites are only two morphogenetic trends differing in the type of tangential etching: through trigonal or ditrigonal layers. This eventually determines the form of crystal resorption. When resorbing through trigonal layers, edges of octahedral crystals are mainly resorbed, and in consequence there form individuals of the series laminar octahedron (octahedron with trigonal layers on faces)–trigon–trioctahedroid with parallel striation on <110>–rhombododecahedroid without a face suture. On etching through ditrigonal layers, tops of octahedral crystals are mainly resorbed to form the morphogenetic series octahedron with ditrigonal striation–rhombododecahedroid with a face suture–tetrahexahedroid, which is determined by substantial refraction of surfaces {110} in the long diagonal. As experimental data show, the second alternative is a possibility only in a water-rich fluid. The process of such a transformation

runs easier if the initial form of a diamond crystal is an octahedron complicated by faces of a cube (Khokhryakov *et al.*, 2001).

The data obtained are additional evidence for the effect of the fluid regime in the system on the morphology of diamond crystals upon etching under conditions of fixed temperature and general pressure. The silicate melt is of minor importance.

STABILITY OF DIAMOND CRYSTALS IN KIMBERLITE AND LAMPROITE DEPOSITS

It is of interest to correlate the data presented with actual material on natural diamonds from kimberlites and lamproites.

Native lamproite diamond deposits are known in Australia (Jakes *et al.*, 1989). Within the problem posed, of great interest are diamonds belonging, according to the classification suggested by Yu.L. Orlov, to the first variety, i.e., crystals of the octahedron–dodecahedroid (a collective name for the morphological series octahedroid–rhombododecahedroid–tetrahexahedroid) series (Orlov, 1973). According to the terminology accepted by Jakes *et al.* (1989), among these are octahedrons, rounded dodecahedrons, and table dodecahedrons. Amidst these crystal types in the Argyle lamproite pipe, the amount of rounded dodecahedrons is higher (45–60%) than that of octahedrons (20–25%) and table dodecahedrons (20–40%). The relationship between H₂O and CO₂ in lamproite samples from the Argyle pipe is unstable: in some samples H₂O exceeds CO₂, but there exist reverse relationships as well.

An alternative situation is observed in the Western Kimberley province. For instance, in the Ellendale-4 and Ellendale-9 pipes, the amount of rounded dodecahedrons (65–70%) exceeds that of table dodecahedrons (25–30%) and octahedrons (3–5%) in the octahedron–dodecahedroid series as compared to the Argyle pipe. This relationship is accompanied by a considerable excess of H₂O over CO₂: by a factor of 4–60 and 12–60 respectively, in lamproite samples from the Ellendale-4 and Ellendale-9 pipes.

Octahedrons predominate amidst crystals of fine classes (less than 1 mm) both in the Argyle pipe and in the Ellendale-4 and Ellendale-9 pipes, whereas large diamond crystals are mainly represented by rounded dodecahedroids. It should be pointed out that the average content of diamonds makes up 5 carat/t in the Argyle pipe and 0.14 and 0.05 carat/t in the Ellendale-4 and Ellendale-9 pipes, respectively (Jakes *et al.*, 1989).

The morphological spectrum of diamonds in kimberlite pipes of South Africa is rather stable. Most diamonds represent crystals of the tetrahexahedroid type with a minor amount of table octahedrons (Robinson *et al.*, 1986). According to the terminology suggested by Robinson, the tetrahexahedroidal class of natural diamonds involves rounded diamond crystals of the octahedroid–rhombododecahedroid–tetrahexahedroid

Table 4. Correlation of the diamond crystal morphology with the content of volatile matters in kimberlites from the deposit of the Zolotits field of the ADP (according to data from tables 3.1.2 and 4.3 from (Bogatikov *et al.*, 1999))

Pipe	Total amount of diamonds of variety I, %	Individuals of the series octahedron–dodecahedroid with ditrigonal layers and a face suture, %	Individuals of the series octahedron–dodecahedroid with trigonal layers without a face suture, %	Table octahedrons, %	H ₂ O/CO ₂
Lomonosov	82.4	85.1	9.8	5.1	2–30
Pomorsk	72.6	83.7	12.3	4	nd
Pioneer	84.4	81.6	13.9	4.5	4–15
Karpinsky-1	75	96.9	2.3	0.8	6
Karpinsky-2	81.3	85.5	11.9	2.6	4–54
Arkhangel'sk	59.2*	83.8	15.9	0.3	4–7

* The deposit has a higher amount of cubic crystals of variety II, according to the classification of Yu.L. Orlov.

series by the Russian classification. In pipes in which morphological types of diamond crystals were statistically treated (the Premier, De Beers, Dutoitspan, Bultfontein, and Wesselton pipes), the H₂O content in kimberlites is considerably higher than the CO₂ content (Dawson, 1983; Ilupin *et al.*, 1978).

A considerable excess of H₂O content over CO₂ content was found in the Madjgawan pipe (India): 87-fold in kimberlite samples from the surface and 18-fold in underground workings (Ilupin *et al.*, 1978). Diamonds of this deposit are characterized by a very high content of rounded crystals (Sobolev *et al.*, 1993; Patel and Agarwal, 1965).

Representative data on the morphology of diamond crystals and the chemical composition of highly diamondiferous kimberlites of the Zolotitsk field of the Arkhangel'sk diamond province (ADP) are presented in (Bogatikov *et al.*, 1999). This allows necessary correlations to be made for crystals of variety I according to the classification suggested by Orlov. Despite the fact that the authors cite no goniometric data, which are the most reliable when establishing types of diamond morphogenesis, a comprehensive description of the morphology makes it possible to unite the identified groups by types of morphogenesis in accord with (Sonin *et al.*, 2002). Such individuals distinguished by the authors as smooth-edged (crypto- and thinly laminar) dodecahedroids or dodecahedroids with a splinter sculpture and shagreen, a tear-shaped sculpture, a mosaic-blocky sculpture, or a sheaflike striation, as well as combination crystals with a splinter striation and blocky ornamentation, fall within the group of diamond crystals with the morphogenesis octahedron–dodecahedroid with a face suture. Belonging to another morphogenetic type (octahedron–dodecahedroid without a face suture) are diamond crystals with a trigonal striation and, probably, judging from the description of crystals, with a polycentric sculpture (terminology from the work by Bogatikov *et al.* (1999). Correlation results are presented in Table 4. Amidst diamonds of size more than 0.5 mm from the deposit of the Zolotitsk

field, crystals of variety I, according to the classification suggested by Orlov, predominate, and, amidst them, the maximum amount falls to diamonds belonging to the first of the above-mentioned morphogenesis types (81.6–96.9%). About 2.3–15.9% of diamonds fall within the second morphogenesis type, the main amount being concentrated in the class 0.5–1 mm. This correlates with the ratio H₂O/CO₂ (Table 4), as the H₂O content in kimberlite predominates.

In the V. Grib pipe, with a high diamond potential (the Verkhotinsk field), kimberlites contain very little CO₂; therefore, as in kimberlites of the Zolotitsk field, H₂O dominates over CO₂, but, nevertheless the content of phlogopite as a water concentrator is shown to be much lower (Garanin *et al.*, 2001; Bogatikov *et al.*, 2001). The morphological spectrum of diamonds is also different. As compared to pipes of the Zolotitsk field, in diamonds of higher classes of dimensions from the V. Grib deposit, the content of octahedrons makes up 37%, dodecahedroids 26%, and crystals of the transitional type 20%, according to data of Bogatikov *et al.* (1999), or 40.8%, 36.1%, and 20.6%, respectively, according to data of Sergeeva (2000). The share of octahedral crystals increases as the size decreases. These are especially abundant amidst crystals less than 0.5 mm in size.

More diverse relationships between morphological types of diamond crystals are observed in the Yakutia diamond province (YDP). In particular, the following regularity has been established: the amount of rounded crystals increases as one moves farther away from the central regions of the province northwards (Bartoshinskii, 1961; Milashev, 1965; Bartoshinskii and Kvasnitsa, 1991). Moreover, for kimberlite deposits of the YDP, the so-called morphological criterion of diamond potential has been empirically established: "if the share of curve-faced rhombododecahedroids in the diamond association exceeds 18–20%, the kimberlite body belongs to the category of low diamond potential" (Koptil, 1994).

Table 5. Correlation of the diamond crystal morphology with the amount of micaceous varieties of kimberlites in YDP deposits, according to data from (Milashev, 1965, 1972)

Kimberlite fields and regions	Diamond content	Octahedrons, %	Transitional forms, %	Dodecahedroids, %	Ratio between mica-free and micaceous rocks
Malobotuobinsk	Very high	65.4	20.9	13.7	10.11
Markhino–Alakit	High	25.4	19.2	56.3	6.09
Daldyn	"	23.8	16.3	59.9	3.59
Upper Mun	"	24.8	10.3	64.9	2.32
Omonos–Kutugun	Low	(40)	(5)	(55)	0.12
Luchakan	Very low	15	10	75	0.17
Kuranakh					0.41
Ogon'or–Motorchun	"	11	5	84	2.41
Chomurdakh					0.95
Lower Kunam	"	2.2	10.6	87.2	0.21
Middle Kunam					0.84

The chemical composition of the YDP kimberlites is characterized by close amounts of H₂O and CO₂, but in some pipes a sharp excess of one component over another is a possibility (Ilupin *et al.*, 1978). Variations in the CO₂ content are especially high (up to 30%), whereas in kimberlite pipes of South Africa the concentration of CO₂ is less pronounced and rarely exceeds 2–5% (Khar'kiv *et al.*, 1991). Nevertheless, in kimberlites of the Verkhnemusk region, the H₂O content often exceeds the CO₂ content compared to kimberlites of the Malobotuobinsk and Daldyno–Alakit regions (Khar'kiv *et al.*, 1991). The content of table octahedrons correspondingly decreases and the amount of rounded crystals increases (Bartoshinskii, 1961).

It was pointed out by Bobrievich *et al.* (1959) that the amount of rounded diamonds increases as the mica content in kimberlites rises. Table 5 displays data obtained by Milashev (1965, 1972), who established the dependence of diamond morphology and content on the amount of micaceous varieties of kimberlites.

We relate the tendency described in (Bobrievich *et al.*, 1959; Milashev, 1965, 1972) to the effect of water on the diamond preservation since phlogopite in unaltered kimberlites is the main H₂O concentrator. The morphological subdivision of diamonds into the series octahedrons–transitional forms–dodecahedroids, which was used by Milashev and other authors, disregards the type of diamond crystal etching through trigonal or ditrigonal layers. Systematization of morphological types is based on physiographic principles (Gneushev and Bartoshinskii, 1959); therefore, the subdivision of diamonds into morphogenetic types involves difficulties. In particular, most diamonds in some YDP deposits are represented by individuals with the polycentric structure of faces (Bartoshinskii, 1961). The basis for the subdivision of individuals of that type is a crystal defectiveness that results in the polycentric

nature of faces on lit-par-lit resorption of diamonds. Individual lamellae on faces with the polycentric structure may have both trigonal and ditrigonal contours. The established regularity (Table 5) is determined by the fact that in YDP deposits diamond crystals are mainly composed of ditrigonal layers. This is also true for crystals with the polycentric structure of faces since “they involve diamonds of the octahedral habit or, more rarely, diamonds of the transitional form, with numerous embossed, clearly laminated ditrigonal (more rarely, trigonal) knots on octahedron faces” (Gneushev and Bartoshinskii, 1959). Moreover, the authors of this classification assign individuals with visible signs of laminated structure to the group of octahedrons, “outlines of layers ... being in most cases ditrigonal” (Gneushev and Bartoshinskii, 1959).

Thus, we can infer that transitional forms and dodecahedroids of the YDP kimberlite deposits mainly belong to the morphological series octahedron–dodecahedroid with a face suture (Sonin *et al.*, 2002₂). Hence, there exists a dependence of the diamond morphology on the content of micaceous varieties of kimberlites, i.e., on the amount of phlogopite as a water concentrator. The higher the water content in kimberlite magma, the more intense are processes of diamond resorption and the higher will be the content of rounded diamond crystals—products of resorption.

Milashev's data, as well as data obtained by Vasilenko *et al.* (1997) (Table 6) are correlatable. The table also involves K₂O contents since phlogopite in kimberlites is a concentrator of not only water but also potassium.

In light of the aforesaid, the dependence of diamond potential on what is called the mica ratio, which was established by Vasilenko *et al.*, becomes understandable. Judging by the data in Table 6, the diamond potential of native deposits decreases as the share of mica-bearing rocks increases (and, correspondingly, the K₂O

Table 6. Correlation of the diamond content with the amount of micaceous varieties of kimberlites in productive deposits of the YDP, according to data from (Vasilenko *et al.*, 1997)

Kimberlite pipe	Alkalinity type	K ₂ O content, wt %	Diamond content, conventional units
Aikhal	Ultrabasic	0.42	48.85
	Micaceous	0.90	40.96
	Sublamprophyric + lamprophyric	1.70	28.33
Internatsional'naya	Ultrabasic	0.45	42.88
	Micaceous	0.94	38.12
	Sublamprophyric + lamprophyric	1.47	22.08
Mir	Ultrabasic	0.38	22.30
	Micaceous	0.93	16.0
	Sublamprophyric + lamprophyric	1.68	19.92
Western Udachnaya body	Ultrabasic	0.45	11.18
	Micaceous	0.90	10.38
	Sublamprophyric + lamprophyric	1.70	14.62
Eastern Udachnaya body	Ultrabasic	0.39	10.73
	Micaceous	0.89	7.29
	Sublamprophyric + lamprophyric	1.51	2.92
Sytykan	Ultrabasic	0.20	5.29
	Micaceous	0.85	5.41
	Sublamprophyric + lamprophyric	1.78	0.10

content increases). The exception is the western body of the Udachnaya pipe. If we consider the western body and the eastern body of the Udachnaya pipe as a single deposit, then the above dependence will be valid.

According to the petrochemical model suggested by Vasilenko *et al.* (1997), the entire YDP kimberlite association is subdivided into seven discrete groups or populations depending on the depth of kimberlite magma generation. The subdivision of the populations is based on changes in the TiO₂ content. The diamond potential of kimberlites rises in more deep-seated populations, i.e., as the titanium content decreases, and in more magnesian varieties. The K₂O content has also been established to vary from 0.8 to 0.2% inversely as the TiO₂ content. However, as the authors point out, higher contents of K₂O are formed beyond the population trend. This means that kimberlites with an elevated alkalinity do not fit into the suggested model, although they do affect the diamond potential of kimberlite pipes. It is quite evident that the diamond potential trend related to the depth of formation of kimberlite melts is superimposed by another trend, namely, the dependence of the diamond content on the amount of H₂O as the main reagent having affected the stability of diamonds during the formation of kimberlite deposits.

CONCLUSIONS

During the formation of kimberlite and lamproite deposits, diamond crystals were subject to resorption,

the process being so intense that it affected not only the morphology of crystals, but the diamond potential in kimberlites as well. The main reagent resorbing diamonds was H₂O. The intensity of the process grew as the water concentration increased. At high pressure and temperature, as well as in the presence of a water-rich fluid, the rate of diamond crystal etching in silicate melts has been established to be higher by about a factor of 1.5 than in a "dry" system (Zhimulev *et al.*, 1998; Chepurov *et al.*, 1997). The increase in the CO₂ content contributed not only to a change in the type of diamond morphogenesis upon resorption but also to a decrease in the depth of the process itself. This tendency has been revealed experimentally on etching of diamond crystals, and it is clearly established by using natural materials despite the fact that initial (primary) contents of H₂O and CO₂ in kimberlites were changed due to superimposition of secondary processes: assimilation of carbonaceous xenoliths, which is more characteristic of the YDP kimberlites, and a low-temperature hydrothermal reworking of the kimberlite substance under the effect of groundwater.

Moreover, it is significant that diamond crystals are likely to have entered the kimberlitic melt in the course of disintegration of mantle xenoliths. Because of this, smaller crystals had a better chance to survive with unchanged growth morphology, which is seen in some deposits.

REFERENCES

1. M. Arima, "Experimental Study of Growth and Resorption of Diamond in Kimberlitic Melts at High Pressure and Temperatures," in *Proceedings of the 3rd NIRIM International Symposium on Advanced Materials (ISAM'96)* (1996), pp. 223–228.
2. Z. V. Bartoshinskii, "Comparative Characteristics of Diamonds from Different Diamond-Bearing Regions of Western Yakutia," *Geol. Geofiz.*, No. 6, 40 (1961) [in Russian].
3. Z. V. Bartoshinskii and V. N. Kvasnitsa, *Crystallomorphology of Diamond from Kimberlites* (Nauk. Dumka, Kiev, 1991) [in Russian].
4. A. P. Bobrievich, M. N. Bondarenko, M. A. Gnevushev, *et al.*, *Diamond Deposits of Yakutia*, Ed. by V. S. Sobolev (Gosgeoltekhizdat, Moscow, 1959) [in Russian].
5. O. A. Bogatkov, V. K. Garanin, V. A. Kononova, *et al.*, *Arkhangel'sk Diamond Province (Geology, Petrography, Geochemistry, and Mineralogy)* (Mosk. Gos. Univ., Moscow, 1999) [in Russian].
6. O. A. Bogatkov, V. A. Kononova, V. A. Pervov, D. Z. Zhuravlev, "Sources, Geodynamic Formation Conditions, and Diamond Potential of Kimberlites from the Northern Margin of the Russian Plate: SR–ND Isotopy and ICP–MS Geochemistry," *Petrologiya* **9** (3), 227 (2001).
7. A. I. Chepurov, I. I. Fedorov, and V. M. Sonin, *Experimental Modeling of Processes of Diamond Formation* (Sib. Otd. Ross. Akad. Nauk, NITs OIGGM, Novosibirsk, 1997) [in Russian].
8. J. Dawson, *Kimberlites and Their Xenoliths* (Mir, Moscow, 1983; Springer, Heidelberg, 1980).
9. V. K. Garanin, G. P. Kudryavtseva, T. V. Posukhova, *et al.*, "Two Types of Diamond-Bearing Kimberlites in the Arkhangel'sk Province," *Geol. Razved.*, No. 4, 36 (2001) [in Russian].
10. M. A. Gnevushev and Z. V. Bartoshinskii, "On the Morphology of Yakutian Diamonds," in *Materials on the Geology of Mineral Resources of Yakutia* (Akad. Nauk SSSR, Moscow, 1959), pp. 74–92 [in Russian].
11. J. W. Harris and E. R. Vance, "Studies of the Reaction Between Diamond and Heated Kimberlite," *Contribs. Mineral. Petrol.* **47** (4), 237 (1974).
12. I. P. Ilupin, F. V. Kaminskii, and E. V. Frantsesson, *Geochemistry of Kimberlites* (Nedra, Moscow, 1978) [in Russian].
13. A. Jakes, J. Luis, and K. Smith, *Kimberlites and Lamproites of Western Australia* (Mir, Moscow, 1989).
14. A. D. Khar'kiv, V. V. Zuenko, N. N. Zinchuk, *et al.*, *Petrochemistry of Kimberlites* (Nedra, Moscow, 1991) [in Russian].
15. A. F. Khokhryakov, Yu. N. Pal'yanov, and N. V. Sobolev, "Evolution of Crystal Morphology of Natural Diamond in Dissolution Processes: Experimental Data," *Dokl. Akad. Nauk* **380** (5), 656 (2001) [*Dokl. Earth Sci.* **381** (8), 888 (2001)].
16. A. F. Khokhryakov, Yu. N. Pal'yanov, and N. V. Sobolev, "Crystal Morphology as Indicator of Redox Conditions of Natural Diamond Dissolution at the Mantle PT Parameters," *Dokl. Akad. Nauk* **384** (5), 670 (2002) [*Dokl. Earth Sci.* **385** (5), 534 (2002)].
17. V. I. Koptil, Candidates Dissertation in Geology and Mineralogy (Novosibirsk, 1994) [in Russian].
18. V. A. Milashev, *Petrochemistry of Yakutian Kimberlites and Factors of Their Diamond Potential* (Nedra, Leningrad, 1965) [in Russian].
19. V. A. Milashev, *Physicochemical Conditions of Kimberlite Formation* (Nedra, Leningrad, 1972) [in Russian].
20. Yu. L. Orlov, *Mineralogy of Diamond* (Nauka, Moscow, 1973) [in Russian].
21. N. Yu. Osorgin, I. I. Fedorov, V. M. Sonin, and D. G. Bagryantsev, "The Study of the Chemical and Molecular Composition of Fluid of the System C–O–H in Experiments at PT parameters of Diamond Synthesis," in *Materials on Genetic and Experimental Mineralogy* (Sib. Otd. Ross. Akad. Nauk, Novosibirsk, 1995), Vol. 11, pp. 74–80 [in Russian].
22. A. R. Patel and M. K. Agarwal, "Microstructures on Panna Diamond Surfaces," *Amer. Mineralogist* **50** (1/2), 124 (1965).
23. D. N. Robinson, J. A. Scott, A. Van Niekerk, and V. G. Anderson, "The Sequence of Events Reflected in the Diamonds of Some Southern African Kimberlites," in *Kimberlites and Related Rocks*, Vol. 2, No. 14, GSA Special Publication, *Proceedings of the Fourth International Kimberlite Conference* (Perth, 1986), pp. 990–1000.
24. O. S. Sergeeva, "Morphological Peculiarities of Diamonds from the V.P. Grib Pipe," in *Essays on Geology and Mineral Resources of the Arkhangel'sk Oblast* (Pomor Gos. Univ., Arkhangel'sk, 2000), pp. 97–102 [in Russian].
25. N. V. Sobolev, E. M. Galimov, E. S. Efimova, *et al.*, "Crystalline Inclusions, Isotopic Composition of Carbon, Nitrogen Centers of Diamonds, and Peculiar Features of the Composition of Garnet from the Madjgavan Pipe (India)," *Geol. Geofiz.*, No. 12, 85 (1993).
26. V. M. Sonin, E. I. Zhimulev, I. I. Fedorov, and N. Yu. Osorgin, "Diamond Crystal Etching in Silicate Melt with Water-Rich Fluid at High PT Parameters," *Geokhimiya*, No. 4, 451 (1997).
27. V. M. Sonin, E. I. Zhimulev, I. I. Fedorov, *et al.*, "Diamond Crystal Etching in 'Dry' Silicate Melt at High PT Parameters," *Geokhimiya*, No. 3, 305 (2001).
28. V. M. Sonin, E. I. Zhimulev, A. I. Chepurov, and V. P. Afanas'ev, "Morphology of Diamond Crystals Etched in Kimberlitic Melt at High PT Parameters," *Geol. Razved.*, No. 1, 60 (2002₁) [in Russian].
29. V. M. Sonin, E. I. Zhimulev, V. P. Afanas'ev, and A. I. Chepurov, "Genetic Aspects of the Diamond Morphology," *Geol. Rudn. Mestor.* **44** (4), 331 (2002₂) [*Geol. Ore Depos.* **44** (4), 291 (2002)].
30. V. B. Vasilenko, N. N. Zinchuk, and L. G. Kuznetsova, *Petrochemical Models of Yakutian Diamond Deposits* (Nauka, Novosibirsk, 1997) [in Russian].
31. S. Yamaoka, H. Kanda, and N. Setaka, "Etching of Diamond Octahedrons at High Temperatures and Pressure with Controlled Oxygen Partial Pressure," *J. Mater. Sci.* **15** (2), 332 (1980).
32. E. I. Zhimulev, V. M. Sonin, and A. I. Chepurov, "Rates of Diamond Crystal Resorption in Silicate Melt at High Pressure," *Crystallography-96, Second Urals Conference on Crystallography* (Syktyvkar, 1998), p. 90 [in Russian].