

“EQUILIBRIUM” AND “NON-EQUILIBRIUM” DIAMOND CRYSTALS FROM DEPOSITS IN THE EAST EUROPEAN PLATFORM, AS REVEALED BY INFRARED ABSORPTION DATA

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ABSTRACT

Almost 600 diamond crystals from Western Russian kimberlite pipes of the Arkhangelsk area and Kola Peninsula and from placer deposits of the Urals and Timan areas were studied with IR spectrometry methods, in order to evaluate the presence of nitrogen and other impurity centers. The crystals differ in their total nitrogen contents and in the concentration of individual structural impurities according to their provenance. There are differences in the temperature of formation of diamond from each deposit: from 1075–1100°C for the Arkhangelsk suite to 1125–1150°C for the Timan and Urals suites. Diamond crystals with octahedral zoning (tangential mechanism of growth) are characterized by the lowest contents of nitrogen, and have a rather uniform distribution of impurity centers. Samples with combined mechanisms of growth demonstrate a paradoxical relationship between temperatures of formation for the central and marginal zones of the crystals; temperatures calculated for the cores are 15–50°C lower than those estimated for the marginal zones. This paradox is caused by differences in the mechanism of growth. Diamond crystals with octahedral zoning were formed under equilibrium conditions, whereas crystals with normal or combined mechanisms of growth had a rate of crystallization probably higher than the rate of aggregation of nitrogen atoms in the crystals. The latter were formed under non-equilibrium conditions. As a result, values of the temperature of formation determined by IR spectroscopy are only realistic for those crystals that grew under equilibrium conditions. For crystals with normal and combined mechanisms of growth, temperature values calculated from IR data may be unrealistic, as they also depend on the kinetics of the crystallization process.

Keywords: diamond, nitrogen, hydrogen, infrared absorption, crystal growth, East European platform, Russia.

SOMMAIRE

Nous avons examiné près de 600 cristaux de diamant provenant des pipes de kimberlite de la Russie occidentale, de la région d'Arkhangelsk et de la péninsule de Kola, ainsi que des gisements de type placer des régions de l'Oural et de Timan, par spectrométrie infra-rouge afin d'en évaluer l'importance des impuretés, y compris l'azote. Les cristaux diffèrent dans leur teneur totale d'azote et dans la concentration d'impuretés spécifiques dans la structure, selon leur provenance. Nous notons des différences dans la température de formation du diamant dans chaque gisement, allant de 1075–1100°C pour la suite provenant d'Arkhangelsk jusqu'à 1125–1150°C pour la suite provenant de Timan et des Ourales. Les cristaux ayant une zonation octaédrique (mécanisme de croissance tangentielle) possèdent les teneurs les plus faibles en azote, et la distribution de leurs centres d'impuretés est plutôt uniforme. Les échantillons ayant des mécanismes de croissance mixtes démontrent une relation paradoxale entre température de formation du coeur et de la bordure des cristaux. Les températures calculées pour le coeur sont environ 15–50°C plus faibles que celles pour les zones de bordure. Ce paradoxe refléterait les différences en mécanisme de croissance. Les cristaux de diamant ayant une zonation octaédrique se sont formés sous conditions d'équilibre, tandis que pour les cristaux formés par mécanisme de croissance normal ou combiné, le taux de croissance était plus rapide que le taux d'aggrégation des atomes d'azote dans les cristaux. Ceux-ci témoignent de conditions de déséquilibre. Les valeurs de la température de formation estimées d'après les spectres d'absorption infra-rouge ne sont réalistes que pour les cristaux dont la croissance était à l'équilibre. Pour les cristaux formés par mécanisme de croissance normal ou combiné, les valeurs de température pourraient bien être non réalistes, parce qu'elles dépendent aussi de la cinétique de cristallisation.

(Traduit par la Rédaction)

Mots-clés: diamant, azote, hydrogène, absorption infra-rouge, croissance cristalline, plateforme de l'Europe orientale, Russie.

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INTRODUCTION

Western Russia hosts a number of diamond deposits. They are located within the East European (Russian) platform, mostly along its marginal zones. Among these deposits are diamond pipes of the Arkhangelsk (East European) diamond province (including the commercial Lomonosov and Grib pipes) and diamond placers of Timan and the western slope of the Urals (Fig. 1); the primary sources of those placers are as yet unknown.

Most of the diamond crystals from the East European platform deposits have rounded habits (dodecahedrons and combination-type forms in the octahedron to rhombic dodecahedron series), with octahedra, cubes, cuboids and tetrahexahedroids present in minor amounts.

Two distinct "populations" of diamond crystals have been identified in the kimberlite pipes of the Lomonosov deposit: (1) small (<1 mm), flat-faced octahedra, and (2) larger, rounded dodecahedral crystals. Along with this difference, the concentration of nitrogen structural

impurity in diamond also differs, which may be evidence of differences in temperature of formation for the diamond crystals in that suite, and possibly a sequence of different stages in the formation of natural diamond (Kaminsky & Khachatryan 2001). Our main objective in this study is to thoroughly examine nitrogen centers in diamond crystals from a number of deposits within the East European platform, to gain further insight into the conditions of their formation. For reliable genetic interpretation, we used the results of our previous study (Kaminsky & Khachatryan 2001); in addition, we examined the distribution of nitrogen centers in diamond with zonal internal structures, paying particular attention to nitrogen impurities in diamond microcrystals.

BACKGROUND INFORMATION

Robertson *et al.* (1934), pioneers in the examination of structural defects (impurities) in diamond, identified two types of crystals, I and II. Their ultraviolet transparency and infrared (IR) absorption spectra revealed

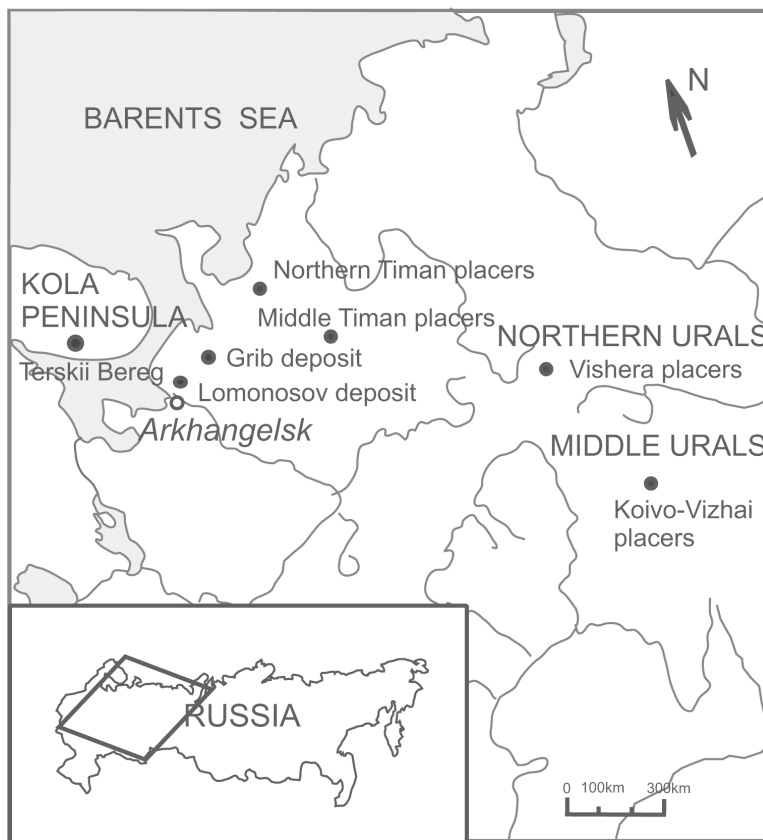


FIG. 1. Sketch map of the diamond deposits in the East European (Russian) platform.

that type-I diamond contains nitrogen in a number of forms, whereas type-II diamond is considered to be "nitrogen-free" (probably containing less than 20 at.ppm nitrogen, which is below the detection limits of IR spectroscopy). Type-I diamond was further subdivided into type Ia and type Ib depending on the mode of occurrence or aggregation of the nitrogen within the structure. In type-Ia diamond, nitrogen is considered to be present in various aggregated forms, whereas in type-Ib diamond, nitrogen atoms are dispersed in isolated substitutional sites, such that in each structural defect, one nitrogen atom replaces one carbon atom. Synthetic diamond is mostly of Type Ib. A good overview of this subject, along with representative IR spectra for each type of diamond, is given by Scarratt & Fritsch (1992).

In type-Ia diamond, two major forms of aggregation of nitrogen are found, A and B. Depending on the predominance of A or B centers, this type of diamond is classified as type IaA and type IaB, respectively. The majority of natural crystals belong to the transitional type IaAB. According to present views, an A center refers to a pair of neighboring atoms of nitrogen substituting for carbon (Davies 1976, Sobolev 1978), and a B center implies a group of nitrogen atoms tetrahedrally arranged around a vacancy (Bursill & Glaisher 1985). Recent trends in diamond investigation have increasingly involved the use of IR spectroscopy, which provides a means of assessing the concentrations not only of nitrogen (A and B) impurity centers, but also of hydrogen (H) centers and platelets (P centers), which are most typical of kimberlite-hosted diamond (Woods 1986).

ANALYTICAL METHODS

IR absorption spectra of the diamond samples in our study were recorded using the Specord M-80 spectrophotometer (Carl Zeiss, Jena), with a beam condenser operating within the spectral range of 4000 to 400 cm^{-1} . Spectral resolution is 6–10 cm^{-1} . The relative error in the concentration of nitrogen impurity is ± 10 to 20%. Local IR analyses of diamond crystals were made with plates cut off along the [110] direction from rounded crystals (dodecahedroids), which were selected from a representative collection of Uralian samples of diamond.

In order to evaluate the concentrations of A and B nitrogen centers, we used the analytical formulae of Boyd *et al.* (1994, 1995), according to which the concentration of A + B nitrogen centers in diamond is directly proportional to IR absorption coefficient values for the spectral peak at 1282 cm^{-1} . As in most cases, natural diamond belongs to the combined IaAB type; we decided to follow the method of interpretation of spectral characteristics proposed by Mendelssohn & Milledge (1995). The relative proportions of the "platelets" (P) and the hydrogen (H) structural impurities in the diamond were estimated in this study in arbitrary units, more precisely, in absorption coefficient values measured, respectively, at 1365 and 3107 cm^{-1} .

CHARACTERISTICS OF THE DIAMOND SAMPLES

In this study, we dealt with diamond crystals from the following areas and deposits (Fig. 1, Table 1): 1) kimberlites of the Lomonosov deposits (pipes: Pomorskaya, Arkhangelskaya, Karpinsky-1 and Lomonosov), 2) kimberlites of the Terskii Bereg from the Kola Peninsula (pipe Yermakovskaya-7), 3) placers of the Northern Timan, 4) placers of the Middle Timan, 5) placers of the Northern Urals (Vishera area), and 6) placers of the Middle Urals (Koivo-Vizhai area).

In general, the number of diamond samples taken for study, to represent each of the aforementioned areas, varied from 15 to 159 crystals. The greatest quantity of diamond crystals (414, including 37 microcrystals) was selected from kimberlite pipes of the commercial Lomonosov deposit. For these pipes, we examined representative groups of diamond crystals of differing grain-size, morphology and internal structure. Among crystals exceeding 1 mm is a group of flat-faced octahedral crystals with trigonal faces and rectilinear edges (26 crystals). Diamond crystals of this type are present in very minor amounts in comparison to dodecahe-

TABLE 1. AVERAGE CONCENTRATIONS OF NITROGEN AND HYDROGEN IMPURITIES IN DIAMOND CRYSTALS FROM EAST EUROPEAN DEPOSITS

Deposit	Nitrogen, at.ppm						N _B	P	H
	#	A	σ	A	B	σ	Total	%	cm^{-1}
	ave.			mode*	ave.		ave.		
Lomonosov deposit, Arkhangelsk area									
Pomorskaya pipe	159	939	472		1300	356	331	1295	28 6.5 3.9
Arkhangelskaya pipe	39	966	363		950	326	248	1292	25 25.3 2.9
Karpinsky-1 pipe	77	698	646		500	300	221	998	30 6.1 3.4
Lomonosov pipe	102	625	507	140	(645)	202	205	827	24 19.8 2.1
All pipes, microcrystals	37	261	244		125	177	146	438	40 5.7 4.4
All pipes, octahedra with trigonal faces	26	211	268		95	120	133	331	36 3.8 1.2
Terskii Bereg, Kolskii Peninsula									
Yermakovskaya-7 pipe	31	868	870		580	386	340	1254	31 11.1 4.1
Northern Timan									
Placers	15	223	178		160	127	173	350	36 n.d. n.d.
Middle Timan									
Placers	22	383	298		250	345	340	728	47 12.3 1.3
Northern Urals									
Vishera placers	32	598	229		525	260	115	858	30 8.0 1.5
Middle Urals									
Koivo-Vizhai, popul. I	19	216	68		175	304	152	520	52 9.5 1.0
Koivo-Vizhai, popul. II	21	845	77		925	262	177	1107	23 9.1 0.4

Additional mode is shown in brackets. n.d.: not detected. #: number of samples.

droids. The +1 mm octahedra are similar in morphology to the octahedra of diamond in the -1 mm size class.

The set of diamond crystals from the Yermakovskaya-7 pipe (Terskii Bereg) consisted of 31 crystals, with approximately equal proportions of +1 mm crystals and -1+0.5 mm microcrystals. Diamond microcrystals from this pipe, like the diamond microcrystals from the Lomonosov deposit, are dominated by octahedra. However, the proportion of dodecahedroids among the Yermakovskaya-7 microcrystals is also considerable.

Data on the distribution of optically active centers in diamond from Northern Timan were partly obtained during this study, and partly taken from Klyuev *et al.* (1974, 1979) and recalculated using the method described above. With the exception of the collection of diamond crystals from Northern Timan (15 crystals), suites from the other pipes and placers included in this study are statistically representative: the proportion of different morphological varieties of diamond in these

collections agrees with corresponding parameters of the statistical distribution of habits according to the observations of Zakharchenko *et al.* (1993).

RESULTS

The Lomonosov suite

IR analyses were performed on 377 large (+1 mm) crystals and 37 microcrystals (-1 mm) of diamond from the Pomorskaya, Arkhangelskaya, Karpinsky-1 and Lomonosov pipes. The total concentration of nitrogen (N_{tot}) in the +1 mm diamond crystals varies from 10 to 2900 at.ppm, with peak values higher than 4000 at.ppm in a few crystals from the Pomorskaya pipe. Samples of nitrogen-free (*i.e.*, type-IIa) diamond are rare; most of them were found in the collection of crystals from the Lomonosov pipe, where they account for not more than 5% of the suite. Diamond crystals with the highest values of N_{tot} occur in the Pomorskaya and Arkhangelskaya pipes (Figs. 2, 3, 4). In the microcrystals, N_{tot} varies from 20 to 1300 at.ppm.

In +1 mm crystals of diamond, nitrogen defects are dominated by A centers, with the average proportion of aggregated nitrogen ($\%N_B$) generally accounting for not more than 30% of total concentration of the nitrogen impurity. The bimodal distribution of diamond crystals from the Lomonosov and Karpinsky-1 pipes, in plots of concentrations of nitrogen A centers (Fig. 4, lines 25 and 26), suggest the presence of two distinct "populations" of macrocrystals of diamond in each of these pipes. The high-nitrogen population mode in the Karpinsky-1 pipe [$N_A = 1300$ at.ppm, $\%B = 100$ $N_B/(N_A + N_B) = 13$] correlates with the main modes for diamond crystals from the Arkhangelskaya and Pomorskaya pipes (Fig. 4, lines 27 and 28). As was shown in our previous studies for the Pomorskaya and Lomonosov pipes (Blinova *et al.* 1989), "small" (-1 mm) crystals have a more uniform distribution of nitrogen impurity-centers. These crystals are characterized by lower N_{tot} values than macrocrystals and lower concentrations of A centers ($N_A \approx 260$ at.ppm) (Figs. 3, 4), and higher concentrations of aggregated nitrogen ($\%B = 40$) and hydrogen structural impurity ($H = 4.4$ cm⁻¹). Figure 5 shows that average concentrations of impurities in -1 mm crystals falls outside the field of values typical of the bulk of +1 mm diamond crystals from pipes of the Lomonosov deposit. As regards the concentration of nitrogen B centers, both small and large crystals with trigonal faces from pipes of the Lomonosov deposit are similar in N_B to crystals from the Daldyn-Alakit area in Yakutia (Fig. 4, lines 4-11).

A peculiar feature of the diamond crystals from the Lomonosov deposit, which distinguishes them from material from Yakutia and other regions, is their above-average concentration of hydrogen structural impurities (2.1-4.4 *versus* 0.2-1.9 cm⁻¹).

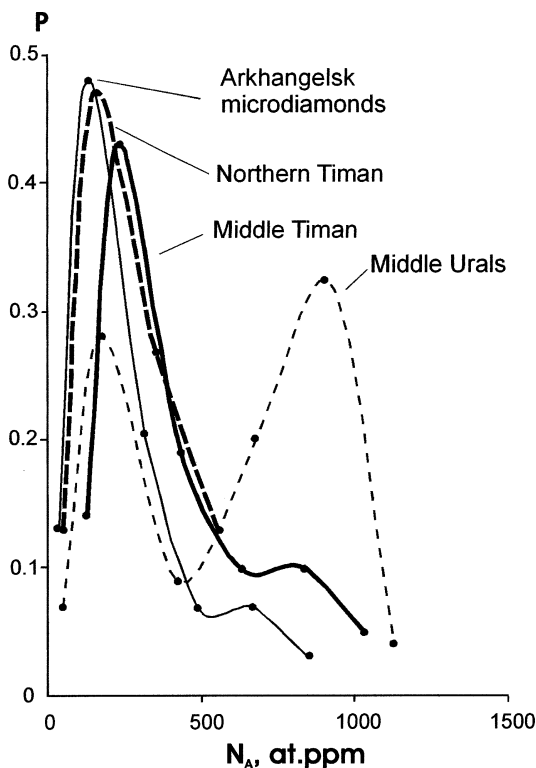


FIG. 2. Distribution of diamond crystals from kimberlite pipes of the Arkhangelsk region and Uralian placers according to the concentration of nitrogen A centers in diamond crystals. P represents the frequency of variation.

Terskii Bereg

About 60 pipe-like, dike-like and stock-like melilitites and, more rarely, mica kimberlite bodies are known in Terskii Bereg area of the Kola Peninsula. The Yermakovskaya-7 pipe included in this study is a mica kimberlite.

Both, macro- ($-2+1$ mm) and microcrystals of diamond ($-1+0.5$ mm) are found in the Yermakovskaya-7 kimberlite, the microcrystals being slightly more abundant. Morphologically, the diamond crystals are dominated by dodecahedroids and transitional habits. Diamond values of N_{tot} vary widely, attaining 4700 at.ppm. In the majority of crystals, N_A also varies quite widely, with average values between 400 and 600 at.ppm (Figs. 3, 4), with highs at 3312 at.ppm and lows of 6–46 at.ppm. B centers are present in Yermakovskaya-7 pipe diamond in minor proportions, with N_B values typically between 57 and 171 at.ppm.

A peculiar feature of Terskii Bereg crystals is their above-average concentrations of P and H centers, making them similar to diamond from Arkhangelsk. In most

of the material from the Yermakovskaya-7 pipe, the concentration of P centers varies between 1 and 28 cm^{-1} , with an average of approximately 10 cm^{-1} . The concentration of H centers attains 13–19 cm^{-1} , with average values between 2 and 4 cm^{-1} . In general, diamond from the Yermakovskaya-7 pipe is similar to +1 mm crystals from the Lomonosov deposit.

Northern Timan

In this area, diamond crystals were found in recent river alluvium, coastal-marine deposits and Devonian conglomerates as far back as the 1970s (Klyuev *et al.* 1974, 1979, Kaminsky *et al.* 1976). However, only 15 crystals have been found (and studied).

Diamond crystals greater than 1 mm across from Northern Timan are mostly dodecahedroids, whereas among the -1 mm crystals, 50% are octahedra. A feature common of diamond in both size classes is its generally lower-than-average concentration of nitrogen A centers. More than 70% of these crystals have N_A not higher than 300 at.ppm (Figs. 2, 4).

Middle Timan

We examined 22 crystals from recent alluvium and Late Devonian conglomerates from Middle Timan. Most of these crystals are +1 mm and rounded, of rhombic dodecahedral habit.

As seen from IR spectroscopy data (Fig. 3), most of the crystals, like those from Northern Timan, are characterized by a lower-than-average concentration of nitrogen in A centers, although some crystals have relatively high N_A values (up to 900 at.ppm). The modal amount of aggregated nitrogen is rather high, %B = 47 on average. The distribution of nitrogen centers at Middle Timan is similar to that in diamond crystals from the Daldyn-Alakit area in Yakutia (Figs. 4, 5).

The Urals

Along the western slope of the Urals, the largest diamondiferous placers occur in the Vishera area (Northern Urals) and in the Koivo-Vizhai area (Middle Urals). The latter-mentioned placers are now mined out. Most of the Uralian samples are fine- and crypto-lamellar crystals with convex faces (dodecahedroids), many of them being perfectly pure and clear. The Northern Urals crystals differ from those the Middle Urals in weight, crystal habit, surface features, coloration and UV luminescence characteristics (Gnevushev & Shemanina 1967).

According to our data, the Northern Urals diamond crystals and the Middle Urals ones differ in their nitrogen concentration as well. In particular, the average total concentration of nitrogen impurity (N_{tot}) for Northern Urals diamond is 858 at.ppm, whereas among the Middle Urals suite, there are two distinct "populations"

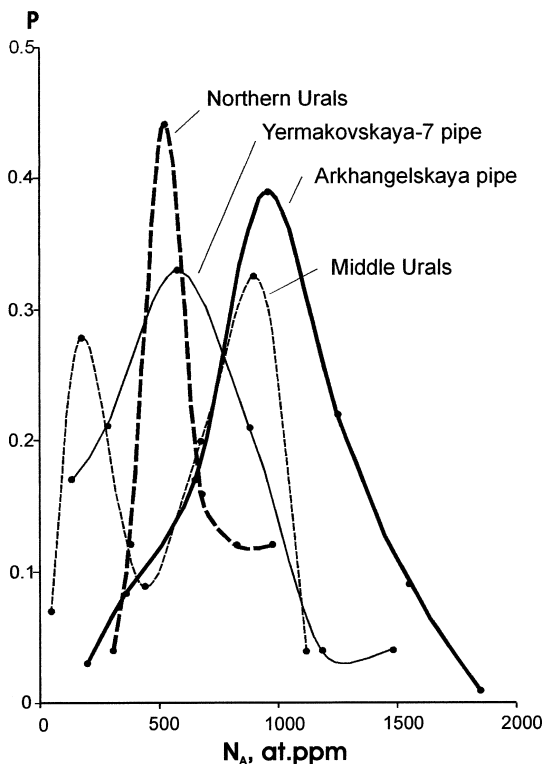


FIG. 3. Distribution of diamond crystals from Timan and Middle Urals placers to the concentration of nitrogen A centers in diamond crystals. P is defined as the frequency of variation.

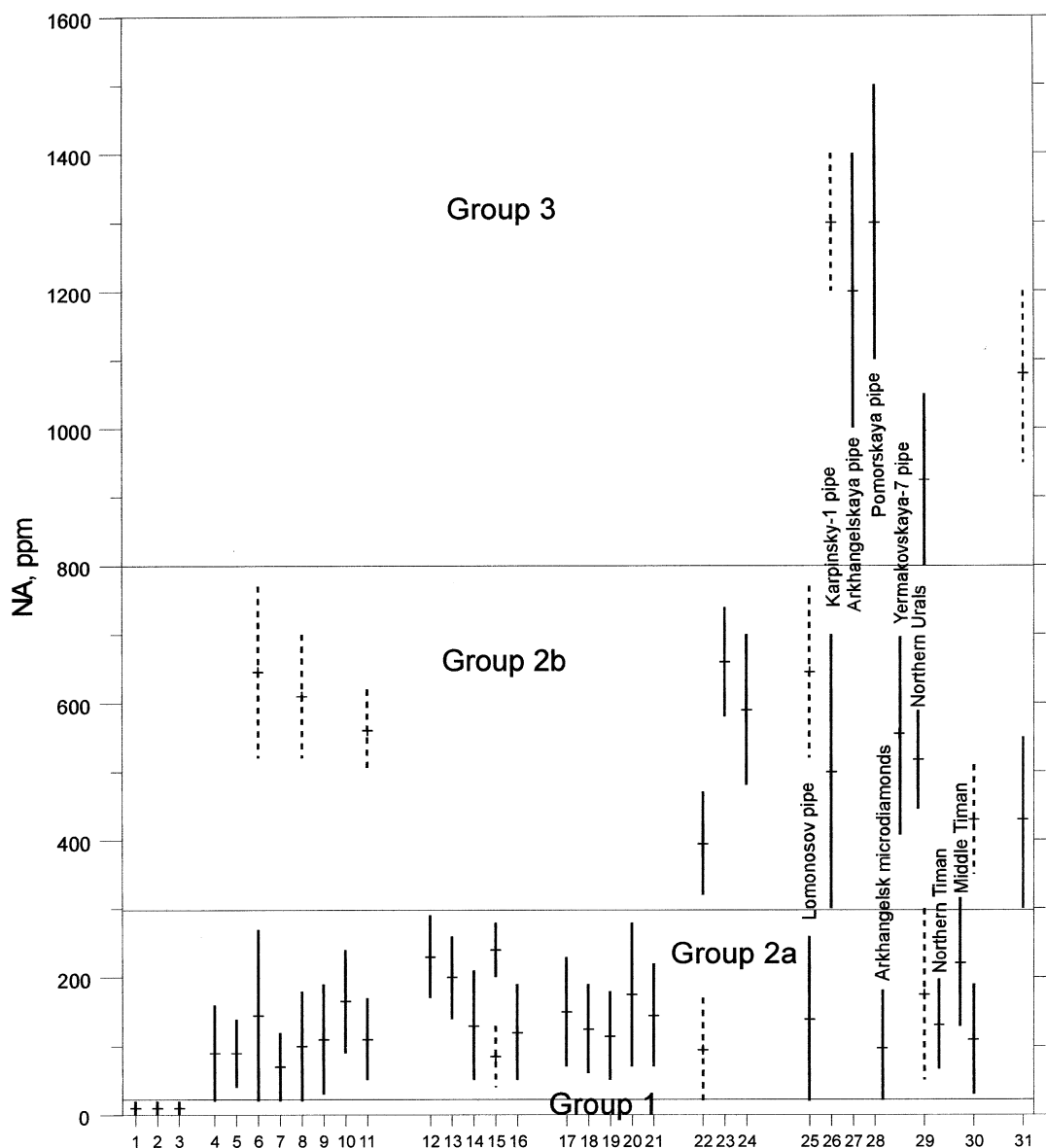


FIG. 4. Groupings of diamond crystals from East European platform deposits based on concentration of nitrogen A centers, taking into account data from Kaminsky & Khachatryan (2001). Brazil, Juina area: 1: Rio Sao Luis ($n = 31$), 2: Rio Vermelho ($n = 33$), 3: Cor. Chicoria ($n = 34$). Daldyn-Alakit area of Yakutia: 4: Prognoznaja ($n = 40$), 5: Aykhal ($n = 35$), 6: Zarnitsa ($n = 36$), 7: Dalnyaya ($n = 35$), 8: Sytkanskaya ($n = 32$), 9: Krasnopresnenskaya ($n = 43$), 10: Komsomolskaya ($n = 39$), 11: Udachnaya ($n = 39$). Coromandel area in Brazil: 12: Grota do Pimpim ($n = 31$), 13: Cor. Sto. Antonio, Cor. Espirito Santo, Cor. Charcao ($n = 32$), 14: Cor. Imbe ($n = 31$), 15: Cor. Da Criminosa ($n = 32$). Venezuela: 16: Kimberlite sills ($n = 47$), 17: Quebrada Grande ($n = 35$), 18: Centella ($n = 36$), 19: Chihuahua ($n = 30$), 20: Ringi-Ringi ($n = 30$), 21: Guaniamito ($n = 38$). Malo-Botuobiya area in Yakutia: 22: Sputnik ($n = 34$), 23: the XXIII Congress CPSU ($n = 62$), 24: International ($n = 57$). Arkhangelsk area: 25: Lomonosov pipe ($n = 102$), 26: Karpinsky-1 ($n = 77$), 27: Arkhangelskaya ($n = 39$), 28: Pomorskaya ($n = 159$), 29: Middle Urals placers ($n = 55$), 30: Pipe DO-27, Canada ($n = 201$). 31: Northeastern Yakutia, Triassic placers ($n = 43$). Solid lines: main modes, dotted lines: additional modes.

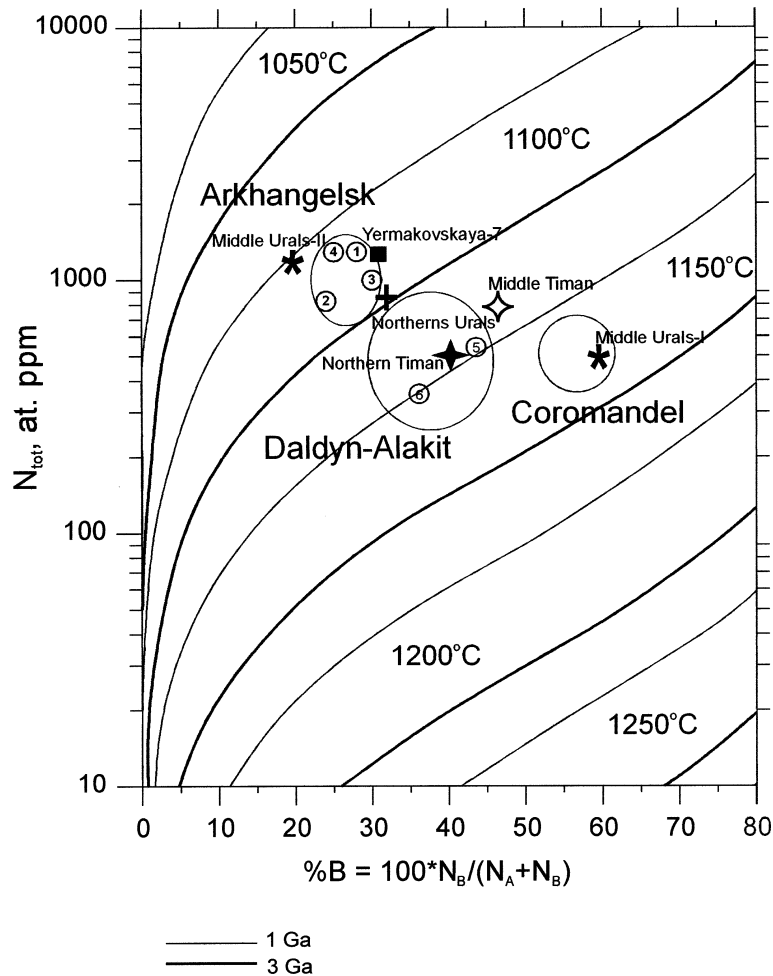


FIG. 5. Average temperatures of formation for crystals of diamond from different locations. Circles outline the Arkhangelsk, the Daldyn-Alakit and the Coromandel areas; some locations are numbered: 1: Pomorskaya pipe, 2: Lomonosov pipe, 3: Karpinsky-1 pipe, 4: Arkhangelskaya pipe, 5: microcrystals of diamond from all pipes, 6: large octahedra with trigonal faces from all pipes. Isotherm curves for 1 and 3 Ga after Taylor & Milledge (1995).

of crystals: (I) low-nitrogen diamond, and (II) high-nitrogen diamond (with average N_{tot} values of 520 and 1108 at.ppm, respectively). The concentration of nitrogen A centers in the first population varies from 20 to 350 at.ppm, whereas for the second population, N_A is between 650 and 1000 at.ppm (Figs. 3, 4, Table 1).

The two populations significantly differ from each other in the amount of B nitrogen center: 52% for population I and 23% for population II (Table 1). Average concentrations of H centers also differ: 1.5 cm^{-1} for diamond from the Northern Urals, 1.0 cm^{-1} for population-I diamond of the Middle Urals, and 0.4 cm^{-1} for

population II (Table 1). On the basis of these characteristics, placer diamond crystals of the Northern Urals and population-II diamond crystals of the Middle Urals are similar to diamond crystals from the Lomonosov deposit kimberlites, whereas population-I crystals from Middle Uralian placers are similar to placer diamond crystals from the Coromandel area in Brazil (Figs. 2, 4, 5).

In order to examine the correlation between the characteristics of nitrogen impurity centers and structural features of diamond crystals, we thoroughly studied the distribution of optically active centers in diamond plates cut from seven dodecahedroids from the Northern Urals.

These seven crystals were selected as typical representatives from several hundred diamond crystals from the Northern Uralian placers. The internal structure of the crystals was previously studied by Gurkina (1980) using the method of anomalous birefringence and X-ray topography after Lang (1965).

Among the analyzed samples were representatives of the following varieties of diamond (Fig. 6): 1) crystals with layer-by-layer step-like octahedral zoning (samples #49 and #5; Figs. 6A, B); 2) crystals with sectorial structure of almost the entire volume of the crystal (samples #1 and #2; Figs. 6C, D); 3) crystals with sectorial-zonal structures consisting of a cubo-octahedral core (up to 20% of the crystal volume) and octahedrally zonal marginal areas (samples #36, #35 and #4; Figs. 6E, F, G). During the final stage of evolution, each of the diamond crystals, regardless of its internal structure, was transformed into a rounded dodecahedral crystal as a result of resorption.

Results of the local IR analysis of zonal diamond crystals from the Northern Urals are presented in Table 2. Diamond crystals with octahedral zoning (samples #49 and #5) have the lowest nitrogen contents and a rather uniform distribution of nitrogen in the volume of a crystal. In contrast, samples with sectorial and zonal-sectorial structures show differences of the nitrogen content in different areas of a crystal. This subject is discussed in detail in the following section.

DISCUSSION

Temperatures and stages of diamond formation

As can be seen from Figures 2, 3 and 4, the diamond crystals examined fall into two distinct groups on the basis of concentration of nitrogen A centers: 1) Diamond crystals from the kimberlite pipes Lomonosov, Karpinsky-1 (low-nitrogen population), Yermakovskiy-7, all small (~1 mm) diamond crystals and octahedral crystals with trigonal faces from the Lomonosov deposit, diamond crystals from placers of Northern and Middle Timan, and population-I diamond crystals from Middle Uralian placers (Fig. 4); all these occurrences belong to Group-2 medium-nitrogen diamond identified in Kaminsky & Khachatryan (2001). 2) Large crystals of diamond from the pipes Pomorskaya, Arkhangelskaya and Karpinsky-1 (high-nitrogen population), and population-II diamond crystals of the Middle Urals; these crystals belong to Group-3 high-nitrogen diamond identified in Kaminsky & Khachatryan (2001). Most of the large crystals from the Lomonosov deposit differ from diamond from Timan and Uralian placers in having relatively high concentrations of hydrogen and low modal abundances of aggregated nitrogen (B centers).

These nitrogen peculiarities relate to specific internal structural features of these diamond crystals, which reflect the multistage character of their formation. Diamond crystals of the Lomonosov deposit are character-

ized by a higher-than-average proportion of crystals with normal or combined mechanisms of growth. Flat-faced octahedral macrocrystals are quite rare (Zakharchenko *et al.* 1993). In contrast, Uralian crystals, according to data reported in Genshaft *et al.* (1977), Gurkina (1980) and Beskrovanov (1992), are characterized by octahedral zoning resulting in the tangential mechanism of growth.

The diagram proposed by Taylor & Milledge (1995) allows us to estimate the temperatures of formation of all diamond crystals from the deposits included in this study. We assume that the "mantle residence time" is the same in all cases, and we have taken a conservative figure of about 3.0 Ga. According to this estimate, the formation of diamond macrocrystals from pipes of the Lomonosov deposit took place in the range 1080–1090°C, and that of diamond microcrystals, at approximately 1125°C, *i.e.*, almost 40°C higher (Fig. 5). However, these observed differences, for octahedral microcrystals and macrocrystals of diamond with trigonal faces and large dodecahedroids, may be related to kinetic factors. In some cases, the degree of nitrogen aggregation (% N_B) may disagree with actual values of temperature of crystallization. This issue is treated below in greater detail.

Nearly identical temperatures of formation (approximately 1200°C) were obtained for diamond from placers of Northern and Middle Timan (Fig. 5). Estimated temperatures of formation of diamond from the Northern and Middle Urals (population II) are close to those of diamond crystals from pipes of the Lomonosov deposit, and diamond crystals from the Daldyn-Alakit area in Yakutia. Middle Uralian diamond crystals of population I are similar in this respect to diamond crystals from the Coromandel area in Brazil (Fig. 5).

Distribution of nitrogen centers in zoned crystals and the problem of thermometry of "non-equilibrium" diamond

Most of the crystals studied were analyzed as a single entity, such that data on concentrations of nitrogen impurity were integral, characterizing the average amount of optically active centers in the whole crystal. However, it is well known that crystals with zonal and zonal-sectorial internal structures are common (*e.g.*, Takagi & Lang 1964, Orlov 1963, Gurkina & Miuskov 1971, Lang 1974, Milledge *et al.* 1989).

More than an order-of-magnitude variation in nitrogen concentrations and in degree of nitrogen aggregation in diamond crystals has repeatedly been observed (Klyuev *et al.* 1969, Sobolev 1974, 1978, Suzuki & Lang 1976, Taylor *et al.* 1995a, b, Davies *et al.* 1999, Hauri *et al.* 1999). In general, those investigators related such differences to variations in nitrogen and carbon isotope composition. In our opinion, variations of nitrogen content and its aggregation are related to internal structural features of the crystals.

tent of hydrogen, with maximum concentrations usually confined to central zones of the crystal (Orlov *et al.* 1978, Bokii *et al.* 1986, Plotnikova & Klyuev 1986, Blinova 1987).

As can be seen from Table 2, diamond crystals with octahedral zoning (samples #49 and #5) are characterized by the lowest nitrogen contents, and have a rather uniform distribution of %N_B, N_{tot} and hydrogen. A determination of temperature of formation using the method proposed in Taylor & Milledge (1995) reveals no difference between the core and the marginal zones in these crystals (Table 2, Fig. 6).

In contrast, samples with sectorial and zonal-sectorial structures demonstrate a paradoxical relationship between temperatures of formation for the central and marginal zones of the crystals. For these cases, the temperature of formation calculated for the core is 15–50°C lower than that estimated for the marginal zones of these crystals. It is a small difference, but it demonstrates an obvious trend of increasing temperature of formation from the core to the rim. However, even provided that the temperature of the environment may have increased during the latter stages of growth, the temperature of formation of the outermost zone of a crystal plays an important role in imposing an annealing temperature for all the internal zones of this crystal. Hence, the temperature of formation of the outer (marginal) zone cannot be higher than that of the internal zones of the same crystal, as appears to be the case in samples #35, #4, #1 and #2 (Table 2).

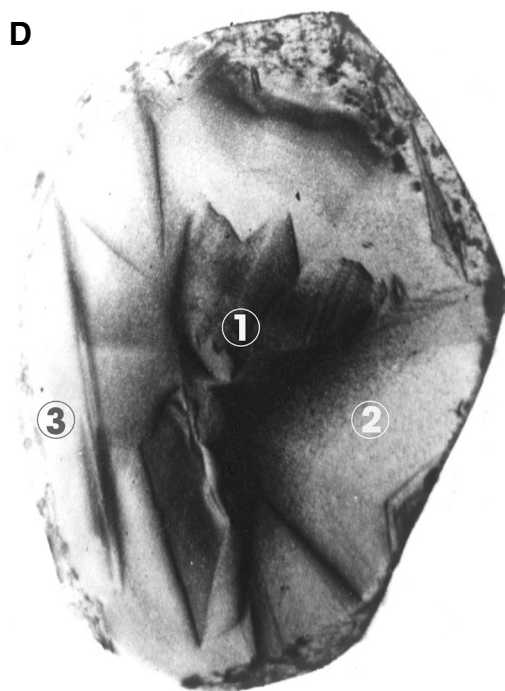
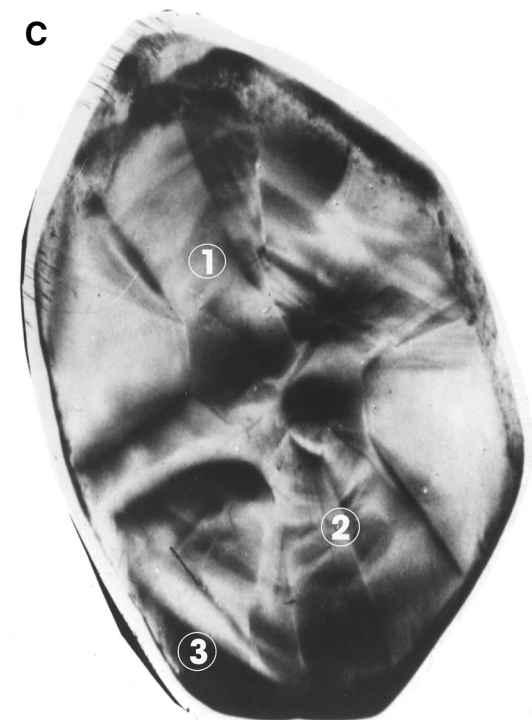
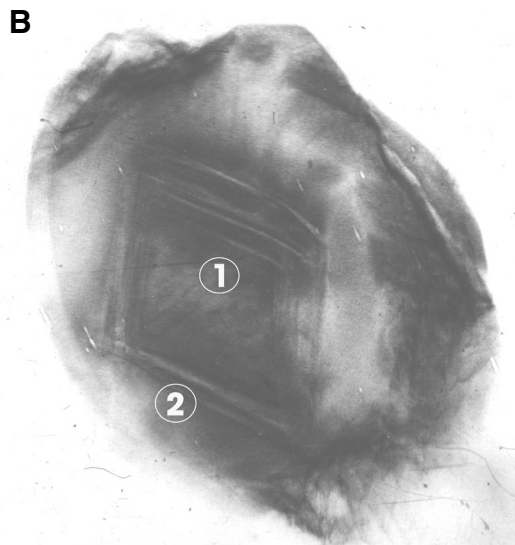
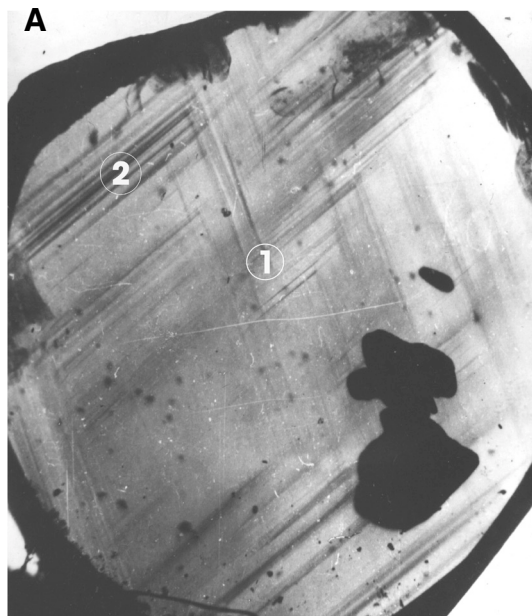
In our opinion, the distribution of nitrogen centers in crystals with layer-by-layer octahedral (tangential) zoning, which reflects slow crystallization under sub-equilibrium conditions, can also be considered as an equilibrium, reflecting an actual dependence on temperature of formation. Unlike crystals of this sort, those

No.		Center					Internal zone										Marginal zone				
							<111>					<100>, <hht>									
Sam-ple	Area *	N _{tot} ppm	N _B %	H cm ⁻¹	T °C	Area *	N _{tot} ppm	N _B %	H cm ⁻¹	T °C	Area *	N _{tot} ppm	N _B %	H cm ⁻¹	T °C	Area *	N _{tot} ppm	N _B %	H cm ⁻¹	T °C	
1	49	A-1	368	38	0.6	1125											A-2	340	38	0.5	1125
2	5	B-1	507	41	1.6	1125											B-2	549	42	1.2	1125
3	1						C-1	1549	25	0.5	1075	C-2	1582	21	0.9	1070	C-3	886	42	0.2	1110
4	2	D-1	1040	18	4.7	1075						D-2	658	20	9.4	1090	D-3	222	26	0.9	1125
5	36	E-1	473	37	4.1	1120											E-2	n.d.	n.d.	2.7	n.d.
6	35	F-1	563	30	2.0	1105											F-2	485	15	0.5	1090
7	4						G-1	1103	52	10.9	1115	G-2	1088	50	14.9	1110	G-3	451	41	0.9	1125

* See areas in Figure 6.

with predominantly normal or combined mechanism of growth are characterized by a high rate of crystallization, probably higher than the rate of aggregation of nitrogen atoms. The zonal distribution of nitrogen

impurities indicates that the aggregation of nitrogen may have occurred (at least partly) in the course of diamond crystallization.



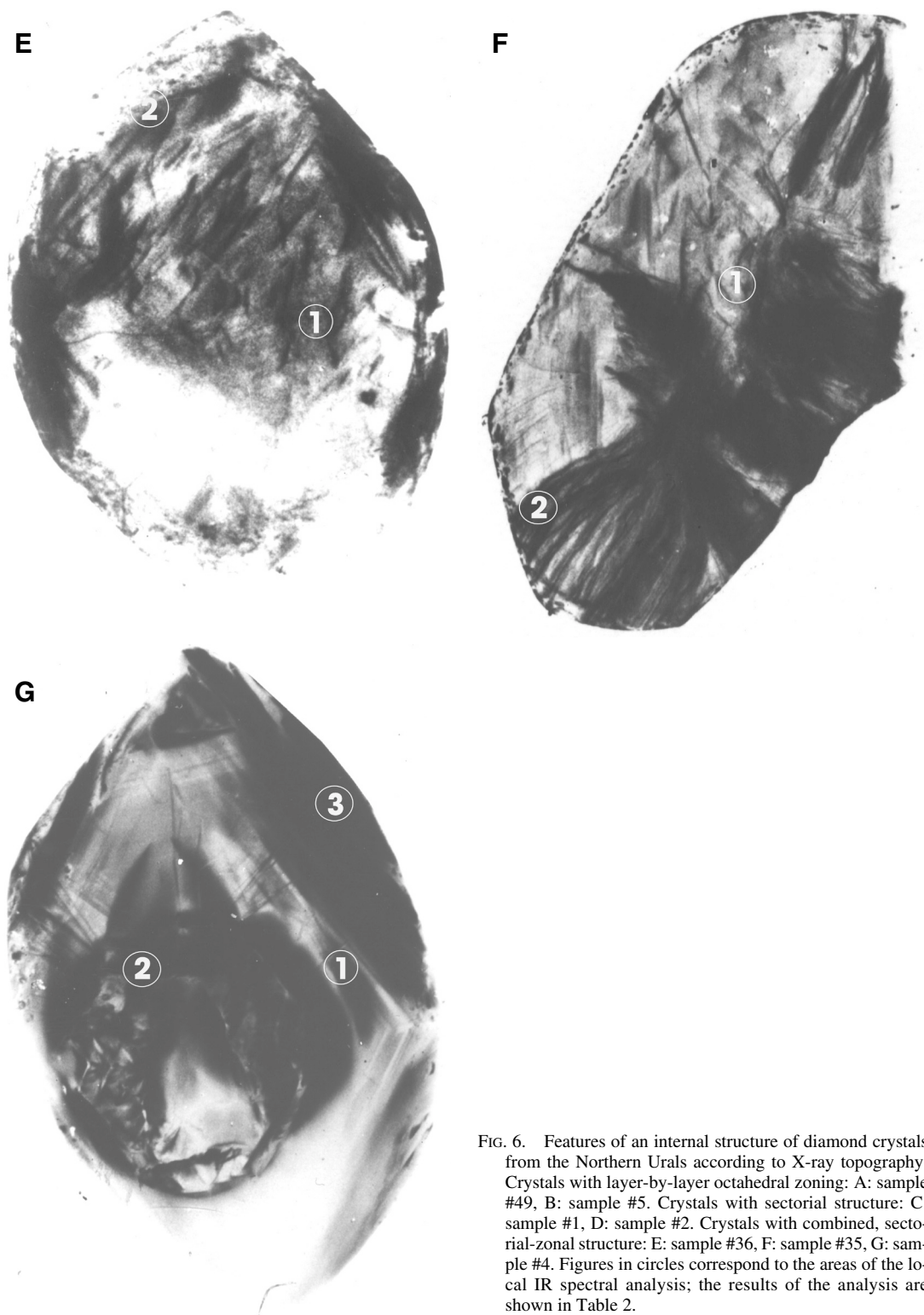


FIG. 6. Features of an internal structure of diamond crystals from the Northern Urals according to X-ray topography. Crystals with layer-by-layer octahedral zoning: A: sample #49, B: sample #5. Crystals with sectorial structure: C: sample #1, D: sample #2. Crystals with combined, sectorial-zonal structure: E: sample #36, F: sample #35, G: sample #4. Figures in circles correspond to the areas of the local IR spectral analysis; the results of the analysis are shown in Table 2.

As a result, for the cases of predominantly normal or combined mechanism of growth, we obtain non-equilibrium, *i.e.*, lower than actual modal amounts of nitrogen B centers and, respectively, lower than realistic values of temperature of formation. In general, the influence of kinetic factors on the constitutional characteristics of a mineral during the process of formation is significant. For example, with feldspars, albite in low-temperature, hydrothermal-metasomatic rocks is represented by its completely disordered, "high-temperature" modifications (Rusinov 1965). High albite forms as a result of metastable crystallization within the stability field of the low-temperature polymorph (low albite), with a rate of crystallization significantly higher than the rate of structural ordering.

To summarize, temperature values determined by IR spectroscopy are only realistic values for those crystals that grew under equilibrium conditions. For crystals with normal and combined mechanisms of growth, temperature values calculated from IR data may be unrealistic, as they also depend on the kinetics of the crystallization process.

The problem of thermometry for "small" crystals of diamond

Taking into account the above discussions and limitations on thermometry of "non-equilibrium" crystals of diamond, it should be noted that our previous assumption regarding the sequence of formation of diamond crystals from the Arkhangelsk region (Kaminsky & Khachatryan 2001) should be interpreted as being tentative. We have deduced, from the distribution of nitrogen centers in diamond crystals, that temperatures of formation of microcrystals of diamond from the Lomonosov deposit are higher than those of macrocrystals (+1 mm) from the same deposit. This view is contrary to the opinion of some other investigators, as deduced from the results of detailed examination of crystal morphology (*cf.* Garanin & Posukhova 1995).

As was noted above, many of the +1 mm dodecahedrons formed through combined and normal mechanisms of growth. Therefore, the temperature of formation calculated from IR data may be lower than real, in contrast to those temperatures determined for octahedral macro- and microcrystals. There is no doubt that this problem warrants further investigation, which must include detailed examination of both the internal structure and the composition of mineral inclusions in microcrystals of diamond at Arkhangelsk.

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