ISSN 2078-6220. Мінералогічний збірник. 2015. № 65. Випуск 1. С. 41–52
Mineralogical Review. 2015. N 65. Issue 1. P. 41–52

UDC 552.323.6

POSTMAGMATIC FACTORS OF KIMBERLITES DIAMOND CONTENT

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The results of comparative analysis of data about kimberlite composition and kimberlites' diamond potential are presented. The quantity and size of diamond crystals associate with grade of kimberlite postmagmatic transformations. The model of diamond hydrothermal-metasomatic dissolution or recrystallization is proposed.

Key words: kimberlite, diamond, normative quartz, postmagmatic transformations, hydrothermal-metasomatic dissolution, recrystallization.

This article follows the studies of diamond potential factors of kimberlites started in our previous papers (see Mineralogical Review. 2014. N 64. Is. 1, 2). Most of geologists and mineralogists interpret the terms “diamond” and “armor” as synonyms. According to their opinion, a diamond armours the inclusions of mineral forming medium and delivers them to us in a state of nature. The subject matter experts dealing with diamonds have a thorough knowledge of the fact that diamonds undergo disintegration and recrystallization at the magmatic stage. Aim of this work is to demonstrate that the processes of diamond interaction with the enclosing rocks go on at the post-magmatic stage of kimberlite formation.

Secondary changes of kimberlite bodies under the near-surface conditions were previously characterized in the papers of E. Shamshina [23] and N. Zinchuk et al. [4, 6, 11]. V. Vasilenko et al. focused their attention on the changes of kimberlites in deep-seated parts of the pipes due to the influence of post-magmatic hydrothermal solutions [2, 3, 9, 17–19].

It is critical to emphasize that E. Shamshina [23] defined the most important petrochemical trend of post-magmatic change in the kimberlites – reverse correlation of SiO_2 and MgO – for the first time. In her opinion, accumulation of SiO_2 and loss MgO took place over the whole period of kimberlites hydration. The relation of SiO_2 to MgO indicates the rate of secondary change in kimberlites. This feature in the petrochemical interpretation is expressed as a well-defined negative dependence between MgO and excess silicic acid. The amount of excess silicic acid (defined as normative secondary quartz Q) has been calculated by formula

$$Q = SiO_2 - 0.81\ MgO - 2.8\ K_2O\ [9].$$

Based on the empirical distribution of Q, the following groups of altered rocks can be distinguished: dolomitized rocks ($Q < 1.0$ %); unaltered rocks ($1.0\ \% < Q < 4.0$ %); quartz con-

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taining (4.0 % > Q < 12.0 %) and quartzous rocks (Q > 12.0 %) in the general aggregate of compositions of the Yakut province kimberlites [12].

Let us present the mean compositions of the pipes separated by the rate of rock change (Table 1) using the mean compositions of the Yakut kimberlites (see [25]) in relation to the levels of post-magmatic changes in kimberlites presented above.

Table 1

Mean compositions of unaltered, quartz containing and quartzous kimberlites of the Yakut diamond deposits

Components	Kimberlites-I, pipes					
	Aykhal			Udachnaya-West		
	U*	QC	Q	U	QC	Q
SiO_2	23.84** 5.04	26.01 4.06	36.31 7.71	25.36 3.66	26.57 3.72	20.37 10.38
TiO_2	0.42 0.15	0.43 0.17	0.32 0.14	0.89 0.28	0.80 0.23	0.73 0.274
Al_2O_3	2.29 0.82	2.66 1.43	4.49 2.83	2.28 0.49	2.39 0.58	3.76 4.20
Fe_2O_3	4.50 1.35	4.63 1.36	3.64 1.90	6.27 2.19	5.83 1.93	2.87 1.742
MgO	24.15 6.15	21.89 5.78	15.89 5.92	26.02 4.69	23.91 5.47	24.28 9.14
CaO	16.30 8.29	17.55 6.44	14.92 8.07	15.10 5.40	15.70 5.77	9.55 6.99
Na_2O	0.18 0.21	0.12 0.18	0.19 0.13	0.80 0.27	0.17 0.16	0.37 0.58
K_2O	0.95 0.62	0.80 0.38	1.06 0.25	0.65 0.35	0.71 0.47	1.29 1.30
P_2O_5	0.69 0.29	0.88 0.22	1.07 0.24	0.31 0.16	0.27 0.15	0.34 0.174
|LOI	27.46 5.52	25.42 4.39	27.03 6.86	23.16 4.15	23.80 4.55	26.26 7.74
n	113	91	7	488	432	24

Components	Kimberlites-I, pipes					
	Udachnaya-East			Yubileynaya		
	U	QC	Q	U	QC	Q
SiO_2	25.87 2.82	27.39 3.58	31.38 9.98	28.17 3.73	28.97 4.77	42.62 13.35
TiO_2	1.17 0.41	1.09 0.40	1.11 0.57	1.07 0.33	0.95 0.37	0.87 1.74
Al_2O_3	2.10 0.43	2.33 0.86	6.78 6.44	1.68 0.55	2.09 0.90	3.52 1.74
Fe_2O_3	7.10 1.69	69.35 1.90	9.00 9.55	7.53 1.78	6.79 1.65	6.99 2.51
MgO	27.99 3.83	24.75 5.46	17.57 11.08	30.07 4.90	26.24 6.46	18.44 7.32

* Here and below the type of kimberlite: U – unaltered, QC – quartz containing, Q – quartzous.

** Here and below the average value is in the numerator and the standard deviation – in the denominator.

Continuation of Table 1

Components	Kimberlites-I, pipes					
	Udachnaya-East			Yubileynaya		
	U	QC	Q	U	QC	Q
CaO	13.38 4.33	14.89 6.04	10.78 4.67	9.39 6.01	13.24 7.58	8.25 8.56
Na_2O	0.28 0.47	0.18 0.36	0.84 1.02	0.09 0.09	0.09 0.10	0.34 0.49
K_2O	0.57 0.30	0.65 0.50	1.48 0.88	0.28 0.21	0.34 0.28	0.62 0.60
P_2O_5	0.32 0.15	0.354 0.16	0.42 0.26	0.41 0.15	0.36 0.15	0.26 0.24
|LOI	21.40 3.48	22.23 4.14	17.70 11.20	20.54 3.17	21.20 4.41	17.99 5.79
n	470	122	10	346	554	111

Components	Kimberlites-I, pipes			Kimberlites-II, pipes		
	Syktykanskaya			Botuobinskaya		
	U	QC	Q	U	QC	Q
SiO_2	28.28 3.90	28.83 3.35	31.40 7.73	27.12 5.39	30.13 3.65	47.49 16.07
TiO_2	1.81 0.50	1.77 0.48	1.44 0.57	0.52 0.16	0.40 0.13	0.69 0.35
Al_2O_3	1.83 0.63	1.87 0.79	2.54 1.92	3.36 0.72	3.65 0.77	9.70 5.68
Fe_2O_3	9.07 3.17	7.94 2.14	10.93 11.90	5.78 3.36	5.29 1.11	7.14 4.89
MgO	31.12 5.22	26.89 5.02	17.43 6.67	26.24 7.22	24.14 5.26	7.59 7.86
CaO	7.60 6.75	12.04 5.75	14.73 6.04	13.22 7.30	14.00 5.20	9.59 10.76
Na_2O	0.10 0.05	0.11 0.08	0.13 0.03	0.01 0.01	0.01 0.02	0.00 –
K_2O	0.26 0.15	0.20 0.19	0.32 0.60	1.13 0.51	1.19 0.52	1.85 1.51
P_2O_5	0.27 0.11	0.24 0.19	0.22 0.12	0.54 0.16	0.44 0.12	0.24 0.22
|LOI	25.56 10.40	29.41 8.29	32.44 10.08	21.96 6.43	20.81 3.79	15.38 8.36
n	102	395	21	104	831	36

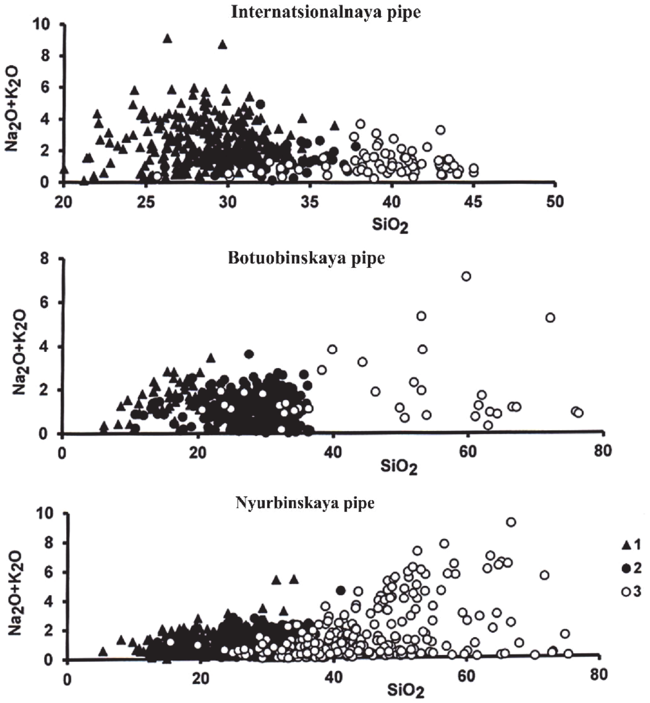
Components	Kimberlites-II, pipes					
	Internatsionalnaya			Mir		
	U	QC	Q	U	QC	Q
SiO_2	29.53 2.36	33.51 1.91	39.10 3.93	27.80 2.97	32.53 2.83	37.18 2.91
TiO_2	0.41 0.13	0.40 0.06	0.42 0.20	1.68 0.53	1.42 0.45	1.08 0.43

The end of Table 1

Components	Kimberlites-I, pipes					
	Udachnaya-East			Yubileynaya		
	U	QC	Q	U	QC	Q
Al_2O_3	2.53 0.90	2.77 0.98	3.77 1.28	2.08 0.57	2.41 0.71	3.15 1.40
Fe_2O_3	6.00 1.48	6.26 1.13	5.63 0.99	8.98 1.74	17.29 0.09	7.64 1.38
MgO	30.75 2.22	28.45 1.89	22.88 3.34	28.29 3.55	27.18 3.15	24.18 3.61
CaO	6.19 2.49	7.30 2.79	9.57 4.45	10.51 4.77	8.16 3.25	7.86 3.01
Na_2O	1.48 1.28	0.85 1.05	0.37 0.47	0.26 0.39	0.23 0.43	0.50 1.05
K_2O	1.02 0.51	0.97 0.43	0.85 0.40	0.90 0.50	0.61 0.51	0.80 0.62
P_2O_5	0.41 0.13	0.43 0.14	0.33 0.16	0.55 0.20	0.32 0.14	0.26 0.09
|LOI	21.34 2.87	20.51 2.35	17.75 3.60	19.13 3.09	17.81 2.62	17.29 0.09
n	237	31	87	104	453	147

Components	Kimberlites-II, pipes					
	Nyurbinskaya			Maiskaya		
	U	QC	Q	U	QC	Q
SiO_2	23.11 4.51	29.54 5.63	44.90 11.03	19.97 5.65	28.72 4.87	34.10 9.71
TiO_2	0.42 0.26	0.43 0.15	0.82 0.59	0.33 0.13	0.39 0.10	0.43 0.27
Al_2O_3	3.79 1.02	3.79 0.73	8.84 5.53	3.68 1.21	3.69 1.12	6.75 4.45
Fe_2O_3	4.97 1.80	6.04 1.58	8.88 4.66	3.10 1.49	5.24 2.11	6.48 5.72
MgO	21.52 4.00	24.31 5.02	14.21 7.24	16.15 7.28	22.31 7.09	13.40 6.61
CaO	17.48 5.52	13.25 5.97	6.81 5.94	24.67 9.01	15.89 7.13	14.32 8.50
Na_2O	0.01 0.01	0.01 0.05	0.37 0.77	0.09 0.14	0.10 0.17	0.03 0.06
K_2O	1.20 0.85	0.93 0.69	1.24 1.22	1.48 0.81	1.09 0.80	1.53 1.09
P_2O_5	0.49 0.22	0.47 0.18	0.39 0.59	0.45 0.14	0.46 0.14	0.32 0.17
|LOI	27.03 4.78	21.25 5.38	13.45 6.82	29.55 5.34	22.17 5.52	21.62 6.85
n	124	552	271	14	117	18

Table 1 presented clearly distinguishes the main feature of post-magmatically altered rocks – an increase of the silicic acid content in rocks and a reduction of MgO with growth of the rate of the post-magmatic change. In most cases, this process is accompanied by the increase of Al_2O_3 and K_2O contents in the changed rocks and the reduction of TiO_2, CaO and P_2O_5 contents. The gross increase of alkaline amount in quartzous kimberlites demonstrates the distributions of alkaline amount contents in single analyses quite effectively (see Figure). An increase in the alkalinity of altered rocks calls attention, which enables to consider the origin of averaged alkaline character of these rocks due to the secondary processes. An increase in the alkaline amount contents of Internatsionalnaya pipe seems perceived, since the changed kimberlites of this pipe are enriched with Na_2O due to evaporates of enclosing carbonate thicknesses.



Distribution of imaging points of alkaline amount contents and silicic acid of single analyses of kimberlite pipe rocks:
1 – unaltered; *2* – quartz containing; *3* – quartzous kimberlites.

The processes of secondary change in diamond field kimberlites also affect their diamond potential (Table 2).

In moderately alkaline kimberlites–I, the diamond potential of rocks reduces, as the rate of the secondary change increases. In a number of pipes (group A) of more alkaline kimberlites – II, the diamond potential reduces in the same way, and in other pipes (group B) it increases gradually.

The process of diamond potential increase in the changed kimberlites can be characterized with more detail by the data on fractional composition of diamonds from the pipes of Nakyn field being changed by the secondary processes to the greater extent. Let us elaborate the features of obtaining the initial data on fractional composition of core sampling intervals of the drill holes.

Table 2

Diamond potential of unaltered and altered kimberlites

Pipe	Type of kimberlite						The percentage of altered rocks*
	Unaltered		Quartz containing		Quartzous		
	n	*D*, car/t	*n*	*D*, car/t	*n*	*D*, car/t	
Kimberlite-I							
Aykhal	55	4.54 2.36	22	3.64 2.57	2	1.85 0.35	46.4
Udachnaya-West	44	1.53 3.48	21	0.93 0.87	–	–	48.9
Udachnaya-East	106	0.71 0.66	10	0.53 0.42	2	0.56 0.47	21.9
Yubileynaya	59	0.53 0.37	135	0.37 0.93	7	0.17 0.22	65.8
Syktykanskaya	66	0.56 0.61	195	0.26 1.39	12	0.23 0.20	80.3
Kimberlite-II, group A							
Botuobinskaya	10	8.59 9.24	406	7.51 6.26	15	3.87 3.82	89.3
Internatsionalnaya	64	4.33 2.36	16	4.29 2.28	31	3.42 2.53	33.3
Kimberlite body-II, group B							
Mir	53	2.02 1.93	108	1.96 1.36	16	2.60 1.31	85.2
Nyurbinskaya	28	5.55 3.61	249	6.99 4.68	80	7.98 6.05	78.6
Maiskaya	8	4.51 5.89	42	8.08 4.77	10	7.81 8.13	90.6

* Ratio of unaltered and altered rocks in the samples of Table 1.

For example, there is such fractional composition of diamonds from one of the sampling intervals of one pipe (depth interval – 221.4–228.0 m; sample weight – 82.1 kg; *D* – 18.12 car/t):

–8+4 mm: pcs – 1, fraction weight – 126.7 mg;

–4+2 mm: 1 and 51.3;

–2+1 mm: 14 and 62.3;

–1.0+0.5 mm: 77 and 53.9.

The data presented, if required, can be used for calculating the average crystal weight in each fraction. Using the descriptions from Table 2, it is possible to trace the trends of change in the grains of average size both in the unaltered and in altered (with various Q) to different extent kimberlites (Table 3) for 431 rock sampling intervals of Botuobinskaya pipe, 356 – of Nyurbinskaya pipe and 60 – of Maiskaya pipe.

The average grain sizes of a number of fractions change in the direction from the unaltered rocks to the changed ones in a different way. For example, in fractions –8+4 and –4+2 mm of Botuobinskaya pipe the grain sizes reduce, as the rate of rock change increases. Similarly, in the Nyurbinskaya pipe, the average grain sizes increase in two largest fractions and reduce in two finest ones. In the Maiskaya pipe, on the contrary, the fractions –4+2 and –2+1 mm are counter-conjugated. These trends remind the interrelations of large and fine fractions of one mineral in a metasomatic process. D. Korzhynskiy remarked that "Growth of extra large crystals takes place under the opposite conditions – in dissolution and subtraction of the components of this mineral, which is possible both in the diffusion and infiltration metasomatism. As concentration of components in the solution reduces fine grains of this mineral would dissolve…, the largest and more perfect crystals would grow" [7].

Table 3

The average value and the standard deviation of diamond grains in relation to fraction size in unaltered and altered kimberlites

Pipes and type of kimberlite		Fractions, mm							
		–8+4		–4+2		–2+1		–1.0+0.5	
		n	Grain weight	*n*	Grain weight	*n*	Grain weight	*n*	Grain weight
Botuobinskaya	U	4	434 507	37	34.6 21.5	60	4.30 0.57	60	0.75 0.12
	CQ	29	242 136	291	34.5 16.4	395	5.00 1.73	400	0.80 0.13
	Q	–	–	7	30.9 12.6	11	4.80 1.11	15	1.21 1.26
Nyurbinskaya	U	3	198.0 100.9	23	27.9 8.5	26	5.10 0.54	28	0.76 0.08
	CQ	17	236.0 133.7	186	36.3 17.6	242	5.00 1.41	248	0.75 0.14
	Q	4	235.0 37.9	52	34.5 16.4	79	4.90 1.45	79	0.74 0.11
Maiskaya	U	–	–	3	34.7 8.5	5	4.60 0.24	8	0.69 0.08
	CQ	2	157 –	24	28.6 1.2	38	4.00 1.38	42	0.73 0.11
	Q	1	1.38 –	4	32.4 13.6	9	4.60 1.24	9	0.66 0.16

Based on the similarity of a metasomatic model to the mentioned regularities of change in grain sizes of diamonds from different fractions (see Table 3), it is possible to assume that the diamond recrystallization with formation of large grains takes place in the process of secondary change in kimberlites. The authors understand that the conclusion proposed contradicts to the traditional views on diamond crystallization at high values of thermodynamic parameters. However, we think that our hypothesis on diamond recrystallization at the post-magmatic stage explains the actual material more completely. If it is true, then the diamond grains formed due to the secondary processes should differ from the diamond grains formed under endogenous conditions. Anomalously high contents of diamonds and anomalously large sizes of their crystals in the places with high quartz should be considered as artifact for kimberlites, i.e. occurring under other thermodynamic conditions.

In this case, we can observe the phenomenon of increase in the volume of elementary cell of kimberlite secondary quartz, as compared to the quartz from the rocks of endogenous genesis [1, 2, 8], i.e., the morphology and other physical properties of the diamonds formed as a result of secondary processes should differ from the same properties of endogenous diamonds. In fact, according to [5, p. 155], "the contents of crystals with the signs of natural etching in the Botuobinskaya pipe are increased in comparison with the same for the mined Yakutian fields".

Outside the conditions defining the origin of kimberlites, for example, under the Earth's crust conditions, the diamond crystallization is reproduced in a number of experiments.

R. Dunin-Barkovskii et al. [15] implemented the growth of diamonds on diamond seeds using the mixture of sulphuric, nitric and acetic acids in aqueous solution medium under atmospheric pressure.

A new acicular shape of diamond has been discovered in natural rubies of one Vietnamese deposit [26]. The diamond formation under the Earth's crust conditions is also described in the works [10, 24]. The work of R. Dunin-Barkovskii et al. [15] deserves special attention, since from 20 to 60 % of strongly changed diamondiferous rocks described by them occur at the depths typical for the weathering crusts (less than 60 m). In this connection, let us remind that D. Korzhynskiy [7] considered sulphate argillization to be one of the manifestations of low-temperature stages of contact leaching. He associated the change of hydromicaceous zone by argillization zone with the increase in the acidity of solutions, when ascending post-magmatic waters mixed with the oxygen-rich surface waters. Later on, V. Razumova [14] used this model for constructing a hydrothermal-vadose hypothesis on formation of the weathering cores of local and areal type by the example of serpentinites from the Southern Urals. According to V. Razumova's representations, natrolitization of kerolitized serpentinites has been realized in the interaction between the hydrothermal solutions arriving from the depths and vadose waters. Similarly, it is possible to assume that weathering cores of kimberlites also formed in the interaction between post-magmatic hydrothermal solutions and oxygen-rich vadose waters. The neutral and acidic media arising at that moment could possibly favour to recrystallization and accumulation of diamonds.

The processes of eluvial change of rocks joined hydrothermal-metasomatic processes at the upper levels; these processes, mostly, took part in the secondary change of kimberlites and their diamond potential.

As is remarked above, in most kimberlite pipes of diamond fields, silicification of rocks causes the reduction of their diamond content. Interpretation of this phenomenon as the consequence of diamond dissolution process seems evident. However, we failed to find the mineralogical descriptions of the aftermath of dissolution process in the references. Therefore, let us address to the data on experimental dissolution of a diamond in kimberlite and basalt melts and in other media to confirm the reality of diamond dissolution in principle.

It is found that synthetic crystals of a diamond partially dissolved in water-containing silicate melts are morphological analogues of natural rounded and semi-rounded diamond crystals. The hypothesis of dissolution proposed by a number of scientists is confirmed experimentally. When the diamonds are carried out by kimberlite melts, the water and carbon dioxide containing in them interact actively with the diamond. The diamond crystals in water-containing silicate melts begin to dissolve, when pyramidal etching figures are formed on the faces. The dissolution layer is formed simultaneously with the etching figures, which results in formation of a round surface. The dissolution hummocks are specific elements of the microrelief [20].

In the $CaCO_3$ melt, the octahedral crystals transform to trigon-trioctahedroids, and tetrahexahedroids in combination with the surfaces of tetragon-trioctahedroids are formed on the basis of cuboctahedrons [16].

The morphological characteristics of diamonds including the orientation of etching figures, the features of striaeing and crystallography of round surfaces are the indicators of oxidation-reduction conditions in the process of interaction between a diamond and melts or fluids of the upper mantle [22].

When the kimberlite melts are hoisted to the upper levels at the temperature 700–900 °C, catalytic dissolution of diamonds is possible, when the part of diamonds could be degraded and the remaining diamonds would have corrosion marks in the form of caverns. The caverns are developed predominantly on the round crystals of rhombic dodecahedral habitus. In diamond crystals dissolution, the weight loss can reach 80 %. The alternation of growth and dissolution processes both in magmatic and metasomatic processes can take place in different systems at *PT*-parameters of natural diamond formation [21]. Some investigators remark that the change of crystallographic shapes during the growth of diamonds has a reverse character, as related to the change of shapes in dissolution.

Thus, the dissolution of a diamond is a real process. The part of diamonds can be dissolved completely [13].

It is natural to assume that in case of post-magmatic change of kimberlites, the dissolution of crystals would take place, but considerably slower than at high thermodynamic parameters. The geological time levels the difference in the rates of growth and dissolution of crystals at high and low values of thermodynamic parameters.

The materials presented make it possible to ascertain confidently, that a diamond doesn't behave indifferently in relation to the actively changing rock-forming minerals. The diamond participates in the processes of hydrothermal-metasomatic change of rocks actively, which is expressed in its dissolution or recrystallization.

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Стаття: надійшла до редакції 19.03.2015
прийнята до друку 04.09.2015

ПІСЛЯМАГМАТИЧНІ ЧИННИКИ АЛМАЗОНОСНОСТІ КІМБЕРЛІТІВ

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Наведено результати порівняльного аналізу даних щодо складу кімберлітів і вмісту в них алмазів. Доведено, що кількість і розмір кристалів алмазу залежать від ступеня післямагматичних змін кімберліту. Запропоновано модель гідротермально-метасоматичного розчинення або перекристалізації алмазу.

Ключові слова: кімберліт, алмаз, нормативний кварц, післямагматичні зміни, гідротермально-метасоматичне розчинення, перекристалізація.

ПОСТМАГМАТИЧЕСКИЕ ФАКТОРЫ АЛМАЗОНОСНОСТИ КИМБЕРЛИТОВ

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Приведено результаты сравнительного анализа данных по составу кимберлитов и содержанию в них алмазов. Показано, что количество и размер кристаллов алмаза зависят от степени постмагматического изменения кимберлита. Предложено модель гидротермально-метасоматического растворения или перекристаллизации алмаза.

Ключевые слова: кимберлит, алмаз, нормативный кварц, постмагматические изменения, гидротермально-метасоматическое растворение, перекристаллизация.