

The Nature and Compositional Peculiarities of Volcanogenic Diamonds

E.M. Galimov^{a,✉}, F.V. Kaminsky^a, G.A. Karpov^b, S.N. Shilobreeva^a, V.S. Sevast'yanov^a,
S.A. Voropaev^a, L.P. Anikin^b, R. Wirth^c, G.K. Khachatryan^d, V.V. Saraikin^e

^a Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, ul. Kosygina 19, Moscow, 119991, Russia

^b Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences,
bul'v. Piipa 9, Petropavlovsk-Kamchatsky, 683006, Russia

^c Helmholtz Centre Potsdam, GFZ German Research Center for Geosciences, D-14473 Potsdam, Germany

^d Central Research Institute of Geological Prospecting for Base and Precious Metals, Varshavskoe sh. 129, bld. 1, Moscow, 117545, Russia

^e Lukin Institute of Physical Problems, Zelenograd, Georgievskii pr. 5, bld. 1, 124460, Russia

Received 25 March 2020; received in revised form 10 June 2020; accepted 29 July 2020

Abstract—We have studied volcanogenic diamonds in the context of a discussion of their genesis, including some assumption on their artificial origin. The carbon isotope composition of diamonds collected from the eruption products of Tolbachik volcano ($\delta^{13}\text{C}_{\text{VPDB}}$ from -22 to -29‰) is within the range of the $\delta^{13}\text{C}_{\text{VPDB}}$ values of natural diamonds, including those from kimberlites. The $\delta^{15}\text{N}_{\text{Air}}$ values of the Tolbachik diamonds, measured for the first time (-2.58 and -2.32‰), correspond to $\delta^{15}\text{N}_{\text{Air}}$ of volcanic gases and differ from that of atmospheric nitrogen ($\delta^{15}\text{N}_{\text{Air}} = 0\text{‰}$), which may be expected in synthetic diamonds. In the studied volcanogenic diamonds, as in synthetic ones, the nitrogen impurity is unaggregated. However, such an unaggregated form of nitrogen is specific to many natural diamonds (e.g., variety II diamonds, according to Orlov's classification). Impurity elements (Cl, F, O, S, Si, Al, Ca, and Na) are locally concentrated in volcanogenic diamonds; they are a constituent of micro- and nano-inclusions in them. The high contents of F and Cl in the studied diamonds are correlated with the composition of volcanic gases; there is no reason to expect a similar correlation in synthetic diamonds. Moreover, the studied cube-octahedral Tolbachik diamonds have a number of accessory forms, some of which are not observed in synthetic diamonds. Their surfaces are frequently covered with films composed of Mg–Fe and Ca–Mg silicates, aluminosilicates, sulfates, metal alloys, and native Al. Mineral inclusions in the studied diamonds are Mn–Ni–Si alloys and silicides varying in composition from $(\text{Mn,Ni})_4\text{Si}$ to $(\text{Mn,Ni})_5\text{Si}_2$, Mn_5Si_2 , and pure Mn silicide MnSi. Summing up the obtained data, we conclude that volcanogenic diamonds form in a strongly reducing environment, in which silicides and native metals and their alloys are stable. The predominant cube-octahedral morphology of these diamonds and the unaggregated nitrogen impurity point to their short-term residence under high-temperature conditions. This makes them similar, to some extent, to synthetic diamonds. There are, however, clear differences as well. Volcanogenic diamonds are similar in compositional peculiarities, including isotope compositions, to natural diamonds that form under most unfavorable conditions, such as cuboids, balases, carbonado, and some diamonds of the eclogite paragenesis. They also resemble diamonds found *in situ* in harzburgite and chromitite of ophiolites. This suggests a specific mechanism of formation of both volcanogenic and ophiolitic diamonds in the oceanic lithosphere.

Keywords: diamond; volcano; ophiolite; metal inclusions; silicide; carbon; isotope composition; oceanic lithosphere

INTRODUCTION

The finds of diamonds in lavas and pyroclastic materials of Kamchatka volcanoes (Russia) have been known since the 1970s, when the first diamonds were identified in basalts of the Icha volcanic structure (Kutyev and Kutyeva, 1975; Kaminsky et al., 1979). The unusual character of these finds brought much attention to them, as well as

strengthening efforts in the continued search for diamonds in Kamchatka. These explorations proved fruitful with new diamond finds in the products of eruptions of six other volcanoes, as well as in placer deposits and ultramafic rocks of Kamchatka (Shilo et al., 1979; Seliverstov and Kaminsky, 1994; Baikov et al., 1995; Seliverstov, 2009; Gordeev et al., 2014; Karpov et al., 2014; Silaev et al., 2015; Kaminsky et al., 2016, 2019; Anikin et al., 2018a,b). The grains of polycrystalline diamond, cemented with tilleyite, silicon carbide and silicides, were discovered in the Valizhgen Peninsula, Koryakia and are called “kamchatites” (Kaminsky et al., 2019). Recently, three diamonds were found in lavas from

✉ Corresponding author.

E-mail address: galimov@geokhi.ru (E.M. Galimov)

the Alaid volcano on the Atlasov Island, northern Kuril Ridge (Anikin et al., 2018a).

We return to the discussion on the peculiarities of the composition and the origin of volcanogenic diamonds, including those from the Tolbachik area, in connection with the assumptions expressed by some authors about their unnatural formation (Litasov et al., 2019a,b; Pokhilenko et al., 2019).

In this paper, we focus our attention on the facts (mainly on diamonds from the Tolbachik volcano) that allow us to make conclusions on the conditions of their formation, and, in our opinion, clearly indicate the natural origin of volcanogenic diamonds.

GEOLOGICAL DATA AND FIELD OBSERVATIONS

Volcanogenic diamonds in Kamchatka have been identified in basaltoids of the Icha volcano (Kutyev and Kutyeva, 1975) (Fig. 1), in meimechites and lamproite-like tuffs of the Valagin Ridge (Seliverstov and Kaminsky, 1994; Seliverstov, 2009), and in melanocratic basalts of the Avacha volcano (Baikov et al., 1995).

In the 2012–2013 products of the Fissured Tolbachik eruption, diamonds were also found. The first crystals were identified by L.P. Anikin in December 2012 in samples of porous basalt, selected by A.V. Sokorenko from the Leningradskii lava flow. In February 2013, G.A. Karpov discovered three grains of yellowish-green diamond in a sample of freshly fallen ash, weighing about 10 grams, collected di-

rectly from the Naboko crater during a powerful pyroclastic eruption. During the course of the sampling, the pyroclastic materials were still hot, approximately at 70 °C. The samples were taken at sites located several kilometers away from each other. In total, more than 100 basalt samples were tested by L.P. Anikin; in 30 of them some 700 diamond grains were recovered.

Diamonds were identified within the pyroclastic material, infilling porous areas of scoriaceous basalt. To preclude any sample contamination, only geological hammers were used in the sample recovery (i.e., without the use of any cutting, drilling and other tools that could be armored with synthetic diamonds). Basalt samples were rinsed to remove surface dust, air-dried, and then each were subdivided into granulometric classes prior to examination under a MPSU-1 microscope.

Along with the diamond finds were elongated, sometimes peculiarly swirling grains of native iron (often with an admixture of Ti, Mn, Cr, Ni and Si), as well as elongated grains of native aluminum (pure, or with an admixture of Mn, Cu and Si), equidimensional grains of native copper (sometimes with Fe and Sn admixtures), native zinc, native molybdenum, as well as grains of deltalumite (without or with impurities of Fe and Cu), and less commonly – grains of moissanite. In the pore spaces and within the pyroclastic material, irregular and equidimensional grains of volcanic glass predominate, there are as well elongated crystals of plagioclase, and small crystals of pyroxene and olivine. In ashes of the 1988 eruption of the Klyuchevsky volcano, L.P. Vergasova found several grains of diamond intergrown

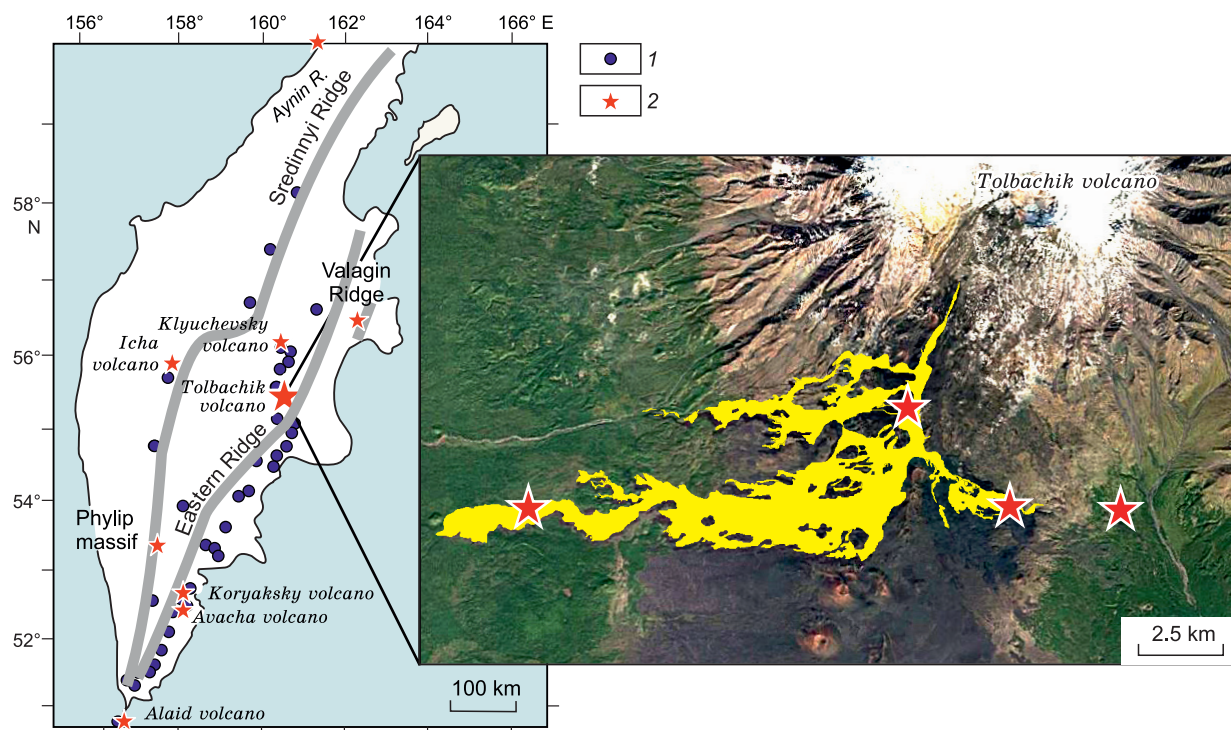


Fig. 1. Map of the eruptions of the Tolbachik volcano in 2012–2013. Left: 1, volcanoes, 2, finds of diamonds. Right: yellow, lava fields, red stars, places of finds of diamonds in samples. The map is based on field work using NASA and JPL satellite imagery. Details in the text.

with native aluminum. During a phreatic eruption of the Koryaksky volcano on July 31, 2009, three vents were formed, located at an altitude of about 3200 m, along a fissure on its NW slope. Two diamond crystals were identified as a result of mineralogical studies of the ash from the central vent, including *in situ* diamond crystal overgrowing deltalumite (Anikin et al., 2018b).

RESEARCH METHODOLOGY AND RESULTS

Identification of diamond was facilitated with a Tescan Vega 3 scanning electron microscope equipped with a X-Max 80 energy-dispersive X-ray spectrometer, and a Cameca Camebax electron microprobe (Anikin et al., 2018b). Analyses of chemical and microelement compositions of ashes were determined utilizing X-ray fluorescence spectrometry (a S4 Pioneer instrument) in the analytical center of the Institute of Volcanology and Seismology.

Crystal-morphology. The most detailed studies of diamond crystals from the Tolbachik volcano show that these are generally represented by isometric, flat-faced cube-octahedral crystals, up to 800 μm in size. On their surfaces were identified not only the equally developed faces of cube {100} and octahedra {111}, but also additional faces of rhombododecahedra {110}, tetragontrioctahedra {131}, and trigontrioctahedra {332}. **Cathodoluminescence** studies of the Tolbachik diamonds, revealed zoning phenomena caused by the presence, in the center of the crystals, of octahedral forms, on which subsequently formed cubic faces that eventually led to the cube-octahedral shape of diamonds (Silaev et al., 2015).

The isotopic composition of carbon and nitrogen in the Tolbachik diamonds was determined at the GEOKHI RAS on their DELTA Plus XP mass spectrometer (Galimov et al., 2016a). The $\delta^{13}\text{C}_{\text{VPDB}}$ values fall within the range from -22 to -27‰ . This data has been supplemented with new analyses on their Cameca IMS-1280-HR. These gave $\delta^{13}\text{C}_{\text{VPDB}}$ values of between -26.70 and -28.66‰ .

We also obtained, for the first time, results for the nitrogen isotopic composition in the Tolbachik diamonds. They are, for two crystals, -2.58 and -2.32 $\delta^{15}\text{N}_{\text{Air}}$. The analyses were carried out on the Cameca IMS-1280-HR instrument; a primary beam of Cs^+ ions had an energy of 20 keV. Signals of $^{12}\text{C}^{13}\text{C}^-$, $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ were measured.

Fourier IR spectroscopy (FTIR) of diamond was carried out with the use of a Nicolet 380 spectrometer (Thermo Electron) combined with a Centarius microscope. The spectral resolution was 6 cm^{-1} after 200 runs. Calculations of nitrogen concentrations were performed using methods by Taylor et al. (1996).

There are absorption bands of the diamond lattice's own oscillations in the range of $1800\text{--}4000\text{ cm}^{-1}$, as well as lines in the area of $1000\text{--}1400\text{ cm}^{-1}$ caused by the structural impurity of single unaggregated nitrogen (C-centers). Absorp-

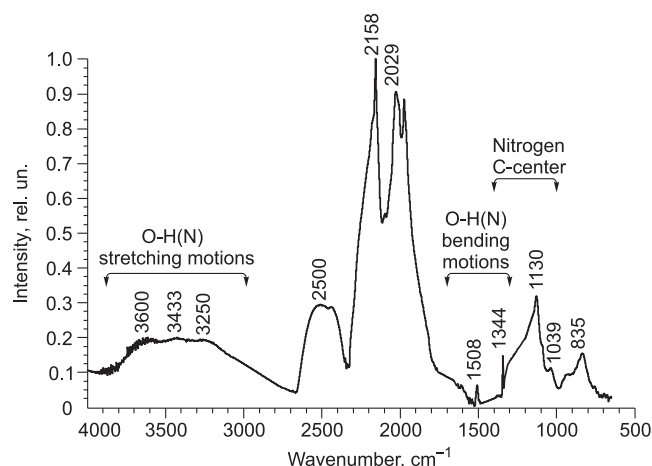


Fig. 2. FTIR spectrum of the TOP diamond from the Tolbachik volcano, after Galimov et al. (2020).

tion lines, characteristic of structural impurities of aggregated nitrogen, in areas 1282 cm^{-1} (A-centers), 1332 , 1175 cm^{-1} (B-centers), as well as lines fixing platelets ($1359\text{--}1378\text{ cm}^{-1}$) and hydrogen centers (3107 cm^{-1}), have not been observed in any of the diamonds analyzed (Fig. 2).

Concentrations of structural nitrogen impurity in the studied diamonds from Tolbachik vary from 126 to 433 at. ppm (Table 1).

The spectra also contain absorption bands in the $3000\text{--}4000\text{ cm}^{-1}$ and $1500\text{--}1600\text{ cm}^{-1}$ ranges, presumably related to stretching and bending motions of O-H or N-H-groups, respectively. In the studied diamonds, these groups cannot be attributed to any phase inclusions. Judging by variations in their relative intensity and configurations of these peaks, the compositions and concentrations of the relevant impurities in different samples are distinct.

Photoluminescence spectra, induced by laser radiation at a frequency of 488 nm, were observed at room temperature utilizing the LabRam spectrometer (Horiba Jobyn Yvon) with a lens of $100\times$; i.e., the size of the beam on the sample was only a few micrometers.

A typical photoluminescence spectrum of one of the Tolbachik diamonds is presented in Fig. 3. The spectrum shows a strong Raman peak from the diamond lattice at 505 nm, although it is usually observed at 1332 cm^{-1} . The difference is likely caused by the recalculation of the wave frequency to nanometres in consideration of the laser's wavelength.

Table 1. Concentrations of unaggregated nitrogen (N-center) in the studied diamonds from the Tolbachik volcano

Sample	Nitrogen, at. ppm
T2	433
T3	131
TOP	126
CH	245
Average	233.8 ± 143.8 (2s)

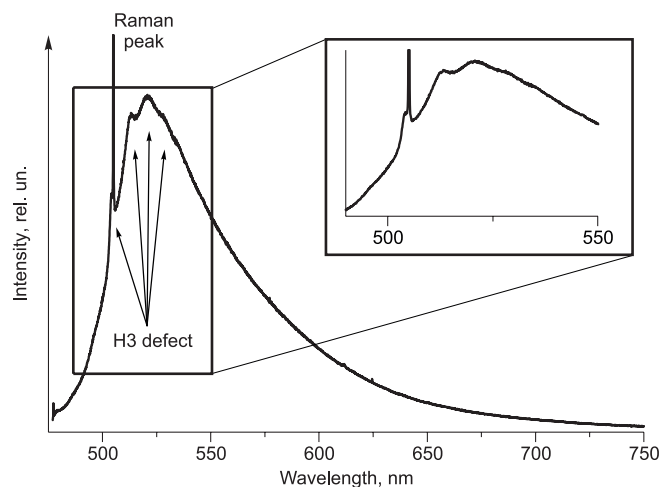


Fig. 3. Typical fluorescence spectrum of one of the Tolbachik diamonds, after Galimov et al. (2020).

Within the range of 520–530 nm, the spectrum shows a series of smooth “humps”. Despite their weak pronouncement, they correspond to the well-known defect H3, which is a combination of nitrogen pair (A-defect) with a site vacancy. The zero-phonon line (504 nm) and the phonon repetitions are clearly visible. The H3 defect is very common for both synthetic and natural diamonds. Unusual is the absence of NV (nitrogen + vacancy) defects, which are also quite common for diamonds. In general, such spectra of luminescence are found in both synthetic and natural diamonds.

The analysis of impurity elements in diamond was carried out by secondary ion mass spectrometry (SIMS) utilizing the Cameca IMS-4f ion probe. The size of the image was determined by the ion beam and was $250 \times 250 \mu\text{m}$. Before the analysis, sample surfaces were cleaned with a primary beam. When the current of negatively charged secondary ions (F, O, Si, Cl, H, S) was recorded, primary ions of Cs^+ were used. When the currents of ions with low potential of ionization were measuring (Na, K, Ca), primary ions of O_2^+ were used, and the current of positively charged secondary ions was recorded.

Translucent electron microscopy (TEM) was produced at the Helmholtz Centre in Potsdam, Germany. Preliminarily, TEM foils were sputtered from host diamonds using a focused ion beam system. Foil sizes were approximately $15 \times 10 \times 0.1 \mu\text{m}$. The foils were studied with the use of TECNAI F20 electron microscope, equipped with an EELS spectrometer (Tridiem™) and an EDAX X-ray microanalyzer, with an ultrathin window and a wide-angle Fishione dark field detector.

From these investigations, mineral inclusions of round or oval grains, 70–450 nm in size were identified. According to the electron diffraction data, they are represented by two mineral groups, Mn-Ni-Si alloys and silicides, with wide compositional variations within each group. The metal alloys vary in composition from MnNi to Mn_2Ni , with an ad-

Table 2. Chemical compositions of films on the surface of diamond from the Tolbachik volcano

Element	Concentration, at. %	
	Point 2	Point 3
C	21.50	10.87
O	49.17	59.6
Na	–	1.21
Mg	–	0.80
Al	1.48	2.54
Si	1.99	5.31
S	–	0.28
Cl	–	0.28
Ca	0.39	0.61
Ti	22.50	15.27
Fe	1.82	2.41
Cu	0.89	0.76
Mo	0.26	–
Total	100.00	100.00

Note. Analyses performed in the Institute of Volcanology and Seismology utilizing the microprobe analyzer Camebax.

mixture of Si (0–5.50 at. %). The silicides, usually associated with alloys and forming overgrowths with them, vary from $(\text{Mn}, \text{Ni})_4\text{Si}$ to $(\text{Mn}, \text{Ni})_5\text{Si}_2$ and Mn_5Si_2 , and further to MnSi, forming pure Mn-silicides (Galimov et al., 2020).

Smears and films on the surfaces of crystals are found in many of the diamonds from the Tolbachik volcano. They are composed of Mg–Fe and Ca–Mg silicates, aluminosilicates, and sulfates (Karpov et al., 2014; Silaev et al., 2015), and are similar in composition and structure with mineral films on surfaces of natural kimberlitic diamonds, for example, from the Ebelyakh placer deposit in northeastern Yakutia (Oleynikov and Barashkov, 2005).

Of particular importance are finds, on surfaces of Tolbachik diamonds, of particles of native Al and alloys of Ni_4Cu_3 , $\text{Cu}_{0.68-0.91}\text{Sn}_{0.07-0.17}\text{Fe}_{0-0.22}$, $\text{Cu}_{4-10}(\text{Sn}_{0.6-1}\text{Fe}_{0.1-0.15})_{1-2}$, $\text{Mn}_3\text{Ni}-\text{Mn}_5\text{Ni}$ (Silaev et al., 2016). Analogous films of the Ni, Fe–Ni, Fe–Mn, Fe–Ni–Mn compositions were observed on surfaces of natural diamonds from the Uralian placer deposits (Makeev and Kriulina, 2012). In addition to such films, we found surfaces enriched with Ti (Table 2; Fig. 4).

DISCUSSION

Volcanogenic diamonds are unusual in many ways. A principal case in fact is that diamonds found within volcanic areas and in ophiolitic rocks bear no indication that high pressures have factored into their environment. The formation of diamonds under the conditions of their thermodynamic stability requires specific P – T conditions attendant to other barophilic minerals formed in paragenesis with diamonds, as is the case of kimberlite and lamproite deposits. Hence, there are divergent views on the mechanism of dia-

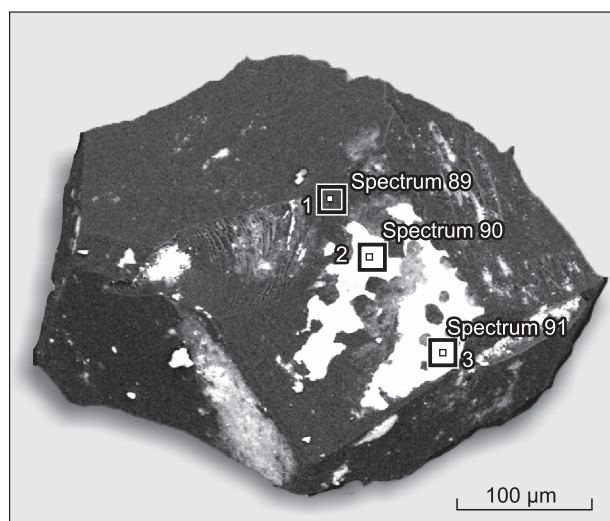


Fig. 4. Film on the surface of one of the cube-octahedral diamonds from the Tolbachik volcano. At point 1, the film has an exclusively carbon (graphite?) composition with a small admixture of Cu (0.11 at.%). The compositions of film at points 2 and 3 are presented in Table 3.

mond formation in such environments, including such extreme ones, as the assumption about their unnatural genesis, i.e., that their findings are nothing more than manifestations of accidental contamination of man-made synthetic diamonds (Litasov et al., 2019a,b; Pokhilenko et al., 2019).

The morphology of volcanogenic diamonds indeed resembles the morphology of synthetic diamonds; in both cases they have a cube-octahedral morphology. However, there are differences in the details. It was noted above that, in addition to cubic and octahedral faces, Kamchatka diamonds also bear facets of other crystal forms: rhombododecahedra, tetragontrioctahedra, and trigontrioctahedra. The last form is not known in synthetic diamonds (Silaev et al., 2015). In general, synthetic diamonds do not exhibit such a variety of additional faces and smears, which are revealed

on the surfaces of any natural diamonds, including the Tolbachik finds. On the other hand, the cube-octahedral diamond crystals are characteristic for many kimberlite and related deposits of diamond (Kvasnytsya, 1985; Orlov, 1987; Sergeeva, 2000; Zinchuk and Koptil, 2003; Kvasnytsya, 2013), as well as for metamorphic diamonds from Kazakhstan (Shatsky et al., 1998). There is also a fairly frequent occurrence of spinel twins among Tolbachik diamonds. Such peculiarities are analogous to cube-octahedral diamonds from Yakutian kimberlites (Zinchuk and Koptil, 2003) and the Grib pipe in the Arkhangelsk Region (Sergeeva, 2000), and in placer deposits of the Ukraine (Kvasnytsya, 1985, 2013). Cathodoluminescence observations of the Tolbachik diamonds demonstrate the existence of octahedral cores, that is not a characteristic of synthetic diamonds.

Isotopic composition of carbon and nitrogen. The isotopic composition of the Tolbachik diamonds is within the range of -22 to -29‰ $\delta^{13}\text{C}_{\text{VPDB}}$. Man-made diamonds, for which the source material in their synthesis is organogenic graphite, may have a similar isotopic composition of carbon. But this is not a distinguishing trait. Natural diamonds have a wide range of variations in isotopic composition (Galimov, 1984). Figure 5 illustrates the $\delta^{13}\text{C}$ values of the Tolbachik diamonds in relation to a general histogram of the $\delta^{13}\text{C}$ values for diamonds across the globe, from the work by Galimov (1991). Many kimberlite-hosted diamonds have the same isotopic composition as those from Tolbachik. As a rule, diamonds formed in the least favorable environment (e.g., those with cuboids, balases, carbonados, as well as some diamonds of the eclogitic paragenesis) are enriched with the light ^{12}C isotope. Their isotopic composition is frequently in the range of values from -15 to -30‰ $\delta^{13}\text{C}_{\text{VPDB}}$. Thus, Tolbachik diamonds (with -22 to -29‰ $\delta^{13}\text{C}_{\text{VPDB}}$) are fairly typical representatives of this group. It is also insightful that, according to Fig. 5, the carbon isotopic composition of Tolbachik diamonds coincides with the carbon isotopic composition of lavas from the same volcano (Karpov et al., 2014;

Table 3. Concentrations of impurity elements in diamond and in volcanic gases from Tolbachik volcano

Element	Diamond		Volcanic gas (after Zelenski et al., 2014)	
	Concentration (ppm)	Normalized to mantle pyrolite	Concentration (ppm)	Normalized to mantle pyrolite
N	304	152		
F	5.6	0.224	4650	186
Na	0.6	0.225	224	83.9
Al	3	0.0001	7.9	0.0003
Si	310	0.0705	74	0.0004
S	11	0.044	36,000	144
Cl	14.6	0.8588	24,000	1411.8
K	1	0.0042	250	1.0417
Ca	3.3	0.0001	4.5	0.0002
O	7382	—	—	—

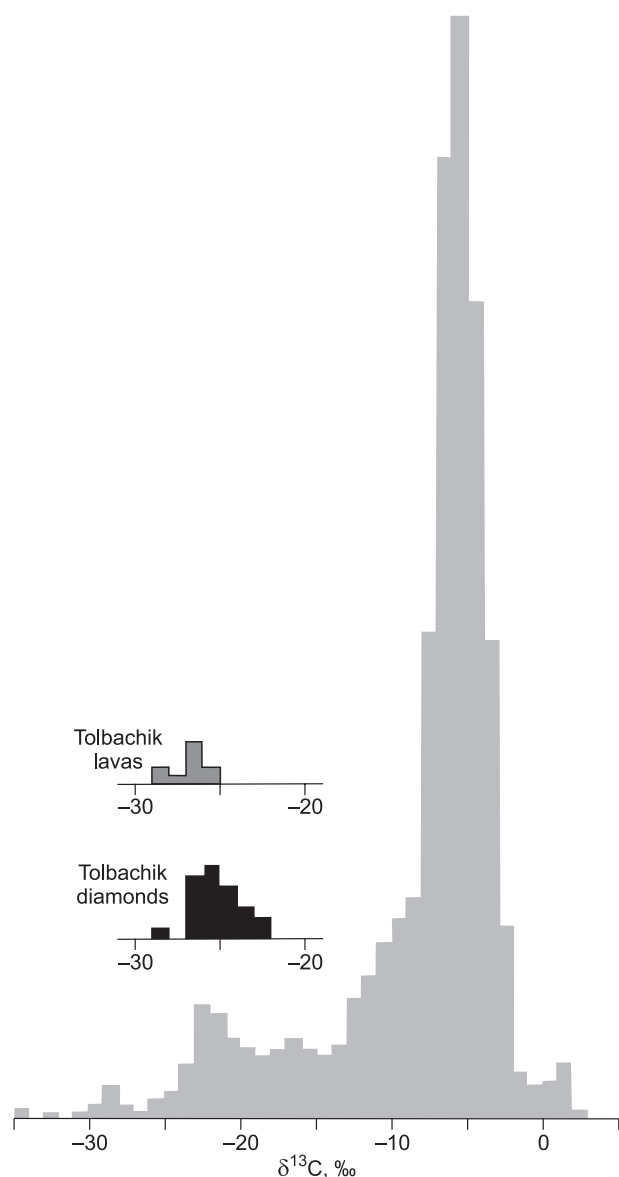


Fig. 5. The carbon isotopic compositions of diamonds and lavas from the Tolbachik volcano on a background general $\delta^{13}\text{C}$ histogram for global diamonds (Galimov, 1991).

Galimov et al., 2016a). This points to a coupled relationship of the Tolbachik diamonds with the volcanic process.

The determined values of the isotopic composition of nitrogen in Tolbachik diamonds yielded values of $\delta^{15}\text{N}_{\text{Air}}$ -2.58 and -2.32‰ (Galimov et al., 2020). These values differ to those of $\delta^{15}\text{N}_{\text{Air}} = 0\text{‰}$, which might be expected in diamonds, synthesized under current atmospheric conditions (Boyd et al., 1988), although, in some cases, nitrogen in graphite may have $\delta^{15}\text{N}_{\text{Air}}$ different from zero values in synthetic diamonds as well. The isotopic composition of nitrogen for natural diamonds, as well as volcanic gases, varies widely. For example, the isotopic composition of nitrogen in volcanic gases from South Kamchatka is in the range of -31 to $+13\text{‰}$ $\delta^{15}\text{N}_{\text{Air}}$ (Volynets et al., 1967). Nitrogen in volcanic

gases from another Kamchatka volcano, Mutnovsky, deviates to $\delta^{15}\text{N}_{\text{Air}} = -3.4\text{‰}$ (Zelenski and Taran, 2011). Analogous isotopic compositions for nitrogen, that differ from zero values, were found in gases from the Oldoinyo-Lengai volcano in East Africa (Fischer et al., 2009). The data on isotopic compositions of carbon and nitrogen are in agreement with each other and, most likely, confirm the natural origin of Tolbachik diamonds.

The presence of unaggregated nitrogen. In synthetic diamonds, the structural admixture of nitrogen occurs in an unaggregated form. However, the presence of nitrogen in diamonds in the form of single atoms, replacing carbon atoms, is also not uncommon for diamonds from natural deposits. These types comprise variety II of natural diamond, according to Orlov's (1987) classification. This variety is characterized by a fast growth rate and a short time residence at high temperatures. Nitrogen impurity does not have time to aggregate and form nitrogen complexes. This is why the trapped nitrogen remains in an atomic form with an unpaired electron, which is expressed in the EPR signal. Usually, diamonds of variety II (physical Type Ib) are represented by crystals of cubic habit with amber-yellow or green coloration. They are common to the Udachnaya kimberlitic pipes in Yakutia, Kimberly in South Africa, as well as some placer deposits in the Urals and Siberia (Afanasyev et al., 2000). Recently, a significant number of Type Ib were identified in the Zimmy placer deposit, Sierra Leone (Smit et al., 2018). It is the presence of the single-atomic nitrogen C(N)-center that causes the yellow-green coloration in diamonds from the Tolbachik volcano. Diamonds from ophiolites have similar characteristics. Moreover, comparable yellow-green diamonds of cube-octahedral habit, almost identical in their spectral properties to Tolbachik diamonds, are found among the impact diamonds of the Popigai astrobleme (Sukharev and Petrovsky, 2019).

The presence of gas-forming elements in the diamond.

Figure 6 provides data on the composition of impurities in the Tolbachik diamond, as compared to the distribution of these elements in volcanic gases from Tolbachik. The latest data is taken from the work of Zelenski et al. (2014); they demonstrate a significant role of S, Cl and F in the associated volcanic gases. There is a clear correlation between the compositions of volcanic gases and impurities in diamond. There is no ground to expect such correlation for synthetic diamonds, particularly for elevated concentrations of Cl and F. Particularly, the concentration of Cl in diamond is close to the concentration of this element in the mantle (e.g., pyrolite model; see Table 2). At the same time, this fact may be considered as evidence for a genetic relationship of the studied diamonds with volcanic fluids.

IR spectra for the Tolbachik diamonds also contain absorption lines, evidencing the presence of CO_3^{2-} inclusions, as well as the band, representing H_2O , which is also characteristic for diamond-bearing fluids.

Inclusions of Fe–Ni–Mn–Co metals. In the Tolbachik diamonds, as well as in ophiolitic ones, inclusions of metal

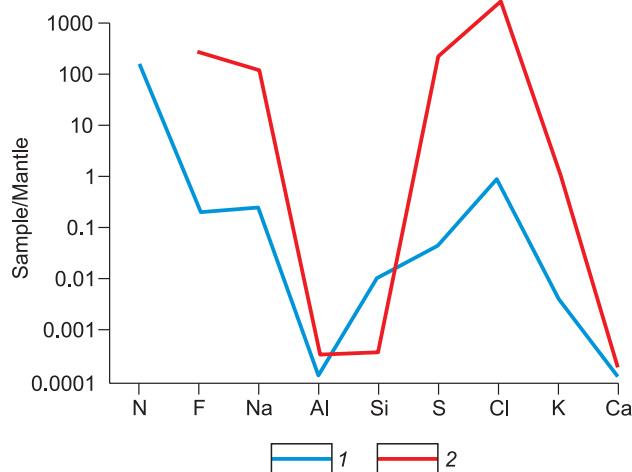


Fig. 6. Mantle-normalized concentrations of impurity elements in diamond No. 1 from Tolbachik volcano and in gases collected during the eruption of Tolbachik in 2013, after Galimov et al. (2020).

alloys occur. These inclusions are similar to the specific composition of catalysts used in the industrial synthesis of diamonds. Metals of the iron group are used for *HPHT* synthesis of diamond because they easily solute carbon. In both the USA and later in the former USSR, during the 1950s, Mn–Ni alloys were used since they are most easily smelted and allow for the production of diamond from graphite under minimal pressure conditions.

Our research demonstrates the presence of metallic inclusions in Tolbachik diamonds. However, their Mn–Ni ra-

tios differ to those used in the industrial catalysis of diamond presently in use in Russia (Shipilo et al., 2005) and China (Tan, 2014) (Fig. 7).

A peculiar feature of volcanic diamonds is the presence, as an admixture, of Si impurity, up to 5 at.%. Even greater concentrations of silica, up to 19 at.% were found in inclusions in the polycrystalline Avacha diamonds (Kaminsky et al., 2019). Along with metallic inclusions, Mn–Ni–Fe(-Ca) silicides were found in a close association with alloys in Tolbachik diamonds; they widely vary in stoichiometric composition from $(\text{Mn,Ni})_4\text{Si}$ to $(\text{Mn,Ni})_5\text{Si}_2$ and Mn_5Si_2 , and further to MnSi, forming pure Mn-silicides. Silicides form a close paragenetic bond with metals. In Figure 7, lines connect compositions of coexisting alloys and silicides. Frequently, the earliest formed, central areas of grains are composed of metal alloys, on which the silicides grow. In addition, mineral-inclusions usually contain pores measuring 20–30 nm. X-ray diffraction spectra from these areas show the presence of Cl, F and O (Galimov et al., 2020). Silicides are common in volcanic ashes (Karpov et al., 2014). At the same time, it is known that silicon is not used in the synthesis of diamond (Pal'yanov et al., 1997). Further, silicides are not known in synthetic diamonds.

Particles of Mn–Ni alloys were also found in a free state in the ashes of the 2013 Tolbachik eruption, indicative of their volcanic origin.

Metallic and silicide inclusions in Kamchatka diamonds are a part of the mineralogical composition of their volcanic eruption (Silaev et al., 2019a,b). In the products of the eruption of the Tolbachik volcano, in addition to metal alloys

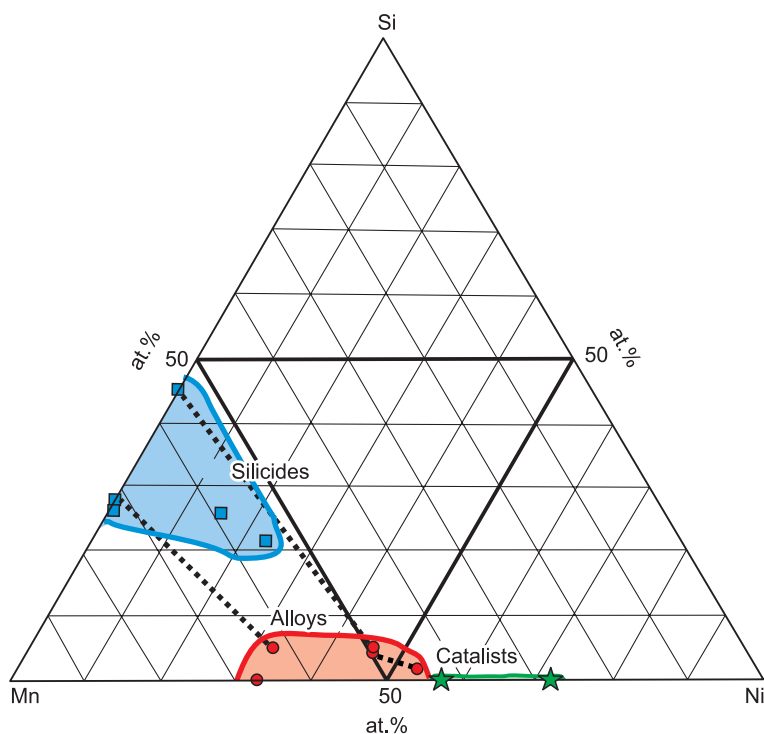


Fig. 7. Compositions of mineral inclusions in Tolbachik diamonds: the compositions of metal alloys (red) and silicides (blue); the composition of metal catalysts for the diamond synthesis (green).

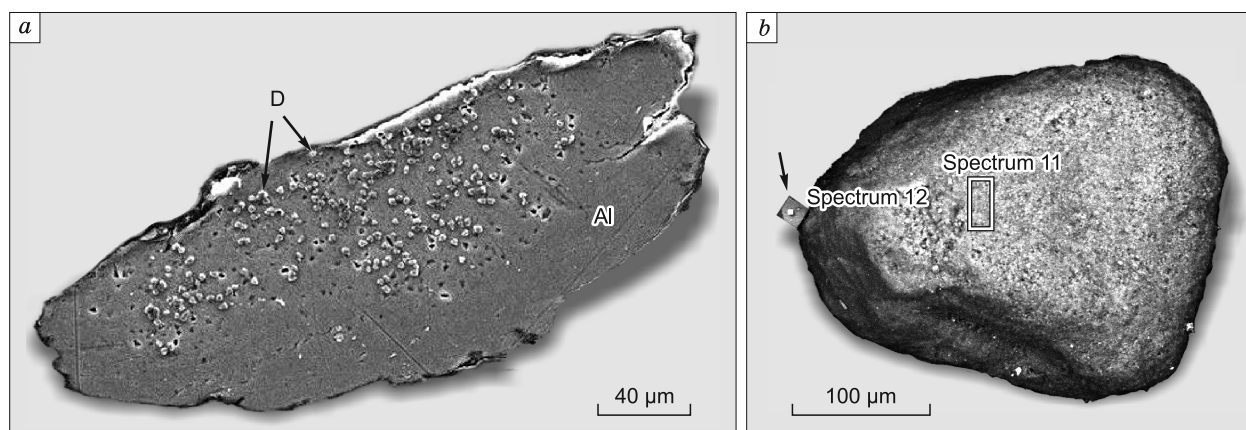


Fig. 8. *In situ* intergrowths of Kamchatka diamonds with products of volcanic activity. *a*, In native Al from the ashes of the Klyuchevsky volcano; *b*, with deltalumite from the ashes of the Koryaksky volcano; diamond is indicated by an arrow (after Anikin et al., 2018b). SEM images in the mode of secondary electrons, after Silaev et al. (2019a).

and silicides, Fe, Ni, Cu, W, and rare native Al are present, as well as carbides of iron, tungsten and silicon (Karpov et al., 2014).

Smears of metals and alloys. As noted above, metals and Mn–Ni alloys were identified on the edges of Kamchatka diamonds. It should also be noted that such adhesions and microinclusions of Mn–Ni alloys were found in diamonds from other regions, for example, in diamonds from placer deposits in the Russian Far East (Shcheka et al., 2006); in Brazilian carbonado, inclusions of $\text{Fe}_{0.38-0.87}\text{Ni}_{0.13-0.62}$ alloys occur regularly (Silaev et al., 2015).

In addition, films enriched in Ti are found on Kamchatka diamonds, as well as intergrowths of diamonds with native Al (Fig. 8).

Diamonds in ophiolites. In this work, we have dealt only with volcanogenic diamonds. However, it should be noted that diamonds, frequently found in rocks of ophiolitic complexes, are very close in their properties to volcanogenic diamonds, including the Tolbachik diamonds. They have comparable cube-octahedral morphologies, are of a similar size, exhibit a yellowish coloration due to the unaggregated nitrogen impurity, as well as near identical isotopic composition of carbon, and host the presence of metallic inclusions (Xu et al., 2017). Thus, it is clear that the authors, attributing an unnatural origin for volcanogenic diamonds, also consider diamonds from ophiolites as artefacts (Litasov et al., 2019b).

Diamonds in ophiolites have been found in many countries, in dozens of places across the Earth, and using various laboratories and techniques. Examples include those from Tibet (Robinson et al., 2004; Howell et al., 2015; McGowan et al., 2015; Yang et al., 2015a; Griffin et al., 2016; Yang et al., 2020) and Inner Mongolia (Huang et al., 2015) in China, in the Polar Urals, Russia (Yang et al., 2015b; Xu et al., 2017), in Turkey (Lian et al., 2017, 2018), in Myanmar (Chen et al., 2018), India (Das et al., 2017), Albania (Xiong et al., 2017; Wu et al., 2019), Cuba (Pujol-Solà et al., 2018), and other areas. In addition to the fact that thousands of dia-

monds have been found by numerous researchers, casting doubt upon any suggestion of their synthetic origin (i.e., the diamonds represent contaminants) it is important to observe that diamonds in ophiolitic complexes were repeatedly found *in situ* in their host rocks (e.g., harzburgites and chromitites). For this reason, the similarity between ophiolitic and volcanogenic diamonds is strong evidence for the natural origin of the latter. Moreover, this provides for the possibility that common type of diamonds are related to the oceanic lithosphere (Galimov et al., 2016b).

CONCLUSIONS

Summarizing this study, we may conclude that volcanogenic diamonds form in a deeply reduced environment: in an environment, where the presence of silicides, native metals, and their alloys is possible. Predominance of the cube-octahedral morphology of these diamonds, and the presence of nitrogen impurity in an unaggregated form indicate their very short residence in a high-temperature environment. In some respects, this makes them similar to synthetic diamonds. But there are also noticeable differences between them, as we have seen. On the other hand, volcanogenic diamonds, by their properties, including the isotopic composition, are close to those kimberlite diamonds that form in the least favorable environment: i.e., the yellow-green cube-octahedral variety II, balases, carbonado, and some diamonds of an eclogitic paragenesis. Volcanogenic diamonds demonstrate important similarities to diamonds from chromitite and harzburgite of ophiolitic complexes. In ophiolites, diamonds not infrequently occur *in situ* in the rocks. Volcanogenic diamonds are geologically specific. Their presence within volcanic rocks of certain facies indicates that exactly in such facies some special conditions occur, which allow for implementation of the special mechanism of their natural origin.

The formation of these diamonds takes place in an environment where there may be no elevated pressure necessary for the formation of other barophilic minerals. This complicates the understanding of the nature of these diamonds. In principle, however, such mechanisms exist. They are known. Their specification related to volcanogenic and ophiolitic diamonds requires special research. We believe that there are grounds to consider both volcanogenic and ophiolitic diamonds as manifestations of a specific mechanism for the formation of diamonds in the oceanic lithosphere.

These studies were partly funded by the RFFR grant № 19-05-00554 and the RAS Presidium Program № 16. The authors thank two anonymous reviewers for their notes, which helped to correct technical errors and improve upon our arguments and in the presentation of this work. We also thank Prof. I. Coulson for his help in English editing of the paper.

REFERENCES

- Afanasyev, V.P., Efimova, E.S., Zinchuk, N.N., Koptil, V.I., 2000. Atlas of Russian Diamond Morphology [in Russian]. Izd. SB RAN, Novosibirsk.
- Anikin, L.P., Delemen, I.F., Rashidov, V.A., Chubarov, V.M., 2018a. Accessory minerals in the products of volcanic eruptions of the Alaid volcano (Kuril Island Arc), in: *Volcanism and Related Processes: Proc. XXI Regional Conference* [in Russian]. IVS DVO RAN, Petropavlovsk, pp. 157–160.
- Anikin, L.P., Silaev, V.I., Chubarov, V.M., Petrovsky, V.P., Vergasova, V.P., Karpov, G.A., Sokorenko, A.V., Ovsyannikov, A.A., Maximov, A.P., 2018b. Diamond and other accessory minerals in the products of 2008–2009 phreatic eruption of Koryaksky volcano, Kamchatka. *Vestnik IG Komi SC UB RAS*, No. 2, 18–27.
- Baikov, A.I., Anikin, L.P., Dunin-Barkovsky, R.L., 1995. Find of carbonado in volcanic rocks of Kamchatka. *Dokl. Akad. Nauk SSSR* 343 (1), 72–74.
- Boyd, S.R., Pillinger, C.T., Milledge, H.T., Mendelsohn, M.J., Seal, M., 1988. Fractionation of nitrogen isotopes in a synthetic diamond of mixed crystal habit. *Nature* 331, 604–607.
- Chen, Y., Yang, J., Xu, Z., Tian, Y., Lai, S., 2018. Diamonds and other unusual minerals from peridotites of the Myitkyina ophiolite, Myanmar. *J. Asian Earth Sci.* 164, 179–193.
- Das, S., Basu, A.R., Mukherjee, B.K., 2017. In situ peridotitic diamond in Indus ophiolite sourced from hydrocarbon fluids in the mantle transition zone. *Geology* 45 (8), 755–758.
- Fischer, T.P., Burnard, P., Marty, B., Hilton, D.R., Füre, E., Palhol, F., Sharp, Z.D., Mangasini, F., 2009. Upper mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonates. *Nature* 459, 77–80.
- Galimov, E.M., 1984. Variations of the isotopic composition of diamonds and their relation with diamond formation conditions. *Geokhimiya*, No. 8, 1091–1117.
- Galimov, E.M., 1991. Isotope fractionation related to kimberlite magmatism and diamond formation. *Geochim. Cosmochim. Acta* 55 (6), 1697–1708.
- Galimov, E.M., Karpov, G.A., Sevast'yanov, V.S., Shilobreeva, S.N., Maksimov, A.P., 2016a. Diamonds in the products of the 2012–2013 Tolbachik eruption (Kamchatka) and mechanism of their formation. *Geochem. Int.* 54 (10), 829–833.
- Galimov, E.M., Sevast'yanov, V.S., Karpov, G.A., Shilobreeva, S.N., Maximov, A.P., 2016b. Microcrystalline diamonds in the oceanic lithosphere and their origin. *Dokl. Earth Sci.* 469 (1), 670–673.
- Galimov, E.M., Kaminsky, F.V., Shilobreeva, S.N., Sevast'yanov, V.S., Voropaev, S.A., Wirth, R., Schreiber, A., Saraykin, V.V., Karpov, G.A., Anikin, L.P., 2020. Enigmatic diamonds from the Tolbachik volcano, Kamchatka. *Am. Mineral.* 105 (4), 498–509.
- Gordeev, E.I., Karpov, G.A., Anikin, L.P., Krivoviev, S.V., Filatov, S.K., Antonov, A.V., Ovsyannikov, A.A., 2014. Diamonds in lavas of the Tolbachin fissure eruption in Kamchatka. *Dokl. Earth Sci.* 454 (1), 47–49.
- Griffin, W.L., Gain, S.E.M., Adams, D.T., Huang, J.X., Saunders, M., Toledo, V., Pearson, N.J., O'Reilly, S., 2016. First terrestrial occurrence of tistarite (Ti₂O₃) ultra-low oxygen fugacity in the upper mantle beneath Mount Carmel, Israel. *Geology* 44, 815–818.
- Howell, D., Griffin, W.L., Yang, J., Gain, S., Stern, R.A., Huang, J.-X., Pearson, N.J., 2015. Diamond in ophiolites: Contamination or a new diamond growth environments? *Earth Planet. Sci. Lett.* 430, 284–295.
- Huang, Z., Yang, J., Robinson, P.T., Zhu, Y., Xiong, F., Liu, Z., Zhang, Z., Xu, W., 2015. The discovery of diamonds in chromitites of the Hegenshan ophiolite, Inner Mongolia. *Acta Geol. Sin.* 89 (2), 341–350.
- Kaminsky, F.V., Patoka, M.G., Sheymovich, V.S., 1979. Geologic and tectonic position of diamond-bearing basalts of Kamchatka. *Dokl. Akad. Nauk SSSR*, No. 246, 55–58.
- Kaminsky, F.V., Wirth, R., Anikin, L.P., Morales, L., Schreiber, A., 2016. Carbonado-like diamond from the Avacha active volcano in Kamchatka, Russia. *Lithos* 265, 222–236.
- Kaminsky, F.V., Wirth, R., Anikin, L.P., Schreiber, A., 2019. «Kamchatite» diamond aggregate from northern Kamchatka, Russia: New find of diamond formed by gas phase condensation or chemical vapor deposition. *Am. Mineral.* 104 (1), 140–149.
- Karpov, G.A., Silaev, V.I., Anikin, L.P., Raikin, V.I., Vasilyev, E.A., Filatov, S.K., 2014. Diamonds and accessory minerals in the products of the 2012–2013 Tolbachik fissure eruption. *J. Volcanol. Seismol.* 8 (6), 323–339.
- Kutyev, F.Sh., Kutyeva, G.V., 1975. Diamonds in basaltoids of Kamchatka. *Dokl. Akad. Nauk SSSR*, No. 221 (1), 183–186.
- Kvasnytsya, V.N., 1985. Small Diamonds [in Russian]. Naukova Dumka, Kiev.
- Kvasnytsya, V., 2013. Crystal forms of natural microdiamonds. *Diamond Relat. Mater.* 39, 89–97.
- Lian, D., Yang, J., Dilek, Y., Wu, W., Zhang, Z., Xiong, F., Liu, F., Zho, W., 2017. Deep mantle origin and ultra-reducing conditions in podiform chromitite: Diamond, moissanite, and other unusual minerals in podiform chromitites from the Pozanti-Karsanti ophiolite, southern Turkey. *Am. Mineral.* 102, 1101–1113.
- Lian, D., Yang, J., Wiedenbeck, M., Dilek, Y., Rocholl, A., Wu, W., 2018. Carbon and nitrogen isotope, and mineral inclusion studies on the diamonds from the Pozanti-Karsanti chromitite, Turkey. *Contrib. Mineral. Petrol.* 173, 72–80.
- Litasov, K.D., Kagi, H., Voropaev, S.A., Hirata, T., Ohfuji, H., Ishibashi, H., Makino, Y., Bekker, T.B., Sevast'yanov, V.S., Afanasiev, V.P., Pokhilenko, N.P., 2019a. Comparison of enigmatic diamonds from the Tolbachik arc volcano (Kamchatka) and Tibetan ophiolites: Assessing the role of contamination by synthetic materials. *Gondwana Res.* 75, 16–27.
- Litasov, K.D., Kagi, H., Bekker, T.B., Hirata, T., Makino, Y., 2019b. Cuboctahedral type Ib diamonds in ophiolitic chromitites and peridotites: the evidence for anthropogenic contamination. *High Pressure Res.* 39 (3), 480–488.
- Makeev, A.B., Kriulina, G.Yu., 2012. Metallic films on surface and within crystals of diamond. *Zapiski VMO*, No. 1, 101–114.
- McGowan, N.M., Griffin, W.L., González-Jiménez, J.M., Belousova, E.A., Afonso, J., Shi, R., McCammon, C.A., Pearson, N.J., O'Reilly, S.Y., 2015. Tibetan chromitites: Excavating the slab graveyard. *Geology* 43 (2), 179–182.

- Oleynikov, O.B., Barashkov, Y.P., 2005. Features of the chemical composition of silicate films on diamond crystals from the Ebelyakh deposits and their genesis. *Otechestvennaya Geologia*, No. 5, 42–47.
- Orlov, Yu.L., 1987. *Mineralogy of Diamond*. John Wiley & Sons, New York.
- Pal'yanov, Yu.N., Khokhryakov, A.F., Borzdov, Yu.M., Sokol, A.G., Gusev, V.A., Rylov, G.M., Sobolev, N.V., 1997. Growth conditions and real structure of synthetic diamond crystals. *Russian Geology and Geophysics (Geologiya i Geofizika)* 38 (5), 920–945 (882–906).
- Pokhilenko, N.P., Shumilova, T.G., Afanas'ev V.P., Litasov, K.D., 2019. Diamonds in the Kamchatka Peninsula (Tolbachik and Avacha volcanoes): Natural origin or contamination? *Russian Geology and Geophysics (Geologiya i Geofizika)* 60 (5), 463–472 (605–618).
- Pujol-Solà, N., Proenza, J.A., Garcia-Casco, A., González-Jiménez, M., Andreazini, A., Melgarejo, J.C., Gervilla, F., 2018. An alternative scenario on the origin of ultra-high pressure (UHP) and super-reduced (SuR) minerals in ophiolitic chromitites: A case study from the Mercedita deposit (Eastern Cuba). *Minerals* 8, 433–440.
- Robinson, P., Bai, W.-J., Malpas, J., Yang, J.-S., Zhou, M.-F., Fang, Q.-S., Hu, X.-F., Cameron, S., Staudigel, H., 2004. Ultra-high pressure minerals in the Luobusa Ophiolite, Tibet, and their tectonic implications, in: Malpas, J., Fletcher, C.J., Aitchison, J.C., All, J. (Eds.), *Aspects of the tectonic evolution of China*. Geological Society of London, Special Publication 226, pp. 247–272.
- Seliverstov, V.A., 2009. Thermobarophilic Mineral Paragenesis Diamond Alkaline-Ultrabasic Volcanic Complex of Eastern Kamchatka. *Vestnik KRAUNC. Earth Sciences*, No. 1, 10–30.
- Seliverstov, V.A., Kaminsky, F.V., 1994. High-pressure mineral associations in alkaline ultramafic volcanics of Kamchatka Peninsula, Russia, in: *Proc. International Volcanological Congress*, Ankara, Turkey. Ankara, pp. 160–163.
- Sergeeva, O.S., 2000. Morphological features of diamonds from the Gryb pipe, in: *Essays on Geology and Minerals of the Arkhangelsk Region* [in Russian]. Izd. Pomorskogo Universiteta, Arkhangelsk, pp. 97–102.
- Shatsky, V.S., Rylov, G.M., Efimova, E.S., De Corte, K., Sobolev, N.V., 1998. Morphology and real structure of microdiamonds from the metamorphic rocks of the Kokchetav massif, kimberlites and alluvial placers. *Russian Geology and Geophysics (Geologiya i Geofizika)* 39 (7), 949–961 (942–955).
- Shcheka, S.A., Ignat'ev, A.V., Nechaev, V.P., Zvereva, V.P., 2006. First diamonds from placers in Primorye. *Petrology* 14 (3), 299–317.
- Shilo, N.A., Kaminsky, F.V., Lavrova, L.D., Dolmatov, B.K., Pleshakov, A.P., Tkachenko, L.A., Shepeleva, K.A., 1979. First diamond find in ultrabasic rocks of Kamchatka. *Dokl. Akad. Nauk SSSR*, No. 248, 176–179.
- Shipilo, V.B., Dutov, A.G., Komar, V.A., Shipilo, N.V., Azarko, I.I., 2005. Crystallization of diamonds in system Mn-Ni-C. *Inorg. Mater.* 41 (3), 293–296.
- Silaev, V.I., Karpov, G.A., Rakin, V.I., Anikin, L.P., Vasiliev, E.A., Filippov, V.N., Petrovskiy, V.A., 2015. Diamonds in the products of Tolbachik fissure eruption 2012–2013, Kamchatka. *Vestnik Permskogo Universiteta*, No. 1 (26), 6–27.
- Silaev, V.I., Vergasova, L.P., Vasil'ev, E.A., Karpov, G.A., Sukharev, A.E., Filatov, S.K., 2016. Microparagenesis of diamond and native aluminum in ejecta of recent volcanism. *J. Volcanol. Seismol.* 10 (1), 64–70.
- Silaev, V.I., Karpov, G.A., Anikin, L.P., Vasiliev, E.A., Vergasova, L.P., Smoleva, I.V., 2019a. Mineral phase paragenesis in explosive ejecta discharged by recent eruptions in Kamchatka and the Kuril Islands. Part 1. Diamonds, carbonaceous phases, and condensed organoids. *J. Volcanol. Seismol.* 13 (5), 323–334.
- Silaev, V.I., Karpov, G.A., Anikin, L.P., Vergasova, L.P., Filippov, V.N., Tarasov, K.V., 2019b. Mineral phase paragenesis in explosive ejecta discharged by recent eruptions in Kamchatka and on the Kuril Islands. Part 2. Accessory minerals of the Tolbachik type diamonds. *J. Volcanol. Seismol.* 13 (6), 376–388.
- Smit, K.V., D'Haenens-Johannsson, U.F.S., Howell, D., Loudin, L.C., Wang, W., 2018. Deformation related spectroscopic features in natural Type 1b-1aA diamonds from Zimmi (West African Craton). *Mineral. Petrol.* 112 (S1), S243–S257.
- Sukharev, A.E., Petrovsky, V.A., 2019. Spectroscopic features of impact diamonds from the Popigai astrobleme, in: *Geology and Mineral Resources of the European Northeast of Russia*. Proc. XVII Geological Congress of the Republic of Komi [in Russian]. Syktyvkar, pp. 243–244.
- Tan, X., 2014. Catalyst alloys processing. *JOM* 66 (10), 2176–2185.
- Taylor, W.R., Canil, D., Milledge, H.J., 1996. Kinetics of Ib to IaA nitrogen aggregation in diamonds. *Geochim. Cosmochim. Acta* 60, 4725–4733.
- Volynets, V.F., Zadorozhny, I.K., Florensky, K.P., 1967. About the isotope composition of nitrogen in the Earth's crust. *Geokhimiya*, No. 5, 587–593.
- Wu, W., Yang, J., Wirth, R., Zheng, J., Lian, D., Qiu, T., Milushi, I., 2019. Carbon and nitrogen isotopes and mineral inclusions in diamonds from chromitites of the Mirdita ophiolite (Albania) demonstrate recycling of oceanic crust into the mantle. *Am. Mineral.* 104, 485–500.
- Xiong, F., Yang, J., Robinson, P.T., Dilek, Y., Milushi, I., Xu, X., Zhou, W., Zhang, Z., Rong, H., 2017. Diamonds discovered from high-Cr podiform chromitites from Bulqiza, eastern Mirdita ophiolite, Albania. *Acta Geol. Sin.* 91 (2), 455–468.
- Xu, X., Cartigny, P., Yang, J., Dilek, Y., Xiong, F., Guo, G., 2017. Fourier transform infrared spectroscopy data and carbon isotope characteristics of the ophiolite-hosted diamonds from the Luobusa ophiolite, Tibet, and Ray-Iz ophiolite, Polar Urals. *Lithosphere* 10 (1), 156–169.
- Yang, J., Robinson, P.T., Dilek, Y., 2015a. Diamond-bearing ophiolites and their geological occurrence. *Episodes* 38 (4), 344–364.
- Yang, J., Meng, F., Xu, X., Robinson, P.T., Dilek, Y., Makeyev, A.B., Wirth, R., Wiedenbeck, M., Cliff, J., 2015b. Diamonds, native elements and metal alloys from chromitites of the Ray-Iz ophiolite of the Polar Urals. *Gondwana Res.* 27, 459–485.
- Yang, J., Simakov, S.K., Moe, K.S., Scribano, V., Lian, D., Wu, W., 2020. Comment on “Comparison of enigmatic diamonds from the Tolbachik arc volcano (Kamchatka) and Tibetan ophiolites: Assessing the role of contamination by synthetic materials” by Litasov et al. 2019. *Gondwana Res.* 79, 301–303.
- Zelenski, M., Taran, Yu., 2011. Geochemistry of volcanic and hydrothermal gases of Mutnovsky volcano, Kamchatka: Evidence for mantle, slab and atmosphere contributions to fluids of a typical arc volcano. *Bull. Volcan.* 73 (4), 373–394.
- Zelenski, M., Malik, N., Taran, Yu., 2014. Emissions of trace elements during the 2012–2013 effusive eruption of Tolbachik volcano, Kamchatka: enrichment factors, partition coefficients and aerosol contribution. *J. Volcanol. Geotherm. Res.* 285, 136–149.
- Zinchuk, N.N., Koptil, V.I., 2003. Features of diamonds of the Siberian Platform [in Russian]. Nedra, Moscow.