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Why Tolbachik diamonds cannot be natural

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Abstract

Taking into account recent publications, we provide additional comprehensive evidence that type Ib cuboctahedral diamonds and some other microcrystalline diamonds from Kamchatka volcanic rocks and alluvial placers cannot be natural and undoubtedly represent synthetic materials, which appear in the natural rocks by anthropogenic contamination. The major arguments provided in favor of the natural origin of those diamonds can be easily disproved. They include the coexistence of diamond and deltalumite from Koryaksky volcano; coexistence with super-reduced corundum and moissanite, Mn-Ni silicide inclusions, F-Cl enrichment and F/Cl ratios, and carbon and nitrogen isotopes in Tolbachik diamonds, as well as microtwinning, Mn-Ni silicides, and other inclusions in microcrystalline diamond aggregates from other Kamchatka placers. We emphasize the importance of careful comparison of unusual minerals found in nature, which include type Ib cuboctahedral diamonds and super-reduced phase assemblages resembling industrial slags, with synthetic analogs. The cavitation model proposed for the origin of Tolbachik diamonds is also unreliable since cavitation has only been shown to cause the formation of nanosized diamonds only.

Keywords: Diamond, Kamchatka, metal catalyst, silicide, super-reduced phases, cavitation, HPHT synthesis

Introduction

Recently, we presented comprehensive evidence that type Ib cuboctahedral diamonds from the 2012–2013 eruption of Tolbachik volcano (Kamchatka) represent anthropogenic contamination based on the data on metallic inclusions, which closely correspond to the typical $Mn_{60}Ni_{40}$ catalyst used for the production of synthetic diamond in the Soviet Union/Russia (Litasov et al. 2019a; Pokhilenko et al. 2019). We also argued that microcrystalline, carbonado-like diamond aggregates found in Kamchatka volcanoes and placers (Kaminsky et al. 2016, 2019) most likely represent contamination by polycrystalline diamond compacts (PDC) and synthetic "carbonado" as they contain Mn-Ni-Fe-bearing inclusions in the proportions of elements close to synthetic catalysts and characteristic Si and SiC inclusions of bonding and reactionary materials used for the fabrication of PDC (Litasov et al. 2020a). Finally, we emphasized the wide appearance of $Ni_{70}Mn_{25}Co_5$ metallic inclusions in similar diamonds from ophiolite peridotite and chromitite, which also indicates their appearance by anthropogenic contamination (Litasov et al. 2019a, 2019b, 2020b) as this composition ($Ni_{70}Mn_{25}Co_5$) corresponds to the widely used catalyst for synthetic diamond production in China. Indeed, these papers caused extensive discussion and criticism (Yang et al. 2020; Kaminsky et al. 2020).

Galimov et al. (2020) provided new interesting data on type Ib cuboctahedral diamonds found on the top of the lava flows at Tolbachik volcano and re-argued that they are of natural origin and could be formed by chemical vapor deposition (CVD) or by hydrodynamic or acoustic cavitation in the gas bubbles, which can collapse and generate intense shock waves. Consequently, we must once again draw the attention of the scientific community to the problem of Tolbachik diamonds and summarize below our criticism of the previously published conclusions (Karpov et al. 2014; Anikin et al. 2018; Silaev et al. 2019a, 2019b; Gordeev et al. 2019; Kaminsky et al. 2020) that these diamonds are natural. In this manuscript, we provide additional comprehensive evidence that type Ib cuboctahedral diamonds and some other microcrystalline diamonds from Kamchatka placers cannot be natural and undoubtedly represent synthetic materials, which appear in the natural rocks by anthropogenic contamination.

Samples and analytical methods

This paper is devoted to the discussion and presentation of some additional original data on synthetic diamonds and diamonds found at Tolbachik volcano. Thus, detailed information on analytical methods can be found in Litasov et al. (2019a) and only a brief summary is provided here. The samples were characterized by Fourier transform infrared (FTIR) spectroscopy using a Bruker VERTEX 70 spectrometer equipped with a HYPERION 2000 microscope at the Institute of Geology and Mineralogy, Siberian Branch Russian Academy of Sciences (IGM SB RAS) in Novosibirsk. Backscattered electron images and chemical analysis of host rock minerals were obtained using a MIRA 3 LMU scanning electron microscope (Tescan Orsay Holding) coupled with an INCA energy-dispersive X-ray microanalysis system 450 equipped with the liquid nitrogen-free Large area EDS X-Max-80 Silicon Drift Detector (Oxford Instruments Nanoanalysis Ltd.) at IGM SB RAS. The laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) data were obtained using an in-house laser ablation system (Cyber Probe) combined with a

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Yb:KGW femtosecond laser (CARBIDE, Light Conversion, Vilnius, Lithuania) and a galvanometric fast scanning laser system at Geochemical Research Center, The University of Tokyo (Makino et al. 2019). A focused ion beam (FIB) system (FEI Scios) was used to prepare thin cross-section foils of approximately 15 × 10 × 0.1 μm for microtexture observation and elemental mapping of inclusions using transmission electron microscopy (TEM) with a high-resolution energy-dispersive X-ray (EDX) spectrometer. The TEM study was performed using JEOL JEM-2100F (Ehime University, Matsuyama, Japan) operated at 200 kV and equipped with two CCD cameras (Gatan, Orius 200D, and UltraScan1000).

RESULTS AND DISCUSSION

Diamond finding and coexistence with deltalumite

Galimov et al. (2020) reported that about 500 diamond grains were recovered from the powdery white coating of deltalumite on the basaltic lava sample from the Leningradskoe flow of the 2012–2013 eruption of Tolbachik volcano. They show cubic or tetragonal carbon pieces on deltalumite from Koryaksky volcano and claimed that this carbon is diamond without confirmation (Fig. 1a). Although diamond crystals can have cubic shapes, in association with deltalumite it is more appropriate for unusual graphite (e.g., Korsakov et al. 2019) (Fig. 1b). Deltalumite is also not confirmed by the original data. The identification of diamond and deltalumite by EDX spectra alone is not sufficient. Nevertheless, the authors conclude that an in situ coexistence of diamond with deltalumite from Koryaksky volcano is the most important proof of the natural origin of diamonds from Tolbachik and other Kamchatka volcanoes. It is difficult to understand how this unidentified carbon grain from Koryaksky volcano can confirm the natural origin of cuboctahedral type Ib diamonds from Tolbachik volcano.

We believe that deltalumite in diamond-bearing samples from Tolbachik and Koryaksky volcano should first be confirmed by spectroscopic methods or by X-ray diffraction. The carbon fragment in Figure 1a is very interesting and should also be identified at least by Raman spectroscopy. It is clear that the morphology of this carbon fragment is completely different from Tolbachik cuboctahedral diamonds. The confirmation of deltalumite in association with diamonds would be extremely important because it clearly indicates that the assemblage cannot be related to high pressures since deltalumite is a low-pressure phase (Wilson and McConnell 1980; Levin and Brandon 1998).

Galimov et al. (2020) note that several tens of diamonds were collected from another place near Naboko vent, a few were collected from the Toludskoe lava field and some from the lava of the 1975 eruption, and that these diamonds have the same size and morphology as those from 2012–2013 lava of the Leningradskoe flow described in their paper. It seems that it is extremely important to present data on these separately found diamonds for comparison of the infrared spectra and composition of the microinclusions with those from Leningradskoe flow. Unfortunately, the authors did not perform this important study.

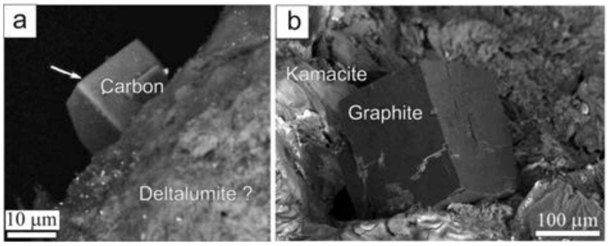

FIGURE 1. Cubic carbon fragment on deltalumite (?) from Koryaksky volcano (modified from Anikin et al. 2018) (**a**) and cliftonite-like cubic graphite coexisting with kamacite from Ozernaya mountain Fe-Ni-bearing basaltic intrusion (Norilsk, Russia) (modified from Korsakov et al. 2019).

P-T stability field of Al_2O_3-deltalumite

Deltalumite, δ-Al_2O_3, was discovered by Pekov et al. (2019) in rounded aggregates from Tolbachik volcano. It is dimorphous to corundum α-Al_2O_3 and has a spinel superstructure with $P\bar{4}m2$ space group. The structural formula is $(Al_{0.67}\square_{0.33})Al_2O_4$. It is a thermodynamically metastable phase with a narrow *P-T* field of crystallization (Wilson and McConnell 1980; Levin and Brandon 1998). Different polymorphs of Al_2O_3 can be synthesized by heating of different aluminum hydroxides. Each of them has its own sequence of transformation in the temperature range of 250–1000 °C that ends with the high-temperature corundum structure (Wefers and Misra 1987).

The δ-Al_2O_3 is a member of the boehmite sequence of transformations: boehmite, γ-AlOOH (<500 °C) → γ-Al_2O_3 (500–700 °C) → δ-Al_2O_3 (700–900 °C) → θ-Al_2O_3 (900–1000 °C) → α-Al_2O_3 (>1000 °C) (Wilson and McConnell 1980; Levin and Brandon 1998). In Tolbachik, the formation of deltalumite may be connected to the reaction of fumarole gases with basaltic magma. It is difficult to determine whether deltalumite was crystallized directly from the reaction or by heating of boehmite and γ-Al_2O_3 (Pekov et al. 2019). The kinetics of transformation is sluggish. At 1000 °C, the δ-Al_2O_3 totally disappears in about 8 weeks (Wilson and McConnell 1980).

High-pressure transformation from boehmite to corundum was not studied; however, it may be similar to that from diaspore to corundum. The kinetics of phase transitions is much faster with increasing pressure, and boehmite becomes unstable relative to diaspore when pressure is applied (e.g., Kennedy 1959). The transition from diaspore to corundum without intermediate phases occurs at 0.18 GPa and 396 °C and at 1.5 GPa and 515 °C in <70 h (e.g., Haas 1972; Fockenberg et al. 1996), i.e., at much lower temperatures than the temperatures of deltalumite existence at 1 atm. Thus, it is clear that diamond and deltalumite cannot be the syngenetic minerals and "the most important proof of the natural origin of diamonds from Tolbachik" (Galimov et al. 2020) is compromised.

The phases coexisting with Tolbachik diamond

In addition to the Al_2O_3-bearing phase, diamond coexists with a moissanite, corundum, sulfides, Mn-Ni and Cu-Sn alloy, native iron, aluminum, silicon, and copper (Galimov et al. 2020). Some other coexisting and associated minerals reported by Karpov et al. (2014) and Silaev et al. (2019b) include Cu-Zn alloy, Fe-Ti-silicide, WC, and many other phases. Some of the metallic particles can be formed by volcanic activity and reactions with fumarole gases; however, they should not be considered all together. For example, Cu, Cu-Sn, and Cu-Zn are common alloy binders for diamond-WC and diamond-Fe abrasives and other industrial tools (e.g., Pekker et al. 1988; Gorbunov et al. 1990), whereas Fe-Ti-silicides are the most common inclusions in Al_2O_3- and SiC-based abrasives and ceramics (Litasov et al. 2019c).

However, the most convincing evidence for anthropogenic contamination, other than diamond itself, is corundum with super-reduced (SR) inclusions. Silaev et al. (2019b) described Ti-bearing corundum grains with TiN (hamrabaevite) and TiC (osbornite) and argue that they are associated with the diamond at Tolbachik volcano.

Recently, we discussed the possibility of anthropogenic contamination of alluvial deposits near Mt. Carmel (Israel) (Griffin et al. 2018a, 2019) by abrasive materials or industrial slags after ferroalloy production (Litasov et al. 2019c, 2019d). The grains of fused alumina and corundum from Mt. Carmel contained nearly the same mineral assemblage, which includes Ti_2O_3-tistarite, $Ti_4Al_2ZrO_{11}$-carmeltazite, Fe-Si-Ti-alloys, TiN_{1-x}, and TiC_{1-x}. Similar Ti-bearing corundum grains with tistarite, carmeltazite, Fe-Si-Ti-alloys, TiN, and Ti-Si-nitrophosphides were described in mineral concentrates from a Tibet ophiolite (Xu et al. 2013, 2015).

Tatarintsev et al. (1987) studied heavy mineral concentrate from Devonian volcanic breccia and Quaternary alluvial deposits of the Donetsk region, which also contain also small remnants of garnet peridotites and mantle minerals, such as pyrope, Cr-spinel, and picroilmenite. The SR phases are represented by metallic iron, Mn-silicides, Fe- and Ti-carbides, moissanite, and Ti-bearing corundum. The microinclusions in corundum contain spinel, Fe-Ti-silicides, silicates, anorthite glass, perovskite, TiN, and carmeltazite (which they named the Ti-Al-Zr phase).

How can Ti-bearing corundum with SR inclusions, which is equivalent to industrial fused alumina (Litasov et al. 2019c), crystallize in such different geological environments? Griffin et al. (2018b) argued that all these findings indicate the widespread occurrence and natural origin of corundum with SR inclusions, however, a reliable model of the origin is difficult to constrain and moreover it should be nearly similar for very contrast geological environments, whereas similarities with industrial alumina-bearing slags are very clear (Litasov et al. 2019c, 2019d). Ballhaus et al. (2017) proposed a lightning strike hypothesis for the origin of the SR phases, but this formation mechanism is applicable to micrometer-sized crystals and hardly explains the observed mineral assemblages with a relatively large grain size up to several centimeters.

Microinclusions in Tolbachik diamonds and "kamchatites"

Galimov et al. (2020) determined similar compositions of metallic inclusions in Tolbachik diamonds to those reported by Litasov et al. (2019), however, they provided more comprehensive data. They show that: (1) Mn-Ni inclusions vary in composition from MnNi to Mn_2Ni with 45–67 wt% Ni; (2) the Mn-Ni inclusions contain up to 5 wt% Si; (3) silicides with 19 at% Si were found in polycrystalline carbonado-like aggregates from other placers in Kamchatka (Kaminsky et al. 2019); and (4) various Mn-silicides appear in the inclusions, which were not reported for synthetic diamonds before, based on very limited reference data (Bezrukov et al. 1972; Pal'yanov et al. 1997; Lang et al. 1995). Thus, Galimov et al. (2020) argued that the Si-bearing nature of metallic inclusions in Tolbachik diamonds undoubtedly proves their natural origin.

In Litasov et al. (2019b), we showed that the trace element composition of the individual diamonds could vary widely with respect to Mn/Ni ratio, from pure Mn to pure Ni. However, most analyses show compositions that are close to those of catalysts. Similar data were obtained by X-ray diffraction, where pure β- or γ-Mn, intermediate alloys, and Ni_3Mn were recognized (e.g., Detchuev et al. 1983). Yet, the average composition of Mn-Ni inclusions in diamonds from Tolbachik reported by Galimov et al. (2020) is $Mn_{57}Ni_{43}$, which is very close to the $Mn_{60}Ni_{40}$ catalyst.

There are more than 50 papers devoted to microinclusions in synthetic diamonds published only in Russian literature, which are available to the authors of Galimov et al. (2020). These papers show that Si impurities are common for industrial synthetic diamonds. We can note only two references, which show up to 0.2 wt% Si in synthetic diamonds (with Mn = 0.3–0.4 wt% and Ni = 0.4–0.6 wt%) determined by emission spectroscopy (Otopkov et al. 1974) and similar data with 0.05–0.2 wt% Si in diamonds (with Mn ≈ 0.2 wt% and Ni ≈ 0.25 wt%) determined by instrumental neutron activation analysis (Novikov et al. 1987). These data indicate that Si/metal ratios can be high enough to produce silicides in the inclusions. One additional study can be mentioned where Vishnevsky et al. (1975) reported NiO, MnO, MnO_2, $MnTiO_3$, metallic γ-Ca, and Ca-silicate or carbonate among inclusions in diamonds synthesized using Mn-Ni catalyst. The inclusions were identified by X-ray diffraction.

Indeed, even in the papers cited by Galimov et al. (2020), we can find some additional information. Bezrukov et al. (1972) noticed up to 5 wt% Fe and Si impurities in the Mn-Ni inclusions from synthetic diamonds. Pal'yanov et al. (1996) described Fe-Ni metal, wüstite, magnetite, chromite, and silicates (garnet, orthopyroxene) as inclusions in diamonds grown using Fe-Ni catalyst. Lang et al. (1995) noticed Fe-Co inclusions coexisting with garnet and pyroxene from synthetic diamond, which indicate the presence of Si in the growth medium. All authors explained the appearance of silicates by the diffusion of surrounding materials into the melt and by impurities in the initial chemical reagents. We also noticed a significant Si-content in synthetic diamonds (Litasov et al. 2019b), however, quantitative calibration was difficult due to the high SiO_2 content in the standard material. We can clearly see the signal from Si in the time-resolved spectra during the LA-ICP-MS measurements both in Tolbachik and synthetic diamonds (Fig. 2). The intensity of the Si signal positively correlates with that from metal, and Si intensities in Tolbachik diamonds are comparable with those from synthetic ones (Fig. 3).

The possible source of Si-impurities in synthetic diamonds is very clear. It is either minor part of Mn-Ni catalyst that, according to the GOST standard, may contain up to 1.5 wt% Fe and Si (Shipilo et al. 2005) or the high-pressure cell material used in diamond synthesis, "catlenite" or "lithographic stone" (Zhigadlo 2014), which is a well-sintered Ca-carbonate containing up to 15 wt% silicates. It was shown that this material could diffuse into the growth medium during industrial synthesis (e.g., Davydov et al. 1982; Litasov et al. 2019a). Importantly, Si, and even Ca, can be reduced to metal during diamond synthesis, and this is confirmed by original data (Vishnevsky et al. 1975). It should be noted that pyrophyllite was also used as a pressure medium for similar experiments (Zhang 1986). In this case, the penetration of Si into the diamond growth medium is even more obvious. We also analyzed several conventional Mn-Ni and Fe-Ni

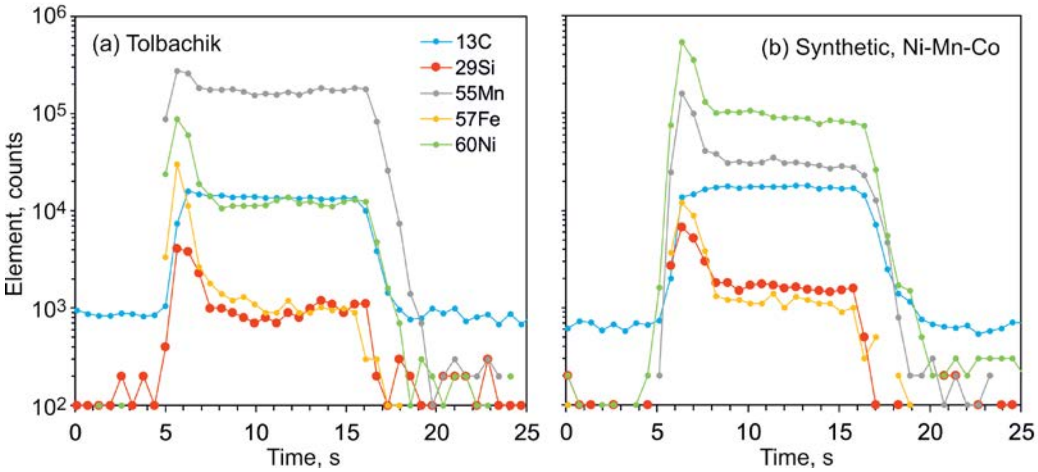

FIGURE 2. Intensity of ^{13}C, ^{29}Si, ^{55}Mn, ^{57}Fe, and ^{60}Ni signals during LA-ICP-MS measurements of (**a**) Tolbachik diamond (Litasov et al. 2019a) and (**b**) synthetic type Ib diamonds grown using $Ni_{70}Mn_{25}Co_5$ catalysts (Litasov et al. 2019b). (Color online.)

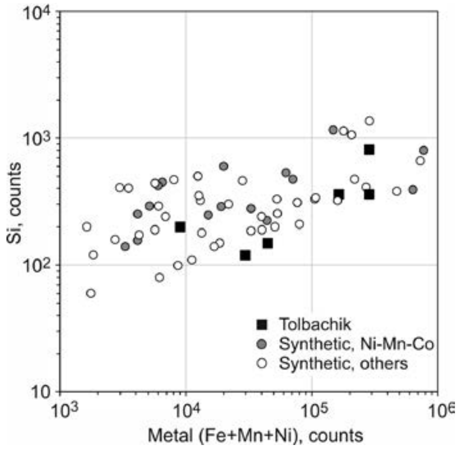

FIGURE 3. Si vs. metal (Fe+Mn+Ni) intensities of LA-ICP-MS measurements in Tolbachik and synthetic type Ib diamonds grown using $Ni_{70}Mn_{25}Co_5$ (Litasov et al. 2019b) and other catalysts.

catalysts for synthetic diamond growth and confirmed that the major impurities are represented by Si and Fe (for Mn-Ni) in the amounts of up to 0.6 wt% (Table 1).

Although Mn-silicides were not reported as inclusions in synthetic diamonds so far, it can be emphasized that silicide phases were described in synthetic diamonds grown using the media other than Mn-Ni alloy. Yin et al. (2000a, 2000b), using transmission electron microscopy, observed $(Fe,Ni)_{23}C_6$, $FeSi_2$, and SiC inclusions in diamonds grown from the Fe-Ni-C system. Later, similar inclusions of Fe_3C, $FeSi_2$, SiO_2, and fcc-SiC were identified in diamonds grown in the Fe-C system (Yin et al. 2001). All these data indicate that Mn/Ni-variability and Mn-silicides cannot be considered as a specific natural feature of inclusions in Tolbachik diamonds.

The high-Si inclusions and interstitial Si and SiC described by Kaminsky et al. (2016, 2019) in microcrystalline diamond aggregates from Kamchatka, named "kamchatite," were discussed in detail by Litasov et al. (2020a), and they have no similarities with the Tolbachik diamonds. Kaminsky et al. (2020) ignore the facts that: (1) diamond aggregates from Avacha volcano and Aynyn river are completely different, the first represents synthetic "carbonado," whereas the second appears to be PDC prepared by impregnation of metallic Si into diamond powder [the images of PDC can be found in Shulzhenko et al. (2000), Shimono and Kume (2004), and Boland and Li (2010)]; (2) Mn-Ni silicides would be a common product of PDC fabrication, due to the migration of Mn-Ni metallic inclusions in diamond crystals toward the surface during high-temperature annealing (e.g., Otopkov et al. 1974; Webb and Jackson 1995), and Mn/Ni ratio in these silicides perfectly matches the $Mn_{60}Ni_{40}$ catalyst (Table 1); (3) almost all other inclusions and interstitial minerals, SiC, SiO_2, Si, $CaCO_3$, β-Mn, W_2C, and B_4C match with industrially synthesized synthetic "carbonado" and PDC; and (4) nanotwinning is a common phenomenon in synthetic diamonds (e.g., Malov 1971; Westraadt et al. 2007). We emphasize that some minor features of microcrystalline diamond aggregates are not yet explained by the synthetic origin, and the major mineral associated with the purported diamonds, tilleyite (Kaminsky et al. 2019), has not been observed in synthetic diamonds. Kaminsky et al. (2020) noticed that "drilling operations occur worldwide every day, but they never produce tilleyite." However, no one has investigated used industrial diamonds to find tilleyite. Tilleyite

TABLE 1. Composition (wt%) of industrial Mn-Ni and Fe-Ni catalysts for synthetic diamonds in USSR/Russia determined by energy-dispersive X-ray microanalysis

	IHPP-1	IHPP-2	PRGN-40[a]	Ukraine	Belarus
N	16	14	20	10	10
Si	0.49(6)	0.18(3)	0.57(8)	0.55(9)	0.13(4)
Ti	–	–	0.19(4)	0.18(6)	0.05(3)
Cr	–	–	0.24(5)	0.37(4)	0.05(4)
Mn	49.3(0.8)	–	59.4(1.0)	49.4(7)	0.16(5)
Fe	0.13(4)	69.5(1.1)	0.51(8)	0.55(12)	59.6(1.0)
Co	0.17(3)	0.14(4)	–	0.21(7)	–
Ni	49.5(1.1)	29.8(5)	38.9(0.8)	49.1(8)	40.2(1.3)
Total	99.6(1.0)	99.6(8)	99.8(1.0)	100.4(9)	100.2(1.1)

Notes: N = number of analyses. IHPP = Institute for High Pressure Physics.
[a] Polema company. The alloys contain also minor carbon and oxygen. The standard deviation is in parentheses.

is a very reasonable product of oxidation and contamination during the synthesis of PDC or synthetic "carbonado" or may be formed during or after the use of a drill bit.

We should also emphasize that Fe-Ni inclusions observed in natural diamonds and mentioned by Galimov et al. (2020) should not be directly extrapolated to Tolbachik diamonds, because they have completely different characteristics. For example, E. Smith et al. (2016) described Fe-Ni-C-S inclusions, which consist of Fe-Ni-metal, $(Fe,Ni)_3C$, and FeS in type IIa diamonds. These metallic aggregates coexist with majorite garnet and Ca-bearing minerals (walstromite, larnite, Ca-Ti perovskite). In other reports (Haggerty 1975; Sobolev et al. 1981) metallic Fe and Fe-Ni inclusions are also associated with Fe-sulfide, which is a characteristic feature of the deep-seated diamonds.

Galimov et al. (2020) also provided the F/Cl ratio determined for one Tolbachik diamond (0.39) and argue for a close relation of diamonds to the gases from the host lava, which have F/Cl = 0.37 (Zelenski et al. 2014). Statistics for such a conclusion based on data from a single diamond are not enough. Surprisingly, the data reported by Galimov et al. (2020) in Table 1 indicate a ratio F/Cl = 0.19 in volcanic gases, whereas for Tolbachik lava Zelenski et al. (2014) reported an average F/Cl ratio of 1.43.

These F/Cl ratios are not compared to F and Cl in synthetic diamonds. The pores around metallic and silicide inclusions in transmission electron microscope (TEM) films are also enriched by F, Cl, and O. This is a common feature for all thin diamond films. It is known that about a third of the surface bonds of the diamond can be saturated with H, F, or Cl. Oxygen is also an important surface impurity (Sappok and Boehm 1968). Figure 4 shows the TEM-EDX spectrum of the area around small Mn-Ni inclusion in a synthetic diamond, which indicates a significant amount of F and Cl.

Figure 5 shows the F- and Cl-enrichment of a Mn-Ni-Si inclusion in the Tolbachik diamond described by Litasov et al. (2019a). The diamond surface itself is slightly enriched by F relative to Cl in both synthetic and Tolbachik diamonds. This indicates that secondary ion mass spectrometry (SIMS) or LA-ICP-MS data can give any F/Cl ratio depending on the amount of the microinclusions ablated under the laser beam. Thus, the F/Cl = 0.39 ratio for Tolbachik diamonds is insufficient evidence for the comparison of the purported diamonds with the host lava or volcanic gases from 2012–2013 eruption.

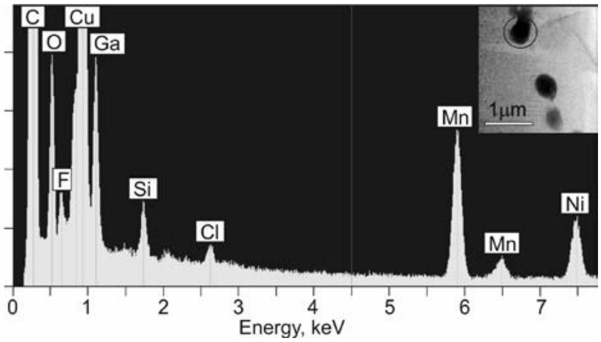

FIGURE 4. Example of TEM-EDX spectrum of the area around Mn-Ni inclusion in a synthetic diamond, grown from Mn-Ni-C system and showing significant O, F, and Cl peaks. Insert shows an SEM image of the inclusions and encircled analyzed spot. Cu and Ga are from TEM grid and ion beam, respectively.

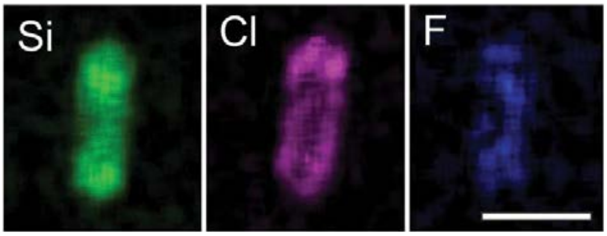

FIGURE 5. TEM-EDX element maps for Si, Cl, and F in the Mn-Ni inclusion in Tolbachik diamond (see Fig. 5 in Litasov et al. 2019a). Scale bar 100 nm. (Color online.)

Similarly, a higher concentration of trace elements in ophiolitic diamonds relative to synthetic one (Howell et al. 2015) is not a criterion for natural origin, as stated by Galimov et al. (2020). Litasov et al. (2019a) noticed that absolute values of the trace element concentrations in diamonds with metallic inclusions have no meaning because they depend on the amount of inclusions captured by the laser beam during analysis. The elemental ratios are instead important and in the case of Tolbachik or ophiolitic diamonds they correlate with the compositions of catalyst used for diamond synthesis (Litasov et al. 2020b).

Infrared and cathodoluminescence spectroscopy

The FTIR spectra of Tolbachik diamonds resemble those from synthetic diamonds and show the abundance of single-nitrogen atom C-centers with total N-content of 100–500 ppm (Figs. 6–7). Diamonds from an ophiolite (Xu et al. 2018) rarely contain minor A-centers (Figs. 6–7), which is also possible for synthetic diamonds. Galimov et al. (2020) suggested that similar type Ib diamonds can rarely be found in nature and noticed as an example those from the Kokchetav massif (Khachatryan 2013). We examined the single spectrum of a presumably Ib diamond from Kokchetav massif reported by Khachatryan (2013) and found that it shows completely different peak positions and extremely low N-contents (Fig. 6). In contrast, the Kokchetav diamonds reported in other works always have significant amounts of A-centers corresponding to type Ib-IaA and, in general, contain very high amounts of total nitrogen (Fig. 7) (e.g., De Corte et al. 1998; Cartigny et al. 2004). The lowest nitrogen aggregation reported for natural diamonds was observed in microdiamonds from Dachine komatiites (French Guiana) (Cartigny 2010) and Zimmi alluvial deposits (West Africa) (Smit et al. 2016, 2018). They may be comparable with Tolbachik and ophiolite diamonds by FTIR spectra, but clearly have some other distinctive features, such as sulfide inclusions (Smit et al. 2016, 2018; C. Smith et al. 2016).

Some minor features from FTIR spectra of Tolbachik diamonds, such as bands near 1508 cm^{-1} and broadband near 3400 cm^{-1}, that are related to water impurities or surface contamination are also common for the synthetic diamonds.

An explanation of the FTIR spectra for Tolbachik and especially for ophiolite diamonds is a serious issue since they indicate very short residence time under high pressures and temperatures (Evans and Qi 1982; Xu et al. 2018). Galimov et al. (2020) noticed that this can be explained by the cavitation hypothesis,

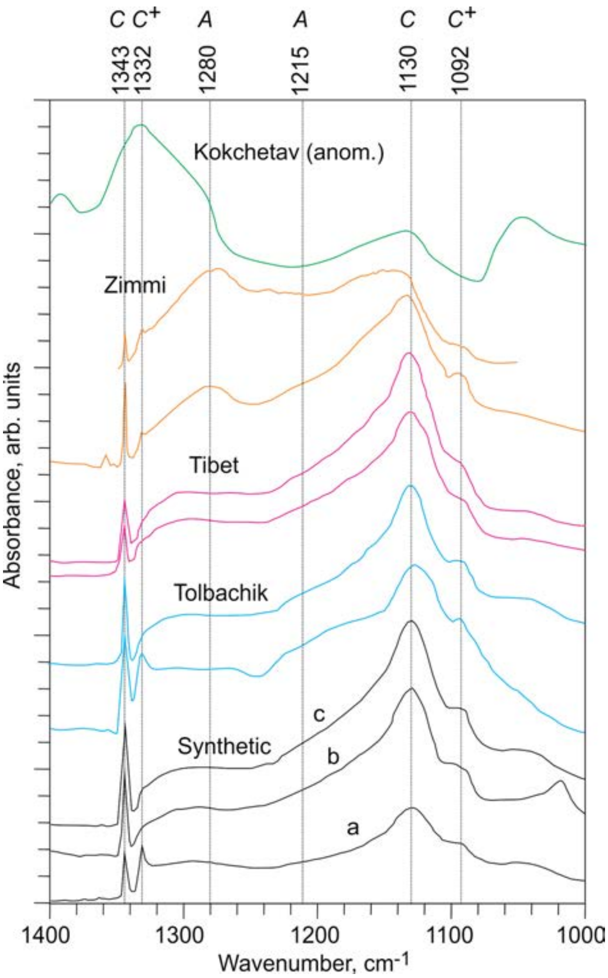

FIGURE 6. FTIR spectra of type Ib and Ib-IaA diamonds from different sources: Synthetic diamonds from (**a**) experiment with Mn-Ni catalyst at 6 GPa and 1400 °C (**b**) saw grit and (**c**) used drill bit. Tolbachik diamonds (Litasov et al. 2019a; Pokhilenko et al. 2019); diamonds from Tibet ophiolite (Xu et al. 2018); diamonds from Zimmi alluvial deposits (West Africa) (Smit et al. 2016, 2018); anomalous metamorphic diamond from Kokchetav massif (Khachatryan 2013). Note that most typical metamorphic diamonds correspond to clear Ib-IaA type with significant degree of A-centers aggregation. (Color online.)

which is described below. Indeed, this idea does not stand up to criticism. Figure 8 shows cathodoluminescence images of Tolbachik and synthetic diamonds with clear sectorial growth zones that, without a doubt, is impossible for fast non-directional growth in a cavitation bubble.

Other evidence for the natural origin of Tolbachik diamonds

Carbon isotope measurements for Tolbachik diamonds are not informative as all type Ib diamonds (with FTIR spectra similar to standard synthetic diamonds) found in nature, including those from ophiolites worldwide, have low $\delta^{13}C$ values in the range from –22 to –30‰ (Karpov et al. 2014; Xu et al. 2018) resembling the range for synthetic diamonds (Boyd et al. 1988; Reutsky et al. 2008; Xu et al. 2018). Rarely, this value in ophiolite diamonds is shifted to –17‰ (Xu et al. 2018).

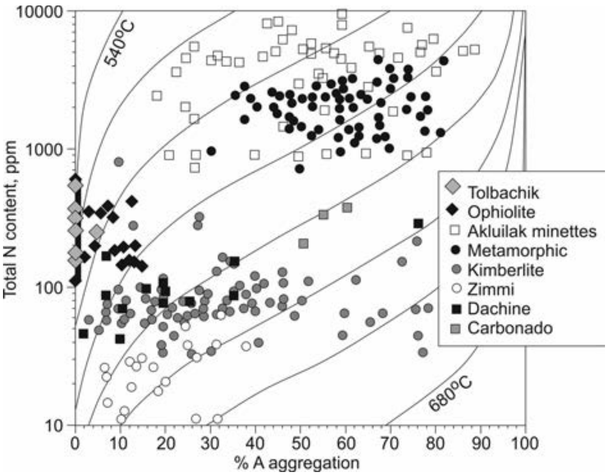

FIGURE 7. Nitrogen aggregation vs. nitrogen content in Tolbachik (this work) and ophiolite-hosted microdiamonds (Xu et al. 2018) in comparison with eclogite diamonds from kimberlite, metamorphic diamonds (mainly from Kokchetav massif), microdiamonds from Akluilak minettes (Canada) (Cartigny et al. 2004), diamonds from Dachine komatiite (French Guiana) and carbonado (Cartigny 2010), and Zimmi (West Africa) alluvial diamond (Smit et al. 2016). Black line from 100 to 500 ppm N indicate a range observed in ophiolite diamonds, which coincide in general with that for Tolbachik diamonds. Isopleths were calculated with the use of a residence time of 1 Ma for temperatures ranging, by steps of 20 °C, from 540 to 680 °C (Evans and Qi 1982).

Galimov et al. (2020) determined $\delta^{15}N = –2.3$ and –2.6‰ for two Tolbachik diamonds and argue that these values are different from synthetic diamonds, which should all have atmospheric $\delta^{15}N = 0$. This conclusion is not correct, because all previous measurements of $\delta^{15}N$ in synthetic diamonds indicate a wider range up to $\delta^{15}N = –2.5$‰ (Boyd et al. 1988), $\delta^{15}N = –5.6$‰ (Howell et al. 2015), and $\delta^{15}N = –10$‰ (Reutsky et al. 2008).

As we can see, the only reliable evidence of the natural origin of Tolbachik diamonds is the assertion of their finding in nature with presumably impossible contamination by anthropogenic materials. Even this single item of evidence becomes less sustainable taking into account the findings of fused alumina with TiN and TiC inclusions (Litasov et al. 2019c), moissanite, and industrial alloys (Cu, Cu-Sn, Al) (Pekker et al. 1988; Gorbunov et al. 1990) in the same probes (Silaev et al. 2019a, 2019b). All these materials may indicate anthropogenic contamination.

A model for the origin

A deep-seated origin of Tolbachik diamonds at static *P-T* conditions in the diamond stability field is not applicable due to the shallow location of magma chambers below the Klyuchevskoy group volcanoes and the short residence times of diamond crystals in basaltic magma before complete dissolution/oxidation (see Litasov et al. 2019a). The CVD model is also refuted by Galimov et al. (2020) as not reliable for the origin of Tolbachik diamonds. Galimov et al. (2020) suggested a cavitation model for the origin of Tolbachik diamonds by epitaxial crystallization from CH_4-bearing gas. No further explanations about the possibility of the cavitation synthesis of diamonds were provided.

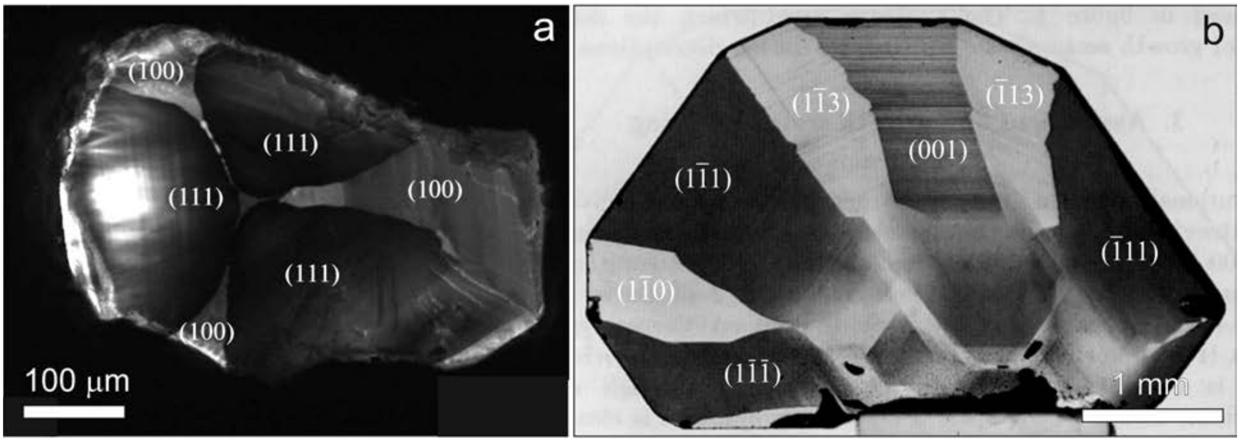

FIGURE 8. Cathodoluminescence images of Tolbachik diamond (modified from Karpov et al. 2014) and synthetic diamonds grown on seed (modified from Lang and Meaden 1991) indicating sectorial growth pattern typical for synthetic diamonds.

The cavitation hypothesis was proposed by Galimov (1973) to explain the origin of kimberlitic diamonds during fast ascent in a magma channel when they encounter constrictions. The limiting stage of crystal growth during the cavitation process is the duration of the shock wave formed by the collapse of a cavitation bubble, which is in the range of microseconds. In other words, it is not much different from the detonation synthesis of nanodiamonds (e.g., Baidakova 2014). Thus, the cavitation model is not applicable for natural relatively large single-crystal diamonds, and it was carefully discussed by Frank et al. (1973) in their comment on Galimov (1973). Similar arguments are still valid against the cavitation hypothesis during the formation of Tolbachik diamonds.

Frank et al. (1973) noticed that Galimov (1973) ignored the fundamental difference in the rate control between the martensitic transformation of crystals from one polymorphic modification to another if the carbon source is graphite or other carbon phases. It is well known that the shock transformation of graphite leads to the formation of thin lenses of nanocrystalline diamonds, such as in the Popigai impact crater (e.g., Ohfuji et al. 2015). If the carbon source is different from graphite, one would need time for diffusive segregation of chemical constituents. Galimov (1973) estimates the duration, t_c of dynamic pressure due to bubble collapse as 2×10^{-3} s (which is indeed overestimated). In this time, diffusive segregation could occur through a thickness of order $x = (Dt_c)^{1/2}$, where D is the diffusion coefficient. With a fairly generous allowance of 10^{-8} m^2 s^{-1} for D we have $x =$ 4.5 μm (Frank et al. 1973). One cannot expect sectorial growth of a 200–300 μm single crystal with metallic inclusions in 10^{-6} to 10^{-3} s, even during repeated cavitation episodes.

In the subsequent paper Galimov (1985) argued that kinetic limitations could be overcome by recrystallization of diamonds by the post-deformation annealing (e.g., Laudise 1970; Humphreys et al. 2017). The driving force of this process is accumulated elastic potential energy. The formation of the single crystal occurs due to the migration of grain boundaries and enlargement of grain size. This mechanism is useful for metals plastically deformed into a non-porous ingot, which further recrystallizes during a long time by post-deformation annealing (e.g., Fe for 1–2 h at 800 °C; Glover and Sellars 1972). Nanocrystalline diamonds or other non-metal materials cannot be deformed into homogenous ingot due to fracturing (Laudise 1970). Besides, post-deformation annealing of diamonds is possible at temperatures of about 3000 °C for a long time, exceeding hours. We conclude that the mechanism of post-deformation annealing does not work for single crystal growth of diamonds at all. Thus, the major arguments against the cavitation hypothesis are large grain size, sectorial growth of diamond crystals, and Mn-Ni-Si metallic inclusions, all features of typical synthetic diamonds.

We should mention that cavitation synthesis of diamond is a very prospective direction, which may be more favorable industrially than the detonation synthesis. At present, there are at least three reports of diamond crystallization during the cavitation process (Flynn 1986; Galimov et al. 2004; Khachatryan et al. 2008). The crystals were usually nanocrystalline and were identified by X-ray diffraction and Raman spectroscopy. However, Khachatryan et al. (2008) reported the formation of 5–10 μm diamond particles after repeated loading of the growth chamber by the cavitation fluid (aromatic compounds). Yet, there was no detailed characterization of those diamonds with transmission electron microscopy.

IMPLICATIONS

We argue that the cuboctahedral type Ib diamonds found in Tolbachik volcano and described in many recent papers, including detailed studies by Litasov et al. (2019a) and Galimov et al. (2020) have an anthropogenic origin. Taking into account the above discussion, the arguments in favor of the formation of Tolbachik diamonds in nature become negligible. There are still many unusual geological findings of diamonds in nontraditional environments, and we believe that their study should be performed by the close collaboration of field geologists with specialists in material science and synthetic diamonds, who can help to distinguish between natural and synthetic materials and perform experiments that can shed a light on the problem. At present, we believe that the amount of similarities between diamonds from Kamchatka and synthetic type Ib diamond is more than enough and leaves little space for further speculations about their origin.

We highlight the need to perform a more careful examination of diamonds and carbon phases from different locations in Kamchatka along with detailed trace element and spectroscopic characteristics of such important minerals as corundum and moissanite with the subsequent study of their microinclusions. These observations and measurements then need to be critically compared with industrially produced analogs. The finding of the unusual minerals in nature does not exclude anthropogenic factors. We emphasize that none of the described minerals were found in situ in the basaltic rocks of Kamchatka.

Another important problem in the description of diamonds from Tolbachik (Litasov et al. 2019a; Galimov et al. 2020), microcrystalline diamonds from other Kamchatka placers (Kaminsky et al. 2016, 2019; Litasov et al. 2020a), diamonds from ophiolite peridotite and chromitite (Howell et al. 2015; Xu et al. 2018; Lian and Yang 2019; Litasov et al. 2019b), some diamonds in metamorphic rocks (Farré-de-Pablo et al. 2019; Massonne 2019), and SR mineral assemblages from alluvium (Griffin et al. 2018a, 2018b, 2019; Litasov et al. 2019c, 2019d) is that authors of the original reports tend to mix all evidence from different rock types and environments together. We show that in many cases the phases from heavy concentrates, diamonds, SR minerals, and metals, have no relation to each other (Litasov et al. 2020a, 2020b). Every case should be carefully considered. There were many examples when new geological findings were approved or disproved with the appearance of additional evidence. We believe that the next important step is the detailed study of moissanite, which was found in many rocks around the globe (e.g., Lyakhovich 1980; Di Pierro et al. 2003; Zhang et al. 2016; Dobrzhinetskaya et al. 2018), and it is very difficult to determine its natural or artificial origin.

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