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Diamonds in the Kamchatka Peninsula (Tolbachik and Avacha Volcanoes): Natural Origin or Contamination?

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Abstract—Lavas of the Kamchatka volcanoes store cubic-octahedral diamonds identical in morphology and structure to synthetic crystals, and their natural origin is doubted. Judging by published data, the diamonds discovered in the Tolbachik lavas are similar to synthetic diamonds made by different producers, and the analyzed samples rather result from contamination with synthetic material. Ophiolite-hosted diamonds reported from Europe, China, Mongolia, and Polar Urals look like the Tolbachik diamonds and are of the same type. The similarity between crystals coming from geologically dissimilar objects indicates that contamination may occur in those cases as well. Thus, diamonds found in unusual hosts or geologic settings require careful checking. These findings have to be reproduced repeatedly in other *in situ* samples and approved by independent experts; with all respect to the priority of the first finders, the sampling sites should be open to many researchers, especially the respective specialists. The inevitable disproval of false diamond findings is discouraging and discredits the true discoveries. Possible contamination with synthetic or natural material from cutting tools has to be excluded in all newly found diamonds before claiming their natural origin.

Keywords: natural diamond, synthetic diamond, carbonado, volcano, ophiolite, contamination

INTRODUCTION

Several recent publications reported data on diamonds found in lavas of Tolbachik volcano in the Kamchatka Peninsula (Anikin et al., 2013; Gordeev et al., 2014; Karpov et al., 2014a,b; Silaev et al., 2015, 2016a,b; Galimov et al., 2016a,b). The evidence of the Tolbachik diamonds complements the previous reports on diamonds from Kamchatka which have appeared since 1975 (Kutyev and Kutyeva, 1975). The very discovery of diamonds in uncommon host rocks and geological settings has important genetic value (Sobolev, 1951) and is worth of close consideration. Several known unusual diamond sources include phyllites from Brazil (Moraes, 1934; Trofimov, 1967, 1980; Skosyrev, 1977; Zubarev, 1989; etc.), diamond-bearing ultrapotassic lamprophyres from Canada (MacRae et al., 1995; etc.), comatiites from French Guiana (Capdevila et al., 1999), the Kokchetav metamorphic rocks in Kazakhstan (Sobolev and Shatsky, 1990; Shatsky and Sobolev, 1993; Shatsky et al., 1995; Lavrova et al., 1999; Schertl and Sobolev, 2013; etc.), and some others. Even in those cases, the origin of diamonds and the ways they got into rocks remain sometimes uncertain. Note that the diamond potential of kimberlites and lamproites can be estimated using universal mineralogical and chemical criteria and explored with known methods based on specific indicators, whereas no indicators are known for exotic diamond hosts, and the respective exploration objectives hardly can be formulated clearly: their discovery is most often a matter of chance.

True diamond hosts of some unknown origin may really exist, and the future finders of such diamonds (especially fine crystals) deserve all respect. Yet, some discoveries appear doubtful, including those in volcanic rocks from Kamchatka, as well as in ophiolites from China, Urals (Xiong et al., 2014; Yang et al., 2014, 2015a,b; Howell et al., 2015; etc.), Bohemia (Naemura et al., 2011), and some other sites. The doubts arise from surprising similarity of these diamonds coming from genetically different rocks and tectonic setting (e.g., ophiolites from geographically dispersed regions and the Tolbachik lavas) to one another and to synthetic varieties used in cutting and polishing tools. Although being fully trustful to the authors of the findings, we suggest checking such diamonds for contamination; all possibilities for incorporation of synthetic diamonds into rocks have to be reviewed even when contamination appears unlikely.

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Unexpectedly discovered diamonds of this kind arouse much interest, sometimes scandalous, but often turn out to anyhow result from contamination. In his special publication on this subject, V. Sobolev (1979) outlined possible ways of contamination, formulated reliability criteria of diamond findings, and stressed the necessity of creating a detailed instruction for the respective checks. The first instruction appeared in the Ukraine, where such discoveries were especially frequent (Palkina and Polkanov, 2008). We know a great number of contamination cases, most often caused by cutting tools, and even a few cases when people implanted diamond crystals into samples deliberately, in order to receive funding for their research. Other ways of contamination and other sources of diamonds may also exist. People who find diamonds in exotic hosts often lack professional expertise but publish their results quickly as a sensation, being eager to "make a discovery". Such claims *a priori* require caution.

Discoveries of new diamond-bearing rocks deserve confidence only provided that the diamonds (a) differ markedly from those of possible contamination sources; (b) are found repeatedly in other samples of the same rock type, and the findings are confirmed by diamond experts; (c) occur *in situ*, inside rock samples or on natural fracture planes rather than on cut or polished surfaces. The latter criterion is optional though being hard to achieve even in usual diamond hosts such as kimberlites.

DIAMONDS FROM TOLBACHIK VOLCANO AND SYNTHETIC DIAMONDS, COMPARED

Methods. The natural origin of diamonds from the Tolbachik lavas likewise causes doubts. Several hundreds of diamond crystals discovered in a sample about 1 kg were characterized in detail (Dunin-Barkovsky et al., 2013), which allowed us to compare them with other varieties. The Tolbachik diamonds are identical to synthetic diamonds which are grown by spontaneous crystallization and are used broadly in tool-making industry (cutting and polishing wheels, drilling bits, abrasive powders, etc.). Below we compare the Tolbachik diamonds, including two samples selected for additional studies, with their synthetic counterparts.

The new diamond samples were analyzed by Fourier-transform infrared (FTIR) spectrometry and laser ablation mass spectrometry with inductively coupled plasma (LA ICP-MS). The FTIR spectra were collected on a Bruker VERTEX 70 spectrometer with a HYPERION 2000 IR microscope within 400–7500 cm^{-1} and an aperture of 100 × 100 μm using KBr pellets, at the V.S. Sobolev Institute of Geology and Mineralogy (IGM, Novosibirsk). LA ICP-MS data were collected on a Thermo Scientific iCAP-Qc mass spectrometer at the Nikolaev Institute of Inorganic Chemistry (IIC, Novosibirsk). The results were checked against the NIST-612 glass standard. Element concentrations were calculated by direct comparison of signals from the sample and the standard. Samples synthesized by the HPHT method at 6.0–7.5 GPa and ~1600 °C and diamonds from various cutting tools were additionally analyzed for comparison.

Crystal morphology. As follows from the description by Dunin-Barkovsky et al. (2013), the diamonds found in the Tolbachik lavas are flat and have well pronounced octahedral and cubic, as well as additional rhombic dodecahedral, tetragon-trioctahedral {311}, and trigon-trioctahedral {332} faces (Fig. 1). Note that these habits are common to synthetic diamonds and never occur in natural crystals. Silaev et al. (2015) compared the Tolbachik samples with synthetic diamonds produced at OAO Orbita-Almazinstrument in Syktyvkar in terms of crystal morphology and denied the synthetic origin of the Tolbachik diamonds for the absence of trigonal-trioctahedral faces. On the other hand, one of coauthors of the same publication (Rakin and Piskunova, 2012, 2014) independently reported the presence of trigonal-trioctahedral faces {221} in synthetic diamonds AS32 630/500 (GOST 9206–80). Furthermore, the indices of trigonal-trioctahedral faces assigned to the Tolbachik diamonds differ in different papers: {332} in (Karpov et al., 2014a; Silaev et al., 2015) and {221} (Rakin and Piskunova, 2012, 2014). Therefore, the presence or absence of trigonal-trioctahedral faces is not as important as (Silaev et al., 2015) claim, and the difference of the Tolbachik diamonds from synthetic samples is thus poorly grounded.

According to available experimental data, synthetic diamonds can develop various shapes upon changes in crystallization conditions and growth media (Bokii et al., 1986; Chepurov et al., 1997; Palyanov et al., 2015; etc.). Thus, comparing the Tolbachik diamond samples with a single variety of synthetic diamonds (actually, those obtained in a single pilot run at Orbita-Almazinstrument, while no serial production has ever occurred) appears unconvincing, as multiple known brands of synthetic diamonds by different producers are neglected. The latter inference is valid also for properties other than crystal morphology. The data reported by Silaev et al. (2015) suggest more similarity than difference between the Tolbachik and HPHT synthetic diamonds.

Silaev et al. (2015) conclude that the cubic-octahedral crystals would crystallize at lower temperatures than the natural diamonds: 1800–2000 °C (!) against 2200–2500 °C (!). Yet, the true crystallization temperature of natural diamonds is at least 1000 °C lower (Bobrievich et al., 1959; Sobolev et al., 1969, 1984, 1986; Bezrukov et al., 1976; Richardson et al., 1984; Pokhilenko et al., 1991, 1993, 2015; Palyanov et al., 2015; etc.). Diamonds that form within the diamond stability field at 1000 to 1400 °C commonly reside in xenoliths of diamond-bearing eclogites first reported from Yakutian kimberlites (Bobrievich et al., 1959), as well as in dunite-harzburgites (Pokhilenko et al., 1977, 1991, 1993, 2014, 2015; Sobolev et al., 1984) and their derivate serpentinites (Sobolev et al., 1969), which are typical rocks of lithospheric mantle.

Color. The greenish-yellow color of the Tolbachik diamonds perfectly matches that of synthetic diamonds and is

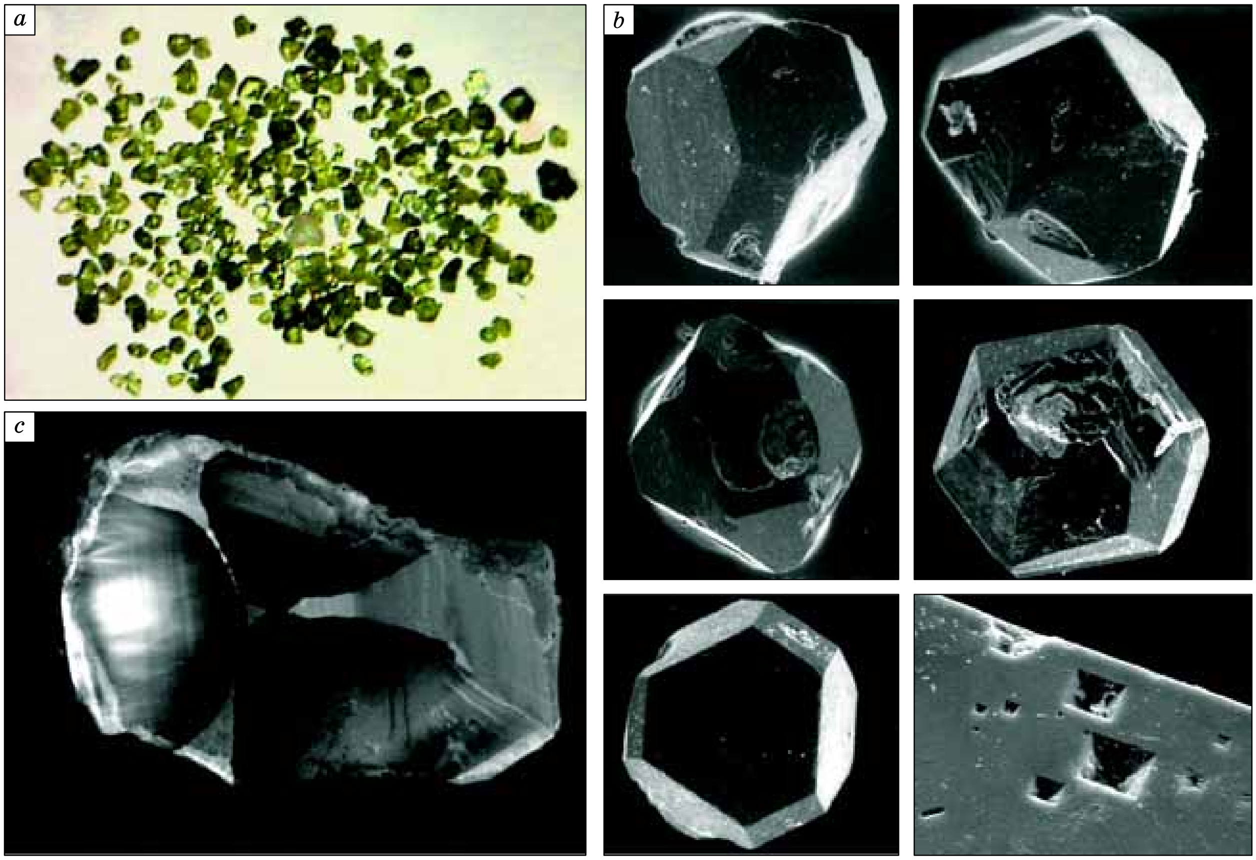

Fig. 1. Crystal morphology of Tolbachik diamonds. *A,* General view (after (Anikin et al., 2013; Dunin-Barkovsky, 2013; Galimov et al., 2016a; Karpov et al., 2014a; Silaev et al., 2015)); *b*, photomicrographs of diamond crystals (after (Gordeev et al., 2014; Karpov et al., 2014a; Silaev et al., 2015)); *c*, sectorial crystal, CL image (after (Anikin et al., 2013; Karpov et al., 2014a; Silaev et al., 2015)).

due to the presence of nitrogen in the diamond structure (Figs. 1, 2).

FTIR spectra. The FTIR spectra show that nitrogen in the Tolbachik diamond occurs as isolated substituting atoms in the C form, at concentrations within 150–500 ppm, which is common to spontaneously crystallized synthetic diamonds, as nitrogen aggregation fails to reach the A form (vapor of N atoms) for the short time of diamond growth (Fig. 3).

Photoluminescence. The Tolbachik diamonds emit no light even under 500 W deuterium lamps. Absent or weak luminescence is a typical property of synthetic diamonds grown by spontaneous crystallization.

Impurities. The types and contents of impurities in the Tolbachik diamonds were analyzed by the LA ICP-MS method. Some elements were found in concentrations 4–5 times those in kimberlitic diamonds, which is common to synthetic diamonds. Abnormal concentrations of Fe, Ni, Co, and Mn reported by Silaev et al. (2015) are consistent with the use of these elements as catalysts in diamond synthesis. The trace element composition of the Tolbachik diamonds, including our new data, is similar to that of diamonds from

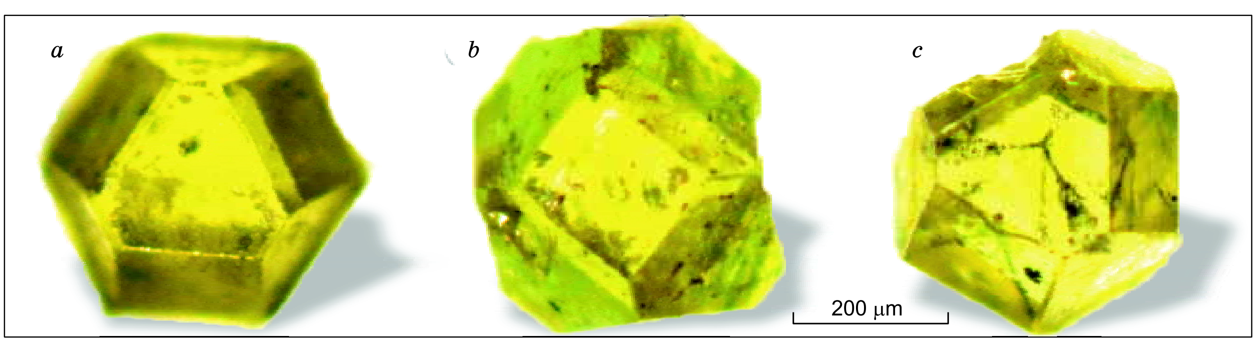

Fig. 2. Color and morphology of Tolbachik (*a*, *b*) and synthetic (*c*) diamonds.

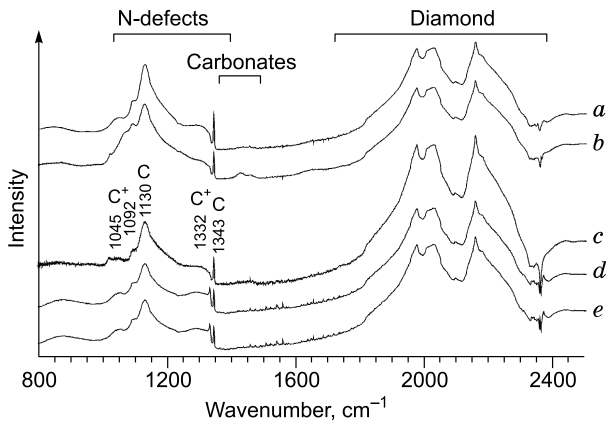

Fig. 3. Typical FTIR spectra. *a*, *b*, Tolbachik and synthetic diamonds from different sources; *c*, HPHT spontaneous crystallization from metal-carbon systems; *d*, diamond cutting wheel; *e*, drilling bit.

Tibet (Howell et al., 2015) and to synthetic varieties (Fig. 4) and shows large random variations.

Note that neither Silaev et al. (2015) nor Howell et al. (2015) paid attention to the presence of microinclusions, which were responsible for high contents of some elements (up to 0.1 wt.% or 10^3 ppm) in the diamond samples. The diamonds we analyzed are poor in transition metals (within 2–50 ppm Mn, Fe, and Ni). Both Tolbachik and synthetic diamonds show quite high As enrichments (never measured previously): 33–53 ppm and 7–22 ppm As, respectively.

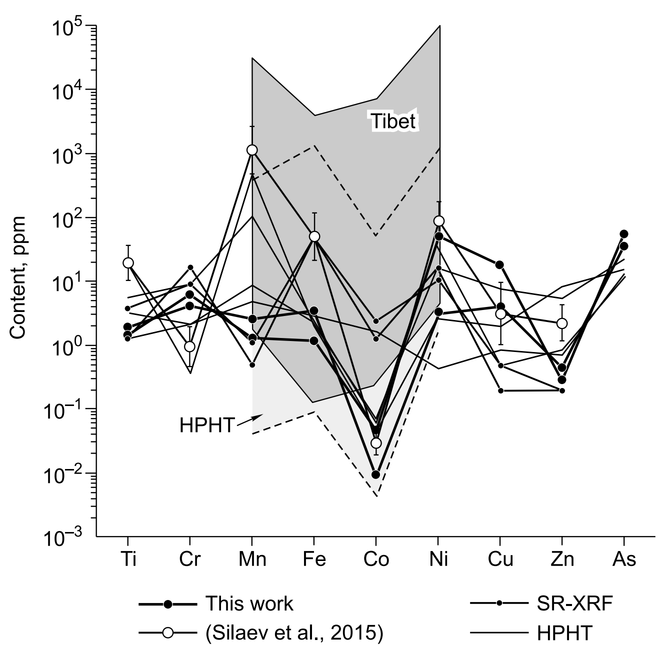

Fig. 4. Trace-element composition of Tolbachik diamonds (according to (Silaev et al., 2015) and this study). Gray fields show compositions of cubic-octahedral diamonds from Tibet and an HPHT diamond (Howell et al., 2015), for comparison. Our data on synthetic diamonds (HPHT in legend) and SR-XRF data by Litasov et al. (2018) on Tolbachik diamonds are provided additionally.

The contribution of transition metals into high contents of impurities results from uptake of microinclusions during synthesis. It is almost impossible to discriminate between the Tolbachik and synthetic diamonds according to impurities, as the latter have technological controls (conditions of growth and refinement, quality of raw material, etc.) and may differ even from run to run. The best known catalyst mixtures used for diamond growth in Russia and China are Mn–Ni–Fe and Fe–Ni–Co, in different proportions. The same elements are present as impurities in all analyzed cubic-octahedral diamonds from Kamchatka and Tibet.

Carbon isotope composition. The carbon isotope composition in the Tolbachik diamonds varies from –22 to –27 ‰ δ^{13}C and corresponds to that of graphite used for diamond synthesis. The similarity of δ^{13}C values in diamonds and in C-bearing phases from the lavas of Tolbachik and its surroundings existing in a subduction setting, with typical low negative δ^{13}C of –25 to –29 ‰ (Galimov et al., 2016a,b), is quite expected and hardly can be a proof for the natural origin of the diamonds.

Thus, the Tolbachik diamonds fully match synthetic varieties grown by spontaneous crystallization and obviously fail to satisfy the criterion (a) implying prominent difference from possible contamination sources.

REPRODUCIBILITY OF DIAMOND FINDINGS

The authors of the Tolbachik diamond discovery first rightfully sent a sample of potentially diamondiferous rock to the ALROSA company to check it for the presence of diamonds, but they never came back to learn the result. The sample was ground manually, without pretreatment in heavy liquids, and was examined many times by ALROSA mineralogists who found no diamonds (as B. Pomazansky, Head of Laboratory, reported in a personal communication). Thus, the Tolbachik diamonds are rather artefacts, also according to criterion (b), which casts more doubt on their natural origin. Meanwhile, Silaev et al. (2016a) extrapolated the Tolbachik diamond potential on Klyuchevskoy volcano though reported findings of metallic duralumin known as a contamination product. As for aluminum, Sobolev (1979) considered it to be the primary target to check, as clearest evidence of contamination, and noted that a special instruction was required for such checking.

Neither Silaev et al. (2015) nor Howell et al. (2015) mentioned findings of diamonds *in situ*, i.e., the criterion (c) has not been satisfied either.

DIAMOND FROM CUTTING TOOLS

In order to check whether the Tolbachik diamonds may result from contamination with material used in cutting tools, we chipped off several pieces of the cutting edge in a stone saw and digested them in acid. The reaction produced

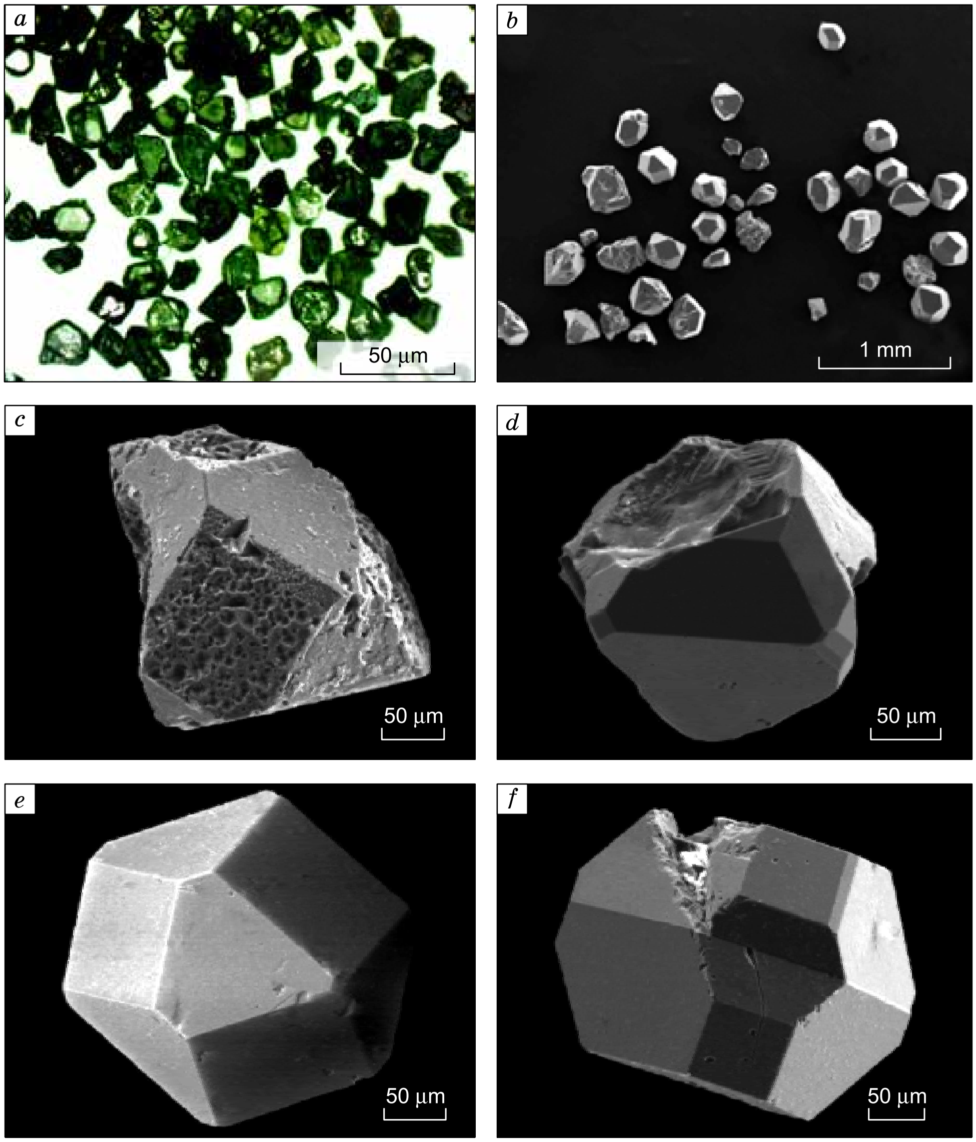

Fig. 5. Synthetic diamonds from a stone saw. *a*, *b*, General view; *c–f*, individual crystals, BSE images.

several thousands (!) of synthetic diamonds looking exactly like those reported for Tolbachik volcano (Fig. 5). Their FTIR spectra confirmed the presence of nitrogen uniquely in the C form (Fig. 3), as in the Tolbachik samples; synthetic diamonds from a drilling bit showed the same spectra. Therefore, lavas from the volcano may have been contaminated with synthetic diamonds from the cutting tools.

Then we checked another saw which had coarser diamonds visible on the surface and found out that they were crushed boart crystals of natural origin (Fig. 6). The debris included whole octahedrons of similar sizes with relic diamond faces; they were colorless and showed common forms of nitrogen (A and B1) in the FTIR spectra (Fig. 7). Thus, such saws likewise can be a source of contamination, which is harder to identify than synthetic diamonds. This possibility has to be taken into account when natural diamonds with features of kimberlitic diamonds are found in unusual rock or mineral hosts.

CARBONADO-LIKE DIAMOND FROM AVACHITE

The case of so-called carbonado diamond from avachite is more complicated. Diamonds of this variety were extracted from the nonmagnetic fraction of 150 kg of avachites in 1993, 26 grains (Dunin-Barkovsky et al. (2013) report more than 100 grains) ranging in size from 0.1–1.0 to 3 mm. The diamonds were described preliminarily by Baikov et al. (1995) and in more detail by Gorshkov et al. (1995). According to Baikov et al. (1995), avachite is a low-silica basaltic rock which comes from an unknown source and occurs as debris or blocks in the U-shaped valley between

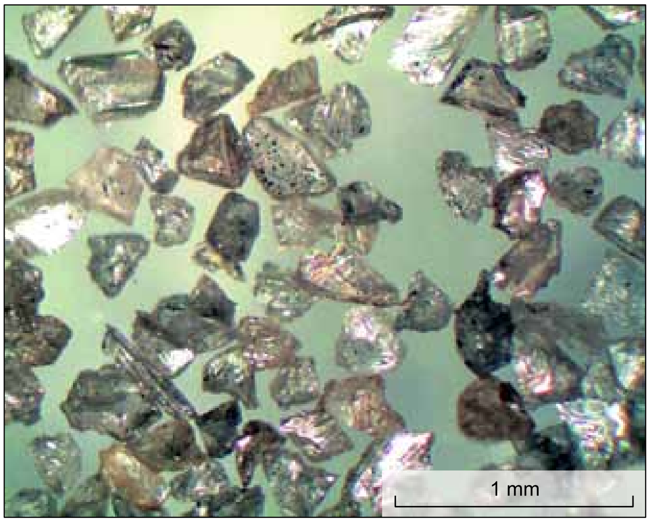

Fig. 6. Chips of natural diamonds from stone saw. See text for explanation.

Avacha and Kozelsky volcanoes. Avachite encloses phenocrysts of forsterite, Cr-diopside, augite, Cr-spinel, and xenoliths of spinel peridotite, olivinite, and pyroxenite that originated at different depths, including in the mantle. The carbonado-like segregations found in avachite comprise twinned micrometer diamond crystals, often with defects (Gorshkov et al., 1995), as well as inclusions of an Mn–Ni–Si–Fe alloy, W and B carbides, and Mn^0 which became cemented with amorphous silica, tridymite, β-SiC and native silica late during formation. These segregations presumably formed in a strongly reduced environment at relatively low pressures and temperatures.

Carbonado diamonds from avachite were also described by Kaminsky et al. (2016). They reported additional sampling, but the samples they discussed were likely the same as in the previous publications, judging by the sampling procedure (from 150 kg of avachite), treatment (manual crushing and magnetic separation), and the number of extracted carbonado grains (26 specimens). The careful study led Kaminsky et al. (2016) to a hypothesis of diamond growth by chemical vapor deposition (CVD mechanism), about the atmospheric pressure, during or shortly after an eruption of Avacha volcano. The carbonado diamonds look original (criterion *a*), and it is hard to imagine a source of manmade contamination for them. Nevertheless, they resemble sintered material of synthetic diamond fused with a binding agent used in tools; the idea of contamination is further supported by the presence of metal alloys commonly employed for diamond synthesis.

However, the natural origin of the carbonado-like particles found in the avachite samples appears doubtful also according to the criterion (b). Specifically, Baikov et al. (1995) noted that the first diamond crystal discovered in avachite by F. Kutyev in 1980 was a 1.7 mm grayish-white single crystal, but all numerous later attempts to reproduce the finding failed. The grains found in 1993 were not single crystals and mismatched Kutyev's finding. The natural origin of these diamonds may be considered reliable only in the case of reproducibility in other independent findings.

Diamonds found in uncommon geological settings and hosts require mandatory checks for possible contamination and reproducibility proofs. If the contamination paths are not obvious or the finding cannot be reproduced for technical reasons, the authors themselves should report possible contamination. That was, for instance the right approach of

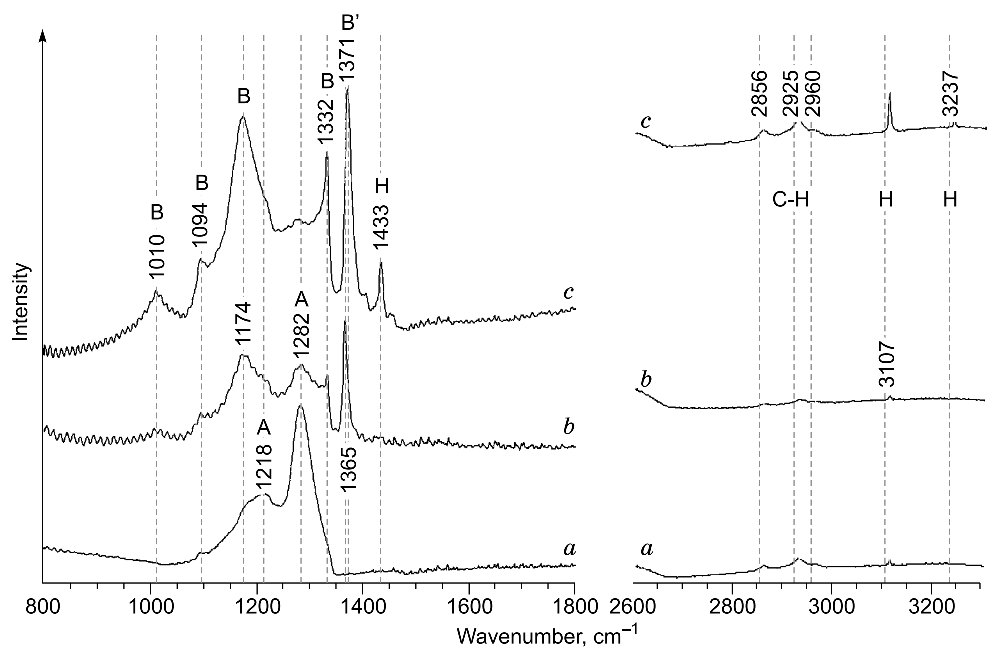

Fig. 7. Typical FTIR spectra of three (*a*–*c*) natural diamonds from stone saw. See text for explanation.

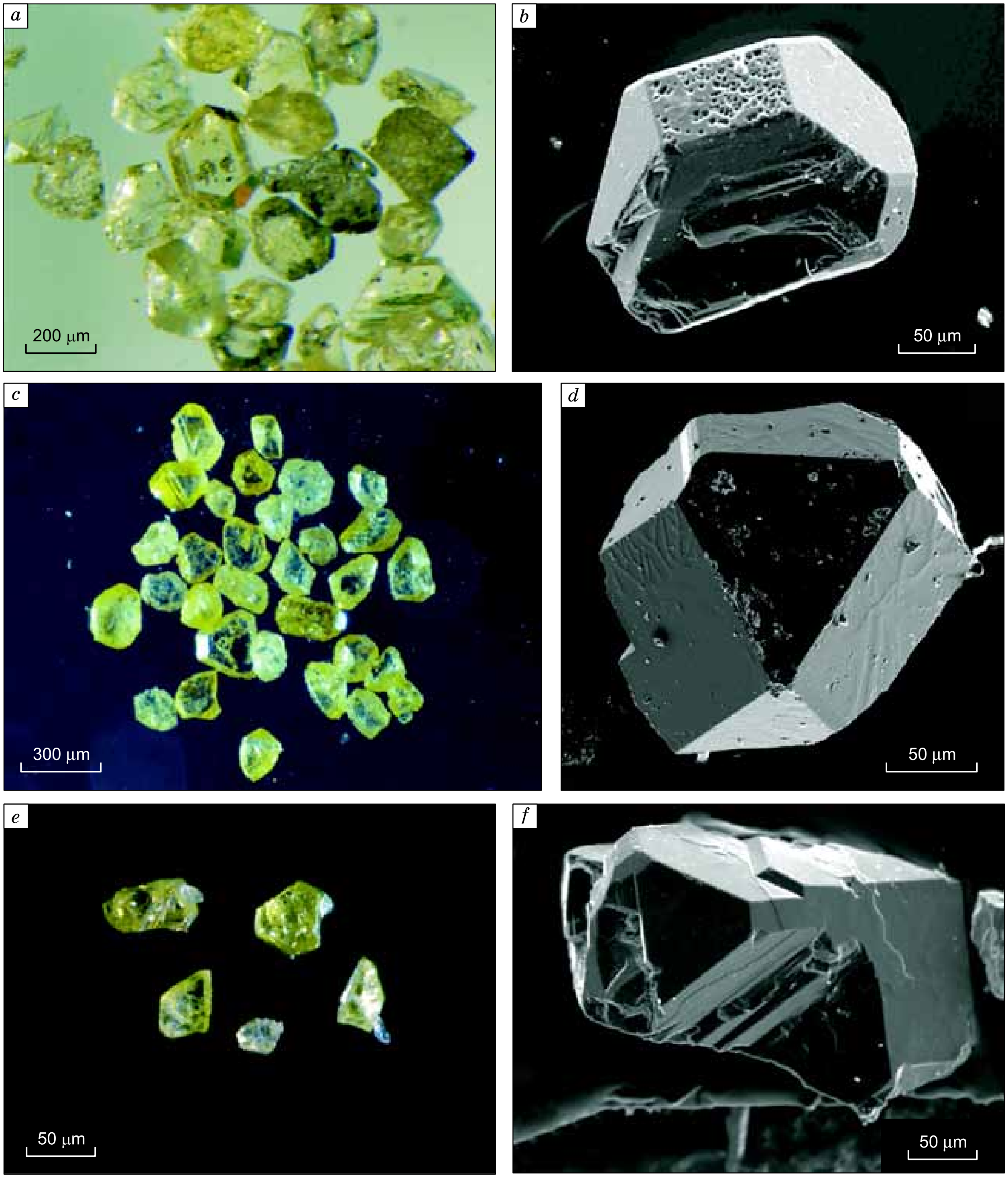

Fig. 8. Diamonds from ophiolites: *a*, *b*, Polar Ural (Yang et al., 2015a); *c*, *d*, Turkey (Lian et al., 2017); *e*, *f*, Tibet (Xiong et al., 2017).

Howell et al. (2015) who admitted the possibility of contamination for diamonds they found in ophiolites from Tibet, which showed similarity with synthetic diamond.

Unfortunately, the diamonds found in abundance in the Kamchatka lavas have never been further investigated in detail (including for genesis issues) and never checked for reproducibility. Their properties are inconsistent with the classical high-pressure high-temperature formation model, while new paradigms of different origin conditions require balanced approaches. The possibility of contamination with synthetic or natural diamonds coming from cutting or polishing tools should be always borne in mind (Figs. 6, 7).

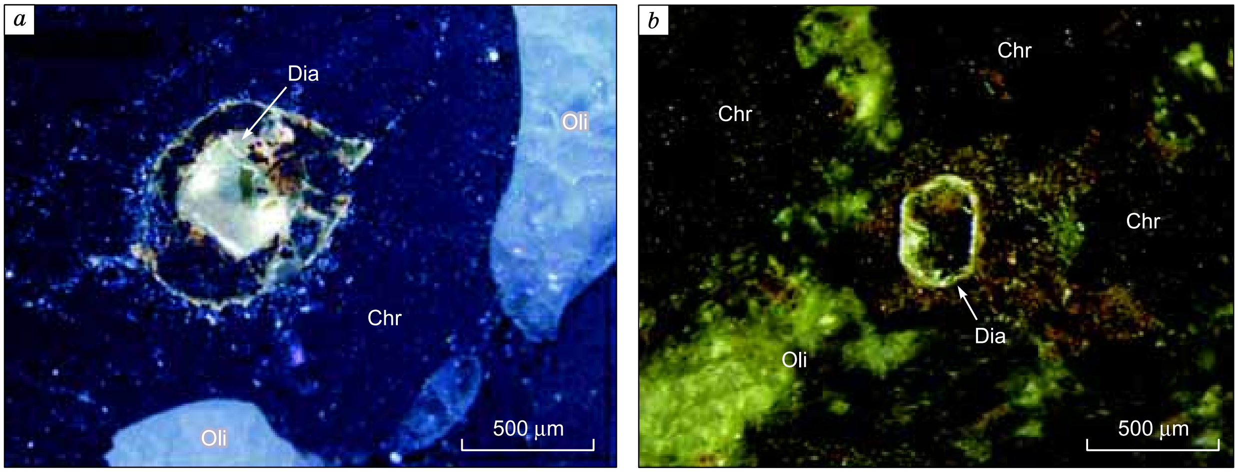

Fig. 9. Diamonds from chromitites: Tibet (Yang et al., 2015b) (*a*) and Polar Ural (Yang et al., 2015a) (*b*) areas in polished thin sections. See a rim of amorphous carbon around the diamond grain. Dia, diamond, Chr, chromite, Oli, olivine.

DIAMONDS FROM PERIDOTITE AND CHROMITITE

There is another recently discussed issue relevant to the problem of the Tolbachik diamonds: diamonds found in peridotite and chromitite hosts from Tibet, Polar Urals, Turkey, and Bohemia (Xu et al., 2009, 2017; Naemura et al., 2011; Howell et al., 2015; Huang et al., 2015; Tian et al., 2015; Lian et al., 2017; Moe et al., 2017; Xiong et al., 2014, 2017; Yang et al., 2014, 2015a,b). Without going into detailed comparisons of their properties, we only note that the ophiolite-hosted diamonds reported in the cited publications are identical to those from the Tolbachik lavas and to synthetic diamonds (Fig. 8). The findings from the Tibet and Ural ophiolites meet none of the three reliability criteria; although they were reproduced, it was done by the original finders and without proper expertise.

Six diamonds found *in situ* (Fig. 9) were located on a cut surface and surrounded by porous amorphous carbonaceous material, while the diamond grains themselves had no evident surface defects, which prompts contamination. The typomorphic similarity of diamonds from the Tolbachik avachites with those from the Tibetan, Ural, Turkish, and Bohemian ophiolites, as well as with synthetic diamonds, is surprising and causes doubt about their natural origin.

CONCLUSIONS

The reliability of diamond discoveries from unusual geological settings and hosts has to be confirmed by special expertise. The priority of the first finders should be fully respected, but checks by independent *in situ* sampling are required; the site and the samples should be open to independent studies and expertise. Contamination with synthetic diamonds from stone cutting tools is easy to establish but that with natural diamonds is harder to discriminate and is thus more critical. Therefore, the contamination possibility has to be always borne in mind and excluded by careful checking the tools and ways of stone cutting and polishing; solid grounds should be provided to prove that contamination is impossible, otherwise, doubts will remain.

The excitement around poorly reliable discoveries is bad for geology as a whole and for the reputation of the authors in particular. It may incur unreasonable costs for exploration and wasting money from grants or government sources. False diamond findings inevitably become disproved, which discredits other potentially true discoveries. Thus, unprofessional boom around doubtful findings obstructs the diamond exploration progress.

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