Revision 2

# 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, carbon and nitrogen isotopes in Tolbachik diamonds; microtwinning, Mn-Ni silicides and other inclusions in microcrystalline diamond aggregates for 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 can 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 2012-2013 eruption of Tolbachik volcano (Kamchatka) represent anthropogenic contamination based on the data on metallic inclusions, closely corresponding 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,b, 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,b; 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, a 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. Back-scattered 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 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 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 Fig.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 Leningradskoe flow described in their paper. It seems that it is extremely important to show 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.

## *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*-4*m*2 space group. The structural formula is $(Al_{0.67}\square_{0.33})Al_2O_4$. It is a thermodynamically metastable phase with a narrow *PT*-field of crystallization (Wilson and McConnell 1980; Levin and Brandon 1998). Different polymorphs of $Al_2O_3$ can be synthesized by heating of different aluminium hydroxides. Each of them has own sequence of transformation in the temperature range of 250-1000 $^{o}$C finalized by high-temperature corundum structure (Wefers and Misra, 1987).

The δ-$Al_2O_3$ is a member of boehmite sequence of transformations: boehmite, γ-AlOOH (<500 $^{o}$C) → γ-$Al_2O_3$ (500—700 $^{o}$C) → δ-$Al_2O_3$ (700—900 $^{o}$C) → θ-$Al_2O_3$ (900—1000 $^{o}$C) → α-$Al_2O_3$ (>1000 $^{o}$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 $^{o}$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 $^{o}$C and at 1.5 GPa and 515 $^{o}$C in less than 70 hours (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 is 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 associate 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,d). 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, Ti-Si-nitrophosphides, were described in mineral concentrates from 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 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,d). Ballhaus et al. (2017) proposed a lightning strike hypothesis for the origin of the SR phases, but it is applicable to μm-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: (a) Mn-Ni inclusions vary in composition from MnNi to $Mn_2Ni$ with 45-67 wt.% Ni, (b) the The Mn-Ni inclusions contain up to 5 wt.% Si, (c) Silicides with 19 at.% Si were found in polycrystalline carbonado-like aggregates from other placers in Kamchatka (Kaminsky et al. 2019), and (d) 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; Palyanov et al. 1997; Lang 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 show that trace element composition of the individual diamonds can 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 catalyst. 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. Palyanov 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, which 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 can diffuse into the growth medium during industrial synthesis (e.g., Davydov 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 (Vishnvesky 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 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,b), 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 (a) 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; Bolad and Li 2010); (b) 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); (c) 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 (d) nano-twinning 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 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 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 (Zelensky 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 Zelensky 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 1/3 of the surface bonds of the diamond can be saturated with H, F, or Cl. Oxygen is also important surface impurity (Sappok and Boehm 1968). Fig.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.

Fig.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.

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 (Fig.6-7). Diamonds from an ophiolite (Xu et al. 2017) rarely contain minor A-centers (Fig.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 peaks 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 broad band 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. 2017). Galimov et al. (2020) noticed that this can be explained by the cavitation hypothesis, which is described below. Indeed, this idea does not stand up to criticism. Fig.8 shows cathodoluminescence images of Tolbachik and synthetic diamonds with clear sectorial growth zones, which 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. 2017) resembling the range for synthetic diamonds (Boyd et al. 1988; Reutsky et al. 2008; Xu et al. 2017). Rarely, this value in ophiolite diamonds is shifted to -17‰ (Xu et al. 2017).

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 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,b). All these materials may indicate anthropogenic contamination.

## A model for the origin

A deep-seated origin of Tolbachik diamonds at static *PT*-conditions in the diamond stability field is not applicable due to shallow location of magma chambers below Klyuchevskoy group volcanoes and short residence time 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.

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 $2 \times 10^{-3}$ 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 $10^{-6} – 10^{-3}$ s even during repeated cavitation episodes.

In the subsequent paper Galimov (1985) argued that kinetic limitations can 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 hours at 800 $^o$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 $^o$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 perspective direction, which may be more favorable industrially than 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 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 diamond 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 rather negligible. There are still many unusual geological findings of diamonds in non-traditional environments and we believe that their study should be performed by 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, which 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 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 2020a), diamonds from ophiolite peridotite and chromitite (Howell et al. 2015; Xu et al. 2017; Lian and Yang 2019; Litasov et al. 2019b), some diamonds in metamorphic rocks (Farre-de-Pablo et al 2019; Massone 2019), and SR mineral assemblages from alluvium (Griffin et al. 2018a,b; 2019; Litasov et al. 2019c,d) is that authors of 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 relations to each other (Litasov et al. 2020a,b). 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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## REFERENCES CITED

Anikin, L.P., Silaev, V.I., Chubarov, V.M., Petrovsky, V.A., Vergasova, L.P., Karpov, G.A., Sokorenko, A.V., Ovsyannikov, A.A., and Maksimov, A.P. (2018) Diamond and other accessory minerals in the products of eruption in 2008–2009. Koryaksky volcano (Kamchatka), Vestnik of the Institute of Geology of the Komi Science Center UB RAS, 32, 18–27 (in Russian). https://doi.org/10.19110/2221-1381-2018-2-18-27

Baidakova, M.V., 2014. Methods of characterization and models of nanodiamond particles. In: Vul, A. and Shenderova, O. (Eds.), Detonation nanodiamonds: Science and applications. CRC Press, Boca Raton, FL, pp. 73-99.

Ballhaus, C., Wirth, R., Fonseca, R.O.C., Blanchard, H., Pröll, W., Bragagni, A., Nagel, T., Schreiber, A., Dittrich, S., and Thome, V. (2017) Ultra-high pressure and ultra-reduced minerals in ophiolites may form by lightning strikes. Geochemical Perspectives Letters, 5, 42-46.

Bezrukov, G.N., Butuzov, V.P., Khatelishvili, G.V., and Chernov, D.B. (1972) Study of the composition of inclusions in synthetic diamond crystals by microanalysis. Soviet Physics-Doklady, 17, 421-424 (Doklady USSR Academy of Science, 204(1), 84-87, in Russian).

Boland, J.N. and Li, X.S. (2010) Microstructural characterisation and wear behaviour of diamond composite materials. Materials, 3(2), 1390-1419.

Boyd, S.R., Pillinger, C.T., Milledge, H.J., Mendelssohn, M.J., and Seal, M. (1988) Fractionation of nitrogen isotopes in a synthetic diamond of mixed crystal habit. Nature, 331, 604-607.

Cartigny, P., Chinn, I., Viljoen, K.F., and Robinson, D. (2004) Early Proterozoic ultrahigh pressure metamorphism: evidence from microdiamonds. Science, 304, 853-855.

Cartigny, P. (2010) Mantle-related carbonados? Geochemical insights from diamonds from the Dachine komatiite (French Guiana). Earth and Planetary Science Letters, 296(3), 329-339.

Davydov, V.A., Revin, O.G., and Slesarev, V.N. (1982) Diffusion of lithographic stone into graphite at high pressures and temperatures. Journal of Superhard Materials, 18(3), 3-7.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.V., and Javoy, M. (1998) Evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan. Geochimica et Cosmochimica Acta, 62, 3765-3773.

Detchuev, Y.A., Zadnevrovsky, B.I., Laptev, V.A., Melekh, M.V., Repnikova, E.A., Shivrin, O.N., and Samoylovich, M.I. (1983) Study of the phase composition of inclusions in single crystals of synthetic diamonds doped by electrically active impurities. Diamonds and Superhard Materials, 13(5), 1-2.

Di Pierro, S., Gnos, E., Grobety, B.H., Armbruster, T., Bernasconi, S.M., and Ulmer, P. (2003) Rock-forming moissanite (natural α-silicon carbide). American Mineralogist, 88, 1817-1821.

Dobrzhinetskaya, L., Mukhin, P., Wang, Q., Wirth, R., O'Bannon, E., Zhao, W., Eppelbaum, L., and Sokhonchuk, T. (2018) Moissanite (SiC) with metal-silicide and silicon inclusions from tuff of Israel: Raman spectroscopy and electron microscope studies. Lithos, 310, 355-368.

Evans, T. and Qi, Z. (1982) The kinetics of the aggregation of nitrogen atoms in diamond. Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 381, 159-178.

Farré-de-Pablo, J., Proenza, J.A., González-Jiménez, J.M., Garcia-Casco, A., Colás, V., Roqué-Rossell, J., Camprubí, A., and Sánchez-Navas, A. (2019) A shallow origin for diamonds in ophiolitic chromitites. Geology, 47(1), 75-78.

Flynn, H.G., 1986. Method and means for converting graphite to diamond. US Patent 4,563,341.

Fockenberg, T., Wunder, B., Grevel, K.-D., and Burchard, M., 1996. The equilibrium diaspore-corundum at high pressures. European Journal of Mineralogy, 8, 1293-1299.

Frank, F.C., Lang, A.R., and Moore, M., 1973. Cavitation as a mechanism for the synthesis of natural diamonds. Nature, 246, 143-144.

Galimov, E.M. (1973) Possibility of natural diamond synthesis under conditions of cavitation, occurring in a fast-moving magmatic melt. Nature, 243, 389-391.

Galimov, E.M. (1985) Some evidences of reality of the cavitation synthesis of diamonds in nature. Geochemistry International, 33(5), 456-471.

Galimov, E.M., Kaminsky, F.V., Shilobreeva, S.N., Sevastyanov, V.S., Voropaev, S.A., Khachatryan, G.K., Wirth, R., Schreiber, A., Saraykin, V.V., Karpov, G.A., and Anikin, L.P. (2020) Enigmatic diamonds from the Tolbachik volcano, Kamchatka. American Mineralogist, 105, 498-509.

Galimov, E.M., Kudin, A.M., Skorobogatskii, V.N., Plotnichenko, V.G., Bondarev, O.L., Zarubin, B.G., Strazdovskii, V.V., Aronin, A.S., Fisenko, A.V., and Bykov, I.V. (2004) Experimental corroboration of the synthesis of diamond in the cavitation process. Doklady Physics, 49(3), 150-153.

Glover, G. and Sellars, C.M. (1972) Static recrystallization after hot deformation of α iron. Metallurgical Transactions, 3(8), 2271-2280.

Gorbunov, A.E., Tsermen, S.I., and Pekker, I.S. (1990) Copper-tin binders for diamond tools. In: Perspective directions for application if diamond tools in engineering. Kolchemanov N.A. Ed., VNIIALMAZ, Moscow, 61-69 (In Russian).

Gordeev, E.I., Silaev, V.I., Karpov, G.A., Anikin, L.P., Vasiliev, E.A., Sukharev, A.E. (2019) On the history of the discovery and nature of diamonds in volcanic rocks of Kamchatka. Bulletin of Perm State University: Geology, 18(4), 307-331 (In Russian). https://doi.org/10.17072/psu.geol.18.4.307.

Griffin, W.L., Gain, S.E.M., Bindi, L., Toledo, V., Cámara, F., Saunders, M., and O'Reilly, S.Y. (2018a) Carmeltazite, $ZrAl_2Ti_4O_{11}$, a new mineral trapped in corundum from volcanic rocks of Mt Carmel, Northern Israel. Minerals, 8(12), 601.

Griffin, W.L., Huang, J.-X., Thomassot, E., Gain, S.E.M., Toledo, V., and O'Reilly, S.Y. (2018b) Super-reducing conditions in ancient and modern volcanic systems: sources and behaviour of carbon-rich fluids in the lithospheric mantle. Mineralogy and Petrology, 112(1), 101-114.

Griffin, W.L., Gain, S.E., Huang, J.-X., Saunders, M., Shaw, J., Toledo, V., and O'Reilly, S.Y. (2019) A terrestrial magmatic hibonite-grossite-vanadium assemblage: Desilication and extreme reduction in a volcanic plumbing system, Mount Carmel, Israel. American Mineralogist: Journal of Earth and Planetary Materials, 104(2), 207-219.

Haas, H. (1972) Diaspore-corundum equilibrium determined by epitaxis of diaspore on corundum. American Mineralogist, 57, 1375-1385.

Haggerty, S.E. (1975) The chemistry and genesis of opaque minerals in kimberlites. Physics and Chemistry of the Earth, p. 295-307.

Howell, D., Griffin, W.L., Yang, J., Gain, S., Stern, R.A., Huang, J.-X., Jacob, D.E., Xu, X., Stokes, A.J., and O'Reilly, S.Y. (2015) Diamonds in ophiolites: Contamination or a new diamond growth environment? Earth and Planetary Science Letters, 430, 284-295.

Humphreys, J., Rohrer, G.S., and Rollett, A. (2017) Recrystallization and related annealing phenomena, 3rd ed. Elsevier, 704 pp.

Kaminsky, F.V., Wirth, R., Anikin, L.P., Morales, L., and 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., and Schreiber, A. (2019) "Kamchatite" diamond aggregate from northern Kamchatka, Russia: New find of diamond formed by gas phase condensation or chemical vapor deposition. American Mineralogist, 104, 140-149.

Kaminsky, F.V., Wirth, R., Anikin, L.P., and Schreiber, A. (2020) On "Kamchatite" diamond aggregate from northern Kamchatka, Russia: New find of CVD-formed diamond in nature - Reply to K.D. Litasov, T.B. Bekker, and H. Kagi. American Mineralogist, 105(1), 144-145.

Karpov, G.A., Silaev, V.I., Anikin, L.P., Rakin, V.I., Vasil'ev, E.A., Filatov, S.K., Petrovskii, V.A., and Flerov, G.B. (2014) Diamonds and accessory minerals in products of the 2012–2013 Tolbachik Fissure Eruption. Journal of Volcanology and Seismology, 8(6), 323-339.

Kennedy, G.C. (1959) Phase relations in the system of $Al_2O_3$-$H_2O$ at high temperatures and pressures. American Journal of Science, 257(8), 563-573.

Khachatryan, G.K. (2013) Nitrogen and hydrogen in diamond crystals in aspect of geological and genetic and exploration problems of diamond deposits. Otechestvennaya Geologia (No 2), 29-42 (In Russian).

Khachatryan, A.K., Aloyan, S.G., May, P.W., Sargsyan, R., Khachatryan, V.A., and Baghdasaryan, V.S. (2008) Graphite-to-diamond transformation induced by ultrasound cavitation. Diamond and Related Materials, 17(6), 931-936.

Korsakov, A.V., Rezvukhina, O.V., Jaszczak, J.A., Rezvukhin, D.I., and Mikhailenko, D.S. (2019) Natural graphite cuboids. Minerals, 9(2), 110.

Lang, A.R. and Meaden, G.M. (1991) Complementary orientation-dependent distributions of 1.40 and 2.56 eV cathodoluminescence on vicinals on {111} in synthetic diamonds. Journal of Crystal Growth, 108(1-2), 53-62.

Lang, A.R., Vincent, R., Burton, N.C., and Makepeace, A.P.W. (1995) Studies of small inclusions in synthetic diamonds by optical microscopy, microradiography and transmission electron microscopy. Journal of Applied Crystallography, 28(6), 690-699.

Laudise, R.A. (1970) The growth of single crystals. Prentice Hall, Inc., Englewood Cliffs, New Jersey 367 pp.

Levin, I., and Brandon, D. (1998) Metastable alumina polymorphs: crystal structures and transition sequences. Journal of the American Ceramic Society, 81, 1995-2012.

Lian, D. and Yang, J. (2019) Ophiolite-hosted diamond: A new window for probing carbon cycling in the deep mantle. Engineering, 5(3), 406-420.

Litasov, K.D., Kagi, H., Voropaev, S.A., Hirata, T., Ohfuji, H., Ishibashi, H., Makino, Y., Bekker, T.B., Sevastyanov, V.S., Afanasiev, V.P., and 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 Research, 75, 16-27.

Litasov, K.D., Kagi, H., Bekker, T.B., Hirata, T., and Makino, Y. (2019b) Cuboctahedral type Ib diamonds in ophiolitic chromitites and peridotites: the evidence for anthropogenic contamination. High Pressure Research, 39(3), 480-488.

Litasov, K.D., Kagi, H., and Bekker, T.B. (2019c) Enigmatic super-reduced phases in corundum from natural rocks: Possible contamination from artificial abrasive materials or metallurgical slags. Lithos, 340-341, 181-190.

Litasov, K.D., Bekker, T.B., and Kagi, H. (2019d) Reply to the discussion of "Enigmatic super-reduced phases in corundum from natural rocks: Possible contamination from artificial abrasive materials or metallurgical slags" by Litasov et al. (Lithos, v.340-341, p.181-190) by W.L. Griffin, V. Toledo and S.Y. O'Reilly. Lithos, 348-349: 105170.

Litasov, K.D., Bekker, T.B., and Kagi, H. (2020a) "Kamchatite" diamond aggregate from northern Kamchatka, Russia: New find of diamond formed by gas phase condensation or chemical vapor deposition – Discussion. American Mineralogist, 105(1), 141-143.

Litasov, K.D., Bekker, T.B., Kagi, H., and Ohfuji, H. (2020b). Reply to the 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 Research, 75, 16–27) by Yang et al. Gondwana Research, 79, 304-307.

Lyakhovich, V.V. (1980) Origin of accessory moissanite. International Geology Review, 22(8), 961-970.

Makino, Y., Kuroki, Y., and Hirata, T. (2019) Determination of major to trace elements in metallic materials based on solid mixing calibration method using multiple spot-laser ablation-ICP-MS. Journal of Analytical Atomic Spectrometry, 34, 1794-1799.

Malov, Y.V., (1971) Microstructure of artificial polycrystalline diamonds. Soviet Physics Crystallography, 15(6), 1042-1044.

Massonne, H.J. (2019) A shallow origin for diamonds in ophiolitic chromitites: Comment. Geology, 47(8), e476.

Novikov, N.V., Kocherzhinsky, Y.A., Shulman, L.A., Ositinskaya, T.D., Malogolovets, V.G., Lysenko, A.V., Malnev, V.I., Nevstruev, G.F., Pugach, E.A., Bogatyreva, G.P., and Vishnevsky, A.S. (1987) Physical properties of diamonds, Handbook. Kiev, Naukova Dumka, 188 p. (in Russian).

Ohfuji, H., Irifune, T., Litasov, K.D., Yamashita, T., Isobe, F., Afanasiev, V.P., and Pokhilenko, N.P. (2015) Natural occurrence of pure nano-polycrystalline diamond from impact crater. Scientific Reports, 5, 14702.

Otopkov, P.P., Nozhkina, A.V., Vasil'eva, L.A., Dul'kina, L.A., Kostikov, V.I., and Andropov, Y.I., (1974) The effect of heat treatment on physical and chemical properties of diamonds. In Physical and chemical properties of diamonds, Proceedings of VNIIALMAZ, Moscow, 3, 15-32 (In Russian).

Pal'yanov, Y.N., Khokhryakov, A.F., Borzdov, Y.M., Sokol, A.G., Gusev, V.A., Rylov, G.M., and Sobolev, N.V. (1997) Growth conditions and real structure of synthetic diamond crystals. Russian Geology and Geophysics, 38(5), 882-906.

Pal'yanov, Y.N., Khokhryakov, A.F., Borzdov, Y.M., Doroshev, A.M., Tomilenko, A.A., and Sobolev, N.V. (1996) Inclusions in synthetic diamonds. Transactions (Doklady) Academy of Sciences: Earth Science Sections, 341(3), 69-72.

Pekker, I.S., Gorbunov, A.E., Balkevich, V.L., Tserman, S.I., and Skidanenko A.I., (1988) Activated sintering of composites of the diamond-copper-tin system. Soviet Powder Metallurgy and Metal Ceramics, 27(12), 934-936.

Pekov, I. V., Anikin, L. P., Chukanov, N.V., Belakovskiy, D.I., Yapaskurt, V.O., Sidorov, E. G., Britvin, S. N., and Zubkova, N.V. (2019) Deltalumite, a new natural modification of alumina with spinel-type structure. Zapiski RMO (Proceedings of the Russian Mineralogical Society) 148(5), 45-58 (In Russian).

Pokhilenko, N.P., Shumilova, T.G., Afanasiev, V.P., and Litasov, K.D. 2019. Diamond in the Kamchatka peninsula (Tolbachik and Avacha volcanoes): Natural origin or contamination? Russian Geology and Geophysics, 60 (5): 463-472.

Reutsky, V.N., Harte, B., Borzdov, Y.M., and Palyanov, Y.N. (2008) Monitoring diamond crystal growth, a combined experimental and SIMS study. European Journal of Mineralogy, 20(3), 365-374.

Sappok, R., and Boehm, H.P. (1968) Chemie der oberfläche des diamanten—I benetzungswärmen, elektronenspinresonanz und infrarotspektren der oberflächenhydride,-halogenide und-oxide. Carbon, 6(3), 283-295.

Shimono, M. and Kume, S. (2004) HIP-Sintered Composites of C (Diamond)/SiC. Journal of the American Ceramic Society, 87(4), 752-755.

Shipilo, V.B., Dutov, A.G., Komar, V.A., Shipilo, N.V., and Azarko, I.I. (2005) Crystallization of diamonds in system Mn–Ni–C. Inorganic Materials, 41(3), 293-296.

Shulzhenko, A.A., Gargin, V.G., Bochechka, A.A., Oleinik, G.S., and Danilenko, N.V., (2000) Diamond nanopowders used to improve strength of diamond- and silicon carbide-based composites. Journal of Superhard Materials, 22(3), 3-15.

Silaev, V.I., Karpov, G.A., Anikin, L.P., Vasiliev, E.A., Vergasova, L.P., and 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. Journal of Volcanology and Seismology, 13(5), 323-334.

Silaev, V.I., Karpov, G.A., Anikin, L.P., Vergasova, L.P., Filippov, V.N., and Tarasov, K.V. (2019b) Mineral phase paragenesis in explosive ejecta discharged by recent eruptions in Kamchatka and the Kuril Islands. Part 2. Accessory minerals of Tolbachik-type diamonds. Journal of Volcanology and Seismology, 13(6), 323-334.

Smit, K.V., Shirey, S.B., and Wang, W. (2016) Type Ib diamond formation and preservation in the West African lithospheric mantle: Re–Os age constraints from sulphide inclusions in Zimmi diamonds. Precambrian Research, 286, 152-166.

Smit, K.V., D'Haenens-Johansson, U.F., Howell, D., Loudin, L.C., and Wang, W. (2018) Deformation-related spectroscopic features in natural Type Ib-IaA diamonds from Zimmi (West African craton). Mineralogy and Petrology, 112(1), 243-257.

Smith, E.M., Shirey, S.B., Nestola, F., Bullock, E.S., Wang, J., Richardson, S.H., and Wang, W. (2016) Large gem diamonds from metallic liquid in Earth's deep mantle. Science, 354(6318), 1403-1405.

Smith, C.B., Walter, M.J., Bulanova, G.P., Mikhail, S., Burnham, A.D., Gobbo, L., and Kohn, S.C. (2016) Diamonds from Dachine, French Guiana: A unique record of early Proterozoic subduction. Lithos, 265, 82-95.

Sobolev, N.V., Efimova, E.S., and Pospelova, L.N. (1981) Native iron in diamonds of Yakutia and its paragenesis. Soviet Geology and Geophysics, 22(12), 25-29.

Tatarintsev, V.I., Sandomirskaia, S., and Tsymbal, S.N. (1987). 1st find of titanium nitride (osbornite) in rocks of the earth. Transactions (Doklady) of the USSR Academy of Sciences: Earth Science sections, 296 (5-6), 155-159 (p.1458-1461, in Russian).

Vishnevsky, A.S., Lysenko, A.V., and Katsai, M.Y., (1975) Electronographic study of mincroinclusions and phases in synthetic diamonds and reaction mixtures. Synthetic Diamonds, 7(2), 7-13 (In Russian).

Webb, S.W., and Jackson, W.E. (1995) Synthetic diamond crystal strength enhancement through annealing at 50 kbar and 1500 $^oC$. Journal of Materials Research, 10(7), 1700-1709.

Westraadt, J.E., Dubrovinskaia, N., Neethling, J.H., and Sigalas, I. (2007) Thermally stable polycrystalline diamond sintered with calcium carbonate. Diamond and Related Materials, 16(11), 1929-1935.

Wefers, K., and Misra, C. (1987) Oxides and Hydroxides of Aluminum. Alcoa Technical Paper No. 19. Alcoa Laboratories, Pittsburgh, PA, 92 pp.

Wilson, S. J., McConnell, J.D.C. (1980) A kinetic study of the system $\gamma$-AlOOH/$Al_2O_3$. Journal of Solid State Chemistry, 34, 315-322.

Xu, X., Yang, J., Guo, G., and Xiong, F. (2013) Mineral inclusions in corundum from chromitites in the Kangjinla chromite deposit, Tibet. Acta Petrologica Sinica, 29(6), 1867-1877.

Xu, X., Yang, J., Robinson, P.T., Xiong, F., Ba, D., and Guo, G. (2015) Origin of ultrahigh pressure and highly reduced minerals in podiform chromitites and associated mantle peridotites of the Luobusa ophiolite, Tibet. Gondwana Research, 27(2), 686-700.

Xu, X., Cartigny, P., Yang, J., Dilek, Y., Xiong, F., and 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., Simakov, S.K., Moe, K., Scribano, V., Lian, D., and 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 Research, 79, 301-303.

Yin, L.W., Zou, Z.D., Li, M.S., Liu, Y.X., Cui, J.J., and Hao, Z.Y. (2000) Characteristics of some inclusions contained in synthetic diamond single crystals. Materials Science and Engineering A, 293(1-2), 107-111.

Yin, L.W., Zou, Z.D., Li, M.S., Sun, D.S., Liu, Y.X., and Hao, Z.Y. (2000) Impurities identification in a synthetic diamond by transmission electron microscopy. Diamond and Related Materials, 9(12), 2006-2009.

Yin, L.W., Li, M.S., Hao, Z.Y., and Zhang, J.F. (2001) Inclusions related to catalyst and medium for transmitting pressure in diamond single crystals grown at high temperature and high pressure from the Fe-C system. Journal of Physics D, 34(12), L57-L60.

Zelenski, M., Malik, N., and Taran, Y. (2014) Emissions of trace elements during the 2012–2013 effusive eruption of Tolbachik volcano, Kamchatka: enrichment factors, partition coefficients and aerosol contribution. Journal of Volcanology and Geothermal Research, 285, 136-149.

Zhang, R.Y., Yang, J.-S., Ernst, W., Jahn, B.-M., Iizuka, Y., and Guo, G.-L. (2016) Discovery of in situ super-reducing, ultrahigh-pressure phases in the Luobusa ophiolitic chromitites, Tibet: New insights into the deep upper mantle and mantle transition zone. American Mineralogist, 101, 1245-1251.

Zhang, S. (1986) Some phenomena and analyses in growing diamond. Journal of Crystal Growth, 79, 542-546.

Zhigadlo, N. (2014) Spontaneous growth of diamond from MnNi solvent-catalyst using opposed anvil-type high-pressure apparatus. Journal of Crystal Growth, 395, 1-4.

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## Figure captions

Fig.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).

Fig.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).

Fig.3. Si versus 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.

Fig.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 show SEM image of the inclusions and encircled analyzed spot. Cu and Ga are from TEM grid and ion beam, respectively.

Fig.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.

Fig.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.

Fig. 7. Nitrogen aggregation versus nitrogen content in Tolbachik (this work) and ophiolite-hosted microdiamonds (Xu et al. 2017) 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

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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).

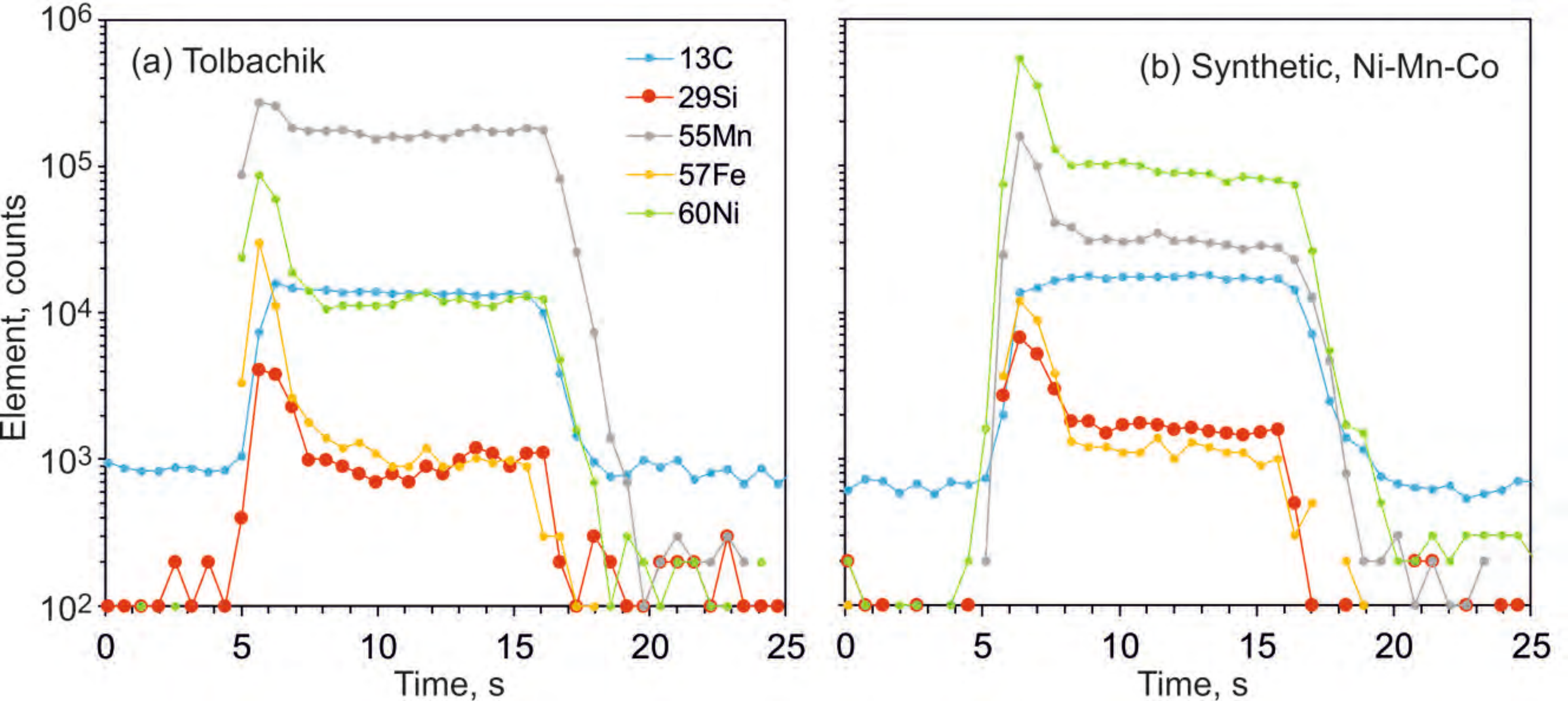
Fig.8. Cathodoluminescence images of Tolbachik diamond (modified from Karpov et al. 2014) and synthetic diamonds grown on seed (modified from Lang and Meaden 1991) indicating sectorial growth pattern typical for synthetic diamonds.

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.

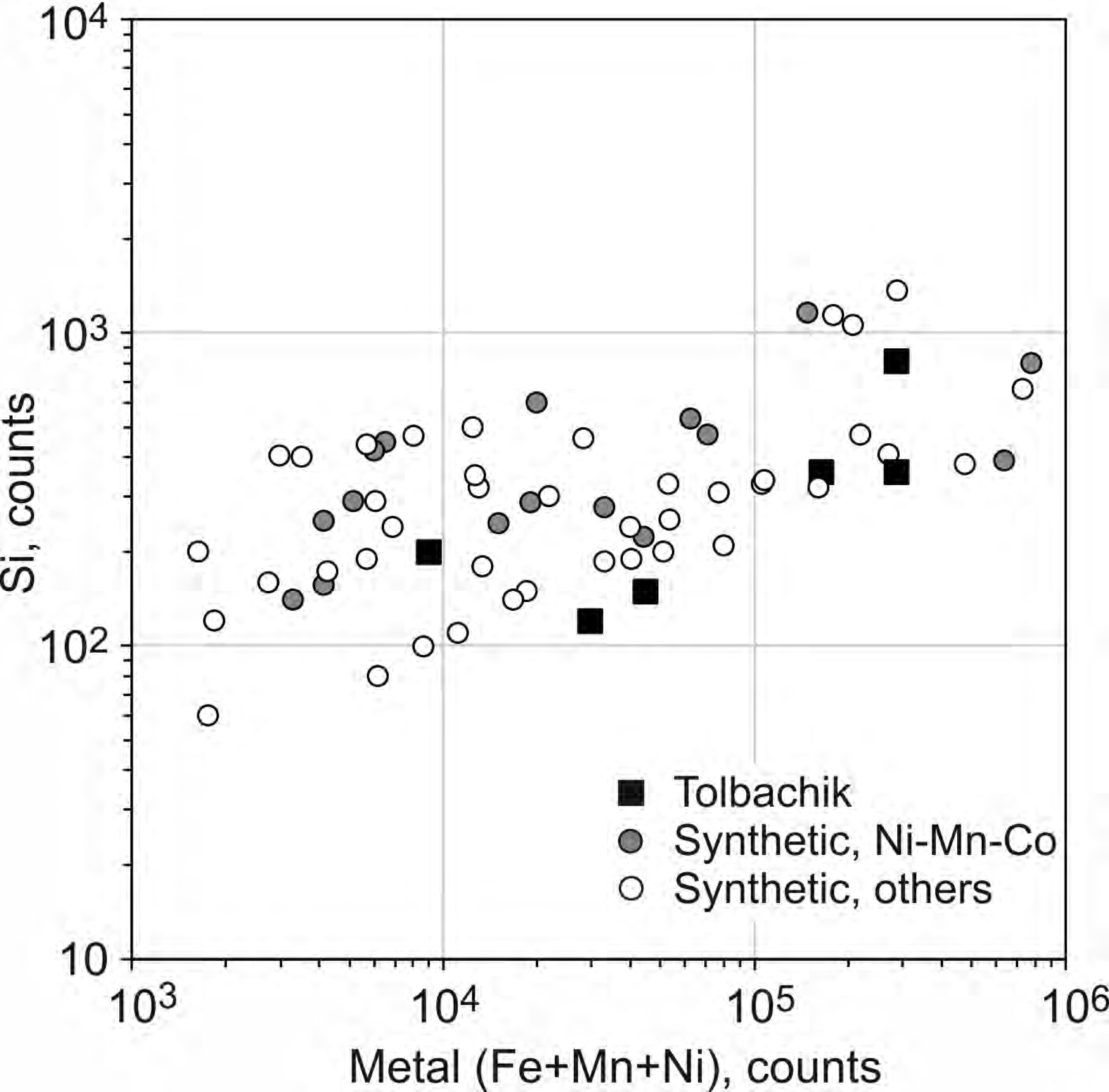
| | IHPP-1 | IHPP-2 | PRGN-40* | Ukraine | Belarus |
|---|---|---|---|---|---|
| N | 16 | 14 | 20 | 10 | 10 |
| Si | 0.49 (6) | 0.18 (3) | 0.57 (8) | 0.55 (9) | 0.13 (4) |
| Ti | - | - | 0.19 (4) | 0.18 (6) | 0.05 (3) |
| Cr | - | - | 0.24 (5) | 0.37 (4) | 0.05 (4) |
| Mn | 49.3 (0.8) | - | 59.4 (1.0) | 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) |

N – number of analyses. IHPP – Institute for High Pressure Physics. *Polema company. The alloys contain also minor carbon and oxygen. The standard deviation is in parentheses.

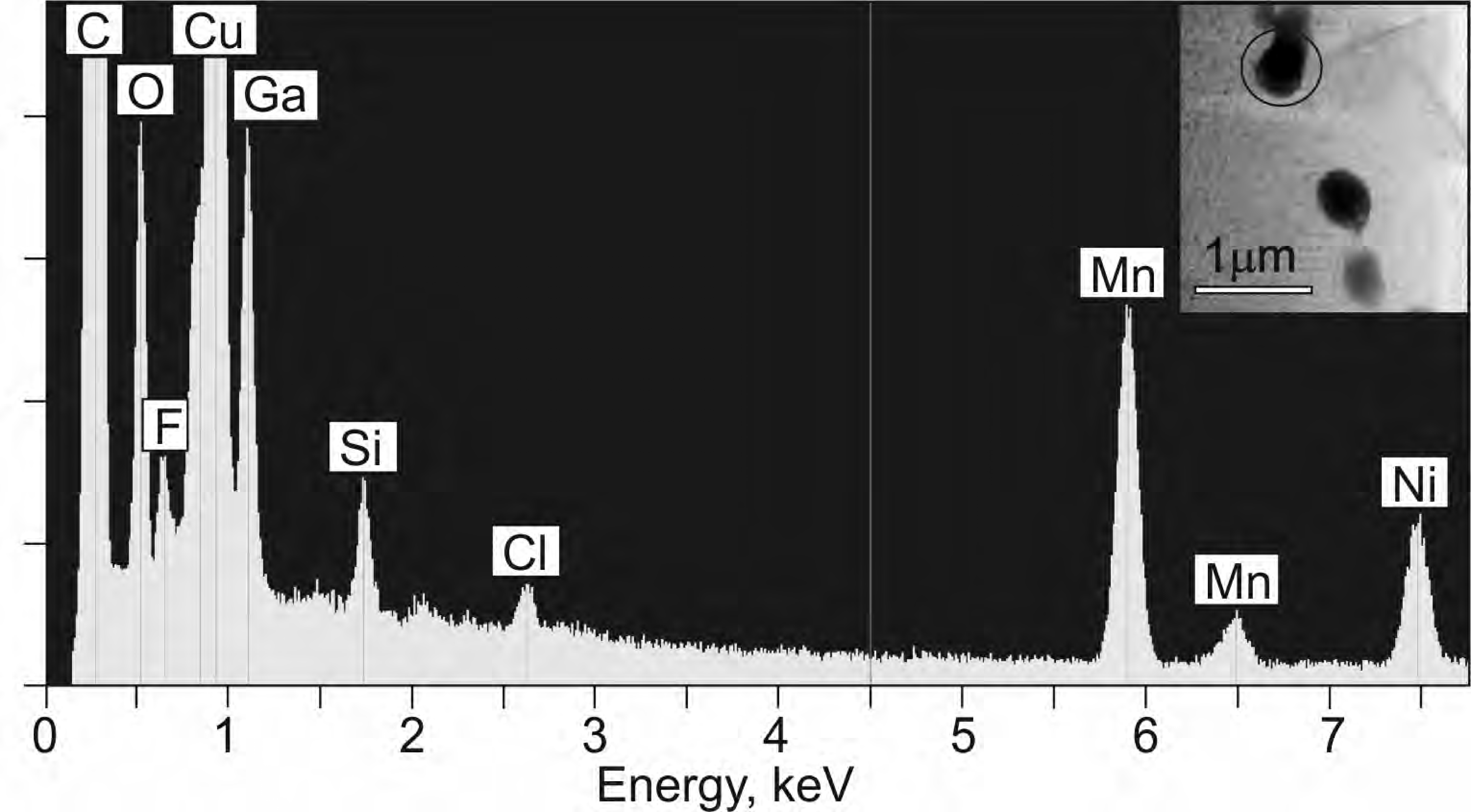

a
Carbon
Deltalumite ?
10 μm
b
Kamacite
Graphite
100 μm

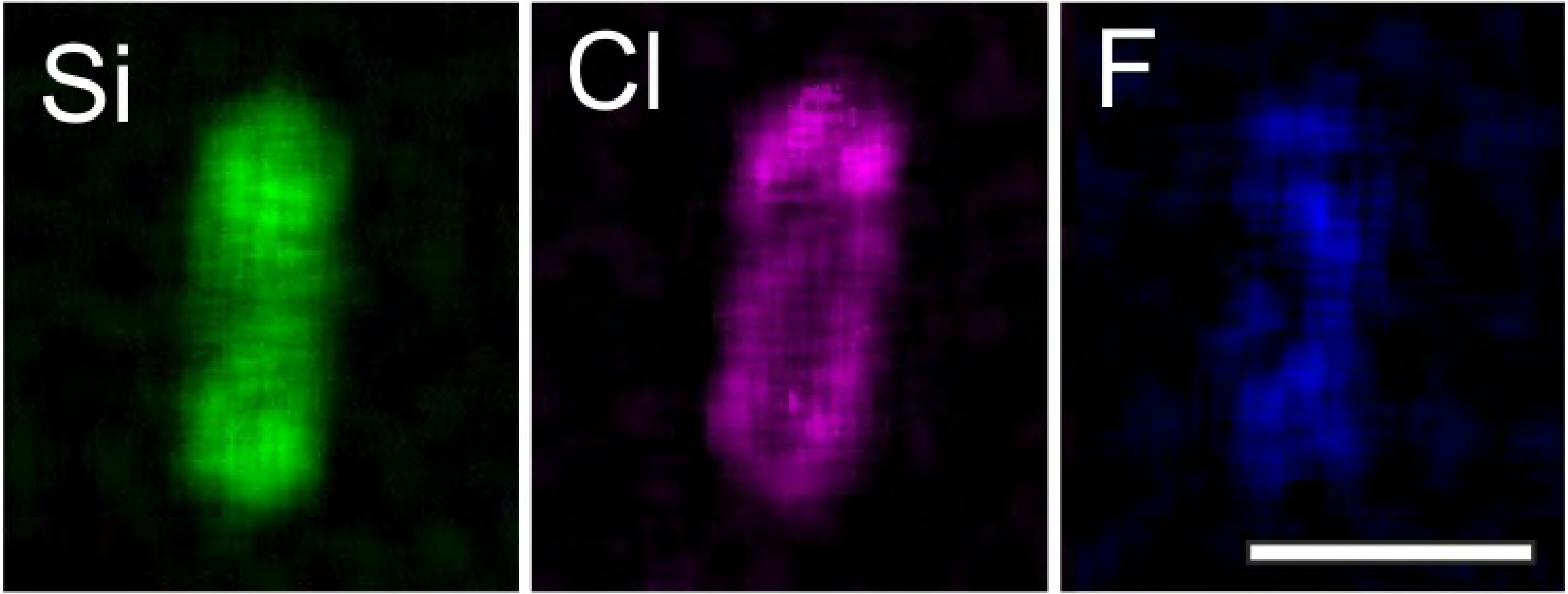


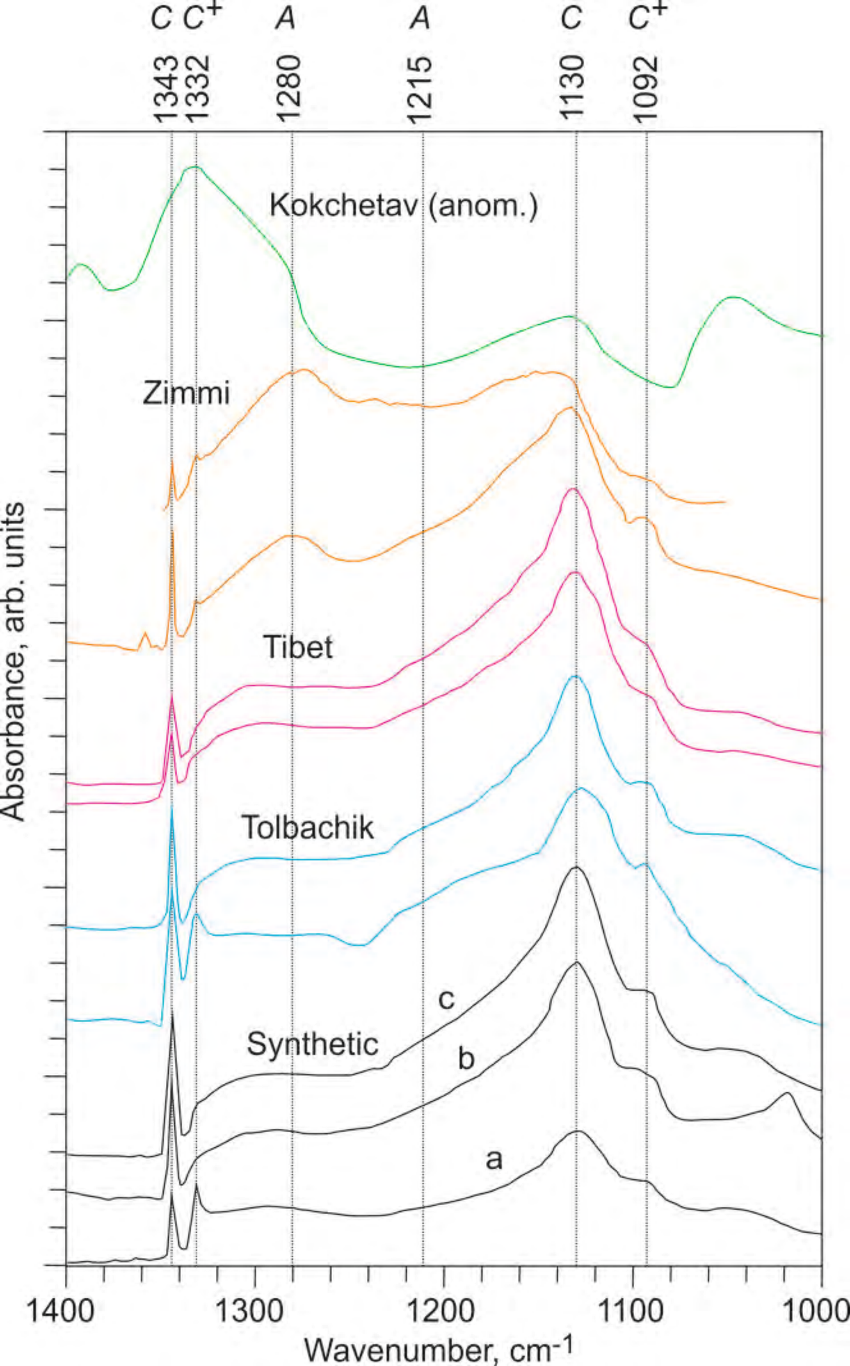
(a) Tolbachik
(b) Synthetic, Ni-Mn-Co
13C
29Si
55Mn
57Fe
60Ni
Element, counts
Time, s
Time, s



Si, counts
Metal (Fe+Mn+Ni), counts
10^4
10^3
10^2
10
10^3
10^4
10^5
10^6
Tolbachik
Synthetic, Ni-Mn-Co
Synthetic, others


C
O
Cu
Ga
F
Si
Cl
Mn
Mn
Ni
1μm
0
1
2
3
4
5
6
7
Energy, keV


Si
Cl
F



C
C+
A
A
C
C+
1343
1332
1280
1215
1130
1092
Kokchetav (anom.)
Zimmi
Tibet
Tolbachik
Synthetic
c
b
a
Absorbance, arb. units
1400
1300
1200
1100
1000
Wavenumber, cm-1

540°C
680°C
Total N content, ppm
% A aggregation
10000
1000
100
10
0
10
20
30
40
50
60
70
80
90
100
Tolbachik
Ophiolite
Akluilak minettes
Metamorphic
Kimberlite
Zimmi
Dachine
Carbonado


a
(100)
(111)
(111)
(100)
(111)
(100)
100 μm
b
(1$\bar{1}$3)
($\bar{1}$13)
(001)
(1$\bar{1}$1)
($\bar{1}$11)
(1$\bar{1}$0)
(1$\bar{1}\bar{1}$)
1 mm