

Extremely Fluorine-Rich Fluoborite from Fumarolic Exhalations of the Tolbachik Volcano, Kamchatka

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Abstract—Fluoborite extremely close to the fluorine endmember of the fluoborite $\text{Mg}_3[\text{BO}_3]\text{F}_3$ –hydroxylborite $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ series has been found in exhalations of the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. The proportion of the molecule $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ in it does not exceed 1 mol %. This borate is associated with halite, sylvite, langbeinite- and apthitalite-group sulfates, anhydrite, krasheninnikovite, sanidine, fluorophlogopite, hematite, tenorite, chubarovite, alluaudite-group arsenates, lammerite, and urusovite. Fluoborite occurs as tiny acicular or hairlike crystals up to 5 mm long assembled in radial, near-parallel or chaotic open-work aggregates up to 10 cm across. Its chemical composition determined by electron microprobe is, wt %: 38.71 Mg, 5.90 B, 25.52 O, 30.83 F, total 100.96; the empirical formula is $\text{Mg}_{2.97}\text{B}_{1.02}\text{O}_{2.98}\text{F}_{3.03}$. The unit-cell parameters calculated from the powder X-ray diffraction pattern are: $a = 8.808(4)$, $c = 3.098(2)$ Å, $V = 208.1(3)\text{Å}^3$. The IR and Raman spectra of borates of the fluoborite–hydroxylborite series are given and discussed. Fluoborite occurring in the Arsenatnaya fumarole crystallized at a temperature no lower than 450°C. The fumarolic genetic type is novel for this borate.

Keywords: fluoborite, hydroxylborite, natural fluoroborate, IR spectrum, Raman spectrum, fumarole, Tolbachik volcano, Kamchatka

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INTRODUCTION

Fluoborite $\text{Mg}_3[\text{BO}_3]\text{F}_3$ –hydroxylborite $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ series minerals are hexagonal orthoborates with triangular BO_3 groups. Their structure is based on columns of coupled edge-shared Mg^{2+} centered octahedra running along the c axis. These columns form 3D framework with two types of through channels. Anions F^- and OH^- occupy hexagonal channels of the first type, whereas channels of the second type having triangular section are occupied by the $[\text{BO}_3]^{3-}$ anion groups (Takeuchi, 1950; Brovkin et al., 1967; Dal Negro and Tadini, 1974; Moore and Araki, 1976; Rudnev et al., 2007).

Magnesium fluorhydroxylborate containing approximately 30 mol % of the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ component and described at the Norberg skarn iron deposit, Sweden in 1926 was initially named as fluoborite (Geijer, 1926). Its richer in F analogue was found in calcite–franklinite–willemite ore at the Sterling Hill

deposit in New Jersey, USA, and was described three years later under the same name (Bauer and Berman, 1929). Numerous findings in subsequent years showed that the F : OH ratio in the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ – $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ series is highly variable (see below for details) although fluorine- and hydroxyl-dominant members of this series were combined under the name of *fluoborite* for almost 80 years. Only in 2005 did V.V. Rudnev and his colleagues, in accordance with the general rules of mineral nomenclature, suggest considering the members of this series with $\text{OH} > \text{F}$ as an individual mineral species, hydroxylborite, retaining the name fluoborite for the fluor-dominant members. This suggestion was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (Rudnev et al., 2007).

It is noteworthy that the study history of this series is almost half a century longer than the history of the name fluoborite. A very high-fluorine sample from carbonate xenoliths among volcanic tuffs of the Nocera locality in Campania, Italy, was described in 1881

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as *nocerite*. Due to close intergrowth with fluorite and difficulties in the determination of boron content, nocerite has long been considered as a $\text{Mg}_3\text{Ca}_3\text{O}_2\text{F}_6$ mineral (Scacchi, 1881; Zambonini, 1919).

Later, Brisi and Eitel (1957) revealed that this is a mineral mixture based on fluoborite; however, the name nocerite is still sometimes used in the literature to refer to the high-fluorine fluoborite variety.

The fluoborite–hydroxylborite series members are not rare minerals. They are common at many magnesian skarn boron, iron, tin and polymetallic deposits and occurrences localized at the outer contact of the boron-bearing granite intrusions. These borates are known at skarn locations in Yakutia, Zabaykalsky Krai, Chukotka, Karelia, Kazakhstan, the United States (deposits in Alaska, New Jersey, and California), China (Aleksandrov, 1990), Sweden (Geijer, 1926), Spain (Cámara and Ottolini, 2000), Romania (Marincea, 2000), Australia (Kwak and Nicholson, 1988), and some other regions. They formed at the end of the early alkali stage of magnesian skarn formation and at the onset of the acidic stage of greisenization (Gramenitsky, 1966; Brovkin et al., 1967; Pertsev, 1971; Aleksandrov, 1990). It is probable that fluoborite in antigoritized ultramafic rocks of the Novoakhemsy massif formed under similar conditions (Oidup and Kudryavtseva, 1999).

Volcano-related fluoborite occurrences are known in Italy. The mineral is associated with altered calcite–dolomite xenoliths hosted by pyroclastic rocks. Aleksandrov (1990) considered metasomatic rock formed during interaction of magnesian carbonate rocks with hot lava or pyroclastic rocks as a specific skarn or skarnoid. Diopside, humite group members, fluorophlogopite, F-rich amphiboles, andradite–grossular garnets, calcite, fluorite, spinel, and iron oxides are the major constituents of this metasomatic rock. Fluoborite is observed in mineralized cavities as fine-acicular crystals intimately associated with fluorite, sellaite, and calcite (Zambonini, 1919; Brisi and Eitel, 1957; Aleksandrov, 1974; Caponera et al., 2003; Lacalamita et al., 2017).

As aforementioned, such fluoborite mineralization was found for the first time in tuffs of the Nocera location south of Vesuvius in 19th century. Later, some more similar fluoborite occurrences were found in southern Campania and in Latium Province near Rome (Caponera et al., 2003; Lacalamita et al., 2017).

Fluoborite is occasionally present in sedimentary sequences. In particular, it was described as spherulites and felt-like aggregates in halite–calcite and halite–anhydrite rocks at the Nepskoe potassium salt deposit in Irkutsk Oblast (Appolonov et al., 1988).

Cation substitutions in the fluoborite series borates are very weakly developed; magnesium is a strongly predominant cation over all studied samples of these minerals, whereas complete isomorphism is supposed between F and OH. Hydroxylborite containing less

than 25 mol % of the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ molecule has still not been found (Aleksandrov, 2007). At the same time, mineral and technogenic and synthetic samples corresponding to the remaining field of this solid solution series are well known. For example, fluoborite of the Nepskoe deposit contains 50–60 mol % of fluorine endmember (Appolonov et al., 1988). According to (Aleksandrov, 1990), the F : OH ratio in the samples from magnesian skarn increases with the F content in mineral-forming fluids from the alkali to acidic stage. Hydroxylborite with 25–50 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$ is primarily precipitated at the alkali substage at the end of skarn borate (usually suanite–kotoite) mineralization proper. It replaces dolomite in calciphyres and near-skarn marbles and is intimately associated with ludwigite and clinohumite. Fluoborite with 50–75 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$ replacing early Mg–Fe borates and kotoite crystallizes at the beginning of the greisen process. High-fluorine (with 75–95 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$) fluoborite varieties are present in greisen replacing dolomite in association with fluorite and sellaite, and less frequent chrysoberyl, cassiterite, tourmaline, fluorophlogopite, and zinnwaldite (Gulyaev, 1971; Aleksandrov, 1990, 2007).

Brisi and Eitel (1957) identified fluoborite from Nocera tuffs as a purely fluorine variety; however, later, Flamini (1966) and Aleksandrov (1990) estimated the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ fraction in it as 91 and 96 mol %, respectively. According to the data from (Lacalamita et al., 2017), the fluorine concentration in the fluoborite samples from altered xenoliths hosted by the Campania volcanic rocks is 24.3 wt % that corresponds to 82 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$.

Hydroxyl-free fluoborite from burnt rocks of the Chelyabinsk coal basin in the South Urals has been described (Chesnokov and Bushmakin, 1995). It was observed at the burning waste pile of the mine no. 45 in Kopeisk within so called “black block”, where it was on the surface of a burnt fragment of petrified wood as acicular crystals together with chondrodite, fluorite, and sellaite. It should be noted that the chemical composition of technogenic fluoborite was not determined and conclusion that it is the fluorine endmember is based on the X-ray diffraction and optical study (Chesnokov and Bushmakin, 1995).

Brisi and Eitel (1957), Brovkin et al. (1967), and Flamini et al. (1979) reported hydroxyl-free fluoborite analog synthesized from dry mixture of MgO , B_2O_3 , and MgF_2 in the 3 : 1 : 3 proportion heated up to 750–1050°C.

Thus, natural members of the fluoborite–hydroxylborite series containing from ~25 to 95 mol % of the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ endmember were reliably identified (supported by the directly determined chemical composition) to date, whereas the hydroxyl-free series member was found among technogenic (burnt rocks from dumps of coal enterprises) and synthetic borates.

This paper is focused on nearly hydroxyl-free natural fluoborite belonging to the fumarole genetic type that is new for borates of this series. The mineral studied came from exhalations of the Arsenatnaya (Arsenate) active fumarole created by the Tolbachik volcano in the Kamchatka Peninsula.

OCCURRENCE OF FUMAROLIC FLUOBORITE AND GENERAL DESCRIPTION OF SAMPLES STUDIED

The Arsenatnaya fumarole is situated in near-summit part of the Second scoria cone of the North Vent of the Great Fissure Tolbachik Eruption (NV GFTE) in 1975–1976 located 18 km South of the Plosky Tolbachik active volcano. This scoria cone, 0.1 km³ in volume and 300 m high, is a monogenic volcano, which arose in 1975 (*Bol'shoe ...*, 1984). It is still exhibiting significant fumarole activity: numerous gas outlets with a temperature up to 500°C according to our measurements in 2012–2018 are observed at the surface. Fumaroles of the Second Cone of the GFTE belong to the oxidizing type through the mixing of volcanic gas and atmospheric air. Here, there are several active mineralized fumaroles, including world unique ones, characterized by an outstanding variety of exhalative minerals, mainly belonging to oxides and oxyalts. The most impressive mineralogical localities here are the Yadovitaya (Vergasova and Filatov, 2016) and Arsenatnaya fumaroles, with the latter being the absolute world record holder in mineral diversity and specifics: at present, almost 200 (!) mineral species (except for poorly documented phases), 50 of which were discovered here (Pekov et al., 2018, 2020), were reliably identified in an area of 15 × 4 m². General information about the Arsenatnaya fumarole as mineralogical location including zoning in distribution of various mineralization types, is given in (Pekov et al., 2018; Shchipalkina et al., 2020). Fluoborite occurs in the so-called polyminerale zone located in the middle part of the Arsenatnaya fumarole. Its clusters were found at the depth of 0.8 to 2 m below surface in open cavities and fractures, in which the temperature measured with chromel-alumel thermocouple ranged from 300 to 400°C at the opening. Earlier, another halogenoborate, chubarovite KZn₂[BO₃]Cl₂, was discovered in this zone (Pekov et al., 2015); in general, within the Arsenatnaya fumarole, this zone is characterized by the greatest diversity of high-temperature minerals resulting from desublimation, i.e., direct precipitation from hot gas or involving gas alteration (Naboko and Glavatskikh, 1983). The latter process, in particular, results in strong replacement of basalt (basalt scoria) making up the walls of fumarole chambers with aggregates of sanidine. including its As-bearing variety and/or fluorophlogopite (Shchipalkina et al., 2020). The richest mineralization is formed in open space. Hematite and tenorite are formed in large amounts; other oxide minerals are pseudobrookite,

rutile, cassiterite, spinels (gahnite, cuprospinel, thermanogenite), and corundum. Sylvinite and halite are common chlorides, whereas fluorides are absent, except for the rarest sellaite. Sulfates primarily represented by the aphantialite (metathenardite, belomarinaitite, aftitalite) and langbeinite (langbeinite, calciolangbeinite) group members are abundant; anhydrite, krashennikovite, euchlorine, wulffite, and arkanite are also frequent. Arsenates, which are observed in great amounts in this zone and are frequently the major constituents of exhalative crusts, are particularly diverse. These are members of the alluaudite group (johillerite, nikenichite, bradachekite, calciojohillerite, badalovite, hatertite, magnesiohatertite), lammerite, lammerite-β, ericlsmanite, kozyrevskite, popovite, urusovite, tilasite, svabite, yurmarinite, shchurovskite, dmisokolovite, arsmirandite, lehmannite, arsenatrotitanite, and some other rarer minerals.

Fluoborite is rather common in this zone of the Arsenatnaya fumarole. In different chambers, it is associated with different minerals; its intimate neighboring was observed with the most aforementioned minerals, including chubarovite.

Tolbachik fluoborite occurs as very thin (occasionally thicker than 1 μm), but sometimes sufficiently long (up to 0.5 cm) hairlike or acicular hexagonal or polygonal crystals with poor formed flat or pyramidal terminations (Fig. 1). As a rule, they are combined into radial (stellate, sheaflike, bushy) (Figs. 2, 3), near-parallel (crystal crusts) or chaotic open-work aggregates. Soft, “velvet” radiated-fibrous segregations up to 1 cm in diameter occasionally forming botroidal clusters up to 10 cm across in cavities are typical. Isolated individuals of the mineral are colorless, whereas aggregates are white with silky luster.

CHEMICAL COMPOSITION

The chemical composition and micromorphology (Figs. 1, 3) of the Tolbachik fluoborite were studied using a JEOL JSM6480LV scanning electron microscope equipped with and INCA-Wave 500 WDS at the Laboratory of Analytical Techniques of High Spatial Resolution at the Department of Petrology and Volcanology, Geological Faculty, Moscow State University. The operating conditions were: 20 kV acceleration voltage, current intensity 10 nA, and beam defocused down to an area of 5 × 5 μm². The following standards were used: diopside (Mg), BN (B), SrSO₄ (O), MgF₂ (F). The contents of other elements with atomic numbers >5 were below detection limits by electron microprobe. Preparing samples for electron microprobe analysis has not been easy, because the Tolbachik fluoborite forms soft and loose, poor-polished aggregates composed of hairlike individuals, between which crystals of other minerals are frequently observed.

The chemical composition of fluoborite from the Arsenatnaya fumarole determined on relatively com-

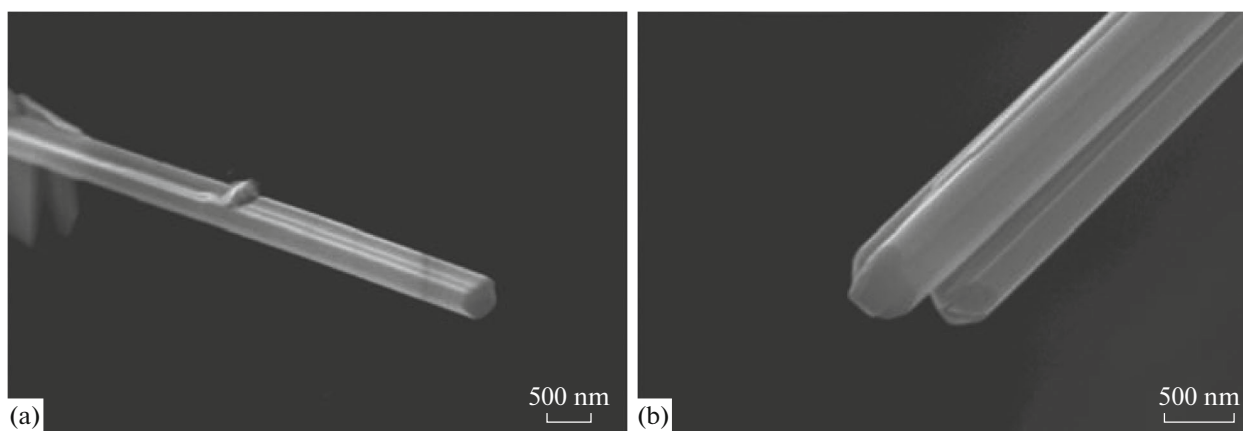


Fig. 1. Secondary electron images of acicular fluoborite crystals from Arsenatnaya fumarole, Tolbachik volcano, Kamchatka. (a) crystal with flat (pinacoidal) termination; (b) parallel intergrowth with poorly formed pyramidal terminations.



Fig. 2. Cluster of stellate fluoborite aggregates on basalt scoria altered by fumarole gas. Arsenatnaya fumarole, Tolbachik.

pact fine-fibrous aggregate is, wt %: 38.71 Mg, 5.90 B, 25.52 O, 30.83 F, total 100.96. The empirical formula calculated on the basis of a total number of ten atoms is $\text{Mg}_{2.97}\text{B}_{1.02}\text{O}_{2.98}\text{F}_{3.03}$. As one can see, it is very close to the idealized formula of the fluoborite endmember, $\text{Mg}_3\text{BO}_3\text{F}_3$.

X-RAY CRYSTALLOGRAPHY

Fine hairlike individuals prevented the single crystal X-ray diffraction study of Tolbachik fluoborite. Powder X-ray diffraction patterns were obtained for several samples using a Rigaku R-AXIS Rapid II diffractometer equipped with cylindrical IP detector (monochromatized $\text{CoK}\alpha$ radiation; Debye-Scherrer geometry, $d = 127.4$ mm, 10 min exposure time). The

initial data from the cylindrical detector were integrated using the osc2tab software package (Britvin et al., 2017).

The powder X-ray diffraction patterns clearly show belonging of the studied mineral to the fluoborite structure type. The hexagonal unit cell parameters calculated from the powder X-ray diffraction data are $a = 8.808(4)$, $c = 3.098(2)$ Å, $V = 208.1(3)$ Å³.

RAMAN SPECTROSCOPY

The Raman spectra were measured with an EnSpectr R532 spectrometer, (Russia) at a 532 nm excitation wavelength and 12 mWt beam power. The spectra were obtained using unoriented (powder)

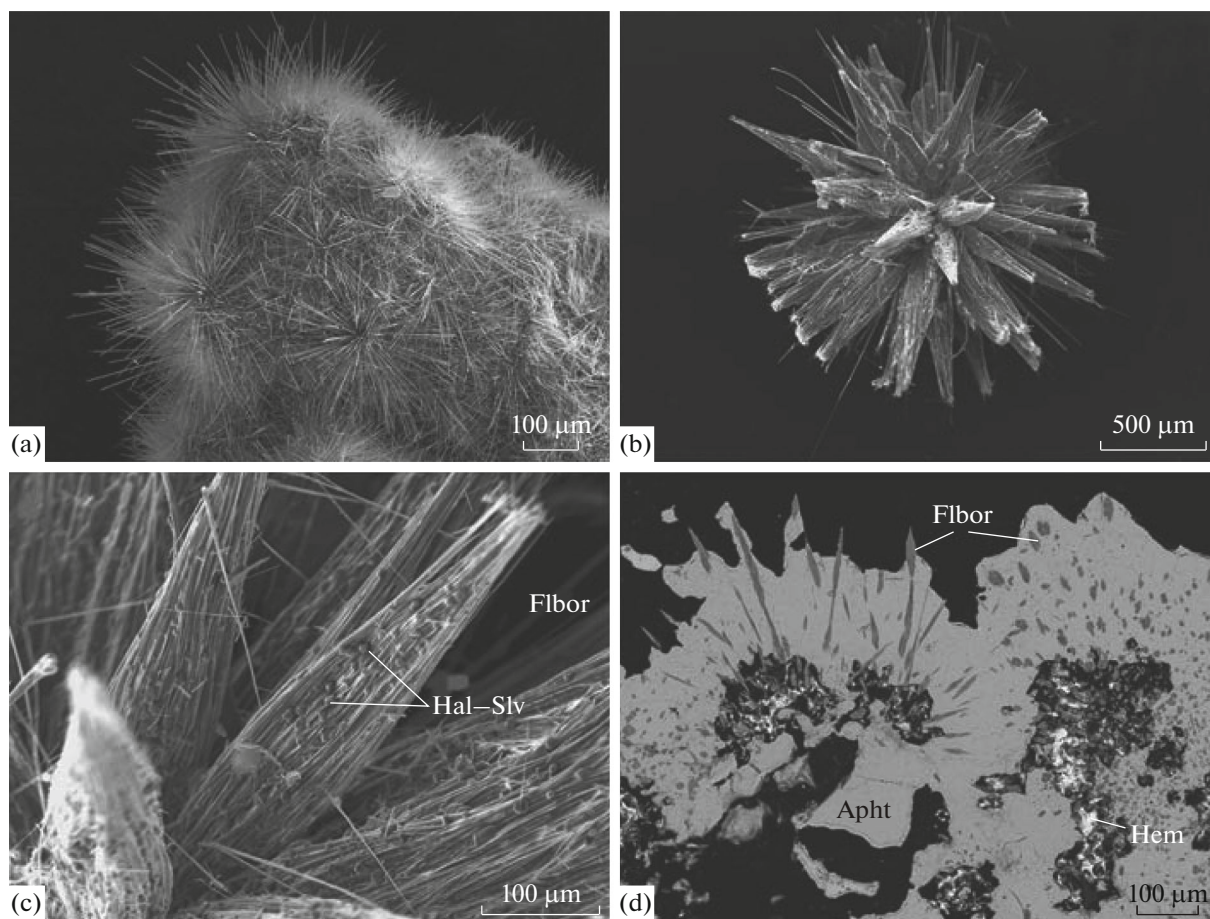


Fig. 3. Secondary electron images of fluoborite aggregates from Arsenatnaya fumarole, Tolbachik. (a) Radial aggregates of thin acicular crystals; (b) stellate aggregate with “rays” consisting of bundles of hairlike crystals; (c) enlarged fragment of the stellate fluoborite (Flbor) aggregate powdered by halite-sylvinite (Hal-Slv); (d) hematite-fluoborite aggregate overgrown by aphtitalite (Apht) crust, (Hem) hematite (polished section). SEM (BSE) images.

samples over the range of 200 to 4000 cm^{-1} with a signal accumulation for 1 s when averaged over 50–70 exposures. The focal spot size was 5–10 μm .

The Raman data for the fluoborite–hydroxylborite series borates were not found in literature and fluoborite spectrum from Ontario, Canada given in the RRUFF electron database (RRUFF project. Database of Raman spectroscopy, X-ray diffraction and chemistry of minerals; <https://rruff.info/fluoborite/>) is limited to the 165–1315 cm^{-1} range. Therefore, for comparison we obtained the spectra of OH-bearing fluoborite sample with ~65 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$ from calciphyre of the Franklin zinc deposit in New Jersey, USA, and hydroxylborite with ~42 mol % of $\text{Mg}_3[\text{BO}_3]\text{F}_3$ from magnesian skarn of the Keberin’ya boron occurrence in the eponymous stream valley, which is tributary of the Dogdo River (Tas-Khayakhtakh Range, Polar Yakutia).

In general, the spectra obtained are similar to each other and to the spectrum from the RRUFF database (Fluoborite R061042). According to (Nakamoto,

2009), the strong band at 950 cm^{-1} corresponds to the symmetric stretching vibrations (ν_1) of the B–O bonds in the borate triangular groups and the weak band at 1350 cm^{-1} corresponds to their asymmetric stretching vibrations (ν_3). Bands in the regions about 860 and 640 cm^{-1} are assigned to the bending symmetric (out-of-plane, ν_2) and asymmetric (degenerate planar, ν_4) B–O vibrations, respectively. As can be seen, these bands are shifting toward higher frequencies with an increase in the proportion of the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ component. Weak bands over the range of 340–550 cm^{-1} correspond to the Mg–O and Mg–F stretching vibrations. The lattice acoustic modes are observed below 300 cm^{-1} .

In the Raman spectrum of the Tolbachik fluoborite, the following bands with maximums at 1350, 958(s), 860, 643, 506, 356, 262, 237(s) cm^{-1} (s denotes strong band) are observed. Its main difference from the other two spectra shown in Fig. 4 is the absence of bands in the region of 3000–4000 cm^{-1} corresponding

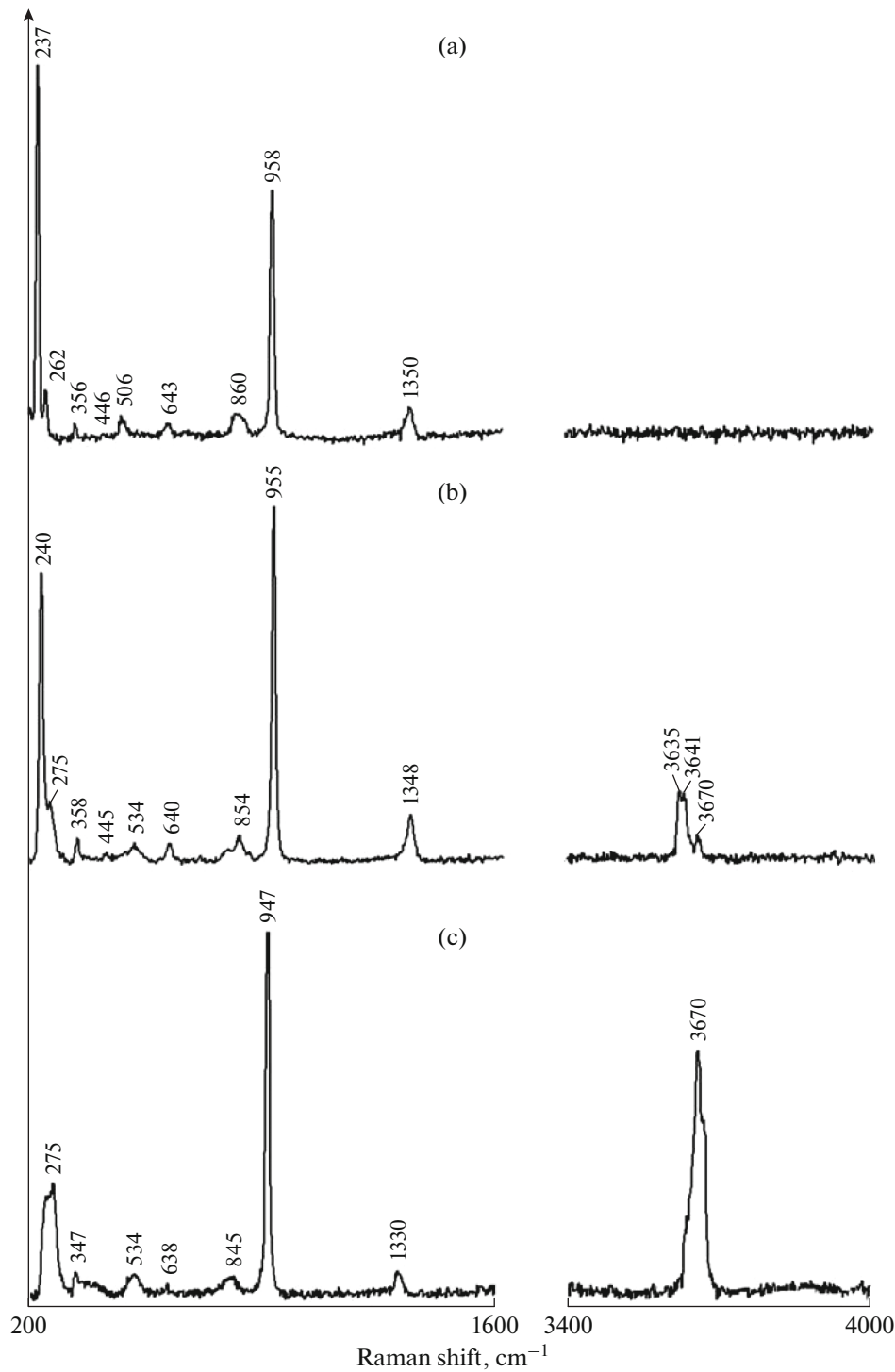


Fig. 4. Raman spectra of: (a) fluoborite from Arsenatnaya fumarole (Tolbachik volcano, Kamchatka), (b) OH-bearing fluoborite from Franklin (New Jersey, USA), and (c) hydroxylborite from Kebirin'ya (Tas-Khayakhtakh Range, Polar Yakutia, Russia).

to hydroxyl group vibrations. In the Raman spectrum of the Franklin sample, just like in its IR spectrum (see below), the band of O–H stretching vibrations is split, while the similar band of hydroxylborite has a high-frequency shoulder, indicating different types of OH groups in these samples.

INFRARED SPECTROSCOPY

The IR spectra of the samples of the fluoborite–hydroxylborite series minerals (Fig. 5) placed in the KBr pellets were recorded with an ALPHA FTIR Bruker Optics spectrometer over a wavenumber range

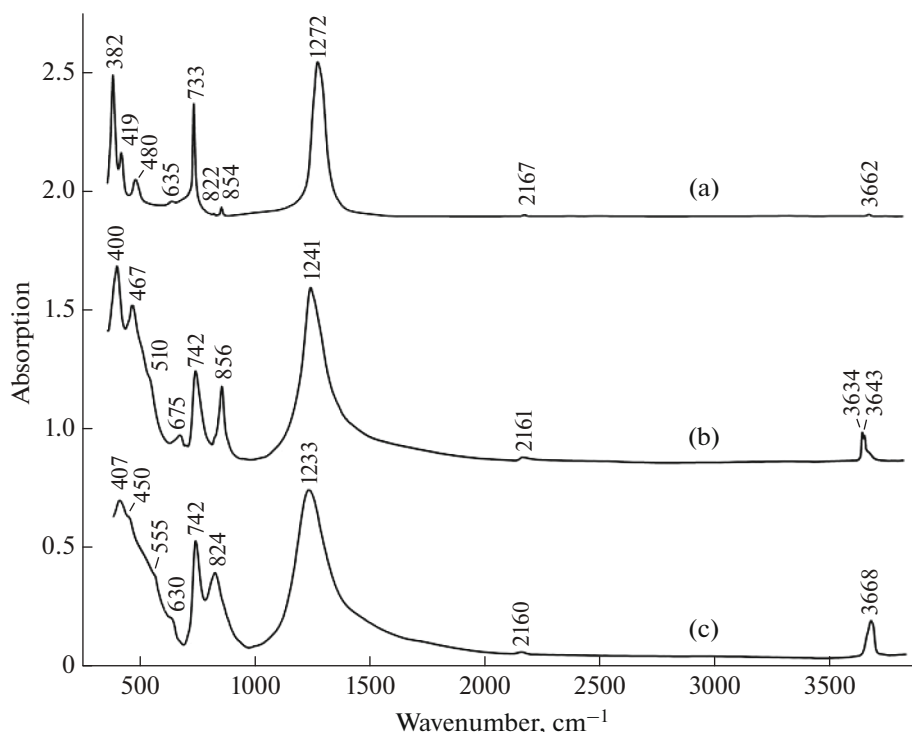


Fig. 5. IR spectra of: (a) fluoborite from the Arsenatnaya fumarole (Tolbachik volcano, Kamchatka), (b) OH-bearing fluoborite from Franklin (New Jersey, USA), and (c) the holotype hydroxylborite from the Titovskoe deposit (Tas-Khayakhtakh Range, Polar Yakutia, Russia).

of 360 to 3800 cm^{-1} with 16 scans at a resolution of 4 cm^{-1} . A similar pellet prepared from pure KBr was used as reference material.

The same samples from Tolbachik and Franklin used in the Raman spectroscopy (Figs. 4a, 4b) were used to record the IR spectra of fluoborite, and the IR spectrum of hydroxylborite was obtained on the best studied holotype sample from the Titovskoe boron deposit in the Tas-Khayakhtakh Range, Polar Yakutia (Rudnev et al., 2007), in which the proportion of the $\text{Mg}_3[\text{BO}_3]\text{F}_3$ molecule is approximately 33 mol %.

All three IR spectra contain bands in the ranges of (cm^{-1}): 3630–3670 (O–H stretching vibrations), 1230–1280 (asymmetric stretching mode of the BO_3^{3-} group), 820–860 (presumably mixed mode involving bending $\text{Mg}\cdots\text{O}$ –H bending vibrations and out-of-plane bending vibrations of the BO_3^{3-} group), 730–750 (out-of-plane bending vibrations of the BO_3^{3-} group possibly involved in the Fermi resonance with overtone of Mg –O stretching vibrations and/or libration vibrations of OH groups), 630–680 (in-plane bending vibrations of the BO_3^{3-} group), 380–560 (stretching vibrations of framework consisting of Mg-centered octahedra and libration vibrations of OH groups). Weak bands at 2160–2167 and 822 (in the sample from Tolbachik) correspond to combination modes.

The integrated intensities of stretching and bending vibrations corresponding to OH groups in the spectrum of the Tolbachik sample are approximately 40–50 times lower than those in the spectrum of hydroxylborite from Polar Yakutia, which suggests that the hydroxylborite molecule proportion in the mineral form Arsenatnaya does not exceed 1%, i.e., it is extremely F-rich fluoborite. This is consistent with the Raman spectrum (Fig. 4a), in which the O–OH stretching vibration bands are not observed due to lower sensitivity of the method.

The minor OH groups in the sample from Arsenatnaya form hydrogen bonds of the unique type as evidenced by singlet at 3662 cm^{-1} . These are possibly $\text{OH}\cdots\text{F}$ or $\text{OH}\cdots\text{O}_{\text{BO}_3}$ bonds. In fluoborite from Franklin, hydroxyl groups are locally diverse and are observed in the IR spectrum as bands with the maximums at 3634 and 3643 cm^{-1} and a weak shoulder at 3665 cm^{-1} . It may be suggested that this diversity is caused by the hydrogen bonding $\text{OH}\cdots\text{F}$, $\text{OH}\cdots\text{OH}$, and $\text{OH}\cdots\text{O}_{\text{BO}_3}$ (possibility of $\text{OH}\cdots\text{OH}$ bonding is close to zero in extremely low-OH Tolbachik fluoborite) Broad bands at 824 and 3648 cm^{-1} in the IR spectrum of hydroxylborite are probable unresolved doublets or multiplets. In general, the increasing content of OH groups is accompanied with broadening of all bands in the IR spectra of the fluoborite–hydroxylborite series minerals, which may be caused by dis-

turbing effect of hydrogen bonds on the vibrations of the framework and orthoborate groups.

DISCUSSION

The published data (Brovkin et al., 1967; Dal Negro and Tadini, 1974; Cámara and Ottolini, 2000; Rudnev et al., 2007) indicate that due to the difference in the F^- and OH^- ion radii, the a unit cell parameter of the purely fluorine member of the fluoborite–hydroxylborite series is the least and increases linearly with the $Mg_3[BO_3](OH)_3$ proportion. The c parameter does not show linear dependence on the $F : OH$ value and substantially less changes in this series. The obtained unit cell parameters of the Tolbachik fluoborite ($a = 8.808$, $c = 3.098 \text{ \AA}$, $V = 208.1 \text{ \AA}^3$) are very close to those of synthetic $Mg_3[BO_3]F_3$ with the fluoborite structure: $a = 8.805$, $c = 3.097 \text{ \AA}$, $V = 208.08 \text{ \AA}^3$ (Brovkin et al., 1967) and $a = 8.805$, $c = 3.100 \text{ \AA}$, $V = 208.14 \text{ \AA}^3$ (Okazaki et al., 1965), as well as technogenic fluoborite from the Chelyabinsk coal basin ($a = 8.802$, $c = 3.097 \text{ \AA}$; Chesnokov and Bushmakin, 1995). Slightly increased a parameter as compared to that of pure $Mg_3[BO_3]F_3$ indicates possible hydroxylborite molecule in the Tolbachik mineral that is consistent with IR data. According to the formula $a = 8.806 + 0.0024h$, where $h = OH/(OH + F) \times 100\%$ suggested by Brovkin et al. (1967), the fraction of the $Mg_3[BO_3](OH)_3$ endmember in the Tolbachik fluoborite is approximately 0.8 mol %. Thus, the X-ray diffraction data support the attribution of the mineral from the Arsenatnaya fumarole to the nearly pure fluorine member of the series.

Since fluoborite with a fraction of the fluoborite endmember of almost 100% was not reliably identified previously, its formation conditions merit attention.

High-temperature fumaroles substantially differ in physicochemical parameters from other mineral-forming systems. The specifics of the exhalation process is governed by such factors as highly variable temperature (up to 1000°C) at low (atmospheric) pressure, gas transport of most chemical elements, and special geochemical environment. In addition, the high-oxidative conditions resulted from mixing of volcanic gas with atmospheric air are characteristic of the Tolbachik fumaroles (Pekov et al., 2020). As a result, the mineral assemblages forming there, including those with fluoborite, are absolutely uncommon in other environments. In magnesian skarn (including greisenized ones) and calciphyre, fluoborite is formed in paragenetic association with fluorides, oxides, borates, and F-rich silicates/aluminosilicates predominantly with Ca, Mg, Fe^{2+} , Fe^{3+} , Al, and K as species-defining cations; chalcophile elements (Cu, Zn, Pb) predominantly incorporate into sulfides and similar compounds. In the oxidizing-type fumarole, fluoborite is accompanied by chlorides, oxides, sulfates, arsenates, silicates, and borates with wide range and

combinations of cations including chalcophile ones with minor fluorides. Fluorine incorporates into complex salts, fluor-silicates, fluor-sulfates, fluor-arsenates and other, among which there are fluoborates whose representative is fluoborite. As shown previously (Pekov et al., 2020), paragenetic assemblages containing these minerals change to the lower-temperature associations with fluorides at 300–350°C.

It is noteworthy that the combination of high temperature and low pressure in the oxidizing environment prevent hydrogen incorporation into crystalline phases and therefore the minerals from fumarole zones with temperature $>200^\circ\text{C}$ do not contain H-bearing groups. This is the case even micas and amphiboles, which are represented by fluorine species (Pekov et al., 2020; Shchipalkina et al., 2020). Thus, the virtual absence of hydroxyl groups in the high-temperature exhalative fluoborite is expected.

Despite the fact that the temperature within fluoborite-bearing cavities was 300–400°C during opening of the Arsenatnaya fumarole, the geothermometric data indicate that the mineral assemblages in them formed at a higher temperature (Pekov et al., 2018; Shchipalkina et al., 2020). Since fluoborite aggregates are frequently overgrown by halite–sylvinitic crusts with an exsolution texture of (K,Na)Cl stable only at the temperatures of $\sim 450^\circ\text{C}$ (Filatov and Vergasova, 2002), the temperature range of the exhalative fluoborite formation appears to be above this value. In magnesian skarns (including xenoliths in volcanic rocks), F-rich fluoborite is formed by the interaction of aqueous fluids saturated in boron and fluorine with magnesian carbonate rocks at 380–450°C under variable lithostatic pressure (Tell, 1972; Lacalmita et al., 2017). It is known that a full fluorine analog of fluoborite was synthesized by A. Flamini in aqueous medium at 400°C and 250 atm. However, under atmospheric pressure, it was synthesized only in the dry Mg–B–O–F system at temperature above 750°C (Flamini et al., 1979). Note that the first stage of dehydroxylation (removal of OH groups from OH-bearing fluoborite) occurs at a temperature about 780°C (Kondrat'eva, 1969), thus suggesting that OH-bearing fluoborite is unstable above this temperature under atmospheric pressure. In contrast, hydroxyl-free fluoborite is formed over wider temperature range. Thus, accurate determination of the temperature range of the fluoborite formation in a such complex natural system as fumarole, is difficult.

The morphology of aggregates and their overgrowth with other exhalation minerals indicate that the Tolbachik fluoborite crystallized immediately from gas phase. Boron and fluorine are introduced by volcanic gas, and basalt is the most likely source of magnesium. The latter is illustrated by the fact that the major Mg-bearing minerals of basalt, pyroxene (diopside–augite) and olivine, are unstable and are easily replaced by cristobalite in the fluoborite-bearing zone

of the Arsenatnaya fumarole. Magnesium released from the rock is low volatile in volcanic gas (Symonds and Reed, 1993; Zelenski et al., 2014); as a consequence, rich and diverse magnesian mineralization is formed in exhalation crusts.

MAIN RESULTS AND CONCLUSIONS

The high-temperature oxidizing-type Arsenatnaya fumarole at the Tolbachik volcano, Kamchatka, is the first (and so far only) natural object, where fluoborite extremely close to the fluorine endmember of the fluoborite $\text{Mg}_3[\text{BO}_3]\text{F}_3$ —hydroxylborite $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ series was established. According to the electron microprobe data, the empirical formula of the Tolbachik fluoborite is $\text{Mg}_{2.97}\text{B}_{1.02}\text{O}_{2.98}\text{F}_{3.03}$. The hexagonal unit cell parameters [$a = 8.808(4)$, $c = 3.098(2)$ Å, $V = 208.1(3)$ Å³] and IR and Raman data clearly indicate that the proportion of the $\text{Mg}_3[\text{BO}_3](\text{OH})_3$ endmember is insignificant in it and does not exceed 1 mol %.

The systematic Raman study of the fluoborite—hydroxylborite series minerals and comparative characteristic of the IR and Raman spectra of these borates were performed for the first time. It was shown that the intermediate members of this series have the most complex structure of the bands in the region of O—H stretching vibrations (3630–3680 cm⁻¹) that is caused by diverse hydrogen bonds.

The new genetic type of the fluoborite mineralization, fumarole, has been established in the exhalation postvolcanic system of Tolbachik. In the Arsenatnaya fumarole, fluoborite is accompanied with diverse oxygen compounds, sulfates, arsenates, silicates, and oxides with a wide range of species-defining cations including chalcophile elements. Other known occurrences of this borate associated with active and extinct volcanoes were formed as result of metasomatic processes at the contact of carbonate xenoliths and effusive rocks rather than proper fumarole activity. Their paragenetic assemblages containing fluoborite differ from those observed in the Arsenatnaya fumaroles both in the chemical composition of minerals and the set of mineral species.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

- Aleksandrov, S.M., Geochemical peculiarities of the occurrences of endogenous borate mineralisation in Italy, *Geokhimiya*, 1974, vol. 10, pp. 1440–1449.
- Aleksandrov, S.M., Geochemistry of Skarn and Ore Formation in Dolomites, Utrecht—Tokyo: VSP, 1998.
- Aleksandrov, S.M., Endogenous transformations of kotoite in calciphyres at magnesian-skarn deposits of boron, *Geochem. Int.*, 2007, vol. 5, no. 7, pp. 666–684.
- Apollonov, V.N., Galkin, G.A., Koshchug, D.G., and Sadovyi, V.F., On boron mineralization in the potassium-bearing member of the Nepskoe Deposit, *Geol. Geofiz.*, 1988, no. 3, pp. 24–30.
- Bauer, L.H. and Berman, H., Mooreite, a new mineral, and fluoborite from Sterling Hill, N.J., *Am. Mineral.*, 1929, vol. 14, no. 5, pp. 165–172.
- Bol'shoe treshchinnoe Tolbachinskoe izverzhenie, Kamchatka, 1975–1976* (The 1975–1976 Great Tolbachik Fissure Eruption in Kamchatka), Fedotov, S.A., Eds., Moscow: Nauka, 1984.
- Brisi, C. and Eitel, W., Identity of nocerite and fluoborite, *Am. Mineral.*, 1957, vol. 42, nos. 3/4, pp. 288–293.
- Britvin, S.N., Dolivo-Dobrovolsky, D.V., and Krzhizhanovskaya, M.G., Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer, *Zap. Ross. Mineral. O-va*, 2017, vol. 146, no. 3, pp. 104–107.
- Brovkin, A.A., Lazebnik, Yu.D., and Lebedeva, L.I., Some results of studying fluoborites of the North-East USSR. In: *Rentgenografiya mineral'nogo Syr'ya* (X-Ray Study of Mineral Raw Materials), Moscow: Nedra, 1967, no. 6, pp. 77–86 (in Russian).
- Cámara, F. and Ottolini, L., New data on the crystal-chemistry of fluoborite, by means of SREF, SIMS and EMP analysis, *Am. Mineral.*, 2000, vol. 85, no. 1, pp. 103–107.
- Caponera, I., Fiori, S., and Pucci, R., Fluoborite, piombo nativo, richterite ed altri interessanti ritrovamenti nei Colli Albani, *Gruppo Mineralogico Roma*, 2003, vol. 1–2, pp. 3–13.
- Chesnokov, B.V. and Bushmakin, A.F., New minerals from the burnt dumps of the Chelyabinsk coal basin. Communication 8., *Ural'sk Mineral. Sbornik*, 1995, no. 5, pp. 3–22.
- Dal Negro, A. and Tadini, C., Refinement of the crystal structure of fluoborite, $\text{Mg}_3[\text{BO}_3]\text{F}_3$, *Tschermaks Mineral. Petrograph. Mitt.*, 1974, vol. 21, pp. 94–100.
- Filatov, S.K. and Vergasova, L.P., Dissociation and homogenization of double salines NaCl—KCl from fumarole deposits based on high-temperature X-ray diffraction data, *J. Volcanol. Seismol.*, 2002, vol. 5, pp. 25–31.
- Flamini, A., Sulla composizione chimica della nocerite, *Periodica di Mineralogia*, 1966, vol. 35, no. 1, pp. 205–222.
- Flamini, A., Graziani, G., and Pagliuca, G., Synthesis of the fluorine end member of the fluoborite series, *Am. Mineral.*, 1979, vol. 64, no. 2, pp. 229–231.
- Geijer, P., Norbergite and fluoborite, two new minerals from the Norberg mining district, *Geologiska Föreningen i Stockholm Föreläsningar*, 1926, vol. 48, pp. 84–85.
- Gramenitskiy, E.N., The analysis of the fluoborite's paragenesis, *Geol. Rudn. Mestorozhd.*, 1966, no. 1, pp. 16–32.
- Gulyaev, A.P., Fluoborite from apodolomitic greisens (Kazakhstan), *Zap. Ross. Mineral. O-va*, 1971, no. 5, pp. 637–640.
- Kondrat'eva, V.V., *Rentgenometricheskii opredelitel's boratov* (A Guide to X-Ray Diffraction Determination of Borates), Leningrad: Nedra, 1969.

- Kwak, T.A.P. and Nicholson, M., Szaibelyite and fluoborite from the St. Dizier Sn-borate skarn deposit, NW Tasmania, Australia, *Mineral. Mag.*, 1988, vol. 52, pp. 713–716.
- Lacalamita, M., Balassone, G., Schingaro, E., Mesto, E., Mormone, A., Piochi, M., Ventrucci, G., and Joachimski, M., Fluorophlogopite-bearing and carbonate metamorphosed xenoliths from the Campanian Ignimbrite (Fiano, southern Italy): crystal chemical, geochemical and volcanological insights, *Mineral. Mag.*, 2017, vol. 81, no. 5, pp. 1165–1189.
- Marincea, St., Fluoborite in magnesian skarns from Baita Bihor (Bihor massif, Apuseni Mountains, Romania), *Neues Jahrb. Mineral., Monatsh.*, 2000, vol. 8, pp. 357–371.
- Moore, P.B. and Araki, T., Painite, $\text{CaZrB}[\text{Al}_9\text{O}_{18}]$: Its crystal structure and relation to jeremejevite, $\text{B}_5[\square_3\text{Al}_6(\text{OH})_3\text{O}_{15}]$, and fluoborite, $\text{B}_3[\text{Mg}_9(\text{F},\text{OH})_9\text{O}_9]$, *Am. Mineral.*, 1976, vol. 61, pp. 88–94.
- Naboko, S.I. and Glavatskikh, S.F., *Posteruptivnyi metasomatoz rudoobrazovanie (Bol'shoe treshchinnoe Tolbachinskoe izverzhenie 1975–1976 gg. At Kamchatka)* (Post-Eruptive Metasomatism and Ore Genesis: the 1975–76 Great Tolbachik Fissure Eruption at Kamchatka), Moscow: Nauka, 1983.
- Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A*, 6th Edition, New Jersey: Wiley & Sons, 2009.
- Oidup Ch.K. and Kudryavtseva, A.I., On the finding of fluoborite in ultramafic rocks of the Novoakhem massif (Western Tuva), In: *Voprosy petrologii, mineralogii, geokhimi i geologii ofiolitov* (Questions of Petrology, Mineralogy, Geochemistry and Geology of Ophiolites), Novosibirsk: Institute of Geology SB RAS, 1999, pp. 146–149.
- Okazaki, H., Nakazima, S., and Mizuno, H., *The crystal structure and the character of fluorescence in fluorescent $\text{MgO}-\text{B}_2\text{O}_3-\text{MgF}_2$* , *Nippon Kagaku Kaishi* (The Chemical Society of Japan, 1965, vol. 86, pp. 1015–1018).
- Pekov, I.V., Zubkova, N.V., Pautov, L.A., Yapaskurt, V.O., Chukanov, N.V., Lykova, I.S., Britvin, S.N., Sidorov, E.G., and Pushcharovsky, D.Yu., Chubarovite, $\text{KZn}_2(\text{BO}_3)\text{Cl}_2$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia, *Can. Mineral.*, 2015, vol. 53, no. 2, pp. 273–284.
- Pekov, I.V., Koshlyakova, N.N., Zubkova, N.V., Lykova, I.S., Britvin, S.N., Yapaskurt, V.O., Agakhanov, A.A., Shchipalkina, N.V., Turchkova, A.G., and Sidorov, E.G., Fumarolic arsenates—a special type of arsenic mineralization, *Eur. J. Miner.*, 2018, vol. 30, no. 2, pp. 305–322.
- Pekov, I.V., Agakhanov, A.A., Zubkova, N.V., Koshlyakova, N.V., Shchipalkina, N.V., Sandalov, F.D., Yapaskurt, V.O., Turchkova, A.G., and Sidorov, E.G., Oxidizing-type fumaroles of the Tolbachik Volcano, a mineralogical and geochemical unique, *Russ. Geol. Geophys.*, 2020, vol. 61, nos. 5–6, pp. 675–688.
- Pertsev, N.N., *Paragenezisy bornykh mineralov magnезial'nykh skarnov* (Boron Mineral Assemblages in Magnesian Skarns), Moscow: Nauka, 1971.
- Rudnev, V.V., Chukanov, N.V., Nechelyustov, G.N., and Yamnova, N.A., Hydroxylborite, $\text{Mg}_3(\text{BO}_3)(\text{OH})_3$, a new mineral species and isomorphous series fluoborite–hydroxylborite, *Geol. Ore Deposits*, 2007, vol. 49, pp. 710–719.
- Scacchi, A. Notizie preliminari intorno ai proietti vulcanici di Nocera e Sarno, In: *Atti della Reale Accademia dei Lincei. Ser. 3*, Transunti, 1881, vol. 5, pp. 270–273.
- Shchipalkina, N.V., Pekov, I.V., Koshlyakova, N.N., Britvin, S.N., Zubkova, N.V., Varlamov, D.A., and Sidorov, E.G., Unusual silicate mineralization in fumarolic sublimates of the Tolbachik Volcano, Kamchatka, Russia,—Part 1: Neso-, cyclo-, ino- and phyllosilicates, *Eur. J. Mineral.*, 2020, vol. 32, no. 1, pp. 101–119.
- Symonds, R.B. and Reed, M.H., Calculation of multicomponent chemical equilibria in gas–solid–liquid systems: calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens, *Amer. J. Sci.*, 1993, vol. 293, pp. 758–864.
- Takeuchi, Y., The structure of fluoborite, *Acta Crystal.*, 1950, vol. 3, pp. 208–209.
- Tell I. Hydrothermal studies of fluorine and boron metamorphic reactions in dolomite, In: *Publications from the Institutes of Mineralogy, Paleontology and Quaternary Geology*, University of Lund, Sweden, 1972, vol. 176, pp. 1–63.
- The Great Tolbachik Fissure Eruption, Fedotov, S.A. and Markhinin, Y.K., Eds., New York: Cambridge University Press, 1983.
- Vergasova, L.P. and Filatov, S.K., A study of volcanogenic exhalation mineralization, *J. Volcanol. Seismol.*, 2016, vol. 10, no. 2, pp. 71–85.
- Zambonini, F., Il tufo pipernoide della Campania e i suoi minerali, In: *Memorie per Dervive alla Decrizione della Carta Geologica d'Italia*, 1919, vol. 7 (II).
- Zelenski, M., Malik, N., and Taran, Yu., Emissions of trace elements during the 2012–2013 effusive eruption of Tolbachik volcano, Kamchatka: enrichment factors, partition coefficients and aerosol contribution, *J. Volcanol. Geotherm. Res.*, 2014, vol. 285, pp. 136–149.

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