

Kononovite, NaMg(SO₄)F, a new mineral from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia

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Abstract: The new mineral kononovite, NaMg(SO₄)F, the first sulphate member of the durangite (tilasite) group, was found in the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is closely associated with langbeinite, hematite, anglesite and euchlorine. Uklonskovite is a product of the supergene alteration of kononovite. The new mineral occurs as prismatic to thick tabular crystals up to 0.04 × 0.06 × 0.1 mm, isolated or, more typically, forming clusters or interrupted crusts up to several cm² in area and up to 0.05 mm thick overgrowing basalt scoria. Kononovite is white, transparent in tiny grains and translucent in blocky crystals, with vitreous lustre. It is brittle but with signs of weak plasticity; one direction of imperfect cleavage is observed. The Mohs' hardness is *ca.* 3. $D_{\text{meas}} = 2.91(1)$, $D_{\text{calc}} = 2.945$ g cm⁻³. Kononovite is optically biaxial (+), $\alpha = 1.488(2)$, $\beta = 1.491(2)$, $\gamma = 1.496(2)$, $2V_{\text{meas}} = 75(5)^\circ$. The IR spectrum is reported. The chemical composition (wt%, electron-microprobe data) is: Na₂O 18.68, K₂O 0.14, MgO 24.77, ZnO 0.28, PbO 0.10, SO₃ 48.44, F 11.82, Cl 0.12, O = (F,Cl) –5.00, total 99.35. The empirical formula calculated on the basis of 5 (O + F + Cl) anions *pfu* is: Na_{0.99}K_{0.01}Mg_{1.01}Zn_{0.01}S_{0.99}O_{3.97}F_{1.02}Cl_{0.01}. The strongest reflections of the powder X-ray diffraction pattern [$d, \text{\AA}(hkl)$] are: 4.766(38)(–111), 3.567(33)(021), 3.233(82)(–112), 3.210(55)(002), 3.041(100)(200), 2.589(53)(130), 2.571(38)(022) and 2.269(33)(131). Kononovite is monoclinic, space group *C2/c* [by analogy with synthetic NaMg(SO₄)F which is practically identical to the mineral in its powder XRD pattern], $a = 6.662(2)$, $b = 8.584(3)$, $c = 7.035(2)$ Å, $\beta = 114.06(3)^\circ$, $V = 367.4(1)$ Å³ and $Z = 4$. The mineral is named in honour of the Russian mineralogist Oleg V. Kononov (born 1932), Moscow State University. Two types of fluorine mineralization in deposits of the Tolbachik fumaroles are discussed.

Key-words: kononovite; new mineral; sodium magnesium fluoride sulphate; durangite / tilasite group; fluorine; volcanic exhalations; fumarole; Tolbachik volcano; Kamchatka.

Introduction

Natural anhydrous fluorosulphates are not numerous. Ten such minerals were known to date, all with large cations: kogarkoite Na₃(SO₄)F, sulphohalite Na₆(SO₄)₂FCl, galeite Na₁₅(SO₄)₅F₄Cl, schairerite Na₂₁(SO₄)₇F₆Cl, thermessaite K₂(AlF₃)(SO₄), thermessaite-(NH₄)(NH₄)₂(AlF₃)(SO₄), shuvalovite K₂(Ca₂Na)(SO₄)₃F, krashennikovite KNa₂CaMg(SO₄)₃F, grandreefite Pb₂(SO₄)₂F, and pseudograndreefite Pb₆(SO₄)₁₀F. Four of them are known only in volcanic fumaroles, namely thermessaite (Demartin *et al.*, 2008), thermessaite-(NH₄) (Garavelli *et al.*, 2012), krashennikovite (Pekov *et al.*, 2012) and shuvalovite (Pekov *et al.*, 2014a);

galeite was also reported from this formation (Óskarsson, 1981; Africano & Bernard, 2000).

This paper is a description of a new anhydrous fluoro-sulphate mineral from fumarole sublimates. It was named kononovite (Cyrillic: кононовит) in honour of the Russian mineralogist Dr. Oleg Vasil'evich Kononov (born 1932), a specialist in general and technological mineralogy. He has been a teacher of mineralogy at Lomonosov Moscow State University for more than 50 years.

Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2013-116). The type specimen is deposited in the systematic collection of the Fersman

Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 94147.

Occurrence and general appearance

Kononovite was found in a single specimen (6 cm in size) collected by us in July 2012 in the southern part of the Arsenatnaya fumarole, located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41'N 160°14'E, 1200 m asl). This scoria cone, formed in 1975, is a monogenetic volcano about 300 m high and approximately 0.1 km³ in volume (Fedotov & Markhinin, 1983). Its fumarole fields are still active; our measurements carried out in 2012–2014 using a chromel–alumel thermocouple showed temperatures of gas up to 430°C. Currently, the fumarolic gases at the Second scoria cone are chemically close to atmospheric air, with the contents of <1 vol.% H₂O vapour and <0.1 vol.% acid species, mainly CO₂, HF and HCl (Zelenski *et al.*, 2012) while in 1976–1977 the gases here were much richer in H₂O, SO₂, CO₂, HCl and, in some fumaroles, HF (Meniaylov *et al.*, 1980). The Arsenatnaya fumarole first uncovered by us in July 2012 is one of the most interesting mineralogical objects related to the Tolbachik volcano. More than eighty mineral species are identified now in this fumarole. Its general description, including the zoning and major mineral assemblages, is given by Pekov *et al.* (2014b).

Strongly mineralized areas in the southern part of Arsenatnaya occur at depths from 0.3 to 0.6 m below the surface. Temperatures measured there, immediately after uncovering of hot fumarole cameras, vary from 360 to 390°C. The major minerals of the sublimate incrustations in this zone are sulphates [langbeinite, apthitalite, krasninnikovite, anhydrite, euchlorine and vanthoffite], arsenates [lammerite, johillerite, urusovite, tilasite and svabite], hematite, tenorite, halite, fluorophlogopite, potassic feldspar (including its As-bearing variety) and fluoborite. Subordinate and rare minerals are lammerite-β, alarsite, bradaczekite, ericlxmanite (IMA 2013–022), kozyrevskite (IMA 2013–023), popovite (IMA 2013–060), wulffite (IMA 2013–035), alumoklyuchevskite, calciolangbeinite, arcanite, anglesite, palmierite, kononovite, shuvalovite, sylvite, fluorite, gahnite (Cu-bearing variety), corundum, zincite, chubarovite (IMA 2014–018) and flinteite (IMA 2014–009).

Kononovite occurs as prismatic to thick tabular crystals up to 0.04 × 0.06 × 0.1 mm. Sometimes they are isolated but typically form clusters or interrupted crusts (Figs 1 and 2) up to several square centimetres in area and up to 0.05 mm thick overgrowing basalt scoria. A specimen with the new mineral is a breccia-like aggregate of scoria pebbles cemented by crusts of kononovite with minor amounts of langbeinite, hematite, anglesite and euchlorine.

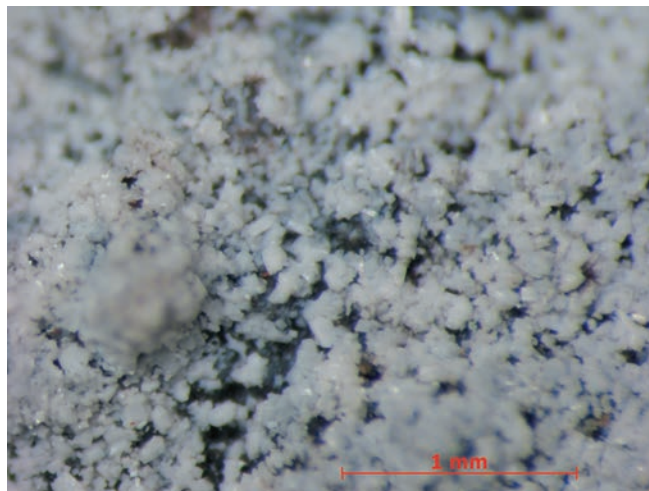


Fig. 1. Clusters of kononovite crystals forming an interrupted crust on basalt scoria. Field of view: 2.8 mm. Photo: I.V. Pekov & A.V. Kasatkin. (online version in colour)

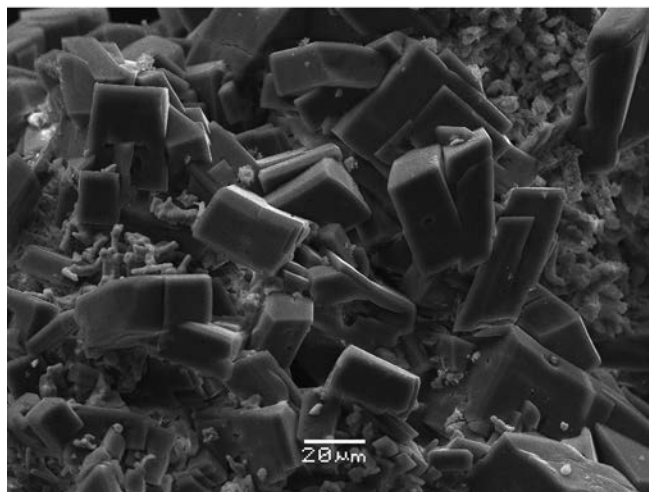
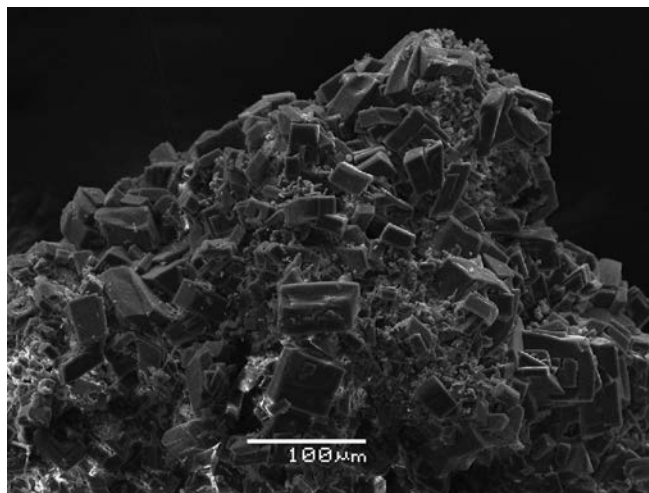


Fig. 2. Crystals of kononovite on basalt scoria: general view (a) and enlarged fragment (b). SEM (SE) images.

Physical properties and optical data

Kononovite is white, transparent in tiny grains and translucent in blocky crystals. Its streak is white. The lustre is vitreous. The mineral is non-fluorescent under ultraviolet light or an electron beam. Kononovite is brittle but with signs of weak plasticity. Its Mohs' hardness is *ca.* 3. One direction of imperfect cleavage was observed under the microscope. The fracture is uneven. The density measured by flotation in heavy liquids (bromoform + dimethylformamide) is 2.91(1) g cm⁻³, the density calculated based on the empirical formula is 2.945 g cm⁻³.

Kononovite is optically biaxial (+), $\alpha = 1.488(2)$, $\beta = 1.491(2)$, $\gamma = 1.496(2)$ (589 nm), $2V_{\text{meas}} = 75(5)^\circ$ and $2V_{\text{calc}} = 76^\circ$. No dispersion of the optical axes was observed. Under the microscope kononovite is colourless and non-pleochroic.

Infrared spectroscopy

The infrared (IR) absorption spectrum of kononovite was obtained for powdered sample mixed with anhydrous KBr and pelletized. The pellet was analyzed using an ALPHA FTIR spectrometer (Bruker Optics) at the resolution of 4 cm⁻¹; the number of sampling scans was 16. The IR spectrum of a pure KBr disc was subtracted from the overall spectrum.

The IR spectrum of kononovite (Fig. 3) is unique and can be used as its diagnostic tool. Absorption bands and their assignments are (cm⁻¹, w – weak band, s – strong band, sh – shoulder): 2132w (combination mode of symmetric and asymmetric vibrations of SO₄²⁻ anions), 1133s [$\nu_3(F_2)$ – asymmetric stretching vibrations of SO₄²⁻ anions], 1010 [$\nu_1(A_1)$ – symmetric stretching vibrations

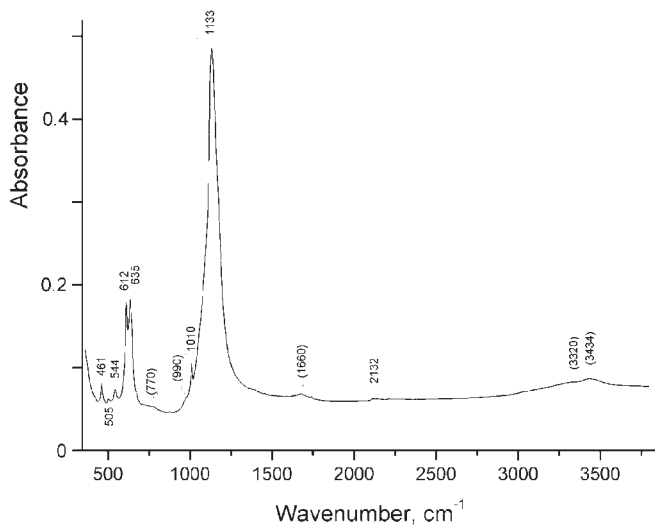


Fig. 3. The IR spectrum of kononovite. Weak bands at 3434, 3320, 1660, 990 and 770 cm⁻¹ (wavenumbers are given in parentheses) belong to minor admixed uklonskovite NaMg(SO₄)F · 2H₂O (see text).

of SO₄²⁻ anions], 635s, 612s [$\nu_4(F_2)$ – bending vibrations of SO₄²⁻ anions], 544, 505w, 461 (lattice modes involving Mg ··· O and Mg ··· F stretching vibrations). The absence of distinct splitting of the degenerate $\nu_3(F_2)$ band and the rather low intensity of the non-degenerate $\nu_1(A_1)$ band indicate a rather weak distortion of SO₄ tetrahedra.

Weak bands at 3434, 3320, 1660, 990 and 770 cm⁻¹ undoubtedly correspond to the minor admixture of uklonskovite NaMg(SO₄)F · 2H₂O. The same bands in the IR spectrum of pure uklonskovite from its type locality, the Kushkanatau salt deposit, Karakalpakstan, Uzbekistan, have maxima at 3430, 3320, 1665, 988 and 768 cm⁻¹ (Chukanov, 2014). The presence of uklonskovite, considered as a product of slight alteration of kononovite in humid air, in the studied sample is confirmed by powder X-ray diffraction (XRD) data (Table 1).

Bands corresponding to NH₄⁺, CO₃²⁻ and NO₃⁻ groups (the range 1300–1500 cm⁻¹) are absent in the IR spectrum of kononovite.

Chemical data

Chemical data for kononovite were obtained using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of local methods of matter investigation, Faculty of Geology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 5 μm beam diameter. The following standards were used: albite (Na), orthoclase (K), MgF₂ (Mg and F), ZnS (Zn), PbTe (Pb), BaSO₄ (S) and scapolite (Cl).

The average (4 spot analyses) chemical composition of kononovite (wt%, ranges/standard deviations are in parentheses) is: Na₂O 18.68 (17.82–19.18/0.60), K₂O 0.14 (0.00–0.31/0.14), MgO 24.77 (24.03–25.43/0.59), ZnO 0.28 (0.00–0.65/0.28), PbO 0.10 (0.00–0.41/0.10), SO₃ 48.44 (47.40–49.14/0.66), F 11.82 (11.45–12.01/0.25), Cl 0.12 (0.00–0.49/0.12), O = (F, Cl) –5.00, total 99.35. Contents of other elements with atomic number higher than carbon are below their detection limits.

The empirical formula of kononovite calculated on the basis of 5 (O + F + Cl) anions *pfu* is: Na_{0.99}K_{0.01}Mg_{1.01}Zn_{0.01}S_{0.99}O_{3.97}F_{1.02}Cl_{0.01}. The idealized formula is NaMg(SO₄)F, which requires Na₂O 19.19, MgO 24.82, SO₃ 49.32, F 11.70, O = F –4.93, total 100.00 wt%.

The Gladstone-Dale compatibility index 1 – (K_p/K_c) (Mandarino, 1981) is 0.033 (excellent) using D_{meas} and 0.045 (good) using D_{calc} .

Kononovite decomposes and partially dissolves in H₂O at room temperature during several hours. In humid air the mineral slowly alters with the formation of uklonskovite NaMg(SO₄)F · 2H₂O.

X-ray crystallography

Numerous attempts to perform a single-crystal X-ray diffraction study of kononovite were unsuccessful because of

Table 1. X-ray powder diffraction data for kononovite and synthetic NaMg(SO₄)F.

Kononovite*			Synthetic NaMg(SO ₄)F**		
I_{meas}	d_{meas}	d_{calc}	I_{calc}	d_{calc}	hkl
3	4.962	4.963	4	4.963	110
38	4.766	4.769	41	4.770	-111
1	4.294	4.292	3	4.290	020
33	3.567	3.569	35	3.568	021
23	3.418	3.416	23	3.416	111
82	3.233	3.231	100	3.231	-112
55	3.210	3.212	32	3.212	002
100	3.041	3.042	97	3.042	200
30	2.870	2.868	28	2.869	-202
18	2.626	2.627	19	2.627	-221
53	2.589	2.589	63	2.588	130
38	2.571	2.572	48	2.571	022
3	2.484	2.482	3	2.482	220
33	2.269	2.269	41	2.268	131
10	2.259	2.258	10	2.259	-113
7	2.211	2.212	10	2.212	-132
3	2.140	2.140	12	2.140	-311
11	2.093	2.093, 2.092	1, 14	2.093, 2.093	221, -312
6	2.035	2.035	10	2.035	041
10	1.979	1.979	14	1.979	-223
10	1.972	1.973	9	1.974	310
7	1.862	1.862	8	1.862	202
2	1.783	1.784	9	1.784	042
2	1.751	1.749	1	1.749	-331
14	1.744	1.744	12	1.744	-204
15	1.719	1.722, 1.718	6, 21	1.723, 1.718	-332, -242
20	1.708	1.708	23	1.708	222
12	1.702	1.703	3	1.703	-114
21	1.654	1.654	24	1.654	330
3	1.649	1.645	1	1.644	-151
3	1.605	1.606	3	1.606	004
2	1.549	1.549	5	1.550	-422
6	1.541	1.540	11	1.540	-152
2	1.525	1.525	4	1.525	133
2	1.521	1.521	4	1.521	400
12	1.485	1.487, 1.485	3, 17	1.487, 1.485	331, -134
7	1.435	1.434	14	1.435	-404
7	1.408	1.410, 1.407	7, 8	1.411, 1.407	-334, 152
4	1.344	1.343	9	1.343	-352
2	1.295	1.295	5	1.294	260
4	1.270	1.270	6	1.270	134

*The powder XRD pattern of kononovite also contains weak reflections at 3.50, 3.15 and 2.97 Å that clearly correspond to the three strongest reflections of uklonskovite NaMg(SO₄)F·2H₂O (Sabelli, 1985), a product of slight alteration of kononovite in humid air. The presence of admixed uklonskovite in the studied sample of kononovite is also confirmed by the IR spectroscopy data (see text and Fig. 3).

**Calculated from the structure data reported by Reynaud *et al.* (2012).

the imperfection of its crystals. Even perfect looking (Fig. 2), they are in fact blocky, have a mosaic structure and consist of differently oriented microdomains.

Powder X-ray diffraction data of kononovite collected with a Rigaku Ultima IV diffractometer (CuK α radiation) are given in Table 1 in comparison with the data on synthetic NaMg(SO₄)F, which is practically identical to the mineral in its powder XRD pattern. By analogy with the synthetic compounds NaM²⁺SO₄F with M²⁺ = Mg, Fe, Co, Cu and Zn (Reynaud *et al.*, 2012), we considered the monoclinic space group C2/c to be correct for kononovite. The calculated unit-cell parameters obtained for the new

mineral are: $a = 6.662(2)$, $b = 8.584(3)$, $c = 7.035(2)$ Å, $\beta = 114.06(3)^\circ$, $V = 367.4(1)$ Å³ and $Z = 4$. These values are very close to those reported for synthetic NaMg(SO₄)F in the above-cited paper: $a = 6.66958(10)$, $b = 8.58747(12)$, $c = 7.05209(10)$ Å, $\beta = 114.090(1)^\circ$ and $V = 368.729(9)$ Å³.

Discussion

Kononovite NaMg(SO₄)F, according to the structure data of its synthetic analogue (Reynaud *et al.*, 2012), is

isostructural with fluoro(hydroxyl)phosphates and fluorarsenates of the durangite group (Back, 2014; some authors prefer the name tilasite group), namely isokite CaMg(PO₄)F, lacroixite NaAl(PO₄)F, panasqueiraite Ca(Mg,Fe)(PO₄)(OH,F), durangite NaAl(AsO₄)F, maxwellite NaFe³⁺(AsO₄)F, and tilasite CaMg(AsO₄)F. We propose to include kononovite into this group as its first sulphate member. The new mineral is also very close, or even identical in terms of structure, to oxosilicates of the titanite group, namely titanite CaTi(SiO₄)O, natrotitanite (Na_{0.5}Y_{0.5})Ti(SiO₄)O, malayaite CaSn(SiO₄)O, and vanadomalayaite CaV(SiO₄)O.

We consider that kononovite was formed as a result of the interaction between fumarolic gas (the obvious source of F and SO₃ and the most probable source of Na) and basalt scoria at a temperature not lower than 360°C rather than deposited directly from the gas phase. The basalt scoria is the likely source of Mg which has low volatility in volcanic gases at temperatures lower than 500°C (Symonds & Reed, 1993).

One of the most important volatile acid species in volcanic gases of the GTFE is HF (Meniaylov *et al.*, 1980; Fedotov & Markhinin, 1983) and fluorine minerals in the Tolbachik fumaroles are diverse and sporadically very abundant. Two main types of fluorine mineralization could be distinguished. For one of them only fluorides, including alumino-fluorides, are typical among minerals with species-defining F. This type was reported earlier at the First and the Second scoria cones of the GTFE (Naboko & Glavatskikh, 1991; Vergasova *et al.*, 2004; Vergasova *et al.*, 2007). We also observed occurrences of fluoride mineralization at both these scoria cones. At the First scoria cone, fluorite and sellaite together with halite and anhydrite are the major components of the sublimate incrustations at the Northern fumarole field (the temperature measured by us in these cameras was 220–290°C). In fumaroles of the Southern field at the First scoria cone (measured temperatures are not higher than 150°C), the hydrous alumino-fluorides ralstonite and meniaylovite, closely associated with gypsum and opal, are the main fluorine minerals.

The second, quite different type of fluorine mineralization in fumaroles related to Tolbachik was not described before. It is studied by us and the Arsenatnaya fumarole is the brightest example of its occurrence. Fluorine does not form fluorides here but plays a role of additional anion F[−] in oxysalts, namely fluorosulphates, fluorosilicates, fluorarsenates and fluoroborates. In Arsenatnaya only one fluoride mineral, fluorite, was found in a single specimen, as several tiny grains on shuvalovite crystals, while oxysalts with species-defining F[−] are abundant and diverse. Fluorophlogopite KMg₃(AlSi₃O₁₀)F₂, krashennikovite KNa₂CaMg(SO₄)₃F, fluorborite Mg₂(BO₃)F₃, tilasite CaMg(AsO₄)F and svabite Ca₅(AsO₄)₃F are common minerals in Arsenatnaya, being in some areas even the major constituents of the sublimate incrustations. Kononovite NaMg(SO₄)F, shuvalovite K₂(Ca₂Na)(SO₄)₃F, durangite NaAl(AsO₄)F and several incompletely characterized F-bearing oxysalts were found in small amounts. All these minerals are very close chemically to their fluorine

end-members, with only insignificant substitutions of F[−] for Cl[−] or O^{2−} but not for OH[−]. The absence of the OH[−] → F[−] substitution is mainly caused by the combination of high temperature and low pressure, close to atmospheric pressure, in this mineral-forming system.

The causes of the strong difference in crystal-chemical behaviour of fluorine in sublimates of different fumaroles at Tolbachik are still not completely clear, but we assume that the temperature could be an important factor determining the mineralogy of F here and in volcanic exhalations in general. All mineral assemblages with abundant fluorite, sellaite and/or alumino-fluorides were earlier described as relatively low-temperature fumarolic products, and we observed fluoride mineralization at both the First and the Second scoria cones of the GTFE only in fumarole cameras with temperatures not higher than 300°C. On the contrary, in Arsenatnaya all mineral associations containing oxysalts with additional anion F[−] were observed in pockets with temperatures not lower than 360°C.

The formation of galeite, Na₁₅(SO₄)₅F₄Cl, as a product of the alteration of halide assemblage under the influence of gaseous SO₃ was reported for fumarolic incrustations at the Surtsey volcano, Iceland (Óskarsson, 1981). Such origin could be also assumed for kononovite in the case of temperature increase in a fumarole camera with primary fluoride (sellaite?) mineralization. However, no signs of this process are observed in Arsenatnaya.

Note in conclusion that synthetic NaMg(SO₄)F doped with REE³⁺ (Ce, Eu, Dy) is now in the focus of numerous studies because of its remarkable photoluminescent properties (*e.g.*, Nagpure *et al.*, 2009; Choubey *et al.*, 2012, 2013).

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