Fumarolic arsenates – a special type of arsenic mineralization

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Abstract: This paper is a review devoted to a special type of arsenic mineralization related to volcanic fumaroles of the oxidizing type. Fifty-four hydrogen-free arsenates (40 valid species and 14 insufficiently characterized phases) with Cu^{2+}, Mg, Al, Fe^{3+}, Ti^{4+}, Zn, Ca, Na, and K are identified here and 46 of them are endemics of fumarolic formation. Fifty-three of them have been found in active fumaroles at the Tolbachik volcano, Kamchatka, Russia. Thirty different structure types have been established for fumarolic arsenates, including 19 previously unknown among minerals. The alkali-richest (>17 wt% $Na_2O + K_2O$) and Ti-richest (12–28 wt% TiO_2) natural arsenates occur in Tolbachik fumaroles. Nineteen fumarolic arsenates with Cu^{2+}, Al, Fe^{3+} or Ti contain additional O^{2-} anions. The major fumarolic arsenates at Tolbachik are alluaudite-group members (johillerite, calciojohillerite, nickenichite, bradaczekite and badalovite), lammerite, svabite, tilasite, berzeliite and urusovite. All Tolbachik arsenates crystallized at temperatures ≥450 °C (the major assumed temperature interval is 500–750 °C), under atmospheric pressure and high oxygen fugacity. They were precipitated directly from the gas phase as volcanic sublimates, or were formed as a result of gas–rock interaction in fumarolic cameras, where the host basalt was the source of the less volatile elements Al, Ti, Mg and Ca. The empirical data on fumarolic As^{5+} minerals are summarized and discussed, including their chemistry, crystal chemistry (with special attention paid to isomorphic substitutions and solid solutions) and occurrence. Electron-microprobe analyses illustrating the chemical diversity and variability of 53 fumarolic arsenates are given as supplementary data, as well as a photographic documentation of their morphology and paragenetic relationships.

Key-words: arsenate mineralization; arsenic mineralogy; arsenic geochemistry; crystal chemistry; isomorphism; alluaudite group; tilasite group; fumarole sublimate; Tolbachik volcano; Kamchatka.

1. Introduction

Arsenic has a specific place in mineralogy, crystal chemistry and geochemistry. It is a metalloid (ground-state electronic configuration: $[Ar]3d^{10}4s^24p^3$) that differs in properties from both metals and non-metals. This determines its geochemical individuality: despite the fact that As is a rare element (its content in the lithosphere is about 0.0002 wt%), its high concentrations are typical, primarily in chalcogenide ores containing arsenopyrite, fahlerz and other arsenosulfides. Among all rare elements, As demonstrates unique mineral diversity: six hundred valid minerals with species-defining As are known today according to the IMA-CNMNC list of minerals (ima-cnmnc.nrm.se/imalist.htm), *i.e.*, almost 12% of the known mineral species. From the geochemical point of view, As is

considered as a typical chalcophile, though 430 of 600 its minerals are oxygen compounds containing As^{5+}, As^{3+} or both. Arsenates are the oxysalts with tetrahedral anion $(AsO_4)^{3-}$, which strongly prevail among O-bearing As minerals, counting for some 360 species including 60 anhydrous ones.

In terms of general volume and species diversity, the majority of oxygen-bearing arsenic minerals form in oxidation zones of As-enriched chalcogenide ore deposits and are represented by H-containing (*i.e.*, with H_2O, OH^-, H^+ or/and H_3O^+) compounds. In endogenic formations, As chalcogenides generally strongly prevail over oxo-compounds. Very few localities where endogenic arsenates are diverse and/or form geochemically significant accumulations are known. The most remarkable examples are famous metamorphic-hydrothermal deposits belong-

ing to the Långban (Värmland, Sweden) and Franklin (New Jersey, USA) ore districts and the alpine-type vein localities in the Italian and Swiss Alps. For an overview on arsenic mineral parageneses see, *e.g.*, Majzlan *et al.* (2014).

Arsenic is a volatile element and, as a result, a characteristic constituent of volcanic gases (Meniaylov *et al.*, 1980; Symonds *et al.*, 1987; Symonds & Reed, 1993; Vicandy & Minoru, 1993; Signorelli, 1997; Signorelli *et al.*, 1998; Cheynet *et al.*, 2000; Africano *et al.*, 2002). Exhalation-type arsenic mineralization is common for volcanic fumaroles of reducing type represented by sulfides, sulfosalts, As-enriched native sulfur and, rarely, As^{3+}-O-bearing phases (*e.g.* Zelenski & Bortnikova, 2005; Campostrini *et al.*, 2011). In fumaroles of the oxidizing type, arsenates were known but only in minor amounts and their described diversity was scanty. For active volcanoes, they were reported only at Tolbachik (Kamchatka Peninsula, Far-Eastern Region, Russia). Before our works on this object, the following data on Tolbachik fumarolic arsenates have been published: a brief description of the P-bearing variety of lammerite, $Cu_3[(As,P)O_4]_2$ (Filatov *et al.*, 1984), data on johillerite, $NaCuMg_3(AsO_4)_3$ (Glavatskikh & Bykova, 1998; Tait & Hawthorne, 2004), and nickenichite Na($\square$, Cu)($\square$,Ca)(Mg,Fe^{3+})$_3$(AsO$_4$)$_3$ (Rybin *et al.*, 2012) and reports of nine new mineral species, alarsite, Al(AsO$_4$) (Semenova *et al.*, 1994), coparsite, $Cu_4O_2[(As,V)O_4]Cl$ (Vergasova *et al.*, 1999), urusovite, $CuAlO(AsO_4)$ (Vergasova *et al.*, 2000), bradaczekite, $NaCu_4(AsO_4)_3$ (Filatov *et al.*, 2001), filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$ (Vergasova *et al.*, 2004), lammerite-β, $Cu_3(AsO_4)_2$ (Starova *et al.*, 2012), hatertite, $Na_2(Ca,Na)(Fe^{3+},Cu)_2(AsO_4)_3$ (Krivovichev *et al.*, 2013b), wrightite, $K_2Al_2O(AsO_4)_2$ (Shablinskii *et al.*, 2016a), and ozerovaite, $KNa_2Al_3(AsO_4)_4$ (Shablinskii *et al.*, 2016b). Data on the occurrences of Tolbachik arsenates known before 2013 were briefly summarized by Vergasova & Filatov (2016).

Arsenates are also known in the deposits of paleofumaroles at extinct Cenozoic volcanoes. Nickenichite was first discovered at Nickenich, Eifel, Germany (Auernhammer *et al.*, 1993). Durangite, $NaAl(AsO_4)F$, reported in intergrowths with hematite and cassiterite in cavities in rhyolite at Thomas Range, Utah, USA (Wilson, 1986), is most likely a product of paleofumarolic activity as well. Majzlan *et al.* (2014) assume the same origin for angelellite, $Fe^{3+}_4O_3(AsO_4)_2$, from the Vela Yareta mine, Jujuy Province, Argentina, where it occurs in cracks in andesite and is associated with hematite and cassiterite (Ramdohr *et al.*, 1959).

Among all known volcanoes, Tolbachik is the world-record holder in both diversity of fumarolic minerals and the number of new mineral species discovered at one volcano. Summarizing the available literature and our data, we evaluate the number of valid mineral species reliably determined to date in Tolbachik fumaroles as about 240. This number includes: (1) fumarolic sublimates, (2) products of gas–rock interaction and (3) secondary minerals formed in the weathering zone of the two former assemblages (we do not include primary constituents of host volcanic rocks in this number). Moreover, 60 minerals were reported/mentioned in the literature for Tolbachik fumaroles, which are not taken into account here because no reliable data on them have been published or their fumarolic origin seems doubtful. Among these 240 minerals, 100 were first discovered at Tolbachik [alumoedtollite (IMA No. 2017-020: see Table 1) became the "anniversary" 100th new mineral species discovered at Tolbachik]. In this respect, the Tolbachik volcano significantly outstripped such famous mineral localities as Tsumeb (Namibia), Långban, and Franklin (<80 for each) and now yields only to two alkaline complexes at Kola peninsula, namely Khibiny (126 new minerals) and Lovozero (112). However, both Khibiny and Lovozero are huge intrusions (1327 and 650 km^2 in area, respectively), with several big operating mines and 130-year history of intense studies. In contrast, all new minerals discovered at Tolbachik have been found in products of fumaroles born by two recent eruptions, 1975–1976 and 2012–2013, and the majority of them were described from the Second and First scoria cones of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–1976 (NB GTFE), in an area less than 1 km^2. Among 240 minerals undoubtedly identified in the Tolbachik fumarole mineral-forming systems, 121 (including 96 species first discovered at Tolbachik) are known only in volcanic exhalations or genetically related sublimates of natural or anthropogenic fires at coal or ore mine dumps.

Our study carried out at Tolbachik in 2012–2016 indicated that the fumarolic arsenate mineralization is much more diverse and much richer than it was thought before. At the Second scoria cone of the NB GTFE we have uncovered hot fumarole cameras extremely enriched in arsenates. Incrustations, continuous or interrupted, up to several square meters in area and up to 2–3 cm thick, containing up to 90 vol% minerals belonging to this chemical class were found, documented and sampled. The gross mass of arsenates there could be estimated as several tons. Thus, taking into account both significant scale of occurrence and unique mineral composition, we now consider fumarolic arsenate assemblages as a special type of rich As mineralization that was never characterized at large. The major topic of the present paper is to provide an overview of this mineralization summarizing the empirical data, primarily for its main object, active fumarole fields of the Tolbachik volcano.

2. General location and diversity of arsenates in Tolbachik fumaroles

All occurrences of arsenate mineralization at Tolbachik, both known earlier and found by us, belong to the main fumarole field of the Second scoria cone of the NB GTFE (55°41′N 160°14′E, 1200 m asl) located at the summit of this scoria cone (Fig. 1), a monogenic volcano about 300 m high and 0.1 km^3 in volume situated 18 km SSW of the

Table 1. Arsenates from fumaroles of the Tolbachik volcano.

Mineral	Simplified formula	Structure type (archetype)	Crystal system Space group	a, Å α, °	b, Å β, °	c, Å γ, °	V, Å³ Z	Distribution	Reference for crystal data
Part I. Valid mineral species and well-studied unnamed mineral phases									
Lammerite	$Cu_3(AsO_4)_2$	lammerite	Monoclinic $P2_1/c$	5.375(4) 111.41(8)	11.600(12)	5.069(3)	294.3(7) 2	+++++	our data
Lammerite-β	$Cu_3(AsO_4)_2$	I-$Cu_3(AsO_4)_2$ STNM	Monoclinic $P2_1/c$	6.306(1) 92.26(1)	8.643(1)	11.310(1)	615.9(1) 4	+++	Starova *et al.*, 2012
unnamed	$Cu_3(AsO_4)_2$	stranskiite	Triclinic P-1	5.0701(8) 70.091(13)	5.4047(8) 86.828(12)	6.3910(8) 68.399(15)	152.61(4) 1	+	our data
Stranskiite	$CuZn_2(AsO_4)_2$	stranskiite	Triclinic P-1	5.09(1) 69.70(5)	5.31(1) 86.69(6)	6.68(1) 67.92(5)	156.4(2) 1	+	our data
Ericlaxmanite*	$Cu_4O(AsO_4)_2$	tricl. $Cu_4O(AsO_4)_2$ STNM	Triclinic P-1	6.4271(4) 98.396(4)	7.6585(4) 112.420(5)	8.2249(3) 98.397(5)	361.11(3) 2	+++	Pekov *et al.*, 2014b
Kozyrevskite*	$Cu_4O(AsO_4)_2$	orth. $Cu_4O(AsO_4)_2$ STNM	Orthorhombic $Pnma$	8.2581(4)	6.4026(4)	13.8047(12)	729.90(9) 4	++	Pekov *et al.*, 2014b
Popovite*	$Cu_5O_2(AsO_4)_2$	*novel*	Triclinic P-1	5.1450(3) 100.064(5)	6.2557(3) 96.351(5)	6.2766(4) 95.100(5)	196.48(2) 1	+++	Pekov *et al.*, 2015b
Coparsite	$Cu_4O_2[(As,V)O_4]Cl$	*novel*	Orthorhombic $Pbcm$	5.440(1)	11.154(2)	10.333(2)	627.0(3) 4	+	Starova *et al.*, 1998
Vasilseverginite*	$Cu_9O_4(AsO_4)_2(SO_4)_2$	*novel*	Monoclinic $P2_1/n$	8.1131(4) 110.855(2)	9.9182(4)	11.0225(5)	828.84(6) 2	++	Pekov *et al.*, 2015f
unnamed	$Ca_3Cu_3(AsO_4)_4$	$Ca_3Cu_3(AsO_4)_4$ STNM	Monoclinic $P2_1/a$** (?)	16.8357(33) 117.388(13)	5.0405(8)	9.1173(17)	686.98 (21) 2	+	our data
Shchurovskyite*	$K_2CaCu_6O_2(AsO_4)_4$	*novel*	Monoclinic $C2$	17.2856(9) 92.953(6)	5.6705(4)	8.5734(6)	839.24(9) 2	++	Pekov *et al.*, 2015e
Dmisokolovite*	$K_3Cu_5AlO_2(AsO_4)_4$	*novel*	Monoclinic $C2/c$	17.0848(12) 91.716(6)	5.7188(4)	16.5332(12)	1614.7(2) 4	++	Pekov *et al.*, 2015e
Edtollite*	$K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$	*novel*	Triclinic P-1	5.1168(6) 110.117(13)	9.1241(12) 102.454(12)	9.6979(14) 92.852(11)	411.32(9) 1	+	Pekov *et al.*, 2016c
Alumoedtollite*	$K_2NaCu_5AlO_2(AsO_4)_4$	edtollite	Triclinic P-1	5.0904(11) 110.334(17)	9.0078(14) 102.461(19)	9.6658(2) 92.788(15)	404.88(14) 1	+	our data: IMA No. 2017-020
Melanarsite*	$K_3Cu_7Fe^{3+}O_4(AsO_4)_4$	*novel*	Monoclinic $C2/c$	11.4763(9) 105.078(9)	16.620(2)	10.1322(8)	1866.0(3) 4	++	Pekov *et al.*, 2016d
Arsmirandite*	$Na_{18}Cu_{12}Fe^{3+}O_8(AsO_4)_8Cl_5$	*novel*	Monoclinic $C2/m$	10.742(2) 117.06(3)	21.019(3)	11.787(2)	2370.0(7) 2	++	Pekov *et al.*, 2015a
unnamed	$Na_{18}Cu_{12}TiO_8(AsO_4)_8FCl_5$	arsmirandite	Monoclinic $C2/m$	10.8236(15) 117.195(8)	21.1077(17)	11.856(11)	2409.2(5) 2	+	our data
Axelite*	$Na_{14}Cu_7(AsO_4)_8F_2Cl_2$	*novel*	Tetragonal $P4bm$	14.5957(2)		8.3433(2)	1777.41(5) 2	+	our data: IMA No. 2017-015
Bradaczekite	$NaCu_4(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.053(2) 117.793(3)	12.432(2)	7.2529(13)	961.5(3) 4	++++	Krivovichev *et al.*, 2001
Zincobradaczekite*	$NaZn_2Cu_2(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.0375(13) 117.506(7)	12.4500(13)	7.2213(8)	959.9(2) 4	++	Pekov *et al.*, 2016f

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Table 1. (continued).

Name	Formula	Structure type	Crystal system / Space group	a	b / β	c	V / Z		Reference
Calciojohillerite*	$NaCaMg_3(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	11.8405(3)	12.7836(2) / 112.425(3)	6.6916(2)	936.29(4) / 4	+++++	Pekov *et al.*, 2016i
Johillerite	$NaCuMg_3(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	11.8589(3)	12.7283(3) / 113.628(2)	6.7702(2)	936.25(4) / 4	+++++	our data
Nickenichite	$Na(\square,Ca)(\square,Cu)(Mg,Fe^{3+})_3(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	11.880(11)	12.796(9) / 112.92(8)	6.734(3)	943(1) / 4	++++	our data
Magnesiohatertite*	$(Na,Ca)_2Ca(Mg,Fe^{3+})_2(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.310(1)	13.002(1) / 113.823(4)	6.7211(5)	984.1(1) / 4	++	Pekov *et al.*, 2016j
Hatertite	$Na_2(Ca,Na)(Fe^{3+},Cu)_2(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.640(2)	13.007(2) / 113.828(3)	6.700(1)	1007.6(3) / 4	++	Krivovichev *et al.*, 2013b
Badalovite*	$Na_2Mg_2Fe^{3+}(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	11.9034(3)	12.7832(2) / 112.523(3)	6.6634(2)	936.59(4) / 4	++++	Pekov *et al.*, 2016g
*unnamed***	$Na_3Fe^{3+}_2(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.2394(7)	12.7967(5) / 112.953(7)	6.6589(4)	960.37(9) / 4	+	our data
*unnamed***	$NaCa_2Mg_2(AsO_4)_3$	alluaudite	Monoclinic $C2/c$	12.3226(11)	13.0638(10) / 113.562(8)	6.7621(5)	997.81(14) / 4	+	our data
Berzeliite*	$(Ca_2Na)Mg_2(AsO_4)_3$	garnet	Cubic $Ia\text{-}3d$	12.369(3)			1892.5(7) / 8	++++	our data
Tilasite*	$CaMg(AsO_4)F$	tilasite/titanite	Monoclinic $C2/c$	6.75(4)	8.91(4) / 113.5(6)	7.08(3)	390(3) / 4	++++	our data
Durangite*	$NaAl(AsO_4)F$	tilasite/titanite	Monoclinic $C2/c$	6.564(8)	8.487(3) / 115.16(8)	7.003(8)	353(1) / 4	++	our data
Arsenatrotitanite*	$NaTiO(AsO_4)$	tilasite/titanite	Monoclinic $C2/c$	6.6979(3)	8.7630(3) / 114.805(5)	7.1976(3)	383.48(3) / 4	++	Pekov *et al.*, 2016h
Katiarsite*	$KTiO(AsO_4)$	KTP (=KTiOPO4) *STNM*	Orthorhombic $Pna2_1$	13.174(4)	6.5635(10)	10.805(2)	934.3(3) / 8	+	Pekov *et al.*, 2016b
*unnamed***	$(K,Na)_3(Fe^{3+},Ti,Al,Mg)_5O_2(AsO_4)_5$	*novel*	Orthorhombic $P222_1$	6.5824(2)	13.2488(4)	10.7613(3)	938.48(5) / 2	+	our data
Wrightite	$K_2Al_2O(AsO_4)_2$	$K_2Fe^{3+}_2O(AsO_4)_2$ *STNM*	Orthorhombic $Pnma$	8.2377(3)	5.5731(6)	17.683(1)	811.8(1) / 4	++	Shablinskii *et al.*, 2016a
Ozerovaite	$KNa_2Al_3(AsO_4)_4$	$K_3Cr_3(AsO_4)_4$ *STNM*	Orthorhombic $Cmce$	10.615(2)	20.937(3)	6.393(1)	1420.9(3) / 4	++	Shablinskii *et al.*, 2016b
Pansnerite*	$K_3Na_3(Fe^{3+},Al)_6(AsO_4)_8$	$K_3Cr_3(AsO_4)_4$	Orthorhombic $Cmce$	10.7372(3)	20.837(1)	6.4734(2)	1448.3(1) / 2	+	our data: IMA No. 2016-103
Yurmarinite*	$Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$	II-$Na_3Fe^{3+}_2(AsO_4)_3$ *STNM*	Trigonal $R\text{-}3c$	13.7444(2)		18.3077(3)	2995.1(2) / 6	++	Pekov *et al.*, 2014a
Anatolyite*	$Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$	II-$Na_3Fe^{3+}_2(AsO_4)_3$	Trigonal $R\text{-}3c$	13.6574(10)		18.2349(17)	2945.6(4) / 6	+	Pekov *et al.*, 2016e
Arsenowagnerite*	$Mg_2(AsO_4)F$	wagnerite-*Ma2bc*	Monoclinic $P2_1/c$	9.8638(3)	12.9830(3) / 109.291(3)	12.3284(3)	1490.15(7) / 16	++	Pekov *et al.*, 2015c
Svabite*	$Ca_5(AsO_4)_3F$	apatite	Hexagonal $P6_3/m$	9.786(5)		6.946(5)	576.1(6) / 2	+++++	our data
Alarsite	$AlAsO_4$	berlinite (quartz)	Trigonal $P3_121$	5.031(1)		11.226(6)	246.1(2) / 3	++	Semenova *et al.*, 1994
Filatovite	$K[(Al,Zn)_2(As,Si)_2O_8]$	celsian (feldspar)	Monoclinic $I2/c$	8.772(1)	13.370(2) / 115.944(6)	14.690(2)	1549.1(4) / 8	++	Filatov *et al.*, 2001

Table 1. (continued).

Mineral	Formula	STNM	Symmetry, space group	a	b / β	c	V, Z	Distribution	Reference
Urusovite	$Cu[AlAsO_5]$	STNM	Monoclinic $P2_1/c$	7.335(1)	10.255(1) 99.79(1)	5.599(1)	415.0(1) 4	++++	Krivovichev et al., 2000
Pharmazincite*	$K[ZnAsO_4]$	megakalsilite	Hexagonal $P6_3$	18.501(4)	8.711(4)		2582.4(8) 24	+	Pekov et al., 2017

Part II. Insufficiently studied unnamed mineral phases with definite chemical composition (based on our electron microprobe data)

Mineral phase (simplified formula)	Relationship with known minerals or synthetic compounds
unnamed* $Ca_2[(As,V)_2O_7]$	Assumed analogue of synthetic monoclinic ($C2/m$) $Ca_2(As_2O_7)$ (Pertlik, 1980)
unnamed* $(Na,Ca)_{1-x}Mg_4[(As,V)O_4]_3$	Assumed analogue of synthetic tetragonal ($I\text{-}42d$) $NaMg_4(AsO_4)_3$ (Anissa et al., 2004) and $NaMg_4(VO_4)_3$ (Murashova et al., 1988)
unnamed* $CaAl_2O(AsO_4)_2$	Chemical analogue of wrightite with Ca^{2+} instead of 2K⁺
unnamed* $K_4Na_2Al_6O_3(AsO_4)_6$	No analogies found
unnamed* $Na_2Ca_2Al(AsO_4)_3$	Based on powder X-ray diffraction data, the mineral phase belongs to wyllieite or alluaudite group
unnamed* $NaMgFe^{3+}_2(AsO_4)_3$	Presumably alluaudite-group member that could be anhydrous analogue of yazganite $NaMgFe^{3+}_2(AsO_4)_3 \cdot H_2O$ (Sarp & Černy, 2005) or As-analogue of synthetic alluaudite-type phosphate with the end-member formula $NaMgFe^{3+}_2(PO_4)_3$ (Hidouri et al., 2008)
unnamed* $Na_3Al_2(AsO_4)_3$	Assumed analogue of synthetic trigonal ($R\text{-}3c$) β-$Na_3Al_2(AsO_4)_3$ isostructural with yurmarinite or its monoclinically distorted ($C2$) modification α-$Na_3Al_2(AsO_4)_3$ (Masquelier et al., 1995)
unnamed* $Na_7(Fe^{3+},Mg)_3Al(AsO_4)_6$	Presumably Al-Fe ordered analogue of yurmarinite

Minerals first discovered at Tolbachik are given in **boldtype** (all these species are Tolbachik endemics); * – minerals first found at Tolbachik by us; ** – space group of synthetic analogue (Osterloh et al., 1994); STNM – structure type earlier known for synthetic compound(s) but novel for minerals. Distribution: +++++ – abundant (sporadically main component of voluminous incrustations); ++++ – common (important component of some incrustations); +++ – subordinate; ++ – rare; + – very rare mineral.

active volcano Ploskiy Tolbachik (Fedotov & Markhinin, 1983). It was formed in 1975 and its fumarole fields are still active: many gas vents with temperatures up to 500 °C (measured by us using chromel-alumel thermocouple in 2012–2016) are now observed. Nowadays the emitted gas is compositionally close to the atmospheric air, with contents of <1 vol% water vapour and <0.1 vol% acid species, mainly CO_2, HF and HCl (Zelenski et al., 2011), while in 1976–1977 it was strongly enriched in H_2O, SO_2, CO_2, HCl and, in some fumaroles, HF. Contents of the "ore components" in fumarolic gases, as well as temperature, have been also decreasing after the eruption. In August 1976 the As content in the gas in the Mednaya-1 fumarole ($t = 710 °C$) at the Second scoria cone was $1.1\ mg \cdot m^{-3}$ while in July 1977 in the same fumarole ($t = 600 °C$) the gas contained $<0.02\ mg \cdot m^{-3}$ As (Meniaylov et al., 1980).

Arsenates occur in several hot fumaroles of this field within a 50 m × 100 m area. The occurrences of the period from 1975 to 2000s were reported mainly from the fumaroles located near the eastern wall of a linear submeridional fault zone, so-called Micrograben, and from the Yadovitaya (Poisonous) fumarole (Vergasova & Filatov, 2016). In July 2012 under the western wall of Micrograben we uncovered a new large fumarole named Arsenatnaya due to the abundance of arsenates as its brightest mineralogical feature (Pekov et al., 2014a).

The diversity of arsenates in Tolbachik fumaroles turned out to be unexpectedly considerable and constitute so far 53 mineral species. This number includes 39 valid mineral species, 6 well-studied but still unnamed mineral phases (Table 1, part I) and 8 undoubtedly individual but so far insufficiently studied (mainly due to the tiny size of crystals or aggregates) (Table 1, part II). Among 39 valid species, 31 are Tolbachik-holotype minerals and 22 of them were discovered by us. The 45 arsenates with known crystal-structure data (listed in part I of Table 1) represent 30 structure types among which 10 are novel and 9 were known before only for synthetic compounds.

Among 53 Tolbachik arsenates, 46 are still endemic to volcanic fumaroles (45 Tolbachik endemics and nickenichite), while only seven species are known in other geological formations: tilasite, durangite, svabite, and berzeliite were reported from endogenic (hydrothermal, skarn or pegmatitic) deposits and lammerite, stranskiite and johillerite from the oxidation zones of As-bearing chalcogenide ores (Majzlan et al., 2014). Our findings of berzeliite, tilasite, stranskiite and svabite were the first from fumarolic formation in general. Besides, our examination of durangite from Thomas Range (Utah) showed that its crystals are chemically heterogeneous and contain areas corresponding to maxwellite, ideally $NaFe^{3+}(AsO_4)F$, a mineral earlier unknown in fumarole deposits.

3. Mineral chemistry

Chemical data were obtained by electron microprobe in Laboratory of Analytical Techniques of High Spatial Resolution of Faculty of Geology, Lomonosov Moscow

Fig. 1. Summit of the Second scoria cone (view from South) of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–1976, Tolbachik volcano, Kamchatka, Russia. Main fumarole field, the locality of 53 arsenates, is the yellowish area marked with arrow.

State University (FG MSU), and in Analytical Laboratory of the Fersman Mineralogical Museum. Single-crystal and powder X-ray diffraction studies, including data collection for determination of crystal structures, were carried out mainly at Dept. of Crystallography and Crystal Chemistry, FG MSU, and in the X-Ray Diffraction Resource Center of St. Petersburg State University. Data on instruments used and analytical conditions are reported in publications devoted to our new arsenate minerals (Pekov *et al.*, 2014a–2017).

Chemical analyses of all arsenates listed in Table 1 are presented in Tables S1–S7 as Supplementary Material (linked to this article and freely available from the GSW website of the journal: https://pubs.geoscienceworld.org/eurjmin/): we selected compact datasets representatively demonstrating chemical variations of the minerals from >1500 of our analyses.

In this paper we summarize the most important chemical and crystal chemical features of fumarolic arsenates. Special attention is paid to major isomorphous substitutions and resulting solid-solution systems. Description of crystal structures is not a goal of this review and the respective data can be found in papers cited in Table 1.

Common chemical features of fumarolic arsenates. The major common chemical feature of all arsenates known in fumarole deposits is the absence of hydrogen. It is a rather remarkable fact, since H-free species constitute 1/6 of the total number of natural arsenates only: 60 valid mineral species out of 360, and 29 of these 60 minerals have been found in fumaroles only. Thus, taking into account unnamed phases (Table 1), more than half of the whole number of H-free arsenate minerals are endemics of the oxidizing-type fumaroles related to Tolbachik.

Species-defining metal cations in fumarolic arsenates are relatively diverse: Cu^{2+}, Mg, Al, Fe^{3+}, Ti^{4+}, Zn, Ca, Na, and K.

Purely alkaline arsenates are generally unknown among minerals, but the alkali-richest natural representatives are Tolbachik endemics: arsmirandite, yurmarinite, wrightite, katiarsite, pharmazincite and several unnamed phases contain >17 wt% $Na_2O + K_2O$ (Tables S3, S5–S7).

An interesting feature of fumarolic mineralization is the presence of titanium-rich arsenates. Katiarsite, arsenatrotitanite and $Na_{18}Cu_{12}TiO_8(AsO_4)_8FCl_5$ contain species-defining Ti^{4+} and, in several minerals, Ti substitutes Al or Fe^{3+} in essential amounts: *e.g.* up to 12.1 wt% TiO_2 in durangite (analysis #14 in Table S5).

Nineteen of 53 Tolbachik arsenates contain O^{2-} as additional anion, *i.e.*, O atoms not bonded to As. There are arsenates containing Cu^{2+} (12) or Al, Fe^{3+}, Ti (7) as the major species-defining cations. This feature is extremely rare for arsenates of other genetic types in which OH^- or/and H_2O groups play a similar crystal-chemical role.

Fluoro- and chloroarsenates are not uncommon in fumaroles: eight such minerals are known from Tolbachik (Table 1), whereas durangite and maxwellite occur in paleofumarole deposits at Thomas Range, Utah (##15–18 in Table S5).

Thus, many fumarolic arsenates with simple, monoelement additional anions (O^{2-}, F^-, Cl^-) are known, but only one species containing a complex additional anion (XO_n) as a separate structural subunit, vasilseverginite, $Cu_9O_4(AsO_4)_2(SO_4)_2$, has yet been found. Unlike this mineral with ordered arrangement of the AsO_4 and SO_4 groups (Pekov *et al.*, 2015f), many Tolbachik arsenates demonstrate wide-range isomorphous substitutions of As^{5+} for V^{5+}, P^{5+}, S^{6+} or Si^{4+}, and even several continuous solid-solution series between arsenate and vanadate, phosphate or silicate have been found. For many other fumarolic arsenates no significant substitutions in the As sites were detected but wide variations in metal-cation composition are typical.

Copper arsenates. Among Tolbachik arsenates, minerals with species-defining Cu^{2+} demonstrate the most striking diversity of chemical compositions and structures: 22 copper arsenates belong to 17 structure types (part I of Table 1). In all these minerals, except johillerite and stranskiite, Cu^{2+} is among the major cations or (in eight species) is the only metal cation. In the majority of the studied samples, Cu^{2+} is a strongly dominant element in corresponding structural sites (Tables S1–S3; ##23–30 in Table S4; ##5–10 in Table S6) with Zn acting as the most common admixture element. Usually Zn content is minor, <5–10% of the sum Cu + Zn, up to 10.1 wt% ZnO (=0.56 *apfu* Zn) only in one sample of lammerite-β, $Cu_3(AsO_4)_2$, from the Yadovitaya fumarole. Melanarsite and minerals with the edtollite structure type contain special sites occupied by Cu^{2+} and trivalent cations (Fe^{3+}, Al) in equal amounts, while in other Cu sites only Cu^{2+} occurs. Urusovite, dmisokolovite and arsmirandite demonstrate ordering of Cu^{2+} and Al or Fe^{3+}. In other fumarolic copper arsenates, Fe^{3+} and Al, as well as Mg and Mn, are only minor admixtures substituting for Cu^{2+} with <2–5% of the sum of Cu and these elements.

Lammerite-β was first described from the Yadovitaya fumarole as a mineral chemically very close to the end-member composition $Cu_3(AsO_4)_2$ (#11 in Table S1: Starova *et al.*, 2012). Our study of this mineral from two fumaroles, Yadovitaya and Arsenatnaya, showed that it forms a continuous isomorphous series with recently

discovered borisenkoite, $Cu_3[(V,As)O_4]_2$ (Pekov *et al.*, 2016a). Typical analyses of the V-rich lammerite-β (17.1–17.8 wt% $V_2O_5 = 0.84$–0.86 V *apfu*) are given in Table S1, ##15–16. The triclinic stranskiite-type modification of $Cu_3(AsO_4)_2$ is also V-enriched (11.6 wt% $V_2O_5 = 0.57$ V *apfu*: #17 in Table S1), being isostructural with mcbirneyite $Cu_3(VO_4)_2$. In contrast, for lammerite, the most widespread form of $Cu_3(AsO_4)_2$ in Tolbachik fumaroles, only V-poor samples have been found (##1–10 in Table S1). Filatov *et al.* (1984) reported a P-rich variety of lammerite (12.4 wt% $P_2O_5 = 0.76$ P *apfu*: #10 in Table S1) transitional to its P-dominant analogue $Cu_3[(P,As)O_4]_2$.

Alluaudite-type minerals form the largest structural group among fumarolic arsenates: eight valid species and two unnamed phases have been structurally characterized (Table 2). In addition, there is at least one poorly studied phase that belongs to this group (Part II of Table 1). Alluaudite-group members are the major As minerals in the Arsenatnaya fumarole. As^{5+} highly prevails in tetrahedrally coordinated sites in the overwhelming majority of our samples (##1-62 in Table S4). The typical contents of V_2O_5 or P_2O_5 are <1.0 wt%; only one calciojohillerite sample contains 11.6 wt% V_2O_5 (= 0.69 V *apfu*), whereas another sample of the same mineral has 12.3 wt% P_2O_5 (= 0.87 P *apfu*) (Table S4, ## 7 and 6, respectively). The highest contents of admixed SO_3 and SiO_2 found in fumarolic alluaudite-group arsenates (AGA) are less then 2.1 and 0.7 wt%, respectively, and typically their concentrations are <0.3 wt%. In contrast, contents of the major, species-defining metal cations vary in wide ranges (wt%; *apfu* in parentheses): Na_2O 2.3–14.2 (0.53–2.52 Na); CaO 0.0–16.7 (0.00–1.71 Ca); MgO 0.0–22.5 (0.00–3.02 Mg); CuO 0.0–45.3 (0.00–3.86 Cu); ZnO 0.0–26.3 (0.00–2.18 Zn); Fe_2O_3 0.0–21.1 (0.00–1.62 Fe) (Table S4).

Garnet-group minerals. Berzeliite, $(Ca_2Na)Mg_2(AsO_4)_3$, is the only arsenate garnet-type mineral known in fumarole deposits. In the Tolbachik samples, only V^{5+} is detected as a significant admixture. Fumarolic berzeliite forms a continuous solid solution with its vanadium analogue schäferite, $(Ca_2Na)Mg_2(VO_4)_3$. In its arsenate part, this series is almost complete: 0.3–23.4 wt% $V_2O_5 = 0.02$–1.24 V *apfu*. No significant substitutions was observed for constituents that occupy non-tetrahedral positions (##63–66 in Table S4).

Arsenates belonging to the tilasite/titanite structure type are represented in fumaroles by tilasite, durangite, maxwellite, and arsenatrotitanite (##1–19 in Table S5). We have found no significant P or Si admixtures in these minerals and only one sample of durangite is enriched in V (7.8 wt% $V_2O_5 = 0.19$ V *apfu*: analysis #11 in Table S5). The highest contents of admixed components were found in different tilasite specimens from Tolbachik (wt%, *apfu* in parentheses; the lowest value is 0.00 for all these components): Na_2O 3.9 (0.30 Na); CuO 1.3 (0.30 Cu); Al_2O_3 7.4 (0.31 Al); Fe_2O_3 15.1 (0.45 Fe); TiO_2 2.0 (0.13 Ti); SO_3 5.2 (0.14 S). The statistics of chemical data for Tolbachik durangite is poorer than that for tilasite, but we

have found a durangite variety strongly enriched in Ti (12.1 wt% $TiO_2 = 0.33$ Ti *apfu*), Fe, Mg and Ca (#14 in Table S5). Durangite and maxwellite from Thomas Range form a continuous isomorphous series (##15–18 in Table S5).

Feldspars Unexpectedly, important arsenic concentrators in the Tolbachik fumaroles turned out to be feldspars. Filatovite $K[(Al,Zn)_2(As,Si)_2O_8]$, a proper arsenate (with As>Si, in *apfu*) feldspar adopts a celsian structure type (Vergasova *et al.*, 2004; Filatov *et al.*, 2004). Our data show that in the Tolbachik fumaroles filatovite (##17–18 in Table S6) and "ordinary", aluminosilicate potassic feldspar form a continuous, complete solid-solution series (Koshlyakova *et al.*, 2014), in which As_2O_5 content varies from 0.0 to at least 42 wt% (0.00–1.25 As *apfu*). Potassic feldspar containing up to 2–3 wt% As_2O_5 is common here as well, forming voluminous incrustations in fumarole chambers, whereas its more As-rich varieties and filatovite are rarer.

The representatives of the *II-NA$_3$Fe$_2^{3+}$(AsO$_4$)$_3$ structure type*, well-studied as synthetic compounds due to their ion-conductor properties, were first discovered in Nature in the Arsenatnaya fumarole. These are yurmarinite, anatolyite (Pekov *et al.*, 2014a, 2016e), and an insufficiently studied phase with the simplified formula $Na_7(Fe^{3+},Mg)_3Al(AsO_4)_6$. These minerals demonstrate significant variations in the contents of major *M* cations: Fe^{3+}, Al, Mg and Cu (#19–23 in Table S6).

Wrightite, $K_2Al_2O(AsO_4)_2$, and ozerovaite, $KNa_2Al_3(AsO_4)_4$, recently described by (2016a and b), were found by us independently in the Arsenatnaya fumarole. In our samples, ozerovaite and pansnerite, both belonging to the $K_3Cr_3(AsO_4)_4$ structure type (Friaa *et al.*, 2003), demonstrate a solid-solution series (##13–15 in Table S6).

The apatite structure type is represented in the Arsenatnaya fumarole by svabite, $Ca_5(AsO_4)_3F$, forming almost complete isomorphous series with fluorapatite. In the arsenate part of the series, P_2O_5 contents vary from 0.0 to 15.1 wt% (up to 1.24 P *apfu*). Among other constituents substituting As, only V is significant: up to 3.4 wt% $V_2O_5 = 0.24$ V *apfu*. In svabite F can be partially substituted by Cl: up to 2.3 wt% = 0.42 Cl *apfu* (##1–7 in Table S7).

4. Occurrence

The Arsenatnaya fumarole at Tolbachik, the world-largest occurrence of sublimate arsenate mineralization, was briefly characterized by Pekov *et al.* (2014a). However, only its southern part was well-examined in the 2012–2013 period. As it turned out later, the As-richest and highly diverse in arsenates area is located at the northern flank of Arsenatnaya. It was uncovered during our 2014–2016 fieldworks. Updated information on the fumarole and its arsenate mineralization is given below.

The Arsenatnaya fumarole is a near-meridional linear system of mineralized pockets (up to 10–15 cm wide) and cracks located between blocks of basalt scoria and volcanic bombs that compose the near-surface part of

Table 2. Distribution of dominant cations and vacancies (□) between sites in crystal structures of alluaudite-group arsenates from fumarole deposits*.

Site	$A(1)$	$A(1)'$	$A(1)''$	$A(2)$	$A(2)'$	$A(2)''$	$M(1)$	$M(2)$	Ref.
Wyckoff site	4b	4e	8f	4a	4e	8f	4e	8f	
Coordinates	½ 0 0	$0\,y\,¼$ $(y \sim ½)$	$x\,y\,z$ $(x \sim ½, y, z \sim 0)$	0 0 0	$0\,y\,¼$ $(y \sim 0)$	$x\,y\,z$ $(x, y, z \sim 0)$	$0\,y\,¼$	$x\,y\,z$	
Badalovite $Na_2Mg_2Fe^{3+}(AsO_4)_3$	Na	□	□	□	Na	□	Mg	$(Mg_{0.5}Fe^{3+}_{0.5})$	1
Bradaczekite $NaCu_4(AsO_4)_3$	□	Cu	□	□	Na	□	Cu	Cu	2
Calciojohillerite $NaCaMg_3(AsO_4)_3$	Ca	□	□	□	Na	□	Mg	Mg	1
Hatertite $Na_2(Ca,Na)(Fe^{3+},Cu)_2(AsO_4)_3$	Na	□	□	□	Na	□	(Ca,Na)	(Fe^{3+},Cu)	3
Johillerite $NaCuMg_3(AsO_4)_3$	□	Cu	□	□	Na	□	Mg	Mg	4
Magnesiohatertite $(Na,Ca)_2Ca(Mg,Fe^{3+})_2(AsO_4)_3$	(Na,Ca)	□	□	□	Na	□	Ca	(Mg,Fe^{3+})	1
Nickenichite $Na(□,Ca)(□,Cu)(Mg,Fe^{3+})_3(AsO_4)_3$	(□,Ca)	(□,Cu)	□	□	Na	□	(Mg,Fe^{3+})	(Mg,Fe^{3+})	5
Zincobradaczekite $NaCu_2Zn_2(AsO_4)_3$	□	Cu	□	□	Na	□	Cu	Zn	1
Unnamed $Na_3Fe^{3+}_2(AsO_4)_3$	Na	□	□	□	Na	□	Na	Fe^{3+}	1
Unnamed $NaCa_2Mg_2(AsO_4)_3$	Ca	□	□	□	Na	□	Ca	Mg	1

References: 1–our data; 2–Krivovichev *et al.*, 2001; 3–Krivovichev *et al.*, 2013b; 4–Tait & Hawthorne, 2004, and our data; 5–Auernhammer *et al.*, 1993;. *The table is organized in accordance with the scheme suggested by Krivovichev *et al.* (2013b).

the scoria cone. The length of the hot area belonging to Arsenatnaya is about 15 m and its width varies from 1–1.5 m in its southern to 3–4 m in its northern part. Numerous strongly mineralized pockets occur depths of 0.3–4 m. The fumarolic minerals, including arsenates, form incrustations in the open space of the pockets, fill cracks and small vugs or replace basalt. Arsenatnaya is now one of the hottest fumaroles known at the Second scoria cone of the NB GTFE: the temperature measured by us using chromel-alumel thermocouple in 2012–2016 in different pockets with arsenate mineralization immediately after their partial uncovering varies from 360 to 450 °C and, in general, increases with depth.

About 140 valid minerals and >20 insufficiently studied mineral phases have been identified in this mineralogically unique fumarole and 51 of them are arsenates. Arsenatnaya is the type locality of 34 IMA-approved mineral species. It is a world record in the number of new minerals per area unit (<50 m²). The presence of minerals with only high-valent states of indicator elements (S^{6+}, Mo^{6+}, As^{5+}, V^{5+}, Fe^{3+}, *etc.*) demonstrates that the sublimate mineralization was formed here under strongly oxidizing conditions.

Various mineral assemblages are unevenly distributed in Arsenatnaya. However, despite their rather complicated, "spotty" character in general, a distinct vertical zonality was observed in the northern part of the fumarole (Fig. 2). The zones 1–4 in Fig. 2 belong to the area where chemical interactions involving sublimate mineralization, host rock, fumarole gas and meteoric water/vapour happen. We define this area as "a hot supergene-alteration zone of

fumarole deposits". The temperature measured in its different points varies from 30–40 (near day surface) to 120–150 °C. The secondary hydrous sulfates and opal prevail here among newly formed phases. At the same time, no arsenates or other As-bearing minerals were found here that could be caused by the relative stability of primary sublimate arsenates under supergene conditions in comparison with primary alkali- or Cu-bearing sulfates (note that no water-soluble arsenates have been found in Tolbachik fumaroles). The zones 5–15 show no signs of the influence of meteoric agents. The measured temperature in zones 5 and 6 is 180–250 °C and only H-free fumarolic minerals are observed there, as well as in all deeper zones, 7–15 (Fig. 2). The temperature in the area including zones 7–15 varies from 250 to 450 °C. All 5–15 zones contain arsenate mineralization, but its composition strongly changes from deeper to upper zones, as well as the general mineral composition of sublimates. The major mineral associations (with special attention paid to arsenates) in the northern part of Arsenatnaya are characterized in Table 3 and their spatial distribution is schematically shown in Fig. 2.

In the deep zones (15–13 in Fig. 2, IV in Table 3), arsenates with only species-defining Mg, Ca and Na have been found. There, arsenate mineralization is complemented by badalovite and further nickenichite and Cu-depleted johillerite (zones 10, 12 and 9 in Fig. 2, III in Table 3). The highest diversity of arsenates is observed in the zones located higher and marked 7, 8 and 11 in Fig. 2 (II in Table 3). Cu-bearing species are dominant there;
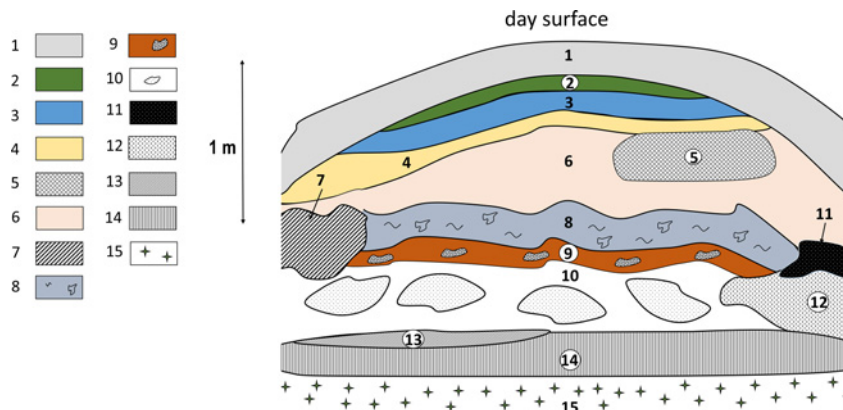
Fig. 2. Section across the northern part of the Arsenatnaya fumarole, Tolbachik volcano: (1) solid outer crust mainly composed by volcanic bombs and lapilli cemented by opal; (2) solid zone mainly consisting of gypsum and opal; (3) loose zone mainly consisting of secondary hydrous Ca, Mg and Cu sulfates; (4) cavernous zone enriched with hydrous Cu sulfates (chalcantite, kaliochalcite, *etc.*) and gypsum; (5) area strongly enriched with H-free Cu sulfates (euchlorine, wulffite, *etc.*), langbeinite and tenorite; (6) breccia-like material: volcanic bombs and scoria fragments are mainly cemented by H-free sulfates of Mg, Cu, Ca, K and Na; (7) area with abundant johillerite; (8) polymineralic zone enriched with sylvite, halite, aphthitalite, various arsenates, As-bearing potassic feldspar, tenorite, fluoborite, *etc.*; (9) zone enriched with aphthitalite, metathénardite and (in its lower part) nickenichite; (10) zone with abundant calciojohillerite; (11) area with bradaczekite and other Cu-rich arsenates; (12) area enriched with calciojohillerite and badalovite; (13) hematite-anhydrite area with fluorophlogopite, calciojohillerite and cassiterite; (14) hematite-anhydrite zone with calciojohillerite; (15) hematite-diopside-anhydrite zone enriched with svabite, calciojohillerite and berzeliite–schäferite series garnets. For more detailed mineralogical data see Table 3.

however, all valid arsenate minerals known in Arsenatnaya have been detected (in different amounts) as constituents of different parageneses belonging to this zone. In sulfate zones (5 and 6 in Fig. 2, I in Table 3), arsenates occur rather rarely and in minor amounts.

The change of cationic composition of arsenates from deep to upper levels of Arsenatnaya can be illustrated by alluaudite-group minerals, which are the main As hosts in this fumarole. They form crystalline crusts up to several m^2 in area. From bottom to upper zones major alluaudite-group minerals evolve in the following sequence: calciojohillerite, $NaCaMg_3(AsO_4)_3 \rightarrow$ calciojohillerite (Fig. 3) + badalovite, $Na_2Mg_2Fe^{3+}(AsO_4)_3$ (Fig. 4) $\rightarrow$ nikenichite, $Na(\square,Ca)(\square,Cu)(Mg,Fe^{3+})_3(AsO_4)_3$ (Fig. 5) $\rightarrow$ johillerite, $NaCuMg_3(AsO_4)_3$ (Fig. 6) + bradaczekite, $NaCu_4(AsO_4)_3$ (Fig. S1). Thus there is a gradual increase in the Cu content and decrease in the Ca content, while Mg remains a permanent essential component of these minerals in all the parageneses studied. This geochemical tendency is general and is confirmed by the distribution of other arsenates, as well as sulfates, between mineral assemblages of different zones (Table 3).

The crystallization sequence of arsenates can vary significantly. For instance, we have observed the replacement of Cu-bearing alluaudite-group minerals by lammerite and *vice versa*. However, some regularities can be detected. In the deepest zone (IVa in Table 3), Na-bearing arsenates typically crystallize later than minerals containing alkaliearth cations (Ca, Mg) only (Fig. 7a and b). In the polymineralic zone (II in Table 3), the evolution of arsenate mineralization proceeds with decreasing Al and increasing Cu content. The generalized sequence found for major Cu- and Al-rich As minerals is: potassic feldspar, $K[AlSi_3O_8]$ $\rightarrow$ As-enriched potassic feldspar, $K[Al(Si,As,Al)_3O_8] \rightarrow$

alarsite, $AlAsO_4 \rightarrow$ urusovite, $Cu[AlAsO_5] \rightarrow$ lammerite, $Cu_3(AsO_4)_2 \rightarrow$ ericlaxmanite, $Cu_4O(AsO_4)_2 \rightarrow$ kozyrevskite, $Cu_4O(AsO_4)_2 \rightarrow$ popovite, $Cu_5O_2(AsO_4)_2$. Different stages of this evolution series are illustrated in Fig. 8a–d.

In the Yadovitaya fumarole, arsenate mineralization is not as considerable as in Arsenatnaya, though lammerite-bearing crystalline crusts up to several hundreds cm^2 in area are common. In Yadovitaya, all seven arsenates are Cu-rich: there are three modifications of $Cu_3(AsO_4)_2$, ericlaxmanite, bradaczekite, zincobradaczekite, and coparsite with the latter two minerals occurring as endemics in the fumarole.

Description of individual arsenate minerals is beyond the scope of this review. We simply provide a series of illustrations (Figs. S2–S1) showing morphologies of arsenate crystals and their aggregates for the species that were so far unknown or poorly characterized in Tolbachik samples.

Many fumarolic sulfates, chlorides and some other minerals are water-soluble, unstable in moist air and easily alter in the upper zones of fumarole deposits due to the influence of surficial agents. In contrast, all Tolbachik arsenates are water-insoluble and stable under atmospheric conditions. We have not found any sign of their supergene chemical alteration, as well as of the presence of As (in amount detectable by electron microprobe) in secondary minerals from the Tolbachik fumaroles.

5. Discussion

Fumarolic arsenates form an unusual type of arsenic mineralization. Their gross mass, being minor on the scale of the Earth's crust is, however, not negligible: at least several tons occur in Tolbachik fumaroles only, where these minerals form very rich, relatively compact accumulations

Table 3. Zonal distribution of arsenate minerals in northern part of the Arsenatnaya fumarole.

Zone[*]	**Predominant**/ common arsenates	Minor arsenates	**Major** and some *characteristic* non-arsenate sublimate minerals	Notes
I. Zone of copper sulfates (≈ 5 and 6 in Fig. 2)	–	lammerite, lammerite-β, urusovite, johillerite	**euchlorine, wulffite, langbeinite, tenorite**, *chalcocyanite, fedotovite, dolerophanite, dravertite, alumoklyuchevskite, anglesite*	sulfates with Cu, Mg and/or K strongly prevail over other minerals; arsenates are very scarce
II. Polymineralic zone (≈7, 8 and 11 in Fig. 2)	**johillerite, bradaczekite, lammerite**, lammerite-β, tilasite, urusovite, ericlaxmanite, popovite	all other arsenates with species-defining Cu and Al listed in Table 1[**], arsenowagnerite, arsenatrotitanite, svabite, nickenichite, magnesiohatertite, hatertite, yurmarinite, pharmazincite, pansnerite, unnamed phases $(K,Na)_3(Fe^{3+}, Ti,Al,Mg)_5O_2(AsO_4)_5$, $Na_3Fe^{3+}_2(AsO_4)_3$ and $NaMgFe^{3+}_2(AsO_4)_3$	**As-bearing potassic feldspar, sylvite, halite, aphthitalite, langbeinite, hematite, tenorite, fluorophlogopite**, *fluoborite, krasheninnikovite, calciolangbeinite, metathénardite, euchlorine, wulffite, pseudobrookite, rutile, flinteite*	zone with the greatest specific and chemical diversity of minerals; Cu minerals are abundant; Ti minerals are mainly concentrated here
IIIa. Zone of alluaudite-group arsenates (upper part) (≈ 9 in Fig. 2)	**nickenichite**	johillerite, calciojohillerite, badalovite, tilasite	**hematite, potassic feldspar, fluorophlogopite, aphthitalite, metathénardite**, *sylvite, halite*	alluaudite-group arsenates are usually Cu-poor
IIIb. Zone of alluaudite-group arsenates (lower part) (≈ 10 and 12 in Fig. 2)	**calciojohillerite, badalovite**	svabite, tilasite	**hematite, fluorophlogopite**, *aphthitalite, metathénardite, cassiterite*	alluaudite-group arsenates can be main constituents of sublimates; Cu minerals are absent
IVa. Anhydrite zone (upper part) (≈13 and 14 in Fig. 2)	calciojohillerite	svabite, tilasite, arsenowagnerite	**anhydrite, hematite, fluorophlogopite, diopside**, *cassiterite*	Cu minerals are absent; cassiterite is sporadically abundant
IVb. Anhydrite zone (lower part) (≈15 in Fig. 2)	**svabite, berzeliite, calciojohillerite**	tilasite, unnamed phases $NaCa_2Mg_2(AsO_4)_3$, $Ca_2[(As,V)_2O_7]$ and $(Na,Ca)_{1-x}Mg_4[(As,V)O_4]_3$	**anhydrite, diopside, hematite**, *As-bearing schäferite, As-bearing fluorapatite, W-bearing powellite, forsterite, ludwigite, magnesioferrite*	Cu minerals are absent; K minerals are minor; the only zone in which V-, P- and W-rich minerals occur

[*] Zones are separated in vertical section and depth increases from zone I (0.3–0.5 m from day surface) to zone IV (2–4 m from day surface); only areas without signs of supergene alteration are included, see Fig. 2, zones 5–15.
[**] Except of coparsite and zincobradaczekite only known in the Yadovitaya fumarole.

and locally show centimetre-sized crystals. A remarkable feature of this mineralization is the great diversity of arsenate species and their crystal structures. More than fifty arsenates have been found in the fumarolic formation: 54 have been included in the present paper and 53 of them, except maxwellite, are reliably known at Tolbachik. Thirty structural types are already determined for fumarolic arsenates, including 19 so far unknown in minerals.

5.1. Isomorphous substitutions and other crystal-chemical features

Various isomorphous substitutions are common for fumarolic arsenates but their type and range are quite different in

minerals with different structures. The affinity to one or the other chemical elements substituting for As^{5+} or/and metal cations and the difference in selectivity of arsenates crystallized simultaneously, under similar conditions, towards admixed constituents can be very significant. Thus the Tolbachik fumaroles, in which arsenates are structurally diverse, seem a unique natural arena for investigations of individual crystal-chemical features of arsenates formed as a result of high-temperature gas-transport reactions.

Continuous solid-solution series between arsenates and minerals of other chemical classes have been observed for minerals with the lammerite, lammerite-β, garnet, apatite and feldspar structure types formed in Tolbachik fumaroles.

Fig. 3. Greenish to bright green calciojohillerite crystal crust overgrowing volcanic bomb extracted from zone 10 (see Fig. 2) of the Arsenatnaya fumarole.

Fig. 5. Violet-blue nickenichite crystal crust (partially covered by white aphthitalite) on volcanic scoria. Photo *in situ*: zone 9 (see Fig. 2) of the Arsenatnaya fumarole.
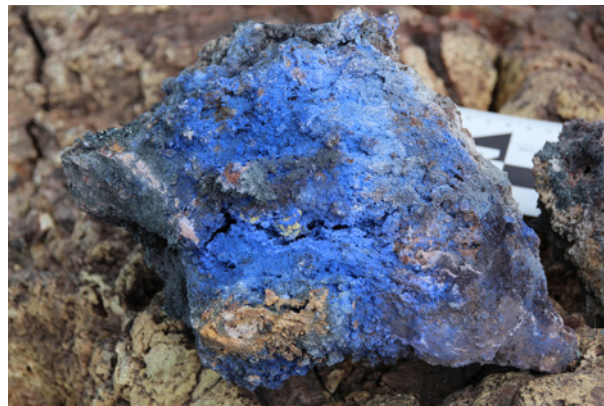

Fig. 4. Green to dark green badalovite crystal crust on volcanic scoria. Photo *in situ*: zone 12 (see Fig. 2) of the Arsenatnaya fumarole. Field of view (FOV) width: 10 cm.

Fig. 6. Blue johillerite crust overgrowing volcanic bomb extracted from zone 7 (see Fig. 2) of the Arsenatnaya fumarole.

Lammerite structure type Filatov *et al.* (1984) reported electron microprobe analyses and crystal-structure data for Tolbachik samples chemically corresponding to the medium part of a hypothetical series between lammerite and its P-dominant analogue, $Cu_3[(P,As)O_4]_2$, with both As >P and P >As (in *apfu*). In our material, no P-rich variety of lammerite or other modifications of $Cu_3(AsO_4)_2$ was found.

*Lammerite-*β *structure type* This modification of $Cu_3(AsO_4)_2$ forms a continuous solid solution with isotypic borisenkoite, $Cu_3[(V,As)O_4]_2$ (Pekov *et al.*, 2016a). Besides the major substitution scheme $As^{5+} \leftrightarrow V^{5+}$, a homovalent substitution $Cu^{2+} \leftrightarrow Zn$ is essential.

Garnet structure type The berzeliite–schäferite series demonstrates significant $As^{5+} \leftrightarrow V^{5+}$ substitution, whereas isomorphism in other sites is minor.

Apatite structure type There is a svabite–fluorapatite solid-solution series with $As^{5+} \leftrightarrow P^{5+}$ as a major substitution scheme. In Tolbachik svabite, a significant F^--for-Cl^- substitution has been observed.

Alluaudite structure type Alluaudite-group minerals having the same $Me_5(TO_4)_3$ general stoichiometry as garnets [we have found, in particular, the alluaudite-type
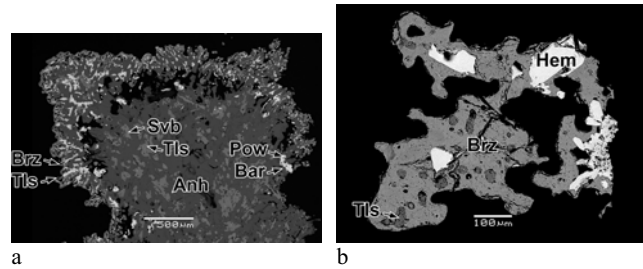
Fig. 7. Berzeliite (Brz) overgrowing Ca and Mg arsenates and associated minerals: (a) berzeliite crust covering anhydrite (Anh) nodule with numerous ingrowths of svabite (Svb), tilasite (Tls), baryte (Bar) and W-bearing powellite (Pow); (b) berzeliite overgrows tilasite and hematite (Hem). Zone 15 (see Fig. 2) of the Arsenatnaya fumarole. SEM (BSE) image.
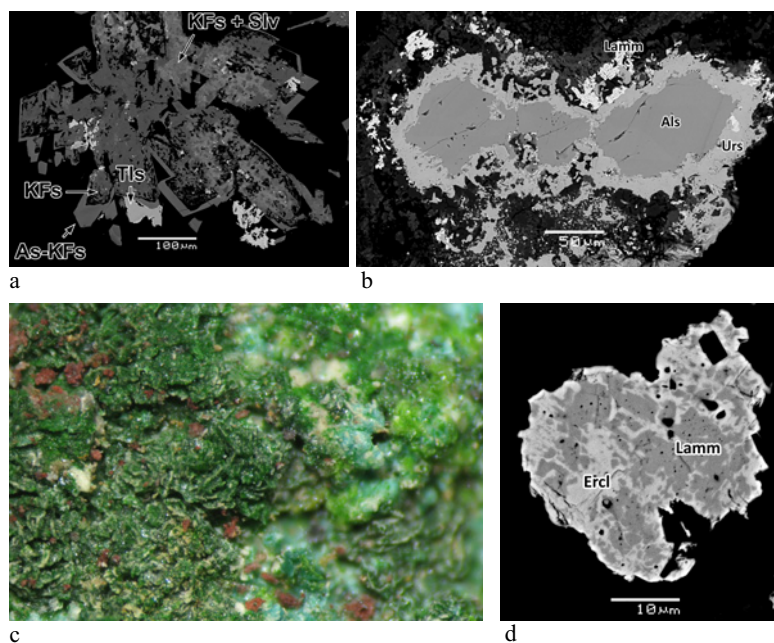
Fig. 8. Crystallization sequence of different arsenates and As-bearing potassic feldspar: (a) As-rich (16 wt% As_2O_5) potassic feldspar (As-KFs) overgrowing As-poor (<2 wt.% As_2O_5) potassic feldspar (KFs), with tilasite (Tls) and sylvite (Slv); (b) alarsite (Als) surrounded by urusovite (Urs) replacement rim and overgrown by lammerite (Lamm); (c) deep-green ericlaxmanite replaces urusovite crystal crust (pale blue urusovite relics and light green kozyrevskite occur in the right part of the photograph); (d) ericlaxmanite (Ercl) overgrows lammerite. Arsenatnaya fumarole. (c) FOV width: 5.8 mm; (a, b and d) SEM (BSE) image.

phase $NaCa_2Mg_2(AsO_4)_3$ dimorphous with berzeliite: see analysis #62 in Table S4], are quite different from the latter in terms of structure and, as a result, the two groups differ strongly in the schemes and ranges of isomorphic substitutions. Substitutions in the As site is, in general, not typical for fumarolic alluaudites, whereas substitutions in the $Me = M + A$ sites [with distribution of dominant cations between different M and A sites] are significant (Table 2); for crystal-chemical analysis see Krivovichev *et al.* (2013b). Our data demonstrate that ten arsenates

listed in Table 2 and the phase $NaMgFe^{3+}_2(AsO_4)_3$ (Table 1, Part II) form two separate continuous solid-solution systems: (1) a binary bradaczekite–zincobradaczekite series with $Cu^{2+} \leftrightarrow Zn$ in the $M(2)$ site as main substitution scheme and (2) a multicomponent system between all other nine arsenates with complicated coupled substitutions involving all constituents that may be present in both M (Fe^{3+}, Mg, Ca and Na) and A (Na, Ca, Cu^{2+}) sites (Table 2). A gap between these solid-solution systems (namely, between the Cu-rich johillerite and the Mg-rich

bradaczekite: Table S4, ##20 and 28, respectively) can be due to some differences in the unit-cell parameters of the members of the Cu^{2+}-rich bradaczekite–zincobradaczekite series ($\beta = 117.5-118°$, due to the strong influence of the Jahn-Teller effect: Krivovichev et al., 2001; Pekov et al., 2016f) and other alluaudite-type arsenates known here ($\beta = 112-114°$) (Table 1). Unlike the $M(1)$ and $A(1)'$ sites, the $M(2)$ site displays significant Cu^{2+}-for-Mg (johillerite, magnesiohatertite) or Cu^{2+}-for-Fe^{3+} (hatertite) substitution (Table 2) (Tait & Hawthorne, 2004; Krivovichev et al., 2013b; our data).

Tilasite/titanite structure type Similar to alluaudite-group minerals, in fumarole deposits, these arsenates are characterized by a rather narrow substitution range for As^{5+} but a wide-range substitution for other metal sites. Fumarolic tilasite, durangite, maxwellite and arsenatrotitanite form a complex multicomponent solid-solution system with the main coupled hetero- and homovalent substitutions involving all species-defining elements occupying two cation sites: (1) Na^+, Ca^{2+} and (2) Mg^{2+}, Al^{3+}, Fe^{3+}, and Ti^{4+}. Substitution in the additional anion site ($O^{2-} \rightarrow F^-$) is minor, except for the samples with significant Ti content. It is also noteworthy that the highest content of S^{6+} substituting As^{5+} among all known fumarolic arsenates was found in tilasite, where S demonstrates a clear positive correlation with Na: tilasite in Arsenatnaya contains up to 14 mol% of kononovite, $NaMg(SO_4)F$, the first sulfate mineral with the tilasite/titanite structure type recently discovered in the same fumarole (Pekov et al., 2015d).

Arsenates with mixed tetrahedral frameworks In the structures of four fumarolic arsenates, As^{5+} forms mixed frameworks with tetrahedrally coordinated Al or/and Zn. Minerals with this type of structures include filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$, alarsite, $[AlAsO_4]$, urusovite, $Cu[AlAsO_5]$, and pharmazincite, $K[ZnAsO_4]$ (part I of Table 1). Among them, filatovite as a feldspar-group mineral demonstrates significant heterovalent substitutions in tetrahedral sites forming continuous solid-solution series with the As-free potassic feldspar. In the As-poor members of this series, the major substitution scheme is $As^{5+} + Al^{3+} \leftrightarrow 2Si^{4+}$ (Koshlyakova et al., 2014), whereas in the As-rich phases there is an additional scheme that involves divalent components: $2As^{5+} + (Zn,Cu)^{2+} \leftrightarrow 3 Si^{4+}$ (Filatov et al., 2004; our data). In alarsite, the AsO_4 and AlO_4 tetrahedra form a neutral berlinite-type framework, an Al-As ordered derivative of quartz (Semenova et al., 1994). In the tetrahedral layer in the structure of urusovite, As and Al are also ordered (Krivovichev et al., 2000). Both alarsite and urusovite have fairly constant chemical compositions (Table S6). Pharmazincite belongs to the stuffed derivatives of tridymite. This arsenate is isostructural to megakalsilite, $K[AlSiO_4]$, but, in the tridymite-type $[ZnAsO_4]^-$ tetrahedral framework, Zn (with distinct Cu admixture) and As occupy sites corresponding to the Si and Al sites in megakalsilite, respectively (Pekov et al., 2017).

All above-mentioned wide-range solid-solution systems, except for the apatite–svabite series, are unknown in minerals of other genetic types. The majority of them have not been reported for synthetic compounds (*e.g.*, the berzeliite–schäferite series, despite the extensive studies of garnet-type minerals and compounds)

Cu^{2+} coordination in fumarolic arsenates The complicated crystal-chemical behaviour of Cu in fumarolic arsenates as well as in sulfates and vanadates is related to the diversity of Cu^{2+} coordination polyhedra in these minerals. Unlike supergene hydrous arsenates and related oxysalts, where Cu^{2+} forms $CuO_x(OH)_y(H_2O)_{6-x-y}$ octahedra ($x \leq 4$), H-free fumarolic copper arsenates contain Cu in different coordination environments with the coordination numbers varying from 4 to 6 (Pekov & Zubkova, 2015). The Cu^{2+}-centred polyhedra known in fumarolic arsenates include almost planar CuO_4 square, CuO_5 and CuO_4Cl square pyramids, CuO_5 trigonal bipyramid, and CuO_6 and CuO_4Cl_2 octahedra with different degrees of distortion, mainly due to the Jahn-Teller effect (Fig. 9). If a structure contains several geometrically different Cu^{2+}-centred polyhedra then the substitution of Cu^{2+} for another cation will mainly occur in less distorted octahedra, whereas four- or five-fold Cu-centred polyhedra in all cases remain practically admixture-free. This is, in particular, illustrated by melanarsite, edtollite-type and Cu-rich alluaudite-group arsenates (Tables 1 and 2).

Complexes of anion-centred tethahedra in fumarolic copper oxyarsenates The crystal structures of H-free copper oxyarsenates, *i.e.*, arsenates with additional O^{2-} anions (O_{add}) could be described in terms of anion-centred tetrahedra (Krivovichev et al., 2013a). Topologically different motifs of O^{2-}-centred (oxocentred) tetrahedra in such minerals discovered in Tolbachik fumaroles are shown in Fig. 10. Dimorphous ericlaxmanite and kozyrevskite, oxyarsenates with the highest ratio Cu: $O_{add} = 4$, contain isolated OCu_4 tetrahedra. In dmisokolovite with $(Cu+Al):O_{add} = 3$, two $[OCu_3Al]$ tetrahedra share a common Cu–Al edge to form isolated dimers $[O_2Cu_5Al]$. In shchurovskyite $(Cu:O_{add} = 3)$, the same dimers include only Cu cations and have the formula $[O_2Cu_6]$. In contrast to dmisokolovite and shchurovskyite, in their stoichiometric analogues edtollite and alumoedtollite not all Cu atoms are involved in oxocentred tetrahedral motifs. These two arsenates contain $[O_2Cu_2M_2]^\infty$ chains $[M = (Fe^{3+}/Al)_{0.5}Cu_{0.5}; \ (Cu+M):O_{add} = 3]$ formed by edge sharing of OCu_2M_2 tetrahedra. The OCu_3M tetrahedra $(M = Fe^{3+}_{0.5}Cu_{0.5})$ also connected *via* common edges form topologically identical $[O_4Cu_6 M_2]^\infty$ chains in melanarsite $[(Cu+M):O_{add} = 2]$. Topologically the same chain involving only Cu^{2+}, $[O_2Cu_6]$ was reported by Starova et al. (1998) for coparsite (Cu: $O_{add} = 2$). Popovite (Cu:$O_{add} = 2.5$) contains the $[O_2Cu_5]^\infty$ chains built by OCu_4 tetrahedra with alternating edge and corner linkages. All above-listed complexes of anion-centred tetrahedra have been already known in other
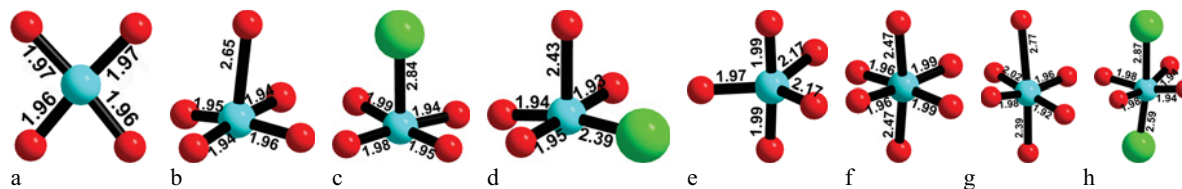
Fig. 9. Diversity of Cu^{2+}-centred coordination polyhedra in oxyarsenates from Tolbachik fumaroles: almost planar square in dmisokolovite (a); square pyramids in ericlaxmanite (b), axelite (c), and coparsite (d); trigonal bipyramid in kozyrevskite (e); distorted octahedra in shchurovskyite (f), edtollite (g), and coparsite (h). Bond lengths (in Å) are marked. Blue circles are Cu, red circles are O and green circles are Cl atoms; d, h − drawn after Starova *et al.* (1998), others − our data.

natural or synthetic oxysalts (Krivovichev *et al.*, 2013a). Vasilseverginite and arsmirandite possess topologically novel oxocentred tetrahedral motifs that have no analogues among minerals. The crystal structure of vasilseverginite ($Cu:O_{add} = 2.25$) is based upon complex layers formed by the $[O_4Cu_9]^\infty$ sheets built by edge- and corner-sharing OCu_4 tetrahedra. In arsmirandite $[(Cu + Fe):O_{add} = 1.625]$, the OCu_3Fe tetrahedra share common edges and one corner to compose the isolated cluster $[O_8Fe^{3+}Cu_{12}]$ with Fe^{3+} cation in the centre of 13-nuclear clusters composed from eight oxocentred tetrahedra. An identical complex with Ti instead of Fe^{3+}, $[O_8TiCu_{12}]$ was recently found in the unnamed Ti-analogue of arsmirandite, $Na_{18}Cu_{12}TiO_8 (AsO_4)_8FCl_5$.

The presence of anion-centred OCu_4 tetrahedra in the crystal structures of fumarolic oxysalt minerals is very common (Krivovichev *et al.*, 2013a). Some authors suppose that it could be a consequence of the existence of such complexes in volcanic gases and their participation in transport of Cu in the form of polynuclear oxocentred clusters (Kovrugin *et al.*, 2015).

5.2. Notes on genesis

The remarkable mineral diversity and unique character of the mineralization formed in the oxidizing-type fumaroles is caused by their unusual formation conditions, namely, by the combination of: (1) high temperature and, typically, significant temperature gradient, (2) low, atmospheric pressure, (3) very high oxygen fugacity (as a result of mixing of volcanic gases with air: Meniaylov *et al.*, 1980; Zelenski *et al.*, 2011), (4) gaseous transport of the majority of constituents, and (5) special geochemistry of volcanic exhalations. As a result, a specific, mixed, "endogenous-supergene" type of mineralization is observed that is formed near the surface at high temperature and with direct endogenous source of most chemical elements including "ore" metals. No analogue of this mineral-forming system is known in nature. The combination of high temperature and low pressure is definitely the cause of the absence of hydrogen (and carbonate groups) in minerals formed in the hot ($>150–200\,°C$) fumarolic environments. High oxygen fugacity definitely favors the formation of high-temperature oxysalts with additional $O^{2−}$ anions that are so typical for the Tolbachik arsenates.

Our measurements show that the temperature range in arsenate-bearing pockets of both Arsenatnaya and Yadovitaya fumaroles is now 250–450 °C. In Arsenatnaya, in zones marked I-IIIa in Table 3, arsenates are intimately associated with sylvite crystals containing oriented halite intergrowths and halite with similarly intergrown sylvite lamellae. This is the obvious result of the breakdown of (K,Na)Cl and (Na,K)Cl solid solutions, respectively. The KCl–NaCl series is well-studied and, in particular, numerous samples from the Tolbachik fumaroles were examined in detail in comparison with the experimental data. It was shown that the formation of homogeneous intermediate phases of the halite–sylvite solid-solution series in Tolbachik fumaroles happen at temperatures $\geq450\,°C$ and exsolution starts at $425 \pm 15\,°C$ (Filatov & Vergasova, 2002). Sylvite/halite crystals with clear exsolution signs typically overgrow arsenates in open spaces of the fumarole cameras but the reverse situation is not uncommon. In fact, simultaneous crystallization of the K-Na chloride solid solution and arsenates has also been observed. In the deeper, hotter zones (IIIb-IV in Table 3), sylvite and halite are absent, whereas arsenates are abundant. Thus, the lowest formation temperature of Tolbachik arsenates could be evaluated as 450 °C. The upper limit is definitely lower than 1000 °C (the maximal temperature measured for the gas emitted directly from lava in 1975, when the scoria cone was formed: Fedotov & Markhinin, 1983), but it is difficult to determine it exactly. We assume, taking into account data on gas temperature and chemistry in fumaroles of the Second scoria cone of the NB GFTE in 1975–1977 (Meniaylov *et al.*, 1980), that arsenates probably crystallized between 500 and 750 °C. High-temperature X-ray diffraction studies of bradaczekite and urusovite (Filatov *et al.*, 2009) indicated that both minerals remained stable in air till 700 °C, which provides indirect support for the estimate given above.

Fumarolic arsenates can be formed as a result of a direct deposition from gases as volcanic sublimates or by a gas–rock interaction. Aluminium, Ti and even Mg and Ca, unlike S, halogens, alkali metals and some "ore" components (As, Cu, Zn, *etc.*), have low volatilities even at temperatures $>500\,°C$ (Symonds & Reed, 1993; Churakov *et al.*, 2000) and they are most probably extracted by hot gases from the host basalt matrix inside fumarole cameras.

Our observations of arsenate mineralization in the Tolbachik fumaroles provide new empirical data on relative volatilities of Cu and As in the oxidizing-type fumaroles. Copper is concentrated in only upper parts of
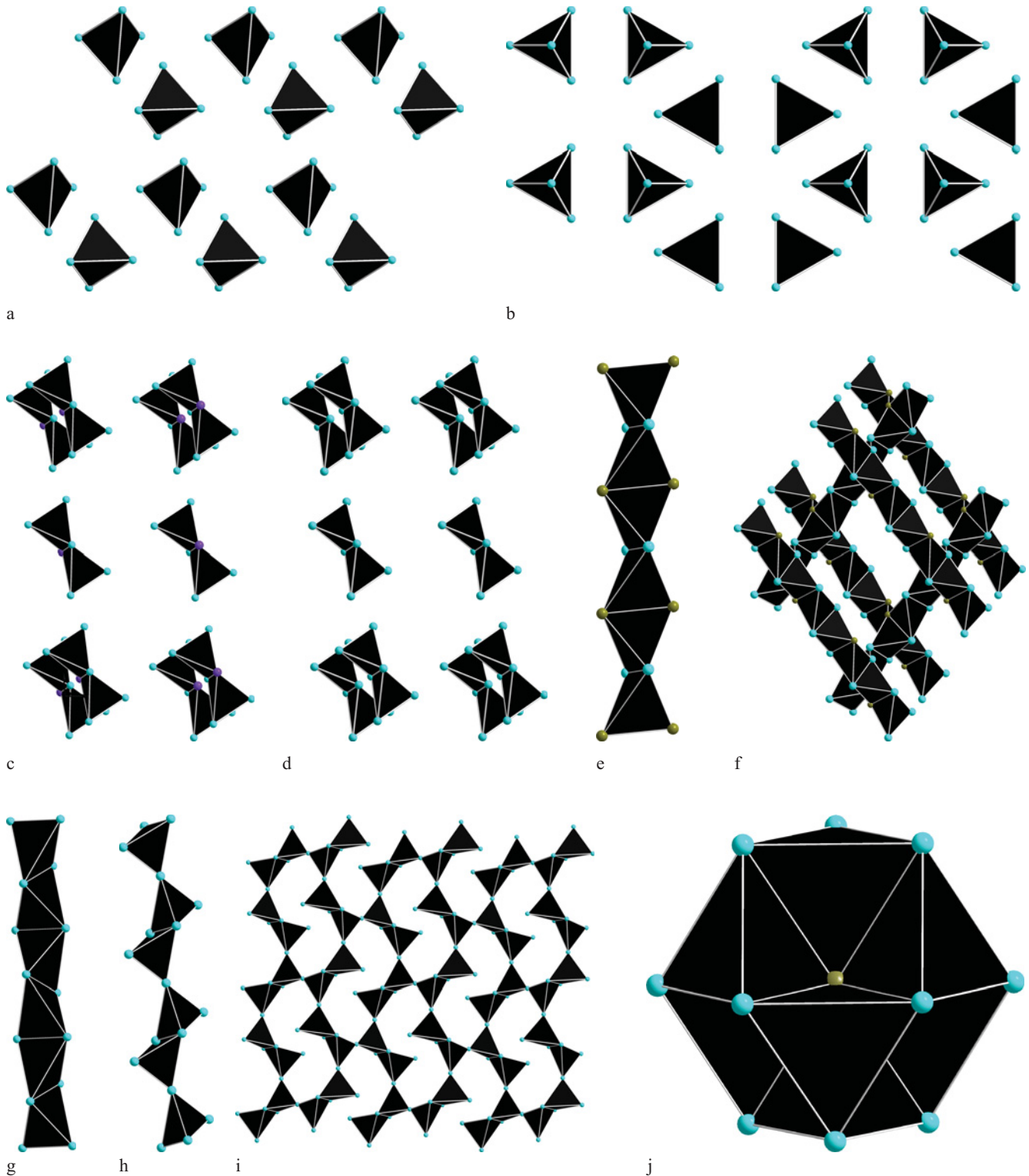
Fig. 10. Diversity of complexes formed by oxocentred tetrahedra in oxyarsenates with species-defining Cu^{2+} from Tolbachik fumaroles: ericlaxmanite (a), kozyrevskite (b), dmisokolovite (c), shchurovskyite (d), edtollite (e), melanarsite (f), coparsite (g), popovite (h), vasilseverginite (i), and arsmirandite (j). Blue circles are Cu, olive green circles are Fe^{3+} (j) or (Fe^{3+},Cu) (e, f) and lilac circles are Al sites; g − drawn after Starova et al. (1998), others − our data.

these fumarole systems: sublimate Cu^{2+} mineralization typically disappears at depths of 1.5–2 m, whereas Ca and Mg arsenates persist even in deeper zones of the fumaroles (Table 3), which reflects the higher volatility of Cu compared to As at temperatures >450–500 °C under high oxygen fugacity conditions.

6. Conclusions

Fumarolic arsenates represent a special type of As mineralization which strongly differs from all other known types of occurrence of As minerals in both composition and crystal chemistry. It is characterized by its significant mineral diversity and originality: 54 arsenates, including 40 valid species and 14 phases with definite chemical compositions were reliably identified in fumarole deposits; 53 of them occur in active fumaroles at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption of 1975–1976 (Tolbachik volcano, Kamchatka, Russia), where their gross mass is evaluated as several tons. Among 30 structure types already determined for fumarolic arsenates, 10 are novels and 9 were previously identified for synthetic compounds only. Forty-six of the 54 arsenates are endemic to fumarolic formations, all but one to Tolbachik.

All fumarolic arsenates are hydrogen-free. This is their major common chemical feature. Metal cations known as species-defining in these minerals are diverse: Cu^{2+}, Mg, Al, Fe^{3+}, Ti^{4+}, Zn, Ca, Na, and K. The alkali-richest (>17 wt% $Na_2O + K_2O$) and Ti-richest (12–28 wt% TiO_2) natural arsenates are among the Tolbachik endemics. Nineteen minerals with Cu, Al, Fe or/and Ti contain additional O^{2-} anions not bonded to As^{5+}, which is very rare for arsenates from other geological formations. The crystal chemical individuality of fumarolic Cu arsenates is mainly due to the strong influence of the Jahn-Teller effect on Cu^{2+}-centred polyhedra in the absence of OH or H_2O groups: Cu^{2+} cations have either four-, five- and sixfold coordination and geometries of the $Cu(O,Cl)_{4-6}$ polyhedra are highly variable. The As^{5+} ion and all metal cations are involved in numerous isomorphous substitutions; some fumarolic arsenates form continuous solid-solution series unknown in other natural systems, *e.g.*, potassic feldspar − filatovite and berzeliite − schäferite.

The uniqueness of the arsenate mineralization formed in the oxidizing-type fumaroles is mainly caused by the unique combination of high temperature, low (in fact, atmospheric) pressure, very high oxygen fugacity and gas transport of most constituents. All Tolbachik arsenates crystallize at temperatures higher than 450 °C. They are deposited directly from fumarolic gases as sublimates, or form as a result of gas–rock interaction. Volcanic gases play the role of a carrier for As, Cu, Zn, Na, K, S, Cl, F, O and probably Fe, whereas the basalt hosting fumarole cameras can be the source of Al, Ti, Mg and Ca.

We believe that the fumarolic type of arsenate mineralization, being unique in different aspects, has a heuristic potential for chemistry, crystal chemistry and geochemistry of arsenic and would be useful for materials science as a possible source of natural prototypes of novel crystalline materials with technologically important properties.

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