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Oxidizing-Type Fumaroles of the Tolbachik Volcano, a Mineralogical and Geochemical Unique

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Abstract—We overview recent data on the mineralogy of oxidizing-type fumaroles of the Tolbachik Volcano (Kamchatka, Russia), with the main focus on the chemical specifics of the minerals. The active fumarole fields of Tolbachik are the most prominent mineral-forming exhalative system of this type in the world. About 350 mineral species, including 123 minerals first discovered here, are reliably identified in the Tolbachik fumaroles. The species diversity and the specifics of this mineralization are due to the unique combination of the physicochemical conditions and mechanisms of its formation: high temperatures, atmospheric pressure, superhigh oxygen fugacity, gas transport of most of chemical elements, and direct deposition of many high-temperature minerals from volcanic gases with a specific geochemical composition, including strong enrichment in alkaline metals and chalcophile ("ore") elements. Sublimate silicates and minerals of As, Cu, Zn, Mn, Ti, Sn, Sb, Se, Au, Ag, Cs, Tl, and F are briefly described in terms of mineral geochemistry.

Keywords: fumarole, volcanic sublimate, exhalative mineral formation, highly oxidizing conditions, new mineral, Tolbachik Volcano, Kamchatka

INTRODUCTION

This research work is a brief review of recently obtained data on the mineralogy of oxidizing-type fumaroles generated by the Tolbachik Volcano in Kamchatka. It focuses on the specific features that make this object unique not only in mineralogical but also in geochemical aspects. The main attention is given to the chemical features of minerals as the key to the development of mineralogical geochemistry[1] of postvolcanic oxidizing-type exhalation systems.

The great interest in the minerals of fumaroles is mostly due to the fact that they have no natural analogues in the physicochemical conditions of formation and therefore are unusual and can be abundant and diverse. Fumarole mineral genesis is characterized by a unique combination of several factors; the main ones are: (1) high temperature (up to 900–1000 ºC) and low atmospheric pressure; (2) gas transport of most of chemical components, including chalcophile and siderophile metals; and (3) specific geochemistry of volcanic exhalations. Most fumarole minerals crystallize through desublimation[2], i.e., direct deposition from hot gas, or by the reaction between gas and the material of the walls of fumarole chambers (gas metasomatism, according to Naboko and Glavatskikh (1983)). Mineral-forming fumaroles are divided into two types according to oxygen fugacity in hot gas: (1) reducing, with only gas of volcanic origin, and (2) oxidizing, in which primary volcanic gas mixed with hot atmospheric air before mineral formation. Thus, a high f_{O_2} value is an additional physicochemical factor of mineral genesis in oxidizing-type fumaroles (Menyailov et al., 1980; Africano et al., 2002). Mineral assemblages (first of all, high-temperature ones) formed in reducing- and oxidizing-type fumaroles differ considerably in compounds of chemical elements that easily change the oxidation state. Sulfur, abundant in almost all volcanic sublimates, can be considered the main

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[1] The term "mineralogical geochemistry", as we understand it, is applicable to the geochemistry of separate elements in the systems where they are present mainly in a concentrated state, as mineral-forming components or significant impurities in minerals. The mineralogical geochemistry approach, which takes into account the fundamental difference in the crystallochemical behavior of an element in scattered and concentrated states, is effective primarily for trace elements whose contents in concentrating minerals are two–three or more orders of magnitude higher than their clarkes.

[2] Such minerals are usually called volcanic sublimates.

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indicator of the oxidative potential in this system: It forms high-temperature sulfides in reducing-type fumaroles and sulfates in oxidizing-type ones.

Fumarole activity is specific to all active volcanoes in the world. In most cases, fumarole gas emission on the Earth's surface results in exhalative mineralization, but the minerals are usually not diverse and have a small set of major chemical components composing minerals (mainly S, O, Cl, F, Na, K, NH_4, Mg, Ca, Al, and Fe). This is evident from reviews of the mineral composition of fumaroles of many volcanoes (Naboko, 1959; Stoiber and Rose, 1974; Serafimova, 1979; Balić-Žunić et al., 2016). There are exceptions, however: A few volcanoes are characterized by exhalative mineralization with more diverse mineral and chemical compositions. At present, there are only five active volcanoes with unique mineralization of fumaroles, which are located in southern Italy and in the Russian Far East. The fumaroles of each of them contain more than fifty minerals. Three of these volcanoes are characterized by mineral-rich reducing-type fumaroles: These are Vulcano (La Fossa crater) in the Lipari Archipelago (Italy) (Campostrini et al., 2011), Kudryavyi on Iturup Island (Kuril Archipelago) (Chaplygin, 2009), and Mutnovskii in the south of Kamchatka (Zelenski and Bortnikova, 2005). The other two have oxidizing-type fumaroles: These are the famous Vesuvius Volcano, which can be called the cradle of fumarole mineralogy as a scientific field (Zambonini, 1935; Russo and Punzo, 2004), and the Tolbachik Volcano[3] in the Klyuchevskaya volcano group in Kamchatka.

The diversity of fumarole minerals is directly related to the chemical composition of fumarole gas. Note that the main geochemical feature of the exhalative systems of the above five volcanoes is a significant enrichment in a wide range of "ore" (first of all, chalcophile) elements: S, Pb, As, Bi, Cu, Zn, Se, Cd, Tl, etc., which are responsible for the fumarole mineral diversity. Fumaroles of most of other volcanoes are poorer in "ore" elements or lack them.

FUMAROLE FIELDS OF THE TOLBACHIK VOLCANO AS A MINERALOGICAL OBJECT: AN OVERVIEW

Tolbachik has become famous as a mineralogical object owing to its active fumarole fields formed after the Great Fissure Tolbachik Eruption of 1975–1976 (GFTE). This geologic event resulted in the scoria cones of the Northern and Southern Breakthroughs, i.e., monogenetic volcanoes, where fumarole fields with widely diverse exhalative minerals formed (Fedotov and Markhinin, 1983; Fedotov, 1984). Before this eruption, Tolbachik was not considered a volcano with specific sublimate mineralogy. For example, Serafimova (1979), who summarized data on fumaroles in Kamchatka in the pre-GFTE period, paid almost no attention to Tolbachik.

The GFTE is not only one of the largest but also the best studied basalt eruption over the history of world volcanology. Details about this event and the Tolbachik Volcano can be found in the monograph edited by Fedotov (1984), who organized and led a research into the GFTE.

Study of the mineralogy of the GFTE fumarole fields began immediately after their formation. The oxidizing-type fumaroles were investigated mainly by a joint team of researchers from the Institute of Volcanology and Seismology, Petropavlovsk-Kamchatsky, and Leningrad State University (L.P. Vergasova, E.K. Serafimova, S.K. Filatov, and their colleagues), who found ten new minerals here by 1990 (Table 1). In the early 1990s, the first brief summary reports on the found minerals were published based on the results of study of the GFTE fumaroles (Serafimova, 1992; Vergasova and Filatov, 1993). In particular, the presented list of exhalative minerals from oxidizing-type fumaroles and of products of their supergene transformation (Vergasova and Filatov, 1993) includes sixty known species and more than ten new ones. By the time we began studying the exhalative minerals of the Tolbachik fumaroles (2009), thirty-one new mineral species had already been discovered here (Table 1), and the total number of minerals (including hypergene ones) that were reliably identified in these fumaroles exceeded a hundred. Moreover, the greatest mineral diversity was observed in the fumaroles of the Second scoria cone of the Northern Breakthrough (NB) of the GFTE (Vergasova and Filatov, 2016).

Most data on the mineralogy of the Tolbachik fumaroles have been obtained in the recent decade. Since 2009, ninety-two (!) new minerals have been discovered here, which were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA CNMNC); seventy-four of these minerals have been found by our research team or with the participation of its members. No other locality in the world has ever shown such dynamics of the increase in the number of new minerals just over a decade. By September 2019, the number of new minerals here reached 123 (the full list of the new Tolbachik minerals is published for the first time; see Table 1[4]). In 2018, Tolbachik was second in the world in this regard, being behind only the Khibiny alkaline massif on the Kola Peninsula (127 new minerals), and left behind the Lovozero alkaline massif (112 new minerals) in the same region. Note that the three record holders (Khibiny, Tolbachik, and Lovozero) are in Russia, while the other localities famous for numerous first discovered minerals, namely, Långban in Sweden, Tsumeb in Namibia, and the Franklin ore district in New Jersey (USA), are far behind: The number of their new minerals ranges from 70 to 75.

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[3] In this work, the name Tolbachik Volcano (or Tolbachik) implies the part of the Tolbachik volcanic massif that includes the active Ploskii (Flat) Tolbachik Volcano and the Tolbachik Dale, an active volcanism zone bordering this volcano in the south (Fedotov, 1984).

[4] Unfortunately, the limited space of the paper does not permit us to describe the new Tolbachik minerals in detail and give all references.

Table 1. New minerals discovered in the fumaroles of the Tolbachik Volcano

Mineral	Formula	IMA No.	Reference
1	2	3	4
Tolbachite	$CuCl_2$	1982-067	Vergasova et al. (1983)
Piypite	$K_4NaCu_4O_2(SO_4)_4Cl$	1982-097	Vergasova et al. (1984)
Nabokoite	$KCu_6CuTe^{4+}O_4(SO_4)_5Cl$	1985-013a	Popova et al. (1987)
Fedotovite	$K_2Cu_3O(SO_4)_3$	1986-013	Vergasova et al. (1988)
Atlasovite	$KCu_6Fe^{3+}BiO_4(SO_4)_5Cl$	1986-029	Popova et al. (1987)
Ponomarevite	$K_4Cu_4OCl_{10}$	1986-040	Vergasova et al. (1988)
Kamchatkite	$KCu_3O(SO_4)_2Cl$	1987-018	Vergasova et al. (1988)
Klyuchevskite	$K_3Cu_3Fe^{3+}O_2(SO_4)_4$	1987-027	Vergasova et al. (1989)
Sofiite	$Zn_2(SeO_3)Cl_2$	1987-028	Vergasova et al. (1989)
Leningradite	$PbCu_3(VO_4)_2Cl_2$	1988-014	Vergasova et al. (1990)
Alarsite	$AlAsO_4$	1993-003	Semenova et al. (1994)
Alumoklyuchevskite	$K_3Cu_3AlO_2(SO_4)_4$	1993-004	Gorskaya et al. (1995)
Vlodavetsite	$Ca_2Al(SO_4)_2F_2Cl \cdot 4H_2O$	1993-023	Vergasova et al. (1995)
Averievite	$Cu_6O_2(VO_4)_2Cl_2 \cdot n(K,Cs,Rb)Cl$	1995-027	Vergasova et al. (1998)
Lesukite	$Al_2Cl(OH)_5 \cdot 2H_2O$	1996-004	Vergasova et al. (1997)
Chlorartinite	$Mg_2(CO_3)(OH)Cl \cdot 2H_2O$	1996-005	Vergasova et al. (1998)
Georgbokiite	$Cu_5O_2(Se^{4+}O_3)_2Cl_2$	1996-015	Vergasova et al. (1999)
Ilinskite	$(Na,K)Cu_5O_2(Se^{4+}O_3)_2Cl_3$	1996-027	Vergasova et al. (1997)
Chloromenite	$Cu_9O_2(Se^{4+}O_3)_4Cl_6$	1996-048	Vergasova et al. (1999)
Coparsite	$Cu_4O_2[(As,V)O_4]Cl$	1996-064a	Vergasova et al. (1999)
Vergasovaite	$Cu_3O(MoO_4)(SO_4)$	1998-009	Bykova et al. (1998)
Urusovite	$CuAlAsO_5$	1998-067	Vergasova et al. (2000)
Bradaczekite	$NaCu_4(AsO_4)_3$	2000-002	Filatov et al. (2001)
Burnsite	$KCdCu_7O_2(Se^{4+}O_3)_2Cl_9$	2000-050	Krivovichev et al. (2002)
Prewittite	$KPb_{1.5}ZnCu_6O_2(Se^{4+}O_3)_2Cl$	2002-041	Shuvalov et al. (2013)
Meniaylovite	$Ca_4AlSi(SO_4)F_{13} \cdot 12H_2O$	2002-050	Vergasova et al. (2004)
Filatovite	$K(Al,Zn)_2(As,Si)_2O_8$	2002-052	Vergasova et al. (2004)
Allochalcoselite	$PbCu^{+}Cu^{2+}{}_5O_2(Se^{4+}O_3)_2Cl_5$	2004-025	Vergasova et al. (2005)
Pauflerite	$(V^{4+}O)SO_4$	2005-004	Krivovichev et al. (2007)
Avdoninite$^{\Upsilon}$	$K_2Cu_5Cl_8(OH)_4 \cdot 2H_2O$	2005-046a	Chukanov et al. (2006)
Parageorgbokiite	$Cu_5O_2(Se^{4+}O_3)_2Cl_2$	2006-001	Vergasova et al. (2006)
Lammerite-β	$Cu_3(AsO_4)_2$	2009-002	Starova et al. (2011)
Pseudolyonsite*	$Cu_3(VO_4)_2$	2009-062	Zelenski et al. (2011)
Cupromolybdite*	$Cu_3Mo_2O_9$	2011-005	Zelenski et al. (2012)
Steklite*$^{\Upsilon}$	$KAl(SO_4)_2$	2011-041	Murashko et al. (2012)
Krasheninnikovite*	$KNa_2CaMg(SO_4)_3F$	2011-044	Pekov et al. (2012)
Calciolangbeinite*	$K_2Ca_2(SO_4)_3$	2011-067	Pekov et al. (2012)
Starovaite*	$KCu_5O(VO_4)_3$	2011-085	Pekov et al. (2013)
Yaroshevskite*	$Cu_9O_2(VO_4)_4Cl_2$	2012-003	Pekov et al. (2013)
Markhininite	$TlBi(SO_4)_2$	2012-040	Siidra et al. (2014)
Grigorievite*	$Cu_3Fe^{3+}{}_2Al_2(VO_4)_6$	2012-047	Pekov et al. (2014)
Hatertite	$Na_2Ca(CuFe^{3+})(AsO_4)_3$	2012-048	Krivovichev et al. (2013)
Nicksobolevite	$Cu_7O_2(Se^{4+}O_3)_2Cl_6$	2012-097	Vergasova et al. (2014)
Sanguite*	$KCuCl_3$	2013-002	Pekov et al. (2015)
Chrysothallite*	$K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$	2013-008	Pekov et al. (2015)
Ericlaxmanite*	$Cu_4O(AsO_4)_2$	2013-022	Pekov et al. (2014)
Kozyrevskite*	$Cu_4O(AsO_4)_2$	2013-023	Pekov et al. (2014)
Yurmarinite*	$Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$	2013-033	Pekov et al. (2014)
Wulffite*	$K_3NaCu_4O_2(SO_4)_4$	2013-035	Pekov et al. (2014)

(*continued on next page*)

Table 1 (*continued*)

Mineral	Formula	IMA No.	Reference
1	2	3	4
Parawulffite*	$K_5Na_3Cu_8O_4(SO_4)_8$	2013-036	Pekov et al. (2014)
Kaliochalcite*	$KCu_2(SO_4)_2[(OH)(H_2O)]$	2013-037	Pekov et al. (2014)
Karpovite	$Tl_2VO(SO_4)_2(H_2O)$	2013-040	Siidra et al. (2014)
Evdokimovite	$Tl_4(VO)_3(SO_4)_5(H_2O)_5$	2013-041	Siidra et al. (2014)
Popovite*	$Cu_5O_2(AsO_4)_2$	2013-060	Pekov et al. (2015)
Shchurovskyite*	$K_2CaCu_6O_2(AsO_4)_4$	2013-078	Pekov et al. (2015)
Dmisokolovite*	$K_3Cu_5AlO_2(AsO_4)_4$	2013-079	Pekov et al. (2015)
Kononovite*	$NaMg(SO_4)F$	2013-116	Pekov et al. (2015)
Ivsite	$Na_3H(SO_4)_2$	2013-138	Filatov et al. (2016)
Flinteite*	K_2ZnCl_4	2014-009	Pekov et al. (2015)
Mellizinkalite*	$K_3Zn_2Cl_7$	2014-010	Pekov et al. (2015)
Romanorlovite*	$K_{11}Cu_9Cl_{25}(OH)_4 \cdot 2H_2O$	2014-011	Pekov et al. (2016)
Zincomenite*	$ZnSeO_3$	2014-014	Pekov et al. (2016)
Pharmazincite*	$KZnAsO_4$	2014-015	Pekov et al. (2017)
Chubarovite*	$KZn_2(BO_3)Cl_2$	2014-018	Pekov et al. (2015)
Katiarsite*	$KTiO(AsO_4)$	2014-025	Pekov et al. (2016)
Melanarsite*	$K_3Cu_7Fe^{3+}O_4(AsO_4)_4$	2014-048	Pekov et al. (2016)
Shuvalovite*	$K_2(Ca_2Na)(SO_4)_3F$	2014-057	Pekov et al. (2016)
Cryobostryxite*	$KZnCl_3 \cdot 2H_2O$	2014-058	Pekov et al. (2015)
Arsmirandite*	$Na_{18}Cu_{12}Fe^{3+}O_8(AsO_4)_8Cl_5$	2014-081	Pekov et al. (ICN-23_2015)
Arsenowagnerite*	$Mg_2(AsO_4)F$	2014-100	Pekov et al. (2018)
Dravertite*	$CuMg(SO_4)_2$	2014-104	Pekov et al. (2017)
Cryptochalcite*	$K_2Cu_5O(SO_4)_5$	2014-106	Pekov et al. (2018)
Bubnovaite	$K_2Na_8Ca(SO_4)_6$	2014-108	Gorelova et al. (2016)
Puninite	$Na_2Cu_3O(SO_4)_3$	2015-012	Siidra et al. (2017)
Saranchinaite*	$Na_2Cu(SO_4)_2$	2015-019	Siidra et al. (2018)
Itelmenite*	$Na_4Mg_3Cu_3(SO_4)_8$	2015-047	Nazarchuk et al. (2018)
Hermannjahnite*	$CuZn(SO_4)_2$	2015-050	Siidra et al. (2017)
Kainotropite*	$Cu_4Fe^{3+}O_2(V_2O_7)(VO_4)$	2015-053	Pekov et al. (ICN-27_2015)
Feodosiyite*	$Cu_{11}Mg_2Cl_{18}(OH)_8 \cdot 16H_2O$	2015-063	Pekov et al. (2018)
Vasilseverginite*	$Cu_9O_4(AsO_4)_2(SO_4)_2$	2015-083	Pekov et al. (ICN-28_2015)
Metathénardite*	Na_2SO_4	2015-102	Pekov et al. (ICN-30_2016)
Dioskouriite*	$CaCu_4Cl_6(OH)_4 \cdot 4H_2O$	2015-106	Pekov et al. (ICN-30_2016)
Philoxenite*	$(K,Na,Pb)_4(Na,Ca)_2(Mg,Cu)_3(Fe^{3+}_{0.5}Al_{0.5})(SO_4)_8$	2015-108	Pekov et al. (ICN-30_2016)
Borisenkoite*	$Cu_3[(V,As)O_4]_2$	2015-113	Pekov et al. (ICN-30_2016)
Eleomelanite*	$(K_2Pb)Cu_4O_2(SO_4)_4$	2015-118	Pekov et al. (ICN-30_2016)
Wrightite	$K_2Al_2O(AsO_4)_2$	2015-120	Shablinskii et al. (2018)
Cesiodymite*	$CsKCu_5O(SO_4)_5$	2016-002	Pekov et al. (2018)
Edtollite*	$K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$	2016-010	Pekov et al. (2019)
Arsenatrotitanite*	$NaTiO(AsO_4)$	2016-015	Pekov et al. (2019)
Ozerovaite	$KNa_2Al_3(AsO_4)_4$	2016-019	Shablinskii et al. (2018)
Marinaite*	$Cu_2Fe^{3+}O_2(BO_3)$	2016-021	Chaplygin et al. (ICN-32_2016)
Deltalumite*	$\delta\text{-}Al_2O_3$	2016-027	Pekov et al. (ICN-32_2016)
Anatolyite*	$Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$	2016-040	Pekov et al. (2019)
Zincobradaczekite*	$NaZn_2Cu_2(AsO_4)_3$	2016-041	Pekov et al. (ICN-33_2016)
Belousovite	$KZn(SO_4)Cl$	2016-047	Siidra et al. (2018)
Badalovite*	$Na_2Mg_2Fe^{3+}(AsO_4)_3$	2016-053	Pekov et al. (ICN-33_2016)
Calciojohillerite*	$NaCaMg_3(AsO_4)_3$	2016-068	Pekov et al. (ICN-34_2016)
Magnesiohatertite*	$Na_2Ca(MgFe^{3+})(AsO_4)_3$	2016-078	Pekov et al. (ICN-34_2016)

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Table 1 (*continued*)

Mineral	Formula	IMA No.	Reference
1	2	3	4
Pansnerite*	$K_3Na_3Fe^{3+}_6(AsO_4)_8$	2016-103	Pekov et al. (ICN-36_2017)
Axelite*	$Na_{14}Cu_7(AsO_4)_8F_2Cl_2$	2017-015a	Pekov et al. (ICN-38_2017)
Alumoedtollite*	$K_2NaCu_5AlO_2(AsO_4)_4$	2017-020	Pekov et al. (2019)
Kalithallite*	$K_3Tl^{3+}Cl_6 \cdot 2H_2O$	2017-044	Pekov et al. (ICN-39_2017)
Lehmannite*	$Na_{18}Cu_{12}TiO_8(AsO_4)_8FCl_5$	2017-057a	Pekov et al. (ICN-46_2018)
Novograblenovite	$(NH_4)MgCl_3 \cdot 6H_2O$	2017-060	Okrugin et al. (2018)
Belomarinaite	$KNaSO_4$	2017-069a	Filatov et al. (ICN-43_2018)
Khrenovite*	$Na_3Fe^{3+}_2(AsO_4)_3$	2017-105	Pekov et al. (ICN-42_2018)
Rhabdoborite-(V)*	$Mg_{12}(V^{5+},Mo^{6+},W^{6+})_{1\frac{1}{3}}O_6\{[BO_3]_{6-x}[(P,As)O_4]_xF_{2-x}\}$ ($x < 1$)	2017-108	Pekov et al. (ICN-42_2018)
Rhabdoborite-(W)*	$Mg_{12}(W^{6+},V^{5+})_{1\frac{1}{3}}O_6\{[BO_3]_{6-x}[(P,As)O_4]_xF_{2-x}\}$ ($x < 1$)	2017-109	Pekov et al. (ICN-42_2018)
Paraberzeliite*	$NaCa_2Mg_2(AsO_{4)}3$	2018-001	Pekov et al. (ICN-43_2018)
Zubkovaite*	$Ca_3Cu_3(AsO_4)_4$	2018-008	Pekov et al. (ICN-43_2018)
Achyrophanite*	$(K,Na)_3(Fe^{3+},Ti,Al,Mg)_5O_2(AsO_4)_5$	2018-011	Pekov et al. (ICN-43_2018)
Dokuchaevite	$Cu_8O_2(VO_4)_3Cl_3$	2018-012	Siidra et al. (ICN-43_2018)
Koryakite	$KNaMg_2Al_2(SO_4)_6$	2018-013	Nazarchuk et al. (ICN-43_2018)
Aleutite*	$Cu_5O_2(AsO_4)(VO_4)\bullet 0.5CuCl_2$	2018-014	Siidra et al. (ICN-43_2018)
Elasmochloite*	$Na_3Cu_6BiO_4(SO_4)_5$	2018-015	Pekov et al. (ICN-43_2018)
Majzlanite	$K_2Na(ZnNa)Ca(SO_4)_4$	2018-016	Siidra et al. (ICN-43_2018)
Thermaerogenite*	$CuAl_2O_4$	2018-021	Pekov et al. (2018)
Pliniusite*	$Ca_5(VO_4)_3F$	2018-031	Pekov et al. (ICN-44_2018)
Udinaite*	$NaMg_4(VO_4)_3$	2018-066	Pekov et al. (ICN-45_2018)
Arsenudinaite*	$NaMg_4(AsO_4)_3$	2018-067	Pekov et al. (ICN-45_2018)
Natroaphthitalite*	$KNa_3(SO_4)_2$	2018-091	Shchipalkina et al. (ICN-46_2018)
Glikinite	$Zn_3O(SO_4)_2$	2018-119	Nazarchuk et al. (ICN-47_2019)
Nishanbaevite*	$KAl_2O(AsO_4)(SO_4)$	2019-012	Pekov et al. (ICN-50_2019)

Note. IMA No. – the minerals (123 mineral species as of September 2019) are listed in chronological order of their discovery, with their numbers registered by the Commission on New Minerals, Nomenclature and Classification (before 2006, Commission on New Minerals and Mineral Names) of the International Mineralogical Association (IMA CNMNC).

The Reference column lists the senior authors and years of publication of the papers with the first description of the minerals. For recently discovered minerals that have not yet been described in literature, we present the senior authors of reports on these mineral species, with the corresponding IMA CNMNC Newsletter No. (ICN = IMA Commission Newsletter) in the journal Mineralogical Magazine and on the IMA CNMNC official website (http://nrmima.nrm.se).

* Minerals were discovered by the authors of this paper or with their participation.

ϒ Avdoninite and steklite were first described under these names in anthropogene systems. Both minerals were approved by the IMA CNMNC based on results of study of the natural samples from the Tolbachik fumaroles.

Moreover, Khibiny and Lovozero are huge intrusive complexes, 1327 and 650 km^2 in area, respectively, and new minerals were found there over a large territory. Large mines have been operating both in Khibiny and in Lovozero for many years, continuously supplying material to researchers, and the systematic mineralogical work on these alkaline intrusions has been ongoing for more than 130 years. As for Tolbachik, all new minerals have been discovered here for 40 years, and more than 110 new minerals were found on an area of ~1 km^2, where the fumarole fields of the Second and First scoria cones of the NB GFTE are located (these fumaroles are still active: The temperature of emitted gases reaches 500 ºC, as shown by results of our field measurements in 2012–2018). Moreover, these new minerals were discovered mainly at a site smaller than 50×50 m within the main (apical) fumarole field of the Second scoria cone (Fig. 1), where the Yadovitaya (Poisonous) and Arsenatnaya (Arsenate-bearing) fumaroles are located. These are the most typical representatives of highly mineralized active exhalative postvolcanic oxidizing-type fumaroles. The above site is the record holder by the concentration of first discovered minerals per unit area of the Earth's surface. The Arsenatnaya fumarole is especially rich in minerals. We were the first to uncover it during the field work in 2012 and named it so because of the rich arsenate mineralization (Pekov et al., 2014b). To date, we have described 49 new minerals in Arsenatnaya (15×4 m in area). We have reliably determined 180 mineral species and found almost 50 mineral phases of fumarolic and supergene origin that must be studied in detail. The highly mineralized fumaroles of the

Fig. 1. The Second scoria cone of the Northern Breakthrough of the GFTE. South view, with the Tolbachik Volcano in the background. White asterisk marks the main fumarole field. Photo by D.A. Varlamov, 2013.

Second scoria cone of the NB GFTE are described by Vergasova and Filatov (2016) and Pekov et al. (2018a), and the fumaroles of the First scoria cone, by Vergasova et al. (2007).

According to our data, the total number of mineral species reliably determined in the Tolbachik fumaroles is about 350, not including the insufficiently studied phases. About fifty of these minerals are surely weathering products formed near the surface at low temperatures (below 30–50 ºC), mainly under impact of atmospheric agents on exhalative minerals. The other three hundred minerals are obviously related to the processes in fumaroles. Note that along with the exhalation phases (sublimates) and gas metasomatism products, we recognized the third genetic group of fumarole minerals, which can be called "hot hypergenesis" products. They result from the interaction of slightly cooled volcanic gas, atmospheric agents, and earlier formed minerals in the apical parts of fumaroles at 50–150 ºC. As shown by Vergasova et al. (2007), thermophile microorganisms can also participate in the mineral genesis processes. Mineral assemblages produced in the zone of "hot hypergenesis" (which we consider to be the low-temperature stage of mineral formation in oxidizing-type fumaroles) have analogues in the oxidation zones of sulfide deposits located in the hottest and arid world regions, e.g., the Atacama Desert (Chile).

Only six of the minerals first discovered in the Tolbachik fumaroles (avdoninite, deltalumite, ivsite, lesukite, pliniusite, and chlorartinite) were earlier found in other geologic formations, whereas the rest 117 are known only in volcanic sublimates or natural (natural coal fires) and anthropogene objects with similar physical conditions. In addition, there are 22 minerals that were first discovered in fumaroles of other volcanoes (bannermanite, blossite, heklaite, hieratite, dolerophanite, carobbiite, knasibfite, leonardsenite, lyonsite, litidionite, mcbirneyite, melanothallite, mitcherlichite, nickenichite, fingerite, chalcocyanite, chlorothionite, ziesite, shäferite, shcherbinaite, and jacobssonite) or in sublimates of burning mine dumps (cuprospinel) and are not known elsewhere. Such a large number (almost 140) of endemic minerals emphasizes the mineralogical and genetic uniqueness of oxidizing-type fumaroles.

The age of most of the Tolbachik fumarole minerals can be determined precisely: They are not older than the GFTE, which occurred in 1975–1976. Was the GFTE a unique event in terms of mineralogy and geochemistry? Could the fumaroles formed by other eruptions of the Tolbachik Volcano also have "ore" elements and be rich in diverse minerals? Today these questions can be answered unambiguously: Other eruptions of Tolbachik also resulted in such "mineral-productive" fumaroles. This is confirmed both by the findings of oxides, chlorides, sulfates, arsenates, vanadates, phosphates, and molybdates of chalcophile metals in the extinct paleofumarole fields of the scoria cones of the ancient Tolbachik eruptions (Naboko and Glavatskikh, 1992; Serafimova et al., 1994) and by direct observations, including ours, of the fissure eruption on the southern slope of Ploskii Tolbachik in 2012–2013, when copper oxosalts and chlorides crystallized in large amounts in the formed active fumaroles (Karpov et al., 2013; Pekov et al., 2014a; Siidra et al., 2018a).

Minerals of the Tolbachik oxidizing-type fumarole systems show a significant chemical diversity. Many of them concentrate elements of different geochemical groups at once, e.g., mineral-forming lithophile and chalcophile elements composing oxosalts, chlorides, and oxides. Below, we present a list of species-defining (i.e., predominant in particular crystal structure positions) components reliably identified in the high-temperature (>200–250 ºC) fumarole minerals (they are listed in order of increasing atomic number of the element; the components present in five or more minerals are bold-typed): **B**, **O**, **F**, **Na**, **Mg**, **Al**, **Si**, P, **S^{6+}**, **Cl**, **K**, **Ca**, **Ti^{4+}**, V^{4+}, **V^{5+}**, Mn^{2+}, Mn^{3+}, Mn^{4+}, **Fe^{3+}**, Cu^{+}, **Cu^{2+}**, **Zn**, **As^{5+}**, **Se^{4+}**, Se^{6+}, Y, Mo^{6+}, Ag^{+}, Cd, Sn^{4+}, Sb^{5+}, Te^{4+}, Te^{6+}, Cs, Ba, Ce^{4+}, W^{6+}, Au^{0}, Tl^{+}, **Pb^{2+}**, and Bi^{3+}. Minerals with species-defining components **H**, C, N (NH_4^+), **O**, **F**, **Na**, **Mg**, **Al**, **S^{6+}**, **Cl**, **K**, **Ca**, V^{4+}, Mn^{4+}, **Fe^{3+}**, **Cu^{2+}**, Zn, Se^{4+}, Tl^{3+}, and U^{6+} were found in the "hot hypergenesis" zone (note that own minerals of H, C, N, Tl^{3+}, and U have not yet been found in high-temperature parageneses of the Tolbachik oxidizing-type fumaroles). Minerals with species-defining Ti^{4+}, Mn, Se^{6+}, REE, Ag^{+}, Sn^{4+}, Sb, Te^{6+}, Ba, W^{6+}, Tl^{3+}, and U had not been revealed in the Tolbachik fumaroles before our research work.

Oxidizing-type fumarole minerals are also characterized by great structural diversity. For example, the new Tolbachik minerals approved by the IMA CNMNC (123 mineral species, Table 1) are of 103 structural types.

THE TOLBACHIK FUMAROLE MINERALS: CHEMICAL COMPOSITION

It is impossible to describe in detail the diversity of the Tolbachik fumarole minerals in one paper, even focusing only on their chemical composition. We will dwell only on some specific mineralogical and geochemical features of oxidizing-type fumaroles, mainly the Tolbachik ones (with emphasis on the recently obtained data), that clearly demonstrate their uniqueness.

Silicates are commonly present in assemblage with typical fumarole minerals, such as chlorides, sulfates, sulfides, etc., but are seldom given attention. Usually they are referred to[5] as products of earlier mineral crystallization from melt (lava) or gases released from it. Therefore, silicate mineralization is almost completely ignored in reviews of fumarole mineralogy (Stoiber and Rose, 1974; Serafimova, 1979, 1992; Vergasova and Filatov, 1993, 2016; Balić-Žunić et al., 2016). Indeed, silicate mineralization in these systems usually precedes "saline" and/or sulfide mineralization, which helps one to separate them. Our study of the Tolbachik fumaroles has shown that this separation can sometimes be artificial; therefore, ignoring all or most of silicates associated with "classical" exhalative minerals is erroneous.

The earlier published lists of the Tolbachik fumarole minerals included silicates, such as diopside, orthoclase, and albite (Serafimova, 1992; Vergasova and Filatov, 1993, 2016), but no characteristics of these minerals were given. Our systematic research works in the fumarole fields of the Second scoria cone of the NB GFTE and of the ancient scoria cone of Mount 1004 showed a wide spread and a great diversity of silicates. The absence of signs of melt crystallization and, most importantly, the unambiguously interpreted relative age of silicates, based on their relations with typical fumarole minerals of other chemical classes (growth of silicates over crystals and crusts of anhydrite, langbeinite, sylvite, hematite, arsenates, vanadates, borates, etc. and their joint growth with these minerals), permit us to consider silicates (by analogy with sulfates, chlorides, or oxides) an undoubted component of fumarole mineralization. Study of the chemical composition of silicates from these parageneses showed that most of them are significantly (or, sometimes, strongly) different from their analogues in other geologic formations. This confirms their belonging to a specific genetic type, namely, sublimates forming in oxidizing-type fumaroles with "ore" elements.

By now, we have identified 24 silicate species (not including the insufficiently studied mineral phases) in the exhalative parageneses of the Tolbachik fumarole systems. They represent all main structural and topological (in terms of crystal structure) types of natural compounds of this chemical class, most of which belong to the groups of major rock-forming or accessory minerals. These are *nesosilicates* belonging to the olivine (forsterite, Fig. 2), garnet (andradite), and titanite (titanite) groups, *cyclosilicate* of the cordierite group (indialite), *single-chain inosilicates* of the pyroxene group (enstatite, clinoenstatite, diopside, aegirine, and esseneite), *double-chain inosilicates* of the amphibole group (potassic-magnesio-fluoro-arfvedsonite and potassic–fluoro-richterite), *phyllosilicates* of the mica group (fluorophlogopite and yangzumingite), and *tectosilicates* of the feldspar (K-, Na-, and Ba-feldspars and intermediate and basic plagioclases) and feldspathoid (nepheline, kalsilite, leucite, sodalite, and haüyne) groups. All these silicates lack hydrogen-containing groups (amphiboles and mica are represented by fluorine-dominant species) and ferrous iron (the calculated empirical formulae and structure identification results show that all iron in the silicates is present as Fe^{3+}). This is in agreement with the mineral formation environment: high temperature (all silicates are present in parageneses with formation temperatures no lower than 500 ºC) and low pressure, preventing localization of hydrogen in crystalline phases, and a high fO_2 value. It is remarkable that the Tolbachik fumaroles contain silicate parageneses specific to agpaitic environments: feldspathoids + alkali feldspars + aegirine (+ Ca-free alkali amphibole).

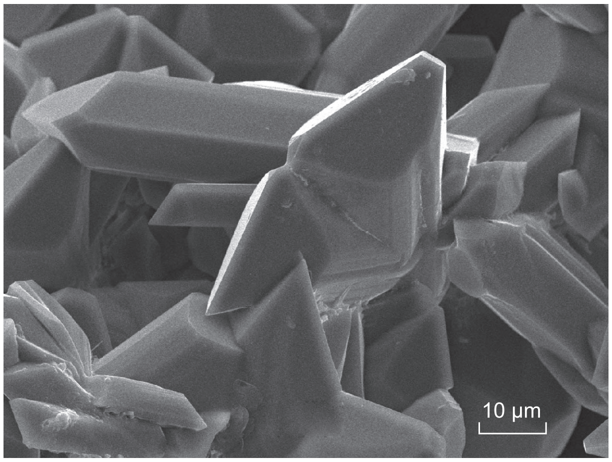

Fig. 2. Crystals of exhalative As-containing forsterite and its twin on (110). Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. Secondary-electron SEM image.

The most specific individual feature of the Tolbachik fumarole silicates is that most of them have significant impurities of ore components: As, Cu, Zn, Sn, Mo, and W. Arsenic is the most typical chalcophile trace element substituting silicon in tetrahedral positions mainly by the scheme $M^{3+} + As^{5+} \rightarrow 2Si^{4+}$ (M^{3+} = Al, Fe). There is also subordinate substitution with the participation of low-valence cations: $Na^{+} + As^{5+} \rightarrow Ca^{2+} + Si^{4+}$ (in clinopyroxenes), $(Zn,Cu)^{2+} + As^{5+} \rightarrow Al^{3+} + Si^{4+}$ (in feldspars), and $[vac]^{0} + As^{5+} \rightarrow A^{+} + Si^{4+}$ (A = K or Na; vac is vacancy) (in feldspars and feldspathoids). The content of As_2O_5 reaches 16.0 wt.% in forsterite, 2.6 wt.% in diopside, 5.1 wt.% in mica, and 10.4 wt.% in feldspathoids; K-feldspar is the As-richest fumarole silicate (Shchipalkina et al., 2019, 2020b,c). Earlier, filatovite $K[(Al,Zn)_2(As,Si)_2O_8]$ (arsenate mineral of the feldspar group) and K-feldspar containing up to 18 wt.% As_2O_5 were discovered in the Tolbachik fumaroles (Vergasova et al., 2004b). We revealed a continuous series of solid solutions intermediate between abundant sanidine and much rarer fila-

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[5] Apparently, from intimate impulse (without any arguments).

tovite, with the content of As_2O_5 varying from 0.0 to 44.6 wt.% (Shchipalkina et al., 2020a). Haüyne from the Arsenatnaya fumarole has significant impurities of Mo (up to 4.2 wt.% MoO_3) and W (up to 1.7 wt.% WO_3). By analogy with synthetic sodalites, we assume that these elements, in contrast to As^{5+} substituting Si in the tetrahedral positions of the AlSiO framework, are part of extra-framework anions and substitute S^{6+}: $(MoO_4)^{2-}/(WO_4)^{2-} \rightarrow (SO_4)^{2-}$ (Shchipalkina et al., 2018). The Tolbachik fumaroles contain the P-richest natural olivine (forsterite with 12.9 wt.% P_2O_5 (Shchipalkina et al., 2019)) and feldspar (sanidine with 5.0 wt.% P_2O_5 (Shchipalkina et al., 2020a)).

Most silicates are volcanic exhalative minerals most resistant to weathering and thus can be preserved as relics of ancient fumarole mineralization on active and extinct volcanoes. We think that the above specific chemical features of such silicates may be of use in paleomineralogical reconstructions.

Arsenic minerals in the Tolbachik oxidizing-type fumaroles are greatly diverse, as evidenced by the research results of the last seven years. This element has been found here only in the form of As^{5+}, and its minerals are represented only by arsenates. In addition, much arsenic is present as an impurity in fumarole silicates, mainly in As^{5+}-enriched K-feldspar (see the text above). At present, there are 55 reliably identified arsenate phases in the Tolbachik fumaroles; eight of them call for additional study. Among 47 arsenates identified here, eight were first discovered in other objects (lammerite, stranskiite, johillerite, nickenichite, svabite, berzeliite, tilasite, and durangite), and the other 39 were found in fumaroles of the Second scoria cone of the NB GFTE, with 29 of them being discovered by us (Table 1). The Tolbachik arsenates are of 32 structural types, including 21 that were not known earlier. We summarized the available data on arsenate minerals in volcanic sublimates, with a focus on the Tolbachik fumaroles (Pekov et al., 2018a), and reviewed the crystal chemistry of greatly diverse fumarole copper arsenates (Pekov et al., 2018d). The Arsenatnaya fumarole is the world's largest occurrence of arsenate minerals of this origin. Coparsite, zincobradaczekite, and aleutite are the only species of the 55 Tolbachik arsenates that have not yet been found in Arsenatnaya. We estimate the total mass of arsenate minerals here at several tons. The most widespread are arsenates of the alluaudite group (johillerite, calciojohillerite, nickenichite, bradaczekite, and badalovite), svabite, berzeliite, tilasite, lammerite, and urusovite. Thus, the Tolbachik oxidizing-type fumaroles "presented" a new, earlier unknown genetic type of rich arsenic mineralization.

All arsenates found in the Tolbachik fumaroles formed at high temperatures (>450–500 ºC; most likely, within 500–750 ºC). None of them contains hydrogen, which is atypical of most of other minerals of this chemical class (more than 370 species): Natural arsenates that formed at low temperatures in the oxidation zone of ore deposits are the most diverse, and almost all of these minerals have components with H-containing groups (H_2O^0, OH^-, H^+, and/or H_3O^+). At present, there are 71 natural anhydrous arsenates, including 47 found in the Tolbachik fumaroles, with 39 of them being endemics of this object.

Cations Cu^{2+}, Mg, Al, Fe^{3+}, Ti^{4+}, Zn, Ca, Na, and K in the Tolbachik fumarole arsenates are species-defining. In addition, twenty arsenates contain O^{2-} (it is present in three minerals with Ti^{4+} and in a few minerals with Cu^{2+}, Al, and Fe^{3+}), F^-, and/or Cl^- not bonded with As^{5+}. The Tolbachik arsenates have two more specific chemical features: They are the richest in alkali metals (>17 wt.% $Na_2O + K_2O$) and titanium (up to 28 wt.% TiO_2) among the minerals of this chemical class (Pekov et al., 2018a).

All Tolbachik arsenates, including those rich in alkali cations, are insoluble in water and stable in air. The same is specific to the Tolbachik silicates, phosphates, and vanadates containing a significant impurity of As^{5+}. This is apparently why arsenic takes a minor part in the low-temperature mineral genesis processes in this system. No newly formed phases with As contents detectable by an electron microprobe were found in the "hot hypergenesis" zone or among the weathering products here.

Copper minerals. Copper holds a special place in the mineralogy and geochemistry of the Tolbachik fumarole systems. It is the main chalcophile metal here, both by its total mass and by the species, chemical, and structural diversity of its minerals. The fumarole fields of the Second scoria cone of the NB GTFE were even regarded as a copper ore occurrence of practical interest, because they are rich in exhalative tenorite CuO and Cu^{2+} sulfates (Naboko and Glavatskikh, 1983). The abundance of tenorite, copper sulfates, and copper chlorides is also typical of many fumaroles generated by other eruptions of the Ploskii Tolbachik Volcano (Naboko and Glavatskikh, 1992b; Serafimova et al., 1994; Karpov et al., 2013). At the same time, copper and, correspondingly, its minerals are unevenly distributed among different fumarole fields within the Tolbachik Dale. For example, the Second and First scoria cones of the NB GTFE adjoin each other and are located on the same active fissure (Fedotov, 1984), but the mineralogy and geochemistry of their fumaroles are strongly different, which is best evident from copper mineralization. The main fumarole field of the Second scoria cone is undoubtedly the major object of the Tolbachik Dale by its mineral richness and mineral diversity, whereas the First scoria cone fumaroles, located no more than a kilometer from it, lack copper minerals: We found not a single grain (!) or any copper mineral during seven fieldwork seasons. Chalcophile-metal minerals of the First scoria cone are mainly oxosalts and chlorides of Pb, Zn, and Tl.

Analysis of literature data showed the absence of copper minerals from reducing-type fumaroles but their presence in oxidizing-type fumaroles of many world volcanoes. Usually, these are tenorite and/or one or two sulfates (chalcocyanite, euchlorine, and simple hydrous sulfates). Ten copper oxosalts, including seven new vanadates, were found on the Izalco Volcano in El Salvador, several copper minerals are known in the paleofumaroles of the Eifel volcanic region in Germany, and a dozen copper minerals (not including supergene ones) were discovered in the Vesuvius fumaroles. The exhalative copper minerals of the Tolbachik Volcano are the most diverse: There are 90 species, including 15 found in the "hot hypergenesis" zone (the products of "ordinary" low-temperature weathering of sublimates are not included). Sixty-eight of these ninety minerals were first discovered in the Tolbachik fumaroles; moreover, 41 of them were discovered by us or with our participation (Table 1). A total of 96 exhalative copper (Cu^{2+}) minerals were found in oxidizing-type fumaroles of the world volcanoes, with 81 of them being endemic to a fumarole formation. These 96 minerals represent 80 (!) structural types, which highlights the specific crystal chemistry of exhalative copper minerals. It is remarkable that the total mass of Cu concentrated in the world's volcanic exhalations is incomparably smaller than its mass in most of other geologic formations. However, endemic copper minerals in fumaroles amount to ~12% of all known copper minerals (~700). A crystallochemical review of fumarole copper minerals was made by us earlier (Pekov et al., 2018d).

Thus, the Tolbachik fumarole fields, especially those of the Second scoria cone of the NB GTFE, are the world's largest and richest occurrence of exhalative copper minerals, with the greatest diversity of the latter. These minerals belong to the following chemical classes: sulfates (27 species), arsenates (22), vanadates (14), chlorides (12), selenites (8), oxides (3), molybdates (2), borates (1), and silicates (1). They crystallize over a wide range of temperatures, from 750 to 50 ºC. We subdivide them into two chemical genetic groups according to their crystallization temperatures. The first group includes 75 minerals forming at temperatures above 200 ºC (mainly within 400–700 ºC), and the second group includes 15 minerals produced in the "hot hypergenesis" zone at temperatures below 200 ºC (mostly within 70–150 ºC). Minerals of these groups are strongly different in chemical and crystallochemical features. The second group (relatively low-temperature minerals) comprises seven sulfates and eight chlorides, with 13 of these 15 minerals having OH groups and/or H_2O molecules. In crystallochemical features, first of all, the high tendency of Cu^{2+} to enter the regular coordination octahedron formed by $O^{2-}/Cl^{-}/OH^{-}/H_2O^0$, they are similar to supergene copper minerals. Most of the high-temperature minerals (the first group) are endemic to fumaroles. These are minerals of all the above-listed chemical classes, and all of them are anhydrous. Forty-five oxosalts of this group have an additional O^{2-} anion, i.e., oxygen atom not bonded with S^{6+}, Mo^{6+}, As^{5+}, V^{5+}, Se^{4+}, or B^{3+}. The Cu^{2+} cations in their structures are coordinated by only two ligands, O^{2-} or Cl^{-}, and are localized mostly in four-fold and five-fold polyhedra, while octahedra, if any, are strongly distorted (Pekov et al., 2018d).

We also discovered Cu-containing oxides of the spinel group in high-temperature (600–800 ºC) parageneses of the active fumaroles of the Second scoria cone of the NB GTFE and the paleofumaroles of Mount 1004. The content of Cu in earlier found natural oxide spinels did not exceed few tenths of a percent. The Tolbachik Cu-containing spinels are nine mineral species (their maximum contents of CuO (wt.%) are given in parentheses): new mineral thermaerogenite $CuAl_2O_4$ (26.9), cuprospinel $CuFe_2O_4$ (28.6), gahnite (21.4), magnesioferrite (14.7), spinel (10.9), magnesiochromite (9.0), franklinite (7.9), chromite (5.9), and zincochromite (4.8). Al- and Fe^{3+}-dominant minerals crystallized directly from gas as sublimates, and Cu-containing chrome-spinels formed through the partial replacement of magnesiochromite in ultrabasite microxenoliths altered by fumarole gas (Pekov et al., 2018b). Copper-containing magnesioferrite (up to 17.3 wt.% CuO) was also found in the fumarole sublimates of the 2012–2013 Tolbachik fissure eruption (Sharygin et al., 2018).

Zinc minerals. Ten years ago, the diversity of zinc mineralization in the Tolbachik exhalations was not the matter of discussion: Only sofiite $Zn_2(SeO_3)Cl_2$ was found in large amounts in several GTFE fumaroles (Vergasova et al., 1989). The situation has changed significantly in recent years, when 20 zinc minerals were found in the Tolbachik fumaroles, including 12 new species (Table 1). Unlike copper or arsenic minerals, zinc minerals do not form large clusters here, but some of them (sofiite, flinteite, zincite, and gahnite) are abundant in some fumaroles. In addition, Zn is scattered as a significant (few wt.%) isomorphic impurity in the Tolbachik fumarole minerals, primarily substituting Cu^{2+} in various copper oxosalts (Pekov et al., 2018a, d) and, to a lesser extent, substituting Al in As-containing K-feldspars (Vergasova et al., 2004b; Shchipalkina et al., 2018) and Mg in spinel (Pekov et al., 2018b). Moreover, earlier unknown zinc minerals containing K, Zn, and Cl together were first found in the Tolbachik fumarole exhalations: three chlorides — mellizinkalite $K_3Zn_2Cl_7$, flinteite K_2ZnCl_4, and cryobostryxite $KZnCl_3·2H_2O$ (Pekov et al., 2014d), chloroborate — chubarovite $KZn_2(BO_3)Cl_2$ (Pekov et al., 2015e), and chlorosulfate — belousovite $KZn(SO_4)Cl$ (Siidra et al., 2018b); all of these elements are also species-defining in prewittite $KPb_{1.5}ZnCu_6O_2(SeO_3)_2Cl$ (Shuvalov et al., 2013). Note that sublimates of compositions K_2ZnCl_4 (an analogue of flinteite?), $KRbZnCl_4$, and $K_{1.5}Cs_{0.5}ZnCl_4$ were earlier obtained during the experiments in quartz tubes placed into the active fumaroles of the Satsuma-Iwojima Volcano in Japan (Africano et al., 2002). Tolbachik is the only volcano where zinc minerals were found in oxidizing-type fumaroles, whereas reducing-type fumaroles of various volcanoes often contain sphalerite and wurtzite (Chaplygin, 2009; Campostrini et al., 2011).

Manganese minerals. In contrast to Vesuvius, where fumarole manganese mineralization has been known for a century and a half (Zambonini, 1935), it has been only recently discovered on Tolbachik during our research on the First (with the main occurrence of manganese minerals) and the Second scoria cones of the NB GTFE. Exhalation origin (crystallization temperatures no lower than 200–280 °C) was established for saltonseaite $K_3NaMnCl_6$, bixbyite Mn_2O_3, hollandite $Ba(Mn^{4+}, Mn^{3+}/Mn^{2+})_8O_{16}$, and cryptomelane (with a composition close to $K_2(Mn^{4+}, Mn^{3+}/Mn^{2+})_8O_{16}$) found in different parageneses. Transformation of saltonseaite in the "hot hypergenesis" zone yields vernadite $(Mn^{4+}, Mn^{3+}/Mn^{2+})(O,OH)_2 \cdot nH_2O$ (Turchkova et al., 2017). Manganese in these fumarole minerals is present in three different valence states (Mn^{2+}, Mn^{3+}, and Mn^{4+}); therefore, manganese mineralization can serve as an indicator of f_{O_2} here.

Titanium, tin, and antimony minerals. Titanium is not highly mobile in volcanic gases (Churakov et al., 2000); nevertheless, its minerals are common in high-temperature parageneses of a number of the Tolbachik oxidizing-type fumaroles. Arsenates are the most interesting form of titanium occurrence here. We discovered three oxoarsenates with mineral-forming Ti^{4+} in the Arsenatnaya fumarole: katiarsite $KTiO(AsO_4)$, arsenatrotitanite $NaTiO(AsO_4)$, and lehmannite $Na_{18}Cu_{12}TiO_8(AsO_4)_8FCl_5$; up to 8.0 wt.% TiO_2 (as an impurity) was found in achyrophanite $(K,Na)_3(Fe^{3+},Ti,Al,Mg)_5O_2(AsO_4)_5$, and up to 12 wt.% TiO_2 was revealed in durangite (Pekov et al., 2018a). Other oxosalts of the Tolbachik fumaroles, including silicates (except for titanite), are not rich in Ti. As in many other geologic formations, oxides are the main form of titanium occurrence here, with pseudobrookite being the most abundant mineral of this chemical class. Much TiO_2 (up to 6.1 wt.%) is present as an impurity in hematite, the main oxide mineral of the Tolbachik fumaroles. Hematite also serves as the main concentrator of tin in the Tolbachik fumaroles. For example, up to 4.5 wt.% SnO_2 was revealed in this mineral from the Mount 1004 paleofumarole (Serafimova and Anan'ev, 1992). We found up to 7.1 wt.% SnO_2 in homogeneous hematite from the Arsenatnaya fumarole; other hematite samples contain emulsion and lattice cassiterite exsolution structures. This suggests that hematite that crystallized from gas at high temperatures initially contained even more tin. The discovery of rich exhalative cassiterite mineralization in the Arsenatnaya fumarole (Sandalov et al., 2017) became a surprise: The crusts of fine orange and red crystals of this mineral locally reach tens of cm^2 in area. Rutile is another oxide that co-concentrates titanium, tin, and antimony in the Tolbachik fumaroles. The highest content of SnO_2 recorded here is 11.8 wt.%. In the Arsenatnaya and Yadovitaya fumaroles, rutile forms a continuous isomorphic series with isostructural tripuhyite $FeSbO_4$ (the main substitution scheme is as follows: $Sb^{5+} + Fe^{3+} \rightarrow 2Ti^{4+}$); the maximum content of Sb_2O_5 (52.5 wt.%) was found in Ti-containing tripuhyite from the Yadovitaya fumarole (Sandalov et al., 2018). It is remarkable that high content of Sb has been revealed here only in the fumarole minerals of this isomorphic series.

Selenium minerals. Selenium mineralization of the Tolbachik fumaroles is unique. Ten selenites were found here (not including supergene molybdomenite), and all of them are Tolbachik endemics. Copper minerals of this chemical class are the most diverse: There are eight species, and all of them are oxochloroselenites (besides the main anion $(SeO_3)^{2-}$, they contain O^{2-} and Cl^- not bonded to Se^{4+} (Table 1)). These minerals are overviewed by Vergasova et al. (2014), and the motifs formed by copper atoms in their structures are described by Pekov et al. (2018d). All Tolbachik copper selenites are very rare minerals, whereas zinc chloroselenite sofiite $Zn_2(SeO_3)Cl_2$ (Vergasova et al., 1989) is common here. In particular, we observed the intense formation of sofiite in the Northern fumarole field of the First scoria cone of the NB GTFE, which took place during the 2012–2013 Ploskii Tolbachik eruption. It was probably related to the intense gas release from the fissure beneath the First scoria cone. The open-work sofiite crusts that formed in this period reached few tens of cm^2 in area, and sofiite crystals in them were up to 3 cm (!) across. Zincomenite $ZnSeO_3$, the only simple selenite known in volcanic exhalations, formed there at the same time (Pekov et al., 2016). Selenate mineralization is minor on Tolbachik. It is represented by olsacherite $Pb_2(SeO_4)(SO_4)$ discovered by us in a small amount in the Northern fumarole field of the First scoria cone of the NB GTFE. We did not find literature data on the presence of oxygen-containing selenium minerals in fumaroles of other world volcanoes.

Gold and silver minerals. Gold is the only representative of native metals reliably identified in the Tolbachik oxidizing-type fumaroles[6]. It was found in many fumaroles generated by the GTFE and the 2012–2013 Tolbachik eruption. This gold occurs as perfect crystals usually no larger than few tenths of a millimeter and seldom reaching 2–3 mm. It was described in more detail by Vergasova et al. (2000). Exhalative gold is of high chemical purity: The earlier published and our results of electron microprobe analyses showed no detectable impurities. The only silver mineral here is chlorargyrite AgCl found by us in the Arsenatnaya fumarole. It occurs as flattened octahedral microcrystals epitactically overgrowing gold, with their {111} faces over the {111} face of flattened or elongated gold cuboctahedra (Fig. 3).

Cesium minerals. Cesium is the only lithophile rare metal whose minerals and their geochemistry have a significant relationship with oxidizing-type fumaroles. For example, avogadrite $(K,Cs)BF_4$ was described as a new mineral from the Vesuvius fumarole sublimates as early as 1926 (Zambonini, 1935). On Tolbachik, the first mineral in which a significant amount of cesium was detected was averievite $Cu_5O_2(VO_4)_2 \times nACl$ (A = K, Rb, or Cs) containing up to 4.1 wt.% Cs_2O (Vergasova et al., 1998). Our data showed that cesium is a typical impurity component that substitutes potassium in many high-temperature (>250–500 ºC) sulfates (e.g., wulffite contains up to 1.1 wt.% Cs_2O; parawulffite, up

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[6] There are many publications concerned with findings of metals (iron, nickel, aluminum, cadmium, tungsten, titanium, tin, lead, silver, etc.), silicon, carbon of different modifications, intermetallic compounds, carbides, and silicides in the products of both the recent and ancient Tolbachik eruptions. Without going into the discussion about their origin that has been lasting over two decades, we note that they, in contrast to native gold, are definitely not related to the oxidizing-type fumaroles considered in this paper.

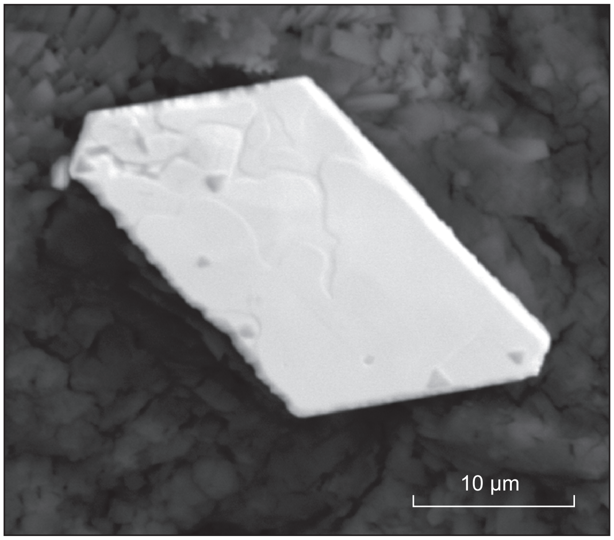

Fig. 3. Distorted (flattened along [111]) crystal of exhalative native gold (bright white), whose {111} face is epitactically overgrown by [111]-flattened octahedral chlorargyrite crystals (light gray triangles). Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. Back-scattered-electron SEM image.

to 1.4 wt.%; and cryptochalcite, up to 3.0 wt.% (Pekov et al., 2014a, 2018c)) and chlorides (flinteite contains up to 2.2 wt.% Cs (Pekov et al., 2015c)). Minerals with species-defining cesium also crystallize in these fumaroles, e.g., cesiodymite with an ideal formula $CsKCu_5O(SO_4)_5$ (with up to 14.3 wt.% Cs_2O), which is isostructural to cryptochalcite $K_2Cu_5O(SO_4)_5$. The cryptochalcite–cesiodymite structure contains four large-cation AO_n polyhedra of different sizes and configurations (A = K or Cs; n = 8–10), with cesium localized in two of them (Pekov et al., 2018c). Recently, we have found a phase Cs_2ZnCl_4 with 44 wt.% Cs in the Arsenatnaya fumarole (Fig. 4). At present, it is the Cs-richest natural compound. Thus, the results of study of the Tolbachik fumarole mineralization show that cesium can concentrate in natural exhalative systems, forming its minerals of different compositions, which crystallize directly from volcanic gas at atmospheric pressure and temperatures above 500 ºC.

Thallium minerals. Thallium is a chalcophile element, but in oxidizing media it is in a monovalent state (most typical of this metal in nature) and is similar in geochemical behavior to potassium and thus can scatter in potassium minerals. In reducing-type fumaroles, halide minerals with species-defining Tl^+ occur; the best-known locality of this mineralization is the La Fossa crater on Vulcano Island (Campostrini et al., 2011). Recently, a new mineral nataliyamalikite TlI has been discovered as microinclusions in As-containing native sulfur in the fumaroles of the Avachinsky Volcano (Kamchatka) (Okrugin et al., 2017). The minerals of high-temperature parageneses of the Tolbachik oxidizing-type fumaroles contain only monovalent thallium. Thallium-enriched flinteite $(K,Tl)_2ZnCl_4$ (27.7 wt.% Tl (Pekov et al., 2015c)) and saltonseaite $(K,Tl)_3NaMnCl_6$ (3.5 wt.% Tl (Turchkova et al., 2017)) and a new mineral markhininite $TlBi(SO_4)_2$ (Siidra et al., 2014a) were discovered on the First scoria cone of the NB GTFE. Thallium mineralization in the Tolbachik fumaroles changes significantly with decreasing temperature. Thallium-enriched hydrous minerals crystallize instead of anhydrous ones. The valence state of Tl in them clearly reflects the oxidation potential of the system at these stages. At moderate oxygen fugacity (f_{O_2}), thallium remains monovalent: For example, 4.1 wt.% Tl substituting K was found in cryobostryxite $KZnCl_3 \cdot 2H_2O$, a product of flinteite alteration in the "hot hypergenesis" zone (Pekov et al., 2015d); Tl^+ also forms low-temperature minerals karpovite $Tl_2VO(SO_4)_2(H_2O)$ and evdokimovite $Tl_4(VO)_3(SO_4)_5(H_2O)_5$ (Siidra et al., 2014b), in which vanadium is present as V^{4+}. When the f_{O_2} value in the "hot hypergenesis" zone is high, minerals of trivalent thallium appear, which are among the best indicators of highly oxidizing conditions. These are chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$ (Pekov et al., 2015b) in the fumaroles of the Second scoria cone and kalithallite $K_3Tl^{3+}Cl_6 \cdot 2H_2O$ recently discovered by us in the fumaroles of the First scoria cone. It is remarkable that both of these chlorides (two of the three known natural minerals of Tl^{3+}; the third is avicennite Tl_2O_3 described earlier) contain not only thallium but also potassium, but the K^+ cations are strictly ordered because of the trivalent state of Tl. The thallium mineralization of the Tolbachik fumaroles, like the cesium one, has no analogues in nature.

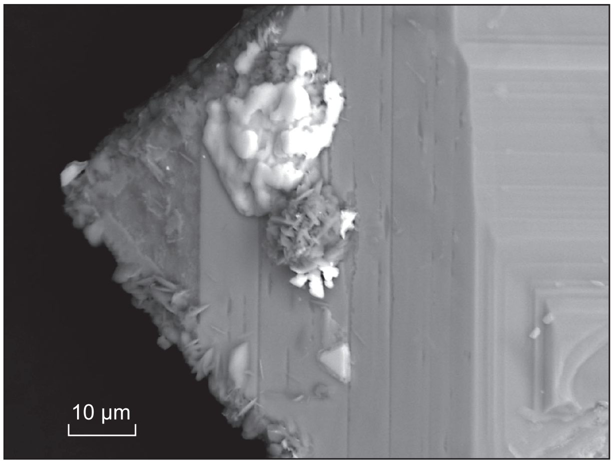

Fig. 4. Cs_2ZnCl_4 aggregate (white) overgrowing, together with cryptochalcite (gray plates and their intergrowths), the face of nabokoite crystal. Arsenatnaya fumarole, Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. Back-scattered-electron SEM image.

Fluorine minerals. Fluorine is a component of forty minerals of the Tolbachik oxidizing-type fumaroles. Eleven of these minerals were first discovered here; these are meniaylovite (aluminofluoride) and ten oxosalts with an additional F^- anion: krasheninnikovite, kononovite, and shuvalovite (fluorosulfates), vlodavetsite (chlorofluorosulfate), arsenowagnerite (fluorarsenate), axelite and lehmannite (fluorochloroarsenates), pliniusite (fluorovanadate), and rhabdoborite-(V) and rhabdoborite-(W) (fluoroborates) (Table 1). Fluorides, including aluminofluorides[7], form large clusters in the Tolbachik fumarole fields; for example, abundant crusts with ralstonite as one of prevailing minerals were found on the scoria cones of the NB GTFE, especially on the First scoria cone (Naboko and Glavatskikh, 1992a; Vergasova et al., 2007). We found widespread sellaite–fluorite crusts and two aluminofluorides new for Tolbachik, jakobssonite and leonardsenite, in the Northern fumarole field of the First scoria cone. Such a diversity of fluorine minerals and their large clusters are primarily due to the strong fluorine (HF) enrichment of the Tolbachik fumarole gases (Menyailov et al., 1980; Fedotov, 1984).

It is remarkable that the mineralogy and genesis of fluorides of the GTFE fumaroles have been well studied (Naboko and Glavatskikh, 1992a; Vergasova et al., 2004a, 2007), whereas literature data on oxosalts with additional F^- are absent, except for vlodavetsite $Ca_2Al(SO_4)_2F_2Cl \cdot 4H_2O$ (Vergasova et al., 1995). The diversity and abundance of F-containing oxosalts were "discovered" only during our work at the deep levels of fumaroles, mainly in Arsenatnaya. Besides the above nine new oxosalts with additional F^-, we found ten more of such minerals here: svabite, tilasite, and durangite (fluoroarsenates), fluorapatite and wagnerite (fluorophosphates), micas (fluorophlogopite and yangzhumingite) and amphiboles (potassic-magnesio-fluoro-arfvedsonite and potassic-fluoro-richterite) (fluorosilicates), fluoborite (fluoroborate), and uklonskovite (fluorosulfate). All these minerals, except for the latter (formed in the "hot hypergenesis" zone), are anhydrous minerals formed at temperatures above 300–400 ºC. Sporadically, fluorophlogopite and svabite are among prevailing minerals in fumarolic incrustations; krasheninnikovite, tilasite, and fluoborite are also common. Analysis of the found parageneses and the measured temperatures in the fumarole chambers led us to the conclusion that fluorine minerals in the Tolbachik oxidizing-type fumaroles are of two types: (1) fluorides (including aluminofluorides) and (2) oxosalts (silicates, sulfates, arsenates, phosphates, vanadates, and borates) with additional $F^–$. These types are close in the number of mineral species (about twenty) and in the scale of occurrence. Temperature turned out to be the factor determining the type of mineralization: Fluorides are low-temperature minerals, and oxosalts with additional anion $F^–$ form at higher temperatures. The temperature boundary between these mineral types is 300–350 ºC. There are only two exceptions: hydrous fluorosulfates vlodavetsite and uklonskovite, which form in small amounts in zones with temperatures below 200 ºC. This empirical conclusion about the relationship between the fluorine mineral species and the temperature in oxidizing-type fumaroles was first reported by Pekov et al. (2015a) and was confirmed by following observations.

CONCLUSIONS

The Tolbachik oxidizing-type fumaroles are unique in the total number of minerals, the number of first discovered mineral species and the dynamics of its increase, and the chemical and structural diversity and specifics of the minerals. They are much superior in these characteristics to all other objects of this genetic type, including the fumarole fields of Vesuvius, where 40 new mineral species have been discovered, with the total number of minerals approaching 150.

The data obtained for the entire period after the Great Tolbachik Fissure Eruption (1975–1976), especially for the last decade, unambiguously show that it is Tolbachik that should be considered a major reference object when characterizing mineral-forming systems in oxidizing-type fumaroles.

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REFERENCES

Africano, F., Van Rompaey, G., Bernard, A., Le Guern, F., 2002. Deposition of trace elements from high temperature gases of Satsuma-Iwojima volcano. Earth Planets Space 54, 275–286.

Balić-Žunić, T., Garavelli, A., Jakobsson, S.P., Jonasson, K., Katerinopoulos, A., Kyriakopoulos, K., Acquafredda, P., 2016. Fumarolic minerals: an overview of active European volcanoes, in: Nemeth, K. (Ed.), Updates in Volcanology — From Volcano Modelling to Volcano Geology. InTech Open Access Publishers, London, pp. 267–322.

Campostrini, I., Demartin, F., Gramaccioli, C.M., Russo, M., 2011. Vulcano: Tre Secoli di Mineralogia. Associazione Micro-mineralogica Italiana, Cremona.

Chaplygin, I.V., 2009. Ore Mineralization of the High-Temperature Fumaroles of the Kudryavyi Volcano. PhD Thesis [in Russian]. IGEM RAN, Moscow.

Churakov, S.V., Tkachenko, S.I., Korzhinskii, M.A., Bocharnikov, R.E., Shmulovich, K.I., 2000. Evolution of composition of high-temperature fumarolic gases from Kudryavy Volcano, Iturup, Kuril Islands: the thermodynamic modeling. Gechem. Int. 38 (5), 436–451.

Fedotov, S.A. (Ed.), 1984. The Great Tolbachik Fissure Eruption, Kamchatka, 1975–1976 [in Russian]. Nauka, Moscow.

Fedotov, S.A., Markhinin, Y.K. (Eds.), 1983. The Great Tolbachik Fissure Eruption. Cambridge University Press, New York.

Karpov, G.A., Krivovichev, S.V., Vergasova, L.P., Chernyat'eva, A.P., Anikin, L.P., Moskaleva, S.V., Filatov, S.K., 2013. Oxysulfates of

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[7] Another name for these compounds, whose structures are usually formed by $(AlF_6)^{3-}$ octahedra, are fluoroaluminates. However, the term "aluminofluoride" (as well as the terms "silicofluoride" and "borofluoride" for compounds with octahedral $(SiF_6)^{2-}$ and tetrahedral $(BF_4)^–$ anionic groups, respectively) is preferable to avoid confusion, because aluminates (silicates, borates, etc.) are usually understood as oxygen compounds. For example, the term "fluorosilicate" is widely used for norbergite $Mg_2(SiO_4)F_2$ or topaz $Al_2(SiO_4)(F,OH)_2$; "fluorocarbonate", for bastnaesite $REE(CO_3)F$; and "fluorophosphate", for fluorapatite $Ca_5(PO_4)_3F$. With this traditional approach, the term "fluoroaluminate" as applied to oxygen-free minerals, e.g., cryolite Na_3AlF_6, is somewhat contradictory.

copper, sodium, and potassium in the lava flows of the 2012–2013 Tolbachik Fissure Eruption. J. Volcanol. Seismol. 7 (6), 362–370.

Menyailov, I.A., Nikitina, L.P., Shapar', V.N., 1980. Geochemical Specifics of the Exhalations of the Great 2013 Tolbachik Fissure Eruption [in Russian]. Nauka, Moscow.

Naboko, S.I., 1959. Volcanic Exhalations and Their Reaction Products. Proceedings of the Laboratory of Volcanology, Issue 16 [in Russian]. Izd. AN SSSR, Moscow.

Naboko, S.I., Glavatskikh, S.F., 1983. Posteruptive Metasomatism and Ore Formation [in Russian]. Nauka, Moscow.

Naboko, S.I., Glavatskikh, S.F., 1992a. Posteruptive fluoride mineral formation, in: Posteruptive Mineral Formation on Active Volcanoes in Kamchatka [in Russian]. DVO AN SSSR, Vladivostok, Part I, pp. 65–91.

Naboko, S.I., Glavatskikh, S.F., 1992b. Relics of posteruptive activity on the old cones of the Tolbachik Dale, Kamchatka. Vulkanologiya i Seismologiya, Nos. 5–6, 66–86.

Okrugin, V., Favero, M., Liu, A., Etschmann, B., Plutachina, E., Mills, S., Tomkins, A.G., Lukasheva, M., Kozlov, V., Moskaleva, S., Chubarov, M., Brugger, J., 2017. Smoking gun for thallium geochemistry in volcanic arcs: Nataliyamalikite, TlI, a new thallium mineral from an active fumarole at Avacha Volcano, Kamchatka Peninsula, Russia. Am. Mineral. 102, 1736–1746.

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Belakovskiy, D.I., Chukanov, N.V., Lykova, I.S., Saveliev, D.P., Sidorov, E.G., Pushcharovsky, D.Yu., 2014a. Wulffite, $K_3NaCu_4O_2(SO_4)_4$, and parawulffite, $K_5Na_3Cu_8O_4(SO_4)_8$, two new minerals from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. Can. Mineral. 52, 699–716.

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Belakovskiy, D.I., Lykova, I.S., Vigasina, M.F., Sidorov, E.G., Pushcharovsky, D.Yu., 2014b. New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. I. Yurmarinite, $Na_7(Fe^{3+}, Mg, Cu)_4 (AsO_4)_6$. Mineral. Mag. 78, 905–917.

Pekov, I.V., Krzhizhanovskaya, M.G., Yapaskurt, V.O., Belakovskiy, D.I., Chukanov, N.V., Lykova, I.S., Sidorov, E.G., 2015a. Kononovite, $NaMg(SO_4)F$, a new mineral from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. Eur. J. Mineral. 27, 575–580.

Pekov, I.V., Zubkova, N.V., Belakovskiy, D.I., Yapaskurt, V.O., Vigasina, M.F., Lykova, I.S., Sidorov, E.G., Pushcharovsky, D.Yu., 2015b. Chrysothallite $K_6Cu_6Tl^{3+}Cl_{17}(OH)_4{\cdot}H_2O$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia. Mineral. Mag. 79, 365–376.

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Britvin, S.N., Vigasina, M.F., Sidorov, E.G., Pushcharovsky, D.Yu., 2015c. New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. II. Flinteite, K_2ZnCl_4. Eur. J. Mineral. 27, 581–588.

Pekov, I.V., Zubkova, N.V., Britvin, S.N., Yapaskurt, V.O., Chukanov, N.V., Lykova, I.S., Sidorov, E.G., Pushcharovsky, D.Yu., 2015d. New zinc and potassium chlorides from fumaroles of the Tolbachik volcano, Kamchatka, Russia: mineral data and crystal chemistry. III. Cryobostryxite, $KZnCl_3{\cdot}2H_2O$. Eur. J. Mineral. 27, 805–812.

Pekov, I.V., Zubkova, N.V., Pautov, L.A., Yapaskurt, V.O., Chukanov, N.V., Lykova, I.S., Britvin, S.N., Sidorov, E.G., Pushcharovsky, D.Yu., 2015e. Chubarovite, $KZn_2(BO_3)Cl_2$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia. Can. Mineral. 53, 273–284.

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Britvin, S.N., Chukanov, N.V., Lykova, I.S., Sidorov, E.G., Pushcharovsky, D.Yu., 2016. Zincomenite, $ZnSeO_3$, a new mineral from the Tolbachik volcano, Kamchatka, Russia. Eur. J. Mineral. 28, 997–1004.

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., Sidorov, E.G., 2018a. Fumarolic arsenates — a special type of arsenic mineralization. Eur. J. Mineral. 30, 305–322.

Pekov, I.V., Sandalov, F.D., Koshlyakova, N.N., Vigasina, M.F., Polekhovsky, Y.S., Britvin, S.N., Sidorov, E.G., Turchkova, A.G., 2018b. Copper in natural oxide spinels: the new mineral thermaerogenite $CuAl_2O_4$, cuprospinel and Cu-enriched varieties of other spinel-group members from fumaroles of the Tolbachik volcano, Kamchatka, Russia. Minerals 8 (11), paper 498.

Pekov, I.V., Zubkova, N.V., Agakhanov, A.A., Pushcharovsky, D.Yu., Yapaskurt, V.O., Belakovskiy, D.I., Vigasina, M.F., Sidorov, E.G., Britvin, S.N., 2018c. Cryptochalcite $K_2Cu_5O(SO_4)_5$ and cesiodymite $CsKCu_5O(SO_4)_5$ — two new isotypic minerals and the K–Cs isomorphism in this solid-solution series. Eur. J. Mineral. 30, 593–607.

Pekov, I.V., Zubkova, N.V., Pushcharovsky, D.Yu., 2018d. Copper minerals from volcanic exhalations — a unique family of natural compounds: crystal chemical review. Acta Crystallogr. B74, 502–518.

Russo, M., Punzo, I., 2004. I minerali del Somma-Vesuvio. AMI, Cremona, Italy.

Sandalov, F.D., Koshlyakova, N.N., Pekov, I.V., Khanin, D.A., Sidorov, E.G., 2017. Cassiterite in the fumarole exhalations of the Tolbachik Volcano (Kamchatka), in: Congress of the Russian Mineralogical Society Dedicated to Its 200th Anniversary. International Scientific Conference, St. Petersburg, 10–13 October 2017 [in Russian]. VSEGEI, St. Petersburg, Vol. 2, p. 316.

Sandalov, F.D., Pekov, I.V., Koshlyakova, N.N., Sidorov, E.G., 2018. Rutile as a concentrator of antimony in fumarolic exhalations of the Tolbachik volcano (Kamchatka, Russia), in: Proc. XXXV Intern. Conf. "Magmatism of the Earth and Related Strategic Metals Deposits". GEOKHI RAS, Moscow, pp. 263–264.

Serafimova, E.K., 1979. Mineralogy of Volcanic Sublimates in Kamchatka [in Russian]. Nauka, Moscow.

Serafimova, E.K., 1992. Parageneses of volcanic sublimates, in: Posteruptive Mineral Formation on Active Volcanoes in Kamchatka [in Russian]. DVO AN SSSR, Vladivostok, Part I, pp. 31–52.

Serafimova, E.K., Anan'ev, V.V., 1992. Tin-containing hematite of Mount 1004 (Tolbachik Dale, Kamchatka), in: Posteruptive Mineral Formation on Active Volcanoes in Kamchatka [in Russian]. DVO AN SSSR, Vladivostok, Part I, pp. 115–121.

Serafimova, E.K., Semenova, T.F., Sulimova, N.V., 1994. Copper and lead minerals of the ancient fumarole fields of Mount 1004 (Kamchatka). Vulkanologiya i Seismologiya, No. 3, 35–49.

Sharygin, V.V., Kamenetsky, V.S., Zhitova, L.M., Belousov, A.B., Abersteiner, A., 2018. Copper-containing magnesioferrite in vesicular trachyandesite in a lava tube from the 2012–2013 eruption of the Tolbachik volcano, Kamchatka, Russia. Minerals 8 (11), p. 514.

Shchipalkina, N.V., Pekov, I.V., Koshlyakova, N.N., Sidorov, E.G., 2018. Feldspars and feldspathoids from fumarole sublimates of the Tolbachik volcano (Kamchatka, Russia), in: Proc. XXXV Intern. Conf. "Magmatism of the Earth and Related Strategic Metals Deposits". GEOKHI RAS, Moscow, pp. 278–281.

Shchipalkina, N.V., Pekov, I.V., Zubkova, N.V., Koshlyakova, N.N., Sidorov, E.G., 2019. Natural forsterite strongly enriched by arsenic and phosphorus: chemistry, crystal structure, crystal morphology and zonation. Phys. Chem. Mineral. 46, 889–898.

Shchipalkina, N.V., Pekov, I.V., Britvin, S.N., Koshlyakova, N.N., Sidorov, E.G., 2020a. Arsenic and phosphorus in feldspar framework: sanidine–filatovite solid-solution series from fumarolic exhalations of the Tolbachik volcano, Kamchatka, Russia. Phys. Chem. Mineral. 47 (1), paper 1. doi: 10.1007/s00269-019-01067-5

Shchipalkina, N.V., Pekov, I.V., Koshlyakova, N.N., Britvin, S.N., Zubkova, N.V., Varlamov, D.A., Sidorov, E.G., 2020b. Unusual silicate mineralization in fumarolic sublimates of the Tolbachik volcano, Kamchatka, Russia — Part I: Neso-, cyclo-, ino- and phyllosilicates. Eur. J. Mineral. 32, 101–119. doi: 10.5194/ejm-32-101-2020

Shchipalkina, N.V., Pekov, I.V., Koshlyakova, N.N., Britvin, S.N., Zubkova, N.V., Varlamov, D.A., Sidorov, E.G., 2020c. Unusual silicate mineralization in fumarolic sublimates of the Tolbachik volcano, Kamchatka, Russia — Part II: Tectosilicates. Eur. J. Mineral. 32, 121–136. doi: 10.5194/ejm-32-121-2020

Shuvalov, R.R., Vergasova, L.P., Semenova, T.F., Filatov, S.K., Krivovichev, S.V., Siidra, O.I., Rudashevsky, N.S., 2013. Prewittite, $KPb_{1.5}Cu_6Zn(SeO_3)_2O_2Cl_{10}$, a new mineral from Tolbachik fumaroles, Kamchatka Peninsula, Russia: description and crystal structure. Am. Mineral. 98, 463–469.

Siidra, O.I., Vergasova, L.P., Krivovichev, S.V., Kretser, Y.L., Zaitsev, A.N., Filatov, S.K., 2014a. Unique thallium mineralization in the fumaroles of Tolbachik volcano, Kamchatka Peninsula, Russia. I. Markhininite, $TlBi(SO_4)_2$. Mineral. Mag. 78, 1687–1698.

Siidra, O.I., Vergasova, L.P., Kretser, Y.L., Polekhovsky, Y.S., Filatov, S.K., Krivovichev, S.V., 2014b. Unique thallium mineralization in the fumaroles of Tolbachik volcano, Kamchatka Peninsula, Russia. III. Evdokimovite, $Tl_4(VO)_3(SO_4)_5(H_2O)_5$. Mineral. Mag. 78, 1711–1724.

Siidra, O.I., Lukina, E.A., Nazarchuk, E.V., Depmeier, W., Bubnova, R.S., Agakhanov, A.A., Avdontseva, E.Y., Filatov, S.K., Kovrugin, V.M., 2018a. Saranchinaite, $Na_2Cu(SO_4)_2$, a new exhalative mineral from Tolbachik volcano, Kamchatka, Russia, and a product of the reversible dehydration of kröhnkite, $Na_2Cu(SO_4)_2(H_2O)_2$. Mineral. Mag. 82, 257–274.

Siidra, O.I., Nazarchuk, E.V., Lukina, E.A., Zaitsev, A.N., Shilovskikh, V.V., 2018b. Belousovite, $KZn(SO_4)Cl$, a new sulphate mineral from the Tolbachik volcano with apophyllite sheet-topology. Mineral. Mag. 82, 1079–1088.

Stoiber, R.E., Rose, W.I., Jr., 1974. Fumarole incrustations at active Central American volcanoes. Geochim. Cosmochim. Acta 38, 495–516.

Turchkova, A.G., Pekov, I.V., Yapaskurt, V.O., Sidorov, E.G., Britvin, S.N., 2017. Manganese mineralization in fumarole deposits at the Tolbachik volcano (Kamchatka, Russia), in: IX Intern. Sympos. “Mineral Diversity: Research and Preservation”. Sofia, p. 9.

Vergasova, L.P., Filatov, S.K., 1993. Volcanic exhalative minerals, a specific genetic group (from data on the 1975–1976 Tolbachik eruption). Zapiski VMO, No. 4, 68–76.

Vergasova, L.P., Filatov, S.K., 2016. A study of volcanogenic exhalation mineralization. J. Volcanol. Seismol. 10 (2), 71–85.

Vergasova, L.P., Filatov, S.K., Semenova, T.F., Filosofova, T.M., 1989. Sofiite $Zn_2(SeO_3)Cl_2$, a new mineral in volcanic sublimates. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva 118 (1), 65–69.

Vergasova, L.P., Filatov, S.K., Starova, G.L., Matusevich, Z.L., Filosofova, T.M., 1995. Vlodavetsite $AlCa_2(SO_4)_2F_2Cl\cdot 4H_2O$, a new mineral of volcanic exhalations. Dokl. Akad. Nauk 343, 358–360.

Vergasova, L.P., Starova, G.L., Filatov, S.K., Anan’ev, V.V., 1998. Averievite $Cu_5O_2(VO_4)_2{\times}nMX$, a new mineral in volcanic sublimates. Dokl. Akad. Nauk 359, 804–807.

Vergasova, L.P., Starova, G.L., Serafimova, E.K., Filatov, S.K., Filosofova, T.M., Dunin-Barkovskii, R.L., 2000. Natural gold deposited from volcanic exhalations on scoria cones induced by the 1975 Great Tolbachik Fissure Eruption. Vulkanologiya i Seismologiya, No. 5, 19–27.

Vergasova, L.P., Semenova, T.F., Epifanova, V.B., Filatov, S.K., Chubarov, V.M., 2004a. Menyailovite $Ca_4AlSi(SO_4)F_{13}\cdot 12H_2O$, a new mineral in volcanic sublimates. Vulkanologiya i Seismologiya, No. 2, 3–8.

Vergasova, L.P., Krivovichev, S.V., Britvin, S.N., Burns, P.C., Ananiev, V.V., 2004b. Filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$, a new mineral species from the Tolbachik volcano, Kamchatka peninsula, Russia. Eur. J. Mineral. 16, 533–536.

Vergasova, L.P., Filatov, S.K., Dunin-Barkovskaya, V.V., 2007. Posteruptive activity on the First Cone of the Great Tolbachik Fissure Eruption and recent volcanogenic generation of bauxites. J. Volcanol. Seismol. 1 (2), 119–139.

Vergasova, L.P., Semenova, T.F., Krivovichev, S.V., Filatov, S.K., Zolotarev, A.A., Jr., Ananiev, V.V., 2014. Nicksobolevite, $Cu_7(SeO_3)_3O_2Cl_6$, a new complex copper oxoselenite chloride from Tolbachik fumaroles, Kamchatka peninsula, Russia. Eur. J. Mineral. 26, 439–449.

Zambonini, F., 1935. Mineralogia Vesuviana. II edizione. Rendiconti della Reale Accademia delle Scienze fisiche e matematiche di Napoli 20, 1–463.

Zelenski, M., Bortnikova, S., 2005. Sublimate speciation at Mutnovsky volcano, Kamchatka. Eur. J. Mineral. 17, 107–118.

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