

Itelmenite, $\text{Na}_2\text{CuMg}_2(\text{SO}_4)_4$, a new anhydrous sulfate mineral from the Tolbachik volcano

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[Received 8 August 2017; Accepted 24 October 2017; Associate Editor: Stuart Mills]

ABSTRACT

Itelmenite, ideally $\text{Na}_2\text{CuMg}_2(\text{SO}_4)_4$, was found in a fumarole of the Naboko scoria cone of the Tolbachik volcano Fissure Eruption (2012–2013), Kamchatka Peninsula, Russia. Itelmenite occurs as irregularly shaped grains as well as microcrystalline masses associated with anhydrite, saranchinaite, hermannjahnite, euchlorine, thénardite, apthitalite and hematite. Itelmenite is orthorhombic, *Pbca*, $a = 9.568(2)$ Å, $b = 8.790(2)$ Å, $c = 28.715(8)$ Å, $V = 2415.0(11)$ Å³ and $Z = 4$ (from single-crystal diffraction data). The nine strongest lines of the powder X-ray diffraction pattern are $[d(I)(hkl)]$: 7.9614(41)(102), 7.1803(32)(004), 5.9122(64)(112), 3.8455(87)(122), 3.6292(52)(214), 3.3931(62)(215), 3.0003(44)(027), 2.9388(100)(312) and 2.4975(56)(230). The chemical composition determined by the electron-microprobe analysis is (wt.%): Na₂O 10.77, K₂O 0.20, MgO 11.10, CuO 15.38, ZnO 5.61, SO₃ 56.42, total 99.48. The empirical formula based on O = 32 apfu is $(\text{Na}_{3.93}\text{K}_{0.05})_{\Sigma 3.98}\text{Mg}_{3.12}(\text{Cu}_{2.19}\text{Zn}_{0.78})_{\Sigma 2.97}\text{S}_{7.97}\text{O}_{32}$. The simplified formula is $\text{Na}_2\text{CuMg}_2(\text{SO}_4)_4$ taking into account structural data. The crystal structure was solved by direct methods and refined to an agreement index $R_1 = 0.034$ on the basis of 1855 independent observed reflections. The structure of itelmenite is based on a unique type of $[\text{A}_3^{2+}(\text{SO}_4)_4]^{2-}$ ($\text{A} = \text{Mg}, \text{Cu}$ and Zn) heteropolyhedral framework with voids filled by Na^+ cations.

KEYWORDS: itelmenite, new minerals, copper, sulfates, framework structures, Tolbachik volcano.

Introduction

ACTIVE fumaroles of scoria cones related to different eruptions of Tolbachik volcano are well-known for the exceptional diversity of various sulfate mineral species (Vergasova and Filatov, 2016). All of the sulfate minerals found in Tolbachik fumaroles can be divided into three

groups: (1) sulfate minerals with additional O atoms (e.g. dolerophanite $\text{Cu}_2\text{O}(\text{SO}_4)$, Effenberger, 1985); (2) sulfates with no additional O atoms (e.g. chalcocyanite CuSO_4 , Siidra *et al.*, 2018b); and (3) hydrated sulfate minerals containing OH⁻ or/and H₂O (e.g. chalcantite $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

Two first groups of sulfate minerals are primary and usually found in the deeper hot zones of the fumaroles. A diverse suite of sulfates with additional oxygen atoms (Krivovichev *et al.*, 2013) is a characteristic feature for Tolbachik volcano (Siidra *et al.*, 2017) and only a few mineral species

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<https://doi.org/10.1180/minmag.2017.081.089>

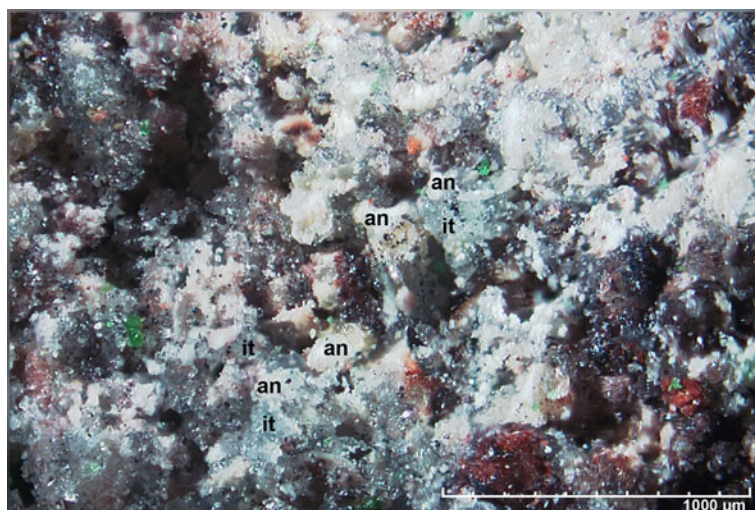


FIG. 1. Itelmenite (it) grey-blue crystalline aggregates associated closely with white anhydrite (an). Green crystals are euchlorine.

related to this group are observed in other active fumaroles on Earth (e.g. Vesuvius, Italy). Hydrated supergene sulfates form as a result of interaction of primary sulfates with water in the surface and subsurface zones. Herein we report on the composition, structure and properties of itelmenite (Cyrillic = ительменит) an anhydrous sulfate belonging to the second group. The mineral is named for the Itelmens, an ethnic group who are the original inhabitants living in the area around Tolbachik volcano and Kamchatka Peninsula. Both the mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015-047). Type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19637).

Occurrence and association

Itelmenite occurs as a product of fumarolic activity. It was found in the summer of 2014 by O.I.S. and E. A.L. in Saranchinaitovaya fumarole on the Naboko scoria cone (N55°46'06", E160°18'59", altitude 1650 m) of the Tolbachik Fissure Eruption that occurred in 2012–2013. The temperature of gases at the sampling location was ~600–620°C, nearly twice that observed in the fumaroles of the Second scoria cone of the Great Tolbachik Fissure Eruption. This means that itelmenite could be deposited directly from the gas phase as a volcanic sublimate. It is also very probable that itelmenite might form as a result of the interaction between gas and basalt scoria.

All the samples recovered were packed and isolated to avoid any contact with the atmosphere.

TABLE 1. Chemical composition (wt.%) of itelmenite.

Constituent	Mean	Range	S.D.	Probe standard
Na ₂ O	10.77	9.97–11.23	0.48	omphacite USNM 110607
K ₂ O	0.20	0.00–0.31	0.10	microcline USNM 143966
MgO	11.10	9.10–11.75	0.54	olivine San Carlos 111312/444
CuO	15.38	14.78–15.71	0.31	Cu
ZnO	5.61	4.15–6.05	0.59	Zn
SO ₃	56.42	55.20–57.02	0.61	SrSO ₄
Total	99.48	98.68–100.07		

S.D. – standard deviation.

TABLE 2. Powder X-ray diffraction data for itelmenite.

<i>I</i>	<i>d</i> _{meas}	<i>I</i> _{calc}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>
41	7.9614	46	7.9619	1	0	2
32	7.1803	39	7.1788	0	0	4
18	6.3200	6	6.3145	1	1	1
64	5.9122	73	5.9010	1	1	2
14	4.3868	24	4.3949	0	2	0
6	4.2933	1	4.2959	1	1	5
28	4.1971	33	4.2019	2	1	0
6	3.9892	0	3.9810	2	0	4
87	3.8455	93	3.8477	1	2	2
21	3.746	18	3.7483	0	2	4
52	3.6292	61	3.6264	2	1	4
26	3.4913	34	3.4902	0	2	5
62	3.3931	54	3.3912	2	1	5
2	3.0650	6	3.0660	2	2	3
44	3.0003	58	2.9988	0	2	7
100	2.9388	100	2.9347	3	1	2
9	2.8620	8	2.8616	1	2	7
31	2.7833	38	2.7801	0	2	8
21	2.7308	27	2.7292	2	1	8
10	2.6903	8	2.6887	1	3	3
5	2.5435	6	2.5411	2	1	9
56	2.4975	60	2.4986	2	3	0
5	2.3965	1	2.4037	2	2	8
2	2.2447	4	2.2445	1	1	12
7	2.2175	8	2.2174	2	1	11
5	2.1905	6	2.1851	1	2	11
2	2.1373	6	2.1358	1	4	1
11	2.1101	15	2.1183	1	4	2
2	1.9932	5	1.9921	2	4	1

The strongest lines are given in bold.

Itelmenite forms irregularly shaped grains as well as microcrystalline masses associated closely with anhydrite (Fig. 1, Supplementary Figure S1) and form intergrowths with it. Other associated minerals are saranchinaite (Siidra *et al.*, 2018a), hermannjahnite (Siidra *et al.*, 2018b), euchlorine, thénardite, aphtitalite and hematite.

General appearance and physical properties

Crystals of itelmenite are brittle with uneven fracture and lack cleavage. Itelmenite has a white streak and a vitreous lustre. Hardness and density could not be measured due to the lack of suitable material. The estimated Mohs' hardness is 2–3. The calculated density for the empirical formula obtained by microprobe is 3.10 g/cm³. The mineral is unstable in air. Itelmenite is light grey-blue and non-pleochroic.

TABLE 3. Crystallographic data and refinement parameters for itelmenite.

Crystal size (mm)	0.15 × 0.15 × 0.15
Space group	<i>Pbca</i>
<i>a</i> (Å)	9.568(2)
<i>b</i> (Å)	8.790(2)
<i>c</i> (Å)	28.715(8)
<i>V</i> (Å ³)	2415.0(11)
μ (mm ⁻¹)	3.514
Radiation wavelength (Å)	0.71073 (MoK α)
θ -range (deg.)	2.837–27.986
Total no. reflections	4558
Unique reflections	2459
Unique $ F_o \geq 4\sigma_F$	1855
R_{int}	0.037
R_1	0.034
R_1 (all data)	0.053
GoF	1.021
$\rho_{max,min}$ (e ⁻ ·Å ⁻³)	+0.675/–0.510

It is biaxial (+), $\alpha = 1.535(2)$, $\beta = 1.555(2)$, $\gamma = 1.585(2)$ (589 nm) and $2V$ (calc.) = 79.82°. The Gladstone-Dale compatibility index (Mandarino, 1981), $1 - (K_p/K_c) = 0.0023$, is superior.

Chemical composition

Three crystals (80 × 40 to 40 × 30 μ m) of itelmenite, previously checked by single-crystal X-ray, were mounted in epoxy resin and polished with an oil suspension. Ten spot analyses on the grains were obtained using a JEOL Superprobe 733 scanning electron microscope equipped with an Oxford Instruments INCA Energy Dispersive Spectrometer. The electron beam accelerating voltage was 20 kV, electron beam current measured with a Faraday cup was 2 nA and X-ray acquisition live-time was 30 s. System calibration was performed on Ni. The mineral is unstable under the focused electron beam with extensive sodium loss during analysis, therefore a defocused beam (5 μ m) was used for analyses. X-ray matrix correction was carried out automatically by the Oxford Instruments INCA version of the XPP routine by Pouchou and Pichoir (1991). No other elements with $Z > 9$ than those reported in Table 1 were detected. The empirical formula based on 32 O atoms per formula unit is (Na_{3.93}K_{0.05}) $\Sigma_{3.98}$ Mg_{3.12}(Cu_{2.19}Zn_{0.78}) $\Sigma_{2.97}$ S_{7.97}O₃₂. The ideal end-member formula is Na₂CuMg₃(SO₄)₄ taking into account structural data discussed below. Itelmenite

TABLE 4. Coordinates and isotropic displacement parameters (\AA^2) of atoms in itelmenite.

Site	Site scattering		Assigned site populations	BVS*	x	y	z	U_{eq}
	Refined	Calc.						
M1	27.30	27.67	Cu _{0.71} Mg _{0.09} Zn _{0.2}	2.06	0.16474(5)	0.25983(6)	0.62640(2)	0.0134(2)
M2	19.14	19.71	Mg _{0.55} Cu _{0.39} Zn _{0.06}	1.90	0.31150(7)	0.4328(1)	0.45028(3)	0.0187(3)
M3	13.62	13.62	Mg _{0.91} Zn _{0.09}	2.18	-0.14980(9)	0.0858(1)	0.69726(4)	0.0102(4)
Na1	11.20	11.20	Na _{0.975} K _{0.025}	0.95	-0.0982(1)	0.4201(2)	0.44265(7)	0.0284(5)
Na2			Na	1.12	-0.0490(1)	0.1392(2)	0.81032(6)	0.0218(4)
S1			S	6.08	-0.12370(9)	0.3899(1)	0.62989(4)	0.0124(2)
S2			S	6.05	0.05841(8)	-0.0726 (1)	0.62062(4)	0.0108(2)
S3			S	6.03	0.12946(8)	0.2851(1)	0.73462(4)	0.0103(2)
S4			S	6.01	0.10424(9)	0.2282(1)	0.51499(4)	0.0155(3)
O1			O	2.05	-0.0163(2)	0.2363(3)	0.7285(1)	0.0149(6)
O2			O	1.93	0.1799(3)	0.0314(3)	0.6167(1)	0.0168(7)
O3			O	2.11	0.1122(3)	-0.2306(3)	0.6170(1)	0.0137(6)
O4			O	2.05	0.1349(2)	0.4504(3)	0.7420(1)	0.0157(6)
O5			O	1.98	0.1865(3)	0.0897(4)	0.5085(1)	0.0216(7)
O6			O	2.00	0.1331(3)	0.3378(4)	0.4771(1)	0.0235(7)
O7			O	2.06	0.1872(2)	0.2053(3)	0.7751(1)	0.0159(6)
O8			O	2.03	-0.1638(3)	0.4452(4)	0.5840(1)	0.0260(8)
O9			O	1.95	-0.0470(3)	0.1999(4)	0.5149(1)	0.0230(7)
O10			O	1.99	-0.0063(3)	-0.0540(4)	0.6665(1)	0.0183(7)
O11			O	2.05	-0.0398(3)	-0.0460(4)	0.5829(1)	0.0221(7)
O12			O	1.75	-0.1445(3)	0.2240(3)	0.6330(1)	0.0240(8)
O13			O	2.12	0.0289(2)	0.4239(3)	0.6361(1)	0.0188(7)
O14			O	2.09	0.2124(2)	0.2446(3)	0.6926(1)	0.0166(7)
O15			O	2.12	-0.1952(3)	0.4700(4)	0.6668(1)	0.0227(7)
O16			O	2.10	0.1462(3)	0.3028(4)	0.5591(1)	0.0234(7)

*Bond-valence sums, calculated using the parameters for Cu–O, Mg–O, Na–O and S–O bonds from Brown and Altermatt (1985).

is soluble in H₂O at room temperature and slowly transforms into a hydrate in humid air.

X-ray crystallography

Powder X-ray diffraction data were collected using a Stoe IPDS II diffractometer (MoK α radiation) at the Department of Crystallography, St. Petersburg State University, Russia after crushing the crystal fragments used for the single-crystal analysis. Data (in Å) are given in Table 2. Unit-cell parameters refined from the powder data are as follows: monoclinic, space group *Pbca*, $a = 9.575(5)$ Å, $b = 8.786(4)$ Å, $c = 28.78(1)$ Å, $V = 2416(1)$ Å³ and $Z = 4$.

A transparent equant crystal fragment of itelmenite was mounted on a thin glass fibre for X-ray diffraction analysis using Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoK α radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multi scan type model implemented in the Bruker programs *APEX* and *SADABS*

(Bruker-AXS, 2014). More than a hemisphere of X-ray diffraction data was collected. The structure was solved by direct methods and successfully refined using *SHELX* (Sheldrick, 2015). The refinement in the *Pbca* space group converged to $R_1 = 0.034$ (Table 3). The final model included anisotropic displacement parameters for all atoms. The final atomic coordinates and anisotropic displacement parameters are given in Tables 4 and 5 and selected interatomic distances in Table 6. Lists of observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

There are four S sites with site-scattering values compatible with occupancy by S⁶⁺ and tetrahedrally coordinated by O anions (Table 6). The <S–O> distances demonstrate very similar values of ~1.47 Å, which is in a good agreement with the <S–O> distance of 1.473 Å reported for sulfate minerals by Hawthorne *et al.* (2000).

Two symmetrically independent Na sites have different coordination environments (Fig. 2). The Na1 atom forms ten Na–O bonds <3.5 Å thus

TABLE 5. Anisotropic displacement parameters (Å²) of atoms in itelmenite.

Site	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
M1	0.0143(3)	0.0159(3)	0.0100(4)	−0.0014(2)	−0.0004(1)	0.0040(1)
M2	0.0112(4)	0.0264(5)	0.0186(6)	0.0080(4)	0.0015(3)	0.0022(3)
M3	0.0075(5)	0.0112(6)	0.0117(8)	−0.0021(5)	−0.0003(4)	−0.0004(4)
Na1	0.0325(9)	0.025(1)	0.028(1)	−0.0052(8)	0.0009(8)	−0.0017(7)
Na2	0.0248(8)	0.023(1)	0.018(1)	−0.0005(7)	0.0016(7)	−0.0011(6)
S1	0.0099(4)	0.0124(5)	0.0149(6)	0.0020(4)	0.0023(4)	0.0015(3)
S2	0.0098(4)	0.0113(5)	0.0113(6)	0.0000(4)	0.0000(4)	0.0015(3)
S3	0.0084(4)	0.0124(5)	0.0100(6)	−0.0012(4)	−0.0001(4)	−0.0003(3)
S4	0.0197(5)	0.0151(5)	0.0117(7)	0.0009(4)	−0.0024(4)	−0.0010(3)
O1	0.011(1)	0.018(1)	0.017(1)	0.000(1)	−0.003(1)	−0.004(1)
O2	0.016(1)	0.014(1)	0.020(2)	−0.003(1)	0.005(1)	−0.003(1)
O3	0.012(1)	0.013(1)	0.017(2)	−0.001(1)	−0.001(1)	0.0016(9)
O4	0.018(1)	0.013(1)	0.016(1)	−0.002(1)	−0.001(1)	−0.002(1)
O5	0.018(1)	0.027(1)	0.019(2)	−0.001(1)	−0.001(1)	0.002(1)
O6	0.031(1)	0.020(1)	0.020(2)	0.006(1)	−0.006(1)	−0.005(1)
O7	0.015(1)	0.021(1)	0.012(1)	0.002(1)	−0.001(1)	0.005(1)
O8	0.023(1)	0.040(2)	0.015(2)	0.003(1)	−0.002(1)	0.010(1)
O9	0.020(1)	0.024(1)	0.025(2)	−0.000(1)	−0.005(1)	0.002(1)
O10	0.018(1)	0.024(1)	0.014(1)	0.000(1)	0.004(1)	0.004(1)
O11	0.023(1)	0.025(1)	0.018(2)	−0.001(1)	−0.009(1)	0.006(1)
O12	0.024(1)	0.012(1)	0.036(3)	0.001(1)	0.004(1)	−0.002(1)
O13	0.010(1)	0.022(1)	0.025(2)	−0.004(1)	−0.000(1)	0.002(1)
O14	0.014(1)	0.027(1)	0.009(1)	−0.002(1)	0.003(1)	0.004(1)
O15	0.022(1)	0.028(1)	0.018(2)	0.000(1)	0.007(1)	0.009(1)
O16	0.034(1)	0.021(1)	0.015(2)	−0.004(1)	−0.008(1)	−0.001(1)

TABLE 6. Selected interatomic distances (in Å) in itelmenite.

M1–O14	1.961(3)	Na2–O4	2.385(3)
M1–O13	1.961(3)	Na2–O13	2.447(4)
M1–O16	1.976(3)	Na2–O3	2.456(3)
M1–O2	2.032(3)	Na2–O14	2.465(3)
M1–O3	2.153(3)	Na2–O1	2.520(3)
<M1–O>	2.017	Na2–O7	2.544(3)
		Na2–O10	2.828(4)
M2–O11	1.980(3)	Na2–O15	2.846(3)
M2–O8	2.028(3)	<Na2–O>	2.561
M2–O9	2.048(3)		
M2–O6	2.050(3)	S1–O15	1.445(3)
M2–O5	2.168(3)	S1–O8	1.457(3)
<M2–O>	2.055	S1–O12	1.475(3)
		S1–O13	1.501(3)
M3–O15	2.000(3)	<S1–O>	1.470
M3–O7	2.041(3)		
M3–O10	2.043(3)	S2–O11	1.453(3)
M3–O1	2.046(3)	S2–O10	1.465(3)
M3–O4	2.116(3)	S2–O2	1.484(3)
M3–O12	2.211(3)	S2–O3	1.484(3)
<M3–O>	2.076	<S2–O>	1.472
Na1–O3	2.393(3)	S3–O7	1.465(3)
Na1–O16	2.480(4)	S3–O4	1.469(3)
Na1–O5	2.493(3)	S3–O1	1.470(2)
Na1–O6	2.528(3)	S3–O14	1.487(3)
Na1–O13	2.725(4)	<S3–O>	1.473
Na1–O2	2.756(3)		
Na1–O8	2.876(4)	S4–O5	1.462(3)
Na1–O9	2.879(4)	S4–O9	1.468(3)
Na1–O16	3.134(4)	S4–O6	1.480(3)
Na1–O6	3.155(4)	S4–O16	1.483(3)
<Na1–O>	2.742	<S4–O>	1.473

forming NaO₁₀ polyhedron with the average <Na1–O> distance of 2.742 Å. Coordination environments of the Na2 atom are different with formation of a NaO₈ irregular polyhedron and <Na2–O> = 2.561 Å. The Na1 site is partly substituted by K⁺ in agreement with microprobe data.

Three *M* sites are characterized by the different cationic substitutions in the structure of itelmenite. The *M1* and *M2* sites form similar MO₅ distorted tetragonal pyramids, whereas *M3* is roughly symmetrically coordinated by six oxygen atoms thus forming MO₆ octahedron (Fig. 2). As the X-ray scattering power of Cu and Zn atoms cannot be distinguished, Cu and Zn were regarded as one group with one scattering factor for the refinement of the *M1* and *M2* site occupancies. Copper and zinc atoms were summed to form Cu* in atomic

fractions. The occupancy of the *M3* atom position was refined using scattering factors for Mg and Zn. All *M*-site occupancies were subsequently fixed at the values given in Table 4 so as to be in agreement with the results of chemical analysis (see above). Refined site scattering and calculated site scattering are in good agreement with each other for all *M* sites in itelmenite. The [5]-coordinated polyhedron as observed for *M1*- and *M2*-centred distorted tetragonal pyramids is rather typical for both Cu²⁺ and Mg²⁺ cations.

A projection of the structure of itelmenite along the *b* axis is shown in Fig. 3. Sulfate tetrahedra are packed into pseudolayered arrangements perpendicular to the *a* axis (Fig. 4). Na1O₁₀ and Na2O₈ polyhedra are also arranged in pseudolayers, but perpendicular to the *c* axis. The structure topology of itelmenite is rather simple. Each MO₅ or MO₆ polyhedron shares all common corners with sulfate tetrahedra thus forming heteropolyhedral framework with voids filled by Na⁺ cations. The framework can be split into *A* and *B* layers as specified in Fig. 3. The *A* layers are formed by M2O₅ polyhedra and sulfate tetrahedra, whereas *B* layers consist of M3O₆ octahedra and sulfate tetrahedra. Chains based on M1O₅ polyhedra occur in the channels between the layers.

Discussion

The [A₃²⁺(SO₄)₄]²⁻ sulfate framework in itelmenite is unique and has not been described before. Itelmenite is the second sulfate mineral after dravertite CuMg(SO₄)₂ (Pekov *et al.*, 2017) with Mg and Cu as essential elements. However itelmenite from the Saranchinoitovaya fumarole formed at significantly higher temperature (~600°C) compared to dravertite (~350°C) from the Arsenatnaya fumarole, Second scoria cone of the Great Tolbachik Fissure Eruption. The temperature of gases in the Saranchinoitovaya fumarole had dropped to ~180°C in the summer of 2016, which resulted in the extinction of a rich Cu-sulfate mineralization.

We have obtained by the solid-state method a synthetic analogue of itelmenite in the CuSO₄–MgSO₄–Na₂SO₄ anhydrous system. The mixed cationic character of the *M1* and *M2* sites is very similar to that observed in the natural sample. The symmetrical *M3* octahedral site is occupied exclusively by Mg, which is also similar to the structure of itelmenite with a minor admixture of zinc reported above. In a symmetrical coordination environment it

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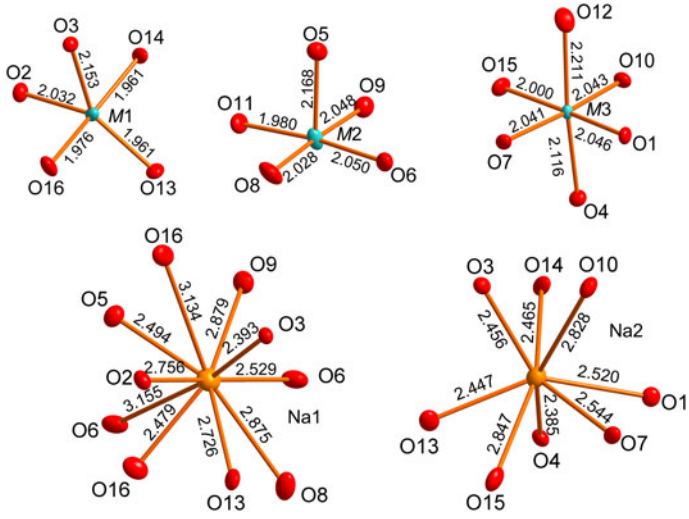


FIG. 2. Coordination of atoms in itelmenite.

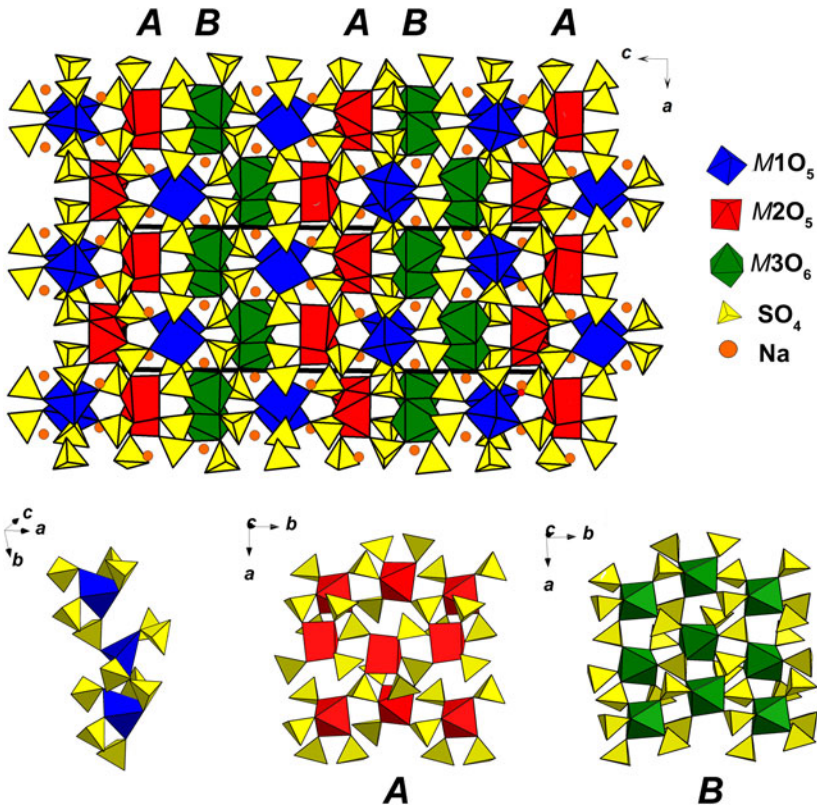


FIG. 3. General projection of the crystal structure of itelmenite along the *b* axis (above). The heteropolyhedral framework structure of itelmenite consists of *A* and *B* corrugated layers formed by $M2O_5$ polyhedra (designated as *A*) and $M3O_6$ octahedra (designated as *B*) and SO_4 tetrahedra with $M1O_5$ -based chains inserted in between.

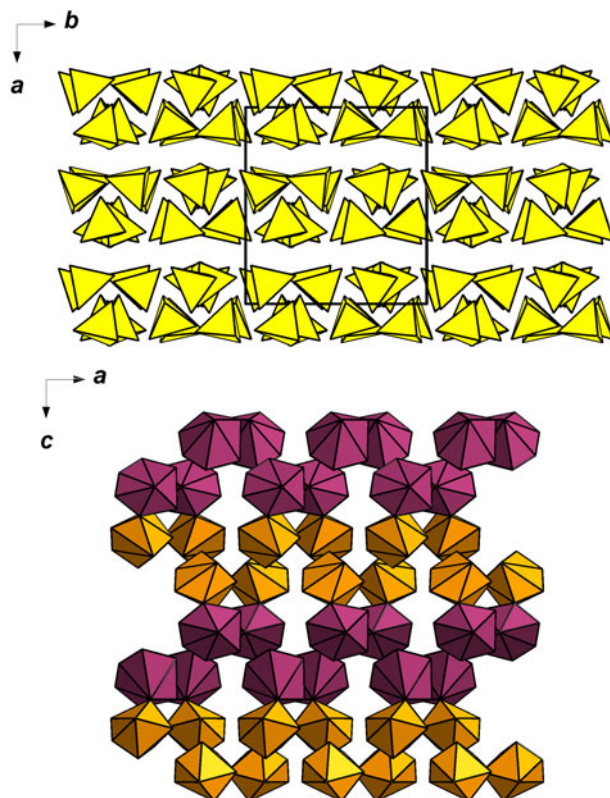


FIG. 4. Sulfate pseudolayers (*above*) ($\text{SO}_4 = \text{yellow}$) and arrangement of Na-centred polyhedra (*below*) ($\text{Na1O}_{10} = \text{purple}$, $\text{Na2O}_8 = \text{orange}$) in the structure of itelmenite.

is not preferable for Cu^{2+} to replace Mg^{2+} , however partial substitution is possible for Zn^{2+} (Siidra *et al.*, 2018b). The following structural formula for synthetic itelmenite was obtained from refinement: $\text{Na}_2(\text{Cu}_{0.81}\text{Mg}_{0.19})(\text{Mg}_{0.78}\text{Cu}_{0.22})\text{Mg}(\text{SO}_4)_4$. The synthetic analogue of itelmenite was obtained from a mixture of anhydrous Na_2SO_4 , MgSO_4 and CuSO_4 by solid-state synthesis in a platinum crucible at 600°C . The temperature of the successful synthesis is in a good agreement with the temperature of gases observed in Saranchinaitovaya fumarole.

It is very probable that a Zn-dominant analogue of itelmenite exists as a mineral species in fumaroles of the Tolbachik Fissure Eruption and the Great Tolbachik Fissure Eruption. Synthetic analogues of Cu exhalative minerals may be of interest from the viewpoint of materials science. Physical properties of the synthetic analogue of itelmenite will be reported in a separate publication in the near future.

Acknowledgements

We are grateful to Nikita Chukanov, Henrik Friis and Peter Leverett for valuable review comments. This work was financially supported by the Russian Science Foundation through the grant 16-17-10085. Technical support by the SPbSU X-ray Diffraction Resource Centre is gratefully acknowledged.

Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.089>

References

- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica B*, **41**, 244–247.

- Bruker-AXS (2014) *APEX2*. Version 2014.11-0. Madison, Wisconsin, USA.
- Effenberger, H. (1985) $\text{Cu}_2\text{O}(\text{SO}_4)$, dolerophanite: Refinement of the crystal structure with a comparison of $\text{OCu}(\text{II})_4$ tetrahedra in inorganic compounds. *Monatshfte für Chemie*, **116**, 927–931.
- Hawthorne, F.C., Krivovichev, S.V. and Burns, P.C. (2000) The crystal chemistry of sulfate minerals. Pp. 1–112 in: *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy & Geochemistry, **40**. Mineralogical Society of America and the Geochemical Society, Washington, DC.
- Krivovichev, S.V., Mentré, O., Siidra, O.I., Colmont, M. and Filatov, S.K. (2013) Anion-centred tetrahedra in inorganic compounds. *Chemical Reviews*, **113**, 6459–6535.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship. IV. The compatibility concept and its application. *Canadian Mineralogist*, **19**, 441–450.
- Pekov, I.V., Zubkova, N.V., Agakhanov, A.A., Yapaskurt, V. O., Chukanov, N.V., Belakovskiy, D.I., Sidorov, E.G. and Pushcharovsky, D.Y. (2017) Dravertite, $\text{CuMg}(\text{SO}_4)_2$, a new mineral species from the Tolbachik volcano, Kamchatka, Russia. *European Journal of Mineralogy*, **29**, 323–330.
- Pouchou, J.L. and Pichoir, F. (1991) Quantitative analysis of homogeneous or stratified microvolumes applying the model “PAP”. Pp. 31–75 in: *Electron Probe Quantitation* (K.F.J. Heinrich and D.E. Newbury, editors). Plenum Press, New York.
- Sheldrick, G.M. (2015) New features added to the refinement program SHELXL since 2008 are described and explained. *Acta Crystallographica C*, **71**, 3–8.
- Siidra, O.I., Nazarchuk, E.V., Zaitsev, A.N., Lukina, E.A., Avdontseva, E.Y., Vergasova, L.P., Vlasenko, N.S., Filatov, S.K., Turner, R. and Karpov, G.A. (2017) Copper oxosulfates from fumaroles of Tolbachik volcano: puninite, $\text{Na}_2\text{Cu}_3\text{O}(\text{SO}_4)_3$ – a new mineral species and structure refinements of kamchatkite and alumoklyuchevskite. *European Journal of Mineralogy*, **29**, 499–510.
- Siidra, O.I., Lukina, E.A., Nazarchuk, E.V., Depmeier, W., Bubnova, R.S., Agakhanov, A.A., Avdontseva, E.Y., Filatov, S.K. and Kovrugin, V.M. (2018a) Saranchinaite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, a new exhalative mineral from Tolbachik volcano, Kamchatka, Russia, and a product of the reversible dehydration of kröhnkite, $\text{Na}_2\text{Cu}(\text{SO}_4)_2(\text{H}_2\text{O})_2$. *Mineralogical Magazine*, **82**, 257–274.
- Siidra, O.I., Nazarchuk, E.V., Agakhanov, A.A., Lukina, E.A., Zaitsev, A.N., Turner, R., Filatov, S. K., Pekov, I.V., Karpov, G.A. and Yapaskurt, V.O. (2018b) Hermannjahnite, $\text{CuZn}(\text{SO}_4)_2$, a new mineral with chalcocyanite derivative structure from the Naboko scoria cone of the 2012–2013 fissure eruption at Tolbachik volcano, Kamchatka, Russia. *Mineralogy and Petrology*, **112**, 123–134.
- Vergasova, L.P. and Filatov, S.K. (2016) A study of volcanogenic exhalation mineralization. *Journal of Volcanology and Seismology*, **10**, 71–85.