Mineralogical Magazine (2019), **83**, 633–638
doi:10.1180/mgm.2019.11

Article

New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XI. Anatolyite, $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$

Igor V. Pekov[1]*, Inna S. Lykova[1], Vasiliy O. Yapaskurt[1], Dmitry I. Belakovskiy[2], Anna G. Turchkova[1], Sergey N. Britvin[3], Evgeny G. Sidorov[4] and Katharina S. Scheidl[5]

[1]Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia; [2]Fersman Mineralogical Museum of the Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia; [3]Department of Crystallography, St Petersburg State University, University Embankment 7/9, 199034 St Petersburg, Russia; [4]Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia; and [5]Institute of Mineralogy and Crystallography, University of Vienna, Althanstrasse 14 (UZA 2), A-1090 Vienna, Austria

Abstract

The new mineral anatolyite $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ was found in the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. It is associated with potassic feldspar, hematite, tenorite, cassiterite, johillerite, tilasite, ericlaxmanite, lammerite, arsmirandite, sylvite, halite, aphthitalite, langbeinite, anhydrite, wulffite, krasheninnikovite, fluoborite, pseudobrookite and fluorophlogopite. Anatolyite occurs as aggregates (up to 2 mm across) of rhombohedral–prismatic, equant or slightly elongated along [001] crystals up to 0.2 mm. The mineral is transparent, pale brownish–pinkish, with vitreous lustre. It is brittle, cleavage was not observed and the fracture is uneven. The Mohs' hardness is *ca* 4½. D_{calc} is 3.872 g cm^{-3}. Anatolyite is optically uniaxial (–), $\omega = 1.703(4)$ and $\varepsilon = 1.675(3)$. Chemical composition (wt.%, electron microprobe) is: Na_2O 16.55, K_2O 0.43, CaO 2.49, MgO 5.80, MnO 0.16, CuO 0.69, ZnO 0.55, Al_2O_3 5.01, Fe_2O_3 7.94, TiO_2 0.18, SnO_2 0.17, SiO_2 0.04, P_2O_5 0.55, As_2O_5 60.75, SO_3 0.03, total 101.34. The empirical formula based on 24 O apfu is $(Na_{5.90}K_{0.10})_{\Sigma 6.00}(Ca_{0.50}Na_{0.13}Zn_{0.08}Mn_{0.03})_{\Sigma 0.74}(Mg_{1.63}Fe^{3+}_{1.12}Al_{0.15}Cu_{0.10})_{\Sigma 3.00}(Al_{0.96}Ti_{0.03}Sn_{0.01})_{\Sigma 1.00}(As_{5.97}P_{0.09}Si_{0.01})_{\Sigma 6.07}O_{24}$. Anatolyite is trigonal, $R\bar{3}c$, $a = 13.6574(10)$, $c = 18.2349(17)$ Å, $V = 2945.6(4)$ Å^3 and $Z = 6$. The strongest reflections of the powder XRD pattern [d,Å(I)(hkl)] are: 7.21(33)(012), 4.539(16)(113), 4.347(27)(211), 3.421(20)(220), 3.196(31)(214), 2.981(17)(223), 2.827(100)(125) and 2.589(18)(410). The crystal structure was solved from single-crystal XRD data to $R = 4.77\%$. The structure is based on a 3D heteropolyhedral framework formed by M_4O_{18} clusters [$M1$ = Al and $M2 = (Mg,Fe^{3+})$] linked with AsO_4 tetrahedra. (Ca,Na) and Na cations centre $A1O_6$ and $A2O_8$ polyhedra in voids of the framework. Anatolyite is isostructural with yurmarinite. The new mineral is named in honour of the outstanding Russian crystallographer, mineralogist and mathematician Anatoly Kapitonovich Boldyrev (1883–1946).

Keywords: anatolyite, new mineral, yurmarinite, crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka

(Received 10 October 2018; accepted 23 January 2019; Accepted Manuscript published online: 22 February 2019; Associate Editor: Daniel Atencio)

Introduction

In this paper, we continue to characterise new arsenate mineral species found in the Arsenatnaya fumarole located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41′N 160°14′E, 1200 m asl). Arsenatnaya is one of the largest and hottest fumaroles at this scoria cone, a monogenetic volcano formed in 1975 (Fedotov and Markhinin, 1983). This fumarole was thus named due to the abundance of arsenate minerals as described by Pekov *et al.* (2014*a*, 2018*a*). In particular, 13 new arsenates from this locality have been characterised: yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al.*, 2014*a*), two polymorphs of $Cu_4O(AsO_4)_2$, ericlaxmanite and kozyrevskite (Pekov *et al.*, 2014*b*), popovite $Cu_5O_2(AsO_4)_2$ (Pekov *et al.*, 2015*b*), structurally related shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2015*c*), katiarsite $KTiO(AsO_4)$ (Pekov *et al.*, 2016*b*), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (Pekov *et al.*, 2016*c*), pharmazincite $KZnAsO_4$ (Pekov *et al.*, 2017), arsenowagnerite $Mg_2(AsO_4)F$ (Pekov *et al.*, 2018*b*), arsenatrotitanite $NaTiO(AsO_4)$ (Pekov *et al.*, 2019*a*), and isostructural minerals edtollite $K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$ and alumoedtollite $K_2NaCu_5AlO_2(AsO_4)_4$ (Pekov *et al.*, 2019*b*).

This paper describes the new mineral anatolyite, $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ (Cyrillic: анатолиит) named in honour of the outstanding Russian crystallographer, mineralogist and mathematician Anatoly Kapitonovich Boldyrev (1883–1946), Professor of Crystallography and Mineralogy in the Leningrad Mining Institute. Both new mineral and its name have been approved

---

***Author for correspondence:** Igor V. Pekov, Email: igorpekov@mail.ru

Cite this article: Pekov I.V., Lykova I.S., Yapaskurt V.O., Belakovskiy D.I., Turchkova A.G., Britvin S.N., Sidorov E.G. and Scheidl K.S. (2019) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XI. Anatolyite, $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$. *Mineralogical Magazine* **83**, 633–638. https://doi.org/10.1180/mgm.2019.11

by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2016–040, Pekov *et al.*, 2016*a*). The type specimens are deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue numbers 95620 and 95913.

Occurrence, mineral association and morphology

Material with the new mineral was collected by us in July 2015 from the northern area of the Arsenatnaya fumarole, at a depth of 1.5 m under day surface. The temperature, measured using a chromel–alumel thermocouple, was 420°C at the time of collecting. Anatolyite was deposited directly from the gas phase as a volcanic sublimate or, more likely, formed as a result of the interaction between hot gas and basalt scoria at a temperature not lower than 420–450°C. The volcanic gas seems to be a carrier of As, Na and Fe while the basalt scoria is the most probable source of Mg, Al and Ca which have low volatilities in volcanic gases (Symonds and Reed, 1993).

Anatolyite is one of the rarest minerals of fumarolic encrustations in the polymineralic zone of Arsenatnaya (Pekov *et al.*, 2018*a*). Closely associated minerals are potassic feldspar (As-bearing), hematite, tenorite, cassiterite, johillerite, tilasite, ericlaxmanite, lammerite, arsmirandite (IMA2014–081, Pekov *et al.*, 2015*a*), sylvite, halite, aphthitalite, langbeinite, anhydrite, wulffite, krasheninnikovite, fluoborite, pseudobrookite and fluorophlogopite.

Anatolyite occurs as clusters (up to 0.3 mm × 0.5 mm × 1.2 mm) or open-work aggregates (up to 2 mm across) of crystals overgrowing crusts of As-bearing potassic feldspar that cover basalt scoria altered by volcanic gas (Fig. 1). The crystals (up to 0.2 mm across) are rhombohedral–prismatic, equant or slightly elongated along [001]. They are well-shaped or, more commonly, crude and blocky, with rough surfaces (Fig. 2). Goniometric measurements were not performed due to the small size of anatolyite crystals, however, based on the scanning electron image (Fig. 2) and by analogy with the isostructural mineral yurmarinite (Pekov *et al.*, 2014*a*), the observed crystal forms could be assigned to the pinacoid {001}, hexagonal prisms {100} and {110} and rhombohedra {101} and {011}.

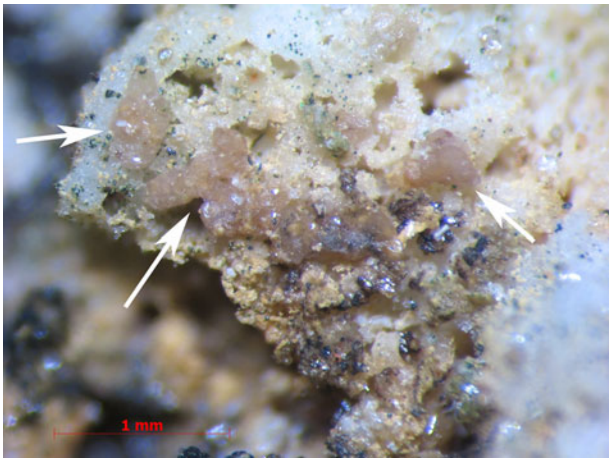

Fig. 1. Clusters of pale brownish–pinkish crystals of anatolyite (marked by arrows) with iron-black hematite on a crust of As-bearing potassic feldspar covering the surface of basalt scoria altered by fumarolic gas. FOV width: 3.6 mm. Photo: I.V. Pekov and A.V. Kasatkin, specimen #4739.

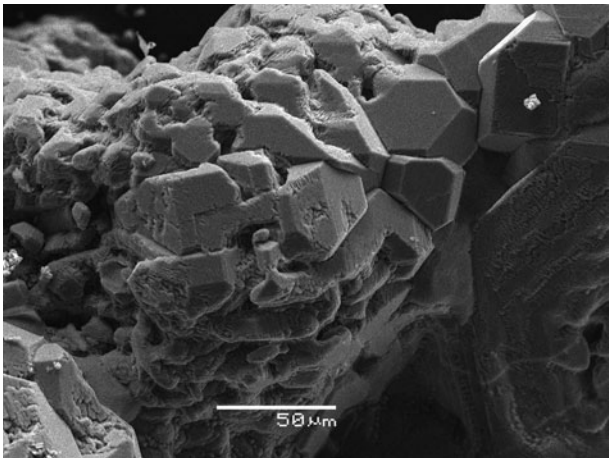

Fig. 2. Crystals of anatolyite forming a crust on the surface of dense cluster of the same mineral. Scanning electron microscopy (secondary electron) image, specimen #4739.

Physical properties and optical data

Anatolyite is transparent, pale brownish–pinkish, with white streak and vitreous lustre. It is brittle, cleavage or parting was not observed, and fracture is uneven. The Mohs' hardness is ~4½. Density calculated using the empirical formula is 3.872 g cm^{-3}.

The mineral is optically uniaxial (–), $\omega = 1.703(4)$ and $\varepsilon = 1.675(3)$ (589 nm). In transmitted, plane-polarised light, anatolyite is colourless and non-pleochroic.

Chemical composition

The chemical composition of anatolyite was determined using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a beam diameter of 3 µm. The chemical composition of anatolyite (average of 6 spot analyses) and the standards used are given in Table 1. Contents of other elements with atomic numbers higher than carbon are below detection limits.

Table 1. Chemical composition of anatolyite.

Constituent	wt.%	Range	S.D.	Probe standard
Na_2O	16.55	15.45–17.04	0.63	NaCl
K_2O	0.43	0.35–0.61	0.10	Orthoclase
CaO	2.49	2.13–3.14	0.42	$CaMoO_4$
MgO	5.80	4.66–6.60	0.91	Diopside
MnO	0.16	0.09–0.22	0.05	Mn
CuO	0.69	0.36–0.98	0.26	$CuFeS_2$
ZnO	0.55	0.40–0.69	0.13	ZnS
Al_2O_3	5.01	4.43–6.86	0.93	Al_2O_3
Fe_2O_3	7.94	5.11–9.60	1.59	FeS
TiO_2	0.18	0.00–0.42	0.05	Ti
SnO_2	0.17	0.00–0.33	0.14	SnO_2
SiO_2	0.04	0.00–0.10	0.04	Diopside
P_2O_5	0.55	0.49–0.60	0.04	GaP
As_2O_5	60.75	60.18–61.79	0.57	FeAsS
SO_3	0.03	0.00–0.11	0.03	ZnS
Total	101.34			

S.D. – standard deviation

Table 2. Powder X-ray diffraction data of anatolyite.

I_{obs}	I_{calc}*	d_{obs}	d_{calc}**	*h k l*
33	27	**7.21**	7.221	0 1 2
4	4	6.84	6.829	1 1 0
16	**15**	**4.539**	**4.540**	**1 1 3**
27	**34**	**4.347**	**4.342**	**2 1 1**
8	6	4.252	4.254	1 0 4
9	10	4.018	4.014	1 2 2
4	4	3.951	3.943	3 0 0
8	1	3.621	3.611	0 2 4
20	**29**	**3.421**	**3.414**	**2 2 0**
9	12	3.241	3.229	1 3 1
31	**31**	**3.196**	**3.192**	**2 1 4**
4	2	3.081	3.087	3 1 2
11	11	3.039	3.039	0 0 6
17	**21**	**2.981**	**2.977**	**2 2 3**
100	**100**	**2.827**	**2.826**	**1 2 5**
12	18	2.692	2.684	3 2 1
10	7	2.671	2.663	1 3 4
18	**36**	**2.589**	**2.581**	**4 1 0**
13	18	2.442	2.439	3 1 5
1	2	2.410	2.407	3 0 6
2	2	2.381	2.376	4 1 3
2	3	2.336	2.332	3 2 4
4	4	2.289	2.290	5 0 2
2	4	2.226	2.219	2 4 1
1	2	2.180	2.177	2 3 5
1	2	2.077	2.069	1 5 2
6	16	1.977	1.971	6 0 0
7	6, 13	1.932	1.933, 1.926	4 3 1, 5 1 4
4	7	1.911	1.906	4 2 5
7	2, 4, 8	1.804	1.808, 1.805, 1.802	2 5 3, 0 4 8, 1 0 10
5	1, 6	1.744	1.743, 1.742	0 2 10, 2 2 9
8	20	1.721	1.716	3 4 5
8	11	1.690	1.688	2 1 10
3	2, 5	1.659	1.661, 1.654	0 7 2, 0 6 6
4	3, 7	1.645	1.644, 1.641	4 4 3, 5 0 8
2	5	1.618	1.617	6 1 5
3	1	1.591	1.594	4 1 9
2	8	1.581	1.584	7 0 4
6	1, 3, 7	1.555	1.554, 1.554, 1.552	1 2 11, 1 5 8, 4 0 10
2	1, 3	1.516	1.517, 1.513	1 7 3, 3 2 10
4	9	1.500	1.496	2 6 5
3	3	1.494	1.494	4 5 2
2	2	1.482	1.480	3 1 11
5	1, 8, 5	1.446	1.447, 1.442, 1.440	3 6 3, 0 5 10, 2 7 1
1	1	1.418	1.415	2 3 11
6	2, 10, 3	1.386	1.392, 1.384, 1.384	1 7 6, 5 1 10, 2 5 9
3	3, 1, 14	1.373	1.377, 1.369, 1.366	2 7 4, 1 8 2, 5 5 0
2	3, 8	1.349	1.353, 1.343	4 6 1, 7 2 5
2	3, 1	1.341	1.338, 1.338	2 1 13, 3 6 6
3	4, 2	1.332	1.330, 1.327	4 3 10, 7 3 1
2	1, 2, 3	1.310	1.314, 1.309, 1.306	9 0 0, 1 4 12, 4 4 9
1	1, 2, 1	1.292	1.295, 1.294, 1.290	0 1 14, 1 8 5, 1 3 13
1	1, 2	1.264	1.262, 1.262	2 8 3, 3 4 11
2	5	1.247	1.246	5 5 6

*For the calculated pattern, only reflections with intensities ≥1 are given; **for the unit-cell parameters calculated from single-crystal data.
The strongest lines are given in bold.

The empirical formula calculated on the basis of 24 O apfu is $Na_{6.03}K_{0.10}Ca_{0.50}Mg_{1.63}Mn_{0.03}Cu_{0.10}Zn_{0.08}Al_{1.11}Fe^{3+}_{1.12}Ti_{0.03}Sn_{0.01}Si_{0.01}P_{0.09}As_{5.97}O_{24}$ or, after the most probable assignment of constituents to positions in accordance with the structure refinement data (see below): $(Na_{5.90}K_{0.10})_{\Sigma 6.00}(Ca_{0.50}Na_{0.13}Zn_{0.08}Mn_{0.03})_{\Sigma 0.74}(Mg_{1.63}Fe^{3+}_{1.12}Al_{0.15}Cu_{0.10})_{\Sigma 3.00}(Al_{0.96}Ti_{0.03}Sn_{0.01})_{\Sigma 1.00}(As_{5.97}P_{0.09}Si_{0.01})_{\Sigma 6.07}O_{24}$. The simplified formula is $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ ($Z = 6$). The formula $Na_6Ca(Mg_2Fe^{3+})Al(AsO_4)_6$ requires Na_2O 16.27, CaO 4.91, MgO 7.05, Al_2O_3 4.46, Fe_2O_3 6.99, As_2O_5 60.32, total 100.00 wt.%.

Table 3. Crystal data, data collection information and structure refinement details for anatolyite.

Formula	$Na_6(Ca_{0.7}Na_{0.2}\square_{0.1})(Mg_{0.5}Fe^{3+}_{0.4}Al_{0.1})_3(Al_{0.9}Fe^{3+}_{0.1})(AsO_4)_6$
Crystal system, space group	Trigonal, $R\bar{3}c$
Temperature (K)	293(2)
a, *c* (Å)	13.6574(10), 18.2349(17)
V (Å^3)	2945.6(4)
Z	6
Calculated density (g cm^{-3})	3.872
Absorption coefficient μ (mm^{-1})	11.632
Data collection	
Diffractometer	STOE StadiVari
Radiation type, wavelength (Å)	(Mo*K*α), 0.71073,
θ range (°)	2.82–31.72
Crystal size (mm)	0.03 × 0.04 × 0.055
No. of measured, independent and observed [*I* >2σ(*I*)] reflections	14594, 1101, 616
R_{int}	0.2007
h, *k*, *l* range	$-20 \le h \le 6$, $-16 \le k \le 19$, $-24 \le l \le 26$
Refinement	
R_1	0.0477
$wR_{2all}(F^2)$	0.0959
GoF	0.794
Number of refined parameters	68
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.0000P]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
$\Delta\rho_{max}$ /$\Delta\rho_{min}$ (e^-/Å^3)	1.309/−1.394

X-ray crystallography and crystal structure

Powder X-ray diffraction data of anatolyite (Table 2) were collected with a Rigaku R-AXIS Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector (radius 127.4 mm) using Debye-Scherrer geometry, Co*K*α radiation (rotating anode with VariMAX microfocus optics), 40 kV, 15 mA, and exposure time of 15 min. Angular resolution of the detector is 0.045°2θ (pixel size 0.1 mm). The data were integrated using the software package *Osc2Tab* (Britvin *et al.*, 2017). The hexagonal unit-cell parameters of calculated from the powder data are: $a = 13.672(1)$, $c = 18.265(3)$ Å and $V = 2957(1)$ Å^3.

Single-crystal X-ray studies of anatolyite were carried out using a STOE StadiVari diffractometer equipped with a Dectris PILATUS 300K pixel detector. The crystal structure was solved by direct methods and refined with the use of the *SHELX-97* software package (Sheldrick, 2008) to $R = 0.0477$. The crystal data and the experimental details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected interatomic distances in Table 5 and bond-valence calculations in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

The crystal structure of anatolyite is based on octahedral clusters M_4O_{18} (Fig. 3*a*) consisting of *M*1- and *M*2-centred octahedra. A regular $M1O_6$ octahedron, occupied predominantly by Al, shares three edges with three slightly distorted mixed-occupied octahedra $M2O_6$ [Mg and Fe^{3+} are major *M*2 cations and Mg > Fe^{3+}: Tables 1 and 4]. The clusters linked *via* AsO_4 tetrahedra to form a heteropolyhedral framework (Fig. 3*b*); each AsO_4 tetrahedron shares two oxygen vertices with one cluster and two other vertices with two adjacent clusters, one per each. Two large cation sites *A*1 and *A*2 are located in the voids of the framework: the regular $A1O_6$ octahedron is

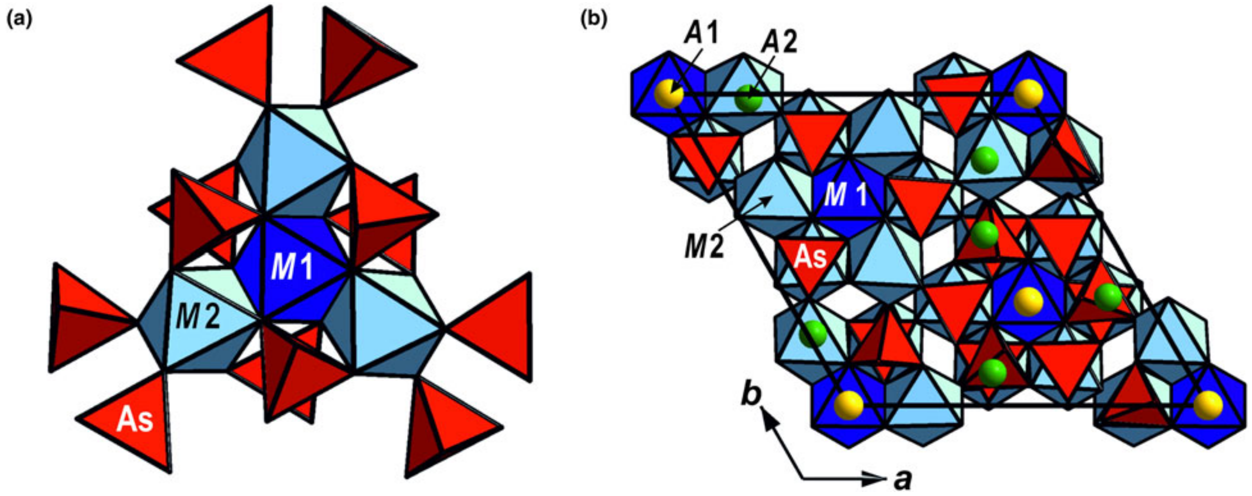

Fig. 3. The main building unit, an octahedral cluster M_4O_{18}, with connected AsO_4 tetrahedra (*a*) in the crystal structure of anatolyite (*b*; the unit cell is outlined). For legend see Table 4.

Table 4. Coordinates and thermal displacement parameters (*U*, Å^2) of atoms and site occupancies and multiplicities (*Q*) for anatolyite.

Site	*Q*	*x*	*y*	*z*	Site occupancy	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
*A*1	6	0	0	0	$Ca_{0.67(3)}Na_{0.19(3)}\square_{0.14}$*	0.0226(15)	0.0194(18)	0.0194(18)	0.029(3)	0	0	0.0097(9)
*A*2	36	0.7861(3)	0.0149(3)	0.05256(19)	Na	0.0276(7)	0.0329(17)	0.0373(18)	0.0198(16)	0.0027(14)	0.0028(13)	0.0228(15)
*M*1	6	0	0	¼	$Al_{0.91(2)}Fe^{3+}_{0.09(2)}$	0.0117(14)	0.0107(17)	0.0107(17)	0.014(3)	0	0	0.0054(8)
*M*2	18	0.77739(14)	0	¼	$Mg_{0.51}Fe_{0.43}Al_{0.06}$**	0.0112(4)	0.0114(6)	0.0136(9)	0.0092(10)	0.0009(7)	0.0004(4)	0.0068(5)
As	36	0.18114(5)	0.98895(5)	0.14623(4)	As	0.01251(18)	0.0125(3)	0.0130(3)	0.0124(3)	−0.0002(2)	0.0011(3)	0.0067(3)
O1	36	0.5239(4)	0.0619(4)	0.1541(3)	O	0.0212(12)	0.012(2)	0.015(2)	0.033(4)	0.004(2)	0.001(2)	0.0040(19)
O2	36	0.7167(4)	0.0617(4)	0.1766(3)	O	0.0193(10)	0.021(2)	0.017(2)	0.024(3)	0.001(2)	−0.004(2)	0.0125(19)
O3	36	0.6000(4)	0.1989(4)	0.0263(3)	O	0.0127(8)	0.013(2)	0.016(2)	0.010(2)	−0.0010(18)	0.0018(17)	0.0083(18)
O4	36	0.0123(5)	0.1534(5)	0.0609(3)	O	0.0232(11)	0.036(3)	0.025(3)	0.011(2)	0.005(2)	0.005(2)	0.017(2)

*Site occupancy was refined as 14% vacant taking into account chemical data (possible minor constituents, such as Mn or Zn, were not taken into consideration during refinement) and presence of vacancies in the *A*1 site in synthetic arsenates and phosphates with the same structure type (Masquelier *et al.*, 1995; Belam *et al.*, 2000); **the *M*2 site was refined assuming full occupancy and refining Mg (including the similarly light Al) against Fe^{3+}, the best agreement was obtained with $Mg_{0.560(14)}Fe^{3+}_{0.440(14)}$. In the final refinement cycles the occupancy was fixed as $Mg_{0.51}Fe_{0.43}Al_{0.06}$ based on the e_{ref} value [18.16] and electron microprobe data.

Table 5. Selected interatomic distances (Å) in the structure of anatolyite.

*M*1–O3	1.900(5) × 6	*A*1–O4	2.302(5) × 6
*M*2–O2	1.972(5) × 2	*A*2–O4	2.303(6)
*M*2–O1	2.005(5) × 2	*A*2–O1	2.555(6)
*M*2–O3	2.121(5) × 2	*A*2–O2	2.560(6)
<*M*2–O>	2.033	*A*2–O4	2.646(7)
		*A*2–O2	2.652(6)
As–O4	1.647(6)	*A*2–O4	2.702(7)
As–O2	1.677(5)	*A*2–O1	2.874(7)
As–O1	1.681(5)	*A*2–O1	2.910(6)
As–O3	1.714(5)	<*A*2–O>	2.650
<As–O>	1.680		

Table 6. Bond-valence calculations* for anatolyite.

	*A*1	*A*2	*M*1	*M*2	As	Σ
O1		0.13 0.05 0.05		0.43 × 2↓	1.26	1.92
O2		0.13 0.10		0.47 × 2↓	1.28	1.98
O3			0.53 × 6↓	0.31 × 2↓	1.15	1.99
O4	0.32 × 6↓	0.26 0.10 0.09			1.38	2.15
Σ	1.92	0.91	3.18	2.42	5.07	

*Bond-valence parameters were taken from (Brese and O'Keeffe, 1991).

partially occupied with predominance of Ca whereas the $A2O_8$ polyhedron, with distances varying in the range 2.303(6)–2.910(6) Å, is Na-centred (Table 4). The prevalence of Al in *M*1 and Ca in *A*1 is clearly confirmed by cation–anion distances in corresponding polyhedra (Table 5) and bond-valence calculations (Table 6), as well as mixed occupancy of *M*2 by bivalent and trivalent cations. The *A*2 site is partially (14%) vacant. In general, the structure refinement results are in good agreement with chemical data obtained for anatolyite using the electron microprobe (Table 1).

Discussion

Anatolyite $Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$ is a structural analogue of yurmarinite, $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$, for comparison see Table 7. Both minerals are isostructural with various synthetic trigonal arsenates and phosphates (space group $R\bar{3}c$, $a = 13.35$–13.8 and $c = 18.3$–18.6 Å for arsenates and $a = 13.4$ and $c = 17.85$–17.9 Å for phosphates). Their general formula is $(Na,\square)_7M_4(T^{5+}O_4)_6$, with T = As or P. All the synthetic compounds, as well as yurmarinite, contain trivalent cations (Fe^{3+}

Table 7. Comparative data for yurmarinite and anatolyite.

Mineral	Yurmarinite	Anatolyite
Formula	$Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$	$Na_6(Ca,Na)(Mg,Fe^{3+})_3Al(AsO_4)_6$
Crystal system, space group	Trigonal, $R\bar{3}c$	Trigonal, $R\bar{3}c$
a (Å)	13.7444(2)	13.6574(10)
c (Å)	18.3077(3)	18.2349(17)
V (Å^3)	2995.1(2)	2945.6(4)
Z	6	6
$D_{calc.}$ (g cm^{-3})	4.00	3.87
Prevailing cations in *A* and *M* sites in structure*		
*A*1 [6b]	Na	Ca
*A*2 [36f]	Na	Na
*M*1 [6a]	Fe^{3+}	Al
*M*2 [18e]	Fe^{3+}	Mg
Strongest reflections of the powder X-ray diffraction pattern: *d* (Å)–*I*	7.28–45	7.21–33
	4.375–33	4.347–27
	3.440–35	3.421–20
	3.217–36	3.196–31
	2.999–30	2.981–17
	2.841–100	2.827–100
	2.598–43	2.589–18
Optical data	Uniaxial (–)	Uniaxial (–)
ω	1.748	1.703
ε	1.720	1.675
Reference	Pekov *et al.* (2014*a*)	This work

*Wyckoff site symbols are given in square brackets.

or Al) as strongly prevailing in the *M* sites. However, if the *M* sites are completely occupied by trivalent cations then ⅐ of Na sites should be vacant, i.e. the general formula of such compounds is $(Na_6\square_1)_{\Sigma7}M_4^{3+}(T^{5+}O_4)_6$, or $Na_3M_2^{3+}(T^{5+}O_4)_3$. The examples are synthetic II-$Na_3Fe_2^{3+}(AsO_4)_3$ (d'Yvoire *et al.*, 1988), $Na_3(Al_{1.89}Y_{0.11})(AsO_4)_3$ (Belam *et al.*, 2000) and $Na_3Fe_2^{3+}(PO_4)_3$ (Belokoneva *et al.*, 2002). However, whereas in $Na_3(Al_{1.89}Y_{0.11})(AsO_4)_3$ the vacant site is *A*1, in II-$Na_3Fe_2^{3+}(AsO_4)_3$ and $Na_3Fe_2^{3+}(PO_4)_3$ the *A*2 site is partially vacant while the *A*1 site is fully occupied. The vacancy at the *A*1 site of $Na_3(Al_{1.89}Y_{0.11})(AsO_4)_3$ could have resulted in underbonding at the O4 site as it does not coordinate *M* sites. At the same time, the admixture of Y distorts the structure and results in the shortening of the *A*2–O4 bonds. Thus, the underbonding is compensated by the bond incidence contribution of the *A*2 site. A topologically close structure characterised by monoclinic distortion (space group *C*2, $a = 14.576$, $b = 13.409$, $c = 9.728$ Å and $\beta = 96.95°$) was reported for α-$Na_3Al_2(AsO_4)_3$, while the high-temperature (> 44°C) β-$Na_3Al_2(AsO_4)_3$ phase is rhombohedral and isotypic with II-$Na_3Fe_2^{3+}(AsO_4)_3$ (Masquelier *et al.*, 1995). All these compounds containing vacancies in Na sites are sodium ion conductors, which are interesting for materials science. The full occupancy of the Na sites is possible only if trivalent cations in the *M* sites are partially substituted by bivalent cations as in synthetic $Na_7(Fe_3^{3+}Fe^{2+})(AsO_4)_6$ (Masquelier *et al.*, 1995) and $Na_7(Fe_3^{3+}Fe^{2+})(PO_4)_6$ (Lii, 1996). Thus, the general formula of the abovementioned synthetic compounds can be written as $(Na_{7-x}\square_x)(M^{3+}_{3+x}M^{2+}_{1-x})(T^{5+}O_4)_2$ with $T =$ As or P, $M^{3+} =$ Fe or Al (±Y) and $M^{2+} =$ Fe and $0 \le x \le 1$.

Anatolyite is the first representative of this structure type in which bivalent cations prevail in both *M*2 [Mg] and *A*1 [Ca] sites. The simplified scheme of cation substitutions defining the relationship between yurmarinite and anatolyite can be written as ${}^{A1}Na^+ + {}^{M1}Fe^{3+} + {}^{M2}Fe^{3+} \leftrightarrow {}^{A1}Ca^{2+} + {}^{M1}Al^{3+} + {}^{M2}Mg^{2+}$. The substitution of significant amount of Fe for Al and Mg and part of Na for Ca causes lower unit-cell dimensions, density and refractive indices of anatolyite in comparison with yurmarinite (Table 7). The substitution of Na for Ca at the *A*1 site could have led to overbonding at the O4 site, but partial occupancy of the cation site alleviates the issue.

Acknowledgements. We thank Peter Leverett, Fernando Camara and anonymous referees for valuable comments. This study was supported by the Russian Foundation for Basic Research, grants nos. 17-05-00179 (mineralogical and structural studies) and 18-29-12007 (crystal chemical analysis). The technical support by the SPbSU X-Ray Diffraction Resource Center in the powder XRD study is acknowledged.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2019.11.

References

Belam W., Madani A., Driss A. and Daoud A. (2000) Elaboration et étude radiocristallographique du trisodium yttrium-aluminium triarsenic dodecaoxyde $Na_3Y_{0.11}Al_{1.89}(AsO_4)_3$. Effet du dopage par Na_2O sur la conductivite electrique. *Journal de la Societe Chimique, Tunis*, **4**, 735–743.

Belokoneva E.L., Ruchkina E.A., Dimitrova O.V. and Stefanovich S.Y. (2002) Synthesis and crystal structure of a new trigonal modification of $Na_3Fe_2(PO_4)_3$. *Zhurnal Neorganicheskoi Khimii*, **47**, 1423–1426 [in Russian].

Brese N.E. and O'Keeffe N.E. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, **B47**, 192–197.

Britvin S.N., Dolivo-Dobrovolsky D.V. and Krzhizhanovskaya M.G. (2017) Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zapiski Rossiiskogo Mineralogicheskogo Obshchestva*, **146**, 104–107 [in Russian].

d'Yvoire F., Bretey E. and Collin G. (1988) Crystal structure, non-stoichiometry and conductivity of II-$Na_3M_2(AsO_4)_3$ (M = Al, Ga, Cr, Fe). *Solid State Ionics*, **28**, 1259–1264.

Fedotov S.A. and Markhinin Y.K. (editors) (1983) *The Great Tolbachik Fissure Eruption*. Cambridge University Press, New York, 341 pp.

Lii K.-H. (1996) $Na_7Fe_4(PO_4)_6$: a mixed-valence iron phosphate containing a tetramer of edge-sharing FeO_6 octahedra. *Journal of the Chemical Society, Dalton Transactions*, **6**, 819–822.

Masquelier C., d'Yvoire F. and Collin G. (1995) Crystal structure of $Na_7Fe_4(AsO_4)_6$ and α-$Na_3Al_2(AsO_4)_3$, two sodium ion conductors structurally related to II-$Na_3Fe_2(AsO_4)_3$. *Journal of Solid State Chemistry*, **118**, 33–42.

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

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2014*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. II. Ericlaxmanite and kozyrevskite, two natural modifications of $Cu_4O(AsO_4)_2$. *Mineralogical Magazine*, **78**, 1527–1543.

Pekov I.V., Britvin S.N., Yapaskurt V.O., Polekhovsky Y.S., Krivovichev S.V., Vigasina M.F. and Sidorov E.G. (2015*a*) Arsmirandite, IMA 2014-081. CNMNC Newsletter No. 23, February 2015, page 57; *Mineralogical Magazine*, **79**, 51–58.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2015*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. III. Popovite, $Cu_5O_2(AsO_4)_2$. *Mineralogical Magazine*, **79**, 133–143.

Pekov I.V., Zubkova N.V., Belakovskiy D.I., Yapaskurt V.O., Vigasina M.F., Sidorov E.G. and Pushcharovsky D.Yu. (2015*c*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IV. Shchurovskyite, $K_2CaCu_6O_2(AsO_4)_4$, and dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$. *Mineralogical Magazine*, **79**, 1737–1753.

Pekov I.V., Lykova I.S., Yapaskurt V.O., Belakovskiy D.I., Turchkova A.G., Britvin S.N., Sidorov E.G. and Scheidl K.S. (2016*a*) Anatolyite, IMA

2016-040. CNMNC Newsletter No. 33, October 2016, page 1137; *Mineralogical Magazine*, **80**, 1135–1144.

Pekov I.V., Yapaskurt V.O., Britvin S.N., Zubkova N.V., Vigasina M.F. and Sidorov E.G. (2016*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. V. Katiarsite, $KTiO(AsO_4)$. *Mineralogical Magazine*, **80**, 639–646.

Pekov I.V., Zubkova N.V., Yapaskurt V.O., Polekhovsky Yu.S., Vigasina M.F., Belakovskiy D.I., Britvin S.N., Sidorov E.G. and Pushcharovsky D.Yu. (2016*c*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VI. Melanarsite, $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$. *Mineralogical Magazine*, **80**, 855–867.

Pekov I.V., Yapaskurt V.O., Belakovskiy D.I., Vigasina M.F., Zubkova N.V. and Sidorov E.G. (2017) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VII. Pharmazincite, $KZnAsO_4$. *Mineralogical Magazine*, **81**, 1001–1008.

Pekov I.V., Koshlyakova N.N., Zubkova N.V., Lykova I.S., Britvin S.N., Yapaskurt V.O., Agakhanov A.A., Shchipalkina N.V., Turchkova A.G. and Sidorov E.G. (2018*a*) Fumarolic arsenates – a special type of arsenic mineralization. *European Journal of Mineralogy*, **30**, 305–322.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Yapaskurt V.O., Chukanov N.V., Belakovskiy D.I., Sidorov E.G. and Pushcharovsky D.Yu. (2018*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VIII. Arsenowagnerite, $Mg_2(AsO_4)F$. *Mineralogical Magazine*, **82**, 877–888.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Belakovskiy D.I., Vigasina M.F., Yapaskurt V.O., Sidorov E.G., Britvin S.N. and Pushcharovsky D.Y. (2019*a*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IX. Arsenatrotitanite, $NaTiO(AsO_4)$. *Mineralogical Magazine*, **83**, 453–458.

Pekov I.V., Zubkova N.V., Agakhanov A.A., Ksenofontov D.A., Pautov L.A., Sidorov E.G., Britvin S.N., Vigasina M.F. and Pushcharovsky D.Yu. (2019*b*) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka Russia. X. Edtollite, $K_2NaCu_5Fe^{3+}O_2(AsO_4)_4$, and alumoedtollite, $K_2NaCu_5AlO_2(AsO_4)_4$. *Mineralogical Magazine*, **83**, 485–495.

Sheldrick G.M. (2008) A short history of *SHELX*. *Acta Crystallographica*, **A64**, 112–122.

Symonds R.B. and Reed M.H. (1993) Calculation of multicomponent chemical equilibria in gas-solid-liquid systems: calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens. *American Journal of Science*, **293**, 758–864.