



Article

New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. XI. Anatolyite, $\text{Na}_6(\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$

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Abstract

The new mineral anatolyite $\text{Na}_6(\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$ was found in the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. It is associated with potassic feldspar, hematite, tenorite, cassiterite, johillerite, tilasite, ericaxmanite, lammerite, arsmirandite, syl-vite, halite, apthitalite, langbeinite, anhydrite, wulfite, krashennikovite, fluorborite, 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 $\epsilon = 1.675(3)$. 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 $(\text{Na}_{5.90}\text{K}_{0.10})_{\Sigma 6.00}(\text{Ca}_{0.50}\text{Na}_{0.13}\text{Zn}_{0.08}\text{Mn}_{0.03})_{\Sigma 0.74}(\text{Mg}_{1.63}\text{Fe}_{1.12}\text{Al}_{0.15}\text{Cu}_{0.10})_{\Sigma 3.00}(\text{Al}_{0.96}\text{Ti}_{0.03}\text{Sn}_{0.01})_{\Sigma 1.00}(\text{As}_{5.97}\text{P}_{0.09}\text{Si}_{0.01})_{\Sigma 6.07}\text{O}_{24}$. Anatolyite is trigonal, $R\bar{3}c$, $a = 13.6574(10)$, $c = 18.2349(17)$ Å, $V = 2945.6(4)$ Å³ and $Z = 6$. The strongest reflections of the powder XRD pattern [d , Å(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 [$\text{M1} = \text{Al}$ and $\text{M2} = (\text{Mg},\text{Fe}^{3+})$] linked with AsO_4 tetrahedra. (Ca,Na) and Na cations centre AlO_6 and Al_2O_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

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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.* (2014a, 2018a). In particular, 13 new arsenates

from this locality have been characterised: yurmarinite $\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$ (Pekov *et al.*, 2014a), two polymorphs of $\text{Cu}_4\text{O}(\text{AsO}_4)_2$, ericaxmanite and kozyrevskite (Pekov *et al.*, 2014b), popovite $\text{Cu}_5\text{O}_2(\text{AsO}_4)_2$ (Pekov *et al.*, 2015b), structurally related shchurovskyite $\text{K}_2\text{CaCu}_6\text{O}_2(\text{AsO}_4)_4$ and dmsokolovite $\text{K}_3\text{Cu}_5\text{AlO}_2(\text{AsO}_4)_4$ (Pekov *et al.*, 2015c), katiarsite $\text{KTiO}(\text{AsO}_4)$ (Pekov *et al.*, 2016b), melanarsite $\text{K}_3\text{Cu}_7\text{Fe}^{3+}\text{O}_4(\text{AsO}_4)_4$ (Pekov *et al.*, 2016c), pharmazincite KZnAsO_4 (Pekov *et al.*, 2017), arsenowagnerite $\text{Mg}_2(\text{AsO}_4)\text{F}$ (Pekov *et al.*, 2018b), arsenatro-titanite $\text{NaTiO}(\text{AsO}_4)$ (Pekov *et al.*, 2019a), and isostructural minerals edtollite $\text{K}_2\text{NaCu}_5\text{Fe}^{3+}\text{O}_2(\text{AsO}_4)_4$ and alumoedtollite $\text{K}_2\text{NaCu}_5\text{AlO}_2(\text{AsO}_4)_4$ (Pekov *et al.*, 2019b).

This paper describes the new mineral anatolyite, $\text{Na}_6(\text{Ca},\text{Na})(\text{Mg},\text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$ (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

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by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2016-040, Pekov *et al.*, 2016a). 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.*, 2018a). Closely associated minerals are potassic feldspar (As-bearing), hematite, tenorite, cassiterite, johillerite, tilasite, ericlxmanite, lammerite, arsmirandite (IMA2014-081, Pekov *et al.*, 2015a), sylvite, halite, aphthitalite, langbeinite, anhydrite, wulfite, krashennikovite, fluorborite, 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.*, 2014a), the observed crystal forms could be assigned to the pinacoid {001}, hexagonal prisms {100} and {110} and rhombohedra {101} and {011}.

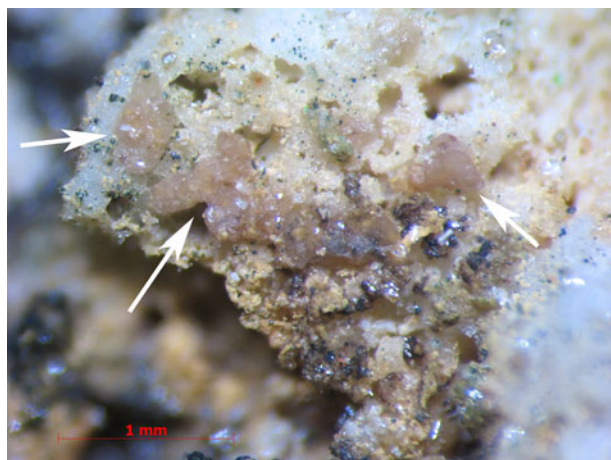


Fig. 1. Clusters of pale brownish–pinkish crystals of anatolyite (marked by arrows) with iron-black hematite on a crust of As-bearing potassic feldspar covering the surface of basalt scoria altered by fumarolic gas. FOV width: 3.6 mm. Photo: I.V. Pekov and A.V. Kasatkin, specimen #4739.

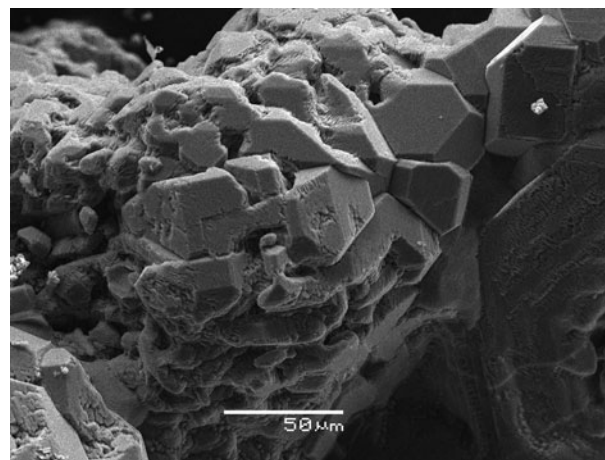


Fig. 2. Crystals of anatolyite forming a crust on the surface of dense cluster of the same mineral. Scanning electron microscopy (secondary electron) image, specimen #4739.

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 $\epsilon = 1.675(3)$ (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 ₂ O	16.55	15.45–17.04	0.63	NaCl
K ₂ O	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 ₂ O ₃	5.01	4.43–6.86	0.93	Al ₂ O ₃
Fe ₂ O 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 ₂ O ₅	0.55	0.49–0.60	0.04	GaP
As ₂ O 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>I</i> _{obs}	<i>I</i> _{calc} *	<i>d</i> _{obs}	<i>d</i> _{calc} **	<i>h k l</i>
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 $\text{Na}_{6.03}\text{K}_{0.10}\text{Ca}_{0.50}\text{Mg}_{1.63}\text{Mn}_{0.03}\text{Cu}_{0.10}\text{Zn}_{0.08}\text{Al}_{1.11}\text{Fe}_{1.12}^{3+}\text{Ti}_{0.03}\text{Sn}_{0.01}\text{Si}_{0.01}\text{P}_{0.09}\text{As}_{5.97}\text{O}_{24}$ or, after the most probable assignment of constituents to positions in accordance with the structure refinement data (see below): $(\text{Na}_{5.90}\text{K}_{0.10})_{\Sigma 6.00}(\text{Ca}_{0.50}\text{Na}_{0.13}\text{Zn}_{0.08}\text{Mn}_{0.03})_{\Sigma 0.74}(\text{Mg}_{1.63}\text{Fe}_{1.12}^{3+}\text{Al}_{0.15}\text{Cu}_{0.10})_{\Sigma 3.00}(\text{Al}_{0.96}\text{Ti}_{0.03}\text{Sn}_{0.01})_{\Sigma 1.00}(\text{As}_{5.97}\text{P}_{0.09}\text{Si}_{0.01})_{\Sigma 6.07}\text{O}_{24}$. The simplified formula is $\text{Na}_6(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$ ($Z = 6$). The formula $\text{Na}_6\text{Ca}(\text{Mg}_2\text{Fe}^{3+})\text{Al}(\text{AsO}_4)_6$ 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	$\text{Na}_6(\text{Ca}_{0.7}\text{Na}_{0.2}\square_{0.1})(\text{Mg}_{0.5}\text{Fe}_{0.4}^{3+}\text{Al}_{0.1})_3(\text{Al}_{0.9}\text{Fe}_{0.1}^{3+})(\text{AsO}_4)_6$
Crystal system, space group	Trigonal, $R\bar{3}c$
Temperature (K)	293(2)
<i>a</i> , <i>c</i> (Å)	13.6574(10), 18.2349(17)
<i>V</i> (Å ³)	2945.6(4)
<i>Z</i>	6
Calculated density (g cm ⁻³)	3.872
Absorption coefficient μ (mm ⁻¹)	11.632
Data collection	
Diffractometer	STOE StadiVari
Radiation type, wavelength (Å)	(MoK α), 0.71073,
θ range (°)	2.82–31.72
Crystal size (mm)	0.03 \times 0.04 \times 0.055
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14594, 1101, 616
<i>R</i> _{int}	0.2007
<i>h</i> , <i>k</i> , <i>l</i> range	$-20 \leq h \leq 6$, $-16 \leq k \leq 19$, $-24 \leq l \leq 26$
Refinement	
<i>R</i> ₁	0.0477
<i>wR</i> _{2all} (<i>F</i> 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, CoK 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°2 θ (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) Å³.

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 $M_4\text{O}_{18}$ (Fig. 3a) consisting of M1- and M2-centred octahedra. A regular M1O₆ octahedron, occupied predominantly by Al, shares three edges with three slightly distorted mixed-occupied octahedra M2O₆ [Mg and Fe³⁺ are major M2 cations and Mg > Fe³⁺; Tables 1 and 4]. The clusters linked via AsO₄ tetrahedra to form a heteropolyhedral framework (Fig. 3b); each AsO₄ tetrahedron shares two oxygen vertices with one cluster and two other vertices with two adjacent clusters, one per each. Two large cation sites A1 and A2 are located in the voids of the framework: the regular AlO₆ octahedron is

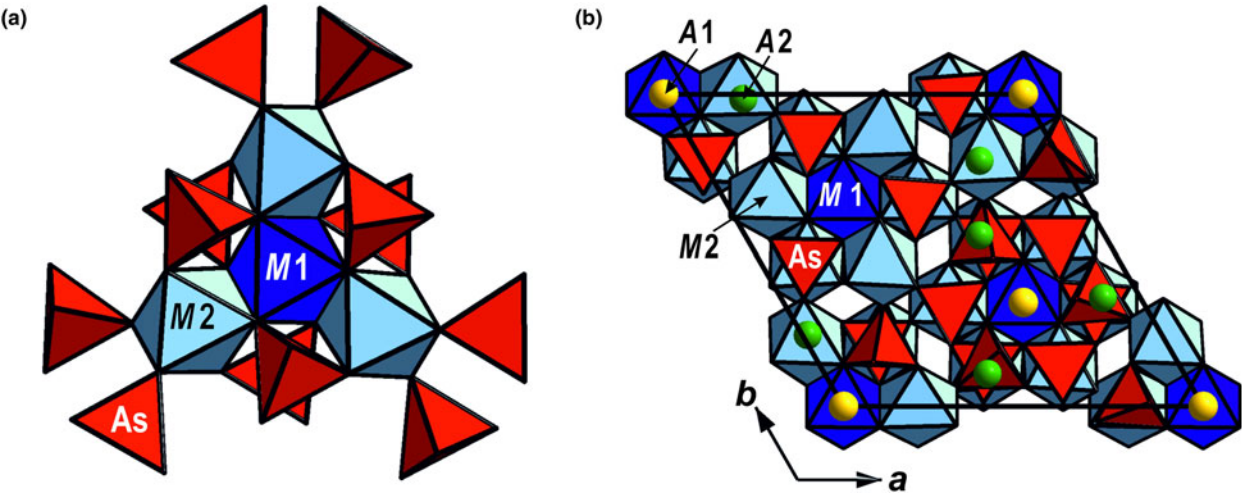


Fig. 3. The main building unit, an octahedral cluster M_4O_{18} , with connected AsO_4 tetrahedra (a) in the crystal structure of anatolyite (b; the unit cell is outlined). For legend see Table 4.

Table 4. Coordinates and thermal displacement parameters (U , Å²) of atoms and site occupancies and multiplicities (Q) for anatolyite.

Site	<i>Q</i>	<i>x</i>	<i>y</i>	<i>z</i>	Site occupancy	<i>U</i> _{eq}	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ²³	<i>U</i> ¹³	<i>U</i> ¹²
A1	6	0	0	0	Ca _{0.67(3)} Na _{0.19(3)} □ _{0.14} *	0.0226(15)	0.0194(18)	0.0194(18)	0.029(3)	0	0	0.0097(9)
A2	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)
M1	6	0	0	¼	Al _{0.91(2)} Fe _{0.09(2)} ³⁺	0.0117(14)	0.0107(17)	0.0107(17)	0.014(3)	0	0	0.0054(8)
M2	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 A1 site in synthetic arsenates and phosphates with the same structure type (Masquelier et al., 1995; Belam et al., 2000); **the M2 site was refined assuming full occupancy and refining Mg (including the similarly light Al) against Fe³⁺, the best agreement was obtained with Mg_{0.560(14)}Fe_{0.440(14)}³⁺. 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.

M1–O3	1.900(5) × 6	A1–O4	2.302(5) × 6
M2–O2	1.972(5) × 2	A2–O4	2.303(6)
M2–O1	2.005(5) × 2	A2–O1	2.555(6)
M2–O3	2.121(5) × 2	A2–O2	2.560(6)
<M2–O>	2.033	A2–O4	2.646(7)
		A2–O2	2.652(6)
As–O4	1.647(6)	A2–O4	2.702(7)
As–O2	1.677(5)	A2–O1	2.874(7)
As–O1	1.681(5)	A2–O1	2.910(6)
As–O3	1.714(5)	<A2–O>	2.650
<As–O>	1.680		

Table 6. Bond-valence calculations* for anatolyite.

	A1	A2	M1	M2	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 A2O₈ polyhedron, with distances varying in the range 2.303(6)–2.910(6) Å, is Na-centred (Table 4). The prevalence of Al in M1 and Ca in A1 is clearly confirmed by cation–anion distances in corresponding polyhedra (Table 5) and bond-valence calculations (Table 6), as well as mixed occupancy of M2 by bivalent and trivalent cations. The A2 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 Na₆(Ca,Na)(Mg,Fe³⁺)₃Al(AsO₄)₆ is a structural analogue of yurmarinite, Na₇(Fe³⁺,Mg,Cu)₄(AsO₄)₆, for comparison see Table 7. Both minerals are isostructural with various synthetic trigonal arsenates and phosphates (space group *R*3̄c, *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,□)₇M₄(T⁵⁺O₄)₆, with T = As or P. All the synthetic compounds, as well as yurmarinite, contain trivalent cations (Fe³⁺

Table 7. Comparative data for yurmarinite and anatolyite.

Mineral	Yurmarinite	Anatolyite
Formula	$\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$	$\text{Na}_6(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}^{3+})_3\text{Al}(\text{AsO}_4)_6$
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
$D_{\text{calc.}}$ (g cm ⁻³)	4.00	3.87
Prevailing cations in A and M sites in structure*		
A1 [6b]	Na	Ca
A2 [36f]	Na	Na
M1 [6a]	Fe^{3+}	Al
M2 [18e]	Fe^{3+}	Mg
Strongest reflections of the powder X-ray diffraction pattern: d (Å)– I	7.28–45 4.375–33 3.440–35 3.217–36 2.999–30 2.841–100 2.598–43	7.21–33 4.347–27 3.421–20 3.196–31 2.981–17 2.827–100 2.589–18
Optical data		
ω	Uniaxial (–)	Uniaxial (–)
ϵ	1.748	1.703
ϵ	1.720	1.675
Reference	Pekov <i>et al.</i> (2014a)	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 $\frac{1}{2}$ of Na sites should be vacant, i.e. the general formula of such compounds is $(\text{Na}_6\Box)_1\text{M}_4^{3+}(\text{T}^{5+}\text{O}_4)_6$, or $\text{Na}_3\text{M}_2^{3+}(\text{T}^{5+}\text{O}_4)_3$. The examples are synthetic $\text{II-Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ (d'Yvoire *et al.*, 1988), $\text{Na}_3(\text{Al}_{1.89}\text{Y}_{0.11})(\text{AsO}_4)_3$ (Belam *et al.*, 2000) and $\text{Na}_3\text{Fe}_2^{3+}(\text{PO}_4)_3$ (Belokoneva *et al.*, 2002). However, whereas in $\text{Na}_3(\text{Al}_{1.89}\text{Y}_{0.11})(\text{AsO}_4)_3$ the vacant site is A1, in $\text{II-Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ and $\text{Na}_3\text{Fe}_2^{3+}(\text{PO}_4)_3$ the A2 site is partially vacant while the A1 site is fully occupied. The vacancy at the A1 site of $\text{Na}_3(\text{Al}_{1.89}\text{Y}_{0.11})(\text{AsO}_4)_3$ 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 A2–O4 bonds. Thus, the underbonding is compensated by the bond incidence contribution of the A2 site. A topologically close structure characterised by monoclinic distortion (space group C2, $a = 14.576$, $b = 13.409$, $c = 9.728$ Å and $\beta = 96.95^\circ$) was reported for $\alpha\text{-Na}_3\text{Al}_2(\text{AsO}_4)_3$, while the high-temperature ($> 44^\circ\text{C}$) $\beta\text{-Na}_3\text{Al}_2(\text{AsO}_4)_3$ phase is rhombohedral and isotypic with $\text{II-Na}_3\text{Fe}_2^{3+}(\text{AsO}_4)_3$ (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 $\text{Na}_7(\text{Fe}^{3+}\text{Fe}^{2+})(\text{AsO}_4)_6$ (Masquelier *et al.*, 1995) and $\text{Na}_7(\text{Fe}^{3+}\text{Fe}^{2+})(\text{PO}_4)_6$ (Lii, 1996). Thus, the general formula of the abovementioned synthetic compounds can be written as $(\text{Na}_{7-x}\Box_x)(\text{M}_{3+x}^{3+}\text{M}_{1-x}^{2+})(\text{T}^{5+}\text{O}_4)_2$ with $T = \text{As}$ or P , $\text{M}^{3+} = \text{Fe}$ or Al ($\pm\text{Y}$) and $\text{M}^{2+} = \text{Fe}$ and $0 \leq x \leq 1$.

Anatolyite is the first representative of this structure type in which bivalent cations prevail in both M2 [Mg] and A1 [Ca] sites. The simplified scheme of cation substitutions defining the relationship between yurmarinite and anatolyite can be written as $^{\text{A1}}\text{Na}^{+} + ^{\text{M1}}\text{Fe}^{3+} + ^{\text{M2}}\text{Fe}^{3+} \leftrightarrow ^{\text{A1}}\text{Ca}^{2+} + ^{\text{M1}}\text{Al}^{3+} + ^{\text{M2}}\text{Mg}^{2+}$. 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 A1 site could have led to overbonding at the O4 site, but partial occupancy of the cation site alleviates the issue.

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