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

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Running title: Anatolyite, a new mineral

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, the fracture is uneven. The Mohs' hardness is *ca* 4½. D_{calc} is 3.872 g cm^{-3}. Anatolyite is optically uniaxial (–), ω = 1.703(4), ε = 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* (assignment of constituents to

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positions is in accordance with the structure refinement data) 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*-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, *R* = 4.77%. The structure is based on a 3D heteropolyhedral framework formed by M_4O_{18} clusters [*M*(1) = Al, *M*(2) = (Mg, Fe^{3+})] linked with AsO_4 tetrahedra. (Ca,Na) and Na cations centre *A*(1)O_6 and *A*(2)O_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.

Introduction

In this paper, we continue to characterize 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, thirteen new arsenates from this locality were characterized: yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al*., 2014a), two polymorphs of $Cu_4O(AsO_4)_2$, ericlaxmanite and kozyrevskite (Pekov *et al*., 2014b), popovite $Cu_5O_2(AsO_4)_2$ (Pekov *et al*., 2015a), structurally related shchurovskyite $K_2CaCu_6O_2(AsO_4)_4$ and dmisokolovite $K_3Cu_5AlO_2(AsO_4)_4$ (Pekov *et al*., 2015b), katiarsite $KTiO(AsO_4)$ (Pekov *et al*., 2016a), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (Pekov *et al*., 2016b), pharmazincite $KZnAsO_4$ (Pekov *et al*., 2017), arsenowagnerite $Mg_2(AsO_4)F$ (Pekov *et al*., 2018b), arsenatrotitanite $NaTiO(AsO_4)$ (Pekov *et al*., 2018c), 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*., in press).

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 by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2016–040). 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 the depth of 1.5 m under day surface. The temperature there, 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 the temperature not lower than 420–450ºC. The volcanic gas seems a carrier of As, Na and Fe while the basalt scoria was 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 variety), hematite, tenorite, cassiterite, johillerite, tilasite, ericlaxmanite, lammerite, arsmirandite (IMA2014–081), sylvite, halite, aphthitalite, langbeinite, anhydrite, wulffite, krasheninnikovite, fluoborite, pseudobrookite, and fluorophlogopite.

Anatolyite occurs as clusters (up to 0.3 x 0.5 x 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 (Figure 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, blocky, with rough surfaces (Figure 2). Goniometric measurements were not performed due to small size of anatolyite crystals, however, based on the SEM image (Figure 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}.

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 approximately 4½. Density calculated using the empirical formula is 3.872 g cm^{-3}.

The mineral is optically uniaxial (–), ω = 1.703(4), ε = 1.675(3) (589 nm). In transmitted, plane-polarized light, anatolyite is colourless and non-pleochroic.

Chemical composition

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, Dept. 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.

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.%.

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 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 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). Parameters of hexagonal unit cell 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 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 crystal structure of anatolyite is based on octahedral clusters M_4O_{18} (Figure 3a) consisting of M(1)- and M(2)-centred octahedra. Regular $M(1)O_6$ octahedron, occupied predominantly by Al, shares three edges with three slightly distorted mixed-occupied octahedra $M(2)O_6$ [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 heteropolyhedral framework (Figure 3b); 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: regular $A(1)O_6$ octahedron is partially occupied with predominance of Ca whereas $A(2)O_8$ polyhedron, with distances varying in the range 2.303(6) – 2.910(6) Å, is Na-centred (Table 4). The prevailing 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 bi- 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 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-3c, a = 13.35 – 13.8, c = 18.3 – 18.6 Å for arsenates and a = 13.4, c = 17.85 – 17.9 Å for phosphates). Their general formula is $(Na,□)_7M_4(T^{5+}O_4)_6$, with T = As or P. All the synthetic compounds, as well as yurmarinite, contain trivalent cations (Fe^{3+} or Al) as strongly prevailing in the M sites. However, if the M sites are completely occupied by trivalent cations then 1/7 of Na sites should be vacant, *i.e.*, the general formula of such compounds is $(Na_6□_1)_{\Sigma 7}M^{3+}{}_4(T^{5+}O_4)_6$, or $Na_3M^{3+}{}_2(T^{5+}O_4)_3$. The examples are synthetic II-$Na_3Fe^{3+}{}_2(AsO_4)_3$ (d'Yvoire *et al.*, 1988), $Na_3(Al_{1.89}Y_{0.11})(AsO_4)_3$ (Belam *et al.*, 2000) and $Na_3Fe^{3+}{}_2(PO_4)_3$ (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-$Na_3Fe^{3+}{}_2(AsO_4)_3$ and $Na_3Fe^{3+}{}_2(PO_4)_3$ 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 O(4) 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)-O(4) bonds. Thus, the underbonding is compensated by the bond incidence contribution of the A(2) site. A topologically close structure characterized by monoclinic distortion (space group C2, a = 14.576, b = 13.409, c

= 9.728 Å, β = 96.95º) was reported for α-$Na_3Al_2(AsO_4)_3$, while the high-temperature (> 44ºC) β-$Na_3Al_2(AsO_4)_3$ phase is rhombohedral and isotypic with II-$Na_3Fe^{3+}_2(AsO_4)_3$ (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 $Na_7(Fe^{3+}_3Fe^{2+})(AsO_4)_6$ (Masquelier *et al.*, 1995) and $Na_7(Fe^{3+}_3Fe^{2+})(PO_4)_6$ (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), 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 $^{A(1)}Na^{+} + {}^{M(1)}Fe^{3+} + {}^{M(2)}Fe^{3+} \leftrightarrow {}^{A(1)}Ca^{2+} + {}^{M(1)}Al^{3+} + {}^{M(2)}Mg^{2+}$. 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 O(4) site, but partial occupancy of the cation site alleviates the issue.

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Table 1. Chemical composition of anatolyite.

Constituent	wt. %	Range	Standard deviation	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			

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

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
33	**7.21**	27	7.221	012
4	6.84	4	6.829	110
16	**4.539**	15	4.540	113
27	**4.347**	34	4.342	211

8	4.252	6	4.254	104
9	4.018	10	4.014	122
4	3.951	4	3.943	300
8	3.621	1	3.611	024
20	**3.421**	29	3.414	220
9	3.241	12	3.229	131
31	**3.196**	31	3.192	214
4	3.081	2	3.087	312
11	3.039	11	3.039	006
17	**2.981**	21	2.977	223
100	**2.827**	100	2.826	125
12	2.692	18	2.684	321
10	2.671	7	2.663	134
18	**2.589**	36	2.581	410
13	2.442	18	2.439	315
1	2.410	2	2.407	306
2	2.381	2	2.376	413
2	2.336	3	2.332	324
4	2.289	4	2.290	502
2	2.226	4	2.219	241
1	2.180	2	2.177	235
1	2.077	2	2.069	152
6	1.977	16	1.971	600
7	1.932	6, 13	1.933, 1.926	431, 514
4	1.911	7	1.906	425
7	1.804	2, 4, 8	1.808, 1.805, 1.802	253, 048, 1.0.10
5	1.744	1, 6	1.743, 1.742	0.2.10, 229
8	1.721	20	1.716	345
8	1.690	11	1.688	2.1.10
3	1.659	2, 5	1.661, 1.654	072, 066
4	1.645	3, 7	1.644, 1.641	443, 508
2	1.618	5	1.617	615
3	1.591	1	1.594	419
2	1.581	8	1.584	704
6	1.555	1, 3, 7	1.554, 1.554, 1.552	1.2.11, 158, 4.0.10
2	1.516	1, 3	1.517, 1.513	173, 3.2.10
4	1.500	9	1.496	265
3	1.494	3	1.494	452
2	1.482	2	1.480	3.1.11
5	1.446	1, 8, 5	1.447, 1.442, 1.440	363, 0.5.10, 271
1	1.418	1	1.415	2.3.11
6	1.386	2, 10, 3	1.392, 1.384, 1.384	176, 5.1.10, 259
3	1.373	3, 1, 14	1.377, 1.369, 1.366	274, 182, 550
2	1.349	3, 8	1.353, 1.343	461, 725
2	1.341	3, 1	1.338, 1.338	2.1.13, 366
3	1.332	4, 2	1.330, 1.327	4.3.10, 731
2	1.310	1, 2, 3	1.314, 1.309, 1.306	900, 1.4.12, 449
1	1.292	1, 2, 1	1.295, 1.294, 1.290	0.1.14, 185, 1.3.13

1	1.264	1, 2	1.262, 1.262	283, 3.4.11
2	1.247	5	1.246	556

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

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, *Z*	Trigonal, *R*-3*c*, 6
a, Å	13.6574(10)
c, Å	18.2349(17)
V, Å^3	2945.6(4)
λ (Mo*K*a) (Å), *T* (K)	0.71073, 293(2)
Diffractometer	STOE StadiVari
θ range (°)	2.82–31.72
Crystal size (mm)	0.03 x 0.04 x 0.055
Absorption coefficient μ (mm^{-1})	11.632
h, *k*, *l* range	$-20 \le h \le 6$, $-16 \le k \le 19$, $-24 \le l \le 26$
Reflections collected	14594
Unique reflections, R_{int}	1101, 0.2007
Reflections with $I > 2\sigma(I)$	616
Number of refined parameters	68
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.0000P]$, $P = [\max(F_o)^2 + 2(F_c)^2]/3$
*R*1	0.0477
w$R2_{all}(F^2)$	0.0959
GoF	0.794
$\Delta\rho_{max}/\Delta\rho_{min}$ (э/Å^3)	1.309/-1.394

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

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

*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)	– O(3)	1.900(5) x 6		*A*(1)	– O(4)	2.302(5) x 6	
M(2)	– O(2)	1.972(5) x 2		*A*(2)	– O(4)	2.303(6)	
	– O(1)	2.005(5) x 2			– O(1)	2.555(6)	
	– O(3)	2.121(5) x 2			– O(2)	2.560(6)	
<*M*(2)-O>		2.033			– O(4)	2.646(7)	
					– O(2)	2.652(6)	
As	– O(4)	1.647(6)			– O(4)	2.702(7)	
	– O(2)	1.677(5)			– O(1)	2.874(7)	
	– O(1)	1.681(5)			– O(1)	2.910(6)	
	– O(3)	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**
O(1)		0.13		$0.43^{x2\downarrow}$	1.26	**1.92**
		0.05				
		0.05				
O(2)		0.13		$0.47^{x2\downarrow}$	1.28	**1.98**
		0.10				
O(3)			$0.53^{x6\downarrow}$	$0.31^{x2\downarrow}$	1.15	**1.99**
O(4)	$0.32^{x6\downarrow}$	0.26			1.38	**2.15**
		0.10				
		0.09				
Σ	**1.92**	**0.91**	**3.18**	**2.42**	**5.07**	

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

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*-3*c*	Trigonal *R*-3*c*
a, Å *c*, Å *V*, Å^3 *Z*	13.7444 (2) 18.3077 (3) 2995.1 (2) 6	13.6574 (10) 18.2349 (17) 2945.6 (4) 6
$D_{calc.}$, g cm^{-3}	4.00	3.87
Prevailing cations in *A* and *M* sites in structure* *A*(1) [6b] *A*(2) [36f] *M*(1) [6a] *M*(2) [18e]	 Na Na Fe^{3+} Fe^{3+}	 Ca Na Al 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 ε	Uniaxial (–) 1.748 1.720	Uniaxial (–) 1.703 1.675
Source	Pekov *et al*., 2014a	this work

*Wyckoff site symbols are given in square brackets.

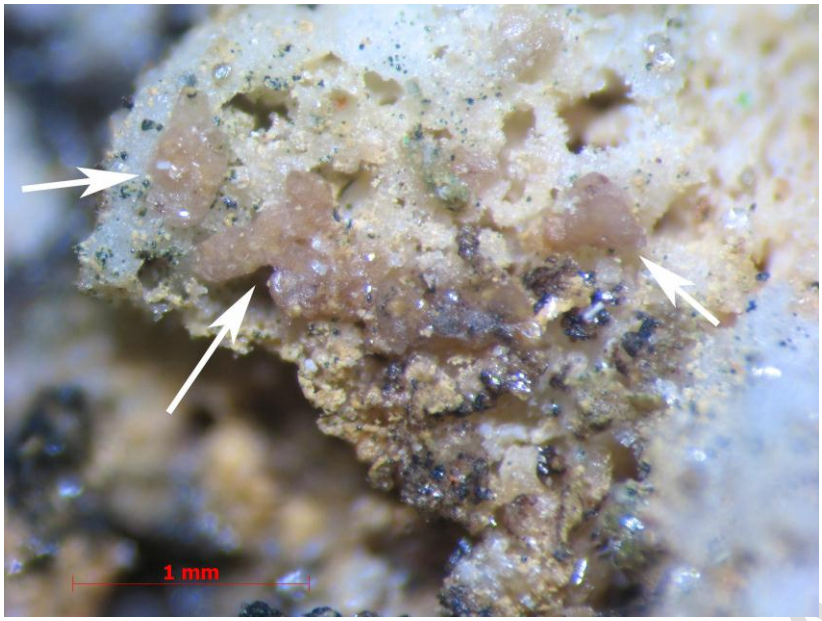


Figure 1. Clusters of pale brownish-pinkish crystals of anatolyite (marked by arrows) with iron-black hematite on a crust of As-bearing potassic feldspar covering surface of basalt scoria altered by fumarolic gas. FOV width: 3.6 mm. Photo: I.V. Pekov & A.V. Kasatkin.

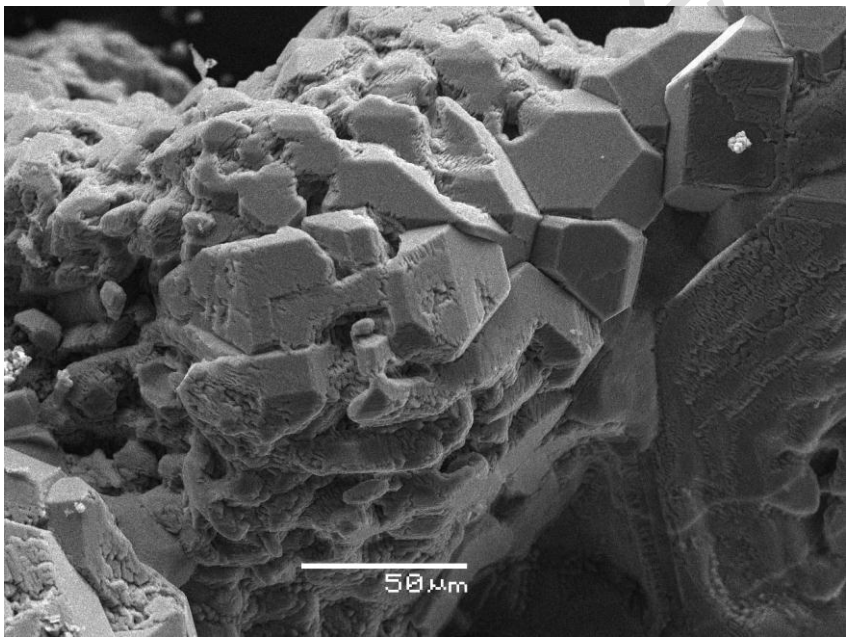
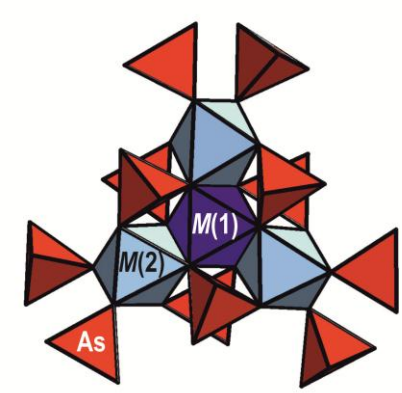
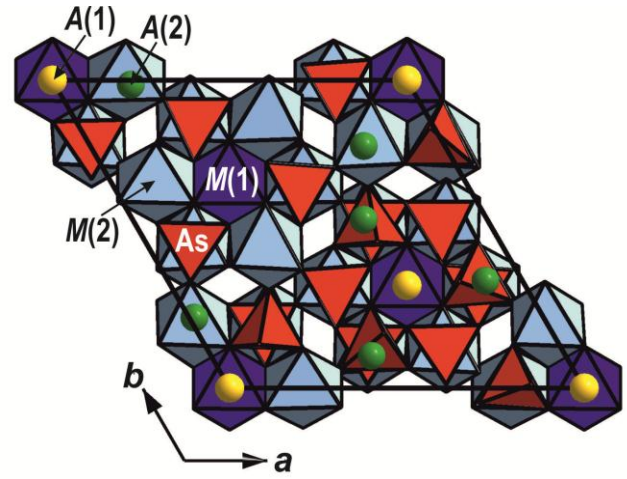


Figure 2. Crystals of anatolyite forming a crust on the surface of dense cluster of the same mineral. SEM (SE) image.



a



b

Figure 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.