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Article

New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IX. Arsenatrotitanite, NaTiO(AsO$_4$)

Igor V. Pekov[1]*, Natalia V. Zubkova[1], Atali A. Agakhanov[2], Dmitry I. Belakovskiy[2], Marina F. Vigasina[1],

Vasiliy O. Yapaskurt[1], Evgeny G. Sidorov[3], Sergey N. Britvin[4] and Dmitry Y. Pushcharovsky[1]

[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]Institute of Volcanology and Seismology, Far Eastern Branch of the Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia; and [4]Department of Crystallography, St Petersburg State University, University Embankment 7/9, 199034 St Petersburg, Russia

Abstract

The new durangite-group mineral arsenatrotitanite, ideally NaTiO(AsO$_4$), was found in the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with orthoclase, tenorite, hematite, johillerite, bradaczekite, badalovite, calciojohillerite, arsmirandite, tilasite, svabite, cassiterite, pseudobrookite, rutile, sylvite, halite, aphthitalite, langbeinite and anhydrite. Arsenatrotitanite occurs as prismatic, tabular, lamellar or acicular crystals up to 0.3 mm × 0.8 mm × 2 mm. They are separated or combined in open-work aggregates up to 2 mm across or interrupted crusts up to 2 mm × 5 mm in area and up to 0.3 mm thick. Arsenatrotitanite is transparent, brownish red to pale pinkish-reddish or almost colourless, with vitreous lustre. It is brittle and the Mohs' hardness is ∼5½. Cleavage is perfect on {110} and the fracture is stepped. D_{calc} is 3.950 g cm^{-3}. Arsenatrotitanite is optically biaxial (+), α = 1.825(5), β = 1.847(6), γ = 1.896(6) (589 nm) and 2V$_{meas.}$ = 70(5)°. Chemical composition (wt.%, electron-microprobe) is: Na$_2$O 12.26, CaO 3.10, Al$_2$O$_3$ 4.39, Fe$_2$O$_3$ 9.57, TiO$_2$ 17.11, SnO$_2$ 1.03, As$_2$O$_5$ 50.17, F 3.29, O = F −2.39, total 99.53. The empirical formula based on 5 (O + F) apfu is (Na$_{0.91}$Ca$_{0.13}$)$_{\Sigma1.04}$(Ti$_{0.49}$Fe$^{3+}_{0.27}$Al$_{0.20}$Sn$_{0.02}$)$_{\Sigma0.98}$(As$_{1.00}$O$_{4.00}$)(O$_{0.60}$F$_{0.40}$). Arsenatrotitanite is monoclinic, C2/c, a = 6.6979(3), b = 8.7630(3), c = 7.1976(3) Å, β = 114.805(5)°, V = 383.48(3) Å^3 and Z = 4. The strongest reflections of the powder X-ray diffraction (XRD) pattern [d,Å(I)(hkl)] are: 4.845(89)($\bar{1}$11), 3.631(36)(021), 3.431(48)(111), 3.300(100)($\bar{1}$12), 3.036(100)(200), 2.627(91)(130) and 2.615(57)(022). The crystal structure was solved from single-crystal XRD data with R = 1.76%. Arsenatrotitanite belongs to the titanite/durangite structure type. It is named as an *arsenat*e of sodium (*natr*ium in Latin) and *titani*um isostructural with *titanite*.

Introduction

This paper continues a series of articles on new arsenate minerals from 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). This active fumarole, discovered by us in July 2012, has already given rise to the new arsenates: yurmarinite Na$_7$(Fe^{3+}, Mg,Cu)$_4$(AsO$_4$)$_6$ (Pekov *et al.*, 2014*a*); two polymorphs of Cu$_4$O (AsO$_4$)$_2$, ericlaxmanite and kozyrevskite (Pekov *et al.*, 2014*b*); popovite Cu$_5$O$_2$(AsO$_4$)$_2$ (Pekov *et al.*, 2015*a*); structurally related shchurovskyite K$_2$CaCu$_6$O$_2$(AsO$_4$)$_4$ and dmisokolovite K$_3$Cu$_5$AlO$_2$(AsO$_4$)$_4$ (Pekov *et al.*, 2015*b*); katiarsite KTiO(AsO$_4$)

(Pekov *et al.*, 2016*a*); melanarsite K$_3$Cu$_7$Fe^{3+}O$_4$(AsO$_4$)$_4$ (Pekov *et al.*, 2016*b*); pharmazincite KZnAsO$_4$ (Pekov *et al.*, 2017); and arsenowagnerite Mg$_2$(AsO$_4$)F (Pekov *et al.*, 2018*a*). The general description of this fumarole and data on the distribution of arsenate mineralisation within it are given by Pekov *et al.* (2014*a*, 2018*b*).

The present paper is devoted to the new mineral arsenatrotitanite, ideally NaTiO(AsO$_4$) (Cyrillic: арсенатротитанит). It is named as an *arsenat*e of sodium (*natr*ium in Latin) and *titani*um isostructural with *titanite*. Both the new mineral and its name have been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA2016–015). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 95614.

Occurrence and general appearance

Specimens with the new mineral were collected by us in July 2015 from two pockets in the northern area of the Arsenatnaya
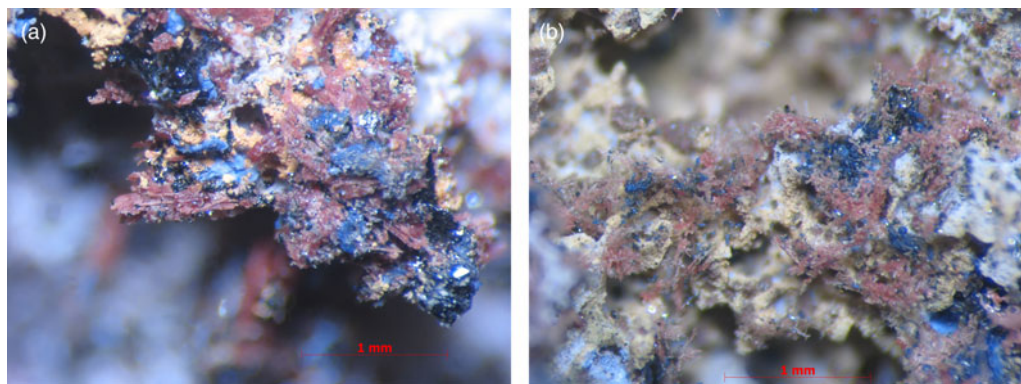
*Author for correspondence: Igor Pekov, Email: igorpekov@mail.ru

Fig. 1. Brownish red to pale pinkish–reddish crystals and their aggregates of arsenatrotitanite with blue johillerite, black tenorite and yellowish fine-grained cassiterite (the latter is visible in (*a*) on white to pale beige crusts of As-bearing orthoclase). Field of view width is 3.5 mm for both images. Photo: I.V. Pekov & A.V. Kasatkin.

fumarole, at the depth of 1–1.5 m under day surface. Temperatures measured using a chromel–alumel thermocouple at the time of collecting in these pockets were 400–420°C. Arsenatrotitanite was deposited directly from the gas phase as a volcanic sublimate or, more likely, formed as a result of the interaction between fumarolic gas and basalt scoria at temperatures not lower than 420–450°C. The basalt scoria seems the most probable source of Ti which has low volatility in volcanic gases, as both thermodynamic calculations (Churakov *et al.*, 2000) and direct measurements carried out for gases present at Tolbachik (Zelenski *et al.*, 2014) show.

Arsenatrotitanite is a minor component of fumarolic encrustations mainly consisting of arsenates, sulfates, oxides, chlorides and silicates. The new mineral is associated closely with orthoclase (As-bearing variety), tenorite, hematite, johillerite, bradaczekite, badalovite (IMA2016–053), calciojohillerite (IMA2016–068), arsmirandite (IMA2014–081), tilasite, svabite, cassiterite, pseudobrookite, rutile, sylvite, halite, aphthitalite, langbeinite and anhydrite.

Arsenatrotitanite occurs as prismatic, tabular or lamellar crystals up to 0.3 mm × 0.8 mm × 2 mm, typically coarse (Fig. 1*a*) and sometimes divergent. They are separate, or combined in open-work aggregates, or interrupted crusts up to 2 mm × 5 mm in area and up to 0.3 mm thick. Crude acicular crystals up to 0.7 mm long form chaotic open-work aggregates up to 2 mm across in cavities (Fig. 1*b*). Well-shaped crystals are small, usually not bigger than 0.01 mm, rarely up to 0.05 mm. They are flattened, wedge-shaped, more rarely multifaceted (Figs 2*a–c*), sometimes skeletal (Fig. 2*c*). Dendrite-like aggregates are common (Figs 2*a* and 2*d*). Arsenatrotitanite overgrows, in close association with johillerite, bradaczekite, tenorite, cassiterite and hematite, incrustations mainly consisting of As-bearing orthoclase that cover basalt scoria altered by fumarolic gas.

Physical properties and optical data

Arsenatrotitanite is transparent, brownish red to pale pinkish–reddish with brown hue or, in the thinnest needles, almost colourless. Its streak is white and its lustre is vitreous. The mineral is brittle. Cleavage is perfect on {110}, the fracture is stepped (observed under the microscope). The Mohs' hardness is *ca* 5½. Density could not be measured because of the small size of crystals without caverns and the open-work character of aggregates

(Fig. 2). Density calculated using its empirical formula is 3.950 g cm^{-3}.

Arsenatrotitanite is optically biaxial (+) with $\alpha = 1.825(5)$, $\beta = 1.847(6)$, $\gamma = 1.896(6)$ (589 nm), $2V_{meas} = 70(5)°$ and $2V_{calc} = 69°$. Other optical data are: dispersion of optical axes is strong, $r > v$; optical orientation: $Y = b$; pleochroism is strong: Z (bright pink to, in thicker grains, carmine red) $> Y$ (very pale pinkish to almost colourless) $\geq X$ (colourless).

Raman spectroscopy

The Raman spectrum of arsenatrotitanite (Fig. 3) was obtained on a randomly oriented crystal using an EnSpectr R532 instrument (Department of Mineralogy, Moscow State University) with a green laser (532 nm) at room temperature. The output power of the laser beam was ~16 mW. The spectrum was processed using the *EnSpectr* expert mode program in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 lines cm^{-1} and a resolution of 6 cm^{-1}. The diameter of the focal spot on the sample was ~10 μm. The back-scattered Raman signal was collected with 40x objective; signal acquisition time for a single scan of the spectral range was 1500 ms and the signal was averaged over 10 scans.

The most intense bands with maxima at 878 and 801 cm^{-1} correspond to As^{5+}–O stretching vibrations of AsO$_4^{3-}$ anions. Bands with frequencies lower than 700 cm^{-1} correspond to bending vibrations of AsO$_4$ tetrahedra, Ti^{4+}–O, Fe^{3+}–O and Al–O stretching vibrations and lattice modes. The absence of bands with frequencies higher than 950 cm^{-1} indicates the absence of groups with O–H, C–H, C–O, N–H, N–O and B–O bonds in the mineral.

Chemical composition

The chemical composition of arsenatrotitanite was determined on 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 3 μm beam diameter. The following standards were used: albite (Na), wollastonite (Ca), Al$_2$O$_3$ (Al), magnetite (Fe), ilmenite (Ti), SnO$_2$ (Sn), InAs (As) and fluorophlogopite (F).
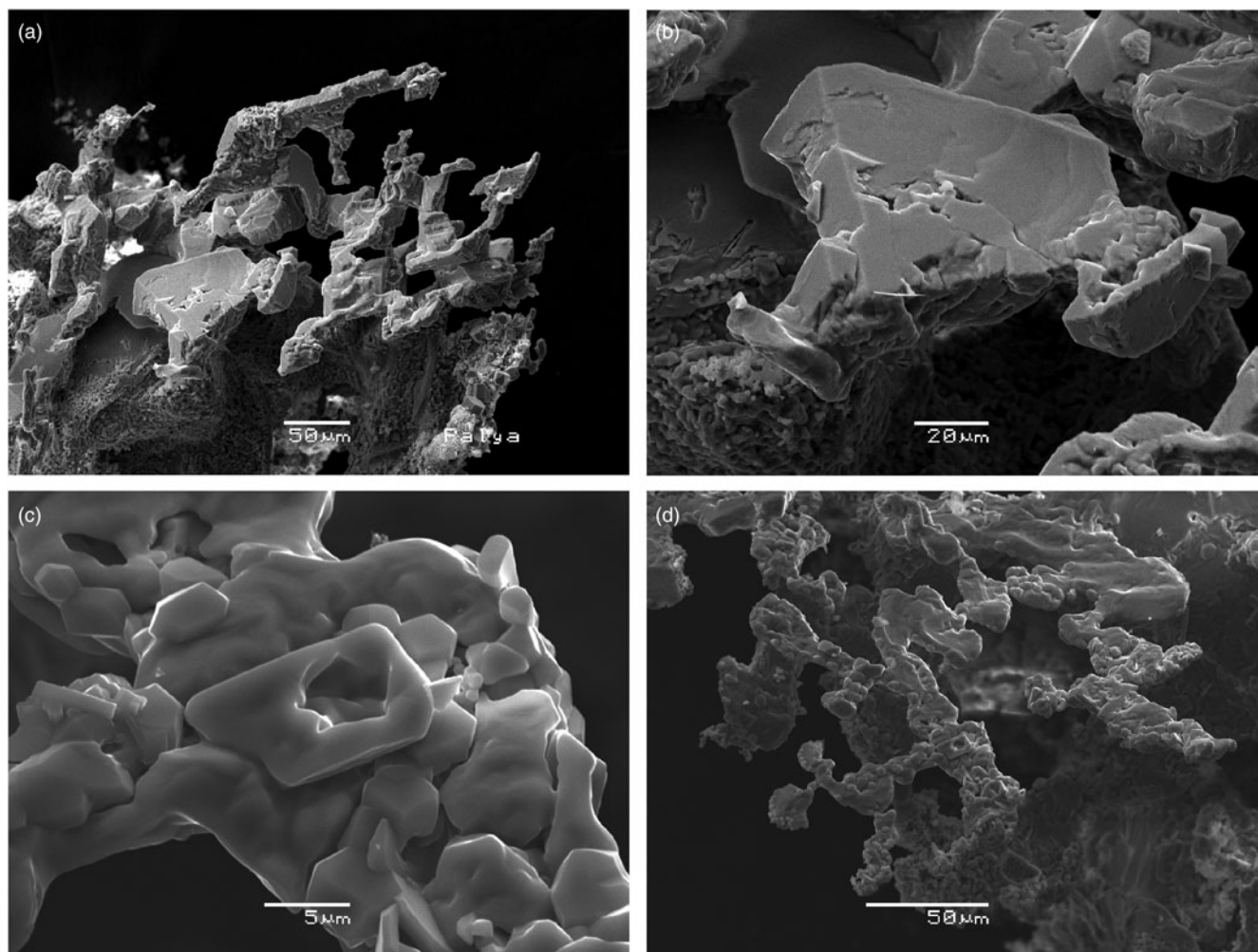
Fig. 2. Crystals and aggregates of arsenatrotitanite. Secondary electron images from scanning electron microscopy.
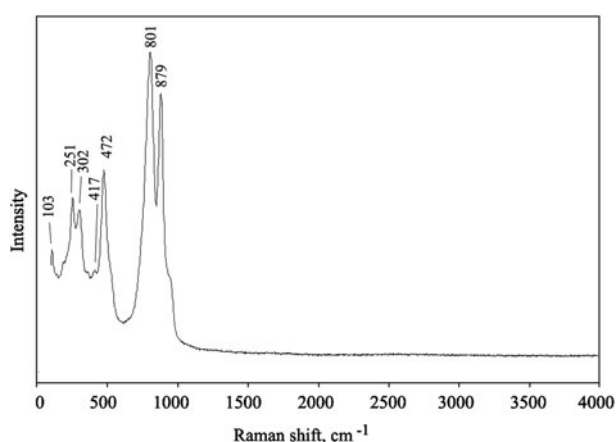

Fig. 3. The Raman spectrum of arsenatrotitanite.

The chemical composition of arsenatrotitanite (average of 6 spot analyses; wt.%, ranges are in parentheses / standard deviation) is: Na_2O 12.26 (11.95–12.84 / 0.30), CaO 3.10 (2.97–3.29 / 0.11), Al_2O_3 4.39 (3.97–4.55 / 0.22), Fe_2O_3 9.57 (9.06–10.11 / 0.44), TiO_2 17.11 (16.81–17.29 / 0.26), SnO_2 1.03 (0.91–1.30 / 0.15), As_2O_5 50.17 (49.48–51.14 / 0.71), F 3.29 (3.21–3.41 / 0.09), O = F −2.39, total 99.53. Contents of other elements with atomic numbers higher than carbon are below detection limits. Fe is calculated as Fe^{3+} taking into account strongly oxidising conditions of mineral formation in the Arsenatnaya fumarole: only minerals of trivalent iron are found there (Pekov *et al.*, 2014*a*, 2018*b*).

The empirical formula calculated on the basis of 5 (O + F) atoms per formula unit is $Na_{0.91}Ca_{0.13}Al_{0.20}Fe^{3+}_{0.27}Ti_{0.49}Sn_{0.02}$ $As_{1.00}O_{4.60}F_{0.40}$ or, after grouping of constituents by structure positions: $(Na_{0.91}Ca_{0.13})_{\Sigma1.04}(Ti_{0.49}Fe^{3+}_{0.27}Al_{0.20}Sn_{0.02})_{\Sigma0.98}(As_{1.00}O_{4.00})$ $(O_{0.60}F_{0.40})$. The simplified, end-member formula is $NaTi(AsO_4)O$, which requires Na_2O 13.72, TiO_2 35.38, As_2O_5 50.90, total 100.00 wt%.

X-ray crystallography and crystal structure

Powder XRD data of arsenatrotitanite (Table 1) 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, CoKα 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). The parameters of the monoclinic

Table 1. Powder XRD data (*d* in Å) of arsenatrotitanite.

I_{obs}	I_{calc}*	d_{obs}	d_{calc}**	*h k l*
12	7	4.981	4.995	1 1 0
89	**85**	**4.845**	**4.858**	**$\bar{1}$ 1 1**
2	2	4.371	4.382	0 2 0
36	**35**	**3.631**	**3.639**	**0 2 1**
48	**47**	**3.431**	**3.438**	**1 1 1**
100	**100**	**3.300**	**3.305**	**$\bar{1}$ 1 2**
19	16	3.262	3.267	0 0 2
100	**97**	**3.036**	**3.040**	**2 0 0**
23	22	2.914	2.918	$\bar{2}$ 0 2
25	24	2.655	2.659	$\bar{2}$ 2 1
91	**92**	**2.627**	**2.633**	**1 3 0**
57	**64**	**2.615**	**2.619**	**0 2 2**
7	6	2.494	2.498	2 2 0
10	11	2.427	2.429	$\bar{2}$ 2 2
5	6	2.381	2.383	1 1 2
23	26	2.299	2.301	1 3 1
12	17	2.258	2.260	$\bar{1}$ 3 2
3	2	2.189	2.191	4 0
16	20	2.114	2.115	$\bar{3}$ 1 2
12	16	2.022	2.023	$\bar{2}$ 2 3
4	4	1.973	1.975	3 1 0
2	4	1.949	1.950	2 3
4	5	1.898	1.899	$\bar{3}$ 1 3
6	7	1.888	1.889	1 3 2
7	10	1.867	1.869	2 0 2
3	4	1.832	1.833	$\bar{2}$ 4 1
5	8	1.819	1.819	0 4 2
16	20	1.784	1.784	$\bar{2}$ 0 4
2	3	1.765	1.766	$\bar{3}$ 3 1
10	11, 10	1.748	1.752, 1.747	$\bar{2}$ 4 2, $\bar{3}$ 3 2
17	27	1.718	1.719	2 2 2
4	4	1.706	1.707	3 1 1
24	40	1.664	1.665	3 3 0
5	9	1.633	1.633	0 0 4
2	3	1.617	1.617	2 4 1
2	2, 2	1.586	1.587, 1.580	1 5 1, $\bar{2}$ 4 3
11	26	1.572	1.573	$\bar{1}$ 5 2
7	14	1.562	1.562	$\bar{4}$ 2 2
5	2, 9	1.544	1.546, 1.545	1 3 3, 0 4 3
1	2	1.536	1.536	$\bar{4}$ 2 1
17	11, 30	1.518	1.520, 1.517	4 0 0, $\bar{1}$ 3 4
1	2	1.494	1.495	3 3 1
12	5, 20	1.460	1.461, 1.459	0 6 0, $\bar{4}$ 0 4
6	8	1.448	1.448	3 1 2
8	15	1.441	1.440	$\bar{3}$ 3 4
9	17	1.430	1.431	1 5 2
3	2, 3	1.418	1.422, 1.417	2 4 2, 2 2 3
2	2	1.387	1.387	$\bar{1}$ 1 5
4	5	1.380	1.380	$\bar{3}$ 1 5
7	21	1.366	1.366	$\bar{3}$ 5 2
2	4	1.337	1.338	$\bar{2}$ 6 1
2	2, 3	1.331	1.333, 1.329	0 6 2, $\bar{4}$ 4 2
3	4	1.326	1.326	3 5 0
3	2	1.323	1.322	$\bar{5}$ 1 2
7	14, 6	1.315	1.316, 1.313	2 6 0, $\bar{4}$ 4 1
2	4	1.299	1.299	4 2 1
5	17	1.288	1.287	1 3 4
1	4	1.253	1.252	0 2 5
2	4	1.248	1.247	$\bar{1}$ 5 4
4	3, 10	1.239	1.242, 1.238	$\bar{4}$ 2 5, 2 0 4

*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.

unit cell calculated from the powder data are: $a = 6.699(3)$, $b = 8.756(2)$, $c = 7.203(3)$ Å, $\beta = 114.81(3)°$ and $V = 383.5(3)$ Å^3.

Single-crystal X-ray studies of arsenatrotitanite were carried out using an Xcalibur S diffractometer equipped with a CCD

Table 2. Crystal data, data collection information and structure refinement details for arsenatrotitanite.

Crystal data	
Formula	$(Na_{0.9}Ca_{0.1})(Ti_{0.5}Fe^{3+}_{0.3}Al_{0.2})(O_{0.6}F_{0.4})AsO_4$
Crystal dimensions (mm)	0.06 × 0.10 × 0.14
Crystal system, space group, Z	Monoclinic, C2/c, 4
Temperature (K)	293(2)
a, *b*, *c* (Å)	6.6979(3), 8.7630(3), 7.1976(3)
β (°)	114.805(5)
V (Å^3)	383.48(3)
Absorption coefficient μ (mm^{-1})	11.105
Formula weight	226.92
Data collection	
Diffractometer	Xcalibur S CCD
Radiation, wavelength (Å)	Mo$K\alpha$, 0.71073
F_{000}	427
θ range for data collection (°)	4.08–30.51
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3420, 591, 583
R_{int}	0.0332
Index ranges for *h*, *k*, *l*	$-9 \le h \le 9$, $-12 \le k \le 12$, $-10 \le l \le 10$
Refinement	
Data reduction	*CrysAlisPro*, version 1.171.37.35 (Agilent Technologies, 2014)
Absorption correction	Gaussian [Numerical absorption correction based on Gaussian integration over a multifaceted crystal model]
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Number of refined parameters	43
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0176$, w$R_2 = 0.0450$
R indices (all data)	$R_1 = 0.0180$, w$R_2 = 0.0452$
GoF	1.142
$\Delta\rho_{max}$, $\Delta\rho_{min}$, (e$^-$/Å^3)	0.70 and −0.59

detector. The crystal structure was solved by direct methods and refined with the use of the *SHELX-97* software package (Sheldrick, 2008) to $R = 0.0176$. The refined numbers of electrons (e_{ref}) for *A* (Na scattering curve), *M* (Ti scattering curve) and (O,F) (O scattering curve) sites were obtained using low-angle reflections and gave the following values: 11.66, 22.22 and 8.88, respectively. The cation distribution [$A = Na_{0.9}Ca_{0.1}$ ($e_{calc} = 11.90$), $M = Ti_{0.5}Fe_{0.3}Al_{0.2}$ ($e_{calc} = 21.40$) and (O,F) $= O_{0.6}F_{0.4}$ ($e_{calc} = 8.40$)] was performed in accordance with both refined numbers of electrons and chemical data. We should note that e_{calc} for the *M* site could be increased due to the Sn admixture, which was not involved in the refinement because of its minor amount. The unit-cell dimensions and the experimental details are presented in Table 2, atom coordinates and displacement parameters in Table 3, selected interatomic distances in Table 4 and bond-valence calculations in Table 5. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Arsenatrotitanite is a representative of the well-known titanite structure type. The crystal structure of the new mineral (Fig. 4) contains infinite chains of the $MO_4(O,F)_2$ (*M* = Ti, Fe or Al) octahedra running along the *c* axis and connected with each other *via* common vertices. Adjacent chains are linked by isolated AsO_4 tetrahedra forming a heteropolyhedral framework with cavities occupied by the *A* cations (*A* = Na and Ca) in seven-fold coordination. The location of admixed F in the (O,F) site on the bridge between the *M*-centred octahedra is confirmed by bond-valence calculations (Table 5).

Table 3. Coordinates, site multiplicites (Q), site occupancy factors (s.o.f.), and equivalent and anisotropic displacement parameters (U_{eq}, in Å^2) of atoms for arsenatrotitanite.

Site	Q	x	y	z	s.o.f.*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
A	4	½	0.17210(14)	¼	$Na_{0.9}Ca_{0.1}$	0.0193(3)	0.0121(6)	0.0092(5)	0.0310(7)	0.000	0.0035(5)	0.000
M	4	0.0	0.0	0.0	$Ti_{0.5}Fe_{0.3}Al_{0.2}$	0.01061(14)	0.0049(2)	0.0067(3)	0.0174(3)	−0.00524(18)	0.0019(2)	0.00045(17)
As	4	0.0	0.31664(3)	¼	1	0.00631(11)	0.00564(16)	0.00619(16)	0.00670(16)	0.000	0.00219(11)	0.000
O1	8	0.1901(3)	0.43415(18)	0.4163(2)	1	0.0117(3)	0.0088(7)	0.0121(7)	0.0120(7)	−0.0044(6)	0.0023(6)	−0.0028(6)
O2	8	0.1047(3)	0.20862(17)	0.1184(2)	1	0.0102(3)	0.0106(7)	0.0096(7)	0.0125(7)	−0.0024(5)	0.0068(6)	−0.0005(5)
(O,F)	4	0.0	0.0684(2)	¾	$O_{0.6}F_{0.4}$	0.0105(4)	0.0123(9)	0.0100(9)	0.0093(9)	0.000	0.0048(7)	0.000

*Site occupancy factors for the A, M and (O,F) sites were fixed on the last stages of the refinement in accordance to both refined numbers of electrons and chemical data.

Table 4. Selected interatomic distances (Å) in the structure of arsenatrotitanite.

A–(O,F)	2.274(2)		As–O1	1.6840(15)	×2
A–O2	2.4304(16)	×2	As–O2	1.6858(15)	×2
A–O1	2.4746(19)	×2	<As–O>	1.685
A–O2	2.6561(16)	×2			
<A–O>	2.485				
M–(O,F)	1.8966(6)	×2			
M–O1	1.9886(15)	×2			
M–O2	2.0145(15)	×2			
<M–O>	1.967				

Table 5. Bond-valence calculations for arsenatrotitanite.

	A	M	As	Σ
O1	0.16 $^{×2↓}$	0.54 $^{×2↓}$	1.26 $^{×2↓}$	1.96
O2	0.19 $^{×2↓}$, 0.09 $^{×2↓}$	0.51 $^{×2↓}$	1.25 $^{×2↓}$	2.04
(O,F)	0.27	0.70 $^{×2↓×2→}$		1.67
Σ	1.15	3.50	5.02	

Bond-valence parameters are taken from Gagné and Hawthorne (2015). All calculations were weighted according to site occupancies given in Table 3.

Discussion

Arsenatrotitanite, ideally $NaTiO(AsO_4)$, is isostructural with minerals of the durangite group [isokite $CaMg(PO_4)F$, lacroixite $NaAl(PO_4)F$, panasqueiraite $Ca(Mg,Fe)(PO_4)(OH,F)$, durangite $NaAl(AsO_4)F$, maxwellite $NaFe^{3+}(AsO_4)F$, tilasite $CaMg(AsO_4)$ F, and kononovite $NaMg(SO_4)F$] and of the titanite group [titanite $CaTiO(SiO_4)$, natrotitanite $(Na_{0.5}Y_{0.5})TiO(SiO_4)$, malayaite $CaSnO(SiO_4)$, and vanadomalayaite $CaVO(SiO_4)$] (Back, 2018). Arsenatrotitanite combines chemical features of members of both groups: it is an arsenate, like durangite-group minerals, and, like representatives of the titanite group, contains tetravalent cation (Ti^{4+}) and additional anion $O^{2−}$ as species-defining components. Comparison of the new mineral with closely related species is given in Table 6. We propose placing arsenatrotitanite into the durangite group rather than the titanite group for three reasons: (1) the titanite group traditionally includes only silicates; (2) in the powder XRD data the new mineral is much closer to durangite-group arsenates than to the silicate titanite (Table 5); and (3) arsenatrotitanite contains significant admixtures of Fe, Al, and F and in fact belongs to the solid-solution system with the end-members $NaTiO(AsO_4)$ – $NaFe^{3+}(AsO_4)F$ (maxwellite) – $NaAl(AsO_4)F$ (durangite). This solid-solution system which also involves tilasite $CaMg(AsO_4)F$ and kononovite $NaMg(SO_4)F$ was discussed, based on data for samples from fumarole deposits, by Pekov *et al.* (2018*b*).
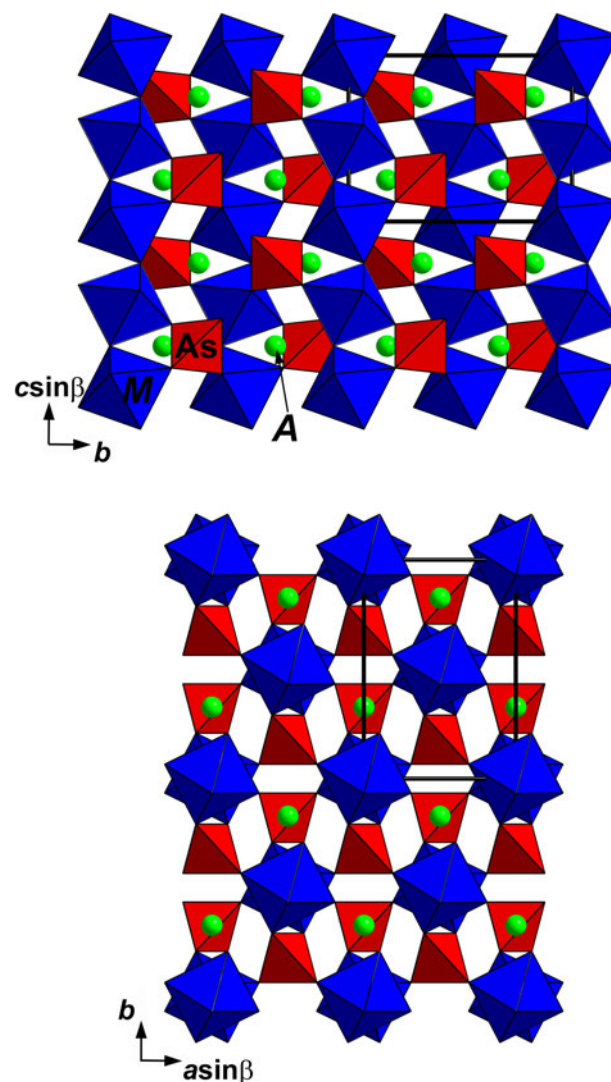
Fig. 4. The crystal structure of arsenatrotitanite in two projections; M = (Ti, Fe and Al), A = (Na and Ca): see Table 3. The unit cell is outlined.

The end-member arsenatrotitanite can be considered as a natural analogue of synthetic $NaTiO(AsO_4)$ reported by Yahia *et al.* (2010).

Arsenatrotitanite has a chemical analogue with K instead of Na, katiarsite $KTiO(AsO_4)$, discovered in the same Arsenatnaya fumarole. However, they are quite different in terms of crystal structure: katiarsite is a representative of the $KTiO(PO_4)$ (KTP) structure type (Pekov *et al.*, 2016*a*).

Table 6. Comparative data for arsenatrotitanite and closely related minerals.

Mineral	Arsenatrotitanite	Maxwellite	Durangite	Titanite
Ideal formula	$NaTiO(AsO_4)$	$NaFe^{3+}(AsO_4)F$	$NaAl(AsO_4)F$	$CaTiO(SiO_4)$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a (Å)	6.698	6.667	6.57–6.58	6.56
b (Å)	8.763	8.781	8.50–8.52	8.71
c (Å)	7.198	7.134	7.02–7.05	7.06
β (°)	114.81	114.50	115.3–115.5	113.8
V (Å^3)	383.5	380.0	355–357	369
Z	4	4	4	4
Strongest reflections	4.845–89	4.844–70	4.76–80	3.233–100
of the powder XRD	3.631–36	3.642–35	3.54–40	2.989–90
pattern:	3.431–48	3.437–35	3.34–50	2.595–90
d (Å) – I	3.300–100	3.290–100	3.237–80	2.058–40
	3.036–100	3.039–75	2.970–100	1.643–40
	2.627–91	2.637–50	2.563–60	1.494–40
	2.615–57	2.614–80	2.549–57	1.418–40
Optical data	Biaxial	Biaxial	Biaxial	Biaxial
α	1.825	1.748	1.597–1.634	1.843–1.950
β	1.847	1.772	1.636–1.663	1.870–2.034
γ	1.896	1.798	1.647–1.685	1.943–2.110
Optical sign, 2V	(+) 70°	(+) 86°	(–) 68–85°	(+) 17–40°
Source	This work	Foord *et al.* (1991); Cooper and Hawthorne (1995)	Foord *et al.* (1985)	Anthony *et al.* (1995)

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