

# New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. VIII. Arsenowagnerite, $Mg_2(AsO_4)F$

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## ABSTRACT

A new mineral arsenowagnerite,  $Mg_2(AsO_4)F$ , the arsenate analogue of wagnerite, was found in sublimates of 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 closely with johillerite, tilasite, anhydrite, hematite, fluorophlogopite, cassiterite, calciojohillerite, apthitalite and fluoborite. Arsenowagnerite occurs as equant to tabular crystals up to 1 mm across combined in interrupted crusts up to 0.1 cm × 1.5 cm × 3 cm. The mineral is transparent, light yellow, lemon-yellow, greenish-yellow or colourless and has a vitreous lustre. Arsenowagnerite is brittle, with Mohs hardness of ~5. Cleavage is distinct, the fracture is uneven.  $D_{\text{calc}} = 3.70 \text{ g cm}^{-3}$ . Arsenowagnerite is optically biaxial (+),  $\alpha = 1.614(2)$ ,  $\beta = 1.615(2)$ ,  $\gamma = 1.640(2)$  and  $2V_{\text{meas}} = 25(5)^\circ$ . Wavenumbers of the strongest absorption bands in the IR spectrum ( $\text{cm}^{-1}$ ) are: 874, 861, 507, 491 and 470. The chemical composition (average of six electron-microprobe analyses, wt. %) is: MgO 38.72, CaO 0.23, MnO 0.32, CuO 0.60, ZnO 0.05,  $Fe_2O_3$  0.11,  $TiO_2$  0.03,  $SiO_2$  0.08,  $P_2O_5$  0.18,  $V_2O_5$  0.03,  $As_2O_5$  54.96,  $SO_3$  0.10, F 8.91 and  $-O=F -3.75$ , total 100.57. The empirical formula calculated on the basis of 5 (O + F) apfu is:  $(Mg_{1.98}Cu_{0.02}Mn_{0.01}Ca_{0.01})_{\Sigma 2.02}(As_{0.99}P_{0.01})_{\Sigma 1.00}O_{4.03}F_{0.97}$ . Arsenowagnerite is monoclinic,  $P2_1/c$ ,  $a = 9.8638(3)$ ,  $b = 12.9830(3)$ ,  $c = 12.3284(3)$  Å,  $\beta = 109.291(3)^\circ$ ,  $V = 1490.15(7)$  Å<sup>3</sup> and  $Z = 16$ . The strongest reflections of the powder X-ray diffraction pattern [ $d, \text{Å}(I)(hkl)$ ] are: 5.80(41)(002), 5.31(35)(120), 3.916(37)(221), 3.339(98)(221, 023), 3.155(65)(202), 3.043(100)( $\bar{1}41$ ), 2.940(72)(204), 2.879(34)(322) and 2.787(51)(320,  $\bar{1}24$ ). The crystal structure was solved from single-crystal X-ray diffraction data,  $R = 0.0485$ . Arsenowagnerite is isostructural to wagnerite- $Ma2bc$ . The crystal structure is built by almost regular  $AsO_4$  tetrahedra, distorted  $MgO_4F_2$  octahedra and distorted  $MgO_4F$  trigonal bipyramids.

**KEYWORDS:** arsenowagnerite, new mineral, magnesium fluoroarsenate, triplite group, wagnerite- $Ma2bc$ , crystal structure, fumarole sublimate, Tolbachik volcano, Kamchatka.

## 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

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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, is described in general in the first paper devoted to yurmarinite  $\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$  (Pekov *et al.*, 2014a). In other articles the following mineral species were characterized: two polymorphs of  $\text{Cu}_4\text{O}(\text{AsO}_4)_2$ , ericlxmanite and kozyrevskite (Pekov *et al.*, 2014b), popovite  $\text{Cu}_5\text{O}_2(\text{AsO}_4)_2$  (Pekov *et al.*, 2015a), structurally related shchurovskyite  $\text{K}_2\text{CaCu}_6\text{O}_2(\text{AsO}_4)_4$  and dmisokolovite  $\text{K}_3\text{Cu}_5\text{AlO}_2(\text{AsO}_4)_4$  (Pekov *et al.*, 2015b), katiarsite  $\text{KTiO}(\text{AsO}_4)$  (Pekov *et al.*, 2016a), melanarsite  $\text{K}_3\text{Cu}_7\text{Fe}^{3+}\text{O}_4(\text{AsO}_4)_4$  (Pekov *et al.*, 2016b) and pharmazincite  $\text{KZnAsO}_4$  (Pekov *et al.*, 2017).

This paper is devoted to the new mineral arsenowagnerite  $\text{Mg}_2(\text{AsO}_4)\text{F}$  (Cyrillic: арсеновагнерит). It is named as an arsenate analogue of wagnerite  $\text{Mg}_2(\text{PO}_4)\text{F}$ . Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA2014–100). The type specimen is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, under the catalogue number 95000.

## Occurrence and general appearance

The first specimen of the new mineral that became the holotype was found by us in July 2014. During fieldwork in 2015 and 2016 we collected more material that gave additional information on the morphology and mineral association of arsenowagnerite.

In the holotype specimen, collected at a depth of two metres below the surface, arsenowagnerite occurs as crude tabular crystals and euhedral grains up to 0.3 mm in size combined in crusts that cover coarse spherulites mainly consisting of johillerite, tilasite and anhydrite (Figs 1a and 2). These complex sulfate–arsenate aggregates overgrow basalt scoria. The crusts of the new mineral, covering botryoidal clusters of the anhydrite–tilasite–johillerite spherulites, are up to 0.5 cm x 1 cm in area and up to 0.4 mm thick. Arsenowagnerite crystals are skeletal, typically case-like, and its aggregates are open-work. Small grains (up to 0.02 mm) of arsenowagnerite are also observed inside the anhydrite–tilasite–johillerite spherulites where they form intimate intergrowths with these three minerals (Fig. 2) and sometimes also with hematite.

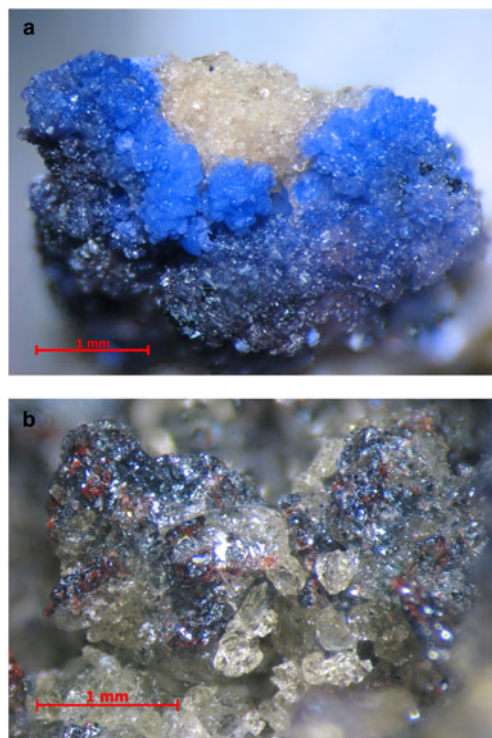


FIG. 1. Morphology of arsenowagnerite aggregates. (a) The holotype: yellowish crust covering an anhydrite–tilasite–johillerite spherulite and surrounded by aggregates of blue johillerite and pinkish-brownish tilasite (in the lower part of the figure); and (b) abundant transparent pale yellowish crystals with deep red cassiterite on iron-black hematite crystal crust. Fields of view: (a) 4.4 mm; (b) 3.5 mm. Photos: I.V. Pekov and A.V. Kasatkin.

At depths of 2.5–3 m below the surface arsenowagnerite was found to be more abundant than at higher levels of the fumarole. In some areas it occurs as interrupted crusts up to 1.5 cm x 3 cm in area and up to 1 mm thick consisting of distorted, typically skeletal crystals up to 1 mm across (Figs 1b and 2). Well-shaped equant or tabular crystals (Fig. 3) up to 0.5 mm are rarer. Arsenowagnerite aggregates cover hematite and fluorophlogopite crystal crusts or directly overgrow basalt scoria. Other associated minerals there are cassiterite, calciojohillerite  $[\text{NaCaMg}_3(\text{AsO}_4)_3]$ , IMA2016-068], johillerite, nickenichite, svabite, berzeliite, tilasite, anhydrite, apthitalite, metathénardite (hexagonal  $\text{Na}_2\text{SO}_4$ , IMA2015-102), krasheninnikovite and fluoborite. Arsenowagnerite crystals commonly contain numerous inclusions of other

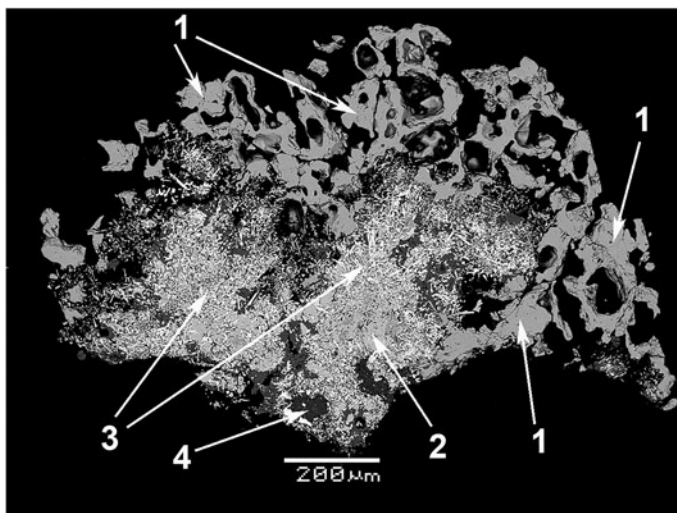


FIG. 2. Back-scattered electron image of a polished section of the holotype specimen showing a crust of skeletal, case-like, crude crystals of arsenowagnerite (1) covering an anhydrite–tilasite–johillerite aggregate with subordinate arsenowagnerite (2–4): 2 – tilasite; 3 – intimate intergrowths of johillerite (white elongated crystals), tilasite and arsenowagnerite (both light grey); 4 – anhydrite.

arsenates, hematite, cassiterite, fluorophlogopite and particles of basalt scoria.

Temperatures measured by us using a chromel–alumel thermocouple in areas with arsenowagnerite at the time of its collecting were 360–450°C. We believe that the new mineral was formed at temperatures not lower than 450°C as a result of the interaction between fumarolic gas (an obvious source of As, O and F) and basalt scoria, the most probable source of Mg which has low volatility at temperatures at least of 500°C (Symonds and Reed, 1993).

### Physical properties and optical data

Arsenowagnerite is transparent with vitreous lustre. It is typically light yellow to lemon-yellow, sometimes pale greenish-yellow or colourless. Its streak is white. Arsenowagnerite demonstrates weak orange-red fluorescence in short-wave ( $\lambda = 245$  nm) ultra-violet (UV) light and does not fluoresce under long-wave (330 nm) UV irradiation. The mineral is brittle. One direction of distinct cleavage was observed under the microscope; by analogy with structurally related wagnerite and sarkinite, we assume that its direction is  $\{001\}$ . The fracture is uneven. The Mohs hardness is  $\sim 5$ . Density could not be measured correctly because of the cavernous, case-

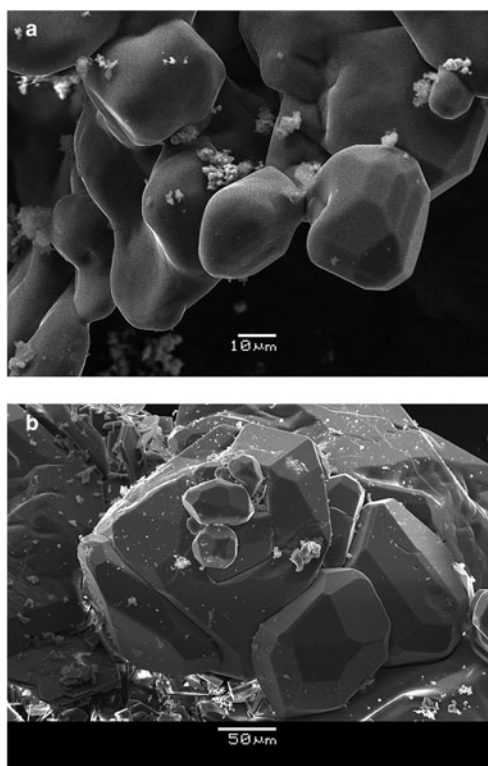


FIG. 3. (a,b) Scanning electron microscopy images of crystals of arsenowagnerite.

like character of individuals of the mineral (Fig. 2) and numerous inclusions in them. Density calculated using the empirical formula is  $3.698 \text{ g cm}^{-3}$ .

In plane polarized light arsenowagnerite is colourless and non-pleochroic. It is optically biaxial (+),  $\alpha = 1.614(2)$ ,  $\beta = 1.615(2)$ ,  $\gamma = 1.640(2)$  (589 nm),  $2V_{\text{meas}} = 25(5)^\circ$  and  $2V_{\text{calc}} = 23^\circ$ . Dispersion of optical axes was not observed.

### Infrared spectroscopy

In order to obtain the infrared (IR) absorption spectrum (Fig. 4), a powdered sample of arsenowagnerite was mixed with dried KBr, pelletized, and analysed using an ALPHA FTIR spectrometer (Bruker Optics) with a resolution of  $4 \text{ cm}^{-1}$  and 16 scans accumulated. The IR spectrum of an analogous pellet of pure KBr was used as a reference.

Wavenumbers of absorption bands in the IR spectrum of arsenowagnerite and their assignments ( $\text{cm}^{-1}$ ; s – strong band, sh – shoulder) are: 900sh, 874s, 861s, 840sh, 820sh (stretching vibrations of  $\text{AsO}_4^{3-}$  groups); 561, 525sh, 507s, 491s, 470s, 443, 417 (bending vibrations of  $\text{AsO}_4^{3-}$  groups combined with Mg–O-stretching vibrations); 375 (lattice mode, possibly involving

Mg–F-stretching vibrations). Weak shoulders at 1090 and  $1140 \text{ cm}^{-1}$  correspond to trace amounts of the sulfate anion.

Numerous bands in the ranges from 800 to 900 and from 400 to  $600 \text{ cm}^{-1}$  reflect the presence of numerous non-equivalent sites of  $\text{AsO}_4^{3-}$  groups and  $\text{Mg}^{2+}$  cations in the crystal structure of arsenowagnerite (see below). Bands corresponding to O–H, C–O and B–O bonds are absent in the IR spectrum of the mineral.

### Chemical composition

Chemical composition of arsenowagnerite 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, Dept. of Petrology, Moscow State University), with an acceleration voltage of 20 kV, a beam current of 20 nA and a  $3 \mu\text{m}$  beam diameter. The standards used are:  $\text{CaWO}_4$  (Ca), diopside (Mg, Si),  $\text{MnTiO}_3$  (Mn, Ti),  $\text{CuFeS}_2$  (Cu, Fe), ZnS (Zn, S), GaP (P), V (V), FeAsS (As) and  $\text{MgF}_2$  (F).

The chemical composition of the new mineral is consistent and only slightly varies in different

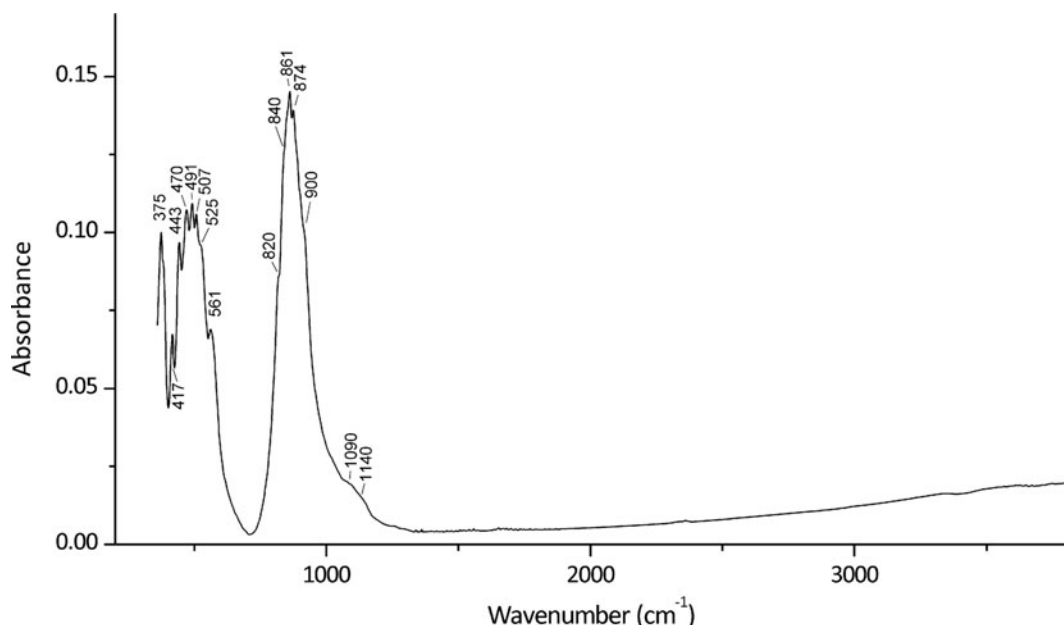


FIG. 4. The powder IR absorption spectrum of arsenowagnerite.

ARSENOWAGNERITE, A NEW MINERAL

TABLE 1. Powder X-ray diffraction data of arsenowagnerite.

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
41	5.80	24	5.818	002
14	5.65	14	5.669	021
35	5.31	21	5.325	120
7	4.65	2	4.655	200
27	4.42	14	4.415	202
37	3.916	27	3.920	221
4	3.584	3	3.604	122
98	3.339	57, 27	3.343, 3.330	221, 023
65	3.155	58	3.161	202
100	3.043	100	3.046	141
72	2.940	68	2.942	204
34	2.879	22	2.881	322
51	2.787	21, 22	2.800, 2.784	320, 124
5	2.610	3	2.615	242
30	2.540	22	2.543	143
12	2.457	9	2.459	402
5	2.407	2	2.407	324
13	2.281	3, 6, 3	2.287, 2.286, 2.272	143, 421, 322
9	2.260	6	2.264	242
11	2.225	10	2.227	423
11	2.175	6, 6	2.180, 2.166	343, 204
32	2.107	24	2.111	341
12	2.040	6, 2, 5	2.046, 2.041, 2.031	206, 421, 162
30	1.932	10, 15, 1, 4	1.939, 1.936, 1.929, 1.921	006, 162, 412, 425
8	1.887	3, 4	1.892, 1.891	261, 440
17	1.848	17	1.851	345
16	1.792	11	1.795	362
23	1.764	2, 16	1.767, 1.763	343, 145
18	1.692	16	1.695	423
12	1.666	10, 2, 1, 1	1.670, 1.666, 1.665, 1.661	543, 541, 046, 364
9	1.616	6, 1, 2	1.623, 1.620, 1.615	080, 461, 362
18	1.592	9, 2, 11	1.598, 1.596, 1.591	463, 181, 526
12	1.573	14	1.576	522
12	1.560	8, 5, 3	1.563, 1.562, 1.551	082, 621, 545
11	1.531	9, 3	1.533, 1.532	147, 280
13	1.520	1, 7, 9	1.525, 1.523, 1.520	461, 282, 347
5	1.504	6	1.506	625
10	1.482	7, 6	1.484, 1.483	328, 166
5	1.468	4	1.471	408
11	1.450	6, 4, 4	1.454, 1.453, 1.449	008, 366, 183
8	1.438	4, 4	1.440, 1.439	644, 621
12	1.416	8, 2, 1, 7, 13	1.421, 1.421, 1.417, 1.417, 1.411	284, 444, 084, 564, 560
15	1.406	2, 13, 2	1.407, 1.402, 1.401	265, 364, 381
7	1.388	8, 2	1.390, 1.389	227, 602
6	1.367	5, 1, 3	1.369, 1.365, 1.364	722, 724, 463
10	1.356	5, 9, 1	1.359, 1.355, 1.355	543, 627, 482
2	1.340	2	1.340	128
3	1.316	5	1.317	385
6	1.303	6, 2	1.307, 1.305	566, 429
8	1.294	7, 3, 3, 1, 2	1.299, 1.299, 1.294, 1.292, 1.291	562, 284, 406, 726, 661
4	1.264	4, 4	1.268, 1.265	029, 741
7	1.256	2, 2, 1, 8	1.259, 1.258, 1.258, 1.255	665, 745, 349, 2.10.1
12	1.241	13, 12	1.245, 1.241	086, 149

(continued)

TABLE 1. (contd.)

$I_{\text{obs}}$	$d_{\text{obs}}$	$I_{\text{calc}}^*$	$d_{\text{calc}}^{**}$	$hkl$
5	1.230	2, 7, 4	1.232, 1.231, 1.228	2.10.1, 0.10.3, $\bar{2}$ .0.10
2	1.211	1, 3, 3	1.213, 1.211, 1.209	604, 823, 486
2	1.205	2	1.205	347

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

samples. The average (over six spot analyses) chemical composition of the holotype specimen (wt.%, ranges are in parentheses) is: MgO 38.72 (38.04–39.28), CaO 0.23 (0.12–0.38), MnO 0.32 (0.08–0.61), CuO 0.60 (0.23–0.85), ZnO 0.05 (0.00–0.14), Fe<sub>2</sub>O<sub>3</sub> 0.11 (0.07–0.22), TiO<sub>2</sub> 0.03 (0.00–0.06), SiO<sub>2</sub> 0.08 (0.04–0.09), P<sub>2</sub>O<sub>5</sub> 0.18 (0.00–0.40), V<sub>2</sub>O<sub>5</sub> 0.03 (0.00–0.07), As<sub>2</sub>O<sub>5</sub> 54.96 (54.27–56.29), SO<sub>3</sub> 0.10 (0.00–0.44), F 8.91

(8.61–9.20), –O=F –3.75, total 100.57. Admixed iron is considered as Fe<sup>3+</sup> because of the extremely oxidizing conditions of mineral formation in the Arsenatnaya fumarole (Pekov *et al.*, 2014a). Contents of other elements with atomic numbers higher than carbon are below detection limits.

The empirical formula, calculated on the basis of 5 anions (O + F) per formula unit, is: (Mg<sub>1.98</sub>Cu<sub>0.02</sub>Mn<sub>0.01</sub>Ca<sub>0.01</sub>)<sub>Σ2.02</sub>(As<sub>0.99</sub>P<sub>0.01</sub>)<sub>Σ1.00</sub>

TABLE 2. Crystal data, data collection information and structure refinement details for arsenowagnerite.

Formula	Mg <sub>2</sub> (AsO <sub>4</sub> )F
Formula weight	206.54
Temperature, K	293(2)
Radiation and wavelength, Å	MoK $\alpha$ ; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/c$ ; 16
Unit-cell parameters, Å, °	$a = 9.8638(3)$ $b = 12.9830(3)$ $c = 12.3284(3)$ $\beta = 109.291(3)$
$V$ , Å <sup>3</sup>	1490.15(7)
Absorption coefficient $\mu$ , mm <sup>-1</sup>	9.375
$F_{000}$	1568
Crystal size, mm	0.09 × 0.11 × 0.15
Diffractometer	Xcalibur S CCD
$\theta$ range for data collection, °	2.69–28.28
Index ranges	$-13 \leq h \leq 13$ , $-17 \leq k \leq 17$ , $-16 \leq l \leq 16$
Reflections collected	24,837
Independent reflections	3696 ( $R_{\text{int}} = 0.0543$ )
Independent reflections with $I > 2\sigma(I)$	2554
Data reduction	<i>CrysAlisPro</i> , Agilent Technologies, Version 1.171.37.34 (Agilent Technologies, 2014)
Absorption correction	Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark and Reid (1995); Empirical absorption correction using spherical harmonics, implemented in <i>SCALE3 ABSPACK</i> scaling algorithm.
Structure solution	direct methods
Refinement method	full-matrix least-squares on $F^2$
Extinction coefficient	0.00029(3)
Number of refined parameters	285
Final $R1$ [ $I > 2\sigma(I)$ ]	0.0485
$wR2$ for all data	0.0694
Goof	1.138
Largest diff. peak and hole, $e/\text{Å}^3$	0.70 and –0.55

O<sub>4.03</sub>F<sub>0.97</sub>. The idealized formula is Mg<sub>2</sub>(AsO<sub>4</sub>)F, which requires MgO 39.03, As<sub>2</sub>O<sub>5</sub> 55.64, F 9.20, –O=F –3.87, total 100.00 wt.%.

The Gladstone-Dale compatibility index  $1 - (K_p/K_c) = -0.018$ , superior (Mandarin, 2007).

### X-ray crystallography and crystal structure

Powder X-ray diffraction data of arsenowagnerite (Table 1) were obtained using a camera RKU-114.6 (Debye-Scherrer geometry,  $d = 114.6$  mm, FeK $\alpha$ -radiation). Monoclinic unit-cell parameters calculated from the powder data are:  $a = 9.858(2)$ ,  $b = 12.964(2)$ ,  $c = 12.332(3)$  Å,  $\beta = 109.32(2)^\circ$  and  $V = 1487.2(8)$  Å<sup>3</sup>.

Single-crystal X-ray studies of the new mineral were carried out using an Xcalibur S diffractometer equipped with a CCD detector. A full sphere of three-dimensional data was collected. Data reduction was performed using *CrysAlisPro* Version 1.171.37.34 (Agilent Technologies, 2014). The data were corrected for Lorentz and polarization effects. The crystal structure of arsenowagnerite was solved by direct methods and refined with the use of the *SHELX-97* software package (Sheldrick, 2008) to  $R = 0.0485$ . The unit-cell parameters and the experimental details are presented in Table 2, atom coordinates and equivalent displacement parameters in Table 3, selected interatomic distances in Table 4 and bond-valence calculations in

TABLE 3. Coordinates and equivalent displacement parameters ( $U_{eq}$ , in Å<sup>2</sup>) of atoms for arsenowagnerite.

Atom	$x$	$y$	$z$	$U_{eq}$
As(1)	0.11375(6)	0.07510(5)	0.42636(5)	0.00441(14)
As(2)	0.87998(6)	0.07035(5)	0.07600(5)	0.00491(14)
As(3)	0.38374(6)	0.17752(5)	0.07630(5)	0.00394(14)
As(4)	0.62083(6)	0.17912(5)	0.42463(5)	0.00366(14)
Mg(1)	0.5446(2)	0.06925(16)	0.91088(16)	0.0054(4)
Mg(2)	0.4733(2)	0.06726(16)	0.60219(16)	0.0064(4)
Mg(3)	0.0408(2)	0.18451(16)	0.91921(16)	0.0044(4)
Mg(4)	0.9739(2)	0.18007(16)	0.61160(16)	0.0060(4)
Mg(5)	0.1964(2)	0.01925(16)	0.19150(16)	0.0055(4)
Mg(6)	0.7806(2)	0.00347(15)	0.30548(16)	0.0055(4)
Mg(7)	0.3000(2)	0.23150(16)	0.31362(16)	0.0058(4)
Mg(8)	0.7153(2)	0.24569(16)	0.19503(16)	0.0065(4)
F(1)	0.4251(3)	0.0434(3)	0.7528(3)	0.0101(7)
F(2)	0.6779(3)	0.0831(3)	0.7124(3)	0.0114(7)
F(3)	0.1802(3)	0.1616(3)	0.7199(3)	0.0129(7)
F(4)	0.9219(3)	0.2085(2)	0.7583(3)	0.0096(7)
O(1)	0.1753(4)	0.1106(3)	0.3191(3)	0.0073(8)
O(2)	0.7934(4)	0.0917(3)	0.1687(3)	0.0067(8)
O(3)	0.3177(4)	0.1434(3)	0.1796(3)	0.0085(9)
O(4)	0.6961(4)	0.1530(3)	0.3246(3)	0.0091(9)
O(5)	0.2514(4)	0.0424(3)	0.5417(3)	0.0097(9)
O(6)	0.7585(4)	0.0524(3)	0.9452(3)	0.0100(9)
O(7)	0.2520(4)	0.2073(3)	0.9523(3)	0.0078(9)
O(8)	0.7509(4)	0.2081(3)	0.5489(3)	0.0063(9)
O(9)	0.9984(4)	0.0232(3)	0.6220(3)	0.0087(9)
O(10)	0.0119(4)	0.0327(3)	0.8835(3)	0.0064(8)*
O(11)	0.4969(4)	0.2233(3)	0.6219(3)	0.0063(8)
O(12)	0.5066(4)	0.2194(3)	0.8786(3)	0.0069(9)
O(13)	0.4757(4)	0.0801(3)	0.0476(3)	0.0096(9)
O(14)	0.5115(4)	0.0854(3)	0.4407(3)	0.0089(9)
O(15)	0.0185(4)	0.1701(3)	0.4585(3)	0.0073(8)
O(16)	0.9935(4)	0.1653(3)	0.0697(3)	0.0060(8)

\* $U_{iso}$ .

**Table 5.** The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

In the crystal structure of arsenowagnerite (Fig. 5) almost regular  $\text{AsO}_4$  tetrahedra, distorted  $\text{MgO}_4\text{F}_2$  octahedra and distorted  $\text{MgO}_4\text{F}$  trigonal bipyramids share either edges or vertices to build up a complex three-dimensional network. The new mineral belongs to the wagnerite-*Ma2bc* structure type (Lazic *et al.*,

2014; Chopin *et al.*, 2014). Its structure is close to those described for wagnerite, ideally  $\text{Mg}_2(\text{PO}_4)\text{F}$  (Coda *et al.*, 1967), its OH-dominant analogue hydroxylwagnerite  $\text{Mg}_2(\text{PO}_4)(\text{OH},\text{F})$  (Chopin *et al.*, 2014), synthetic  $\beta\text{-Mg}_2(\text{PO}_4)\text{OH}$  (Raade and Rømming, 1986), sarkinite, ideally  $\text{Mn}_2^+(\text{AsO}_4)(\text{OH})$  (Dal Negro *et al.*, 1974), and its synthetic analogue (Stock *et al.*, 2002).

Similarly to synthetic  $\beta\text{-Mg}_2(\text{PO}_4)(\text{OH})$ , some deficiency in the valence sums for Mg(6) and Mg(8)

TABLE 4. Selected interatomic distances (Å) in the structure of arsenowagnerite.

As(1)–O(5)	1.664(4)	As(3)–O(13)	1.661(4)
As(1)–O(9)	1.666(4)	As(3)–O(3)	1.671(4)
As(1)–O(15)	1.676(4)	As(3)–O(11)	1.675(4)
As(1)–O(1)	1.692(4)	As(3)–O(7)	1.692(4)
<As(1)–O>	1.675	<As(3)–O>	1.675
As(2)–O(2)	1.661(4)	As(4)–O(4)	1.670(4)
As(2)–O(6)	1.677(4)	As(4)–O(14)	1.681(4)
As(2)–O(10)	1.680(4)	As(4)–O(8)	1.684(4)
As(2)–O(16)	1.685(4)	As(4)–O(12)	1.705(4)
<As(2)–O>	1.676	<As(4)–O>	1.685
Mg(1)–F(1)	1.945(4)	Mg(5)–F(2)	1.933(4)
Mg(1)–O(12)	2.000(5)	Mg(5)–O(1)	2.034(4)
Mg(1)–O(13)	2.020(4)	Mg(5)–O(3)	2.041(4)
Mg(1)–O(6)	2.022(4)	Mg(5)–O(10)	2.068(4)
Mg(1)–O(13)	2.032(5)	Mg(5)–O(6)	2.098(4)
<Mg(1)– $\phi^*$ >	2.004	<Mg(5)– $\phi$ >	2.035
Mg(2)–F(2)	2.037(4)	Mg(6)–F(1)	2.010(4)
Mg(2)–O(11)	2.045(5)	Mg(6)–O(2)	2.076(4)
Mg(2)–O(14)	2.069(5)	Mg(6)–O(9)	2.093(4)
Mg(2)–F(1)	2.086(4)	Mg(6)–O(5)	2.097(4)
Mg(2)–O(5)	2.092(4)	Mg(6)–O(4)	2.156(5)
Mg(2)–O(14)	2.158(4)	Mg(6)–F(3)	2.217(4)
<Mg(2)– $\phi$ >	2.081	<Mg(6)– $\phi$ >	2.108
Mg(3)–F(4)	1.967(4)	Mg(7)–F(3)	1.938(4)
Mg(3)–O(15)	1.979(5)	Mg(7)–O(1)	2.009(4)
Mg(3)–O(7)	2.008(4)	Mg(7)–O(12)	2.030(4)
Mg(3)–O(10)	2.019(5)	Mg(7)–O(3)	2.064(4)
Mg(3)–O(16)	2.072(4)	Mg(7)–O(7)	2.077(4)
<Mg(3)– $\phi$ >	2.009	<Mg(7)– $\phi$ >	2.024
Mg(4)–F(3)	2.046(4)	Mg(8)–F(4)	2.016(4)
Mg(4)–O(9)	2.049(5)	Mg(8)–O(8)	2.037(4)
Mg(4)–F(4)	2.070(4)	Mg(8)–O(4)	2.059(4)
Mg(4)–O(15)	2.079(4)	Mg(8)–O(11)	2.082(4)
Mg(4)–O(16)	2.097(5)	Mg(8)–O(2)	2.205(4)
Mg(4)–O(8)	2.108(4)	Mg(8)–F(2)	2.275(4)
<Mg(4)– $\phi$ >	2.075	<Mg(8)– $\phi$ >	2.112

\*  $\phi$  = unspecified ligand.



TABLE 5. Bond-valence calculations\* for arsenowagnerite.

	As(1)	As(2)	As(3)	As(4)	Mg(1)	Mg(2)	Mg(3)	Mg(4)	Mg(5)	Mg(6)	Mg(7)	Mg(8)	Σ
F(1)					0.37	0.25				0.31			0.93
F(2)						0.29			0.39			0.15	0.83
F(3)								0.28		0.18	0.38		0.84
F(4)							0.35	0.27				0.31	0.93
O(1)	1.22								0.40		0.43		2.05
O(2)		1.33								0.35		0.25	1.93
O(3)			1.30						0.39		0.37		2.06
O(4)				1.30						0.29		0.37	1.96
O(5)	1.32					0.34				0.34			2.00
O(6)		1.27			0.41				0.33				2.01
O(7)			1.22				0.43				0.35		2.00
O(8)				1.25				0.33				0.39	1.97
O(9)	1.31							0.38		0.34			2.03
O(10)		1.26					0.41		0.36				2.03
O(11)			1.28			0.39						0.35	2.02
O(12)				1.18	0.44						0.40		2.02
O(13)			1.33		0.41								2.14
O(14)				1.26	0.40								1.90
						0.36							1.90
						0.28							1.90
O(15)	1.28						0.46	0.35					2.09
O(16)		1.25					0.36	0.34					1.95
Σ	5.13	5.11	5.13	4.99	2.03	1.91	2.01	1.95	1.87	1.81	1.93	1.82	

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

was revealed (Table 5). According to Raade and Rømming (1986), it is related to a higher degree of distortion of these two pseudo-octahedra with the two longest Mg–O distances in the structure (Table 4): Mg(6)–O(4) = 2.156 and Mg(8)–O(2) = 2.205 Å.

## Discussion

Arsenowagnerite  $\text{Mg}_2(\text{AsO}_4)\text{F}$  is a member of the triplite group belonging to the triplite–triploidite supergroup (Chopin *et al.*, 2014). It is an arsenate analogue of wagnerite  $\text{Mg}_2(\text{PO}_4)\text{F}$  and a magnesium and fluorine analogue of sarkinite  $\text{Mn}_2^+(\text{AsO}_4)\text{OH}$ . Comparative data for these three minerals are given in Table 6.

Wagnerite is represented in nature by several polytype modifications (Lazic *et al.*, 2014, and references therein). Their diversity is caused by partial substitutions of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ti}^{4+}$  or  $\text{Fe}^{3+}$  for  $\text{Mg}^{2+}$  and of  $\text{OH}^-$  or  $\text{O}^{2-}$  for  $\text{F}^-$  which causes significant variations in bond lengths. As a result of this, individual coordination polyhedra around cation sites are locally modified with regards

to coordination number and geometry, and this may affect the geometry of the whole structure (Lazic *et al.*, 2014). The structural relationship between wagnerite and triplite, ideally  $\text{Mn}_2^+(\text{PO}_4)\text{F}$ , with  $b \approx 6.45$  Å (Waldrop, 1969) led to the proposal to consider wagnerite as a polytypic series based on the smallest, triplite-type unit cell. In the crystal structure and unit-cell dimensions, arsenowagnerite is close to the polytype modification of wagnerite with  $b \approx 13$  Å ( $\sim 2b$  of triplite) now considered as wagnerite-*Ma2bc* (Lazic *et al.*, 2014; Chopin *et al.*, 2014). It should be noted that this polytype is the only known for wagnerite samples chemically close to the end-member  $\text{Mg}_2(\text{PO}_4)\text{F}$  (Lazic *et al.*, 2014). We do not exclude the same correspondence between chemical composition and structure for arsenowagnerite.

No data on synthetic  $\text{Mg}_2(\text{AsO}_4)\text{F}$  were found by us in the literature and databases. The crystal structures of synthetic  $\text{Fe}_2^+(\text{AsO}_4)\text{F}$  (Berrocal *et al.*, 2006) and  $\text{Cd}_2(\text{AsO}_4)\text{F}$  (Engel, 1989) are generally close to that of triplite (Waldrop, 1969) and synthetic  $\text{Mn}_2(\text{PO}_4)\text{F}$  (Rea and Kostiner, 1972). Thus, arsenowagnerite is the first fluoro-arsenate belonging to the wagnerite-*Ma2bc*

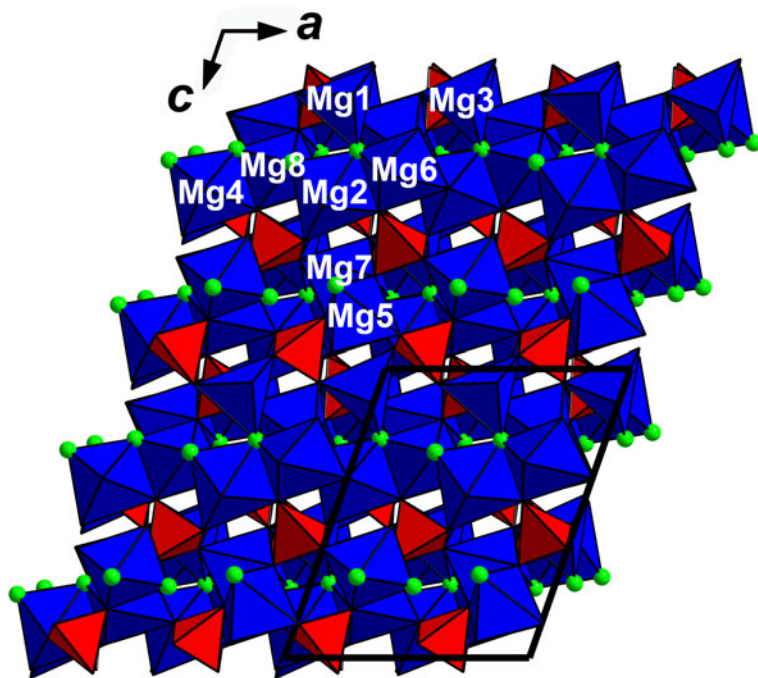


FIG. 5. The crystal structure of arsenowagnerite. Mg-centred polyhedra are blue, red tetrahedra are  $\text{AsO}_4$  groups and green circles are F atoms. The numbers of Mg polyhedra correspond to those in Tables 3–5. The unit cell is outlined.

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TABLE 6. Comparative data of arsenowagnerite, wagnerite and sarkinite.

Mineral	Arsenowagnerite	Wagnerite*	Sarkinite
<b>Crystal data</b>			
Formula	Mg <sub>2</sub> (AsO <sub>4</sub> )F	Mg <sub>2</sub> (PO <sub>4</sub> )F	Mn <sub>2</sub> <sup>2+</sup> (AsO <sub>4</sub> )OH
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i> **
<b>Unit-cell data</b>			
<i>a</i> , Å	9.864	9.64–9.70	10.208
<i>b</i> , Å	12.983	12.68–12.74	13.596
<i>c</i> , Å	12.328	11.94–11.99	12.779
β, °	109.29	108.3–108.6	108.88
<i>V</i> , Å <sup>3</sup>	1490	ca. 1390	1678
<i>Z</i>	16	16	16
<b>Strongest lines in the XRD pattern</b>			
<i>d</i> , Å ( <i>I</i> )	5.80 (41)	3.297 (65)	6.0 (30)
	3.916 (37)	3.123 (63)	3.48 (80)
	3.339 (98)	2.985 (100)	3.29 (90)
	3.155 (65)	2.854 (59)	3.18 (100)
	3.043 (100)	2.758 (25)	3.04 (100)
	2.940 (72)	2.710 (22)	2.90 (70)
	2.787 (51)	1.584 (15)	2.65 (60)
<b>Optical data</b>			
α	1.614	1.568–1.588	1.790–1.793
β	1.615	1.572–1.589	1.794–1.807
γ	1.640	1.582–1.598	1.798–1.809
optical sign, 2V	(+), 25°	(+), 25–35°	(–), 83°
<i>D</i> , g cm <sup>–3</sup>	3.70 (calc.)	3.15	4.08–4.20
<b>Sources</b>			
	This work	Waldrop (1969); Anthony <i>et al.</i> (2000); Lazic <i>et al.</i> (2014); Chopin <i>et al.</i> (2014)	Dal Negro <i>et al.</i> , (1974); Anthony <i>et al.</i> (2000)

\*Wagnerite-*Ma2bc* (Lazic *et al.*, 2014; Chopin *et al.*, 2014). \*\*In the original paper (Dal Negro *et al.*, 1974), the space group *P2<sub>1</sub>/a* was given; we have changed the setting for better comparison with wagnerite and arsenowagnerite.

structure type. In accordance with the nomenclature of polytypes of triplite-group members (Chopin *et al.*, 2014), the new mineral could be considered as arsenowagnerite-*Ma2bc*.

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### Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.067>

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