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

Igor V. Pekov[1]*, Natalia V. Zubkova[1], Atali A. Agakhanov[2], Vasiliy O. Yapaskurt[1], Nikita V. Chukanov[3], Dmitry I. Belakovskiy[2], Evgeny G. Sidorov[4] and Dmitry Yu. Pushcharovsky[1]

[1]Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia

[2]Fersman Mineralogical Museum of Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia

[3]Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1424, 2 Chernogolovka, Moscow Oblast, Russia

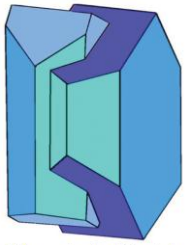
[4]Institute of Volcanology and Seismology, Far Eastern Branch of Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia

*E-mail: igorpekov@mail.ru

Running title: Arsenowagnerite, a new mineral

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 closely associated with johillerite, tilasite, anhydrite, hematite, fluorophlogopite, cassiterite, calciojohillerite, aphthitalite, and fluoborite. Arsenowagnerite occurs as equant to tabular crystals up to 1 mm across, combined in interrupted crusts up to 0.1 x 1.5 x 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 *ca* 5. Cleavage is distinct, the fracture is uneven. D_{calc} = 3.70 g cm^{-3}. Arsenowagnerite is optically biaxial (+), α = 1.614(2), β = 1.615(2), γ = 1.640(2) and $2V_{meas}$ = 25(5)°. Wavenumbers of the strongest absorption bands in the IR spectrum of arsenowagnerite (cm^{-1}) are: 874, 861, 507, 491, and 470. The chemical composition (average of 6 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, –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, β = 109.291(3)°, V = 1490.15(7) Å^3 and Z = 16. The strongest reflections of the powder X-ray diffraction pattern [d,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)(-141), 2.940(72)(-204), 2.879(34)(-322), and 2.787(51)(320, -124). The crystal structure was solved



DOI: 10.1180/minmag.2017.081.067

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 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 in general described in the first paper devoted to yurmarinite $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$ (Pekov *et al.*, 2014a). In other articles the following mineral species were characterized: 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), tiuniteite $KTiO(AsO_4)$ (Pekov *et al.*, 2016a), melanarsite $K_3Cu_7Fe^{3+}O_4(AsO_4)_4$ (Pekov *et al.*, 2016b), and pharmazincite $KZnAsO_4$ (Pekov *et al.*, 2017).

This paper is devoted to the new mineral **arsenowagnerite** $Mg_2(AsO_4)F$ (Cyrillic: арсеновагнерит). It is named as an arsenate analogue of wagnerite $Mg_2(PO_4)F$. Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 2014–100). 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 its holotype was found by us in July 2014. During fieldworks 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 the depth of two meters from day 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 (Figures 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 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 (Figure 2) and sometimes also with hematite.

At depths of 2.5 – 3 m from day surface arsenowagnerite turned out not so rare mineral as at higher levels of the fumarole. In some areas it occurs as interrupted crusts up to 1.5 x 3 cm in area and up to 1 mm thick consisting of distorted, typically skeletal crystals up to 1 mm across (Figures 1b and 2). Well-shaped equant or tabular crystals (Figure 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, calcic johillerite [$NaCaMg_3(AsO_4)_3$, IMA2016-068], johillerite, nickenichite, svabite, berzelite, tilasite, anhydrite, aphthitalite, metathénardite (hexagonal Na_2SO_4, IMA2015-102), urasheninnikovite, and fluoborite. Arsenowagnerite crystals commonly contain numerous inclusions of other 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 the 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 500ºC (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 (λ = 245 nm) ultraviolet (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 *ca* 5. Density could not be correctly measured because of the cavernous, case-like character of individuals of the mineral (Figure 2) and numerous inclusions in them. Density calculated using the empirical formula is 3.698 g cm^{-3}.

In plane polarized light arsenowagnerite is colourless and non-pleochroic. It is optically biaxial (+), α = 1.614(2), β = 1.615(2), γ = 1.640(2) (589 nm), $2V_{meas}$ = 25(5)º and $2V_{calc}$ = 23º. Dispersion of optical axes was not observed.

Infrared spectroscopy

In order to obtain infrared (IR) absorption spectrum (Figure 4), powdered sample of arsenowagnerite was mixed with dried KBr, pelletized, and analyzed using an ALPHA FTIR

spectrometer (Bruker Optics) with a resolution of 4 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 (cm^{-1}; s – strong band, sh – shoulder) are: 900sh, 874s, 861s, 840sh, 820sh (stretching vibrations of AsO_4^{3-} groups); 561, 525sh, 507s, 491s, 470s, 443, 417 (bending vibrations of 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 cm^{-1} correspond to trace amounts of the sulfate anion.

Numerous bands in the ranges from 800 to 900 and from 400 to 600 cm^{-1} reflect the presence of numerous non-equivalent sites of AsO_4^{3-} groups and 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 μm beam diameter. The standards used are $CaVAlO_4$ (Ca), diopside (Mg, Si), $MnTiO_3$ (Mn, Ti), $CuFeS_2$ (Cu, Fe), ZnS (Zn, S), GaP (Ga), V (V), FeAsS (As), and MgF_2 (F).

Chemical composition of the new mineral is stable and only slightly varies in different 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_2O_3 0.11 (0.07–0.22), TiO_2 0.03 (0.00–0.06), SiO_2 0.08 (0.04–0.09), P_2O_5 0.18 (0.00–0.40), V_2O_5 0.03 (0.00–0.07), As_2O_5 54.96 (54.27–56.19), SO_3 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^{3+} because of 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) *pfu*, is: $(Mg_{1.98}Cu_{0.02}Mn_{0.01}Ca_{0.01})_{\Sigma 2.02}(As_{0.99}P_{0.01})_{\Sigma 1.00}O_{4.03}F_{0.97}$. The idealized formula is $Mg_2(AsO_4)F$, which requires MgO 39.03, As_2O_5 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.

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, Fe$K\alpha$-radiation). Monoclinic unit-cell

parameters calculated from the powder data are: a = 9.858(2), b = 12.964(2), c = 12.332(3) Å, β = 109.32(2)°, and V = 1487.2(8) Å^3.

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 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 5.

In the crystal structure of arsenowagnerite (Figure 5) almost regular AsO_4 tetrahedra, distorted MgO_4F_2 octahedra and distorted MgO_4F 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 $Mg_2(PO_4)F$ (Cocco *et al.*, 1967), its OH-dominant analogue hydroxylwagnerite $Mg_2(PO_4)(OH,F)$ (Chopin *et al.*, 2014), synthetic β-$Mg_2(PO_4)OH$ (Raade and Rømming, 1986), sarkinite, ideally $Mn^{2+}_2(AsO_4)(OH)$ (Dal Negro *et al.*, 1974), and its synthetic analogue (Stock *et al.*, 2002).

Similarly to synthetic β-$Mg_2(PO_4)(OH)$, some deficiency in the valence sums for Mg(6) and Mg(8) 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 $Mg_2(AsO_4)F$ is a member of the triplite group belonging to the triplite–triploidite supergroup (Chopin *et al.*, 2014). It is an arsenate analogue of wagnerite $Mg_2(PO_4)F$ and a magnesium and fluorine analogue of sarkinite $Mn^{2+}_2(AsO_4)OH$. 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 probably caused by partial substitutions of Mg^{2+} for Fe^{2+}, Mn^{2+}, Ca^{2+}, Ti^{4+} or Fe^{3+} and of F^- for OH^- or O^{2-} that provokes significant variations in bond lengths. Hereupon, individual coordination polyhedra around cation sites are locally modified regarding coordination number and geometry, and this may affect the geometry of the whole structure (Lazic *et al.*, 2014). Structural relationship between wagnerite and triplite, ideally $Mn^{2+}_2(PO_4)F$, with b ~ 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 $b \sim 13$ Å (~ 2b of triplite) now considered as wagnerite-*Ma*2*bc* (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 $Mg_2(PO_4)F$ (Lazic *et al.*, 2014). We do not exclude the same correspondence between chemical composition and structure for arsenowagnerite.

No data on synthetic $Mg_2(AsO_4)F$ were found by us in literature and databases. The crystal structures of synthetic $Fe^{2+}_2(AsO_4)F$ (Berrocal *et al.*, 2006) and $Cd_2(AsO_4)F$ (Engel, 1989) are generally close to that of triplite (Waldrop, 1969) and synthetic $Mn_2(PO_4)F$ (Rea and Kostiner, 1972). Thus, arsenowagnerite is the first fluoroarsenate belonging to the wagnerite-*Ma*2*bc* 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-*Ma*2*bc*.

Acknowledgements

We thank Evgeny Galuskin, Peter Leverett and anonymous referee for valuable comments. This study was supported by the Russian Foundation for Basic Research, grant no. 17-05-00179.

References

Agilent Technologies (2014) *CrysAlisPro Software system, version 1.171.37.34*, Agilent Technologies UK Ltd, Oxford, UK.

Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols, M.C. (2000) *Handbook of Mineralogy. IV. Arsenates, Phosphates, Vanadates*. Mineral Data Publishing, Tucson.

Berrocal, T., Mesa, J.L., Rojo, J.L., Urtiaga, M.K., Arriortua, M.I. and Rojo, T. (2006) $Fe_2(AsO_4)F$: A new three-dimensional condensed fluoro-arsenate iron(II) compound with antiferromagnetic interactions. *Journal of Solid State Chemistry*, **179**, 1659-1667.

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica B*, **47**, 192-197.

Chopin, C., Armbruster, T., Grew, E.S., Baronnet, A., Leyx, C. and Medenbach, O. (2014) The triplite–triploidite supergroup: structural modulation in wagnerite, discreditation of magniotriplite, and the new mineral hydroxylwagnerite. *European Journal of Mineralogy*, **26**, 553-565

Clark, R. C. and Reid, J. S. (1995) The analytical calculation of absorption in multifaceted crystals *Acta Crystallographica A*, **51**, 887-897.

Coda, A., Giuseppetti, G., Tadini, C. and Carobbi, S.G. (1967) The crystal structure of wagnerite. *Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali*, **43**, 212-224.

Dal Negro, A., Giuseppetti, G. and Pozas, J.M.M. (1974) The crystal structure of sarkinite, $Mn_2AsO_4(OH)$. *Tschermaks Mineralogische und Petrographische Mitteilungen*, **21**, 246-260.

Engel, G. (1989): Die Kristallstruktur von Cd_2AsO_4F und ihre Beziehung zu einer Reihe von Oxidsilicaten und Oxidgermanaten der Seltenen Erden. *Journal of the Less-Common Metals*, **154**, 367-374.

Lazic, B., Armbruster, T., Chopin, C., Grew, E.S., Baronnet, A. and Palatinus, L. (2014) Superspace description of wagnerite-group minerals $(Mg,Fe,Mn)_2(PO_4)(F,OH)$. *Acta Crystallographica*, **B70**, 243-258.

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Belakovskiy, D.I., Lykova, I.S., Vigasina, M.F., Sidorov, E.G. and Pushcharovsky, D.Yu. (2014a) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. I. Yurmarinite, $Na_7(Fe^{3+},Mg,Cu)_4(AsO_4)_6$. *Mineralogical Magazine*, **78**, 909-917.

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

Pekov, I.V., Zubkova, N.V., Yapaskurt, V.O., Belakovskiy, D.I., Vigasina, M.F., Sidorov, E.G. and Pushcharovsky, D.Yu. (2015a) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. III. Popovite, $Cu_5O_2(AsO_4)_2$. *Mineralogical Magazine*, **79**, 135-143.

Pekov, I.V., Zubkova, N.V., Belakovskiy, D.I., Yapaskurt, V.O., Vigasina, M.F., Sidorov, E.G. and Pushcharovsky, D.Yu. (2015b) New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. IV. Shchurovskyite, $K_2CaCu_6O(AsO_4)_4$, and dmisokolovite, $K_3Cu_5AlO_2(AsO_4)_4$. *Mineralogical Magazine*, **79**, 1737-1753.

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

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

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

Raade, G. and Rømming, C. (1986) The crystal structure of β-Mg_2PO_4OH, a synthetic hydroxyl analogue of wagnerite. *Zeitschrift für Kristallographie*, **177**, 15-26.

Rea, J.R. and Kostiner, E. (1972) The crystal structure of manganese fluorophosphate, $Mn_2(PO_4)F$. *Acta Crystallographica*, **B28**, 2525-2529.

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

Stock, N., Stucky, G.D. and Cheetham, A.K. (2002) Synthesis and characterization of the synthetic minerals villyaellenite and sarkinite, $Mn_5(AsO_4)_2(HAsO_4)_2{\cdot}4H_2O$ and $Mn_2(AsO_4)(OH)$. *Zeitschrift für Anorganische und Allgemeine Chemie*, **628**, 357-362.

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

Waldrop, L. (1969) The crystal structure of triplite, $(Mn,Fe)_2FPO_4$. *Zeitschrift für Kristallographie*, **130**, 1-14.

278 Table 1. Powder X-ray diffraction data of arsenowagnerite.
279

I_{obs}	d_{obs}	I_{calc}*	d_{calc}**	*h k l*
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	–[illegible]2
5	2.407	2	2.407	-324
13	2.281	3, 6, 3	2.287, 2.286, 2.272	[illegible]3, –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, 1.7[illegible]	343, 145
18	1.692	16	1.69[illegible]	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, [illegible]9	1.525, 1.523, 1.520	461, –282, –347
5	1.504	[illegible]8	1.506	–625
10	1.482	7, 6	1.484, 1.483	–328, –166
5	1.4[illegible]8	4	1.471	–408
[illegible]	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
5	1.230	2, 7, 4	1.232, 1.231, 1.228	2.10.1, 0.10.3, –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 ≥1 are given; **for the unit-cell parameters calculated from single-crystal data.

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

Formula	$Mg_2(AsO_4)F$
Formula weight	206.54
Temperature, K	293(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $P2_1/c$; 16
Unit cell parameters, Å,°	a = 9.8638(3) b = 12.9830(3) β = 109.291(3) c = 12.3284(3)
V, Å^3	1490.15(7)
Absorption coefficient μ, mm^{-1}	9.375
F_{000}	1568
Crystal size, mm	0.09 × 0.1 × 0.15
Diffractometer	Xcalibur S CCD
θ range for data collection, °	2.69 – 28.28
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 17$, $-16 \le l \le 16$
Reflections collected	24837
Independent reflections	3696 (R_{int} = 0.0543)
Independent reflections with $I > 2\sigma(I)$	2554
Data reduction	CrysAlisPro, 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 SCALE3 ABSPACK 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
w$R2$ for all data	0.0694
GoF	1.138
Largest diff. peak and hole, e/Å^3	0.70 and -0.55

288 Table 3. Coordinates and equivalent displacement parameters (U_{eq}, in Å^2) of atoms for
289 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)	0.010(7)
F(2)	0.6779(3)	0.0831(3)	0.7124(3)	0.014(7)
F(3)	0.1802(3)	0.1616(3)	0.7199(3)	0.012(7)
F(4)	0.9219(3)	0.2085(2)	0.7583(3)	0.006(7)
O(1)	0.1753(4)	0.1106(3)	0.319(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)	0.5467(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)	0.0252(3)	0.6220(3)	0.0087(9)
O(10)	0.0119(4)	0.0027(3)	0.8835(3)	0.0064(8)*
O(11)	0.4963(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)	0.2757(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)

290 *U_{iso}

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)
– O(9)	1.666(4)	– O(3)	1.671(4)
– O(15)	1.676(4)	– O(11)	1.675(4)
– O(1)	1.692(4)	– 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)
– O(6)	1.677(4)	– O(14)	1.681(4)
– O(10)	1.680(4)	– O(8)	1.684(4)
– O(16)	1.685(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)	1.935(4)
– O(12)	2.000(5)	– O(1)	2.034(4)
– O(13)	2.020(4)	– O(3)	2.041(4)
– O(6)	2.022(4)	– O(10)	2.068(4)
– O(13)	2.032(5)	– O(6)	2.098(4)
<Mg(1) – ϕ*>	2.004	<Mg(5) – ϕ>	2.035
Mg(2) – F(2)	2.037(4)	Mg(6) – F(1)	2.010(4)
– O(11)	2.045(5)	– O(2)	2.076(4)
– O(14)	2.069(5)	– O(9)	2.093(4)
– F(1)	2.086(4)	– O(5)	2.097(4)
– O(5)	2.092(4)	– O(4)	2.156(5)
– O(14)	2.158(4)	– F(3)	2.217(4)
<Mg(2) – ϕ>	2.081	<Mg(6) – ϕ>	2.108
Mg(3) – F(4)	1.967(4)	Mg(7) – F(3)	1.938(4)
– O(15)	1.979(5)	– O(1)	2.009(4)
– O(7)	2.008(4)	– O(12)	2.030(4)
– O(10)	2.019(5)	– O(3)	2.064(4)
– O(16)	2.072(4)	– O(7)	2.077(4)
<Mg(3) – ϕ>	2.009	<Mg(7) – ϕ>	2.024
Mg(4) – F(3)	2.046(4)	Mg(8) – F(4)	2.016(4)
– O(9)	2.049(5)	– O(8)	2.037(4)
– F(4)	2.070(4)	– O(4)	2.059(4)
– O(15)	2.079(4)	– O(11)	2.082(4)
– O(16)	2.097(5)	– O(2)	2.205(4)
– O(8)	2.108(4)	– F(2)	2.275(4)
<Mg(4) – ϕ>	2.075	<Mg(8) – ϕ>	2.112

* ϕ - unspecified ligand

295 Table 5. Bond valence calculations* for arsenowagnerite.
296

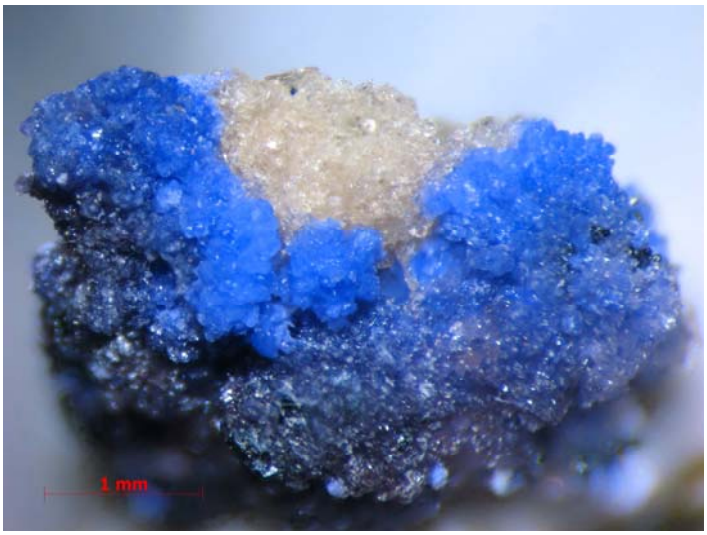
	As(1)	As(2)	As(3)	As(4)	Mg(1)	Mg(2)	Mg(3)	Mg(4)	Mg(5)	Mg(6)	Mg(7)	Mg(8)	Σ
F(1)					0.37	0.25				0.31			0.93
F(2)						0.29			0.39			0.15	0.83
F(3)								0.28		0.18	0.38		0.84
F(4)							0.35	0.27				0.31	0.93
O(1)	1.22								0.40		0.43		2.05
O(2)		1.33								0.35		0.25	1.93
O(3)			1.30						0.39		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 0.40								2.14
O(14)				1.26		0.36 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	

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

298 Table 6. Comparative data of arsenowagnerite, wagnerite and sarkinite.
299

Mineral	Arsenowagnerite	Wagnerite*	Sarkinite
Formula	$Mg_2(AsO_4)F$	$Mg_2(PO_4)F$	$Mn^{2+}_2(AsO_4)OH$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$**
Unit cell data:			
a, Å	9.864	9.64–9.70	10.208
b, Å	12.983	12.68–12.74	13.596
c, Å	12.328	11.94–11.99	12.779
β, °	109.29	108.3–108.6	108.88
V, Å^3	1490	*ca.* 1390	1678
Z	16	16	16
Strongest reflections of the X-ray powder pattern: *d*,Å – *I*	5.80 – 41 3.916 – 37 3.339 – 98 3.155 – 65 3.043 – 100 2.940 – 72 2.787 – 51	3.297 – 65 3.123 – 63 2.985 – 100 2.854 – 59 2.758 – 25 2.710 – 22 1.584 – 15	6.0 – 30 3.48 – 80 3.29 – 9[illegible] 3.18 – 100 3.04 – [illegible]00 2.90 – 79 2.65 – 60
Optical data:			
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	1.582–1.59[illegible]	1.798–1.809
optical sign, 2*V*	(+), 25°	(+), 25–[illegible]°	(–), 83°
D, g cm^{-3}	3.70 (calc.)	3.15	4.08–4.20
Sources	This work	Waldrop, 1969; Anthony *et al*., 2000 Lazic *et al*., 2014; Chopin *et al*., 2014	Dal Negro *et al*., 1974; Anthony *et al*., 2000

300 *Wagnerite-*Ma*2*bc* (Lazic *et al*., 2014; Chopin *et al*., 2014). **In the original paper (Dal
301 Negro *et al*., 1974), the space group $P2_1/a$ was given; we have changed the setting for better
302 comparison with wagnerite and arsenowagnerite.
303
304
305



a

Figure 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 lower part of the figure); b – abundant transparent pale yellowish crystals with deep red cassiterite on iron-black hematite crystal crust. FOV: a – 4.4 mm, b – 3.5 mm. Photo: I.V. Pekov & A.V. Kasatkin.

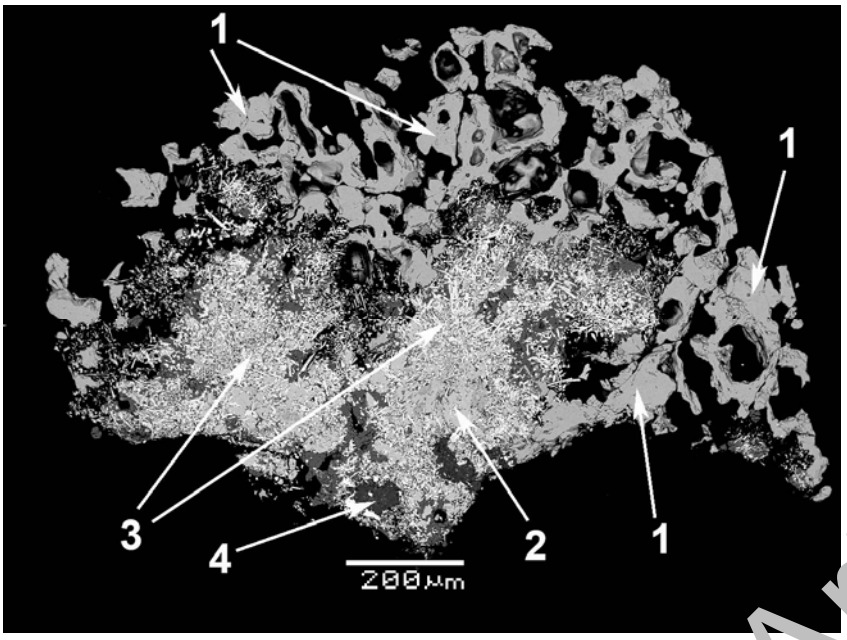


Figure 2. A crust of skeletal, case-like, crude crystals of arsenowagnerite (1) covering an anhydrite-tilasite-johillerite aggregate with subordinate arsenowagnerite (2–4): 2 – tilasite; 3 – intimate intergrowths of johillerite (white elongated crystals), tilasite and arsenowagnerite (both light grey); 4 – anhydrite. The holotype specimen, polished section. SEM (BSE) image.

a b

Figure 3. Crystals of arsenowagnerite. SEM (SE) image.

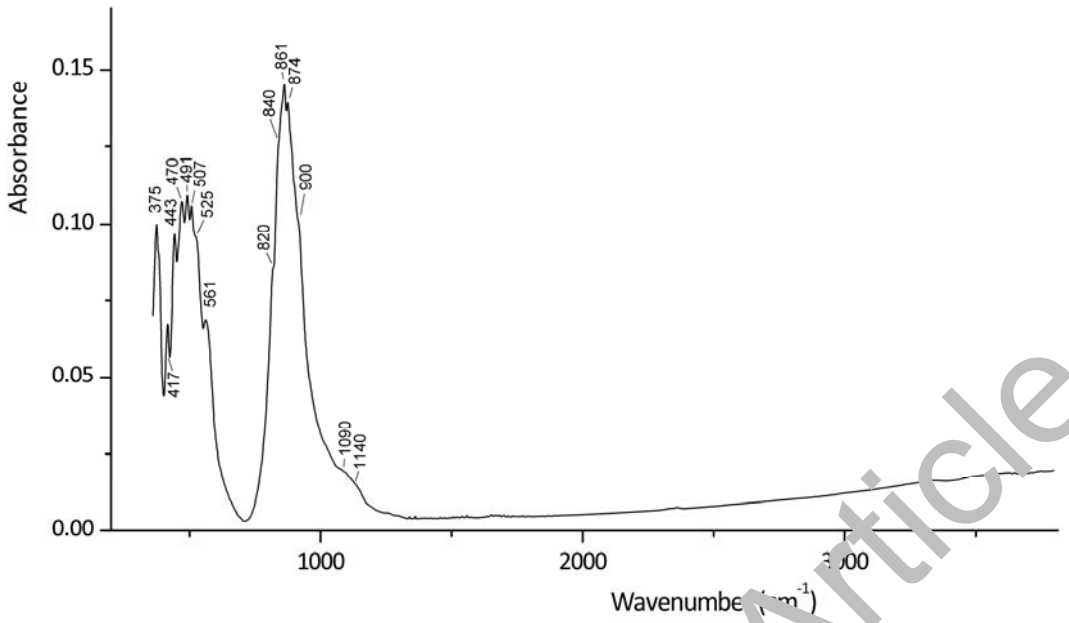


Figure 4. The powder IR absorption spectrum of arsenowagnerite

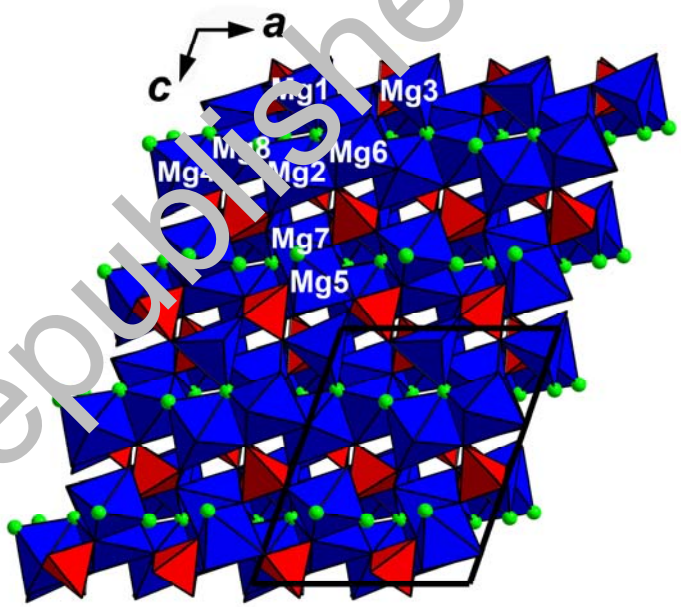


Figure 5. The crystal structure of arsenowagnerite. Mg-centred polyhedra are blue, red tetrahedra are AsO_4 groups and green circles are F atoms. The numbers of Mg polyhedra correspond to those in Tables 3–5. The unit cell is outlined.