

Wrightite, $K_2Al_2O(AsO_4)_2$, a new oxo-orthoarsenate from the Second scoria cone, Northern Breakthrough, Great Fissure eruption, Tolbachik volcano, Kamchatka peninsula, Russia

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ABSTRACT

The new mineral wrightite, $K_2Al_2O(AsO_4)_2$, was found in 1983 at a fumarole on the Second scoria cone, Northern Breakthrough, Great Fissure eruption, Tolbachik volcano, Kamchatka peninsula, Russia, where it occurs as light yellow aggregates of transparent tabular crystals, with an average size of $0.05\text{ mm} \times 0.03\text{ mm} \times 0.005\text{ mm}$. Wrightite is orthorhombic, space group $Pnma$, with the unit-cell parameters $a = 8.230(5)$, $b = 5.555(4)$, $c = 17.584(1)\text{ Å}$, $V = 803.9(6)\text{ Å}^3$ and $Z = 4$ (from powder data). The empirical formula is $(K_{1.69}Na_{0.38})_{\Sigma 2.07}(Al_{1.80}Fe_{0.24})_{\Sigma 2.04}As_{1.96}O_9$. The crystal structure ($R_1 = 0.043$) consists of $Al_2O(AsO_4)_2$ layers in the ab plane with clusters of edge-sharing AlO_6 octahedra. Each layer contains two independent isolated AsO_4 tetrahedra and two AlO_6 octahedra. AlO_6 octahedra are linked by edges, forming zigzag chains along the b axis inside the Al–As layer. Eight- and six-coordinated K atoms are located in the interlayer space between $Al_2O(AsO_4)_2$ layers. The mineral is biaxial (–), $\alpha = 1.679(2)$, $\beta = 1.685(2)$, γ (calc.) = 1.687; $2V$ (meas.) = $62(10)^\circ$ ($\lambda = 589\text{ nm}$). The strongest lines in the powder X-ray diffraction pattern [d , Å (I)(hkl)] are: 8.77(36)(002); 4.458(17)(111); 4.010(19)(201,013); 3.875(19)(104) and 2.972(100)(015). The mineral was named in honour of Adrian Carl Wright, Emeritus Professor at the University of Reading, UK.

KEYWORDS: wrightite, new mineral species, oxo-orthoarsenate, crystal structure, fumarole minerals, Kamchatka peninsula.

Introduction

WRIGHTITE, a new oxo-orthoarsenate mineral, was found by L.P. Vergasova and S.K. Filatov, in 1983, in the fumarole on the east side of the micrograben of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. The temperature of the volcanic gases in the fumarole was 410–420°C and the vent was encrusted

with ponomarevite $K_4Cu_4OCl_{10}$, while piypite $K_4Cu_4O_2(SO_4)_4 \cdot (Na,Cu)Cl$ prevailed at a depth of 0.5 m. The bottom of the visible part of the fumarole was encrusted with sylvite KCl. Minor phases in the sylvite-crust part of the fumarole included dolerophanite Cu_2OSO_4 , euchlorine $KNaCu_3O(SO_4)_3$, lammerite $Cu_3(AsO_4)_3$, johillerite $NaCuMg_3(AsO_4)_3$, urusovite $CuAlO(AsO_4)$, bradaczekite $NaCu_4(AsO_4)_3$, filatovite $K(Al,Zn)_2(As,Si)_2O_8$, hatertite $Na_2(Ca,Na)(Fe^{3+},Cu_2)(AsO_4)_3$, hematite Fe_2O_3 , ozerovaite $Na_2KAl_3(AsO_4)_4$ and tenorite CuO . Based on this mineralogical association, the formation temperature of the arsenate minerals is estimated as 500–600°C.

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Reviews on the mineralization and fumarole activity of the Second scoria cone were reported by Vergasova and Filatov (2012, 2016). The majority of arsenates from Great Fissure Tolbachik Eruption were discovered in the Arsenatnaya fumarole in the period 2014–2016 (Pekov *et al.*, 2014a,b, 2015a,b, 2016a,b). Hatertite (Krivovichev *et al.*, 2013) was only found in the fumarole on the east side of micrograben of the Second scoria cone. The discovery of other arsenate minerals (bradaczekite and filatovite) from the Second scoria cone was reported by Filatov *et al.* (2001, 2004).

The mineral is named wrightite (Russian Cyrillic: райтит) in honour of Adrian Carl Wright, Emeritus Professor at the University of Reading, UK, for many years the Professor in Amorphous Solid State Physics. Professor A.C. Wright was born in 1944. He is a well-known expert in structural studies of glass-forming systems. His works (Wright, 2010; Wright *et al.*, 2010) are very important for understanding processes in both synthetic and natural (volcanic glass) systems. The mineral and its name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2015–120). The type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19653).

Appearance and physical properties

Wrightite crystals are tabular, colourless to light yellow and transparent with an average size of 0.05 mm × 0.03 mm × 0.005 mm (Fig. 1). Well-formed crystals are very rare. Formation of aggregates occurs due to intergrowths of crystals along a flattened plane. The lustre is vitreous and the streak is white. The mineral is brittle; the hardness could not be determined due to the small crystal size. The determination of wrightite

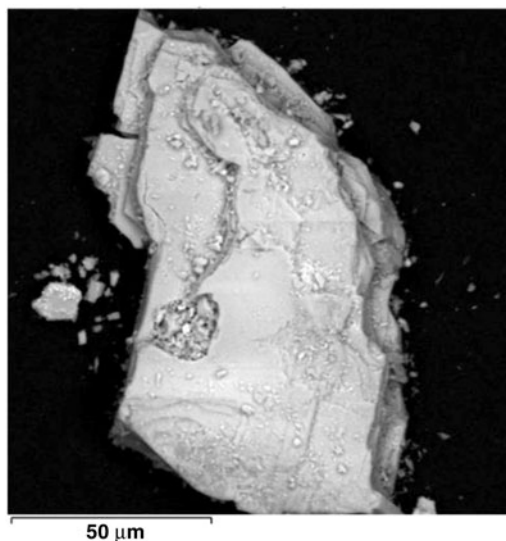


FIG. 1. Scanning electron microscope image of a tabular crystal of wrightite.

properties was in association with other arsenate minerals and in close intergrowth with sylvite. The density calculated from the empirical formula and single-crystal data is 3.499(1) g/cm³.

Optically the mineral is biaxial (–), with $\alpha = 1.679(2)$, $\beta = 1.685(2)$, γ (calc.) = 1.687 and 2V measured using the Wright method = 62(10)° ($\lambda = 589$ nm). The *X* and *Y* directions are located in the plane of tabular crystals, other orientation details are not obvious; tabular crystals have a positive sign of elongation. No pleochroism is observed.

Chemical data

Quantitative elemental microanalysis for 11 grains was carried out using an electron microprobe TESCAN ‘Vega3’ equipped with an Oxford

TABLE 1. Analytical data (in wt.%) for wrightite.

Constituent	Mean	Range	S.D.	Probe standard
Na ₂ O	2.72	2.39–3.03	0.22	NaCl
K ₂ O	18.31	17.75–18.65	0.29	Sanidine
As ₂ O ₅	51.89	51.19–52.99	0.60	GaAs
Al ₂ O ₃	21.14	17.06–23.41	2.05	Sanidine
Fe ₂ O ₃	4.39	1.07–9.06	0.63	NiFe ₂ O ₄
Total	98.45			

S.D. – standard deviation.

TABLE 2. Powder X-ray diffraction data (d in Å) for wrightite (Gandolfi mode, $\text{CoK}\alpha$ radiation).

$I_{\text{meas.}}$	$d_{\text{meas.}}$	$I_{\text{calc.}}$	$d_{\text{calc.}}$	h	k	l
36	8.77	68	8.84	0	0	2
18	6.01	15	6.03	1	0	2
17	4.458	34	4.466	1	1	1
16	4.097	10	4.092	1	1	2
		8	4.119	2	0	0
19	4.010	21	4.012	2	0	1
		3	4.050	0	1	3
19	3.875	11	3.895	1	0	4
5	3.725	13	3.734	2	0	2
10	3.617	14	3.634	1	1	3
13	3.371	23	3.376	2	0	3
		13	3.312	2	1	0
5	3.234	7	3.250	1	0	5
5	3.183	10	3.193	1	1	4
14	3.102	29	3.102	2	1	2
16	3.003	25	3.014	2	0	4
100	2.972	100	2.986	0	1	5
12	2.881	25	2.888	2	1	3
9	2.766	47	2.7866	0	2	0
9	2.709	13	2.7134	3	0	1
15	2.404	11	2.4091	1	2	3
11	2.281	16	2.2886	2	2	1
13	2.140	19	2.1491	2	2	3
7	1.850	3	1.8563	3	2	3
		3	1.8530	1	1	9
5	1.831	10	1.8386	2	1	8
14	1.542	13	1.5465	3	2	7
		2	1.5438	5	0	4
5	1.511	5	1.5159	3	3	2

The strongest lines are given in bold.

TABLE 3. Crystal data and data collection parameters.

Chemical formula (based on single-crystal X-ray diffraction)	$(\text{K}_{1.76}\text{Na}_{0.24})_{\Sigma 2}(\text{Al}_{1.70}\text{Fe}_{0.30})_{\Sigma 2}\text{As}_2\text{O}_9$
M_r	428.5
Crystal system, space group	Orthorhombic, $Pnma$
Temperature (K)	293
a, b, c (Å)	8.2377(3), 5.5731(6), 17.683(1)
V (Å ³)	811.8(1)
Z	4
Radiation type	$\text{MoK}\alpha$
μ (mm ⁻¹)	9.75
Crystal size (mm ³)	0.05×0.03×0.005
Diffractometer	Bruker Smart APEX
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	11,190, 1924, 1204
R_{int}	0.071
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.807
$R_1[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.046, 1.56
No. of reflections	1924
No. of parameters	85
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e ⁻ Å ⁻³)	2.40, -2.33

TABLE 4. Atomic coordinates and isotropic or equivalent displacement parameters ($\text{\AA}^2$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occ.(<1)
As1	0.82486(8)	1/4	0.05869(4)	0.01099(16)	
As2	0.31837(9)	-1/4	0.14499(4)	0.01349(17)	
Al2/Fe2	0.21895(17)	1/4	0.06444(8)	0.0120(4)	0.70/0.30
K1	0.5419(2)	1/4	0.23528(9)	0.0294(5)	
Al1	1/2	0	0	0.0099(5)	
Na2'	0.778(2)	3/4	0.1536(7)	0.0279(7)	0.24(1)
K2'	0.8940(4)	3/4	0.13661(12)	0.0279(7)	0.76(1)
O1	0.4467(5)	1/4	0.0612(2)	0.0122(12)	
O2	0.0137(5)	1/4	0.0255(2)	0.0137(8)*	
O3	0.4609(5)	-1/4	0.0738(2)	0.0115(11)	
O4	0.7284(3)	0.0040(5)	0.02355(17)	0.0123(8)	
O5	0.1988(4)	-0.0050(5)	0.13436(18)	0.0176(9)	
O6	0.8183(6)	1/4	0.1513(3)	0.0235(14)	
O7	0.4178(7)	-1/4	0.2252(3)	0.0304(17)	

**U*_{iso}; Occ. = occupancy

Instruments X-Max 50 silicon drift EDS system operated at 20 kV and 0.445 nA and with a beam size of 0.22 μm . Analytical results are given in Table 1. No elements other than those listed here were detected. The empirical formula based on 9 O atoms per formula unit is $(\text{K}_{1.69}\text{Na}_{0.38})_{\Sigma 2.07}(\text{Al}_{1.80}\text{Fe}_{0.24})_{\Sigma 2.04}\text{As}_{1.96}\text{O}_9$. The simplified formula is $\text{K}_2\text{Al}_2\text{As}_2\text{O}_9$ which requires K_2O 22.1, Al_2O_3 23.9, As_2O_5 54.0, total 100.0 wt.%.

Powder X-ray diffraction data

Powder X-ray diffraction data were collected from three grains using a Rigaku R-AXIS RAPID II

(Gandolfi mode and $\text{CoK}\alpha$ radiation). An additional experiment was performed on a powdered sample of wrightite with sylvite impurities using a Rigaku MiniFlex II with $\text{CuK}\alpha$ radiation. This data was consistent with that collected on the Rigaku R-AXIS RAPID II. The measured and calculated powder diffraction data are given in Table 2. The unit-cell parameters, $a = 8.230(5)$, $b = 5.555(4)$, $c = 17.584(1)$ $\text{\AA}$ and $V = 803.9(6)$ $\text{\AA}^3$, were calculated from these data using the least-squares method in the programme *PDWIN* (Fundamensky and Firsova, 2009). The diagnostic lines are [$d, \text{\AA}(I)(hkl)$] are: 8.77(36)(002); 6.01(18)(102); 4.458(17)(111); 4.097(16)(112); 4.010

TABLE 5. Atomic displacement parameters ($\text{\AA}^2$)*.

	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
As1	0.0053 (3)	0.0067 (2)	0.0210 (3)	0	0.0009 (3)	0
As2	0.0126 (3)	0.0070 (2)	0.0209 (3)	0	0.0015 (3)	0
Al2/Fe2	0.0059 (6)	0.0064 (5)	0.0237 (8)	0	0.0015 (5)	0
K1	0.0229 (9)	0.0318 (8)	0.0336 (9)	0	0.0080 (7)	0
Al1	0.0034 (8)	0.0027 (6)	0.0235 (10)	0.0002 (6)	0.0033 (7)	-0.0005 (6)
Na2'	0.0426 (17)	0.0178 (8)	0.0233 (11)	0	-0.0049 (10)	0
K2'	0.0426 (17)	0.0178 (8)	0.0233 (11)	0	-0.0049 (10)	0
O1	0.008 (2)	0.0093 (17)	0.019 (2)	0	0.0018 (17)	0
O3	0.009 (2)	0.0072 (16)	0.019 (2)	0	0.0041 (17)	0
O4	0.0034 (13)	0.0039 (11)	0.0297 (17)	0.0000 (10)	-0.0005 (12)	-0.0009 (11)
O5	0.0119 (17)	0.0087 (12)	0.0323 (19)	0.0014 (12)	0.0063 (13)	0.0015 (11)
O6	0.016 (3)	0.033 (3)	0.022 (2)	0	0.000 (2)	0
O7	0.033 (3)	0.029 (3)	0.029 (3)	0	-0.007 (2)	0

*Na2' and K2' parameters are constrained to be the same.

TABLE 6. Selected bond lengths (Å) and bond-valence sums.

Bond	Distance	Bond	Distance
As1–O6	1.639(5)	As2–O7	1.638(5)
As1–O2	1.663(4)	As2–O5	1.694(3)
As1–O4	1.702(3)	As2–O5 ⁱ	1.694(3)
As1–O4 ⁱⁱ	1.702(3)	As2–O3	1.722(4)
<As1–O>	1.68	<As2–O>	1.69
Al1–O1	1.818(3)	Al/Fe2–O5 ⁱⁱ	1.826(3)
Al1–O1 ^{ix}	1.818(3)	Al/Fe2–O5 ^v	1.877(4)
Al1–O4 ^{xi}	1.927(3)	Al/Fe2–O2 ⁱⁱ	1.891(3)
Al1–O4 ^{xii}	1.927(3)	Al/Fe2–O1 ⁱⁱ	1.891(3)
Al1–O3	1.936(3)	Al/Fe2–O4 ⁱⁱⁱ	2.148(3)
Al1–O3 ^x	1.936(3)	Al/Fe2–O4 ^{iv}	2.148(3)
<Al1–O>	1.89	<Al2–O>	1.96
K1–O6	2.719(5)	K2–O7 ^{vi}	2.451(5)
K1–O6 ^{vi}	2.723(5)	K2–O4 ^{xiii}	2.804(4)
K1–O7 ⁱⁱ	2.974(2)	K2–O4 ^{xiv}	2.804(4)
K1–O7 ^{viii}	2.974(2)	K2–O5 ^{xiii}	2.858(4)
K1–O5 ^{vi}	3.000(3)	K2–O5 ^{xiv}	2.858(4)
K1–O5 ^{vii}	3.000(3)	K2–O6	2.8671(15)
<K1–O>	2.90	K2–O6 ^{xiii}	2.8671(15)
Na2–O7 ^{vi}	2.434(14)	K2–O2 ^{xv}	2.965(5)
Na2–O4 ^{xiii}	2.731(11)	<K2–O>	2.81
Na2–O4 ^{xiv}	2.731(11)		
Na2–O6	2.807(2)		
Na2–O6 ^{xiii}	2.807(2)		
Na2–O3 ^{viii}	2.965(16)		
<Na2–O>	2.75		

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, y+1/2, -z$; (iii) $x, y-1, z$; (iv) $x, -y+1/2, z$; (v) $x+1, y-1, z$; (vi) $x+1, y, z$; (vii) $x, -y-1/2, z$; (viii) $-x+1, y+1/2, -z$; (ix) $-x+1, -y, -z$; (x) $x-1, -y+1/2, z$; (xi) $x-1/2, -y+1/2, -z+1/2$; (xii) $x-1/2, y, -z+1/2$; (xiii) $x-1, y+1, z$; (xiv) $-x+3, y-1/2, -z$; (xv) $-x+3, y+1/2, -z$; (xvi) $-x+2, -y, -z$; (xvii) $x, y+1, z$.

(19)(201,013); 3.875(19)(104); 3.003(16)(204); and 2.972(100)(015)

Crystal-structure determination

Single-crystal X-ray diffraction data were collected using a Bruker Smart APEX diffractometer equipped with CCD detector. A hemisphere of three-dimensional data was collected using MoK α X-radiation and frame widths of 0.5° in ω , with 60 s used to acquire each frame. The data were corrected for Lorentz, polarization and background effects using the Bruker programs *APEX* and *XPREF*. A semi-empirical absorption-correction based upon

the intensities of equivalent reflections was applied in the Bruker program *SADABS*.

The structure was solved by charge flipping and refined on the basis of 1924 unique observed reflections using the *Jana2006* program suite (Petříček *et al.*, 2014) (Table 3). The crystal structure was refined on the basis of F^2 . Refinement of all atom-position parameters, allowing for the anisotropic displacement of all atoms, and the inclusion of a refinable weighting-scheme of the structure factors, resulted in a final agreement index (R_1) of 0.043, calculated for the 1924 independent reflections, and a goodness-of-fit (S) of 1.56. Atomic coordinates, atomic displacement parameters and selected bond

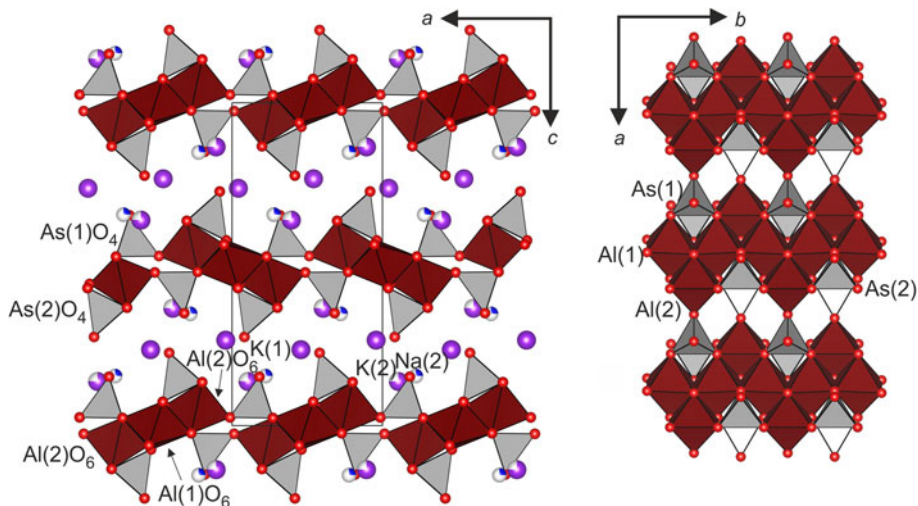


FIG. 2. Crystal structure of wrightite: (left) crystal structure; and (right) zigzag chains of AlO_6 octahedra.

distances are summarized in Tables 4–6. Projections of the crystal structure, coordination polyhedra of alkali cations and coordination of the additional oxygen atom are provided in Figs 2–4. The crystallographic information file has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below).

Discussion

Wrightite is orthorhombic, space group $Pnma$, with $a = 8.2377(3)$, $b = 5.5731(6)$, $c = 17.683(1)$ Å, $V = 811.8(1)$ Å³ and $Z = 4$.

The crystal structure of wrightite is similar to those of the synthetic analogues such as $\text{NaKA}_2\text{O}(\text{AsO}_4)_2$ (Yania *et al.*, 2010; Chang *et al.*, 1997; Boughzala and Jouini, 1997). This structure consists of $\text{Al}_2\text{O}(\text{AsO}_4)_2$ layers in the ab plane (Fig. 2a). Each layer contains two independent isolated AsO_4 tetrahedra and two AlO_6 octahedra. AlO_6 octahedra are linked by edges, forming zigzag chains along the b axis inside the Al–As layer (Fig. 2b). Eight- and seven-coordinated K atoms are located in the interlayer space between layers.

There are two sites for alkaline elements: $M1$ and $M2$. The $M1$ site is only occupied by K atoms. The K1 cation is surrounded by nine oxygen atoms with bond lengths of 2.719–3.632 Å and forms a

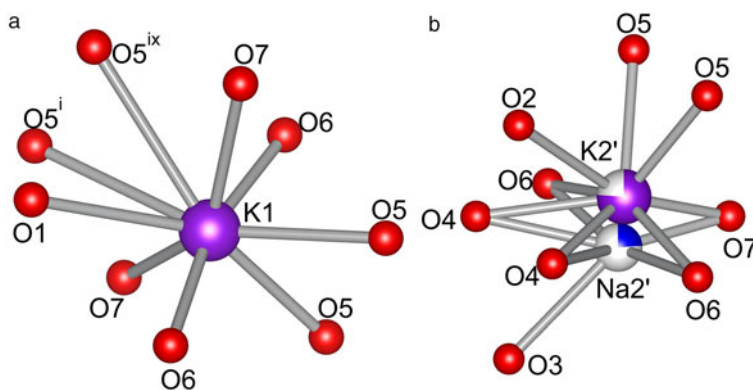


FIG. 3. Coordination of alkali elements in the crystal structure of wrightite: (a) K1O_9 polyhedra; and (b) splitting of the $M2$ site into $\text{Na2}'$ and $\text{K2}'$ sub-positions.

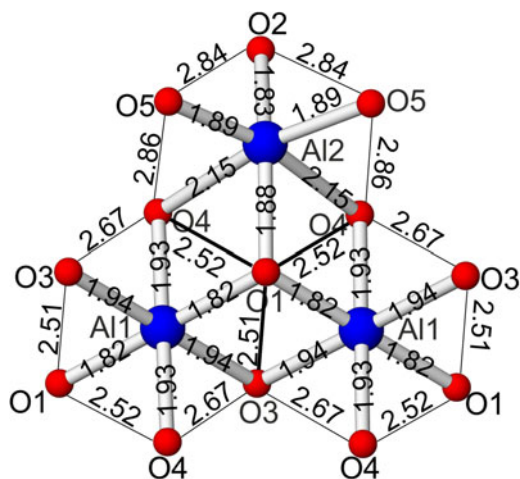


FIG. 4. Coordination of the additional oxygen atom, O1, in the crystal structure of wrightite.

distorted polyhedra $K1O_9$ (Fig. 3a). The bond-valence sum for K1 is 0.89 valence units (vu). The M2 site splits into the K2' and Na2' sub-positions, and the coordination of K2' and Na2' is different. K2' polyhedra are eightfold-coordinated with one short bond length, 2.451 Å, and seven bond lengths varying over the interval 2.804–2.965 Å. The bond-valence sum for K2' is 1.07 vu (Table 7). The excess of the ideal value of 1 is caused mainly by the short bond in the $K2'O_8$ polyhedron. Na2' is coordinated by seven oxygen atoms with bond distances in the range of 2.434–2.965 Å and a bond-valence sum of 0.12 (Fig 3b). The distance between K2'–Na2' sub-positions is 1.00(2) Å.

The $Al1O_6$ octahedron is only occupied by Al. The Al1 site is located in the inversion centre and it

forms an octahedron with bond lengths in the range of 1.818–1.936 Å. The Al2 site occurs in a very distorted octahedron with the distance range varying from 1.826 to 2.148 Å. An additional oxygen O1 is coordinated by three Al atoms with bond lengths ranging from 1.818 to 1.891 Å (Fig. 4).

The connection of AlO_6 octahedra via shared O–O edges leads to the convergence of three Al^{3+} octahedra on the O1 atom. This approach may be excessive and causes the repulsion of Al atoms from each other. There are two ways Al atoms can be repulsed from each other: (1) by extending the Al–O bonds; or (2) the Al–Al distance can be increased by shortening the shared edges O–O of the AlO_6 octahedra. Analysis of the values of the interatomic distances Al–O and O–O allows us to determine which of these mechanisms occurs. In accordance with the first mechanism, the Al–O bonds in the Al–O–Al chains are on average 1.95 Å, which is 0.06 Å more than the average value of the bonds of O atoms with an Al atom (1.89 Å) (Fig. 4). In accordance with the second mechanism, all three shared edges have a reduced length (their average value is 2.52 Å) relative to the average length of the unshared edges of 2.68 Å (Fig. 4). So, both mechanisms of repulsing Al atoms from each other are actually realized in the crystal structure of wrightite.

The AsO_4 tetrahedra are slightly distorted; and the average As–O bond length in the crystal structure is 1.68 Å in $As1O_4$ and 1.69 Å in $As2O_4$. In comparison with the average As^{5+} –O bond length of 1.66 Å indicated in Janssen *et al.* (2006), the above values can be considered as acceptable.

Wrightite, $K_2Al_2O(AsO_4)_2$, is the first mineral of the $K_2Fe_2O(AsO_4)_2$ structure type (Chang *et al.*,

TABLE 7. Bond-valence analysis for wrightite.

	As1	As2	Al1	Al/Fe2	K1	K2'*	Na2'*	Σ
O1			0.586 ^{x2}	0.553	0.059			1.784
O2	1.325			0.635		0.080		1.938
O3		1.129	0.426 ^{x2}				0.010	1.991
O4	1.192 ^{xyz, ii}		0.436 ^{xi, xii}	0.266 ^{iii, iv}		0.124	0.020 ^{xiii, xiv}	1.914
O5		1.218 ^{xyz, i}		0.533	0.096 ^{vi, vii} , 0.017 ^{i, ix}	0.107 ^{xiii, xiv}		1.985
O6	1.413				0.203	0.104 ^{x2}	0.016 ^{x2}	2.044
O7		1.417			0.103 ^{x2}	0.321	0.044	1.944
Σ	5.12	4.98	2.89	2.79	0.89	1.07	0.13	

Bond valences for positions with occupation not equal to unity are marked with an asterisk. Parameters from Brown and Altermatt (1985).

TABLE 8. Crystal chemical parameters of wrightite and synthetic isotypes (space group *Pmna*, *Z* = 4).

Phase	Formula	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³
Single-crystal data [1]	(K _{1.76} Na _{0.24})Σ ₂ (Al _{1.78} Fe _{0.22})Σ ₂ As ₂ O ₉	8.2377(3)	5.5731(6)	17.683(1)	811.8(1)
Powder-diffraction data [1]	(K _{1.69} Na _{0.38})Σ _{2.07} (Al _{1.80} Fe _{0.24})Σ _{2.04} As _{1.96} O ₉	8.230(5)	5.555(4)	17.584(1)	803.9(6)
Synthetic isotype [2]	K ₂ Fe ₂ O(AsO ₄) ₂	8.5219(3)	5.7616(2)	17.9452(6)	881.1(1)
Synthetic isotype [2]	Rb ₂ Fe ₂ O(AsO ₄) ₂	8.5330(2)	5.7945(2)	18.6157(1)	920.4(1)
Synthetic isotype [3]	Rb ₂ Cr ₂ O(AsO ₄) ₂	8.546(3)	5.665(1)	18.464(5)	893.9(4)
Synthetic isotype [4]	NaKAl ₂ O(AsO ₄) ₂	8.2368(6)	5.5228(3)	17.016(1)	774.1(1)

Refs: [1] this work; [2] Chang *et al.* (1997); [3] Boughzala and Jouini (1997); and [4] Yania *et al.* (2010).

1997). The similar inorganic compound, NaKAl₂O(AsO₄)₂, was synthesized by a gas transport reaction method in an alumina tube (Yania *et al.*, 2010). K₂Fe₂O(AsO₄)₂ and Rb₂Fe₂O(AsO₄)₂ have been obtained by the solid-state reaction method from KH₂AsO₄ (or RbH₂AsO₄) and Fe₂O₃ (Chang *et al.*, 1997). Rb₂Cr₂O(AsO₄)₂ has been prepared by solid-state reactions from Rb₂CO₃, Cr₂O₃ and NH₄H₂AsO₄ (Boughzala and Jouini, 1997). All inorganic analogues crystallize in the same space group, *Pmna*, and their unit-cell parameters vary depending on the composition. The comparison of crystal chemical parameters of wrightite and synthetic analogues are listed in Table 8. In the crystal structure of Rb₂Fe₂O(AsO₄)₂, one of the Rb atomic positions is split into two sub-positions (Chang *et al.*, 1997). In the crystal structure of wrightite, the position of K2'/Na2' is also split. A possible reason for splitting is the difference between cation sizes.

The Al2/Fe2–O distances and bond-valence sums indicate clearly that Fe is 3+. In the synthetic analogues of wrightite, K₂Fe₂O(AsO₄)₂ and Rb₂Fe₂O(AsO₄)₂, the trivalent state of Fe has been confirmed by Mössbauer data.

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Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.091>

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