

Natrowalentaite, a new mineral from the Griffins Find gold deposit, Western Australia

Dedicated to the late EH (Ernie) Nickel for his generosity and encouragement in providing mineral specimens for study

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Abstract

Natrowalentaite, $[(\text{Fe}^{3+}, \text{Na}, \square)(\text{H}_2\text{O})_6][\text{NaAs}^{3+}_2(\text{Fe}^{3+}_{3-x}\text{W}^{6+}_x)(\text{PO}_4)_2(\text{O}, \text{OH})_7]$, $x \sim 0.7$, is a new secondary phosphate mineral from the Griffins Find gold deposit, Western Australia. It forms aggregates of extremely thin (1 to 3 μm), bright greenish-yellow blades with lengths up to 200 μm , on natropharmacosiderite. The blades are flattened on {100}, elongated on [010] and exhibit the forms {100}, {001} and {011}. Cleavage is perfect on {100}. The measured density is 2.91(2) g cm^{-3} . Optically, natrowalentaite is biaxial (-), with $\alpha = 1.650(3)$, $\beta = 1.728(3)$, $\gamma = 1.772(3)$ (white light), and $2V$ (meas.) = 71(2)°. The orientation is $X = \mathbf{a}$, $Y = \mathbf{c}$, $Z = \mathbf{b}$. Dispersion is distinct with $r > v$, and pleochroism is imperceptible. Electron microprobe analyses give the empirical formula $\text{Na}_{1.09}\text{K}_{0.07}\text{Ca}_{0.30}\text{Fe}^{3+}_{2.57}\text{W}^{6+}_{0.70}\text{As}^{3+}_{2.10}\text{P}_{2.02}\text{H}_{12.02}$ based on 21 anions per formula unit. Natrowalentaite is orthorhombic, *Imma*, with $a = 25.770(3)$, $b = 7.3250(8)$, $c = 10.522(1)$ Å, $V = 1986.2(4)$ Å³ and $Z = 4$. The structure was solved and refined using single-crystal synchrotron X-ray data to $R_f = 0.062$ for 875 unique reflections to a resolution of 0.7 Å. Natrowalentaite is isostructural with walentaite, which has a structure based on layers of composition $(\text{Fe}, \text{W})_3(\text{PO}_4)_2(\text{O}, \text{OH})_6$, with surface-attached As^{3+}O_3 groups and Na/Ca cations and with interlayer hydrated cations and H_2O . Natrowalentaite differs from walentaite in having dominant Na as a surface-attached cation, rather than Ca, and in having partial replacement of Fe^{3+} by W^{6+} in the layers. The natrowalentaite and walentaite structures are unusual in that they contain $(\text{As}_3\text{O}_6)^{3-}$ trimeric clusters of pyramidal As^{3+}O_3 arsenite groups.

KEYWORDS: natrowalentaite, Griffins Find gold deposit, crystal structure, hydrated sodium ferric tungsten arsenite phosphate, walentaite, $(\text{As}_3\text{O}_6)^{3-}$ clusters

Introduction

Natrowalentaite was first identified by Dr Ernie H Nickel (EHN) (Nickel, 1987) in specimens collected by John Day at the Griffins Find gold deposit, Western Australia. Nickel conducted electron microprobe analyses on the mineral and gave a tentative formula as a ferric tungsten arsenate phosphate, $(\text{Fe}, \text{W}, \text{Ca})_{15}(\text{PO}_4)_4(\text{AsO}_4)_{16}(\text{OH})_2 \cdot 32 \text{H}_2\text{O}$. He indexed the powder X-ray diffraction (PXRD) pattern using the same orthorhombic cell as reported by Dunn et al. (1984) for walentaite and he referred to the mineral as tungsten-bearing walentaite. Nickel noted that further chemical characterization of the mineral, including the valence state of tungsten, could only be resolved by single-crystal structure analysis. To this end, he sent a specimen of the mineral to one of the authors (Ian Grey), but, at the time, the ultra-thin bladed crystals were too tiny (only ~1 μm thick) to collect statistically significant single-crystal X-ray diffraction data. It was only recently, with access to the Australian Synchrotron microfocus beam line, that it has been possible to obtain high-quality diffraction data for a structure determination and refinement. The results of the structure refinement, coupled with electron microprobe analyses, showed that the arsenic is present as As^{3+} , not as As^{5+} . Based on the new data, a new mineral proposal (IMA2018-23) was submitted to the Commission on New Minerals, Nomenclature and Classification

(CNMNC) of the International Mineralogical Association (IMA). The new mineral and its name, based on dominant sodium replacing calcium in walentaite, were subsequently approved by the IMA CNMNC. The holotype specimen is deposited in the collections of the Natural History Museum of Los Angeles County, catalogue number 66703.

Occurrence

The Griffins Find gold deposit (118°19'12" E, 33°4'11" S) is located about 15 km northwest of Lake Grace and 275 km southeast of Perth in Western Australia (Fig. 1). The deposit was discovered in 1957 and gold was mined commercially from two open pits in the 1980s, producing approximately 55 000 troy ounces of gold. The deposit comprises surface-enriched, gold-bearing, quartz–sulfide lodes in a highly metamorphosed greenstone, which has been intruded by recrystallized adamellite. The main ore minerals are pyrrhotite, löllingite and arsenopyrite, with the gold being closely associated with the last two minerals. The ore minerals are dispersed in the rock-forming minerals quartz, potassium-feldspar, plagioclase, biotite and clinopyroxene. The deposit is the only Australian location for walentaite. Since mining ceased the open pits have filled with water and access to minerals in the pits is no longer possible (Fig. 2). However, walentaite has been reported forming dull yellow crusts on ironstone and quartz in the waste dump near the main pit (www.mindat.org, viewed 12/3/19).

According to Nickel (1987), the specimens of natrowalentaite were located at the bottom of one of the pits, about 20 m below the original land surface and 4 m below the original pre-mining water table. Above the

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Figure 1. Location of the Griffins Find gold deposit.

pre-mining water table, the rock has been heavily weathered and the primary sulfides and arsenides have been converted into a range of secondary minerals, including goethite, jarosite, scorodite, arseniosiderite and natropharmacosiderite. The natrowalentaite occurs on fracture surfaces in iron-stained rock, together with natropharmacosiderite and jarosite (Fig. 3). It is a product of supergene alteration and Nickel (1987) concluded that the chemical components were derived from the following primary minerals: apatite (calcium and phosphorus), löllingite and arsenopyrite (arsenic), pyrrhotite and arsenopyrite (iron) and scheelite (tungsten). In addition, natropharmacosiderite is the most likely source of sodium.

Appearance and properties

The specimen supplied by EHN for this study comprised a dense mass of bright greenish-yellow blades on a 1.5 mm wide core of brown natropharmacosiderite. Individual blades are extremely thin, 1 to 3 μm , with widths of typically 10 to 20 μm and lengths up to 200 μm . The blades are flattened on {100} and elongated on [010]. Forms are {100}, {001} and {011} — see Figure 4. Cleavage is perfect on {100}. The density measured by flotation in methylene iodide-toluene is 2.91(2) g cm^{-3} . For comparison, the density calculated from the empirical formula and the PXRD cell is 2.93 g cm^{-3} .

Natrowalentaite crystals are biaxial (-), with $\alpha = 1.650(3)$, $\beta = 1.728(3)$, $\gamma = 1.772(3)$ (white light), and $2V$ (meas.) = $71(2)^\circ$ measured directly on a spindle stage. The orientation is $X = \mathbf{a}$, $Y = \mathbf{c}$, $Z = \mathbf{b}$. Dispersion is distinct with $r > v$, and there is no perceptible pleochroism. The indices of refraction agree with those measured by Nickel (1987) to within the associated errors.



Figure 2. The main open pit at Griffins Find (~55 m deep). It has flooded since mining ceased. Photo Kim Macdonald.

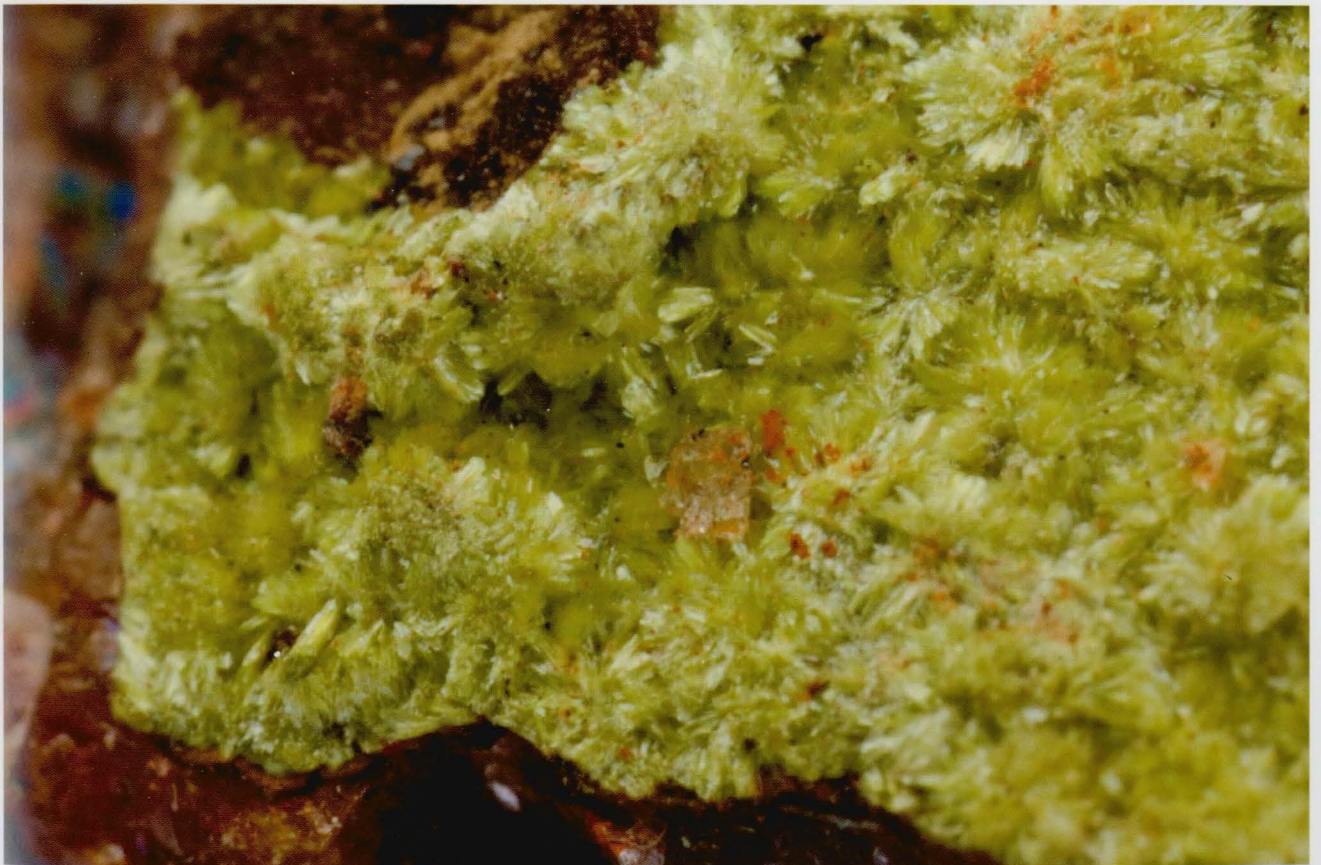
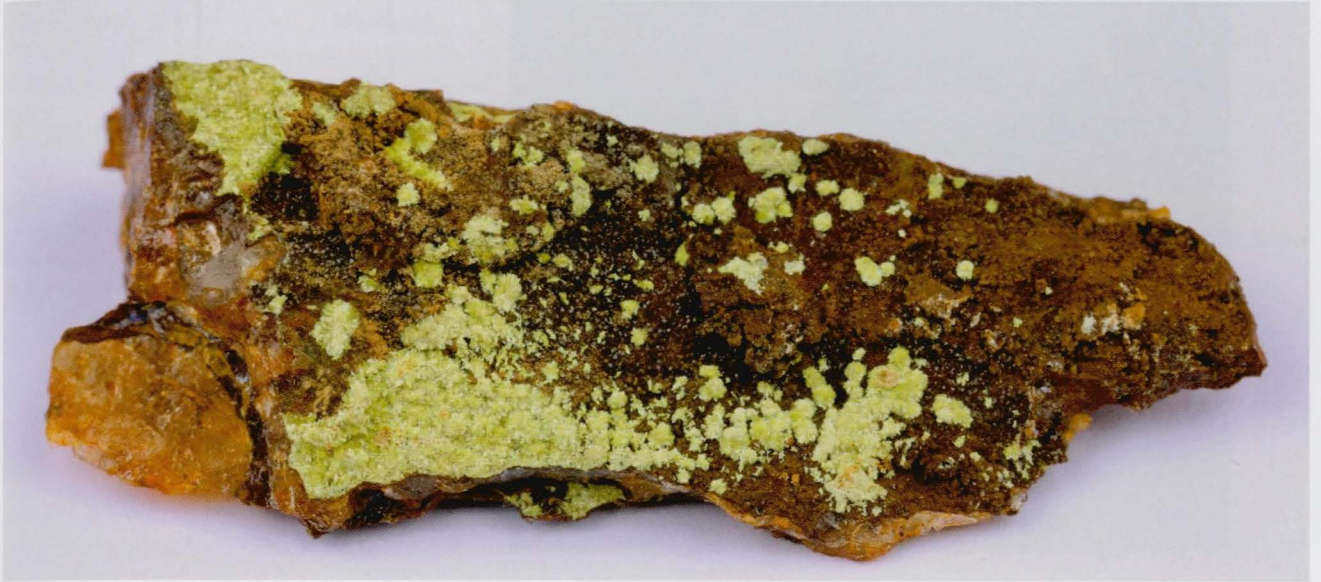


Figure 3. Upper image: yellow aggregates of natrowalentaite on a specimen from Mark Creasy's private collection (originally part of a collection made by Blair Gartrell); field of view is 5 cm wide. Lower image: higher-magnification image, field of view is 0.7 mm wide. Photos Jenna Sharp.

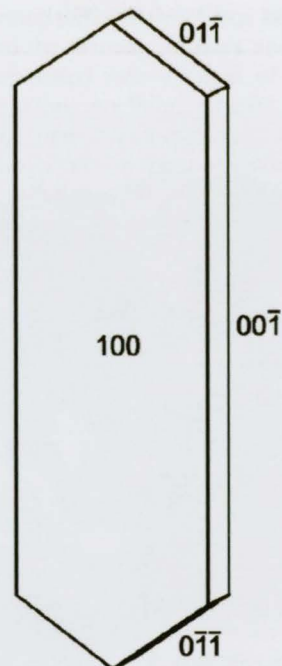
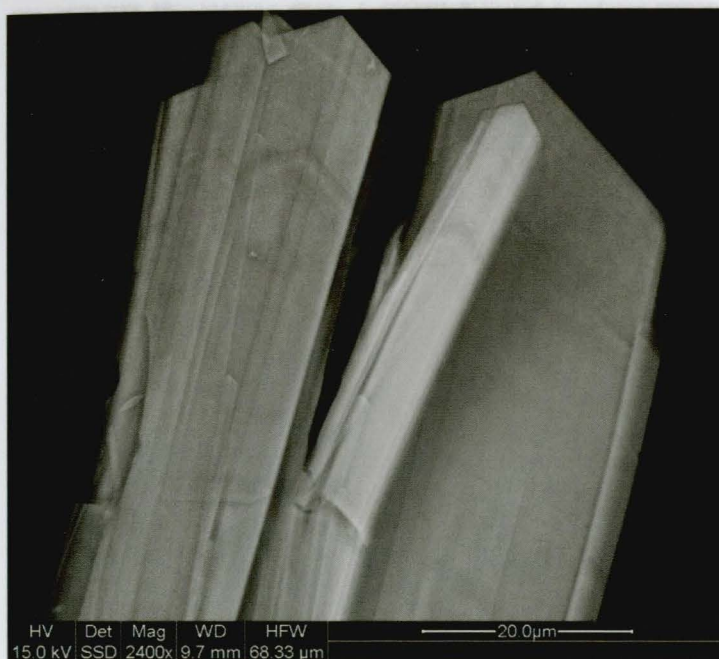


Figure 4. Scanning-electron microscope image of natrowalentaite blades, with clinographic projection showing crystal forms.

Chemical composition

Crystals of natrowalentaite were analysed using wavelength-dispersive spectrometry on a JEOL JXA 8500F Hyperprobe operated at an accelerating voltage of 15 kV and a beam current of 2.5 nA. The beam was defocused to 4 μm . Standards were scorodite (iron and arsenic), wollastonite (calcium), albite (sodium), synthetic MnSiO_3 (manganese), AlPO_4 (phosphorus) and scheelite (tungsten). Analytical results (average of analyses on 4 crystals) are given in Table 1. The H_2O content was calculated based on the results of the crystal structure analysis. The low total is attributed to the beam penetrating through the ultrathin blades. For the calculation of the empirical formula, the oxides were scaled so that their sum with the H_2O content totaled 100%. Also given for comparison in Table 1 are the electron microprobe analyses reported by Nickel (1987) for tungsten-bearing walentaite. The empirical formula, based on 21 anions per formula unit is

$$\text{Na}_{1.09}\text{K}_{0.07}\text{Ca}_{0.30}\text{Fe}^{3+}_{2.57}\text{W}^{6+}_{0.70}\text{As}^{3+}_{2.10}\text{P}_{2.21}\text{O}_{12.02}\text{H}$$

X-ray crystallography

Powder diffraction

X-ray powder diffraction data were obtained using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer, with monochromatized $\text{MoK}\alpha$ radiation. A Gandolfi-like motion on the ϕ and ω axes was used to randomize the sample. Observed d values and intensities were derived by profile fitting using JADE 2010 software. Data (in $\text{\AA}$ for $\text{MoK}\alpha$) are given in Table 2. Unit cell parameters refined from the powder data using JADE 2010 with whole pattern fitting are: $a = 25.788(8)$, $b = 7.336(1)$, $c = 10.519(2)$ $\text{\AA}$, $V = 1990.0(6)$ $\text{\AA}^3$, $Z = 4$. The b and c cell parameters are reversed relative to those reported by Nickel (1987), to correspond to the first setting of orthorhombic space group *Imma* (those reported by Nickel correspond to *Imam*).

Single-crystal study

A thin blade of natrowalentaite, $0.070 \times 0.007 \times 0.002$ mm^3 , was used for single-crystal diffraction data collection made at the macromolecular microfocus beam line MX2 of the Australian Synchrotron. Data were collected using monochromatic radiation with a wavelength of 0.7107 $\text{\AA}$. The crystal was maintained at 100 K in an open-flow nitrogen cryostream. Refined unit cell parameters are $a = 25.770(3)$, $b = 7.3250(8)$, $c = 10.522(1)$ $\text{\AA}$, $V = 1986.2(4)$ $\text{\AA}^3$.

A structure solution in space group *Imma*, was obtained using SHELXT (Sheldrick, 2015). The structural model was essentially the same as that obtained from a recent study of walentaite from the White Elephant mine, USA (Grey et al., 2018). Refinement of the structure was made using SHELXL (Sheldrick, 2015), resulting in convergence at $R_1 = 0.061$ for 872 observed reflections with $I > 2\sigma(I)$ and 0.062 for all 875 reflections, to a resolution of 0.7 $\text{\AA}$.

Compositional and atom positional disorders were encountered, as described in detail for walentaite by Grey et al. (2018). The results are indicative of the crystals being composed of small regions of different compositions that are ordered locally on a very fine scale, so that only the average structure can be obtained from the refinement. Refined coordinates, equivalent isotropic displacement parameters and site occupation factors are given in Table 3.

Discussion

Description of the crystal structure

Natrowalentaite has a layer structure, illustrated in Figure 5. The layers are stacked along $[100]$ with a separation = $0.5a$ of 12.88 $\text{\AA}$. Hydrated-cation polyhedra and H_2O molecules are located between the layers and are hydrogen-bonded to the layers. The heteropolyhedral layers comprise hexagonal rings of corner-connected $(\text{Fe,W})\text{O}_6$ octahedra that are

Table 1. Analytical data (wt%)

	Natrowalentaite			Walentaite	
	Mean	Range	SD	Nickel (1987) ^(a)	Grey et al. (2018)
Na ₂ O	3.52	2.96–4.22	0.47		0.90
K ₂ O	0.34	0.21–0.57	0.20		-
MnO	-				2.69
CaO	1.76	1.48–1.95	0.20	2.3	2.55
Fe ₂ O ₃	21.4	19.4–22.3	1.2	25.3	28.1
WO ₃	17.0	13.4–19.1	2.4	14.5	-
P ₂ O ₅	14.8	13.3–15.6	0.9	16.5	12.9
As ₂ O ₃	21.7	19.4–24.1	1.8		29.1 ^(c)
As ₂ O ₅				24.9	4.23 ^(c)
Σ oxides	80.5			83.5	80.5
H ₂ O	12.3 ^(b)			16.5	
Total	92.8			100.0	

(a) Nickel (1987) did not analyse for Na, and reported As as As₂O₃ and H₂O = 100 – Σ oxides

(b) H₂O from structure

(c) As₂O₃/As₂O₅ from structure

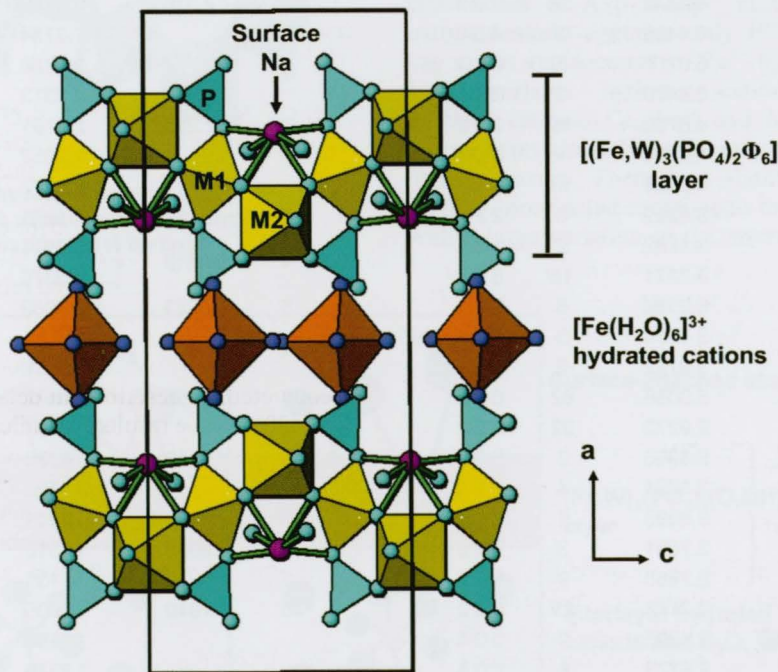


Figure 5. [010] projection of the crystal structure of natrowalentaite, showing saw-tooth layers of corner-connected (Fe,W)O₆ octahedra and PO₄ tetrahedra, together with surface-coordinated sodium and with interlayer Fe³⁺(H₂O)₆ hydrated cations. The surface-coordinated arsenite clusters have been omitted for clarity. They are shown in Figure 6.

decorated with PO₄ tetrahedra. The PO₄ tetrahedra each share three vertices with three octahedra, giving the same topology as in the alunite supergroup mineral kintoreite-1c, PbFe₃(PO₄)₂(OH,H₂O)₆ (Kharisun et al., 1997; Bayliss et al., 2010). The heteropolyhedral layer, with composition (Fe_{2.33}W_{0.67})(PO₄)₂Φ₆, Φ = O,OH, can be described as unit-cell twinned kintoreite, with the twin plane = (001), giving the characteristic saw-tooth layers shown in Figure 5.

There are two independent octahedral sites in the layer, M1 and M2 in Figure 5, with the tungsten ordered preferentially into the M2 site, which has an occupancy of 0.65Fe³⁺ + 0.35W⁶⁺. The tungsten is displaced from the position occupied by iron by 0.4 Å to establish two short bonds of 1.78 Å, characteristic of the tungstenyl (WO₂)²⁺ group (Roy et al., 2015). Substitution of W⁶⁺ for Fe³⁺ occurs in a number of ferric-containing minerals, as discussed by Kolitsch (1998).

Pyramidal arsenite groups, As³⁺O₃, as well as sodium (with minor calcium and potassium), are attached to the surface of the heteropolyhedral layers. These atoms are disordered over several closely-spaced positions, corresponding to different locally-ordered configurations, as discussed in

detail for walentaite (Grey et al., 2018). A locally ordered configuration of the AsO₃ pyramids is shown in Figure 6. It involves trimeric clusters, with composition (As₃O₆)³⁻, which are attached to the (Fe_{2.33}W_{0.67})(PO₄)₂(O,OH)₆ layer by sharing edges with the M2-centred octahedra. The clusters are composed of corner-shared pairs of AsO₃ trigonal pyramids (As2 in Fig. 6), which connect to a third AsO₃ pyramid (As3 in Fig. 6) by edge-sharing. This unusual geometry involves all three As³⁺ cations sharing a common anion, O6 in Figure 6. A trimeric (As₃O₆)³⁻ arsenite cluster has been reported in a heteropolymolybdate crystal structure, but in this case, the three AsO₃ groups share corners in a cyclic arrangement (Martin-Frère et al., 1991). The As2 atoms in the natrowalentaite structure are located only 0.8 Å from the surface-coordinated sodium (plus minor calcium, potassium), so both sites cannot be simultaneously occupied. Locally, when the As2 sites are occupied, trimeric clusters are present, as shown in Figure 6, and the sodium sites are vacant; when the sodium sites are occupied, arsenic can occupy only the As3 site of the clusters, giving 2Na and isolated AsO₃ pyramids on the surface of the layers. The different local structure configurations are shown schematically in Figure 7.

Table 2. Powder X-ray data (*d* in Å) for natrowalentaite. Only calculated lines with *I* > 1 are listed.

<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>hkl</i>	<i>I</i> _{obs}	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{calc}	<i>hkl</i>
100	12.95	12.8850	100	2 0 0					
9	9.72	9.7413	11	1 0 1	2	2.379	2.3787	2	9 1 2
14	6.72	6.6542	28	3 0 1			2.3686	3	10 1 1
8	6.51	6.4425	3	4 0 0	2	2.316	2.3143	6	10 0 2
5	6.03	6.0117	5	0 1 1			2.2734	2	5 2 3
4	5.42	5.4479	3	2 1 1			2.2432	2	6 0 4
9	4.88	4.8706	15	2 0 2			2.2313	2	4 3 1
5	4.64	4.6286	4	5 0 1	7	2.226	2.2181	11	9 0 3
10	4.41	4.3953	10	4 1 1			2.2057	3	9 2 1
4	3.553	3.5229	6	2 2 0			2.1977	4	8 2 2
2	3.450	3.4282	2	1 2 1	3	2.121	2.1076	5	10 2 0
8	3.335	3.3271	18	6 0 2	4	2.0510	2.0544	4	7 1 4
5	3.207	3.2086	6	3 2 1			2.0375	6	8 0 4
		3.1634	3	0 1 3	5	2.0023	2.0039	5	0 3 3
		3.0722	2	2 1 3			1.9882	2	12 0 2
27	3.020	3.0058	62	0 2 2			1.9801	4	2 3 3
15	2.940	2.9273	32	2 2 2	7	1.9559	1.9481	16	11 0 3
3	2.880	2.8996	3	5 0 3			1.9397	5	11 2 1
		2.8721	4	5 2 1	6	1.9159	1.9129	15	6 2 4
		2.8393	3	8 1 1			1.8525	2	12 2 0
5	2.805	2.7891	3	7 1 2			1.8408	2	10 0 4
		2.7868	9	6 2 0	8	1.8389	1.8313	14	0 4 0
11	2.759	2.7472	29	8 0 2			1.8130	5	2 4 0
4	2.621	2.6305	9	0 0 4	10	1.7840	1.7805	21	8 2 4
		2.5773	6	2 0 4			1.7656	3	3 4 1
		2.4297	4	3 2 3			1.7376	2	2 0 6
4	2.433	2.4188	8	8 2 0	7	1.7242	1.7257	2	13 0 3
							1.7200	6	5 2 5



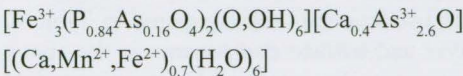
The interlayer hydrated cation polyhedra are of two types, depending on whether they are centred by Fe³⁺ or by sodium. The iron-centred polyhedra have octahedral coordination, as shown in Figure 5. The sodium-centred polyhedra, which contain minor calcium and potassium, are square antiprisms, which share edges to form crankshaft-like chains parallel to [010]. Edge-sharing of sodium-centred square antiprisms have been reported from a neutron diffraction study of the zeolite thomsonite (Pluth et al., 1985). The interlayer Fe³⁺ and sodium cations are separated by only 1.3 Å, and so, analogous to the surface-coordinated As₂/Na sites, the occupations of the two types of interlayer sites are mutually exclusive. Locally, the interlayer region contains either the iron-centred octahedra, or the sodium-centred square-antiprisms. From Table 3, the combined number of interlayer cations is 0.7(2) per formula unit. The structural components present in the interlayer region are most likely dependent on which components are attached to the surface of the layers (As₃O₆ clusters or 2Na + AsO₃). The crystal structure refinement showed that there was approximately equal probability of both of the two types

of interlayer components and the two types of surface components.

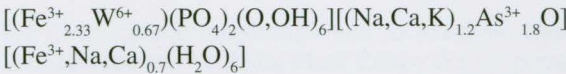
Compositions of walentaite and natrowalentaite

A comparison of the compositions of walentaite and natrowalentaite is assisted by separating the formulae for the two minerals into three compositional components corresponding to the heteropolyhedral layer, the surface-attached components and the interlayer hydrated components. This separation of specific atom sites into the three structural components is shown for natrowalentaite in Table 3. On this basis, the formulae can be separated into the three bracketed components below for walentaite (Grey et al., 2018) and natrowalentaite:

walentaite



natrowalentaite



Both formulae are derived from the crystal structure refinements, combined with the electron microprobe results. In walentaite, the large cations coordinating to the surface of the layers and also occupying the interlayer region are dominantly calcium with minor sodium, whereas in natrowalentaite, sodium is dominant with minor calcium and potassium. The heteropolyhedral layers for the two minerals differ in that walentaite has minor substitution of As⁵⁺ for P⁵⁺ in the tetrahedra, whereas natrowalentaite contains only P⁵⁺ in the tetrahedra, but has minor replacement of Fe³⁺ by W⁶⁺ in the octahedra. The interlayer hydrated cations are predominantly divalent cations, Ca, Fe²⁺ and Mn²⁺ in walentaite, but are an approximately equal mix of Fe³⁺ and Na + Ca in natrowalentaite. There is a significant difference in the surface-coordinated components between the two minerals, with a large variation in the arsenic to (Na+Ca+K) ratio.

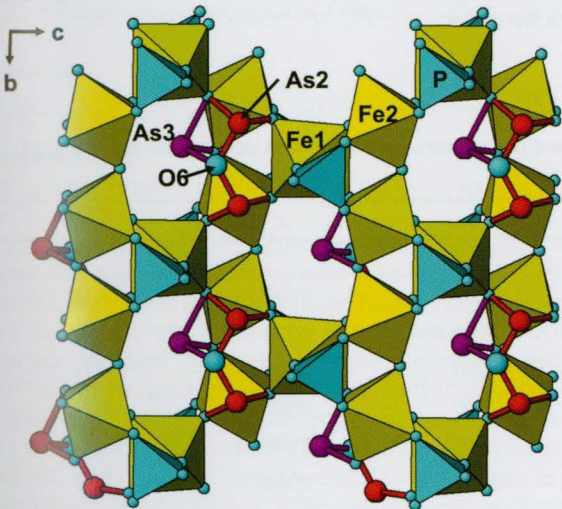


Figure 6. [100] projection of the heteropolyhedral layer in natrowalentaite, with a locally-ordered arrangement of As₃O₆ trimeric clusters attached to the layer.

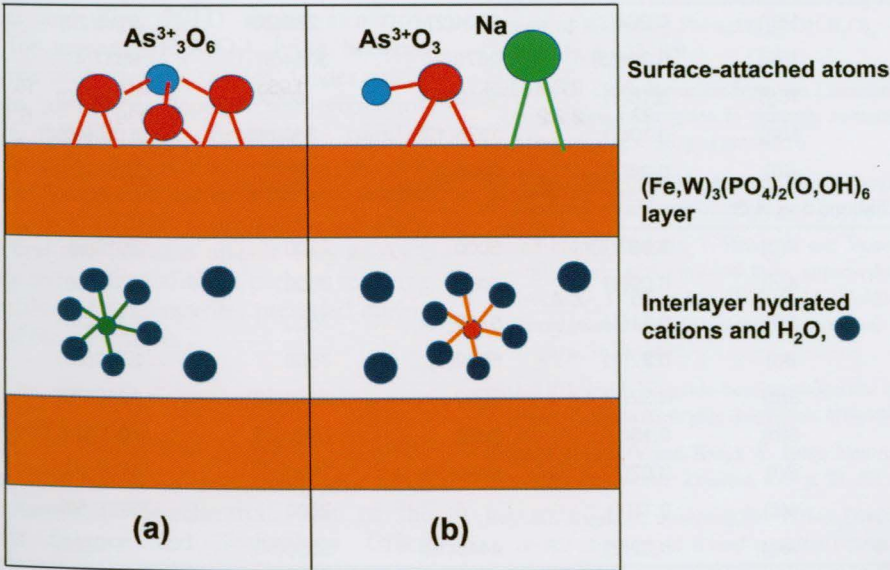
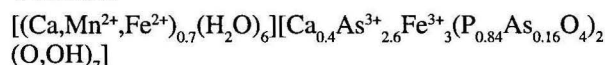


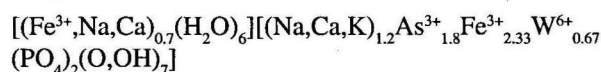
Figure 7. Schematic diagram showing different local structure configurations with (a) As₃O₆ clusters attached to the surface and (b) Na and As₃O₃ attached to the surface. Dark blue circles are H₂O and light blue circles are oxygen.

In both minerals, the surface sites occupied by the large sodium, calcium and potassium cations are located very close to the sites occupied by one of the two independent arsenic atoms (As2 in Fig. 6) and thus can only be occupied when the arsenic site is vacant, so that the distribution of surface components is $[(\text{As})_2\text{AsO}]_1[(\text{Na,Ca,K})_2\text{AsO}]_{1-x}$, that is, locally there are trimeric As_3O_6 clusters, or there are surface Na/Ca/K cations plus isolated AsO_3 pyramids centred on the As3 cations, as shown schematically in Figure 7. In walentaite, $x = 0.8$ and the trimeric clusters dominate, whereas in natrowalentaite, $x = 0.4$ and the surface-coordinated sodium cations dominate. The most likely reason that the concentration of As_3O_6 trimeric clusters is so much lower in natrowalentaite is that they can only be present when Fe^{3+} occupies the *M2* site. When W^{6+} occupies the *M2* site, the valency of anions shared between *M2* and arsenic would be highly oversaturated if arsenic were also present. The crystallographic and optical properties for the two minerals are compared in Table 4. Grouping the layer and surface components in the above formulae and reporting the interlayer composition first gives the following compositions:

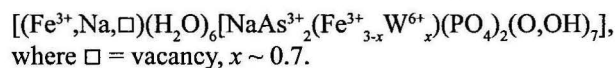
walentaite



natrowalentaite



Reporting only the dominant large cation (sodium), and rounding the surface-attached components to integers gives a simplified formula for natrowalentaite:



Concluding comments

Both walentaite (Dunn et al., 1984) and natrowalentaite (tungsten-bearing walentaite of Nickel, 1987) were originally reported as mixed arsenate–phosphate minerals with their reported formulae, divided by 4 and regrouped, given hereafter:

Table 3. Refined coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\times 10^3$) and site occupation factors (sof) for natrowalentaite

	Site	sof*	x	y	z	Ueq(Å ²)
(Fe,W) ₃ (PO ₄) ₂ O ₆ layer						
Fe1	4(c)	0.25	2500	2500	2500	17(1)
Fe2	8(f)	0.334(5)	3239(2)	5000	5000	18(1)
W2	8(f)	0.166(5)	3083(2)	5000	5000	18(1)
P1	8(i)	0.5	3738(1)	2500	2897(3)	14(1)
O1	8(i)	0.5	4232(3)	2500	2097(8)	29(2)
O2	8(i)	0.5	3256(3)	2500	2052(7)	19(2)
O3	16(j)	1.0	3731(2)	4222(7)	3765(5)	23(1)
O4A	16(j)	0.5	2653(10)	5450(50)	6300(30)	18(2)
O4B	16(j)	0.5	2596(8)	5740(40)	6090(30)	18(2)
O5	8(i)	0.5	3179(3)	2500	5730(8)	20(2)
Surface-attached atoms						
As2	16(j)	0.224(7)	2104(2)	280(20)	5110(20)	23(3)
As3	16(j)	0.218(5)	2670(2)	3044(5)	6937(4)	20(2)
Na2A	16(j)	0.18(1)	1810(20)	-60(30)	5290(30)	29(11)
Na2B	16(j)	0.10(2)	1578(19)	380(60)	5120(40)	29(12)
O6	8(i)	0.24(2)	2086(8)	2500	5980(20)	38(8)
Interlayer hydrated cations and H ₂ O						
Fe3	4(c)	0.087(4)	5000	7500	2912(8)	37(3)
Na1	4(c)	0.09(1)	5000	7500	1640(30)	29(9)
OW1A	8(i)	0.21(1)	5715(10)	7500	3320(30)	40(4)
OW1B	8(i)	0.27(1)	5849(8)	7500	2570(20)	40(4)
OW2A	8(h)	0.32(2)	5000	4640(30)	2940(20)	40(4)
OW2B	8(h)	0.15(2)	5000	4920(50)	2310(50)	40(4)
OW3	8(i)	0.07(1)	5290(30)	7500	4740(70)	40(4)
OW4	4(c)	0.11(1)	0	2500	5970(50)	40(4)
OW5	16(j)	0.22(2)	4445(12)	5660(50)	110(30)	40(4)

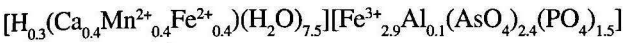
*sof = site occupation factor used in SHELXT. sof = (site multiplicity/general site multiplicity) x site occupancy, where occupancy = 1 for full occupation. sof x 4 gives the atoms per formula unit.

Table 4. Comparison of natrowalentaite and walentaite

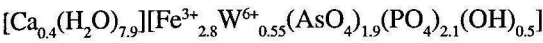
	natrowalentaite	walentaite*
Simplified formula	$[(\text{Fe}^{3+}, \text{Na}, \square)(\text{H}_2\text{O})_6]$ $[\text{NaAs}_{3/2}(\text{Fe}^{3+}, \text{W}^{6+})_3(\text{PO}_4)_2(\text{O}, \text{OH})_7]$	$[(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ca}, \square)(\text{H}_2\text{O})_6]$ $[\text{Ca}_{0.4}\text{As}_{3/2}\text{Fe}_{2.6}^{3+}(\text{P}, \text{As})\text{O}_4)_2(\text{O}, \text{OH})_7]$
Symmetry	Orthorhombic, <i>Imma</i>	Orthorhombic, <i>Imma</i>
a (Å)	25.770(3)	26.188(5)
b (Å)	7.3250(8)	7.360(2)
c (Å)	10.522(1)	10.367(2)
V (Å ³)	1986.2(4)	1998.2(7)
Strongest powder pattern lines	12.95, 100 (200)	12.9, 100 (200)
d, I, hkl	9.72, 9 (101)	9.6, 15 (101)
	6.72, 14 (101)	6.56, 20 (400)
	4.41, 10 (411)	4.43, 30 (411)
	3.020, 27 (022)	3.00, 50 (022)
	2.940, 15 (222)	2.931, 20 (222)
	2.759, 11 (802)	2.776, 20 (802)
	1.784, 10 (824)	
Optics	Biaxial (-) $\alpha = 1.650(3)$, $\beta = 1.728(3)$, $\gamma = 1.772(3)$, $2V(\text{meas}) = 71(2)^\circ$	Biaxial (+) $\alpha = \text{n.d.}$, $\beta = 1.738(4)$, $\gamma = 1.779(4)$, $2V = \text{n.d.}$

* Powder lines and optics from Dunn et al. (1984)

walentaite



natrowalentaite



A comparison with the formulae from the crystal structures, shows that a major difference relates to the valency of the arsenic. Both Dunn et al. (1984) and Nickel (1987) assumed that the arsenic was present as As⁵⁺; however, the crystal structure analyses show that the arsenic is present only as As³⁺ in natrowalentaite, and predominantly (90%) as As³⁺ in walentaite. Another significant difference stems from the fact that the original studies did not include analyses for sodium. In the current study, we analysed for sodium and found that it is the dominant large cation in natrowalentaite, whereas it is subordinate to calcium in our re-analysed walentaite (Grey et al., 2018).

The presence of dominant arsenite in both minerals places some constraints on the paragenetic conditions. A recent presentation of Eh-pH diagrams for the system As–O–H–Fe–S (Lu and Zhu, 2011) shows a narrow Eh stability field for arsenite (H₃AsO₃), lying between those for arsenopyrite and arsenate species. Under acidic conditions likely to prevail in deposits with oxidation of sulfide minerals, the Eh range for arsenite stability is ~+0.3 to 0.5. It is interesting that the sample used for the present study has natrowalentaite as a surface coating on natropharmacosiderite. The natropharmacosiderite must have formed first and contains arsenic only as As⁵⁺, suggesting that more reducing conditions, perhaps resulting from the decomposition of arsenopyrite, prevailed during the crystallization of the walentaite.

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