

The crystal structure of wycheproofite, $\text{NaAlZr}(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$

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Abstract: The previously unknown crystal structure of wycheproofite, $\text{NaAlZr}(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (space group $P\bar{1}$, $a = 5.263(1)$, $b = 9.251(2)$, $c = 9.480(2)$ Å, $\alpha = 109.49(3)$, $\beta = 98.57(3)$, $\gamma = 90.09(3)^\circ$, $V = 429.60(15)$ Å³, $Z = 2$) has been solved using single-crystal X-ray diffractometer data (CCD area detector, Mo- $K\alpha$) and refined to $R1 = 4.18\%$ for 1731 'observed' reflections with $F_o > 4\sigma(F_o)$. The structure determination led to a completely revised unit cell. The atomic arrangement of wycheproofite is characterised by two different alternating layers parallel to (001): the first layer is composed of corner-linked ZrO_6 octahedra and PO_4 tetrahedra. The second layer is built from zigzag chains of edge-sharing $\text{AlO}_2(\text{OH})_4$ octahedra along [100], and of $\text{Na}_{1-x}\text{O}_3(\text{OH})_2(\text{H}_2\text{O})_{2-y}$ ($x \sim 0.1$, $y \sim 0.6$) polyhedra. Adjacent layers are connected by oxygen ligands shared between PO_4 tetrahedra and $\text{AlO}_2(\text{OH})_4$ octahedra. Only very weak hydrogen bonding is necessary to reinforce the structural framework. The Al-, Zr- and P-O polyhedra are all fairly regular and average Al-O, Zr-O and P-O bond lengths are 1.898, 2.063 and 1.529 Å, respectively. The unique Na site is only partially occupied ($\sim 88\%$) and slightly disordered; it is surrounded by three O atoms, two OH groups and two H_2O molecules with Na-O distances ranging from 2.247(14) to 2.725(4) Å. Two of its O ligands (Ow11 and Ow12) are also only partially occupied, and split (Ow11) or somewhat disordered (Ow12), in agreement with bond-valence calculations. The originally given chemical formula, $\text{NaAlZr}(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, is therefore an idealised formula, although it is very close to the presently obtained formula.

Comparisons with the structures of the few other known natural and synthetic zirconium phosphates (*e.g.*, kosnarite - $\text{KZr}_2(\text{PO}_4)_3$; selwynite - $\text{NaK}(\text{Be,Al})\text{Zr}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$; mahlmoodite - $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$; synthetic $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{ZrKH}(\text{PO}_4)_2$ and $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$) demonstrates that a heteropolyhedral layer composed of corner-linked PO_4 tetrahedra and ZrO_6 octahedra is a common structural feature of several of these phosphates, and that it links them closely to the family of yavapaiite-related layered $AM(\text{XO}_4)_2$ compounds.

Key-words: wycheproofite, crystal structure, crystal chemistry, zirconium phosphates, yavapaiite.

Introduction

In a series of studies of the crystal structures of oxysalt minerals from Australia (Kolitsch *et al.*, 1999, 2000; Kolitsch & Giester, 2000a,b, 2001; Kolitsch, 2001a), the presently reported work was conducted to determine the previously unknown crystal structure of wycheproofite, a very rare hydrated Na-Al-Zr-phosphate. The mineral occurs in pegmatite veins of a Devonian granite mined at a quarry at Wycheproof, Victoria, Australia (Birch *et al.*, 1994). No other occurrences are known at present. Wycheproofite forms compact, finely fibrous masses in small cavities in the quartz/feldspar/muscovite/schorl-bearing pegmatite. The fibrous crystals of the type material are 5-10 µm wide and up to several mm long. Accompanying minerals include two other zirconium phosphates, kosnarite, $\text{KZr}_2(\text{PO}_4)_3$, and selwynite, $\text{NaK}(\text{Be,Al})\text{Zr}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$ (Birch *et al.*, 1995), and several other phosphate species not containing zirconium.

Birch *et al.* (1994) reported the formula $\text{NaAlZr}(\text{PO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, triclinic symmetry and the

preliminary unit-cell parameters $a = 10.926(5)$, $b = 10.986(5)$, $c = 12.479(9)$ Å, $\alpha = 71.37(4)$, $\beta = 77.39(4)$, $\gamma = 87.54(3)^\circ$, $V = 1375.9$ Å³, determined with the help of electron diffraction.

The present article reports the results of a single-crystal X-ray diffraction study of wycheproofite, which resulted in a complete revision of the unit cell and provided a detailed view of the atomic arrangement of the mineral. A preliminary account of the results has already been given (Kolitsch, 2001b). The results are compared to the structures of the few other known natural and synthetic zirconium phosphates, and common structural features are pointed out, including the relation to the family of yavapaiite-related layered $AM(\text{XO}_4)_2$ compounds.

Experimental

A very small sample from the type locality, kindly donated by Dr. Bill Birch, Melbourne, was used for the

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Table 1. Crystal data, data collection information and refinement details for wycheproofite.

Crystal data	
Formula (idealised)	NaAlZr(PO ₄) ₂ (OH) ₂ ·H ₂ O
Space group	$P\bar{1}$
a, b, c (Å)	5.263(1), 9.251(2), 9.480(2)
α, β, γ (°)	109.49(3), 98.57(3), 90.09(3)
V (Å ³), Z	429.60(15), 2
$F(000)$, ρ_{calc} (g·cm ⁻³)	368, 2.932
μ (mm ⁻¹)	1.853
Absorption correction	multi-scan*
Crystal dimensions (mm)	0.02 × 0.03 × 0.08
Data Collection and Refinement	
Diffractometer	Nonius KappaCCD system
λ (Mo-K α) (Å), T (K)	0.71073, 293
Detector distance (mm)	28
Rotation axis; rot. width (°)	ϕ, ω ; 1.0
Total no. of frames	412
Collect. time per frame (s)	350
Collection mode	sphere (redundancy 1.5)
$2\theta_{\text{max}}$ (°)	60.00 (used: 56.56)
h, k, l ranges	-6 → 6, -12 → 12, -12 → 10
Total reflections measured	3273
Unique reflections	2117 (R_{int} 3.2 %)
$R1(F)$, $wR2(F^2)$ **	4.18 %, 7.03 %
'Observed' reffs.	1731 [$F_o > 4\sigma(F_o)$]
Extinction coefficient	-
No. of refined parameters	160
GooF	1.062
$(\Delta/\sigma)_{\text{max}}$	0.0001
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e/Å ³)	-0.94, 0.81

Note:

Scattering factors for neutral atoms were employed in the refinement.

* Otwinowski & Minor (1997)

** $w = 1/[\sigma^2(F_o^2) + (0.0P)^2 + 1.0P]$; $P = ([\max(0 \text{ or } F_o^2)] + 2F_c^2)/3$

present study (Museum Victoria collection, sample no. M42853). Owing to the fibrous nature of the mineral and its occurrence as massive aggregates, a great deal of persistence was required to find a suitable single-crystal fragment which was not intergrown with other individuals. A tiny elongate, optically homogeneous fragment with the dimensions $0.02 \times 0.03 \times 0.08$ mm and a good crystal quality was used for intensity data collection. This fragment and the other fragments studied invariably had a triclinic unit cell completely different from the tentative cell reported in the original description. All the single-crystal studies were done with a Nonius KappaCCD single-crystal diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution. Data from a complete sphere of reciprocal space were acquired (see Table 1 for details). The intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarisation, and background effects, and, by the multi-scan method (Otwinowski & Minor, 1997), for absorption. Averaging gave 2117 symmetry-independent reflections. Intensity statistics clearly favoured the centrosymmetric space group $P\bar{1}$ (no. 2). The positions of all non-H atoms (Zr, P, Al, Na, O) were found by direct methods (SHELXS-97, Sheldrick

1997a), followed by the inspection of subsequent difference Fourier maps. A full-matrix anisotropic least-squares refinement on F^2 (SHELXL-97, Sheldrick 1997b) in space group $P\bar{1}$ proceeded smoothly and gave $R1 \sim 5$ %. Three low-angle reflections, 001, 0-11 and 010, whose intensities were strongly affected by the experimental conditions (beamstop interference), were then omitted in the refinement process. At this stage, it was apparent that two of the 12 O sites were disordered and only partially occupied, and could not be refined anisotropically. Furthermore, refinement of the Na site occupancy also revealed incomplete occupancy and indications of slight disorder. Subsequently, the positions of four H atoms belonging to two OH groups and one of the two non-equivalent H₂O molecules were detected from difference Fourier maps. However, the two detected H positions of the one H₂O molecule must be regarded as tentative in view of the observed disorder (see below for discussion). The two remaining H atoms (belonging to the second H₂O molecule) could not be located. The isotropic displacement parameters of all detected H atoms were restrained to a value of $0.04 \text{ \AA}^2$. The O-H distances were freely refined and values between ~ 0.72 and $\sim 1.02 \text{ \AA}$ were obtained. The refinement converged to the final discrepancy factors $R1 = 4.18$ % for 1731 'observed' reflections with $F_o > 4\sigma(F_o)$. Further details are given in Table 1. The final atomic positions and displacement parameters are given in Table 2, selected bond lengths, calculated bond valences and suggested hydrogen bonds in Table 3. A list of observed and calculated structure factors (Table 4) can be obtained from the author or through the E.J.M. Editorial Office in Paris.

The present solution of the crystal structure of a micro-crystal (dimensions $0.02 \times 0.03 \times 0.08$ mm) provides again evidence that CCD area detectors attached to conventional X-ray tubes can be very helpful in elucidating the atomic arrangements of minerals with very small crystal or grain sizes (Burns, 1998), *i.e.*, without having to resort to synchrotron radiation.

Description and discussion of the structure

The revised triclinic unit cell of wycheproofite, $a = 5.263(1)$, $b = 9.251(2)$, $c = 9.480(2) \text{ \AA}$, $\alpha = 109.49(3)$, $\beta = 98.57(3)$, $\gamma = 90.09(3)^\circ$, $V = 429.60(15) \text{ \AA}^3$, bears no relation to the tentative cell reported in the original description, $a = 10.926(5)$, $b = 10.986(5)$, $c = 12.479(9) \text{ \AA}$, $\alpha = 71.37(4)$, $\beta = 77.39(4)$, $\gamma = 87.54(3)^\circ$, $V = 1375.9 \text{ \AA}^3$ (Birch *et al.*, 1994). An X-ray powder diffraction pattern calculated from the presently obtained structure model is, however, in good agreement with the X-ray powder data reported by Birch *et al.* (1994).

The crystal structure of wycheproofite contains one Zr, one Al, one Na, two P, 12 O and six H sites. All detected atoms are on general positions. Two of the O positions represent OH groups (Oh9, Oh10), whereas two others represent H₂O molecules (Ow11, Ow12). This assignment is clearly demonstrated by the calculated bond-valence sums for the ligands O1 to Ow12, which amount to 1.96, 1.94, 1.99, 1.95, 1.94, 1.89, 1.95, 1.90, 1.18, 1.18, 0.24 and

Table 2. Fractional atomic coordinates and displacement parameters for wycheproofite.

Atom	x	y	z	U_{eq}/U_{iso}
Na [§]	0.2639(4)	0.2812(2)	0.4670(3)	0.0320(9)
Zr	0.25452(8)	0.25660(4)	0.01905(5)	0.00557(14)
Al	-0.2475(3)	0.07698(15)	-0.49748(15)	0.0077(3)
P1	0.8058(2)	0.14282(12)	0.19870(12)	0.0062(3)
P2	-0.3072(2)	0.34173(12)	-0.18984(12)	0.0059(3)
O1	0.8291(6)	0.1785(3)	0.3691(3)	0.0093(6)
O2	0.2559(6)	0.0284(3)	-0.1128(4)	0.0139(7)
O3	0.0614(6)	0.1949(4)	0.1675(4)	0.0122(7)
O4	0.5912(6)	0.2356(3)	0.1483(4)	0.0121(7)
O5	0.2613(6)	0.4855(3)	0.1513(4)	0.0139(7)
O6	-0.3350(6)	0.2671(3)	-0.3617(3)	0.0098(7)
O7	-0.0834(6)	0.2770(4)	-0.1115(4)	0.0136(7)
O8	0.4458(6)	0.3097(4)	-0.1344(4)	0.0120(7)
Oh9	0.0970(6)	0.1061(3)	-0.4001(3)	0.0099(7)
Oh10	-0.5899(6)	0.0288(3)	-0.6104(3)	0.0100(7)
Ow11*	0.4306(19)	0.5264(12)	0.5436(12)	0.053(4)
Ow12**	0.103(3)	0.4853(19)	0.629(2)	0.066(7)
H12A	0.170(14)	0.409(9)	0.607(8)	0.040***
H12B	0.951(15)	0.495(8)	0.552(7)	0.040***
H9	0.137(13)	0.157(7)	-0.334(7)	0.040***
H10	-0.621(12)	0.007(7)	-0.688(7)	0.040***

Note: Oxygens of hydroxyl groups are designated as Oh, those of water molecules as Ow.

[§] Refined occupancy 0.884(8). * Refined occupancy 0.507(13); the Ow11 site is also split (Ow11-Ow11 = 1.16(2) Å, see text, Table 3). ** Refined occupancy 0.390(19). *** U_{iso} fixed.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	0.0310(14)	0.0274(13)	0.0573(17)	0.0131(12)	-0.0149(12)	-0.0048(10)
Zr	0.0049(2)	0.0058(2)	0.0061(2)	0.00216(15)	0.00093(15)	0.00050(14)
Al	0.0077(7)	0.0078(6)	0.0079(6)	0.0025(5)	0.0029(5)	0.0013(5)
P1	0.0055(6)	0.0064(5)	0.0072(5)	0.0030(4)	0.0008(4)	0.0005(4)
P2	0.0059(6)	0.0057(5)	0.0064(5)	0.0023(4)	0.0013(4)	0.0012(4)
O1	0.0124(16)	0.0105(15)	0.0059(14)	0.0032(12)	0.0025(12)	-0.0020(12)
O2	0.0212(19)	0.0054(15)	0.0119(16)	-0.0012(12)	0.0018(13)	0.0000(13)
O3	0.0085(16)	0.0166(17)	0.0142(16)	0.0081(13)	0.0033(13)	-0.0004(13)
O4	0.0096(16)	0.0100(15)	0.0164(16)	0.0052(13)	-0.0007(13)	0.0024(12)
O5	0.0191(18)	0.0064(15)	0.0142(16)	0.0007(12)	0.0035(13)	-0.0013(13)
O6	0.0115(16)	0.0101(15)	0.0075(14)	0.0019(12)	0.0030(12)	0.0023(12)
O7	0.0115(17)	0.0161(17)	0.0137(16)	0.0065(13)	0.0000(13)	0.0027(13)
O8	0.0092(16)	0.0159(16)	0.0121(16)	0.0056(13)	0.0035(12)	0.0008(12)
Oh9	0.0103(16)	0.0081(15)	0.0090(15)	0.0000(12)	0.0017(12)	0.0014(12)
Oh10	0.0099(16)	0.0099(15)	0.0105(15)	0.0039(12)	0.0019(12)	-0.0011(12)

0.12 v.u. (valence units), respectively (Table 3). Some anomalous features of Ow11 and Ow12, which are bonded to the Na site, are discussed below. A refinement of the occupancy of the Zr site provided some slight indication for a very minor Hf-for-Zr substitution (1.24 wt% HfO₂ was detected in the type material; Birch *et al.*, 1994), but the Zr:Hf ratio has not been refined.

Cation polyhedra and polyhedral connectivity

The PO₄ tetrahedra are corner-linked to ZrO₆ octahedra so that each corner of the ZrO₆ octahedron is shared with adjacent PO₄ tetrahedra. Thus, a heteropolyhedral layer parallel to (001) (Fig. 1) is formed, which is topologically identical to that in yavapaiite [KFe³⁺(SO₄)₂]- and merwinite [Ca₃Mg(SiO₄)₂]-type compounds. The yavapaiite-type compounds belong to an extensive family of layered $AM(XO_4)_2$ compounds where A = monovalent Na, K, Rb, Cs, Ag or divalent Ca, Sr, Ba, M = trivalent Sc, V, Cr, Mn, Fe, Al, Ga, Rh or tetravalent Mo, Ge, Ti, Zr, Hf, Sn or

pentavalent Ta, and X = hexavalent S, Se, Cr or pentavalent P, As (see Fleck *et al.*, 2002, and Fleck & Kolitsch, 2003, for details and references). The ZrO₆-PO₄ layer in wycheproofite shows strongest similarities with the layers in the high-symmetry trigonal members of the $AM(XO_4)_2$ family.

AlO₂(OH)₄ octahedra share common edges to form zigzag chains parallel to [100] at a height of $z \approx 0.5$. According to single-crystal studies, the chain direction is also the direction of the morphological elongation. These zigzag chains are linked via corners to PO₄ tetrahedra of ZrO₆-PO₄ layers both above and below the chain (Fig. 2). The shortest Al–Al distance within the chain is 2.969(3) Å. The Na atoms occupy voids within the resulting framework. The Al-, Zr- and P-O polyhedra are all fairly regular and average Al–O, Zr–O and P–O bond lengths are 1.898, 2.063 and 1.529 Å, respectively (Table 3).

The unique Na site is only partially occupied [refined occupancy 0.884(8)] and shows some very slight positional disorder, reflected by its anisotropic displacement parameters (Table 2); it is surrounded by three O atoms, two OH

Table 3. Selected bond distances (Å) and calculated bond valences (v.u.) for the coordination polyhedra in wycheproofite, and possible hydrogen bonds.

Zr–O4	2.047(3)	0.743	Al–Oh9	1.876(3)	0.544
–O7	2.057(3)	0.723	–Oh9	1.885(3)	0.531
–O2	2.066(3)	0.709	–O1	1.893(3)	0.520
–O5	2.067(3)	0.704	–O6	1.905(3)	0.503
–O8	2.070(3)	0.700	–Oh10	1.910(3)	0.497
–O3	2.073(3)	0.691	–Oh10	1.917(3)	0.487
<Zr–O>	2.063	4.27 v.u.	<Al–O>	1.898	3.08 v.u.
Na–Ow12	2.247(14)	0.116*	P1–O1	1.522(3)	1.248
–Ow11*	2.267(9)	0.144*	–O2	1.526(3)	1.235
–Oh10	2.367(4)	0.214	–O3	1.530(3)	1.221
–O1	2.403(3)	0.196	–O4	1.535(3)	1.205
–Ow11*	2.433(10)	0.092*	<P1–O>	1.528	4.91 v.u.
–O6	2.498(3)	0.152	P2–O5	1.526(3)	1.235
–Oh9	2.583(4)	0.120	–O6	1.526(3)	1.235
–O3	2.725(4)	0.082	–O7	1.528(3)	1.228
<Na–O>	2.440	1.12 v.u.	–O8	1.536(3)	1.202
			<P2–O>	1.529	4.90 v.u.

Bond-valence sums for the ligands O1 to Ow12 are 1.96, 1.94, 1.99, 1.95, 1.94, 1.89, 1.95, 1.90, 1.18, 1.18, 0.24 and 0.12, respectively.

Note: Bond-valence parameters used are from Brese & O'Keeffe (1991).

* The Ow11 site is split, and both Ow11 and Ow12 sites are only partly occupied (see text and Table 2). The calculated bond-valence contributions have been diminished according to the refined occupancies of the Ow sites (see text).

Possible hydrogen bonds			
Oh9...O8	2.961(4)	Ow11...Ow12	3.02(2)
		Ow11...O4	3.041(9)
Oh9...O7	2.969(4)	Ow12...Ow12	2.65(3)
		Ow12...Ow11	3.02(2)
Oh9–H9...O8	156	Ow12–H12A...Ow12	138
Oh9–H9...O7	130	Ow12–H12B...Ow11	155

Note: Freely refined O–H distances for Ow12–H12A, Ow12–H12B, Oh9–H9 and Oh10–H10 are 0.84(7), 1.02(6), 0.72(6) and 0.73(6) Å. Oh10 is not involved in H bonding: the shortest Oh10–O2 distance, 3.278(5) Å, is too long for a H bond.

groups and two H₂O molecules with Na–O distances ranging from 2.247(14) to 2.725(4) Å (Table 3). The Ow11 site represents a split position (Ow11–Ow11 distance 1.16(2) Å). Furthermore, the Ow11 and Ow12 sites are

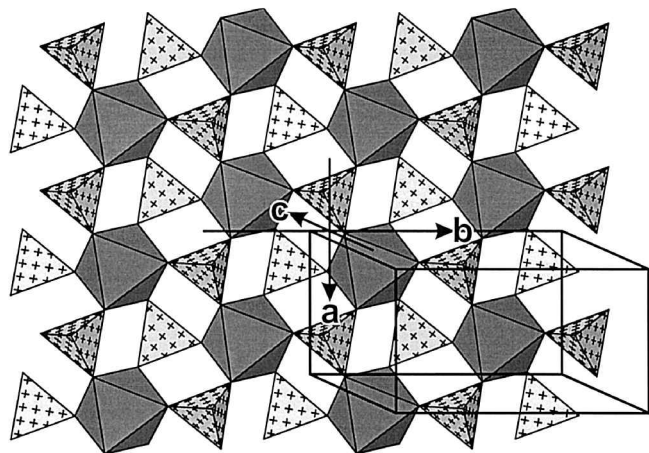


Fig. 1. The yavapaiite-related ZrO₆-PO₄ octahedral-tetrahedral layer parallel to (001) in wycheproofite. All drawings were done with ATOMS (Shape Software, 1999).

only partially occupied; their refined occupancies are 0.507(13) and 0.390(19), respectively. This explains the physically impossible short Ow11–Ow12 distance of 2.09(2) Å, and is in good agreement with bond-valence calculations: if the Ow11 and Ow12 sites, which are both rather close to Na (Table 3), were fully occupied, this would result in strong overbonding of the Na atom (bond-valence sum of 1.52 v.u.). The bond-valence sums given in Table 3 were calculated taking into account the refined occupancies of the Ow sites, and the resulting value for the Na site, 1.12 v.u., is very reasonable.

The positional disorder of Na, Ow11 and Ow12 is apparent from the anisotropic displacement ellipsoid of the Na atom (Table 2) and the fact that the two Ow sites could not be refined anisotropically. Also, the isotropic displacement parameters of the two H atoms bonded to Ow12 had to be fixed to physically reasonable values. Taking into account the refined occupancies of Na, Ow11 and Ow12, the Na–O polyhedron may be described with the 'bulk' chemical formula Na_{1-x}O₃(OH)₂(H₂O)_{2-y}, with x ~ 0.1 and y ~ 0.7. Therefore, the originally given formula for wycheproofite, NaAlZr(PO₄)₂(OH)₂·H₂O, represents only an idealised formula, although it shows fairly good agreement with the structure model. The measured Na (+ Ca,K)

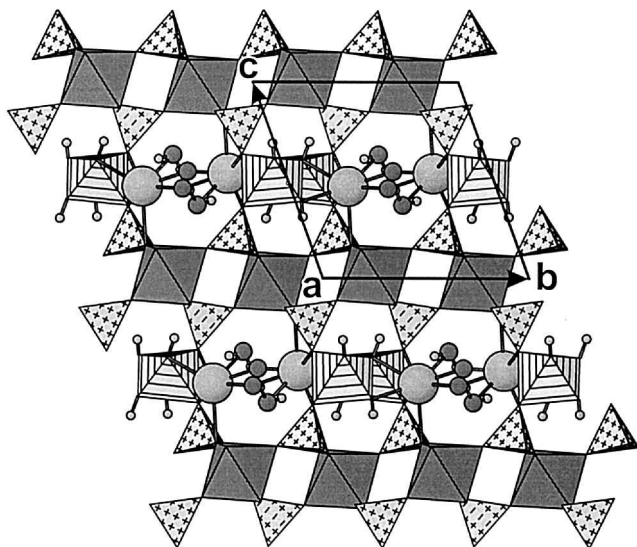


Fig. 2. View of the wycheproofite structure along the a -axis, showing the layered character of the polyhedral arrangement: a layer composed of corner-linked ZrO_6 octahedra and PO_4 tetrahedra, which alternates with a second layer built of $\text{AlO}_2(\text{OH})_4$ (striped) octahedral zigzag chains (parallel to the a -axis, at a height of $z \approx 0.5$) and $\text{Na}_{1-x}\text{O}_3(\text{OH})_2(\text{H}_2\text{O})_{2-y}$ polyhedra. Large, small and very small spheres represent Na, O and H atoms, respectively. Both positions of the split O11 site are shown, and the unit cell is also outlined.

content of the type material was found to be smaller by about 10 % than that required by the ideal formula; the analysis of Birch *et al.* (1994) suggest the occupancy ($\text{Na}_{0.80}\text{Ca}_{0.05}\text{K}_{0.04}$). The present results support this deficiency. The slight disorder of the Na atom and the two O_w ligands might also be related to some minor substitution of K and Ca for Na, and of F for OH (chemical analyses of the type material had shown 0.44 wt% K_2O , 0.66 wt% CaO and 0.34 wt% F; Birch *et al.*, 1994). Partial occupancies of Na sites were also observed in the chemically related mineral gainesite, $\text{NaNa}(\text{Be},\text{Li})(\text{Zr},\text{Zn})_2(\text{PO}_4)_4 \cdot 1\text{-}2\text{H}_2\text{O}$ (Moore *et al.*, 1983). The calculated density for wycheproofite, 2.93 g/cm³ (based on the occupancy refinements), is higher than the measured density, 2.83 g/cm³ (Birch *et al.*, 1994) but this small discrepancy might be attributed to the fibrous nature of the material and the non-stoichiometry of the chemical formula.

The view of the structure along the a -axis in Fig. 2 also shows that the atomic arrangement may be visualised in term of two different layers parallel to (001): a (yavapaiite-related) layer composed of corner-linked ZrO_6 octahedra and PO_4 tetrahedra, which alternates with a second layer built of $\text{AlO}_2(\text{OH})_4$ octahedral chains and $\text{Na}_{1-x}\text{O}_3(\text{OH})_2(\text{H}_2\text{O})_{2-y}$ polyhedra. Hydrogen bonding provides only minor strengthening of the structural framework, because all donor-acceptor distances are > 2.96 Å and the bonding forces are therefore very weak (Table 3).

Comparison with related zirconium phosphates

The atomic arrangement of wycheproofite is unique. However, a comparison with chemically related

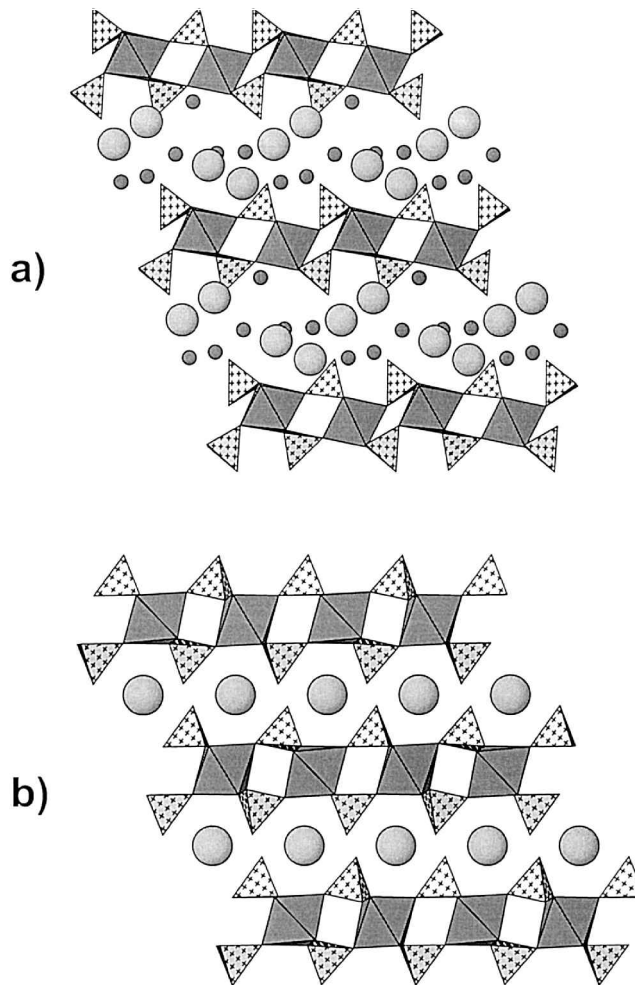


Fig. 3. (a) View of the crystal structure $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$ (Poojary & Clearfield, 1994) along the c -axis and (b) view of $\text{ZrKH}(\text{PO}_4)_2$ (Clearfield *et al.*, 1984) along the b -axis. Large spheres = alkali atoms, small spheres = O atoms of H_2O molecules. The layers built of corner-linked ZrO_6 octahedra and PO_4 tetrahedra present in both compounds are similar to that in wycheproofite (compare Fig. 2).

compounds shows that corner-linkage between ZrO_6 octahedra and PO_4 tetrahedra is a common characteristic in the few known natural and synthetic zirconium phosphates: such linkage is found in, *e.g.*, kosnarite, $\text{KZr}_2(\text{PO}_4)_3$ (Brownfield *et al.*, 1993), synthetic $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$ (Poojary & Clearfield, 1994) and synthetic $\text{ZrMH}(\text{PO}_4)_2$, where $M = \text{K}$ or Na (*e.g.*, Clearfield *et al.*, 1984; Rudolf & Clearfield, 1985). The latter compounds are intercalated modifications of the well-known, layered proton conductor $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (Troup & Clearfield, 1977), whose interlayer protons can be easily exchanged by alkali cations.

Views of the crystal structure of $\text{ZrKH}(\text{PO}_4)_2$ along the b -axis and of $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$ along the c -axis are given in Fig. 3 for comparison with the structural arrangement in wycheproofite (Fig. 2). It is clearly seen that in all three compounds there exist very similar (yavapaiite-related) layers built of ZrO_6 octahedra corner-linked to PO_4 tetrahedra. However, the orientation of the involved polyhedra

in the structures with respect to the layer plane is slightly different (Fig. 2, 3). Also, in wycheproofite the layers are linked *via* both Na atoms and AlO_6 octahedral chains, whereas in the two synthetic compounds the interlayer linkage is achieved only via alkali cations (K^+ and Na^+) and H_2O molecules involved in hydrogen bonding. The fact that the linkage between ZrO_6 and PO_4 polyhedra involves only corner-sharing, but not edge-sharing, is explained by the instability of an edge-sharing arrangement in view of the strong repulsive forces between the highly charged central cations (Zr^{4+} , P^{5+}).

The crystal structures of mahlmoodite $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Milton *et al.*, 1993) and mccrillisite $\text{NaCs}(\text{Be},\text{Li})\text{Zr}_2(\text{PO}_4)_4 \cdot 1-2\text{H}_2\text{O}$ (Foord *et al.*, 1994) are unknown at present, although the former is assumed to be isostructural with $\alpha\text{-MZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ compounds, where $M = \text{Mn}, \text{Ni}, \text{Co}, \text{Cu}$ and Zn (Milton *et al.*, 1993). Selwynite, $\text{NaK}(\text{Be},\text{Al})\text{Zr}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$, is considered to be the K analogue of gainesite and mccrillisite. Single-crystal work done by the author on selwynite from Wycheproof indicated cation disorder and the possibility of microtwinning; no satisfactory structure model could be obtained yet.

The occurrence of a zigzag chain of edge-sharing AlO_6 octahedra is apparently unusual in metal (aluminium) phosphates. A recent review on phosphate minerals by Hawthorne (1998) demonstrates the large variety of different mechanisms of polyhedral linkages in phosphates but linkage mechanisms such as in wycheproofite seem to be very rare.

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References

- Birch, W.D., Pring, A., Kharisun, Bevan, D.J.M. (1994): Wycheproofite: a new hydrated sodium aluminium zirconium phosphate from Wycheproof, Victoria, Australia and a new occurrence of kosnarite. *Min. Mag.*, **58**, 635-639.
- Birch, W.D., Pring, A., Foord, E.E. (1995): Selwynite, $\text{NaK}(\text{Be},\text{Al})\text{Zr}_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$, a new gainesite-like mineral from Wycheproof, Victoria, Australia. *Can. Mineral.*, **33**, 55-58.
- Breese, N.E. & O'Keeffe, M. (1991): Bond-valence parameters for solids. *Acta Cryst.*, **B47**, 192-197.
- Brownfield, M.E., Foord, E.E., Sutley, S.J., Botinelly, T. (1993): Kosnarite, $\text{KZr}_2(\text{PO}_4)_3$, a new mineral from Mount Mica and Black Mountain, Oxford County, Maine. *Am. Mineral.*, **78**, 653-656.
- Burns, P.C. (1998): CCD X-ray area detectors applied to mineral structure analysis. *Can. Mineral.*, **36**, 847-853.
- Clearfield, A., McCusker, L.B., Rudolf, P.R. (1984): Crystal structure from powder data. 1. Crystal structure of $\text{ZrKH}(\text{PO}_4)_2$. *Inorg. Chem.*, **23**, 4679-4682.
- Fleck, M. & Kolitsch, U. (2003): Natural and synthetic compounds with kröhnkite-type chains: an update. *Z. Kristallogr.*, **218**, 553-567.
- Fleck, M., Kolitsch, U., Hertweck, B. (2002): Natural and synthetic compounds with kröhnkite-type chains: review and classification. *Z. Kristallogr.*, **217**, 435-443.
- Foord, E.E., Brownfield, M.E., Lichte, F.E., Davis, A.M., Sutley, S.J. (1994): Mccrillisite, $\text{NaCs}(\text{Be},\text{Li})\text{Zr}_2(\text{PO}_4)_4 \cdot 1-2\text{H}_2\text{O}$, a new mineral species from Mount Mica, Oxford County, Maine, and new data for gainesite. *Can. Mineral.*, **32**, 839-842.
- Hawthorne, F.C. (1998): Structure and chemistry of phosphate minerals. *Min. Mag.*, **62**, 141-164.
- Kolitsch, U. (2001a): Refinement of pyrobelonite, $\text{PbMn}^{\text{II}}\text{VO}_4(\text{OH})$, a member of the descloizite group. *Acta Cryst.*, **E57**, i119-i121.
- (2001b): The crystal structure of wycheproofite, a rare hydrated Na-Al-Zr-phosphate from Wycheproof, Victoria, Australia. *Mitt. Österr. Mineral. Ges.*, **146**, 137-138.
- Kolitsch, U. & Giester, G. (2000a): The crystal structure of namibite, $\text{Cu}(\text{BiO})_2\text{VO}_4(\text{OH})$, and revision of its symmetry. *Am. Mineral.*, **85**, 1298-1301.
- , — (2000b): The crystal structure of faustite and its copper analogue turquoise. *Min. Mag.*, **64**, 905-913.
- , — (2001): Revision of the crystal structure of ulrichite, $\text{CaCu}^{2+}(\text{UO}_2)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. *Min. Mag.*, **65**, 717-724.
- Kolitsch, U., Taylor, M.R., Fallon, G., Pring, A. (1999): Springcreekite, $\text{BaV}^{3+}_3(\text{PO}_4)_2(\text{OH},\text{H}_2\text{O})_6$, a new member of the crandallite group, from the Spring Creek mine, South Australia: the first natural V^{3+} -member of the alunite family and its crystal structure. *N. Jahrb. Mineral. Monatsh.*, **1999**, 529-544.
- Kolitsch, U., Pring, A., Tiekink, E.R.T. (2000): Johntomaite, a new member of the bjarebyte group of barium phosphates: description and structure refinement. *Mineral. Petrol.*, **70**, 1-14.
- Milton, C., McGee, J.J., Evans, H.T., jr. (1993): Mahlmoodyite, $\text{FeZr}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, a new iron zirconium phosphate mineral from Wilson Springs, Arkansas. *Am. Mineral.*, **78**, 437-440.
- Moore, P.B., Araki, T., Steele, I.M., Swihart, G.H., Kampf, A.R. (1983): Gainesite, sodium zirconium beryllophosphate: a new mineral and its crystal structure. *Am. Mineral.*, **68**, 1022-1028.
- Otwinowski, Z. & Minor, W. (1997): Processing of X-ray diffraction data collected in oscillation mode. in "Methods in Enzymology, Volume 276: Macromolecular Crystallography A", C.W. Carter, Jr. & R.M. Sweet, eds. Academic Press, New York, 307-326.
- Poojary, D.M. & Clearfield, A. (1994): Crystal structure of sodium zirconium phosphate, $\text{Zr}_2(\text{NaPO}_4)_4 \cdot 6\text{H}_2\text{O}$, from X-ray powder diffraction data. *Inorg. Chem.*, **33**, 3685-3688.
- Rudolf, P. & Clearfield, A. (1985): The solution of unknown crystal structures from X-ray powder diffraction data. Technique and an example, $\text{ZrNaH}(\text{PO}_4)_2$. *Acta Cryst.*, **B41**, 418-425.
- Shape Software (1999): ATOMS for Windows and Macintosh V5.0.4. Kingsport, TN 37663, U.S.A.
- Sheldrick, G.M. (1997a): SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Germany.
- (1997b): SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany.
- Troup, J.M. & Clearfield, A. (1977): Mechanism of ion exchange in zirconium phosphates. 20. Refinement of the crystal structure of α -zirconium phosphate. *Inorg. Chem.*, **16**, 3311-3314.

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