Wycheproofite: a new hydrated sodium aluminium zirconium phosphate from Wycheproof, Victoria, Australia, and a new occurrence of kosnarite

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Abstract

Wycheproofite is a new hydrated sodium aluminium zirconium phosphate from a pegmatite vein in granite at Wycheproof, in northwestern Victoria, Australia. The mineral occurs as compact, finely fibrous masses in small cavities in the quartz/feldspar/muscovite/schorl-bearing pegmatite. The fibrous crystals are between 5 and 10 μm wide and up to several mm long. Accompanying minerals include two other zirconium phosphates — kosnarite and a new species, selwynite, the K-analogue of gainesite — as well as wardite, eosphorite, cyrilovite, leucophosphite, rockbridgeite, a kidwellite-like mineral and saleeite. The wycheproofite aggregates are pale pinkish to brownish orange, with a vitreous to pearly lustre. The streak is colourless, fracture rough, cleavage not observed and the Mohs hardness is between 4 and 5. Optical data are incomplete due to the fibrous nature of the mineral; the indices of refraction are in the range 1.62–1.64. The measured density is 2.83 g cm^{-3}. Chemical analysis gave (wt.%) Na_2O 6.36, K_2O 0.44, CaO 0.66, FeO 0.36, MnO 0.21, Al_2O_3 12.03, Cs_2O 0.03, ZrO_2 32.43, HfO_2 1.24, P_2O_5 35.85, SiO_2 0.23, F 0.34, H_2O 9.0, less 0=F 0.14, Total 99.04. The simplified formula is $NaAlZr(PO_4)_2(OH)_2{\cdot}H_2O$. Wycheproofite is triclinic with unit cell parameters $a = 10.926(5)$ Å, $b = 10.986(5)$ Å, $c = 12.479(9)$ Å, $\alpha = 71.37(4)°$, $\beta = 77.39(4)°$, $\gamma = 87.54(3)°$, $V = 1375.9$ Å^3. For $Z = 6$, the calculated density is 2.81 g cm^{-3}. The strongest lines in the X-ray powder diffraction pattern are [d_{obs} (Å), I_{obs}, *hkl*] 2.603 (100) 040; 4.128 (80) 121; 3.711 (65) 023; 3.465 (60) 030; 8.865 (40) 101; 3.243 (35) 132. The crystal structure has not been solved due to the finely fibrous nature of the material available. The name is for the locality, which in the local Australian Aboriginal language means 'witchie bushes growing on a hilltop'.

Data on the third occurrence of kosnarite, $KZr_2(PO_4)_3$, at Wycheproof are also given.

KEYWORDS: wycheproofite, new mineral, zirconium phosphate, kosnarite, Wycheproof, Australia.

Introduction

IN late 1990, mineral collectors discovered pegmatite veins in granite boulders in a quarry at Wycheproof, a small town in northwestern Victoria (lat. 36°05′ S, long. 143°14′E). Cavities in the pegmatite veins were lined with well-formed crystals of eosphorite, the first record of this

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mineral in Australia. Closer inspection revealed other minerals which the collectors were unsure of, so representative specimens were sent to the senior author (WDB) for identification. Detailed studies have defined a suite of iron phosphates, as well as three zirconium-bearing phosphate minerals, two of which have now been approved as new species by the I.M.A. Commission on New Minerals and Mineral Names.

This paper describes one of the these new minerals, wycheproofite, named for the locality, which means 'witchie bushes growing on a hilltop' in the Australian Aboriginal language of the region. The chemical formula for wycheproofite is $NaAlZr(PO_4)_2(OH)_2{\cdot}H_2O$. The paper also provides data on the third occurrence of kosnarite, $KZr_2(PO_4)_3$, first discovered in the late 1980s in pegmatites in Maine, USA (Brownfield *et al.*, 1993). The second new species from Wycheproof is selwynite, which is the K-analogue of gainesite and will be described separately (Birch *et al.*, in press).

The type specimen of wycheproofite is in the Museum of Victoria collections (M42853). About 700 mg of wycheproofite is estimated to be present on five specimens.

Occurrence

The granite quarry yielding the wycheproofite and kosnarite is on the eastern side of 'Mount' Wycheproof, a low (43 m high) knoll about 500 m east of the township. The knoll consists of a uniform, pale grey, medium-grained, muscovite-bearing granite, which is a reduced S-type of Devonian age. It projects through flat-lying Tertiary sediments of the Murray Basin covering much of northwestern Victoria. The pegmatite-bearing boulders were found at the base of the southeastern wall of the quarry and were probably close to their original position.

Quartz, white to flesh-coloured orthoclase, albite, muscovite and coarse patches of dark greenish brown schorl form the pegmatite veins, which are between 4 and 12 cm thick. Some veins are rimmed by a zone of fine-grained, quench-textured granite. Irregular pegmatitic patches and miarolitic cavities were also found associated with the veins. All traces of the pegmatite have now been removed.

The pegmatite cavities contain a suite of secondary phosphate minerals, including wardite, eosphorite, cyrilovite, a kidwellite-like mineral, rockbridgeite, leucophosphite and saleeite (Birch, 1993). The zirconium-bearing species tend to occur in small miarolitic or interstitial cavities up to 8 mm across, and may be associated with wardite, eosphorite and cyrilovite. Some larger cavities appear to have resulted from the dissolution of primary phosphates, which included fluorapatite. These cavities are now occupied by skeletal or powdery masses consisting mainly of quartz, muscovite, eosphorite and cyrilovite.

Appearance, physical and optical properties

Wycheproofite forms compact aggregates of finely fibrous crystals, filling cavities in one of the pegmatite veins. The crystals are 5 to 10 μm thick and up to several mm long (Fig. 1). No terminations or single crystals have been observed. The colour of the aggregates ranges from pale pinkish orange to pale brownish orange, and they have a vitreous to pearly lustre. The mineral may be overlooked due to its resemblance to feldspar but the finely fibrous nature is diagnostic. A pale pink platy marginal alteration occurs on some of the aggregates. Crystal fragments of wycheproofite are transparent, the streak is colourless and no fluorescence in UV light occurs. The estimated Moh's hardness is between 4 and 5, there is no observable cleavage and the fracture is rough. The measured density of the fibrous aggregates is 2.81 g cm^{-3}, obtained by suspension in a mixture of methylene iodide and trichloromethane.

Because of the finely fibrous nature of wycheproofite, complete optical data could not be obtained. The indices of refraction range from 1.62 normal to fibres to 1.64 parallel to the fibres, which are length slow. Extinction is parallel to the

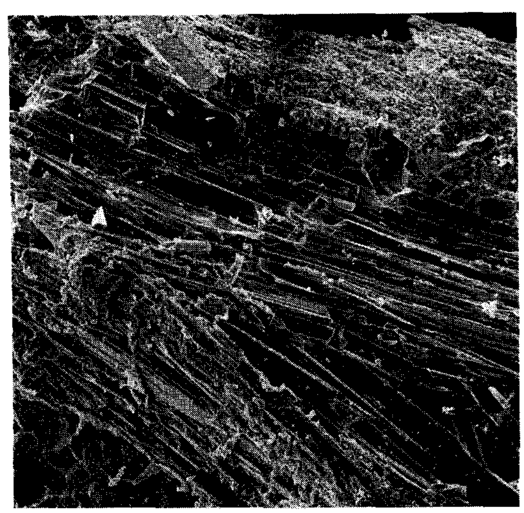

FIG. 1. SEM showing fibrous nature of wycheproofite aggregates. Field of view is 200 × 200 μm.

fibrosity, but is somewhat undulose. No pleochroism is observed.

Kosnarite occurs as translucent, bluish grey rhombohedral crystals between 0.3 and 0.5 mm on edge, lining a small cavity in one of the pegmatite veins. Part of this cavity is filled with iron-stained and altered wycheproofite which encloses some of the kosnarite crystals. Schorl crystals project into the cavity, which also contains euhedral eosphorite crystals and curved whisker-like crystals of an unknown species. A thin coating of cyrilovite occurs on all the cavity minerals. Only about 50 crystals of the kosnarite have been collected. The Wycheproofite kosnarite is similar in appearance to that described from the type locality, the Mt Mica pegmatite in Maine, USA (Brownfield *et al.*, 1993).

Chemical Analysis

Wycheproofite and kosnarite were analysed using a Cameca SX-50 electron microprobe, at 15 kV and specimen current of about 0.2 μA. Standards used were jadeite (Na), synthetic $KTaO_3$ (K), wollastonite (Ca,Si), corundum (Al), hematite (Fe), pure Mn (Mn), monazite (Hf), fluorapatite (P,F), synthetic pollucite (Cs) and kosnarite from the type locality (Zr,P). Water was determined in wycheproofite using a Perkin-Elmer CHN analyser. Lithium, Rb and Be were sought by the ICP-MS method, however contents in excess of 250 ppm were detected only for Rb and Li in kosnarite.

The analytical data and empirical formulae for wycheproofite and kosnarite are shown in Table 1. Small amounts of Hf replace Zr in both minerals, but otherwise there is only limited substitution of major elements. The simplified formula for wycheproofite is $NaAlZr(PO_4)_2(OH)_2{\cdot}H_2O$.

X-ray crystallography

X-ray powder diffraction data for wycheproofite were recorded using a 100 mm diameter Guinier camera with Cu-$K\alpha$ radiation. Due to the finely fibrous nature of the mineral, preliminary precession photographs were unable to shed any light on the unit cell. An initial monoclinic cell was obtained using the computer program 'Visser'. This unit cell was later modified with the aid of electron diffraction patterns to yield a triclinic cell whose parameters were used to index the powder diffraction data. The cell parameters were refined by least squares method to give $a = 10.926(5)$, $b = 10.986(5)$, $c = 12.479(9)$ Å, $\alpha = 71.37(4)°$, $\beta = 77.39(4)°$, $\gamma = 87.54(3)°$, $V = 1375.9$ Å^3. The

TABLE 1. Chemical analyses of wycheproofite and kosnarite

wt.%	1	2	3			4		
Na_2O	6.36	0.04	Na	0.81		K	0.90	
K_2O	0.44	8.46	Ca	0.05	0.90	Li	0.06	0.98
Li_2O	–	0.17	K	0.04		Rb	0.01	
Rb_2O	–	0.11	Al	0.93		Na	0.01	
CaO	0.66	–	Fe	0.02	0.96	Zr	1.88	
BaO	–	0.09	Mn	0.01		Hf	0.17	
SrO	–	0.30	Zr	1.03	1.05	Mn	0.04	2.14
FeO	0.36	0.15	Hf	0.02		Al	0.03	
MnO	0.21	0.54	P	1.99	2.0	Fe	0.01	
Al_2O_3	12.03	0.28	Si	0.01		Sr	0.01	
Cs_2O	0.03	0.03	O	8.06		P	2.98	2.99
ZrO_2	32.43	46.10	OH	1.87	1.94	Si	0.01	
HfO_2	1.24	1.79	F	0.07		O	11.91	
P_2O_5	35.85	42.11	H_2O	1.0		F	0.09	
SiO_2	0.23	0.34						
H_2O	9.0	–						
F	0.34	0.09						
$-O\equiv F$	0.14	0.04						
Total	99.04	100.56						

1. Wycheproofite: average of 5 microprobe analyses
2. Kosnarite: average of 6 microprobe analyses, Li and Rb by ICP-MS
3. Wycheproofite: empirical formula on basis of 11 (O,OH,F)
4. Kosnarite empirical formula on basis of 12 (O,F)

TABLE 2. Powder X-ray diffraction data for wycheproofite

I/I_0	d_{obs}(Å)	d_{cal}(Å)	*hkl*
40	8.865	8.841	101
5	5.359	5.355	$\bar{1}11$
5	4.581	4.623	120
20	4.485	4.483	$\bar{2}01$
10	4.418	4.421	202
20	4.358	4.356	$\bar{2}11$
80	4.128	4.108	$1\bar{2}1$
65	3.711	3.709	023
60	3.465	3.469	030
35	3.243	3.243	$\bar{1}32$
10	2.943	2.947	$\bar{2}30$
30	2.875	2.877	$\bar{1}33$
3	2.709	2.710	$0\bar{2}3$
2	2.680	2.678	$\bar{2}\bar{2}2$
10	2.660	2.659	141
5	2.648	2.646	402
100	2.603	2.602	040
5	2.431	2.433	$\bar{1}43$
3	2.306	2.311	240
2	2.288	2.289	$\bar{1}\bar{4}1$
1	2.262	2.261	$\bar{4}12$
10	2.179	2.179	$\bar{4}22$
10	2.099	{2.100	{$\bar{5}10$
		{2.099	{$4\bar{3}1$
5	2.076	2.076	510
10	2.063	2.063	503
5	2.046	2.046	$3\bar{4}1$
5	1.966	1.966	443
5	1.959	1.958	$\bar{2}50$
5	1.872	{1.873	531
		{1.872	$\bar{5}02$
5	1.855	1.855	$4\bar{3}3$
5	1.841	1.841	$4\bar{4}1$
2	1.737	1.738	$452,5\bar{1}3$
2	1.713	1.714	$\bar{5}03$
6	1.697	1.697	$541,\bar{6}20$
5	1.658	1.657	$3\bar{5}2$
2	1.620	1.620	$4\bar{5}1$
2	1.613	1.612	$\bar{6}12$
5	1.542	1.542	$\bar{1}72,\bar{2}\bar{6}1$
30	1.524	1.524	$\bar{4}\bar{5}1,273$
5	1.378	1.378	561
5	1.328	1.327	$8\bar{1}3$

a = 10.926 (5) b = 10.986 (5) c = 12.479 (9)Å
α = 71.37 (4)° β = 77.39 (4)° γ = 87.54 (3)°

wycheproofite X-ray powder data (Table 2) were indexed on the basis of this cell. The calculated density, for Z=6, is 2.81 g cm^{-3}, in good agreement with the measured density of 2.83 g cm^{-3}.

Structure determination by single crystal X-ray diffraction methods is not possible with the natural material available. Experiments are currently underway to try to synthesize the mineral by hydrothermal methods, with the hope that this will yield suitable crystals for structure analysis.

Much-abbreviated X-ray powder diffraction data were obtained for Wycheproof kosnarite, using the same method as for wycheproofite. Close matches were observed between the major reflections in kosnarite from Wycheproof and the type locality (Brownfield *et al.* 1993).

Paragenesis

Wycheproofite is one of only five known alkali zirconium phosphates. The others are gainesite, $Na_2(Be,Li)Zr_2(PO_4)_4$ (Moore *et al.* 1983), mccrillisite, $NaCs(Be,Li)Zr_2(PO_4)_4 \cdot 1-2H_2O$ (Foord *et al*, in press), selwynite (Birch *et al.* in press) and kosnarite (Brownfield *et al.*, 1993). As well as being known from only a few localities, these minerals occur only in amounts of the order of tens or hundreds of milligrams. In the Wycheproof pegmatite veins, the sequence kosnarite-selwynite-wycheproofite suggests crystallization from secondary hydrothermal solutions with increasing Na/K as temperature decreased. This would be in accordance with the anhydrous (higher temperature) nature of kosnarite, compared with the more hydrated state of wycheproofite. Overall, the Zr phosphates are the earliest formed in the secondary mineral assemblage in the Wycheproof pegmatites. They appear to have crystallized under the reducing conditions which prevailed during the intrusion of the granite. The ubiquitous coating of cyrilovite marks a sudden change to oxidizing conditions, probably due to influx of meteoric fluids, possibly accompanying pressure quenching of the pegmatite veins.

The source of the Zr for these minerals in the Wycheproof pegmatites is uncertain. There appears to be no precursor zircon in the pegmatites, so that the minerals may have resulted from late-stage concentration of Zr in the final pegmatite fluids.

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