Kunatite, $CuFe_2(PO_4)_2(OH)_2 \cdot 4H_2O$, a new member of the whitmoreite group, from Lake Boga, Victoria, Australia.

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ABSTRACT

Kunatite, $CuFe_2(PO_4)_2(OH)_2(H_2O)$, (IMA 2007–057), is a newly defined mineral from a quarry in Late Devonian granite near Lake Boga, northern Victoria, Australia. The mineral occurs as acicular to lath-like microcrystals forming compact to slightly open spheres, hemispheres and flattened sprays up to about 0.25 mm across, with individual fibrous crystals up to 30 µm long and 5 µm thick. Kunatite is associated only with chalcosiderite–turquoise. The crystals are yellow-green with a pale yellow streak and are transparent; the lustre of the aggregates is silky and the estimated Mohs hardness is 3. Kunatite is monoclinic, $P2_1/c$, with a = 9.863(10), b = 9.661(6), c = 5.476(6) Å, $\beta = 92.45(3)^\circ$, V = 521.3(3) Å³ and Z = 2. The calculated density, based on the empirical formula, is 3.063 g/cm³. Crystals are biaxial (–), with $\alpha = 1.703(3)$, $\beta = 1.742(4)$ and $\gamma = 1.762(3)$, and $2V_{calc} = 70^\circ$. Orientation: $Z\sim c$, with straight extinction and slight pleochroism: X = very pale yellow (almost colourless), Y = pale yellowish, Z = yellowish. The strongest five powder-diffraction lines [d in Å, (I/I_o), (hkl)] are: 9.849, (100), (100); 4.386, (90), (210); 6.892, (80), (110); 4.924, (80), (200); 2.697, (60), (320,002,230). Kunatite is a new member of the whitmoreite group and the phosphate-dominant analogue of arthurite. The name is derived from the Australian aboriginal words kunat kunat, meaning cotton weed (sp. Actinobole uliginosum). Kunatite also occurs at the Huber open pit, near Krásno in the Czech Republic. Raman spectra of both type and Czech kunatite and infrared spectra of the Czech kunatite are also presented.

INTRODUCTION

Kunatite is a new secondary phosphate mineral belonging to the whitmoreite group. It occurs in the Late Devonian Lake Boga Granite in north-western Victoria, Australia (Mills et al., 2008a) amongst a diverse assemblage of secondary copper/uranium phosphate minerals (Henry and Birch, 1988), including the three other new species ulrichite (Birch et al., 1988; Kolitsch and Giester, 2001), bleasdaleite (Birch et al., 1999) and lakebogaite (Mills et al., 2008b), as well as several other very rare phosphates including meurigite-(Na) (Kampf et al., 2007), metanatroautunite (Mills, 2004) and a new polymorph of sampleite (Giester et al., 2007). Most of the secondary phosphates occur as millimetre-sized crystals in miarolitic cavities and on joint planes in the granite exposed in a large quarry 10 km south-south-west of Lake Boga township (35° 33'8" S, 143° 38' E) (Figure 1). The secondary phosphates owe their origin to crystallisation from circulating groundwaters charged with P, U and Cu that were derived from oxidation reactions affecting primary apatite-(CaF) (formerly fluorapatite; Burke, 2008), uraninite and chalcopyrite in the uppermost levels of the exposed granite (Mills et al., 2008a).



Figure 1: Map

As well as kunatite, the whitmoreite group contains another two phosphates (whitmoreite and earlshannonite), whilst the related arsenates of the isotypic arthurite group are arthurite, cobaltarthurite and ojuelaite. Several other inadequately described minerals which are likely to be members of these groups were reported by Sejkora *et al.* (2006). All of the minerals are rare, with arthurite the most common. The phosphate members occur mainly as late-stage minerals in granite pegmatites and greisens, whereas the arsenates are found mainly in oxidised zones above ore deposits.

Kunatite was named for the rural district of Kunat around the town of Lake Boga. The mineral data and name were approved by the IMA Commission of New Minerals, Nomenclature and Classification (CNMNC) in March 2008 prior to publication (IMA 2007–057). The name is derived from the Australian aboriginal words *kunat kunat*, meaning 'cotton weed' (in this case the species *Actinobole uliginosum*, which grows in the region). Type material is deposited in the collection of Museum Victoria, Melbourne, Australia (M40728 and M43772).

OCCURRENCE

The new mineral was first found about 1990 by mineral collector John Carey, who donated several specimens to Museum Victoria. At the time, the small amount of material hindered complete description of the mineral, even though it was recognised quite early as being an analogue of arthurite. Kunatite occurs on only about seven or eight small (3 cm or less across) pieces of granite matrix, which may be the contents of a single miarolitic cavity. The only supergene mineral associated with kunatite is chalcosiderite–turquoise, which forms tiny blue-green globules. Thin bladed crystals of manganoan ferberite occur on several of the specimens, but this is regarded as an accidental association. The matrix minerals are smoky quartz, white albite, cream orthoclase and muscovite.

Kunatite has also been found in supergene altered phosphate accumulations in the abandoned Huber open pit, near Krásno (50° 06' N, 12° 48' E) in the Czech Republic

(Sejkora et al., 2006). At this open pit, the apical quartz and greisen part of a cupola of autometamorphosed Li-mica–topaz granite was mined for Sn and W ores. Here, kunatite is associated with apatite-(CaF), isokite, triplite, chalcosiderite–turquoise, leucophosphite, pharmacosiderite, whitmoreite, earlshannonite, kolbeckite, and several unknown minerals, including the F-analogue of perhamite and Zn-Fe³⁺ and Fe²⁺-Al dominant members of the whitmoreite group (see also below).

APPEARANCE AND PROPERTIES

Kunatite from Lake Boga occurs as acicular to lath-like microcrystals that are radially intergrown to form compact to slightly open spheres, hemispheres and flattened sprays up to about 0.25 mm across (Figures 2 and 3). Individual fibrous crystals are up to 30 µm long and 5 µm thick. The small size of the crystals and their indistinct outlines made identification of forms difficult. However, by analogy with other minerals of the whitmoreite group, the crystals are probably flattened on (100), so that prisms belonging to the [001] zone are likely to be present, as well as {100}. The crystals are yellow-green with a pale yellow streak and are transparent; the lustre of the aggregates is silky. The Mohs hardness could not be measured but is estimated to be about 3, based on other members of the whitmoreite group. As observed under the petrographic microscope, kunatite crystals are brittle with an irregular fracture; there is possibly one cleavage direction parallel to [001]. The density could not be measured due to the small size of the crystals, but was calculated to be 3.063 g/cm^3 from the unit cell and empirical formula.

Kunatite crystals are biaxial (-), with $\alpha = 1.703(3)$, $\beta = 1.742(4)$ and $\gamma = 1.762(3)$, measured using white light; 2V could not be measured but was calculated to be 70°. Orientation: Z~c, with straight extinction within error limits; optical orientation (+) (crystals are length slow). In transmitted light crystals show slight pleochroism, from X = very pale yellow (almost colourless), Y = pale yellowish, Z= yellowish. Dispersion is weak, character unknown, and there are slightly anomalous bluish interference colours. Absorption: Z>Y>X. The Gladstone–Dale compatibility index is 0.046, categorised as good.

Table 1: Chemical composition of kunatite from Lake Bo	oga.
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Wt.%	Range	Ideal**	Probe Standard
16.08	14.66-17.29	16.88	copper
0.03	0-0.06		zinc
0.05	0-0.13		wollastonite
27.56	26.62-29.05	33.88	hematite
0.56	0.38 - 0.76		corundum
22.96	22.12-25.42	30.12	apatite-(CaF)
5.14	4.59-5.68		arsenopyrite
16.61		19.12	
88.99		100.00	
	Wt.% 16.08 0.03 0.05 27.56 0.56 22.96 5.14 16.61 88.99	Wt.% Range 16.08 14.66–17.29 0.03 0–0.06 0.05 0–0.13 27.56 26.62–29.05 0.56 0.38–0.76 22.96 22.12–25.42 5.14 4.59–5.68 16.61 88.99	Wt.% Range Ideal** 16.08 14.66–17.29 16.88 0.03 0–0.06 10.05 0.05 0–0.13 27.56 27.56 26.62–29.05 33.88 0.56 0.38–0.76 22.96 22.96 22.12–25.42 30.12 5.14 4.59–5.68 19.12 88.99 100.00 100.00

* $H_2O_{(calc.)}$ content calculated on the basis of the ideal "whitmoreite"-type formula ($H_2O = 4$) and charge balance. ** Theoretical composition calculated from the ideal formula CuFe³⁺₂(PO₄)₂(OH)₂·4H₂O



Figure 2: Radiating aggregates of yellow-green kunatite crystals on quartz from Lake Boga, Victoria. Museum Victoria specimen (M43772). Photograph by Lucy Gibson and Bill Birch. Field of view about 3 mm.

At the Huber open pit, kunatite was found in cavities of strongly altered original triplite accumulations in several morphological types (Sejkora *et al.* 2006). It forms abundant bright yellow-green radiating to semi-spheroidal aggregates up to 1 mm (K1 type; Figure 4) composed of brittle very thin tabular crystals to 0.5 mm long and yellowgreen, well-formed elongate tabular to flattened acicular crystals up to 0.2 mm in length (K2 type; Figures 5 and 6), or light yellowish green, six-sided tabular aggregates up to 0.3 mm composed of fibre-like tabular crystals (K3 type; Figure 7).

CHEMICAL COMPOSITION

Chemical analyses (7) of Lake Boga kunatite were carried out by means of an electron microprobe (CAMECA SX50, WDS mode, 15 kV, 25 nA, 5 µm beam diameter) at the

University of Melbourne. The results, as well as standards, are shown in Table 1. The small size of the crystals, the openness of the crystal aggregates and the high water contents posed problems for the analysis, leading to lower analytical totals than would be

Figure 3: Radiating aggregates of yellow-green kunatite crystals with chalcosiderite-turquoise. Field of view about 4 mm. Photo & specimen: S. Sorrell.

expected from the stoichiometry of other members of the whitmoreite group. This phenomenon has been reported by other authors for members of the whitmoreite and arthurite groups (Raudsepp and Pani, 2002). Raman spectroscopy (see below) showed no carbonate bands, so no CO₂ would be expected in the analyses.

To overcome this problem, the empirical formula has been calculated on the basis of the stoichiometric whitmore ite formula with 14 anions (setting 4 H_2O) and taking into account the contents of non-essential elements. This yields the formula:

$$(Cu_{1,00})_{\Sigma1,00}(Fe^{3+}_{-1.94}Al_{0,06})_{\Sigma2,00}[(PO_{4})_{1.74}(AsO_{4})_{0,26}]_{\Sigma2,00}(OH)_{2}\cdot 4H_{2}O.$$

Density and Gladstone-Dale factors were calculated using this empirical formula. The simplified formula is $CuFe_{2}^{3}(PO_{4})_{2}(OH)_{2}\cdot 4H_{2}O$, which requires CuO16.88, $Fe_{2}O_{3}$ 33.88, $P_{2}O_{5}$ 30.12, $H_{2}O$ 19.12, total 100.00 wt.%.





Figure 4: Radiating aggregates of kunatite (type K1) from Huber open pit. Field of view is 1 mm across. Photo: J. Sejkora.



Figure 5: Elongated tabular crystal of kunatite (type K2) from Huber open pit. Crystal is 0.2 mm long. Photo: J. Sejkora.

The chemical compositions of morphologically different kunatite types (K1–K3) from the Huber open pit were published by Sejkora *et al.* (2006). In comparison with the Lake Boga material, the Czech kunatite shows a more variable chemical composition, with Al concentrations up to 0.23 apfu (Figure 8) and As contents varying considerably between 0.40 (K2) and 0.99 (K3) *apfu* (Figure 9).

CRYSTALLOGRAPHY

X-ray powder-diffraction data of type kunatite (Table 2) were obtained using a Phillips X'Pert diffractometer with CuK α radiation (λ = 1.5406 Å) at CSIRO Minerals, Melbourne, Australia. The unit-cell parameters were

10	1 1(11)	indertee.			
h	k	l	I_{obs}	d_{obs}	d _{cate}
I	0	0	100	9,849	9.854
]	1	0	80	6.892	6.898
2	0	0	80	4.924	4.927
0	2	0	6	4.768	4.761
2	1	0	90	4.386	4.389
1	1	- 1	<5	4.361	4.351
1	2	0	45	4.333	4.336
1	1	l	35	4.225	4.22
2	2	0	16	3.445	3.449
1	2	-1	-	-	3.431
1	2	1	12	3.366	3.362
2	1	1	-	-	3.285
1	3	0	19	3.056	3.061
2	2	-]	14	2.961	2.959
2	2	1	18	2.876	2.879
3	1	- 1	13	2.774	2.775
3	2	0			2.716
0	0	2	60	2.697	2.696
2	3	0			2.686
1	3	1	31	2.654	2.656
1	0	2	-	-	2.602
1	1	-2	26	2.576	2.568
2	3	1	31	2.442	2.441
2	0	-2	-	-	2.437
2	1	-2			2.387
4	0	1	27	2.369	2.38
2	3	1			2.362
3	2	1	-	-	2.349
1	4	0	<1	2.343	2.344

Table 2: X-ray powder-diffraction datafor kunatite.

refined from the powder data using TOPAS (Coelho, 2004) and starting with the unit cell of whitmoreite (Moore *et al.*, 1974). Due to the scarcity of the material and the fluorescence caused by the iron content of the mineral, the pattern was not of a quality suitable for refinement of the atomic positions using the Rietveld method. Kunatite is monoclinic, P2₁/c, with a = 9.863(10), b = 9.661(6), c = 5.476(6) Å, β = 92.45(3)°, V = 521.3(3) Å³ and Z = 2. A more complete (78 diffraction maxima), fully indexed X-ray powder pattern of kunatite from the Huber open pit was published by Sejkora et al. (2006). Its refined unit-cell parameters, a = 9.839(2), b = 9.636(2), c = 5.471(1) Å, β = 92.23(2)°, V = 518.3(1) Å³, agree well with those of type kunatite.

The small size of the crystals on the type material meant that single-crystal X-ray studies could not be carried out.



Figure 6: Scanning electron micrograph showing a group of elongated tabular kunatite crystals (type K2), Huber open pit. Field of view is 120 μ m across. SEM photo: J. Sejkora.

However, because all other properties of kunatite clearly identify it as a new member of the whitmoreite group (see comparative data in Tables 3 and 4), specifically the phosphate analogue of arthurite, some conclusions about the crystal structure of kunatite may be drawn. Members of the group are characterised by a unique corrugated open sheet of Fe³ O_p octahedra, each of which shares four of its six vertices with adjacent octahedra. Vertices with OH ligands are corner-linked to adjacent octahedra, forming a stepped corner-chain parallel to [001]. These chains are linked into a sheet parallel to (100) by sharing O(1)–O(1) edges with equivalent chains. Above and below the sheet of octahedra are (As/P)O₄ tetrahedra, which share three of four vertices with the octahedra, to form a slab.

RAMAN SPECTROSCOPY

Single-crystal laser-Raman spectra were recorded from small aggregates of acicular crystals with random orientation taken from both the type locality and the

Huber occurrence. Type kunatite was studied with a Renishaw MicroRaman Imaging system (M1000) using a laser wavelength of 518 and 633 nm and excitation through a Leica DMLM optical microscope(180° backscatter mode, 'unpolarised' laser light). Spectra were recorded between 100 and 4000 cm⁻¹ with a spectral resolution of ± 2 cm⁻¹ and a minimum lateral resolution of ~2 μ m on the sample. Both wavelengths led to sample damage, but reasonable spectra could be obtained with 633 nm and strongly reduced laser power. Kunatite from Krásno was investigated with a dispersive Raman spectrometer Labram HR (Jobin Yvon) and confocal optics (Olympus microscope). The Raman signal was excited by a 532 nm laser and detected with a multichannel

Figure 8: Plot of Fe³⁺–Al *apfu* in kunatite from Lake Boga and Huber open pit.



Figure 7: Greenish tabular aggregates of kunatite (type K3) from Huber open pit. Field of view is 1.6 mm across.

air-cooled CCD camera. The laser power at the sample was limited to 12 mW to avoid possible thermal destruction of the samples. Spectra were recorded between 400 and 4000 cm⁺ with a spectral resolution of ± 4 cm⁻¹ and a minimum lateral resolution of ~1 μ m on the sample.

Raman spectra of type kunatite and kunatite from the Huber open pit are given in Figure 10. The spectrum of type kunatite shows several peaks in the range between 1140 and 130 cm⁻¹. The peaks at 1130, 1026, ~992 (shoulder), 974, 9.35, 890, 836 and ~782 cm⁻¹ are assigned to v_1 and v_3 vibrations of the PO₄ group; the last three bands may, at least in part, be caused by v_1 and v_3 vibrations of the minor AsO₄ present in the structure. The v_2 and v_4 vibrations of this group would be expected near the observed 445 + 442 and 572 cm⁻¹ bands, respectively. The remaining, partly overlapping peaks below 600 cm⁻¹ (at 494, 307, 243, 188 and 163 cm⁻¹) are attributed to *M*–O (*M* = Cu, Fe) bond and lattice vibrations which are typically observed in this range. A very small peak at ~1654 cm⁻¹ is probably caused by water (H–O–H bending mode). The two more or less





broad peaks at 3342 (with shoulder at ~3150) and 3533 cm⁻ⁱ are attributed to the O–H stretching modes of the H_2O and OH groups, respectively.

Using the correlation of O–H stretching frequencies and O...O hydrogen bond lengths in minerals by Libowitzky (1999), the observed O-H stretching frequencies in kunatite would correspond to approximate O...O bond lengths ranging between roughly 2.7 and 2.95 Å, similar to those observed in whitmoreite (2.72–3.03 Å; Moore *et al.*, 1974).

The Raman spectrum of kunatite from the Huber open pit (Figure 8) is very similar to that of type kunatite. However, some slight band shifts are recognisable in the O–H stretching range (the higher-wavenumber band has shifted to ~3550 cm⁻¹), and most bands below 1200 cm⁻¹ have also shifted somewhat towards higher wavenumbers, possibly as an effect of a different degree of As-for-P substitution.

For comparison purposes Raman spectra were also recorded of a bright green arthurite sample from Cornwall (collection of U.K.) using both 488 and 633 nm laser wavelengths. No sample damage was observed but all spectra showed a high background and a poor signal / noise ratio. Hence, they are not shown but we point out that two bands due to OH stretching vibrations are present at ~3500 and ~3250 cm⁻¹, similar to the situation in kunatite. A very small absorption at ~1600 cm⁻¹ is assigned to the H–O–H bending mode of water. Bands due to several As–O, Cu/Fe–O and lattice vibrations are present in the range <1000 cm⁻¹. We note that Frost *et al.* (2003) reported Raman spectra of arthurite, but these spectra should probably be considered with caution because of the presence of "significant carbonate anions".

INFRARED SPECTROSCOPY

The infrared vibrational spectrum of kunatite from the Huber open pit (Figure 11) was recorded by a micro diffuse-reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range 4000–600 cm⁻¹, resolution 4 cm⁻¹, 128 scans, Happ-Genzel apodization) equipped

Figure 9: Plot of $(PO_4)^{3-}$ $(AsO_4)^{3-}$ apfu in the tetrahedral site of kunatite from Lake Boga and Huber open pit.

with Spectra Tech InspectIR micro FTIR accessory. The sample was dispersed in a mixture with KBr without using any pressure. The Kubelka–Munk units used (Figure 11) formally correspond to absorbance values obtained by the conventional KBr disk technique.

The band at 3332 cm⁻¹ (with a shoulder at 3124 cm⁻¹) was assigned to the v OH stretching vibrations of H₂O groups, and the band at 1649 cm⁻¹ (with a shoulder at 1627 cm⁻¹) was assigned to the δ H–O–H bending vibration of H₂O groups. Shoulders in these regions of the infrared spectrum may indicate that two structurally nonequivalent H₂O groups are present in the structure of kunatite, in accord with the results of the crystal structure study of analogous whitmoreite (Moore *et al.*, 1974) and arthurite (Keller and Hess, 1978). Asharp band at 3534 cm⁻¹ is probably connected to stretching vibrations of OH groups.



Figure 10: Raman spectra of kunatite from Lake Boga and Krásno.

Name Formula	whitmoreite ¹ (Fe ² , Fe ³ , _)Fe (PO ₁) ₂ (OH) 4H O	earlshannonite Min - Fiell (POI) (OH):4H O	kunatite3 Cur Fe (PO) (OH)∙4H O	arthurite ' Culle (AsOl) (OH), 4H O	
a (Å) b (Å) c (Å) β (°) V (Å ³) 5 strongest lines in the powder pattern D(meas.), (calc.) Mohs Hardness α β γ Birefringence Opt. character	10.00(2) 9.73(2) 5.471(8) 93.8(1) 531.2 10.05(100), 7.01(70), 4.98(70), 4.21(70), 2.802(70) 2.87(1), 2.85 3 1.676(3) 1.725(4) 1.745(4) 0.069 neg.	9.910(13) 9.669(8) 5.455(9) 93.95(9) 521.5 9.8(100), 6.9(80), 2.789(70), 4.18(60), 3.45(60), 2.856(60) 2.90(4), 2.92 ~ 3-4 1.696(4) 1.745(4) 1.765(4) 0.069 neg.	9.863(10) 9.661(6) 5.476(6) 92.45(3) 521.3(3) 9.849(100), 4.389(90), 6.898(80), 4.927(80), 2.716(60) n.d., 3.06 ~ 3 (estimated) 1.703(3) 1.742(4) 1.762(3) 0.059 neg.	10.189(2) ^{4,} 9.649(2) ⁴ 5.598(1) ^{4,} 92.16(2) ^{4,} 549.9(2) ^{4,} 6.98(100), 10.14(75), 4.812(60), 2.812(50), 4.305(45) ^{7,} \sim 3.2, 3.29 ^{5,1} not given 1.746(3) ^{4,1} 1.774(3) ^{4,1} 1.806(3) ^{4,1} 0.060 pos. ^{4,1}	
2V (meas.), (calc.)	60-65°, 65.7°	64(4)°, 65.7°	not measurable; 70°	undeterminable ⁽¹⁾ not meas. ⁴⁾ , 88° ⁴⁾ near 90° ⁽⁵⁾ , 88.6° ⁽⁵⁾	
Dispersion OAP Orientation	not given not given Y ~ b, Z ~ c	not given not given Z = c	weak (character unknown) not measurable Z ~ c	not given (010) ⁽⁵⁾ $Y = b, Z^c = 10^{\circ\circ 6}$	
X (colour)	light greenish brown	light yellow brown	very pale yellowish (nearly colourless)	pale yellow ¹⁾ cols. to pale green ¹⁰	
Z (colour)	dark greenish brown	yellow brown	yellowish	grass green ⁵⁷ yellow-green ¹⁷	
Absorption Twinning Cleavage	Z > Y = X (100) (100) fair	Z > X ≅ Y (100) 2 poor cleavages, 1 probably (100)	Z > Y > X not seen not discernible	grassy olive-green ^{**} Z > Y > X not given not given	

1. Moore *et al.* (1974); 2. Peacor *et al.* (1984); 3. This work; 4. Keller and Hess (1978); 5. Davis and Hey (1969), contains P and S (see also Davis and Hey, 1964; Clark and Sillitoe, 1969); 6. Walenta (1975); 7. ICDD-PDF 36-400, contains minor Si and P.

The $(PO_4)^3$ tetrahedron in the crystal structure of kunatite must be distorted from its holosymmetric point symmetry (T_4) since all vibrations are active in the infrared spectrum and degenerate vibrations are split. The bands in the range 900–1200 cm⁻¹ with maxima at 1122, 1085, 1027, 992, 971 and 912 cm⁻¹ are assigned to v_1 and v_3 vibrations of the $(PO_4)^3$ group, while the weak bands at 851, 830 and 784 cm⁻¹ may be connected with v_1 and v_3 vibrations of the $(AsO_4)^3$ groups present as a minor impurity component in the sample studied.

DISCUSSION

Kunatite at Lake Boga crystallised during weathering of the granite in a zone which contains primary hydrothermal apatite-(CaF) and traces of magmatic sulfides, mainly chalcopyrite with minor pyrite. When altered under oxidizing conditions, these minerals contribute Cu^{2-} and PO_4^{3-} to groundwater, from which a suite of secondary copper-based phosphates, including kunatite, have crystallised in cavities and joint planes within the granite. Chalcosiderite–turquoise, libethenite and pseudomalachite are the most common members of this Cu–P assemblage,



Figure 11: Infrared spectra of kunatite from the Huber open pit in the range 4000–600 cm⁻¹.

Table 4. Comparison of X-ray data for whitmoreite-group minerals.

			Kunatite			Kunat	ite ²	e ² Arthurite ³		Whitmoreite⁴		Cobaltarthurite ³		Earlshannoite ⁶		Oujealite ⁷	
h	k	1	d	d _{cale}	1	d_{obs}	I	d_{abs}	I	d_{obs}	I	d_{obs}	I	d _{ub}	I	d_{ob}	
1	0	0	9.849	9.854	100	9.852	100		100	10.05	100	10.2	95	9.8	100	10.207	98
1	1	0	6.892	6.898	80	6.89	35	7.004	97	7.01	70	7.04	100	6.9	80	7.017	100
2	0	0	4.924	4.927	80	4.92	73	4.839	42	4.98	70			4.95	40		
0	2	0	4.768	4.761	16	4.757	7	4.824	45	4.81	40	4.81	65	4.82	5	4.831	47
2	1	0	4.386	4.389	90	4.38	34	4.503	26	4.42	60	4.51	20			4.512	23
] 1	1	-1	4.361	4.351	<5	4.326	9	4.317	92	4.21	70	4.24	60	4.38	40		
<u>}</u> 1	2	0	4.333	4.336	45												
1	1	1	4.225	4.22	35	4.227	24							4.18	60	4.244	91
] 2	2	0	3.445	3.449	16	3.426	20	3.466	24	3.476	50	3.63	<5	3.45	60	3.486	20
} 1	2	-1		3.431								3.5	15				
] 1	2	1	3.366	3.362	12	3.278	20					3.41	10	3.34	2		
} 2	1	1		3.285													
1	3	0	3.056	3.061	19	3.059	16	3.067	17	3.091	30	3.05	20	3.07	5	3.071	14
2	2	-1	2.961	2.959	14	2.949	16	3.003	26	3	20			2.987	30	3.037	28
2	2	1	2.876	2.879	18	2.876	23	2.934	42	2.878	50	2.89	25	2.856	60	2.897	39
3	1	-1	2.774	2.775	13	2.766	35	2.822	72	2.802	70	2.87	55	2.789	70	2.868	72
] 3	2	0	2.697	2.716	60	2.706	30	2.776	18	2.726	40	2.78	10	2.712	40	2.724	20
0	0	2		2.696													
2	3	0		2.686		2.687	27										
] 1	3	1	2.654	2.656	31	2.651	15					2.72	15	2.646	2		
] 1	0	2		2.602		2.602	15	2.671	21	2.585	40	2.622	<5	2.577	30	2.626	18
1	1	-2	2.576	2.568	26	2.563	13	2.621	17			2.619	10				
] 2	3	1	2.442	2.441	31	2.433	5	2.457	22	2.461	20	2.514	5	2.451	2	2.512	15
2	0	-2		2.437						2.4	30						
2	1	-2		2.387		2.397	9			2.329	20	2.43	10	2.389	30	3.427	18
] 4	0	1	2.369	2.38	27	2.394	10										
2	3	1		2.362		2.383	13										
3	2	1		2.349		2.374	9										
1	4	0	2.343	2.344	<1	2.34	12	2.215	14	2.222	30	2.358	<5	2.345	2		

1. This work; 2. Sejkora et al. (2006); 3. Keller and Hess (1978); 4. Moore et al. (1974); 5. Jambor et al. (2002); 6. Peacor et al. (1984); 7. Hughes et al. (1996). The d(obs) for kunatite is only measurable to d = 2.343 Å due in part to the fluorescence caused by the Fe content of the mineral and the amount of sample available for study

accompanied by rarer species ulrichite and a polymorph of sampleite. U/Th dating of ulrichite and other secondary uranium phosphates suggests that much of this assemblage formed in the past 500,000 years (Maas *et al.*, 2006). The presence of a significant amount of As (12^{e_A}) substituting for P in kunatite suggests it has crystallised in proximity to altered arsenopyrite which, while rare, has been recorded as a primary phase in the granite (Mills, 2003).

A phase described from Neubulach, Germany by Walenta (1979) may be the same as kunatite (see unnamed mineral 1455 in the MINERAL database; Nickel and Nichols, 2007). Further unnamed Zn–Fe³⁺ and Fe²⁺–Al members of the whitmoreite group were also reported by Sejkora *et al.* (2006) from Krásno. The latter phase ("UNK8"; Sejkora *et al.* 2006) forms as tiny zones (up to 40 μ m) within kunatite crystals (the presence of divalent iron is deduced from stoichiometry). Besides other supergene minerals, whitmoreite was found in close association. Relics of primary triplite (as Fe²⁺ phosphate) may operate as a local buffer of Fe²⁺ ions in a generally oxidising environment.

A possible Mn²⁻–Mn³⁻–As member from Falotta, Switzerland, which forms small red crystals, is mentioned on http://homepage.hispeed.ch/KlingerMinerals/mineralienfalotta.htm.

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