Cloncurryite, $Cu_{0.56}(VO)_{0.44}Al_2(PO_4)_2(F,OH)_2 \cdot 5H_2O$, a new mineral from the Great Australia mine, Cloncurry, Queensland, Australia, and its relationship to nevadaite

David M. Colchester, Peter Leverett*, Adam R. McKinnon, James L. Sharpe, Peter A. Williams*
School of Natural Sciences, University of Western Sydney
Locked Bag 1797, Penrith South DC, New South Wales, 1797, Australia

David E. Hibbs
School of Pharmacy, University of Sydney
Sydney, New South Wales, 2006, Australia

Peter Turner
School of Chemistry, University of Sydney
Sydney, New South Wales, 2006, Australia

Volker H. Hoppe
46 Dalmor Avenue
Ormond, Victoria, 3204, Australia

ABSTRACT

Cloncurryite, $Cu_x(VO)_{(1-x)}Al_2(PO_4)_2(F,OH)_2 \cdot nH_2O$, with $x = 0.56$, $F \approx OH$ and $n \approx 5$ (IMA 2005-060), is a new mineral from the Great Australia mine, Cloncurry, Queensland, Australia. The name is derived from the locality. It occurs as aggregates of slender, sky-blue needles in silicified goethite-hematite gossan associated with malachite, pseudomalachite, cuprite and native copper. Cloncurryite is monoclinic, space group $P2_1/c$, with $a = 4.9573(2)$, $b = 12.1824(4)$, $c = 18.9749(8)$ Å, $\beta = 90.933(6)°$, $V = 1145.78(14)$ Å^3, $Z = 4$, $D_c = 2.525$ g cm^{-3}, based on the formula $Cu_{0.56}(VO)_{0.44}Al_{1.98}Fe_{0.02}(PO_4)_2F(OH) \cdot 5H_2O$ (analysis and single-crystal X-ray structure), and $a = 4.961(2)$, $b = 12.181(4)$, $c = 18.974(7)$ Å, $\beta = 90.96(4)°$, $V = 1146.4(11)$ Å^3, $Z = 4$ (from least-squares refinement of powder diffraction data). The a:b:c ratio calculated from unit-cell parameters is: 0.4069:1:1.5576. The ten strongest lines in the X-ray powder diffraction pattern [d in Å(I)(hkl)] are: 6.101(100)(020), 5.621(91)(013), 9.515(67)(002), 3.976(21)(031), 3.338(21)(14), 4.753(17)(004), 3.163(17)(006), 3.047(13)(040), 2.903(12)(115) and 2.808(10)(026). An average of 10 microprobe analyses (wt%) gave CuO 10.29; VO_2 8.32; Al_2O_3 23.63; Fe_2O_3 0.32; P_2O_5 32.54; F 4.34; H_2O (by difference) 22.4, less O=F -1.83; total, 100.00. No other metallic elements were detected. The derived empirical formula (based on 2 PO_4 groups pfu and F + OH = 2 pfu) is $[Cu_{0.56}(VO)_{0.44}]_{\Sigma1.00}(Al_{2.02}Fe_{0.02})_{\Sigma2.04}(PO_4)_2F_{1.00}OH_{1.00} \cdot 4.92H_2O$ and the simplified formula is $[Cu_{0.56}(VO)_{0.44}]Al_2(PO_4)_2(F,OH)_2 \cdot 5H_2O$, with $F \approx OH$. The formula is entirely consistent with the results of the single-crystal X-ray structure analysis. Cloncurryite occurs as sky-blue clusters and radiating sprays of extremely acicular prismatic crystals, in a ferruginous, silicified gossan matrix. Isolated needles less than 1 mm long and less than 0.03 mm in thickness are very pale sky-blue in colour and when small appear colourless. Crystals are non-fluorescent, have a white streak and are transparent with a vitreous lustre. Mohs hardness is 2, fracture is uneven and no cleavage was observed. Acicular prisms are elongated along the a axis with forms {010} and {001} and twinning on {100}. Cloncurryite is biaxial (-), with $\alpha = 1.541(2)$, $\beta = 1.548(2)$, $\gamma = 1.550(2)$ (white light), 2V (calc.) = 56°. Dispersion, $r < v$, is very weak. The orientation is X = a, Y ≈ b, Z ≈ c. Pleochroism is faint, but distinct pale blue (β, γ) to very pale greenish blue (α). A characteristic, strong vanadyl (VO^{2+}) stretch is present in the Raman spectrum at 1044 cm^{-1}. The structure of cloncurryite is related to that of the orthorhombic mineral nevadaite, but can be conveniently distinguished from the latter by analysis, the presence of VO^{2+} (in cloncurryite) and a careful examination of X-ray powder diffraction data.

INTRODUCTION

Cloncurryite, $Cu_x(VO)_{(1-x)}Al_2(PO_4)_2(F,OH)_2 \cdot nH_2O$, with $x = 0.56$, $F \approx OH$ and $n \approx 5$, is a new mineral species from the oxidized zone of the Great Australia ore body, Cloncurry, Queensland, Australia. Great Australia, the first copper deposit discovered in the Mt Isa Block, was found in 1867

by Ernest Henry (Blainey, 1970). Small amounts of copper were produced up to 1884, when the mine was purchased by British investors. Some 450 tons of copper were produced to 1897 and the mine closed in 1889. Subsequent mining from 1906 to 1920 yielded approximately 101,000 tons of ore grading 4.3% Cu (Ball, 1907; Carter et al., 1961; Branson, 1998). Apart from minor activities by the 'copper gougers',

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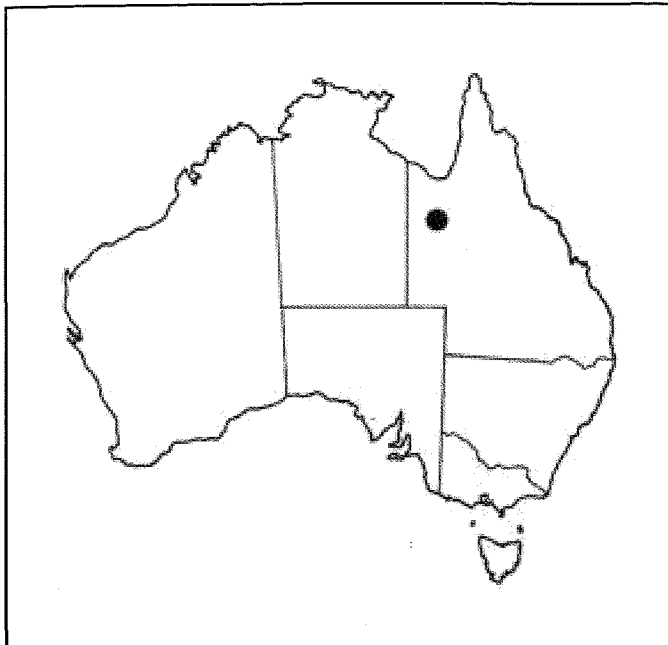*E-mail: p.leverett@uws.edu.au; p.williams@uws.edu.au.

Figure 1 : Map showing the location of Cloncurry.

the mine lay idle until 1995 when the Cloncurry Mining Company NL developed an open-cut oxide resource, producing copper from a heap-leach-SXEW operation. Mining again ceased in 1997. It was during this latter phase of mining that much material from the oxidized zone was exposed, including the zone in which cloncurryite was discovered. All known specimens bearing cloncurryite were recovered from a small dump of silicified, ferruginous gossan removed from the B Tangye lode of the deposit and which had been placed near the entrance to the mining lease for fossicking.

The section of the lode has been mined away and the open cut is currently filled with water. Nevadaite, $(Cu,\square,Al,V)_6[Al_8(PO_4)_8F_8](OH)_2(H_2O)_{22}$ (Cooper *et al.*, 2004), is closely related to cloncurryite, but differs from the former structurally and in the details of its composition. Cloncurryite contains vanadium as the V(IV) vanadyl ion, VO^{2+}, whereas nevadaite contains vanadium as the V^{3+} ion.

The new mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA (IMA 2005-060). The holotype is housed in the collections of the Geosciences Department of Museum Victoria, specimen number M49502. The mineral is named after the town of Cloncurry, Queensland, Australia, founded as the result of the discovery of the copper deposit by Ernest Henry in 1867 that became the Great Australia mine.

OCCURRENCE

The Great Australia deposit is situated at 20° 42' 47" South 140° 30' 0" East, adjacent to the township of Cloncurry, Queensland, Australia (Figure 1). It is one of a large number of fault-hosted deposits of magmatic origin, related to the intrusion of the Williams-Naraku granite suite (Wyborn, 1998). The geology and mineralization of the deposit have

been dealt with in detail by Cannell and Davidson (1998). A simple primary mineralogy comprising cobalt-bearing pyrite and chalcopyrite in a quartz–dolomite–calcite–actinolite–albite–magnetite gangue is confined to the Orphan Shear system, a splay of the Cloncurry Fault, which trends N-S. Host rocks are basaltic meta-andesites with interbedded sediments and intrusive dolerites of the Proterozoic Toole Creek Volcanics. The Naraku granite crops out within 300 m of the ore body (Cannell and Davidson, 1998). The Main lode (Lode A; Ball, 1907) occupies the Orphan Shear and is intersected to the east by three ENE-trending minor faults that are also mineralized. These are the A, B and C Tangye lodes. The most heavily mineralized ground in the upper levels was associated with the intersection of the Main and B Tangye lodes. A well-developed oxidized zone formed the focus of mining in the early days and by Cloncurry Mining NL. Despite the simple nature of the primary mineralization, an extraordinary assemblage of rare secondary copper minerals was recovered from the deposit (Wallace and Pring, 1990; Beyer and Day, 1995; Sharpe and Williams, 1999; Hibbs *et al.*, 2003), mostly lining and filling vughs in cuprite. The setting is rather akin to that of similar mineralization at Bisbee, Arizona (Graeme, 1981, 1993). Cloncurryite was recovered from similar material taken from near the junction of the Main and B Tangye lodes near Bench 6, about 20 m from the surface. Associated minerals were secondary quartz, hematite, goethite, malachite, pseudomalachite, dark-red cuprite and native copper. Its conspicuous sky-blue colour and habit of radiating clusters of acicular crystals initially drew attention. However, the distribution of the mineral was apparently very restricted and only a few dozen specimens were recovered. It formed by oxidation of primary Cu mineralization containing accessory fluorapatite. The origin of the vanadium is uncertain, but may be associated with magnetite; vanadium-rich magnetite is known to occur elsewhere in the region (Wyborn, 1998) and levels of more than 300 ppm V are recorded in the altered Toole Creek Volcanics adjacent to ore (Cannell and Davidson, 1998).

CHEMICAL COMPOSITION

A crystal of cloncurryite was embedded in epoxy resin, polished and carbon-coated. Ten spot analyses were carried out using a Jeol 8600 electron microprobe (WDS mode, 15 kV, 20 nA, 3 μm beam diameter). Due to the very small amount of material available, the H_2O content was not analyzed directly, but was calculated by difference. Analytical results are given in Table 1. No other elements than those reported were detected (Jeol JXA-840 SEM equipped with a light element detector EDS system). The empirical formula (based on 2 PO_4 groups pfu and F + OH = 2 pfu) is: $[Cu_{0.56}(VO)_{0.44}]_{\Sigma1.00}(Al_{2.02}Fe_{0.02})_{\Sigma2.04}(PO_4)_2F_{1.00}OH_{1.00}\cdot4.92H_2O$ and the simplified formula is $Cu_{0.56}(VO)_{0.44}Al_2(PO_4)_2(F,OH)_2\cdot5H_2O$, with F ≈ OH. The formula is entirely consistent with the results of the single-crystal X-ray structure analysis and the presence of vanadium as the vanadyl ion, VO^{2+} (see below). We cannot comment on the extent of any solid solution involving F and OH, although this is likely.
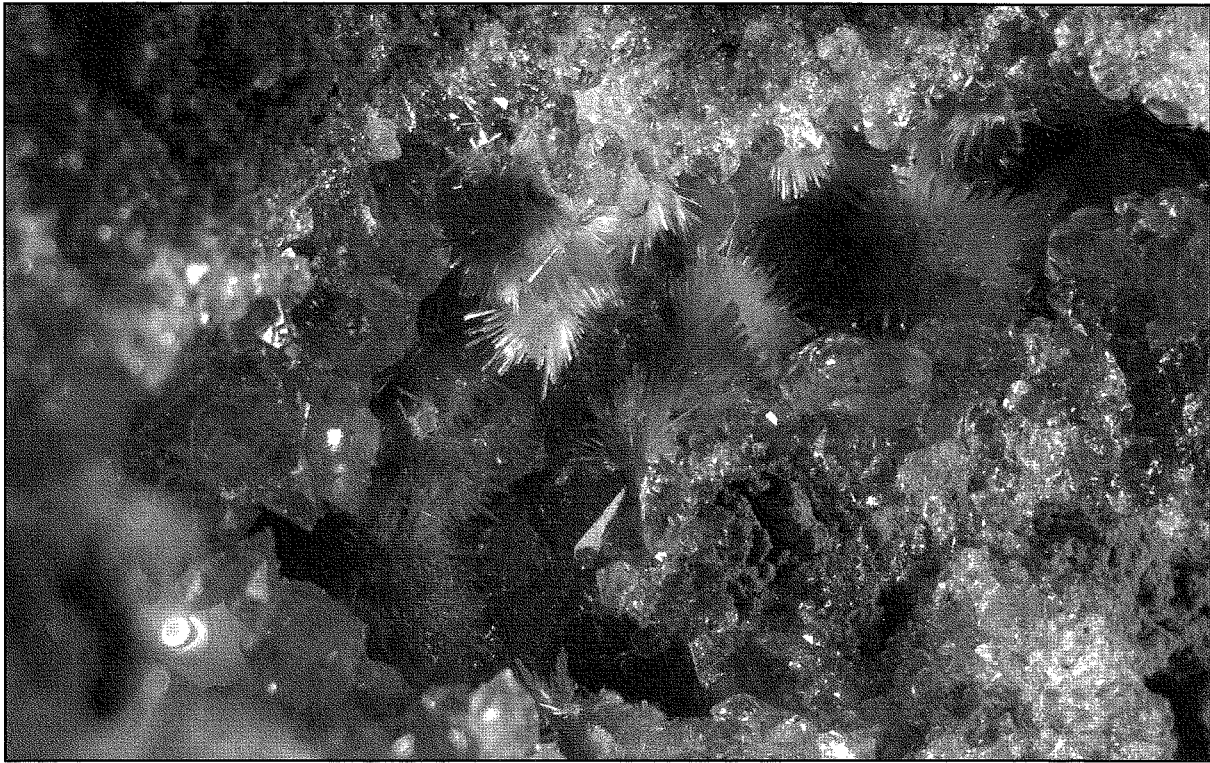
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Figure 2: Cloncurryite from the Great Australia mine. Field of view is 1 mm across. Photo: S. Hinkley. Specimen: V. Hoppe collection.

PHYSICAL AND OPTICAL PROPERTIES

Cloncurryite forms sky-blue clusters and radiating sprays of extremely acicular prismatic crystals less than 1 mm long, in a cuprite-rich, ferruginous, silicified gossan matrix (Figures 2 and 3). The prisms are elongated along the a axis and show the forms {010} and {001}. Twinning is on {100} (see single-crystal structure below). Isolated needles are very pale sky-blue in colour and when small appear colourless. The streak is white and the lustre vitreous. Cloncurryite is transparent and non-fluorescent. Mohs hardness is 2. No cleavage was observed; the mineral is brittle and the fracture is uneven. Density could not be measured because of the small amount of material available and the extremely small crystal size. The calculated density is 2.525 g cm^{-3}, based on the formula $Cu_{0.56}(VO)_{0.44}Al_{1.98}Fe_{0.02}(PO_4)_2F(OH)\cdot5.0H_2O$ (analysis and

Table 1: Analytical data for cloncurryite.

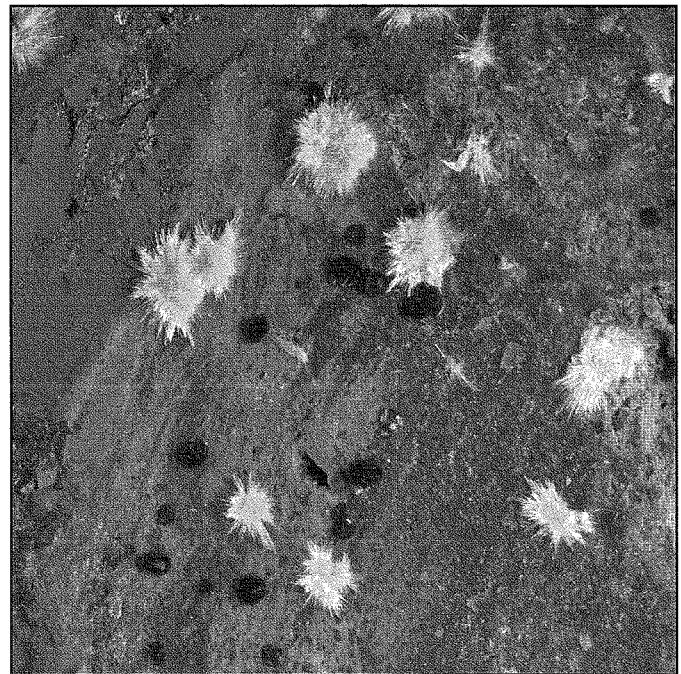| Constituent	Average Wt.%	Range	Probe Standard
CuO	10.29	9.51-10.77	Cu metal
VO$_2$	8.32	7.72-9.10	V metal
Al$_2$O$_3$	23.63	22.82-24.70	orthoclase
Fe$_2$O$_3$	0.32	0.14-0.47	hematite
P$_2$O$_5$	32.54	30.75-34.33	fluorapatite
F	4.34	3.95-5.04	fluorite, fluorapatite
H$_2$O	22.4*		
Less O=F	-1.83		
Total	100.00		

*By difference.

Figure 3: Cloncurryite from the Great Australia mine. Field of view is 5 mm. Photo: D. Henry. Specimen: Museum Victoria, M50605.

single-crystal X-ray structure). The mineral is biaxial (-), with indices of refraction α 1.541(2), β 1.548(2), γ 1.550(2) (white light); 2V (calc.) = 56°; orientation: X = a, Y ≈ b, Z ≈ c; dispersion, r < v, is very weak. The Gladstone-Dale compatibility index is 0.076 (fair) with density calculated using the empirical formula obtained from the microprobe analysis and single-crystal unit-cell dimensions. Pleochroism is faint, but distinct pale blue (β, γ) to very pale greenish blue (α). Raman spectroscopic data (cm$_{-1}$) are

Table 2: Observed and calculated powder diffraction data for cloncurryite and nevadaite.

	Cloncurryite				Nevadaite		
I	d_{meas}	d_{calc}	h k l	I	d_{meas}	d_{calc}	h k l
8	10.226	10.250	0 1 1	**5**	10.193	10.213	1 1 0
67	9.515	9.486	0 0 2	**80**	9.535	9.481	0 2 0
100	6.101	6.090	0 2 0	**100**	6.077	6.061	2 0 0
6	5.832	5.799	0 2 1				
91	5.621	5.612	0 1 3	**90**	5.618	5.604	1 3 0
				5	4.962	4.951	0 0 1
17	4.753	4.743	0 0 4	10	4.751	4.740	0 4 0
				20	4.587	4.583	1 0 1
				5	4.423	4.389	0 2 1
4	4.122	4.110	1 1 2	5	4.123	4.126	1 2 1
21	3.976	3.970	0 3 1	**30**	3.956	3.952	3 1 0
5	3.862	3.846	1 2 0	**20**	3.838	3.834	2 0 1
5	3.748	3.760	1 2 1	10b	3.750	3.758	2 1 1
						3.734	2 4 0
3	3.693	3.690	1 1 3			3.711	1 3 1
3	3.593	3.581	-1 2 2				
3	3.558	3.548	1 2 2	15	3.551	3.555	2 2 1
6	3.461	3.457	-1 0 4	**40**	3.430	3.424	0 4 1
5	3.417	3.417	0 3 3				
21	3.338	3.326	-1 1 4				
5	3.306	3.305	-1 2 3	5	3.287	3.278	2 3 1
17	3.163	3.162	0 0 6	15	3.159	3.160	0 6 0
				3	3.089	3.089	3 1 1
13	3.047	3.045	0 4 0	10	3.033	3.031	4 0 0
8	3.005	3.007	-1 2 4				
7	2.968	2.968	1 2 4	**60**	2.983	2.981	2 4 1
12	2.903	2.903	1 1 5	5	2.933	2.922	1 5 1
				20	2.882	2.887	4 2 0
10	2.808	2.806	0 2 6	**35**	2.805	2.805	3 3 1
						2.802	2 6 0
4	2.777	2.772	0 3 5				
3	2.737	2.744	0 4 3				
6	2.688	2.687	-1 0 6				
4	2.648	2.646	1 0 6	**40**	2.661	2.664	0 6 1
5	2.592	2.595	1 4 0	**20**	2.583	2.585	4 0 1
6	2.564	2.562	0 4 4	5	2.555	2.553	4 4 0
5	2.464	2.458	-1 2 6	**20**	2.476	2.476	0 0 2
				10	2.412	2.414	3 5 1
6	2.370	2.371	0 0 8	10	2.374	2.376	0 7 1
				3	2.341	2.332	1 7 1
2	2.283	2.285	-2 2 1	3	2.301	2.305	0 3 2
				3	2.246	2.250	3 7 0
3	2.217	2.217	1 3 6	3	2.216	2.212	2 7 1
				3	2.189	2.194	0 4 2
						2.187	4 6 0
				15	2.163	2.163	5 1 1
2	2.099	2.100	2 3 1	10	2.098	2.098	3 1 2
				3	2.065	2.063	2 4 2
5	2.048	2.050	0 5 5	5	2.044	2.043	5 5 0
2	2.031	2.031	2 1 5				
				3	2.016	2.020	6 0 0
						2.016	2 8 1
3	1.992	1.991	-1 5 4				
4	1.986	1.985	0 6 2	10	1.976	1.976	6 2 0
				15	1.950	1.949	0 6 2
2	1.928	1.927	-1 1 9	**20**	1.917	1.914	1 1 9
				5	1.889	1.890	3 8 1
4	1.868	1.866	0 6 4				
2	1.838	1.837	2 3 5	**40**	1.844	1.844	3 5 2
4	1.811	1.811	0 2 10	**20**	1.810	1.810	2 10 0
						1.807	1 7 2
				3	1.792	1.794	6 3 1
						1.793	5 6 1
3	1.769	1.771	-2 3 6				
3	1.743	1.743	1 6 4	**40**	1.740	1.740	6 4 1
				5b	1.713	1.712	0 8 2
3	1.707	1.708	0 6 6	3	1.700	1.702	6 6 0
					Plus 11 lines to 1.383 Å		

The 10 strongest lines for cloncurryite and lines for nevadaite with relative intensity ≥20 are marked in bold.

3500s, H_2O stretch; 3330s,b, OH stretch; 1615m, H_2O bending; 1145m, (v_s(V-O-P); 1102m, (v_{as}(V-O-P); 1064s, (v_{as}(P-O); 1044s, V=O; 995s, (v_s(P-O); 851m, 617m, 581m, 502m, 478m, 448,m 411m, 327. Cloncurryite gives positive chemical spot tests for Cu, V, P, and is soluble in acid. It decomposes on heating with liberation of water.

X-RAY POWDER DIFFRACTION

Powder X-ray diffraction data were recorded using a Philips PW1825-20 powder diffractometer (Ni-filtered Cu Kα radiation with pure Si as internal standard; λ = 1.5418 Å). Table 2 lists powder diffraction data, together with those of nevadaite (Cooper et al., 2004) for comparison. Refined unit cell dimensions (Langford, 1973) from the powder diffraction data are a = 4.961(2), b = 12.181(4), c =18.974(7) Å, β = 90.96(4)°, V = 1146.4(11) Å³. The $a:b:c$ ratio calculated from unit cell parameters (see below) is 0.4069:1:1.5576. The ten strongest lines in the X-ray powder diffraction pattern [d in Å(I)(hkl)] are: 6.101(100)(020), 5.621(91)(013), 9.515(67)(002), 3.976(21)(031), 3.338(21)(14), 4.753(17)(004), 3.163(17)(006), 3.047(13)(040), 2.903(12)(115) and 2.808(10)(026).

SINGLE-CRYSTAL X-RAY STRUCTURE

Because of the very small size of the crystals available, single-crystal data were collected using synchrotron radiation at the ChemMatCARS facility at the University of Chicago (Sector 15). A summary of crystallographic and refinement details is given in Table 3. Data were corrected for Lorenz polarization and extinction effects. No absorption correction was applied. The structure was solved using direct methods (Sheldrick, 1997a) followed by a careful sequence of difference syntheses and refined using full-matrix least-squares techniques based on F^2 (Sheldrick, 1997b). Several data sets were collected; although the structure could be solved with each set, in only the present case could it be satisfactorily refined due to crystal quality. The small Fe content indicated by chemical analysis was taken account of in the refinement by including it at the Al(2) site. Acceptable and comparable equivalent isotropic thermal parameters were subsequently obtained for both Al(1) and Al(2) sites. There is no suggestion of ordering of the two (OH,F) sites. To test this, we artificially perturbed the structure analysis by varying site occupancy factors for F and OH between the two sites and by systematically varying the relative amounts of F and OH in each of them. The structure was refined to a final R of 0.103, with largest peak and hole in the final difference map being series termination effects close to Cu(1) and P(1). Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 4. Lists of anisotropic thermal parameters and selected bond lengths and angles are given in Tables 5 and 6, respectively. A perspective drawing of the structure is shown in Figure 4.

The structure of the sheets produced by Al, phosphate, fluoride and hydroxide ions and coordinated water molecules (Figure 4) is comparable to that in nevadaite (Cooper et al., 2004). The two aluminium ions are both

octahedrally coordinated (Table 6). One is bonded to two *trans* water molecules, two *cis* phosphate oxygen atoms and two disordered cis (F,OH) ions. The other is coordinated to four phosphate oxygen atoms and two *trans* disordered (F,OH) ions. $AlO_4(F,OH)_2$ octahedra are linked in chains parallel to the *b* axis by (F,OH) bridges and phosphate oxygen atoms, and the latter also serve to link the chains into sheets parallel to the *ab* plane. The sheets are further linked in the *c* direction via coordination of phosphate oxygen atoms to Cu^{2+} and VO^{2+}. Both phosphate ions are regularly tetrahedral. Cu(1) is coordinated in a square planar fashion to two phosphate oxygen atoms (*cis*-O(3) and O(7)) and two water molecule (*cis*-OW3 and OW4) in fully occupied sites. These four Cu-O bond lengths vary from 1.901 to 2.002 Å. A water molecule (OW5; Cu-O = 2.486 Å) completes the Jahn-Teller distorted square pyramidal coordination sphere. The site occupancy factor (sof) for Cu(1) is 0.53. Cu(2), which is present only in very small amounts, is similarly coordinated to the same atoms, but in a related face-sharing position down the *a* axis (placing it 2.47 and 2.49 Å on either side of the Cu(1) site along *a*); its site occupancy factor is 0.03, giving a total of 0.56 Cu pfu, in line with the analytical data, and consistent with the sof of OW5 of 0.56 (OW5 is bonded to both Cu(1) and Cu(2)).

Table 3: Crystal data and structure refinement details for cloncurryite.

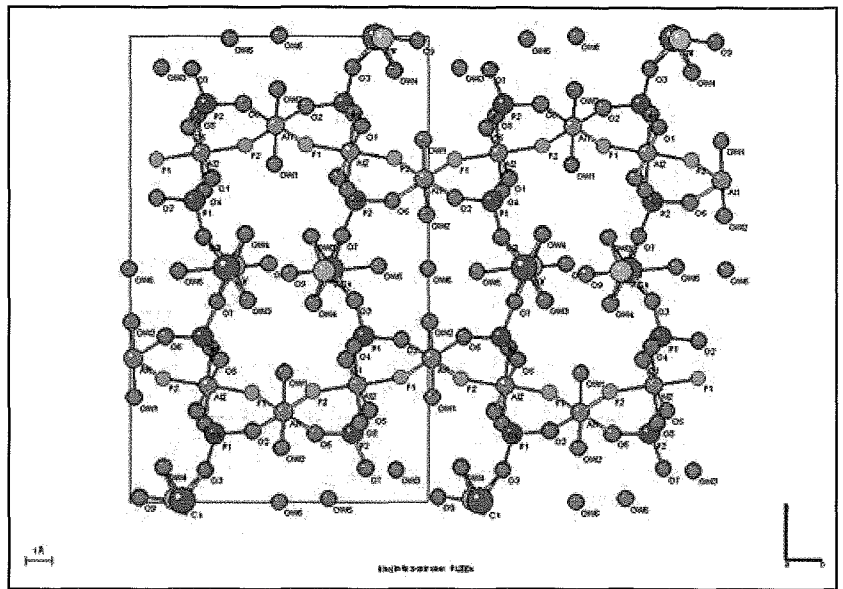|	
Empirical formula	$Cu_{0.56}(VO)_{0.44}Al_{1.98}Fe_{0.02}(PO_4)_2F(OH)\cdot 5.0H_2O$
Formula weight	435.60
Temperature	123(2) K
Wavelength	0.56356 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 4.95730(10) Å
	b = 12.1824(2) Å β = 90.933(2)°
	c = 18.9749(4) Å
V	1145.78(4) Å^3
Z	4
Density (calculated)	2.525 Mg m^{-3}
Absorption coefficient	1.042 mm^{-1}
$F(000)$	873
Crystal size	0.006 x 0.002 x 0.002 mm
θ range for data collection	3.38 to 30.38°.
Index ranges	$-7 \leq h \leq 6, -19 \leq k \leq 19, -30 \leq l \leq 30$
Reflections collected	25795
Independent reflections	5353 [R(int) = 0.0778]
Completeness to θ = 30.38°	77.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5353/36/225
Goodness-of-fit on F^2	1.102
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.1033, $wR2$ = 0.2643
R indices (all data)	$R1$ = 0.1176, $wR2$ = 0.2718
Weighting scheme	$w = 1/(\sigma^2 F_o^2 + 0.01P^2 + 25P)$, where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.000(4)
Largest diff. peak and hole	2.521 and -2.103 e Å^{-3}

Figure 4: Perspective drawing of the structure of cloncurryite viewed down the *a* axis. Cu2 and OW7, present in the structure in very small amounts, are omitted for clarity; Cu(1))(blue), V (orange), Al (grey) P (purple), O (red), F, O of OH (green).

As with Cu(1), Cu(2) is five-coordinate (Table 6) and assumes a Jahn-Teller-distorted square pyramidal geometry. The VO^{2+} ion is coordinated to the same four oxygen atoms (O(3), O(7), OW3 and OW4) as Cu(1) as shown in Figure 5. These four V-O distances range from 1.937 to 2.059 Å, and the vanadyl V=O distance (V-O(9)) is 1.640 Å. The site occupancy factors of the V atom and the vanadyl O atom are equal at 0.44, again in line with the analysis. It is emphasized here that the Cu-OW5 vector is opposite in direction to the V=O vector and that when the
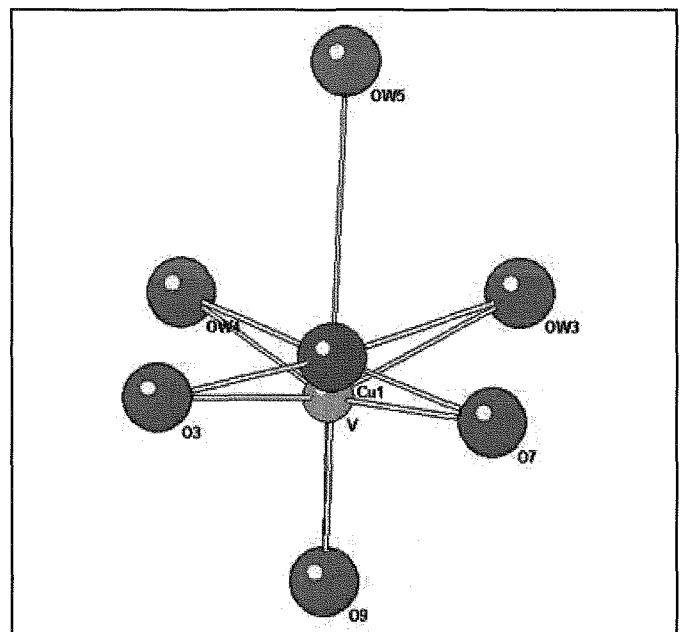

Figure 5: The coordination environment of the coupled Cu(1)–VO^{2+} site. Both ions are coordinated to the same four oxygen atoms (O(3), O(7), OW3 and OW4); the vanadyl oxygen atom is O(9). At any one time either Cu(1) plus OW5, or V plus O(9), are present, but not both.

Table 4: Atomic coordinates (x10⁴), site occupancy factors (sof) and equivalent isotropic displacement parameters (Å²x 10³) for cloncurryite. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	sof	U(eq)
V	1889(16)	1522(6)	49(4)	0.44	12(1)
Cu(1)	2267(11)	1756(4)	26(3)	0.53	11(1)
Cu(2)	-2710(50)	1680(30)	-16(12)	0.03	12(4)
P(1)	9807(3)	2161(1)	-3546(1)	1	4(1)
P(2)	-47(3)	2554(1)	-1468(1)	1	4(1)
Al(1)	7664(4)	4870(1)	-1924(1)	1	5(1)
Al(2)	4905(3)	2387(1)	-2513(1)	0.98	4(1)
Fe(2)	4905(3)	2387(1)	-2513(1)	0.02	4(1)
F(1)	5605(7)	5907(3)	-2340(2)	0.5	4(1)
OH1	5605(7)	5907(3)	-2340(2)	0.5	4(1)
F(2)	5478(7)	3862(3)	-2363(2)	0.5	4(1)
OH2	5478(7)	3862(3)	-2363(2)	0.5	4(1)
O(1)	11851(8)	2758(3)	-3061(2)	1	5(1)
O(2)	10091(9)	902(3)	-3477(2)	1	9(1)
O(3)	111(10)	2530(4)	680(2)	1	11(1)
O(4)	6935(8)	2488(3)	-3334(2)	1	6(1)
O(5)	-2086(8)	1973(3)	-1965(2)	1	6(1)
O(6)	-488(9)	3791(3)	-1460(2)	1	9(1)
O(7)	-374(9)	2096(3)	-713(2)	1	7(1)
O(8)	2843(8)	2289(3)	-1700(2)	1	6(1)
O(9)	340(20)	337(7)	105(5)	0.44	9(2)
OW1	9875(10)	4841(3)	-2761(2)	1	9(1)
OW2	5027(10)	4943(3)	-1157(2)	1	8(1)
OW3	4713(9)	1080(3)	-682(2)	1	9(1)
OW4	4653(12)	1134(4)	753(3)	1	16(1)
OW5	5190(20)	3405(8)	-66(5)	0.56	14(2)
OW6	0	5000	0	0.16	10(3)
OW7	4590(40)	3184(15)	-78(9)	0.28	10(3)

VO^{2+} group is present, Cu(1), Cu(2) and OW5 are absent from the lattice, and vice versa. It is further stressed that the coupled V=O vanadium and oxygen atoms, and Cu(1), Cu(2) and OW5 refine independently with no constraints other than the coupling of the appropriate site occupancy factors. The V atom of the vanadyl ion lies close (0.345 Å) to the position of Cu(1), but is displaced from the square plane formed by O(3), O(7), OW3 and OW4 by a small amount (0.35 Å) towards the vanadyl oxygen atom (Figure 5). It should be noted that only one of the Cu(1), Cu(2) and V sites is occupied at any one time. Finally, a remarkable crystallographic constraint in the structure is that the vanadyl:Cu ratio cannot exceed 1:1 as this would result in an untenable non-bonded steric interaction between the vanadyl oxygen atoms (O(9)⋯O(9')) = 0.97 Å).

A weakly hydrogen-bonded water molecule (OW6) is located at site 2c (0,1/2,0) in tunnels running parallel to a and it is evident that this water is "zeolitic" in nature. An sof of 0.16 for this water molecule is indicated in the single-crystal structure analysis. A further partially occupied water molecule (OW7) with an sof of 0.28 is located near OW5 (0.40 Å distant), but is not present when Cu(1), Cu(2) and OW5 are. OW7 lies 2.81 Å from OW3 and 2.95 Å from

OW4 and is hydrogen bonded to both. Furthermore, it could also interact weakly with vanadium (V⋯OW7 = 2.44 Å; O9-V⋯OW7 = 174°).

A complete bond-valence calculation for nevadaite (Cooper et al., 2004) showed that the structural assignment of OH-, H_2O, F-, Cu^{2+}, Al and V^{3+} is reliable. In cloncurryite, the phosphate ions are regularly tetrahedral with normal bond distances. A bond-valence calculation (Brown and Altermatt, 1985; Hormillosa et al., 1993) for the metal ions in cloncurryite gave bond-valence sums of 3.89 vu (valence units) for V, with the vanadyl contribution amounting to 1.48 vu, 2.04 vu for Cu(1), 2.91 vu for Al(1) and 2.92 vu for Al(2). These values are entirely consistent with the chemistry of the mineral, and in particular for the identity of the oxidation state of vanadium in cloncurryite.

RELATIONSHIP OF CLONCURRYITE TO NEVADAITE

In our initial work on the nature of cloncurryite, we discounted its identity with nevadaite, $(Cu^{2+},\square,Al,V^{3+})_6[Al_8(PO_4)_8F_8](OH)_2(H_2O)_{22}$, on the basis of chemical analyses (VO^{2+} versus V^{3+}, and differing Cu, V, Al, F contents) and the fact that nevadaite is orthorhombic. However, an anonymous member of the IMA Commission on New Minerals and Mineral Names drew to our attention the facts that the optical properties of the two minerals were the same within experimental error, as were the a, b and c unit cell dimensions (Cooper et al., 2004). In line with the member's suggestion that refinement of our data ought to be attempted in the orthorhombic space group $P2_1mn$, as found for nevadaite, we made the appropriate matrix conversion and started with the coordinates given for the structure of nevadaite. This attempt failed and the nevadaite structure is quite incompatible with our data. Indeed, SHELXL (Sheldrick, 1997b) identified some 181 systematic absence violations in our data for space group $P2_1mn$. Of these, all had $I > 5s(I)$ and many had $I > 20s(I)$, especially when the reflections were of high intensity. A re-check of our data reduction routine showed that the true symmetry of cloncurryite is monoclinic. Furthermore, we approached the authors of the published description of nevadaite and they have made it clear that the true symmetry of nevadaite is orthorhombic.

Additionally, we have calculated powder diffraction patterns for nevadaite and cloncurryite using the program PowderCell (Kraus and Nolze, 1996a,b) and have compared the powder diffraction records of both minerals very closely. Data for comparison are given in Table 2. There are marked similarities in the data, but there are also striking differences. The reflection at 5.832 Å (I_{rel} = 6, calc. 5.799 Å, 021) in cloncurryite is not observed in nevadaite. Indeed, in the setting of the latter it is symmetry-forbidden. Similarly, in the powder diffraction record for nevadaite, reflections at 4.962 Å (I_{rel} = 5, calc. 4.951 Å, 001) and at 2.246 Å (I_{rel} = 5, calc. 2.250 Å, 370) correspond to symmetry-forbidden reflections in cloncurryite, space group $P2_1/c$, and peaks in the diffraction trace for cloncurryite are not observed at these d spacings. These differences serve to distinguish between

Table 5: Anisotropic displacement parameters ($Å^2 \times 10^3$) for cloncurryite*. The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	6(2)	26(3)	3(1)	0(2)	1(1)	7(2)
Cu(1)	8(2)	17(2)	8(1)	1(1)	0(1)	4(1)
Cu(2)	4(11)	31(14)	1(7)	2(8)	-2(6)	-8(8)
P(1)	2(1)	5(1)	6(1)	0(1)	0(1)	1(1)
P(2)	3(1)	4(1)	6(1)	0(1)	0(1)	1(1)
Al(1)	2(1)	3(1)	9(1)	0(1)	-1(1)	0(1)
Al(2)	3(1)	2(1)	8(1)	0(1)	0(1)	1(1)
Fe(2)	3(1)	2(1)	8(1)	0(1)	0(1)	1(1)
F(1)	1(2)	2(1)	9(1)	0(1)	-2(1)	1(1)
OH1	1(2)	2(1)	9(1)	0(1)	-2(1)	1(1)
F(2)	3(1)	3(1)	5(1)	0(1)	0(1)	0(1)
OH2	3(1)	3(1)	5(1)	0(1)	0(1)	0(1)
O(1)	4(2)	4(1)	8(1)	1(1)	-2(1)	1(1)
O(2)	7(2)	5(2)	14(2)	-1(1)	-4(1)	3(1)
O(3)	10(2)	20(2)	4(2)	1(1)	1(1)	2(2)
O(4)	2(2)	9(2)	8(2)	1(1)	-1(1)	2(1)
O(5)	4(2)	5(2)	8(1)	0(1)	0(1)	1(1)
O(6)	8(2)	6(2)	12(2)	0(1)	-2(1)	0(1)
O(7)	5(2)	10(2)	7(2)	4(1)	1(1)	2(1)
O(8)	4(1)	7(1)	6(1)	1(1)	0(1)	0(1)
O(9)	11(5)	1(3)	14(4)	3(2)	1(3)	1(2)
OW1	8(2)	8(2)	12(2)	0(1)	4(1)	0(1)
OW2	7(2)	6(2)	13(2)	1(1)	2(1)	1(1)
OW3	8(2)	7(2)	13(2)	2(1)	-1(1)	3(1)
OW4	26(3)	6(2)	15(2)	-3(1)	-10(2)	6(2)
OW5	14(2)	14(2)	14(2)	0(1)	0(1)	0(1)
OW6	11(3)	10(3)	10(3)	0(1)	0(1)	0(1)
OW7	10(3)	10(3)	10(3)	0(1)	0(1)	0(1)

*O(8), F(2), OH2, OW5, OW6 and OW7 were constrained so that their U_{ij} components approximated to isotropic behaviour (Sheldrick, 1997b).

Table 6: Selected bond lengths [Å] and angles [°] for cloncurryite.

V-O(9)	1.640(11)	O(9)-V-O(3)	107.4(5)
V-O(3)	1.937(10)	O(9)-V-O(7)	95.6(5)
V-O(7)	1.946(10)	O(9)-V-OW4	93.9(5)
V-OW3	2.059(9)	O(9)-V-OW3	97.9(5)
V-OW4	1.956(10)	O(7)-V-OW4	169.5(4)
V···OW7	2.44(2)	O(7)-V-O(3)	88.2(4)
O(9)-V···OW7	174.2(8)	O(7)-V-OW3	89.0(3)
OW4-V-O(3)	93.0(4)	OW4-V-OW3	85.4(4)
O(3)-V-OW3	154.6(4)		
Cu(1)-O(3)	1.901(7)	Cu(2)-O(7)	1.84(2)
Cu(1)-O(7)	1.948(7)	Cu(2)-OW3#2	1.93(2)
Cu(1)-OW3	2.002(7)	Cu(2)-OW4#2	2.08(2)
Cu(1)-OW4	1.956(7)	Cu(2)-OW5#2	2.34(3)
Cu(1)-OW5	2.486(11)	Cu(2)-O(3)	2.17(2)
O(3)-Cu(1)-O(7)	89.2(3)	O(7)-Cu(2)-OW3#2	93.0(10)
O(3)-Cu(1)-OW4	94.1(3)	O(7)-Cu(2)-OW4#2	177.2(18)
O(7)-Cu(1)-OW4	169.2(3)	OW3#2-Cu(2)-OW4#2	85.5(10)
O(3)-Cu(1)-OW3	174.5(3)	O(7)-Cu(2)-O(3)	84.2(10)
O(7)-Cu(1)-OW3	90.7(3)	OW3#2-Cu(2)-O(3)	173.9(17)
OW4-Cu(1)-OW3	87.0(3)	OW4#2-Cu(2)-O(3)	97.5(9)
O(3)-Cu(1)-OW5	88.9(3)	O(7)-Cu(2)-OW5#2	90.5(12)
O(7)-Cu(1)-OW5	99.4(3)	OW3#2-Cu(2)-OW5#2	91.6(11)
OW4-Cu(1)-OW5	90.9(3)	OW4#2-Cu(2)-OW5#2	91.9(11)
OW3-Cu(1)-OW5	85.7(3)	O(3)-Cu(2)-OW5#2	83.0(10)
P(1)-O(1)	1.540(4)	P(2)-O(5)	1.542(4)
P(1)-O(2)	1.546(4)	P(2)-O(6)	1.523(4)
P(1)-O(3)#3	1.526(4)	P(2)-O(7)	1.548(4)
P(1)-O(4)	1.538(4)	P(2)-O(8)	1.540(4)
O(3)#3-P(1)-O(4)	107.1(2)	O(6)-P(2)-O(8)	110.1(2)
O(3)#3-P(1)-O(1)	112.6(2)	O(6)-P(2)-O(5)	111.6(2)
O(4)-P(1)-O(1)	108.9(2)	O(8)-P(2)-O(5)	109.5(2)
O(3)#3-P(1)-O(2)	108.4(3)	O(6)-P(2)-O(7)	109.2(2)
O(4)-P(1)-O(2)	108.5(2)	O(8)-P(2)-O(7)	107.5(2)
O(1)-P(1)-O(2)	111.1(2)	O(5)-P(2)-O(7)	108.8(2)
Al(1)-F(1)	1.799(4)	Al(2)-F(1)#5	1.841(4)
Al(1)-O(6)#1	1.821(4)	Al(2)-O(8)	1.868(4)
Al(1)-F(2)	1.829(4)	Al(2)-O(4)	1.873(4)
Al(1)-O(2)#4	1.836(4)	Al(2)-O(5)#1	1.874(4)
Al(1)-OW1	1.944(5)	Al(2)-O(1)#2	1.878(4)
Al(1)-OW2	1.974(5)	Al(2)-F(2)	1.842(4)
F(1)-Al(1)-O(6)#1	175.3(2)	F(2)-Al(2)-F(1)#5	178.98(19)
F(2)-Al(1)-O(2)#4	177.4(2)	O(8)-Al(2)-O(4)	179.3(2)
OW1-Al(1)-OW2	172.6(2)	O(5)#1-Al(2)-O(1)#2	178.31(19)

Symmetry transformations used to generate equivalent atoms are #1: $x+1,y,z$; #2: $x-1,y,z$; #3: $x+1,-y+1/2,z-1/2$; #4: $-x+2,y+1/2,-z-1/2$; #5: $-x+1,y-1/2,-z-1/2$.

the two minerals (see below). It should also be noted that there are significant differences in intensities of strong lines for one or other of the minerals. Thus it is clear that the two minerals, though very similar in structure in terms of the ordered layers as described for nevadaite (Cooper et al., 2004), belong to different crystal systems. This is despite the fact that the a, b and c dimensions of the unit cell are virtually identical, taking into account the different settings. We are thus led to conclude that the adoption of an orthorhombic structure versus a monoclinic one depends upon the nature of substitution in the metal sites between the ordered layers, which must ultimately reflect the compositions of the solutions from which the minerals crystallized. Nevadaite contains V^{3+}, but cloncurryite contains V^{4+}, as vanadyl, VO^{2+}. Nevadaite also contains significant extra amounts of Al in the metal sites (space group $P2_1mn$ generates three metal sites in nevadaite; in cloncurryite two of these are identical and the third is analogous). Cloncurryite contains significantly greater amounts of vanadium and copper and in cloncurryite Al is confined to the two octahedral sites of the ordered layers. The two minerals must reflect the chemical outcomes of

solutions of different redox potential. It may well be the case that the nevadaite lattice is more suitable to stabilize V in the lower oxidation state, but this is a speculation. Finally, in this connection, it may be the case that the adopted symmetry may also be dependent upon the relative amounts of F^- versus OH^- in the ordered layers, but we have no evidence to support this one way or the other. Aside from the structural constraint concerning the

maximum amount of VO^{2+} that can be accommodated by the cloncurryite lattice, mentioned above, the limits of solid solution (involving metal ions, F and OH) in nevadaite and cloncurryite remain to be established.

Nevertheless, there are properties that can be used to distinguish between cloncurryite and nevadaite. The chemical compositions of nevadaite and cloncurryite are significantly different in that each contains V in a different oxidation state. The optical properties of the two species are the same within experimental error and this reflects, fortuitously, contributions of the chemical composition and the related structures. Optical properties therefore are not useful for distinguishing between the two phases. Cloncurryite and nevadaite can be conveniently distinguished crystallographically in that cloncurryite is monoclinic and nevadaite orthorhombic, as confirmed by single-crystal X-ray analysis. A careful examination of the powder diffraction record (see above), especially with respect to observed versus symmetry-forbidden reflections, will discriminate between the two. In addition, the presence of the strong vanadyl V=O stretch in the IR spectrum of cloncurryite at 1044 cm^{-1} is diagnostic. In the vanadyl ion, the V-O bond length varies from 1.55 to 1.68 Å and the V=O stretching frequency (950-1050 cm^{-1}) is correlated with it (Cotton et al., 1999). Higher wavenumbers correspond to longer bond distances and the present V-O distance (1.64 Å) is consistent with the IR data.

SUPPLEMENTARY DATA

Full lists of crystallographic data excluding structure factor tables have been deposited with the Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum, Karlsruhe, Germany; CRYSDATA@FIZ-Karlsruhe.DE. Any request to the ICSD for this material should quote the full literature citation and the CSD-number 416728 (filename CloncurryiteCIF). Lists of observed and calculated structure factors are available from the authors upon request.

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