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NEVADAITE, $(Cu^{2+}, \square, Al, V^{3+})_6$ $[Al_8 (PO_4)_8 F_8]$ $(OH)_2$ $(H_2O)_{22}$, A NEW PHOSPHATE MINERAL SPECIES FROM THE GOLD QUARRY MINE, CARLIN, EUREKA COUNTY, NEVADA: DESCRIPTION AND CRYSTAL STRUCTURE

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Abstract

Nevadaite, $(Cu^{2+}, \square, Al, V^{3+})_6$ $(PO_4)_8$ F_8 $(OH)_2$ $(H_2O)_{22}$, is a new supergene mineral species from the Gold Quarry mine, near Carlin, Eureka County, Nevada, U.S.A. Nevadaite forms radiating clusters to 1 mm of prismatic crystals, locally covering surfaces more that 2 cm across; individual crystals are elongate on [001] with a length:width ratio of >10:1 and a maximum diameter of ~30 μm. It also occurs as spherules and druses associated with colorless to purple-black fluellite, colorless wavellite, strengite–variscite, acicular maroon-to-red hewettite, and rare anatase, kazakhstanite, tinticite, leucophosphite, torbernite and tyuyamunite. Nevadaite is pale green to turquoise blue with a pale powder-blue streak and a vitreous luster; it does not fluoresce under ultraviolet light. It has no cleavage, a Mohs hardness of ~3, is brittle with a conchoidal fracture, and has measured and calculated densities of 2.54 and 2.55 g/cm^3, respectively. Nevadaite is biaxial negative, with α 1.540, β 1.548, γ 1.553, $2V$(obs.) = 76°, $2V$(calc.) = 76°, pleochroic with X pale greenish blue, Y very pale greenish blue, Z blue, and with absorption $Z >> X > Y$ and orientation $X = c$, $Y = a$, $Z = b$. Nevadaite is orthorhombic, space group $P2_1mn$, a 12.123(2), b 18.999(2), c 4.961(1) Å , V 1142.8(2) Å ^{3}, $Z = 1$, $a:b:c$ = 0.6391:1:0.2611. The strongest seven lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are: 6.077(10)(200), 5.618(9)(130), 9.535(8)(020), 2.983(6)(241), 3.430(4)(041), 2.661(4)(061), and 1.844(4)(352). A chemical analysis with an electron microprobe gave P_2O_5 32.54, Al_2O_3 27.07, V_2O_3 4.24, Fe_2O_3 0.07, CuO 9.24, ZnO 0.11, F 9.22, H_2O (calc.) 23.48, OH ≡ F –3.88, sum 102.09 wt.%; the valence states of V and Fe, and the amount of H_2O, were determined by crystal-structure analysis. The resulting empirical formula on the basis of 63.65 anions (including 21.65 H_2O *pfu*) is $(Cu^{2+}_{2.00}$ $Zn_{0.02}$ $V^{3+}_{0.98}$ $Fe^{3+}_{0.01}$ $Al_{1.15})_{\Sigma 4.16}$ Al_8 $P_{7.90}$ O_{32} $[F_{8.37}$ $(OH)_{1.63}]_{\Sigma 10}$ $(H_2O)_{21.65}$. The crystal structure of nevadaite was solved by direct methods and refined to an R index of 4.0% based on 1307 observed reflections collected on a four-circle diffractometer with Mo$K\alpha$ X-radiation. The structure consists of ordered layers of vertex-sharing octahedra and tetrahedra alternating with layers of disordered vertex-sharing and face-sharing octahedra in the b direction. $[Al\phi_5]$ chains of octahedra are decorated by (PO_4) tetrahedra that share vertices with octahedra adjacent in the chain. These chains link in the c direction by sharing vertices between octahedra and tetrahedra to form an ordered layer of the form $[Al_8(PO_4)_8F_8(H_2O)_8]$. In the disordered layer, octahedra

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containing positionally disordered Cu^{2+}, V^{3+}, Al and □ (vacancy) share *trans* faces to form columns that link by sharing octahedron vertices to form ribbons extending in the *c* direction; the resulting layer has the form $\{(Cu^{2+}{}_2\square_2V^{3+},Al)_{\Sigma 6}\,(H_2O)_{12}\,(OH)_2\,(H_2O)_x\}$, $x \approx 2$. The layers link in the *b* direction by sharing vertices between octahedra and tetrahedra. Although decorated chains topologically equivalent to that in nevadaite are common in many oxysalt minerals, its chain is geometrically distinct from those topologically equivalent chains. The *M–M* linkage along the $[M\phi_5]$ chains in most minerals take place through *trans* vertices of the octahedra, with one example of linkage through *cis* vertices; in nevadaite, the *M–M* linkage involves both *trans* and *cis* vertices, as does the chain in slavíkite. In most of these decorated chains, alternate tetrahedra along the chain occur either in a *trans* or a *cis* arrangement. In nevadaite and slavíkite, the tetrahedra are arranged in both *trans* and *cis* arrangements; the arrangements in these two minerals are geometrically distinct, however.

Keywords: nevadaite, new mineral species, phosphate, Gold Quarry mine, Nevada, crystal structure, $[M\phi_5]$ chains, geometrical isomerism.

SOMMAIRE

La névadaïte, $(Cu^{2+}, \square, Al, V^{3+})_6\,(PO_4)_8\,F_8\,(OH)_2\,(H_2O)_{22}$, est une nouvelle espèce minérale d'origine épigénétique découverte à la mine Gold Quarry, près de Carlin, comté d'Eureka, Nevada, aux Etats-Unis. Elle forme des groupements radiaires de cristaux prismatiques de 1 mm, couvrant ici et là des surfaces atteignant 2 cm; les cristaux individuels sont allongés sur [001], avec un rapport longueur à largeur dépassant 10:1 et un diamètre maximum d'environ 30 μm. Elle se présente aussi en sphérules et dans des cavités, associée à la fluellite allant d'incolore à violette ou noire, la wavellite incolore, strengite–variscite, hewettite aciculaire maron à rouge et, plus rarement, anatase, kazakhstanite, tinticite, leucophosphite, torbernite et tyuyamunite. Il s'agit d'un minéral vert pâle à bleu turquoise, à la rayure bleu poudre pâle et un éclat vitreux; il n'y a aucune fluorescence en lumière ultra-violette. La névadaïte est sans clivage; la dureté de Mohs est environ 3. Elle est cassante avec une fracture conchoïdale, et la densité mesurée et calculée est de 2.54 et 2.55 g/cm³, respectivement. Elle est biaxe négative, avec α 1.540, β 1.548, γ 1.553, 2*V*(obs.) = 76°, 2*V*(calc.) = 76°, pléochroïque, avec *X* bleu verdâtre pâle, *Y* bleu verdâtre très pâle, et *Z* bleu, et avec une absorption $Z >> X > Y$ et orientation $X = c$, $Y = a$, $Z = b$. La névadaïte est orthorhombique, groupe spatial $P2_1mn$, *a* 12.123(2), *b* 18.999(2), *c* 4.961(1) Å , *V* 1142.8(2) Å³, $Z = 1$, $a:b:c = 0.6391:1:0.2611$. Les sept raies les plus intenses du spectre de diffraction X (méthode des poudres) [*d* en Å(I)(*hkl*)] sont: 6.077(10)(200), 5.618(9)(130), 9.535(8)(020), 2.983(6)(241), 3.430(4)(041), 2.661(4)(061), et 1.844(4)(352). Une analyse chimique avec une microsonde électronique a donné P_2O_5 32.54, Al_2O_3 27.07, V_2O_3 4.24, Fe_2O_3 0.07, CuO 9.24, ZnO 0.11, F 9.22, H_2O (calc.) 23.48, OH ≡ F –3.88, somme 102.09% (poids); les valences du V et du Fe, et la quantité de H_2O, ont été déterminées par analyse de la structure cristalline. Il en résulte la formule empirique suivante, sur une base de 63.65 anions (y inclus 21.65 H_2O *pfu*): $(Cu^{2+}{}_{2.00}\,Zn_{0.02}\,V^{3+}{}_{0.98}\,Fe^{3+}{}_{0.01}\,Al_{1.15})_{\Sigma 4.16}\,Al_8\,P_{7.90}\,O_{32}\,[F_{8.37}\,(OH)_{1.63}]_{\Sigma 10}\,(H_2O)_{21.65}$. La structure de la névadaïte a été résolue par méthodes directes et affinée jusqu'à un résidu *R* de 4.0% sur une base de 1307 réflexions observées, prélevées avec un diffractomètre à quatre cercles et un rayonnement Mo*K*α. La structure est faite de feuillets ordonnés d'octaèdres et de tétraèdres à coins partagés en alternance avec des couches plutôt désordonnées d'octaèdres partageant coins et arêtes le long de *b*. Les chaînes d'octaèdres $[Al\phi_5]$ sont décorées avec des tétraèdres (PO_4) partageant des coins avec des octaèdres de la chaîne adjacente. Ces chaînes sont liées le long de *c* par partage de coins entre octaèdres et tétraèdres pour former une couche ordonnée de la forme $[Al_8(PO_4)_8F_8(H_2O)_8]$. Dans la couche désordonnée, les octaèdres contenant les cations Cu^{2+}, V^{3+}, Al et □ ont une position désordonnée, et partagent des faces en position *trans* pour former des colonnes liées par partage de coins d'octaèdres ce qui donne des rubans le long de *c*; la couche qui en résulte possède la forme $\{(Cu^{2+}{}_2\square_2V^{3+},Al)_{\Sigma 6}\,(H_2O)_{12}\,(OH)_2\,(H_2O)_x\}$, $x \approx 2$. Les feuillets sont connectés dans la direction *b* par partage de coins entre octaèdres et tétraèdres. Quoique de telles chaînes décorées topologiquement équivalentes sont répandues dans plusieurs minéraux oxysels, la chaîne dans la névadaïte est géométriquement distincte. L'agencement *M–M* le long des chaînes $[M\phi_5]$ dans la plupart des minéraux impliquent les coins des octaèdres en position *trans*, avec un exemple connu de couplage par les coins *cis*; dans la névadaïte, le couplage *M–M* implique à la fois des coins *trans* et *cis*, tout comme dans la slavíkite. Dans la plupart de ces chaînes décorées, les tétraèdres en alternance le long de la chaîne sont disposés en position *trans* ou *cis*. Dans la névadaïte et la slavíkite, les tétraèdres sont disposés en position *trans* et *cis*; les dispositions dans ces deux minéraux sont géométriquement distincts, toutefois.

(Traduit par la Rédaction)

Mots-clés: névadaïte, nouvelle espèce minérale, phosphate, mine Gold Quarry, Nevada, structure cristalline, chaînes $[M\phi_5]$, isomérisme géométrique.

INTRODUCTION

In a detailed description of the mineralogy of the Gold Quarry mine, Carlin Trend, Eureka County, Nevada, Jensen *et al.* (1995) reported two unknown minerals, both of which are transition-metal phosphates. Unknown #1 is a (Cu,Al,V,Fe)-bearing phosphate, and unknown #2 is goldquarryite (Roberts *et al.* 2003). Solution of the crystal structure of unknown #1 complemented the data reported by Jensen *et al.* (1995), resulting in approval of the new mineral by the Commission on New Minerals and Mineral Names, International Mineralogical Association (IMA 2002–35). The mineral is named *nevadaite* after the state in which it occurs. The holotype specimen of nevadaite is stored in the Systematic Reference Series of the National Mineral Collection of Canada at the Geological Survey of Canada, catalogue #NMCC68091.

OCCURRENCE

Nevadaite was found by MCJ during the period February, 1992, through January, 1993, on the 5425 (elevation in feet) through 5375 benches of the Gold Quarry open-pit mine near Carlin, Eureka County, Nevada. This deposit and its mineralogy have been described in detail by Jensen *et al.* (1995), and nevadaite is referred to as unknown #1 in that report. The Gold Quarry mine, operated by Newmont Mining Corporation, exploits one of the largest gold deposits occurring along the well-known Carlin-trend gold belt in northeastern Nevada. These deposits are typified by large volumes of hydrothermally altered sedimentary rocks containing low-grade micrometer-size (disseminated) gold. Mining began at Gold Quarry in 1985, and, at the present daily rate of about 250,000 metric tonnes, should continue for at least another ten years.

A large suite of phosphate, vanadate, arsenate, and uranate minerals occur in the upper supergene zone of the deposit and have provided nevadaite and goldquarryite (Roberts *et al.* 2003) as mineral species new to Science. Mining has exposed brecciated and silicified silty carbonate rocks (jasperoid) of the Devonian Rodeo Creek unit; these rocks contain an abundance of mineral species deposited on fractures and in open spaces.

Nevadaite was first recognized on the 5425 bench as rare, pale green to turquoise-blue spherules and druses associated with black crystals of fluellite and colorless crystals of wavellite. As mining continued, richer and more prolific examples were encountered, especially at the 5375 level. Here, radiating clusters to 1.0 mm of prismatic, turquoise-blue crystals were found, locally covering surfaces more than 2 cm across. Associated minerals were abundant, most commonly consisting of intermediate members of the strengite–variscite series, colorless to purple fluellite, and maroon to red acicular hewettite; rarer species included anatase, kazakhstanite, leucophosphite, tinticite, torbernite, and tyuyamunite.

PHYSICAL PROPERTIES

Nevadaite consists of radiating clusters (to 1 mm) of turquoise-blue prismatic crystals, locally covering surfaces more than 2 mm across, and as pale green to turquoise-blue spherules and druses associated with black fluellite and colorless wavellite. Individual crystals are elongate along the *c* direction, with a length:width ratio exceeding 10:1 and a maximum diameter of 30 μm. The streak is pale powder-blue, and the luster is vitreous. No cleavage, parting or twinning was observed; nevadaite is brittle with a conchoidal fracture. The Mohs hardness is ~3. The measured density (by suspension in a bromoform–acetone mixture) is 2.54 g/cm^3; the calculated density is 2.55 g/cm^3. Optical properties were measured with the Bloss spindle stage for the wavelength 590 nm using a gel filter. The indices of refraction are α 1.540, β 1.548, γ 1.553, the calculated birefringence γ–α is 0.013, (+)2*V* (meas.) 76°, 2*V* (calc.) 76°; orientation $X = c$, $Y = a$, $Z = b$; the Gladstone–Dale compatibility index is 0.008 (superior). Pleochroism is moderate with *X* pale greenish blue, *Y* very pale greenish blue, and *Z* blue, absorption $Z >> X > Y$.

CHEMICAL COMPOSITION

Crystals were analyzed with a Cameca SX–50 electron microprobe operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 10 μm. The following standards were used: VP_2O_7 (V), mariĉite (P), brazilianite (Al), fayalite (Fe), cuprite (Cu), fluorite (F), gahnite (Zn). The data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1984, 1985).

The presence and quantity of (OH) and (H_2O) groups were established by crystal-structure solution and refinement. In addition, infrared spectroscopy indicated a broad intense band at 3359 cm^{-1} and a sharper band at 1630 cm^{-1}, indicative of H_2O, together with a shoulder at 3539 cm^{-1}, which is conformable with the presence of OH. Table 1 gives the chemical composition (mean of two determinations) and formula unit based on 63.65 anions (including 21.65 H_2O groups) *pfu* (per formula unit). The excess of wt.% total over 100 is probably caused by slight dehydration of the mineral during electron-microprobe analysis, which would increase the percentages of non-H_2O components.

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND EMPIRICAL FORMULA (*apfu*) FOR NEVADAITE

P_2O_5	32.54	P	7.90
Al_2O_3	27.07		
V_2O_3	4.24	Al	8.00
Fe_2O_3	0.07		
CuO	9.24	Cu^{2+}	2.00
ZnO	0.11	V^{3+}	0.98
F	9.22	Zn	0.02
H_2O*	(23.48)	Fe^{3+}	0.01
O ≡ F	−3.88	Al	1.15
TOTAL	102.09	Σ	4.16
		F	8.37
		OH	1.63
		Σ	10.00
		H_2O	21.65

* calculated from the crystal structure

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR NEVADAITE

	$I_{obs.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	h	k	l		$I_{obs.}$	$d_{meas.}$ (Å)	$d_{calc.}$ (Å)	h	k	l
	5	10.193	10.213	1	1	0	*	15	2.163	2.163	5	1	1
	80	9.535	9.481	0	2	0	*	10	2.098	2.098	3	1	2
	100	6.077	6.061	2	0	0		3	2.065	2.063	2	4	2
	90	5.618	5.604	1	3	0		5	2.044	2.043	5	5	0
	5	4.962	4.951	0	0	1		3	2.016	2.020	6	0	0
	10	4.751	4.740	0	4	0		"	"	2.016	2	8	1
	20	4.587	4.583	1	0	1	*	10	1.976	1.976	6	2	0
	5	4.423	4.389	0	2	1	*	15	1.950	1.949	0	6	2
	5	4.123	4.126	1	2	1	*	20	1.917	1.914	1	9	1
*	30	3.956	3.952	3	1	0		5	1.889	1.890	3	8	1
*	20	3.838	3.834	2	0	1	*	40	1.844	1.844	3	5	2
	10b	3.750	3.758	2	1	1		20	1.810	1.810	2	10	0
	"	"	3.734	2	4	0		"	"	1.807	1	7	2
	"	"	3.711	1	3	1		3	1.792	1.794	6	3	1
*	15	3.551	3.555	2	2	1		"	"	1.793	5	6	1
*	40	3.430	3.424	0	4	1	*	40	1.740	1.740	6	4	1
	5	3.287	3.278	2	3	1		5b	1.713	1.712	0	8	2
*	15	3.159	3.160	0	6	0		3	1.700	1.702	6	6	0
	3	3.089	3.089	3	1	1		"	"	1.700	2	10	1
*	10	3.033	3.031	4	0	0		"	"	1.697	5	7	1
*	60	2.983	2.981	2	4	1		5	1.665	1.665	3	7	2
	5	2.933	2.922	1	5	1		3b	1.629	1.627	5	4	2
*	20	2.882	2.887	4	2	0	*	15	1.610	1.610	6	6	1
	35	2.805	2.805	3	3	1		20	1.585	1.586	3	11	0
	"	"	2.802	2	6	0		"	"	1.580	0	12	0
*	40	2.661	2.664	0	6	1		20	1.561	1.565	6	0	2
*	20	2.583	2.585	4	0	1		"	"	1.559	0	4	3
	5	2.555	2.553	4	4	0		3	1.527	1.529	2	12	0
*	20	2.476	2.476	0	0	2		"	"	1.523	3	1	3
*	10	2.412	2.414	3	5	1		35	1.508	1.510	2	4	3
*	10	2.374	2.376	0	7	1		"	"	1.505	0	10	2
	3	2.341	2.332	1	7	1	*	15	1.491	1.491	4	8	2
	3	2.301	2.305	0	3	2	*	20	1.460	1.461	2	10	2
	3	2.246	2.250	3	7	0		5	1.399	1.399	7	7	1
	3	2.216	2.212	2	7	1		30	1.384	1.384	7	3	2
	3	2.189	2.194	0	4	2		"	"	1.383	6	10	0
	3	"	2.187	4	6	0							

114.6 mm Debye-Scherrer powder camera, Cu radiation, Ni-filter (λCu$K\alpha$ = 1.54178 Å);
intensities estimated visually, b = broad line; not corrected for shrinkage and no internal standard;
* = reflections used for unit-cell refinement; indexed with a 12.122(4), b 18.961(8), c 4.951(2) Å.

TABLE 3. MISCELLANEOUS INFORMATION CONCERNING THE SOLUTION AND REFINEMENT OF THE CRYSTAL STRUCTURE OF NEVADAITE

a (Å)	12.123(1)	crystal size (μm)	20 x 32 x 104
b	18.999(2)	radiation	Mo$K\alpha$
c	4.9613(5)	No. of reflections	2089
V (Å^3)	1142.8(2)	No. $\lvert F_o \rvert > 5\sigma F$	1307
Space Group	$P2_1mn$	R (%)	4.0
Z	1	wR (%)	4.5

$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert) / \Sigma\lvert F_o\rvert$

$wR = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma F_o^2]^{1/2}$, $w = 1$

X-Ray Powder Diffraction

The powder-diffraction pattern was recorded with Ni-filtered Cu$K\alpha$ X-radiation (λ = 1.54178 Å) and a 114.6 mm Debye–Scherrer powder camera. Table 2 shows the X-ray powder-diffraction data for nevadaite, together with the refined unit-cell dimensions. Unit-cell dimensions were also determined on a Bruker diffractometer using graphite-monochromated Mo$K\alpha$ X-radiation: a 12.123(2), b 18.999(2), c 4.961(1) Å , V 1142.8(2) Å ^{3}, and a:b:c = 0.6381:1:0.2611.

Crystal-Structure Solution and Refinement

A crystal was attached to a glass fiber and mounted on a Bruker $P4$ diffractometer equipped with a serial detector and a Mo$K\alpha$ X-ray tube. A total of 2089 reflections was measured out to 50° 2θ with index ranges $\overline{14} \le h \le 14$, $0 \le k \le 22$, $0 \le l \le 5$ and a fixed scan-speed of 0.60° 2θ/min. Of the 2089 unique reflections, 1307 reflections were considered as observed [$\lvert F_o\rvert \ge 5\sigma F$]. Absorption corrections were done by the Gaussian method. The data were then corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. After data collection, the crystal used for X-ray diffraction was attached to the surface of a Perspex disc, polished, carbon-coated and analyzed with a Cameca SX–50 electron microprobe as described above.

All calculations were done with the SHELXTL PC (Plus) system of programs; R indices are of the form given in Table 3 and are expressed as percentages. Systematic absences in the single-crystal X-ray-diffraction data are consistent with general diffraction-symmetry $P{*}{*}n$, and the structure was originally solved in $Pmmn$. This refinement model (R = 5.6%) consisted of an ordered Al–(PO_4)–F layer and a disordered Cu–V–Al–(H_2O) layer. The chemical data (Table 1) indicate a fairly simple stoichiometry for the (Cu, V, Al) content of the disordered layer (*i.e.*, ~ 2:1:1), and we were able to successfully refine (R = 4.0%) a partly ordered model in $P2_1mn$. Because the Al–(PO_4)–F layer is conformable with $Pmmn$ symmetry, refinement in $P2_1mn$ was unstable because of highly correlated position and displacement parameters. We managed to attain satisfactory convergence by constraining the anisotropic-displacement parameters for the pseudosymmetric sites to be the same. The coupled sites from the Al–(PO_4)–F component are as follows: P(1)–P(2), F(1)–F(2), O(1)–O(5), O(2)–O(6), O(3)–O(7), O(4)–O(8) and O(9)–O(10). In addition, displacement parameters for the O(11)–O(12), O(15)–O(16) and O(17)–O(18) pairs were also coupled. The O(15)–O(16) and O(17)–O(18) pairs represent two positionally disordered (H_2O) groups. The O(15) and O(16) anions bond to the M(3) cation, whereas the O(17) and O(18) anions are not bonded to any cations. We constrained the z coordinates of the O(15) and O(16) sites to be equal, and allowed

TABLE 4. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR NEVADAITE

Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M(1)	0.5774(9)	1/2	0.2888(16)	0.033(2)	0.055(5)	0.011(3)	0.032(5)	0	0.015(5)	0
M(2)	0.5934(9)	1/2	0.7206(10)	0.0288(18)	0.057(4)	0.004(2)	0.025(3)	0	–0.027(3)	0
M(3)	0.4258(8)	0	0.7098(9)	0.0082(13)	0.015(2)	0.005(2)	0.004(2)	0	0.006(3)	0
Al(1)	1/2	0.2502(5)	–0.0017(13)	0.0074(5)	0.0086(10)	0.0074(9)	0.0063(9)	0.0000(9)	0.0000(10)	0.0003(7)
Al(2)	0.749(1)	0.19131(11)	0.2619(5)	0.0097(6)	0.0069(10)	0.0139(10)	0.0084(11)	0.0034(9)	–0.001(4)	0.001(2)
P(1)	0.5192(8)	0.1467(3)	0.4955(8)	0.0088(3)	0.0099(5)	0.0084(6)	0.0082(6)	0.0011(6)	0.0012(7)	–0.0004(5)
P(2)	0.4817(8)	0.3545(3)	0.4960(8)	0.0088(3)	0.0099(5)	0.0084(6)	0.0082(6)	0.0011(6)	0.0012(7)	–0.0004(5)
F(1)	0.6464(11)	0.2346(6)	0.051(2)	0.0133(9)	0.0106(14)	0.0166(15)	0.013(2)	0.0037(13)	0.003(5)	–0.004(4)
F(2)	0.8512(11)	0.2360(6)	0.059(2)	0.0133(9)	0.0106(14)	0.0166(15)	0.013(2)	0.0037(13)	0.003(5)	–0.004(4)
O(1)	0.6451(12)	0.1448(7)	0.450(3)	0.0163(12)	0.0086(16)	0.020(2)	0.021(2)	0.009(2)	0.0030(16)	–0.0005(16)
O(2)	0.4753(15)	0.0709(7)	0.456(2)	0.0163(12)	0.028(2)	0.0102(17)	0.010(2)	–0.0002(18)	–0.001(2)	–0.0065(16)
O(3)	0.4591(11)	0.1961(5)	0.291(2)	0.0093(10)	0.0109(17)	0.0101(16)	0.007(2)	0.0043(15)	0.0012(15)	0.0031(14)
O(4)	0.4910(11)	0.1700(5)	0.788(3)	0.0116(10)	0.0157(18)	0.0101(17)	0.0089(16)	–0.0021(15)	0.0028(15)	–0.0026(14)
O(5)	0.3570(12)	0.3497(7)	0.533(3)	0.0163(12)	0.0086(16)	0.020(2)	0.021(2)	0.009(2)	0.0030(16)	–0.0005(16)
O(6)	0.5217(14)	0.4295(7)	0.524(2)	0.0163(12)	0.028(2)	0.0102(17)	0.010(2)	–0.0002(18)	–0.001(2)	–0.0065(16)
O(7)	0.5378(12)	0.3062(5)	0.697(2)	0.0093(10)	0.0109(17)	0.0101(16)	0.007(2)	0.0043(15)	0.0012(15)	0.0031(14)
O(8)	0.5092(11)	0.3322(5)	0.212(3)	0.0116(10)	0.0157(18)	0.0101(17)	0.0089(16)	–0.0021(15)	0.0028(15)	–0.0026(14)
O(9)	0.7496(17)	0.2736(3)	0.4979(12)	0.0175(11)	0.015(2)	0.0193(17)	0.0181(18)	–0.005(2)	0.003(4)	–0.006(5)
O(10)	0.7582(13)	0.1156(3)	–0.0122(13)	0.0175(11)	0.015(2)	0.0193(17)	0.0181(18)	–0.005(2)	0.003(4)	–0.006(5)
O(11)	0.6449(14)	0.4244(8)	0.009(2)	0.0277(18)	0.027(3)	0.013(3)	0.042(3)	0.000(3)	–0.001(3)	0.003(2)
O(12)	0.3690(14)	0.0663(8)	0.975(2)	0.0277(18)	0.027(3)	0.013(3)	0.042(3)	0.000(3)	–0.001(3)	0.003(2)
O(13)	0.404(3)	1/2	0.008(5)	0.109(12)	0.08(2)	0.084(16)	0.16(3)	0	0.001(17)	0
O(14)	0.7225(12)	1/2	0.528(3)	0.039(5)	0.044(10)	0.025(5)	0.049(8)	0	–0.005(7)	0
O(15)	0.597(3)	0	0.998(3)	0.022(5)						
O(16)	0.546(4)	0	0.998(3)	0.022(5)						
O(17)	0.705(6)	0	0.635(18)	0.075(12)						
O(18)	0.768(4)	0	0.460(7)	0.075(12)						

their site occupancies to refine with the sum constrained to unity. Coordinates and occupancies were refined independently for the O(17) and O(18) sites. Refined coordinates and displacement factors are listed in Table 4, selected interatomic distances are given in Table 5, and site-scattering values and assigned site-populations are given in Table 6, and bond valences are given in Table 7. Observed and calculated structure-factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

CRYSTAL STRUCTURE

Coordination of cations

There are two P sites completely occupied by P; these sites are coordinated by tetrahedral arrays of anions with <P–O> distances of 1.52 and 1.55 Å , close to the grand <P–O> distance for phosphate minerals of 1.537 Å (Huminicki & Hawthorne 2002). There are two Al sites, each of which is coordinated by an octahedral array of four O atoms and two F atoms. The <Al–O,F> distances are 1.86 and 1.87 Å , consistent with complete occupancy of each of these sites by Al.

M-site assignments

From the results of the chemical analysis (Table 1), there are approximately four cations (Cu^{2+}_2, Al, V^{3+}) to assign to three sites [M(1), M(2), M(3)]. All three M-sites are located at Wyckoff *2a* sites, so there must be a total of two vacancies in addition to the four cations *pfu* occupying these sites. The associated scattering (2Cu + Al + V = 94 *epfu*, electrons per formula unit) is in good agreement with the total observed scattering (91.6 *e*) at the three M-sites (Table 6). We are therefore presented with a reasonable opportunity to assign Cu, V and Al to the three M-sites on an electron-counting basis, keeping in mind that Cu and V have similar scattering, and that their assignment will be less accurate. The M(1) and M(2) sites are coordinated by octahedra that share faces along the *c* axis. The distances between the M(1) and M(2) sites along the *c* axis result in close approaches (2.15 Å) between adjacent sites. Therefore, only locally alternate M(1)–M(2) sites may be simultaneously occupied [M(1)–M(2) = 2.83Å], resulting in a maximum possible occupancy of two atoms per formula unit (*apfu*) for the combined M(1) and M(2) sites. The refined scattering at the M(1) and M(2) sites, 28.1 and 26.1 *e*, respectively, are very similar, and the only pattern of order possible that avoids unreasonably short approaches between *M*(1) and *M*(2) sites involves 1 *apfu* at each of the *M*(1) and *M*(2) sites. As there are four cations to assign, the *M*(3) site must therefore be fully occupied (2 *apfu*). Let us first examine the scattering at *M*(3); the lowest possible scattering assigned to *M*(3) would result from $Al_{1.0} + V_{1.0} = 36$ *e*, and the observed scattering is only marginally greater at 37.4 *e* (Table 6). We can therefore confidently assign all available Al to *M*(3), as any significant reduction in Al at *M*(3) (while maintaining full occupancy), would cause an increase in the number of assigned electrons above that observed. The scattering at *M*(1), 28.1 *e*, is close to the scattering value for Cu, and hence we have assigned $Cu_{1.0}$ to this site. The scattering at *M*(2) is intermediate between Cu and V at 26.1 *e*. Thus we then modified the Cu:V ratios at *M*(2) and *M*(3) so as to minimize the differences between assigned and refined scattering values at these sites (Table 6).

Anion identity: the O sites

There are eight sites [O(1)–O(8)] that are occupied by O^{2-} anions that bond to the two *P*-sites. Six of these O sites link to one *P* and one *Al*, and have incident bond-valences from 1.75 to 1.90 *vu* (valence units) (Table 7). The O(2) site links to *P*(1) and the fully occupied *M*(3) site, and has an incident bond-valence sum of 1.70 *vu*. The O(6) site links to *P*(2) and also to either *M*(1) or *M*(2), and has a corresponding bond-valence sum of either 1.89 or 1.98 *vu*. Thus several of these O sites are probable hydrogen-bond acceptors.

Anion identity: the F sites

The F(1) and F(2) sites link to *Al*(1) and *Al*(2), respectively, and have incident bond-valence sums of 0.96 and 0.93 *vu*, respectively. The F(1) and F(2) sites also have greater scattering relative to the O sites, consistent with their occupancy by F. In addition, the F content established by chemical analysis (Table 1) also supports occupancy of F(1) and F(2) by a total of eight F *apfu*.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) IN NEVADAITE

M(1)–O(6),e	1.901(15)	x2	*Al*(1)–F(1)	1.818(13)
M(1)–O(11),e	2.157(15)	x2	*Al*(1)–F(2)a	1.845(13)
M(1)–O(14)	2.120(17)		*Al*(1)–O(3)	1.847(13)
<$^{[5]}$*M*(1)–O>	2.047		*Al*(1)–O(4)c	1.851(13)
			Al(1)– O(7)c	1.891(13)
M(1)–O(13)	2.52(3)		*Al*(1)–O(8)	1.887(13)
			<*Al*(1)–ϕ>	1.857
M(2)–O(6),e	1.871(15)	x2		
M(2)–O(11)f,g	2.122(14)	x2	*Al*(2)–F(1)	1.821(15)
M(2)–O(14)	1.833(17)		*Al*(2)–F(2)	1.810(15)
<$^{[5]}$*M*(2)–O>	1.964		*Al*(2)–O(1)	1.799(16)
			Al(2)–O(5)d	1.834(16)
M(2)–O(13)f	2.71(3)		*Al*(2)–O(9)	1.953(6)
			Al(2)–O(10)	1.982(6)
M(3)–O(2),b	1.941(13)	x2	<*Al*(2)–ϕ>	1.867
M(3)–O(12),b	1.948(15)	x2		
M(3)–O(15)	2.52(3) *			
M(3)–O(16)	*2.04(3)* *			
<$^{[5]}$*M*(3)–O>	2.06 *1.96*			
M(3)–O(14)h	2.732(16)			
P(1)–O(1)	1.543(18)		*P*(2)–O(5)	1.526(17)
P(1)–O(2)	1.548(15)		*P*(2)–O(6)	1.512(15)
P(1)–O(3)	1.563(13)		*P*(2)–O(7)	1.516(13)
P(1)–O(4)	1.556(13)		*P*(2)–O(8)	1.508(13)
<*P*(1)–O>	1.553		<*P*(2)–O>	1.516

a: $x-½, \bar{y}+½, \bar{z}$; b: $x, \bar{y}, z$; c: $x, y, z-1$; d: $x+½, \bar{y}+½, \bar{z}+1$; e: $x, \bar{y}+1, z$; f: $x, y, z+1$; g: $x, \bar{y}+1, z+1$; h: $x-½, y-½, \bar{z}+1$.

* *M*(3) bonds either to O(15) or to O(16) (bond lengths in italics)

TABLE 6. *M*-SITE ASSIGNMENTS IN NEVADAITE

Site	Cu	V	Al	□	Assigned scattering	Refined scattering
M(1)	1			1	29.0	28.1(7)
M(2)	0.6	0.4		1	26.6	26.1(6)
M(3)	0.4	0.6	1		38.4	37.4(6)
Σ					94.0	91.6

TABLE 7. BOND-VALENCE* TABLE FOR NEVADAITE

	P(1)	*P*(2)	*Al*(1)	*Al*(2)	*M*(1)	*M*(2)	*M*(3)**	Σ	
F(1)			0.48	0.48				0.96	
F(2)			0.44	0.49				0.93	
O(1)	1.23			0.67				1.90	
O(2)	1.20						$0.50^{x2}\downarrow$	1.70	
O(3)	1.17		0.58					1.75	
O(4)	1.17		0.58					1.75	
O(5)		1.27		0.62				1.89	
O(6)**		1.34			$0.55^{x2}\downarrow$	*0.64*$^{x2}\downarrow$		1.89	*1.98*
O(7)		1.30	0.52					1.82	
O(8)		1.34	0.52					1.86	
O(9)				0.45				0.45	
O(10)				0.41				0.41	
O(11)					$0.27^{x2}\downarrow$	$0.33^{x2}\downarrow$		0.60	
O(12)							$0.49^{x2}\downarrow$	0.49	
O(13)					0.10	0.07		0.17	
O(14)**					0.30	*0.72*	0.06	0.36	*0.78*
O(15)							0.11	0.11	
O(16)							*0.38*	*0.38*	
O(17)									
O(18)									
Σ	4.77	5.25	3.12	3.12	2.04	2.73	2.15 *2.42*		

* curves (*vu*) from Brown & Altermatt (1985)

** *M*(3) bonds either to O(15) or O(16); O(6) bonds either to *M*(1) or *M*(2); O(14) bonds either to *M*(1) or *M*(2).

Anion identity: the (H_2O) sites

The O(9) and O(10) sites link only to Al at the *Al*(2) site and are therefore (H_2O) groups. The O(13) anion is weakly bonded to *M*(1) and *M*(2), and also must be an (H_2O) group. The O(15) and O(16) sites are 0.62(6) Å apart and represent a split (H_2O) site linked only to the cation at *M*(3). The O(17) and O(18) sites are also a split (H_2O) group with a separation of 1.15(9) Å; they are not linked to any cation.

Anion identity: the (OH) sites

The remaining anions, O(11), O(12) and O(14), form shorter bonds than the (H_2O) groups to the cations at the *M* sites (Table 5), and will therefore have greater incident bond-valences (Table 7), depending upon the specific local order of Cu^{2+}, V^{3+} and Al. It is clear from the chemical data (Table 1) that there must be two (OH, F) groups present to achieve electroneutrality. The O(11), O(12) and O(14) sites constitute 10 sites *pfu*, and thus must be occupied by $(H_2O)_8 + (OH,F)_2$.

Structure topology

Nevadaite is a heteropolyhedral framework structure, but has prominent ordered and disordered layers alternating along the *b* direction, and will be described on that basis.

The ordered layer: $\{Al(1)\phi_6\}$ octahedra are linked by pairs of (PO_4) tetrahedra to form a brandtite-like $[M(TO_4)_2\phi_2]$ chain that extends in the *c* direction (Fig. 1). The repeat distance along this chain is ~5 Å and defines the *c* dimension of the nevadaite structure. These chains are cross-linked in the *a* direction by sharing both octahedron and tetrahedron vertices with $\{Al(2)\phi_6\}$ octahedra. The latter are four-connected to the chains, and the remaining anions, bonded only to one Al atom, are (H_2O) groups, to give a sheet of general stoichiometry $[M_8\ (TO_4)_8\ \phi_{16}]$ and specific formula $[Al_8\ (PO_4)_8\ F_8\ (H_2O)_8]$ (Fig. 1). Alternatively, one may describe the sheet in terms of $[M\phi_5]$ chains. Both $Al\phi_6$ [ϕ: O^{2-}, F, (H_2O)] octahedra share one set of vertices to form an $[M\phi_5]$ chain that extends in the *a* direction. This chain is decorated by (PO_4) tetrahedra that bridge *vertices*

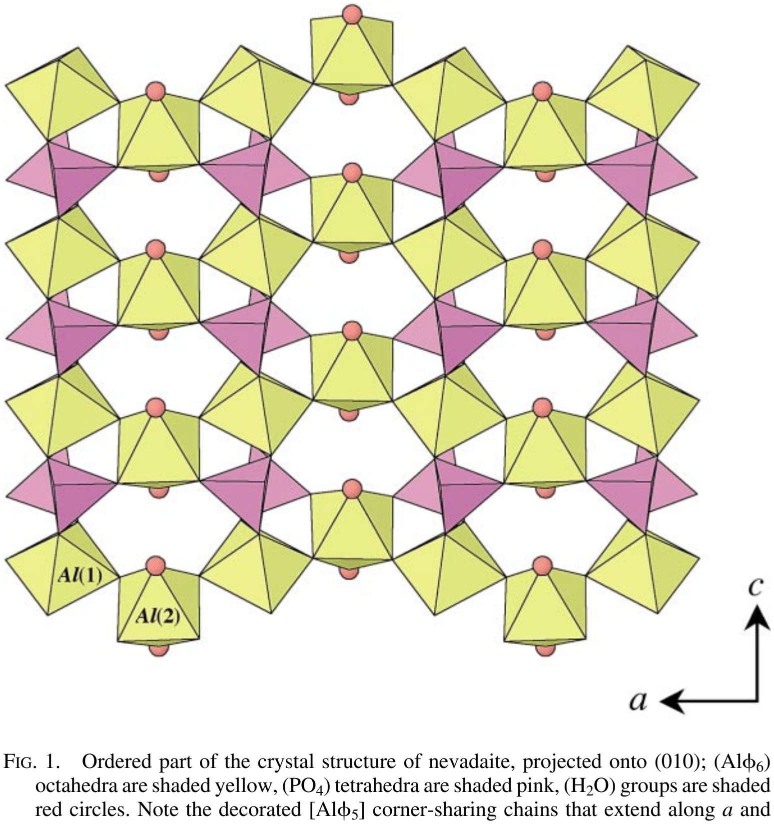

FIG. 1. Ordered part of the crystal structure of nevadaite, projected onto (010); ($Al\phi_6$) octahedra are shaded yellow, (PO_4) tetrahedra are shaded pink, (H_2O) groups are shaded red circles. Note the decorated $[Al\phi_5]$ corner-sharing chains that extend along *a* and link by sharing octahedron–tetrahedron vertices along *c*.

from adjacent octahedra to form a chain of general stoichiometry [M (TO_4) ϕ_3] (Fig. 1). Chains of this topology have been called the 7 Å chains (Moore 1970) because the repeat distance of the chain (and the unit cell in the chain direction) is a multiple of ~7 Å . However, the cell dimension defined by the [$M\phi_5$] chain is significantly shorter than ~7n Å in nevadaite as a result of a novel geometrical feature of the chain. Most [$M\phi_5$] chains link through *trans* vertices of their component octahedra. However, inspection of Figure 1 shows that the {$Al(1)\phi_6$} octahedron links to the {$Al(2)\phi_6$} octahedron by *trans* vertices, the {$Al(2)\phi_6$} octahedron links to the {$Al(1)\phi_6$} octahedron by *cis* vertices. As the *cis* vertices of an octahedron are much closer together than the *trans* vertices, this linkage has the effect of shortening the repeat distance of the [$M\phi_5$] chain. The mean repeat distance of an [$M\phi_5$] chain is 7.1 Å (Moore 1970). If one of the (two) linkages in the repeat distance along the chain is *cis* instead of *trans*, this reduces the repeat length to $7.1 / 2 + 7.1 / 2\sqrt{2} = 6.06$ Å ; twice this length (doubling due to the decorating tetrahedra) is 12.12 Å, which is the a dimension of nevadaite.

The disordered layer: The disordered layer is shown in Figure 2, with the (PO_4) linkages from the ordered [Al–(PO_4)–F (H_2O)] sheet shown above and below. The $M(1)$ and $M(2)$ octahedra share *trans* faces to form columns extending in the c direction. Only alternate $M(1)$–$M(2)$ pairs are occupied in order to avoid close (2.15 Å) $M(1)$–$M(2)$ approaches. The pattern of occupancy of the octahedra is disordered over adjacent columns. Each $M(1)$ or $M(2)$ octahedron shares a vertex [O(14)] with an adjacent $M(3)$ octahedron. Most of the anions in this layer are (H_2O) groups, and the general formula of the disordered layer is $\{(Cu^{2+}{}_2\square_2V^{3+},Al)_{\Sigma 6}\,(H_2O)_{12}\,(OH)_2\,(H_2O)_x\}$, where $x \approx 1.65$ and $0 \leq x \leq 2$.

Linkage between the two layers: The ordered and disordered layers alternate along the b direction (Fig. 3). The ordered layer links to the (MO_6) octahedra through vertices of the (PO_4) tetrahedra that are not involved in linkage to the ($Al\phi_6$) octahedra. There are most probably extensive hydrogen bonds linking the two layers, but the disordered nature of the structure prevented resolution of these details. It is apparent in Figure 3 that there is one (H_2O) group [O(17) + O(18)] that occurs in a

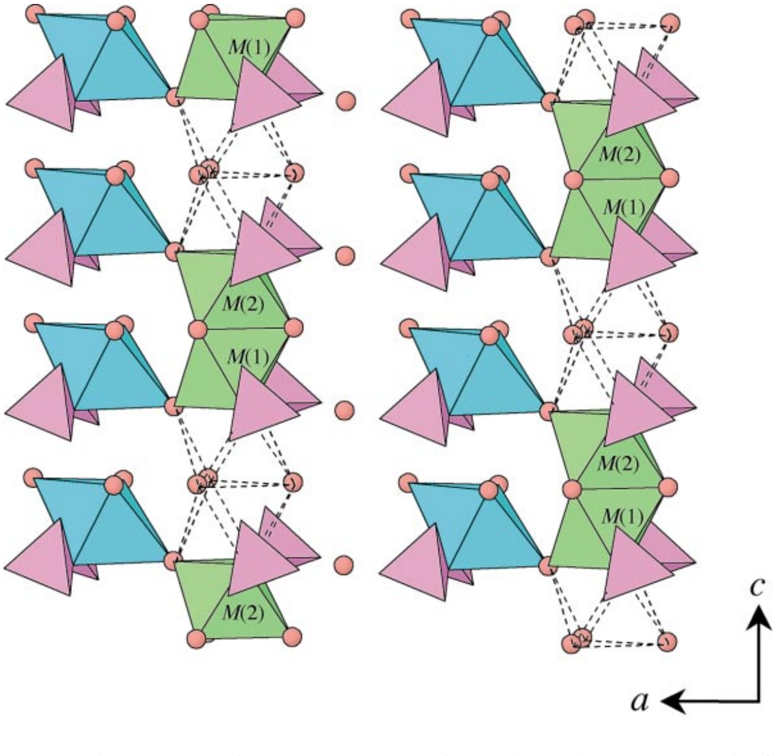

FIG. 2. Disordered part of the crystral structure of nevadaite, projected down an axis 8° from [010]; occupied $M(1)$ and $M(2)$ octahedra are shaded green, unoccupied $M(1)$ and $M(2)$ octahedra are outlined by dashed lines, and $M(3)$ octahedra are shaded blue. The (H_2O) groups at O(16) and O(17) are not shown.

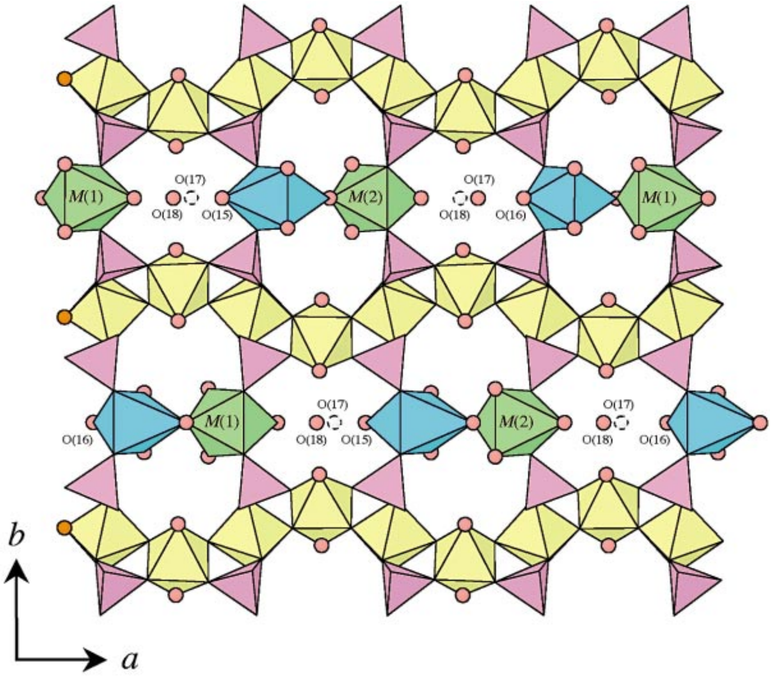

FIG. 3. The crystal structure of nevadaite projected onto (001); legend as in Figures 2 and 3. Note that the disordered layers are shown in an arbitrarily ordered fashion. Vacant O(17) and O(18) sites are shown with dashed circles.

large interstice of the structure and is held in the structure solely by hydrogen bonding; this is the 'variable' (H_2O) in the formula. It is constrained to be within the limits 0 and 2 *apfu*, and the electron density observed in this region of the structure indicates that there is ~1.65 H_2O groups per formula unit for this crystal.

Ordering over the O(15)–O(16) and O(17)–O(18) split sites

The relative interatomic distances and occupancies of the O(15) → O(18) anion sites is shown in Figure 4. The O(15) and O(16) sites were refined with the sum of their occupancies equal to 1.0 (*i.e.*, 2 H_2O *pfu*), and the O(17) and O(18) occupancies were refined independently. One might anticipate that the *M*(3) site would be occupied by a smaller cation (*i.e.*, $^{[6]}\text{Al} = 0.535$, $^{[6]}\text{V}^{3+} = 0.64$ Å) where the locally adjacent O(16) position is occupied. However, there is no agreement between the occupancy of the *M*(3) site by (Al, V^{3+}) (Table 6) and the occupancy of the O(16) site by (H_2O) (Fig. 4). The (H_2O) groups at O(15) and O(17) are mutually interfering [with a separation of 2.23(9) Å], and their refined occupancies suggest that these two sites are never simultaneously occupied. The sum of the (H_2O) over the O(17) and O(18) sites is 1.65 (H_2O) *pfu*. The three *M*-

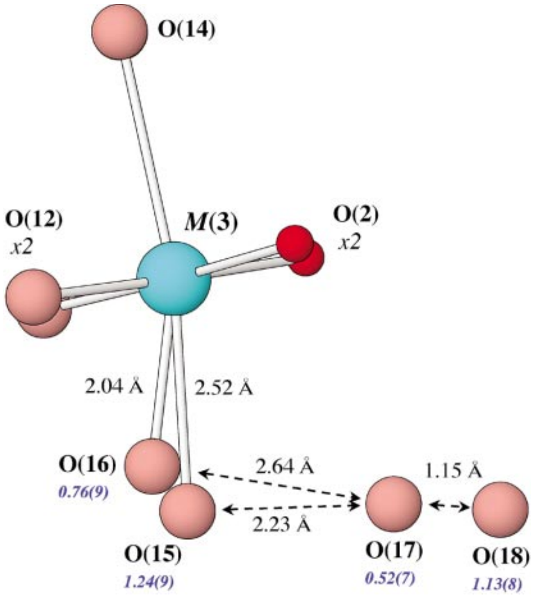

FIG. 4. Local configuration associated with the two positionally split (H_2O) groups, O(15)–O(16) and O(17)–O(18). Legend as in Figure 3; smaller darker red circles are O^{2-}. The interatomic distances are indicated with dashed lines, and site occupancies are given in purple text.

sites and the O(13) → O(18) sites all lie on the mirror plane perpendicular to the *b* axis (at $y = 0, ½$). A possible ordered arrangement involving (H_2O) groups at O(13) → O(18) is shown in Figure 5. There is a complex relation involving occupancy of the *M*(1) and *M*(2) sites, cation ordering at *M*(3), and hydrogen bonding between the various (H_2O) groups. Although the exact role of the isolated (H_2O) remains unclear, the structure places an upper limit of two such isolated (H_2O) groups *pfu*.

(*OH*)–(*H_2O*) *disorder*

The bond-valence values at the *M* sites (Table 7) are mean values calculated from the *M*-site assignments in Table 6. The local environments and corresponding bond-valences for each of the O(11), O(12) and O(14) anion sites are shown in Figure 6. Two O(11) sites lie along the shared edge of the *M*(1)–*M*(2) dimer. The incident bond-valence at O(11) varies slightly from 0.57 to 0.63 *vu*, depending upon the occupancy of the *M*(2) site (Fig. 6a). In either case, the O(11) site will likely require three hydrogen-bonds for occupancy by an (OH) group. Two O(12) sites occur along the edge of the *M*(3) octahedron, and the incident bond-valence at O(12) ranges from 0.45 to 0.57 *vu*, depending upon the occupancy of *M*(3) (Fig. 6b). Again, it is likely that the O(12) site will require three hydrogen-bonds to be occupied by an OH group.

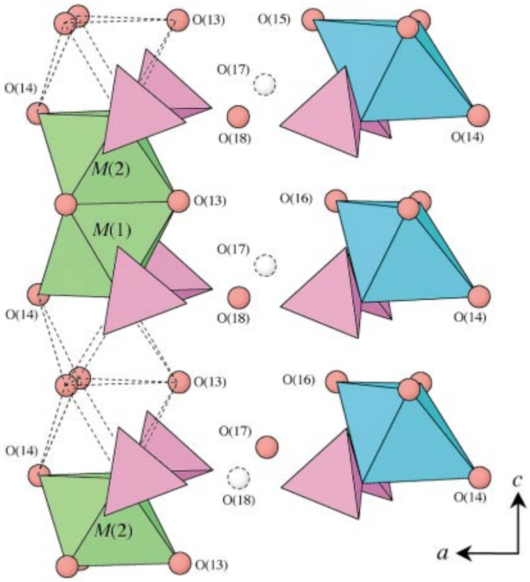

FIG. 5. Example of a locally ordered arrangement within the disordered layer; legend as in Figures 3 and 4.

The O(14) site is associated with either (1) a medium-length bond to *M*(1) and a long bond to *M*(3), or (2) a short bond to *M*(2) and a long bond to *M*(3) (Fig. 6c). Because the bond to *M*(3) is so long (2.73 Å), variation in incident bond-valence at O(14) as a function of the *M*(3) cation type is very small, and we give only the mean value in Figure 6c. Of all possible candidate sites for occupancy by (OH), the O(14) site receives the greatest incident bond-valence (0.72–0.85 *vu*) when bonded to M(2); however, it is still bond-valence-deficient and requires two more hydrogen-bonds. An additional complexity arises from the constraint that only half of the O(14) sites can be bonded to an occupied *M*(2) site (Fig. 2), limiting the number of such (OH) groups (requiring only two hydrogen-bonds) to a maximum of 1 (OH) group *pfu*.

In summary, the O(14) site seems a strong candidate for occupancy by up to 1 (OH) group *pfu*. The other necessary (OH) group must reside at O(11), O(12) or O(14), where three hydrogen-bonds are likely directed toward the donor O-atom.

MORE DIVERSITY IN 7 Å [$M\Phi_5$] CHAINS

In his pioneering paper, Moore (1970) examined some general features of a chain of octahedra that shares *trans* vertices, and subsequent work has shown that

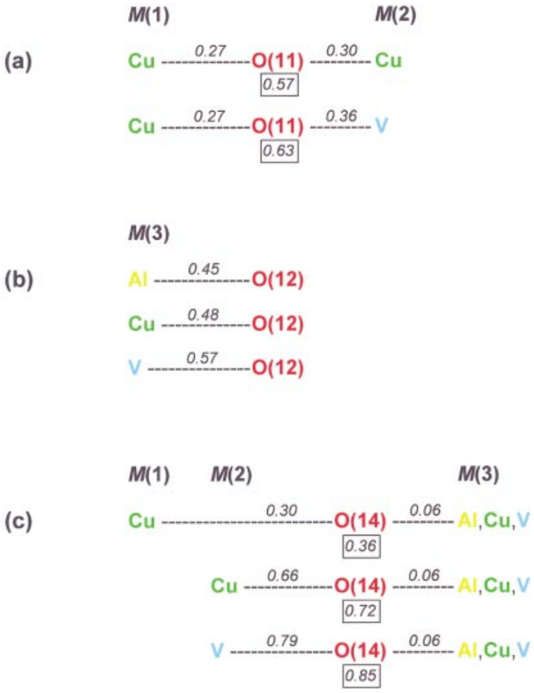

FIG. 6. Bond valences associated with Cu, V and Al at the *M* sites for (a) O(11), (b) O(12), and (c) O(14).

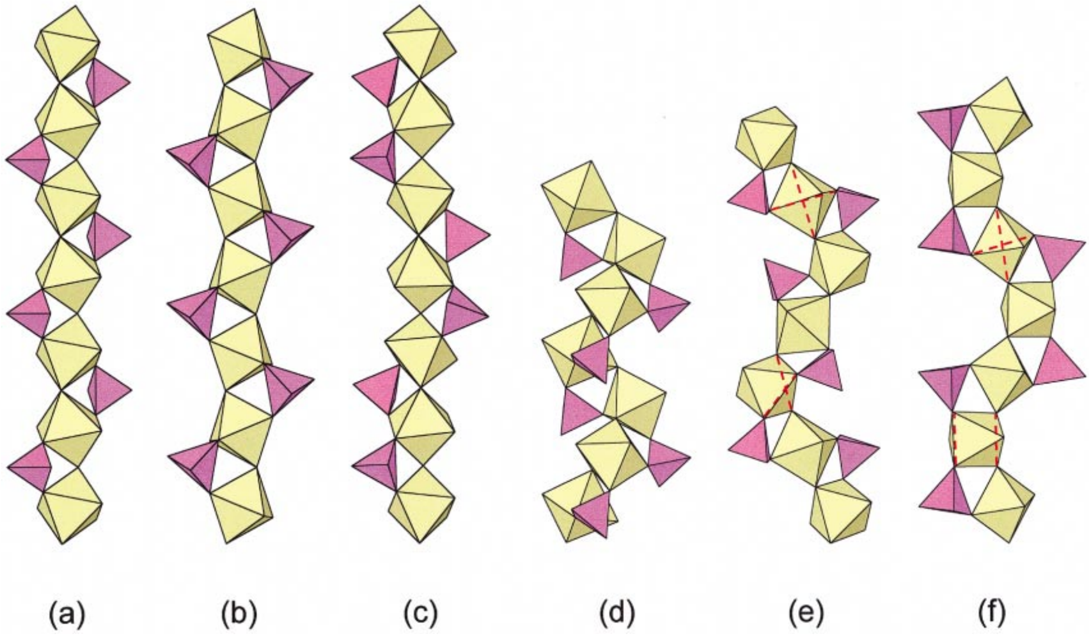

FIG. 7. [$M(TO_4)\phi_3$] chains in selected mineral structures: (a) butlerite, (b) metavauxite, (c) stewartite, (d) fibroferrite, (e) slavíkite, and (f) nevadaite.

variations of this arrangement are common in a wide variety of oxysalt structures (*e.g.*, Moore & Araki 1974a, b, 1977, Fanfani *et al.* 1971, 1978, Giuseppetti & Tadini 1984, Sabelli 1985, Hawthorne 1985, 1990, Burns & Hawthorne 1995). Some typical chains found in minerals are shown in Figure 7. Comparison of these chains (Fig. 7, Table 8) shows that the [$M\phi_5$] octahedron linkage may be through *trans* vertices (Figs. 7a, b, c), through *cis* vertices (Fig. 7d), or through alternate *cis* and *trans* vertices (Figs. 7e, f). The decorating tetrahedra may share *trans* vertices of an octahedron (Fig. 7a), or *cis* vertices (Figs. 7b, d), or alternating *cis* and *trans* vertices (Figs. 7c, e, f). The [$M(TO_4)\phi_3$] chains of slavíkite (Süsse 1975) and nevadaite are similar: both contain alternate *cis* and *trans* vertex-sharing involving (1) the [$M\phi_5$] octahedra, and (2) the decorating tetrahedra. Their patterns of *trans* connections are the same; however, the patterns of *cis* connections differ for these two chains, as shown by the broken red lines used to highlight the *cis* and *trans* connections in Figures 7e and f. In nevadaite (Fig. 7f), the *cis* connections occur between octahedron vertices along two parallel opposite sides of the constituent octahedra; in slavíkite, the *cis* connections occur along non-adjacent non-parallel edges of the constituent octahedra (Fig. 7e). It is also noteworthy in Figure 7 that there is an increased contraction along the chain length with increasing number of octahedra involved in *cis* connections.

CHEMICAL FORMULA

The positional disorder in nevadaite makes the writing of the chemical formula rather ambiguous with regard to the constituents at the $M(1)$ through $M(3)$ sites. The Al-phosphate framework can be written as [Al_8 $(PO_4)_8$ F_8]. There are three distinct octahedrally coordinated M sites that have the occupancies given in Table 6, together with the monovalent anions, to give a general formula $^{M(1)}(Cu^{2+}, \square)_2$ $^{M(2)}(\square, Cu^{2+}, V^{3+})_2$ $^{M(3)}(Al, V^{3+}, Cu^{2+})_2$ $(OH,F)_2$ $(H_2O)_{20}$ $(H_2O)_{1.65}$ [Al_8 $(PO_4)_8$ F_8]. As both the $M(1)$ and $M(2)$ sites are half-occupied, it is somewhat arbitrary which site is assigned dominant Cu^{2+}, but one must have dominant Cu^{2+} and the other must have dominant $\square$ (vacancy) in order to maintain electroneutrality. Alternatively, one could sum the $M(1)$ and $M(2)$ sites and express the interstitial cations as $(Cu^{2+}, V^{3+})_2$ $\square_2$ $(Al, V^{3+}, Cu^{2+})_2$. Taking the first formula given above, the resultant end-member compositions are as follows, taking into account that $M(1)$ and $M(2)$ cannot be locally occupied simultaneously:

$$Cu^{2+}{}_2\ \square_2\ Al_2\ (OH)_2\ (H_2O)_{22}\ [Al_8\ (PO_4)_8\ F_8]$$

$$\square_2\ Cu^{2+}{}_2\ Al_2\ (OH)_2\ (H_2O)_{22}\ [Al_8\ (PO_4)_8\ F_8]$$

$$\square_2\ V^{3+}{}_2\ Cu^{2+}{}_2\ (OH)_2\ (H_2O)_{22}\ [Al_8\ (PO_4)_8\ F_8]$$

The first composition, $Cu^{2+}_2 \square_2 Al_2 (OH)_2 (H_2O)_{22} [Al_8 (PO_4)_8 F_8]$, is the end-member composition of nevadaite.

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References

Baur, W.H. & Rao, R.R. (1967): Crystal structure of metavauxite. *Naturwiss.* **54**, 561-562.

Brown, I.D. & Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

Burns, P.C. & Hawthorne, F.C. (1995): The crystal structure of sinkankasite, a complex heteropolyhedral sheet mineral. *Am. Mineral.* **80**, 620-627.

Fanfani, L., Nunzi, A. & Zanazzi, P.F. (1971): The crystal structure of butlerite. *Am. Mineral.* **56**, 751-757.

________, Tomassini, M., Zanazzi, P.F. & Zanzari, A.R. (1978): The crystal structure of strunzite, a contribution to the crystal chemistry of basic ferric-manganous hydrated phosphates. *Tschermaks Mineral. Petrogr. Mitt.* **25**, 77-87.

Giuseppetti, G. & Tadini, C. (1984): The crystal structure of childrenite from Tavistock (S.W. England), $Ch_{89}Eo_{11}$ term of childrenite–eosphorite series. *Neues Jahrb. Mineral., Monatsh.*, 263-271.

Hawthorne, F.C. (1985): Towards a structural classification of minerals: the $^{VI}M^{IV}T_2\phi_n$ minerals. *Am. Mineral.* **70**, 455-473.

________ (1990): Structural hierarchy in $^{[6]}M^{[4]}T\phi_n$ minerals. *Z. Kristallogr.* **192**, 1-52.

Huminicki, D.M.C. & Hawthorne, F.C. (2002): The crystal chemistry of the phosphate minerals. *In* Phosphates: Geochemical, Geobiological, and Materials Importance (M.L. Kohn, J. Rakovan & J.M. Hughes, eds.). *Rev. Mineral. Geochem.* **48**, 123-253.

Jensen, M.C., Rota, J.C. & Foord, E.E. (1995): The Gold Quarry mine, Carlin trend, Eureka County, Nevada. *Mineral. Rec.* **26**, 449-469.

Moore, P.B. (1970): Structural hierarchies among minerals containing octahedrally coordinating oxygen. I. Stereoisomerism among corner-sharing octahedral and tetrahedral chains. *Neues Jahrb. Mineral., Monatsh.*, 163-173.

________ & Araki, T. (1974a): Jahnsite, $CaMn^{2+}Mg_2(H_2O)_8 Fe^{+}(OH)_2[PO_4]_4$: a novel stereoisomerism of ligands about octahedral corner-chains. *Am. Mineral.* **59**, 964-973.

________ & ________ (1974b): Stewartite, $Mn^{2+}Fe^{3+}_2(OH)_2 (H_2O)_6[PO_4]_2•2H_2O$: its atomic arrangement. *Am. Mineral.* **59**, 1272-1276.

________ & ________ (1977): Overite, segelerite, and jahnsite: a study in combinatorial polymorphism. *Am. Mineral.* **62**, 692-702.

Pouchou, J.L. & Pichoir, F. (1984): A new model for quantitative analysis. I. Application to the analysis of homogeneous samples. *La Recherche Aérosp.* **3**, 13-38.

________ & ________ (1985): "PAP" ($\phi\rho Z$) procedure for improved quantitative microanalysis. *In* Microbeam Analysis – 1985. San Francisco Press, San Francisco, California (104-106).

Roberts, A.C., Cooper, M.A., Hawthorne, F.C. Gault, R.A., Jensen, M.C. & Foord, E.E. (2003): Goldquarryite, a new Cd-bearing phosphate mineral from the Gold Quarry mine, Eureka County, Nevada. *Mineral. Rec.* **34**, 237-240.

Sabelli, C. (1985): Uklonskovite, $NaMg(SO_4)F•2H_2O$: new mineralogical data and structure refinement. *Bull. Minéral.* **108**, 133-138.

Scordari, F. (1981): Fibroferrite, a mineral with a $\{Fe(OH)(H_2O)_4SO_4\}$ spiral chain and its relationship to $Fe(OH)SO_4$, butlerite and parabutlerite. *Tschermaks Mineral. Petrogr. Mitt.* **28**, 17-29.

Süsse, P. (1975): Structure and crystal chemistry of slavikite, $NaMg_2Fe_5(SO_4)_7(OH)_6•33H_2O$. *Neues Jahrb. Mineral., Monatsh.*, 27-40.

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