NEVADAITE, (Cu$^{2+}$, Al, V$^{3+}$)$_6$ [Al$_8$ (PO$_4$)$_8$ F$_8$] (OH)$_2$ (H$_2$O)$_{22}$, A NEW PHOSPHATE MINERAL SPECIES FROM THE GOLD QUARRY MINE, CARLIN, EUREKA COUNTY, NEVADA: DESCRIPTION AND CRYSTAL STRUCTURE

MARK A. COOPER AND FRANK C. HAWTHORNE§

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

EUGENE E. FOORD*

U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225, U.S.A.

RICHARD C. ERD**

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, U.S.A.

HOWARD T. EVANS, JR.**

U.S. Geological Survey, National Center 959, Reston, Virginia 22092, U.S.A.

MARTIN C. JENSEN

1412-1891 Denver West Court, Lakewood, Colorado 80401, U.S.A.

ABSTRACT

Nevadaite, (Cu$^{2+}$, Al, V$^{3+}$)$_6$ [Al$_8$ (PO$_4$)$_8$ F$_8$] (OH)$_2$ (H$_2$O)$_{22}$, 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 than 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 $\alpha$ 1.540, $\beta$ 1.548, $\gamma$ 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$_1$mn, 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)] 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$_2$O$_5$ 32.54, Al$_2$O$_3$ 27.07, V$_2$O$_3$ 4.24, Fe$_2$O$_3$ 0.07, CuO 9.24, ZnO 0.11, F 9.22, H$_2$O (calc.) 23.48, OH $\equiv$ F –3.88, sum 102.09 wt.%; the valence states of V and Fe, and the amount of H$_2$O, were determined by crystal-structure analysis. The resulting empirical formula on the basis of 63.65 anions (including 21.65 H$_2$O pfu) is (Cu$^{2+}$)$_{2.00}$ Zn$_{0.02}$ Fe$^{3+}_{0.01}$ Al$_{1.15}$ Si$_{24.16}$ Al$_8$ P$_7.90$ O$_{32}$ [F$_{8.37}$ (OH)$_{1.63}$]$_{20}$ (H$_2$O)$_{21.65}$. 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 MoKα X-radiation. The structure consists of ordered layers of vertex-sharing octahedra and tetrahedra alternating with layers of disordered vertex-sharing octahedra and tetrahedra in the $b$ direction. [Al$_8$] 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$_4$)$_3$F$_6$(H$_2$O)$_{13}$]. In the disordered layer, octahedra

§ E-mail address: frank_hawthorne@umanitoba.ca

* deceased 1998

** deceased 2000
containing positionally disordered Cu²⁺, 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 \(|(\text{Cu}^{2+})_6\text{Y}^{18+}\text{Al}_{8} (\text{H}_2\text{O})_{32} (\text{OH})_2 (\text{H}_2\text{O})_x, x \approx 2\). 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 oxyysalt minerals, its chain is geometrically distinct from those topologically equivalent chains. The \(M–M\) linkage along the \([\text{Mb}]_5\) 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, \([\text{Mb}]_5\) chains, geometrical isomerism.

**SOMMAIRE**

La névadaïte, \((\text{Cu}^{2+}, \text{Al}, \text{V}^{3+}, \text{Fe}^{3+})_6 (\text{PO}_{12})_5 \text{F}_8 (\text{OH})_2 (\text{H}_2\text{O})_{32}\), est une nouvelle espèce minérale d’origine épigénétique découverte à la mine Gold Quarry, près de Carlin, comté d’Eureka, Nevada, aux États-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 ultra-violette. La névadaïte est sans clivage; la dureté de Mohs est environ 3. Elle est cassante avec une fracture conchoïdale, et 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 ultraviolette. Elle est faite de feuillets ordonnés d’octaèdres et de tétraèdres à coins partagés en alternance avec des couches plutôt désordonnée s

**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 \((\text{Cu},\text{Al},\text{V},\text{Fe})\)-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, Interna-
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 goldquarzite (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 fluelite, and maroon to red accicular hewettite; rarer species included anatase, kazakhstanite, leucophosphate, tincite, torbernite, and tuyumamnite.

**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 fluelite 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/cm³, the calculated density is 2.55 g/cm³. Optical properties were measured with the Blass 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, (+)2V(meas.) 76°, 2V(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: VP2O7 (V), maricite (P), braziliante (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 (H2O) 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 3331 cm⁻¹, indicative of H2O, 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 H2O 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-H2O components.

**Table 1. Chemical Composition (wt.%) and Empirical Formula (pfu) for Nevadaite**

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2O5</td>
<td>32.54</td>
</tr>
<tr>
<td>Al2O3</td>
<td>27.07</td>
</tr>
<tr>
<td>V2O5</td>
<td>4.24</td>
</tr>
<tr>
<td>FeO</td>
<td>0.70</td>
</tr>
<tr>
<td>CuO</td>
<td>9.24</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.11</td>
</tr>
<tr>
<td>F</td>
<td>9.22</td>
</tr>
<tr>
<td>H2O</td>
<td>23.48</td>
</tr>
<tr>
<td>O = F + 2H2O</td>
<td>1.15</td>
</tr>
<tr>
<td>TOTAL</td>
<td>102.09</td>
</tr>
<tr>
<td>F</td>
<td>8.37</td>
</tr>
<tr>
<td>OH</td>
<td>1.63</td>
</tr>
<tr>
<td>Σ</td>
<td>10.00</td>
</tr>
</tbody>
</table>

*calculated from the crystal structure
The powder-diffraction pattern was recorded with Ni-filtered CuKα 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 MoKα X-radiation: a 12.123(2), b 18.999(2), c 4.961(1) Å, V 1142.8(2) Å³, 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 MoKα X-ray tube. A total of 2089 reflections was measured out to 50° 2θ with index ranges 1 ≤ h ≤ 14, 0 ≤ k ≤ 22, 0 ≤ l ≤ 5 and a fixed scan-speed of 0.60° 2θ/min. Of the 2089 unique reflections, 1307 reflections were considered as observed [|Fo| ≥ 5σ(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 P2₁mn, and the structure was originally solved in Pmmn. This refinement model (R = 5.6%) consisted of an ordered Al–(PO₄)–F layer and a disordered Cu–V–Al–(H₂O) 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 P2₁mn. Because the Al–(PO₄)–F layer is conformable with Pmmn symmetry, refinement in P2₁mn 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–(PO₄)–F component are as follows: P(1)–P(2), P(1)–P(2), O(1)–O(5), O(2)–O(6), O(3)–O(7), O(4)–O(8), and O(9)–O(10). Because the Al–(PO₄)–F layer is conformable with Pmmn symmetry, refinement in P2₁mn 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–(PO₄)–F component are as follows: P(1)–P(2), P(1)–P(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 (H₂O) 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
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.

TABLE 4. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR NEVADAITE

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U12</th>
<th>U13</th>
<th>U23</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)</td>
<td>0.183</td>
<td>0.577</td>
<td>0.096</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001001</td>
<td>0.001001</td>
</tr>
<tr>
<td>M(2)</td>
<td>0.577</td>
<td>0.183</td>
<td>0.600</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001001</td>
<td>0.001001</td>
</tr>
<tr>
<td>M(3)</td>
<td>0.600</td>
<td>0.600</td>
<td>0.096</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001</td>
<td>0.001001</td>
<td>0.001001</td>
</tr>
</tbody>
</table>

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+}, 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 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)

<table>
<thead>
<tr>
<th>Site</th>
<th>Distance (Å)</th>
<th>Bond Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)–O(6,6)</td>
<td>1.901(15)</td>
<td>1.618(13)</td>
</tr>
<tr>
<td>M(1)–O(11,6)</td>
<td>2.157(15)</td>
<td>1.845(13)</td>
</tr>
<tr>
<td>M(1)–O(14)</td>
<td>2.120(17)</td>
<td>2.047(13)</td>
</tr>
<tr>
<td>M(1)–O(13)</td>
<td>2.52(3)</td>
<td>1.897(13)</td>
</tr>
<tr>
<td>M(2)–O(8,6)</td>
<td>1.87(17)</td>
<td>1.82(13)</td>
</tr>
<tr>
<td>M(2)–O(11,f)</td>
<td>2.12(14)</td>
<td>1.91(15)</td>
</tr>
<tr>
<td>M(2)–O(14)</td>
<td>1.83(17)</td>
<td>1.897(13)</td>
</tr>
<tr>
<td>M(3)–O(2)</td>
<td>1.94(8)</td>
<td>1.897(13)</td>
</tr>
<tr>
<td>M(3)–O(15)</td>
<td>2.52(3)*</td>
<td></td>
</tr>
<tr>
<td>M(3)–O(18)</td>
<td>2.04(3)*</td>
<td></td>
</tr>
<tr>
<td>M(3)–O(14,h)</td>
<td>2.732(16)</td>
<td></td>
</tr>
<tr>
<td>P(1)–O(1)</td>
<td>1.54(18)</td>
<td>1.526(17)</td>
</tr>
<tr>
<td>P(1)–O(2)</td>
<td>1.54(15)</td>
<td>1.512(15)</td>
</tr>
<tr>
<td>P(1)–O(3)</td>
<td>1.56(13)</td>
<td>1.516(13)</td>
</tr>
<tr>
<td>P(1)–O(4)</td>
<td>1.56(13)</td>
<td>1.516(13)</td>
</tr>
<tr>
<td>P(1)–O(5)</td>
<td>1.56(13)</td>
<td>1.516(13)</td>
</tr>
</tbody>
</table>

### Table 6. M-Site Assignments in Nevadaite

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu</th>
<th>V</th>
<th>Al</th>
<th>Assigned</th>
<th>Refined</th>
<th>Scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1)</td>
<td>1</td>
<td>1</td>
<td>29.0</td>
<td>28.1(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M(2)</td>
<td>0.6</td>
<td>0.4</td>
<td>26.8</td>
<td>26.1(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M(3)</td>
<td>0.4</td>
<td>0.6</td>
<td>38.4</td>
<td>37.4(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Σ</td>
<td>94.0</td>
<td>91.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 7. Bond-Valence* Table for Nevadaite

<table>
<thead>
<tr>
<th>Site</th>
<th>P(1)</th>
<th>P(2)</th>
<th>P(3)</th>
<th>P(4)</th>
<th>P(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(1)</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>F(2)</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
<td>0.44</td>
</tr>
<tr>
<td>O(1)</td>
<td>1.23</td>
<td>1.00</td>
<td>1.23</td>
<td>1.00</td>
<td>1.23</td>
</tr>
<tr>
<td>O(2)</td>
<td>1.20</td>
<td>0.50(2)</td>
<td>1.70</td>
<td>0.50(2)</td>
<td>1.70</td>
</tr>
<tr>
<td>O(3)</td>
<td>1.17</td>
<td>1.75</td>
<td>1.17</td>
<td>1.75</td>
<td>1.17</td>
</tr>
<tr>
<td>O(4)</td>
<td>1.17</td>
<td>1.75</td>
<td>1.17</td>
<td>1.75</td>
<td>1.17</td>
</tr>
<tr>
<td>O(5)</td>
<td>1.27</td>
<td>1.89</td>
<td>1.27</td>
<td>1.89</td>
<td>1.27</td>
</tr>
<tr>
<td>O(6)**</td>
<td>1.34</td>
<td>0.65(2)</td>
<td>1.99</td>
<td>0.65(2)</td>
<td>1.99</td>
</tr>
<tr>
<td>O(7)</td>
<td>1.30</td>
<td>1.82</td>
<td>1.30</td>
<td>1.82</td>
<td>1.30</td>
</tr>
<tr>
<td>O(8)</td>
<td>1.34</td>
<td>1.96</td>
<td>1.34</td>
<td>1.96</td>
<td>1.34</td>
</tr>
<tr>
<td>O(9)</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>O(10)</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>O(11)</td>
<td>0.27(2)</td>
<td>0.33(2)</td>
<td>0.60</td>
<td>0.33(2)</td>
<td>0.60</td>
</tr>
<tr>
<td>O(12)</td>
<td>0.49(2)</td>
<td>0.49</td>
<td>0.49</td>
<td>0.49</td>
<td>0.49</td>
</tr>
<tr>
<td>O(13)</td>
<td>0.10</td>
<td>0.17</td>
<td>0.10</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>O(14)**</td>
<td>0.30</td>
<td>0.36(2)</td>
<td>0.78</td>
<td>0.36(2)</td>
<td>0.78</td>
</tr>
<tr>
<td>O(15)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>O(16)</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>O(17)</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>O(18)</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>Σ</td>
<td>4.77</td>
<td>5.25</td>
<td>3.12</td>
<td>3.12</td>
<td>2.04</td>
</tr>
</tbody>
</table>

* 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$_2$O) sites

The O(9) and O(10) sites link only to Al at the Al(2) site and are therefore (H$_2$O) groups. The O(13) anion is weakly bonded to $M$(1) and $M$(2), and also must be an (H$_2$O) group. The O(15) and O(16) sites are 0.62(6) Å apart and represent a split (H$_2$O) site linked only to the cation at $M$(3). The O(17) and O(18) sites are also a split (H$_2$O) 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$_2$O) 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$_2$O)$_8$ + (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)\Phi_6]_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$_2$O) 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 \([M\Phi_3]\) chains. Both Al$\Phi_6$ [\(\Phi: O^{2-}, F, (H_2O)\)] octahedra share one set of vertices to form an \([M\Phi_3]\) 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$_2$O) groups are shaded red circles. Note the decorated [Al$\Phi_3$] corner-sharing chains that extend along a and link by sharing octahedron–tetrahedron vertices along c.](image-url)
from adjacent octahedra to form a chain of general sto-
ichiometry \( [M \text{(TO}_4 \text{)}] \) (Fig. 1). Chains of this topol-
ogy have been called the \( 7 \text{ Å} \) chains (Moore 1970) be-
cause the repeat distance of the chain (and the unit
cell in the chain direction) is a multiple of \( \approx 7 \text{ Å} \). How-
ever, the cell dimension defined by the \([M\text{To}_5]\) chain is sig-
nificantly shorter than \( \approx 7n \text{ Å} \) in nevadaite as a result
of a novel geometrical feature of the chain. Most \([M\text{To}_5]\)
chains link through \textit{trans} vertices of their component
octahedra. However, inspection of Figure 1 shows that the
\([\text{Al}(1)\text{To}_6]\) octahedron links to the \([\text{Al}(2)\text{To}_6]\) octa-
hedron by \textit{trans} vertices, the \([\text{Al}(2)\text{To}_6]\) octahedron links
to the \([\text{Al}(1)\text{To}_6]\) octahedron by \textit{cis} vertices. As the \textit{cis}
vertices of an octahedron are much closer together than the
\textit{trans} vertices, this linkage has the effect of shorten-
ing the repeat distance of the \([M\text{To}_5]\) chain. The mean
repeat distance of an \([M\text{To}_5]\) chain is \( 7.1 \text{ Å} \) (Moore 1970).
If one of the (two) linkages in the repeat distance along
the chain is \textit{cis} instead of \textit{trans}, this reduces the repeat
length to \( 7.1 / 2 + 7.1 / 2 \sqrt{2} = 6.06 \text{ Å} \); twice this length
doubling due to the decorating tetrahedra is \( 12.12 \text{ Å} \), which
is the \( a \) dimension of nevadaite.

\textbf{The disordered layer}: The disordered layer is shown
in Figure 2, with the \( (\text{PO}_4) \) linkages from the ordered
\([\text{Al}-(\text{PO}_4)\text{F}-(\text{H}_2\text{O})] \) sheet shown above and below. The
\([M(1)]\) and \([M(2)]\) octahedra share \textit{trans} faces to form col-
umns extending in the \( c \) direction. Only alternate \([M(1)]\)–
\([M(2)]\) pairs are occupied in order to avoid close (2.15 \text{ 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 \((\text{H}_2\text{O})\) groups, and the general formula of the
disordered layer is \(([(\text{Cu}^{2+})_{2}\text{V}^{5+}\text{Al})_{26}\text{H}_2\text{O}]_{12}\text{OH})_{2}\text{H}_2\text{O})_{x}\text{H}_2\text{O}\), where \( x \approx 1.65 \) and \( 0 \leq x \leq 2 \).

\textbf{Linkage between the two layers}: The ordered and
disordered layers alternate along the \( b \) direction (Fig. 3).
The ordered layer links to the \((\text{MO}_6)\) octahedra through
vertices of the \((\text{PO}_4)\) tetrahedra that are not involved
in linkage to the \((\text{AlTo}_6)\) octahedra. There are most
probably extensive hydrogen bonds linking the two layers,
but the disordered nature of the structure prevented reso-
lution of these details. It is apparent in Figure 3 that there
is one \((\text{H}_2\text{O})\) group \([O(17) + O(18)]\) that occurs in a

![Fig. 2](image-url)

Disordered part of the crystal structure of nevadaite, projected down an axis \( 8^\circ \)
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
\((\text{H}_2\text{O})\) groups at \( O(16) \) and \( O(17) \) are not shown.
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' \((\text{H}_2\text{O})\) in the formula. It is constrained to be within the limits 0 and 2 \(\text{apfu}\), and the electron density observed in this region of the structure indicates that there is \(\sim1.65\) \(\text{H}_2\text{O}\) 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 \(\text{H}_2\text{O}\) \(\text{pfu}\)), 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 \((\text{Al}, \text{V}^{3+})\) (Table 6) and the occupancy of the O(16) site by \((\text{H}_2\text{O})\) (Fig. 4). The \((\text{H}_2\text{O})\) 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 \((\text{H}_2\text{O})\) over the O(17) and O(18) sites is 1.65 \((\text{H}_2\text{O})\) \(\text{pfu}\). The three \(M-\)
sites and the $O(13) \rightarrow O(18)$ sites all lie on the mirror plane perpendicular to the $b$ axis (at $y = 0, 1/2$). A possible ordered arrangement involving ($H_2O$) groups at $O(13) \rightarrow O(18)$ 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.

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 [$M$=Al] 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
NEVADAITE, A NEW SPECIES FROM THE GOLD QUARRY MINE, NEVADA

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 \([M_{[\delta]} O_3]_{\beta}\) 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 \([M(TO_4)]_{\beta}\) chains of slavíkite (Süsse 1975) and nevadaite are similar: both contain alternate cis and trans vertex-sharing involving (1) the \([M_{[\delta]}]\) 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 \([Al_8 (PO_4)_{18} F_8]\). 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 \(M(1)[Cu^{2+}, \square]_2 M(2)[\square, Cu^{2+}, V^{3+}]_2 M(3)[Al, V^{3+}, Cu^{2+}]_2 (OH, F)_2 (H_2O)_{20} (H_2O)_{1.65} [Al_8 (PO_4)_{18} F_8]\). 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:

\[
\begin{align*}
Cu^{2+}_2 & \square_2 Al_2 (OH)_2 (H_2O)_{22} [Al_8 (PO_4)_{18} F_8] \\
\square_2 & Cu^{2+}_2 Al_2 (OH)_2 (H_2O)_{22} [Al_8 (PO_4)_{18} F_8] \\
\square_2 & V^{3+}_2 Cu^{2+}_2 (OH)_2 (H_2O)_{22} [Al_8 (PO_4)_{18} F_8]
\end{align*}
\]

FIG. 7. \([M(TO_4)]_{\beta}\) chains in selected mineral structures: (a) butlerite, (b) metavauxite, (c) stewartite, (d) fibroferrite, (e) slavíkite, and (f) nevadaite.
The first composition, \( \text{Cu}^{2+}2 \text{Al}_2(\text{OH})_2(H_2\text{O})_{22}[^{\text{Al}_4}\text{(PO}_4)_{8}F_{8}] \), is the end-member composition of nevadaite.

ACKNOWLEDGEMENTS

This work was supported by a Canada Research Chair in Crystallography and Mineralogy and by Natural Sciences and Engineering Research Council of Canada Discovery, Equipment and Major Installation grants to FCH.

REFERENCES


________ (1990): Structural hierarchy in \( \text{M}_4\text{T}_8\text{P}_8 \) minerals. Z. Kristallogr. 192, 1-52.


________ & ARAKI, T. (1974a): Jahnside, \( \text{CaMn}^{2+}\text{Mg}_2(\text{H}_2\text{O})_8\text{Fe}^{+}(\text{OH})_2[\text{PO}_4]_4 \); a novel stereoisomerism of ligands about octahedral corner-chains. Am. Mineral. 59, 964-973.

________ & ________ (1974b): Stewartyte, \( \text{Mn}^{3+}\text{Fe}^{3+}_2(\text{OH})_2(\text{H}_2\text{O})_6[\text{PO}_4]_4\cdot2\text{H}_2\text{O} \); its atomic arrangement. Am. Mineral. 59, 1272-1276.


SUSS, P. (1975): Structure and crystal chemistry of slavikite, \( \text{NaMg}_2\text{Fe}_3(\text{SO}_4)_{17}((\text{OH})_8\cdot33\text{H}_2\text{O} \). Neues Jahrb. Mineral., Monatsh., 27-40.

Received October 1, 2003, revised manuscript accepted April 8, 2004.