

## HUGHESITE, $\text{Na}_3\text{Al}(\text{V}_{10}\text{O}_{28})\cdot 22\text{H}_2\text{O}$ , A NEW MEMBER OF THE PASCOITE FAMILY OF MINERALS FROM THE SUNDAY MINE, SAN MIGUEL COUNTY, COLORADO

JOHN RAKOVAN<sup>§</sup> AND GREGORY R. SCHMIDT

*Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.*

MICKEY E. GUNTER

*Department of Geological Sciences, University of Idaho, Moscow, Idaho 83844, U.S.A.*

BARBARA NASH

*Department of Geology, University of Utah, Salt Lake City, Utah 84112, U.S.A.*

JOE MARTY

*3457 E. Silver Oak Road, Salt Lake City, Utah 84108, U.S.A.*

ANTHONY R. KAMPF

*Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.*

WILLIAM S. WISE

*Department of Earth Science, University of California, Santa Barbara, California 93106, U.S.A.*

### ABSTRACT

We report on the discovery, description and solution of the structure of a new member of the pascoite family of minerals, hughesite, from the Sunday mine, Gypsum Valley, San Miguel County, Slick Rock District, Colorado, USA (38°4'19" N, 108°48'15" W). Orange to golden orange crystals of hughesite occur in efflorescent crusts, averaging 2 mm thick, on the sandstone walls of mine workings and in rock fractures. Hughesite forms through the oxidation of corvusite,  $(\text{Na,Ca,K})_{1-x}(\text{V}^{5+}, \text{V}^{4+}, \text{Fe}^{2+})_8\text{O}_{28}\cdot 4\text{H}_2\text{O}$ , and montrosite,  $(\text{V}^{3+}, \text{Fe}^{2+}, \text{V}^{4+})\text{O}(\text{OH})$ , the primary vanadium oxide phases present, as they react with acidic, oxidizing groundwater. Crystals vary in habit, including blocky, spear-shaped, and platy, with one good cleavage on (001). Crystals are transparent to translucent with a subadamantine luster, and upon partial dehydration, they become opaque. Hughesite is biaxial (–), with  $\alpha$  1.698(5),  $\beta$  1.740(5),  $\gamma$  1.770(5), and the measured  $2V_{589\text{nm}}$  is 84(2)°. It exhibits a strong  $r > v$  dispersion, and is pleochroic with  $X = Y$  light golden yellow, and  $Z$  dark golden yellow. Its absorption is characterized by  $Z > Y > X$ . Electron-probe microanalysis and the crystal-structure solution provided the empirical formula  $\text{Na}_{2.99}\text{Al}_{1.05}(\text{V}_{10}\text{O}_{28})\cdot 22\text{H}_2\text{O}$  (based upon  $V = 10$  apfu). The ideal formula of hughesite is  $\text{Na}_3\text{AlV}_{10}\text{O}_{28}\cdot 22\text{H}_2\text{O}$ . The density calculated from the empirical formula using the single-crystal cell data is 2.29 g/cm<sup>3</sup>. Hughesite is triclinic, space group  $P\bar{1}$ , with  $a$  8.668(4),  $b$  10.295(4),  $c$  12.908(5),  $\alpha$  105.826(9),  $\beta$  97.899(9),  $\gamma$  103.385(9)°,  $V$  1053.0(8) Å<sup>3</sup>, and  $Z = 1$ . The strongest four lines in the powder-diffraction pattern [ $d$  in Å( $hkl$ ): are 12.24(100)00 $\bar{1}$ , 8.25(38)100, 9.50(30)0 $\bar{1}$ 0, and 8.99(28)0 $\bar{1}$ 1]. The crystal structure, refined to  $R_1 = 0.0496$ , consists of two components, the structural unit, which contains the decavanadate  $(\text{V}_{10}\text{O}_{28})^{6-}$  polyanion, and the fully hydrated interstitial complex, composed of two separate components, a  $\text{Na}_3(\text{OH})_2\text{O}_2$  trimer with two distinct cation sites, and a  $\text{Al}(\text{OH})_6$  monomer.

*Keywords:* hughesite, crystal structure, Raman spectrum, decavanadate, pascoite family, Sunday mine, Slick Rock district, Colorado.

<sup>§</sup> E-mail address: rakovajf@muohio.edu

## SOMMAIRE

Nous présentons la description d'un nouveau membre de la famille de la pascoïte, hughesite, découverte à la mine Sunday, vallée de Gypsum, comté de San Miguel, district de Slick Rock, au Colorado (38°4'19" N, 108°48'15" W), ainsi que de sa structure. Les cristaux de hughesite, de couleur orange à orange doré, se présentent en croûtes efflorescentes, ayant en moyenne une épaisseur de 2 mm, sur les parois de grès de la mine et le long de fractures. La hughesite résulte de l'oxydation de la corvusite,  $(\text{Na,Ca,K})_{1-x}(\text{V}^{5+}, \text{V}^{4+}, \text{Fe}^{2+})_8\text{O}_{28} \cdot 4\text{H}_2\text{O}$ , et de la montrosite,  $(\text{V}^{3+}, \text{Fe}^{2+}, \text{V}^{4+})\text{O}(\text{OH})$ , les oxydes primaires de vanadium, qui ont réagi en présence de l'eau souterraine oxygénée. Les cristaux possèdent un bon clivage sur (001), et peuvent avoir un habitus en blocs, en aiguilles ou en plaquettes. Ils sont transparents à translucides avec un éclat sub-adamantin; suite à une déshydratation partielle, ils deviennent opaques. La hughesite est biaxe négative, avec  $\alpha$  1.698(5),  $\beta$  1.740(5),  $\gamma$  1.770(5), et un angle  $2V_{589\text{nm}}$  égal à 84(2)°. Elle montre une forte dispersion  $r > v$  et un pléochroïsme,  $X = Y$  jaune doré pâle, et  $Z$  jaune doré foncé. L'absorption se traduit par  $Z > Y = X$ . Une analyse avec une microsonde électronique et la solution de sa structure ont fourni la formule empirique,  $\text{Na}_{2.99}\text{Al}_{1.05}(\text{V}_{10}\text{O}_{28}) \cdot 22 \text{H}_2\text{O}$  (sur une base de  $V = 10$  *apfu*). La formule idéale de la hughesite est  $\text{Na}_3\text{AlV}_{10}\text{O}_{28} \cdot 22\text{H}_2\text{O}$ . La densité calculée à partir de la formule empirique, en utilisant les données obtenues sur monocristal à propos de la maille élémentaire, est 2.29 g/cm<sup>3</sup>. La hughesite est triclinique, groupe spatial  $P\bar{1}$ , avec  $a$  8.668(4),  $b$  10.295(4),  $c$  12.908(5),  $\alpha$  105.826(9),  $\beta$  97.899(9),  $\gamma$  103.385(9)°,  $V$  1053.0(8) Å<sup>3</sup>, et  $Z = 1$ . Les quatre raies les plus intenses du spectre de diffraction X [ $d$  en Å( $hkl$ )] sont: 12.24(100)00 $\bar{1}$ , 8.25(38)100, 9.50(30)0 $\bar{1}$ 0, et 8.99(28)0 $\bar{1}$ 1. La structure, affinée jusqu'à un résidu  $R_1$  de 0.0496, comprend deux composantes, l'unité structurale qui contient le groupe polyanionique décavanadate,  $(\text{V}_{10}\text{O}_{28})^{6-}$ , et le complexe interstitiel pleinement hydraté, lui-même à deux composantes, un trimère ayant deux sites cationiques distincts,  $\text{Na}_3(\text{OH})_2\text{O}_2$ , et un monomère,  $\text{Al}(\text{OH})_2\text{O}$ .

(Traduit par la Rédaction)

**Mots-clés:** hughesite, structure cristalline, spectre de Raman, décavanadate, famille de la pascoïte, mine Sunday, district de Slick Rock, Colorado.

## INTRODUCTION

Typically bright yellow to orange, owing to octahedrally coordinated pentavalent vanadium, the pascoite family of minerals includes gunterite, huemulite, hughesite, hummerite, lasalite, magnesiopascoite, pascoite, and rakovanite (Table 1). Common to each of these minerals is the  $[\text{V}_{10}\text{O}_{28}]^{6-}$  decavanadate anionic complex, which is weakly bonded to cation complexes, commonly alkali and alkaline earth cations, as well as to  $\text{H}_2\text{O}$  molecules (Hughes *et al.* 2008). Collecting by Joe Marty at the Sunday mine, Gypsum Valley, Colorado, yielded several samples initially presumed to be huemulite. However, the unit-cell parameters measured through single-crystal X-ray diffraction did not match those of huemulite or any other known phase. Data presented in this paper show that this is a new mineral and a member of the pascoite family of minerals. We are pleased to name the mineral *hughesite* in honor of Dr. John Michael Hughes (b. 1952), formerly Professor of Mineralogy at Miami University and now Professor of Mineralogy and former Provost at the University of Vermont, for his long and outstanding career in mineralogy, including his extensive work on the pascoite family of minerals and vanadium bronzes. The Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) has approved the new mineral and name. The holotype specimen, composed of numerous crystals on matrix, resides in the collection of the National Museum of Natural History of the Smithsonian Institution (NMNH #174253).

## OCCURRENCE

Hughesite occurs as crystalline druses on the sandstone walls, usually in organic-carbon-rich zones, of mine workings and on fracture surfaces at the Sunday mine, Gypsum Valley, San Miguel County, Slick Rock District, Colorado, USA (38°4'19" N, 108°48'15" W). Associated minerals are rossite, lasalite, hewettite, sherwoodite, corvusite, montroseite, rakovanite, gunterite, and unidentified vanadium phases. The mineral forms through the oxidation of corvusite,  $(\text{Na,Ca,K})_{1-x}(\text{V}^{5+}, \text{V}^{4+}, \text{Fe}^{2+})_8\text{O}_{28} \cdot 4\text{H}_2\text{O}$ , and montrosite,  $(\text{V}^{3+}, \text{Fe}^{2+}, \text{V}^{4+})\text{O}(\text{OH})$ , the primary vanadium oxide phases present, as they react with acidic, oxidizing groundwater. Secondary mineralization occurs during its evaporation, leaving a crust of hughesite and other oxidized vanadium minerals on rock surfaces. The exact phases that form depend on the Eh–pH conditions and the concentration of other cations of the interstitial

TABLE 1. MINERALS OF THE PASCOITE FAMILY

Mineral	Formula	Reference
gunterite	$\text{Na}_4(\text{H}_2\text{O})_{16}(\text{H}_2\text{V}_{10}\text{O}_{28}) \cdot 6\text{H}_2\text{O}$	(Kampf <i>et al.</i> 2011)
huemulite	$\text{Na}_4\text{Mg}(\text{V}_{10}\text{O}_{28}) \cdot 24\text{H}_2\text{O}$	(Colombo <i>et al.</i> 2011)
hughesite	$\text{Na}_3\text{Al}(\text{V}_{10}\text{O}_{28}) \cdot 22\text{H}_2\text{O}$	(this paper)
hummerite	$\text{K}_2\text{Mg}_2(\text{V}_{10}\text{O}_{28}) \cdot 16\text{H}_2\text{O}$	(Hughes <i>et al.</i> 2002)
lasalite	$\text{Na}_4\text{Mg}_2(\text{V}_{10}\text{O}_{28}) \cdot 20\text{H}_2\text{O}$	(Hughes <i>et al.</i> 2008)
magnesiopascoite	$\text{Ca}_2\text{Mg}(\text{V}_{10}\text{O}_{28}) \cdot 16\text{H}_2\text{O}$	(Kampf & Steele 2008)
pascoite	$\text{Ca}_3(\text{V}_{10}\text{O}_{28}) \cdot 17\text{H}_2\text{O}$	(Hughes <i>et al.</i> 2005)
rakovanite	$\text{Na}_3\{\text{H}_3[\text{V}_{10}\text{O}_{28}]\} \cdot 15\text{H}_2\text{O}$	(Kampf <i>et al.</i> 2011)

complex, that act to balance the charge of the decavanadate polyanion.

The Sunday mine complex, which consists of the Topaz, Sunday, West Sunday, Carnation, and St. Jude mines, is located on the northeastern boundary of the Slick Rock mining district (Fig. 1). This, in turn, is part of the Uravan mineral belt, an arcuate zone of uranium–vanadium deposits in San Miguel, Montrose, and Mesa

counties, Colorado, and Grand County, Utah (Fischer & Hilpert 1952). The Slick Rock mining district was the location of the first uranium production in the Colorado Plateau geological province and the most productive uranium mining area in the United States in the early 20th century (Fischer & Hilpert 1952, Shawe 2011). Uranium–vanadium ore production within the Sunday mine complex is confined to the Upper Jurassic Salt

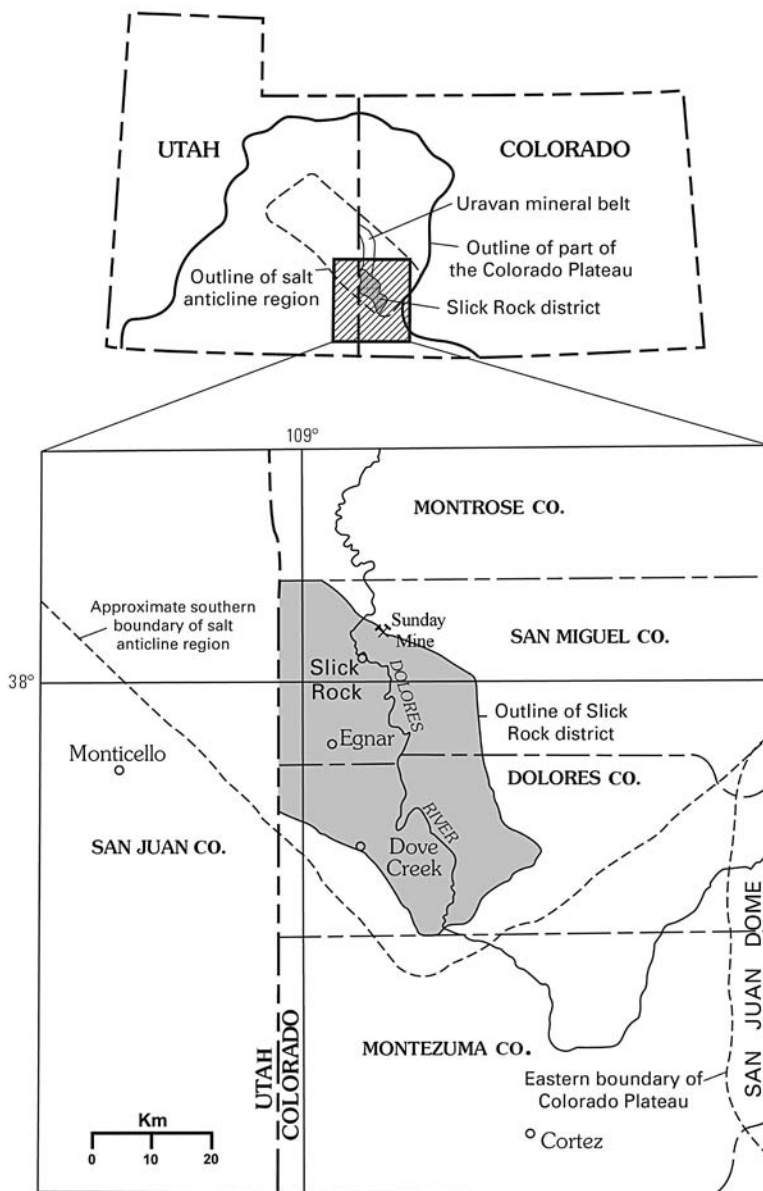


FIG. 1. Map showing the location of the Slick Rock mining district and the Sunday mine. Modified from Shawe (2011).

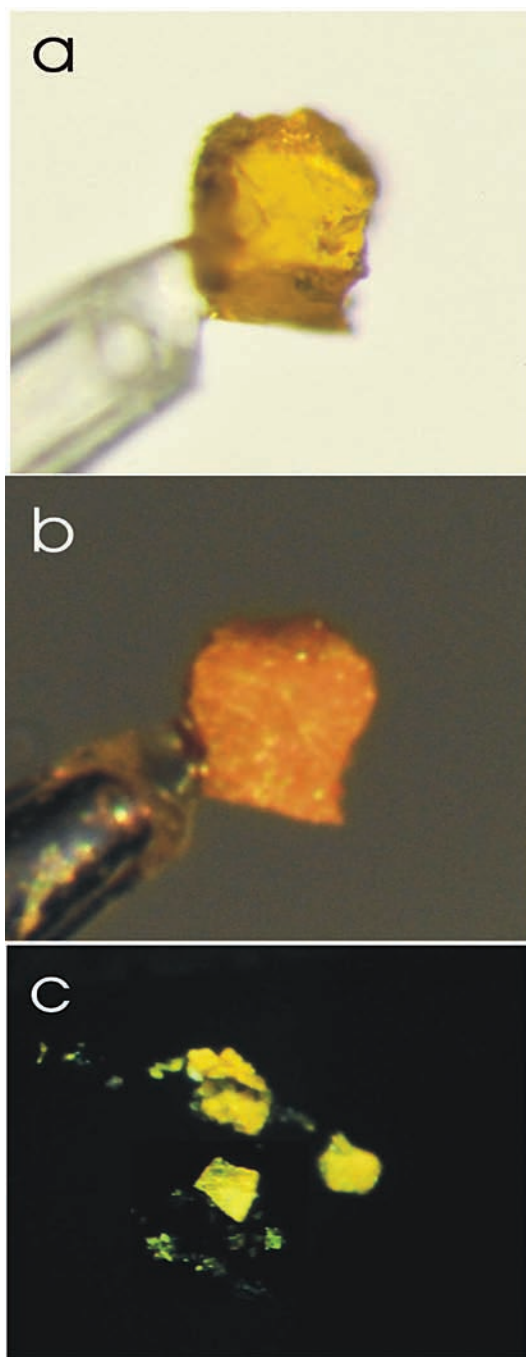


FIG. 2. a) Transparent hughesite (fully hydrated) mounted on glass fiber used for single-crystal XRD, Raman spectroscopy and optical measurements. b) The crystal pictured in a) after partial dehydration. c) The dehydrated crystal pictured in b) after fragmentation on microprobe mount.

Wash Member, a permeable, carbonaceous fluvial sandstone (Shawe 2011) of the Morrison Formation; all mines are located along a common mineralized system (Jim Fisher, pers. commun., 2010). The Sunday, St. Jude, and West Sunday mines are interconnected. Hughesite has also been identified on samples from the West Sunday mine (Kampf *et al.* 2011), and the Blue Streak mine in Montrose County, Colorado.

Within the Slick Rock district and elsewhere on the Colorado Plateau, uranium and vanadium minerals occur in tabular and irregularly shaped ore deposits, commonly referred to as rolls, or roll-front deposits (Shawe 2011). The epigenetic ore deposits in the Slick Rock district occur within carbonaceous strata, where extensive chemical reduction caused precipitation of uranium and vanadium minerals from groundwater. Later oxidation of near-surface deposits resulted in the formation of secondary and tertiary uranium and vanadium minerals. The V:U ratio in Colorado Plateau sediment-hosted ore deposits varies regularly from east to west, with the East exhibiting a dominance of vanadium. In the Slick Rock district, the V:U ratio varies from 3 : 1 to 15 : 1 (Weeks 1956). Recent increases in the price of uranium have resulted in the re-evaluation of data from the Slick Rock mining district. A detailed model of the history and mechanism of ore formation is presented by Shawe (2011).

#### PHYSICAL AND OPTICAL PROPERTIES

Efflorescent crusts of hughesite and other related minerals are between 1 and 3 mm thick. The surface of samples glistens from exposed crystal faces, with very minimal rounding from dissolution. In some instances, single crystals up to 2 mm in length are found. Hughesite is orange to golden orange, and its streak is yellow. The thinnest layers of hughesite appear orange, whereas the thickest layers are golden orange. Crystals are variable in habit, from blocky (Fig. 2) to spear-shaped (Fig. 3) and platy. An idealized crystal drawing is shown in Figure 4. They are transparent to translucent with a subadamantine luster where hydrated, and opaque and chalky where dehydrated. Hughesite is brittle and exhibits one good direction of cleavage parallel to (001). The hardness is estimated to be about 1. Hughesite is highly soluble in water, acetone and alcohol, making it difficult to handle for analytical work. The calculated density using the ideal formula and single-crystal unit cell is 2.29 g/cm<sup>3</sup>.

Optical properties, Raman spectra, and single-crystal X-ray diffraction data were all collected on a single, gemmy, equant fragment of hughesite (Fig. 2a). During the winter months, while relative humidity was low in Oxford, Ohio, the crystal partially dehydrated. Commensurate with dehydration, the crystal became opaque and orange (Fig. 2b), and X-ray diffraction yielded a powder ring pattern. The dehydrated crystal was transferred to a carbon sticky tab for electron-probe

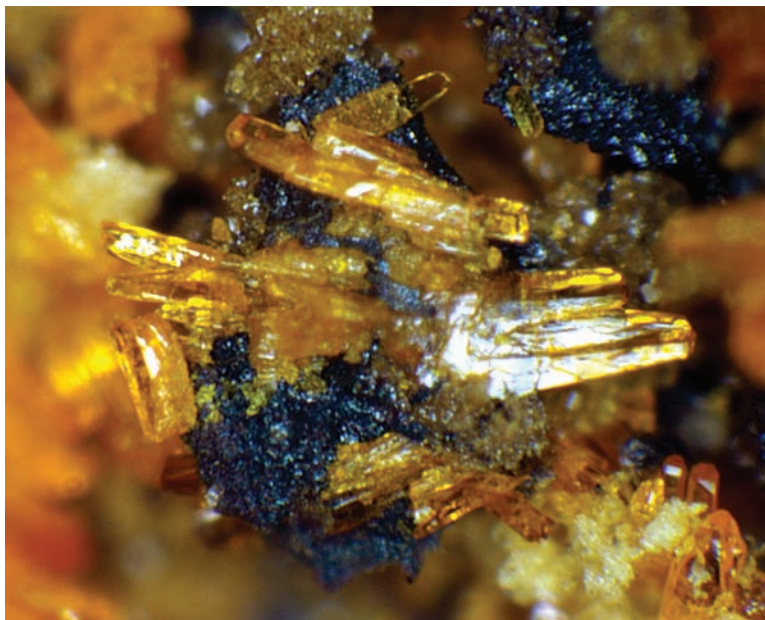


FIG. 3. Hughesite crystals on matrix, West Sunday mine, Gypsum Valley, San Miguel County, Slick Rock District, Colorado.

microanalysis. During transfer, it cleaved into numerous small platy fragments that exhibited a lemon-yellow color (Fig. 2c). Single-crystal X-ray-diffraction data were also collected on a second crystal and were used in the structure solution and refinement presented here.

Optical properties of hughesite were determined from the crystal mounted on a goniometer head and in known orientation, determined by X-ray diffraction. Hughesite is biaxial negative with  $\alpha$  1.698(5),  $\beta$  1.740(5),  $\gamma$  1.770(5), as determined at 589 nm. The measured  $2V_{589\text{nm}}$  is  $84(2)^\circ$ , and the calculated value is  $79(2)^\circ$ . It has a strong dispersion, with  $r > v$ . Hughesite is pleochroic with  $X = Y$  light golden yellow, and  $Z$  dark golden yellow. Absorption in hughesite is described by  $Z > Y = X$ . The optical orientation (Parr *et al.* 2009) is ( $\pm 1^\circ$ ):

	<b>a</b>	<b>b</b>	<b>c</b>
$X$	$110^\circ$	$88^\circ$	$145^\circ$
$Y$	$36^\circ$	$74^\circ$	$56^\circ$
$Z$	$118^\circ$	$16^\circ$	$96^\circ$

#### RAMAN SPECTROSCOPIC ANALYSIS

A Raman spectral analysis of the single crystal of hughesite used for optical measurements (Fig. 2a)

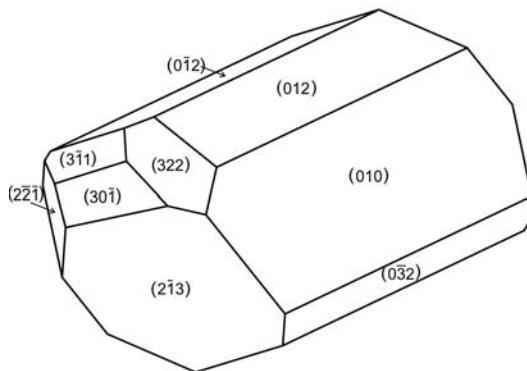


FIG. 4. Crystal drawing of hughesite.

was conducted with a Renishaw InVia Raman microscope. The spectrometer interfaced to the microscope employed a 1800 groove/mm grating and a charge-coupled detector. The sample was excited using a HeNe laser (632 nm) that was focused onto the sample using a  $20\times$  (0.40 N.A.) objective. The same objective was employed to collect the back-scattered Raman radiation. Spectra were collected at 4 wavenumber resolution over the range of  $100\text{--}1500\text{ cm}^{-1}$  using an integration time of 30 seconds per point. Three individual spectra were

averaged to produce the final Raman spectrum. Abscissa values were calibrated using the phonon band of single-crystal silicon located at  $520.7 \pm 0.3$  wavenumber. Raman spectra (Fig. 5) were collected at two perpendicular crystallographic directions. The first spectrum was collected with the laser beam perpendicular to the (001) cleavage surface (orientation 1, Fig. 2a) at 10% total laser power (1.0 mW). The crystal was then rotated  $90^\circ$  (orientation 2) and a second spectrum was collected with the laser beam parallel to the cleavage surface. In this orientation, the laser left a burn mark on the sample when run at 10% total power. The laser was then moved to a new, unaltered area of the crystal, and data were collected at 5% total power (0.50 mW) with no observable decomposition. The following intense Raman bands (in  $\text{cm}^{-1}$ ) are observed at (centroid positions): orientation 1: 191.7, 200.5, 218.1, 234.6, 246.6, 269.6, 318.5, 362.8, 470.6, 595.5, 877.1, 945.4, 959.1, 971.9, 994.4, 1007.1; orientation 2: 181.7, 213.7, 231.3, 259.8, 317.5, 361.8, 468.5, 591.4, 854.2, 971.8, 999.3.

#### THE COMPOSITION OF HUGHESITE

Chemical analysis proved difficult because of the instability of hughesite under the electron beam in a vacuum. Individual crystals were glued to double-sided conductive carbon adhesive, attached to a solid

microprobe mount 2.5 cm in diameter, and coated with carbon prior to analysis. Analyses were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers. Analytical conditions were: 15 keV accelerating voltage, 10 nA beam current, and a nominal beam-diameter of  $10 \mu\text{m}$ , although larger diameters of 15 and  $20 \mu\text{m}$  were occasionally used on larger fragments. Counting times were 10 seconds for each element. Where the size of the crystal permitted, the sample was slowly translated under the beam to minimize the effects of beam damage and sodium migration. Standards were as follows: albite (Na), diopside (Mg and Ca), sanidine (Al and K), vanadium metal (V). Raw X-ray intensities were corrected for matrix effects with a phi-rho-z algorithm (Pouchou & Pichoir 1991).

The analyses were undertaken on a sample confirmed by X-ray structure analysis to be hughesite. The crystal fragmented during transfer to the microprobe mount (Fig. 2c). This crystal was also used for optical measurements and Raman spectroscopy before partial dehydration during the winter. Hughesite can dehydrate under conditions of low humidity, and dehydrates rapidly under the vacuum and electron beam of the microprobe. In addition, under the electron beam, Na was found to migrate over time. Thus, the analyses yielding the highest Na totals are likely to be the most reliable.

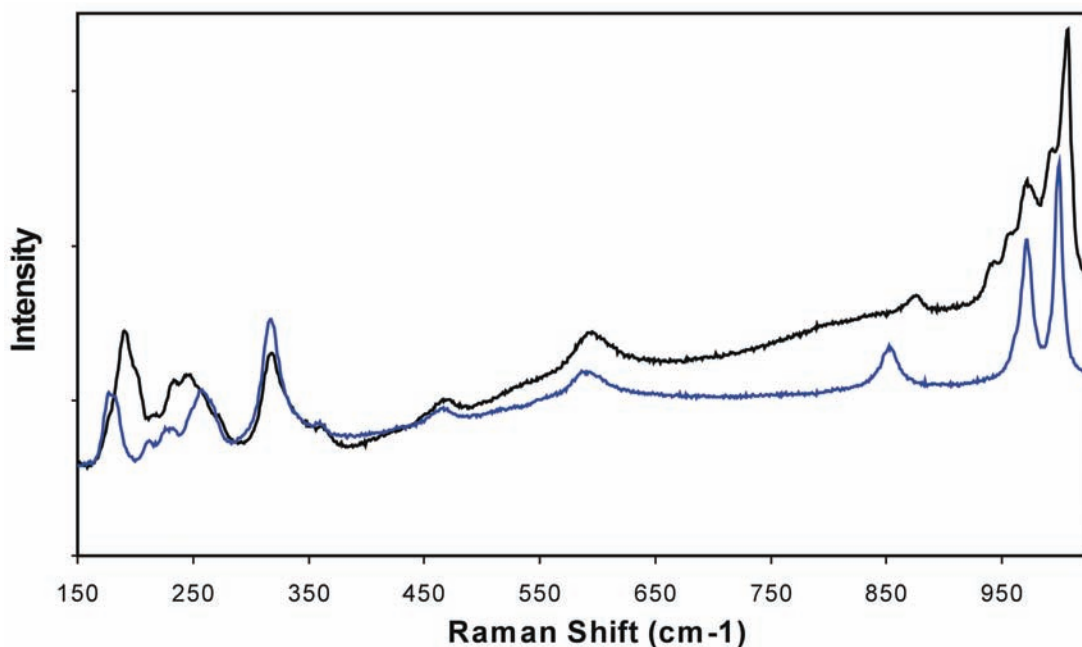


FIG. 5. Raman spectra of hughesite. Black line collected with laser beam perpendicular to the cleavage surface (position 1) at 1.0 mW power. Blue line collected parallel to the cleavage surface (position 2) at 0.5 mW power.

Magnesium, Ca, and K were sought in the analyses, but were not detected in concentrations greater than 0.02 wt.% metal, the lower detection limit for these elements.

Table 2 presents the average results of four analyses of four subcrystals of the partially dehydrated hughesite that broke up upon mounting. Different portions of the fragmented crystal exhibited different extents of dehydration; consequently, the standard deviations of the oxide analyses are unusually high. Analysis of other crystals supported the stoichiometry determined in the crystal-structure analysis. The empirical formula of the partially dehydrated hughesite, based on a total of 10 V atoms per formula unit and a H<sub>2</sub>O content determined by difference, is Na<sub>2.99</sub>Al<sub>1.05</sub>(V<sub>10</sub>O<sub>28</sub>)•5.70 H<sub>2</sub>O. This analysis yields a proportion of Na : Al : V that is applicable to both the dehydrated and hydrated hughesite. Table 2 also presents the ideal oxide weight percentages calculated for hughesite based on a total of 10 V atoms per formula unit and a full content of H<sub>2</sub>O (22 H<sub>2</sub>O), determined from the crystal-structure solution. The empirical formula based on the proportion of cations established by analysis is in excellent agreement with the results of the crystal-structure study, which yielded Na<sub>3</sub>Al(V<sub>10</sub>O<sub>28</sub>)•22H<sub>2</sub>O for a non-dehydrated crystal.

#### CRYSTAL STRUCTURE: EXPERIMENTAL

A crystal of hughesite was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochromated MoK $\alpha$  radiation. Data collection, structure-refinement parameters, refined cell-parameters, and other crystal data are reported in Table 3. Data were collected for a full sphere of reciprocal space, and absorption corrections were applied using semi-empirical methods using the SADABS (Bruker AXS, Inc. 2003) program. Data were integrated as well as corrected for Lorentz and polarization factors using the program SAINTPLUS (Bruker AXS, Inc. 2003).

TABLE 2. CHEMICAL COMPOSITION OF PARTIALLY DEHYDRATED HUGHESITE (A), AND CALCULATED COMPOSITION OF FULLY HYDRATED HUGHESITE (B)

	A		B*
	wt.%	$\sigma$	wt.%
Na <sub>2</sub> O	8.00	0.9	6.41
Al <sub>2</sub> O <sub>3</sub>	4.63	0.2	3.52
V <sub>2</sub> O <sub>5</sub>	78.51	5.5	62.73
H <sub>2</sub> O (by difference)	8.86		27.34
Total	100.00		100.00

A: Empirical formula ( $V = 10$  apfu): Na<sub>2.99</sub>Al<sub>1.05</sub>(V<sub>10</sub>O<sub>28</sub>)•5.70 H<sub>2</sub>O.  
 B\*: Ideal chemical formula: Na<sub>3</sub>Al(V<sub>10</sub>O<sub>28</sub>)•22 H<sub>2</sub>O. \* Assuming the ideal chemical formula, based on  $V = 10$  apfu and 22 H<sub>2</sub>O molecules determined from the crystal-structure solution.

The crystal structure was solved by direct methods and difference-Fourier maps using the Bruker SHELXTL v. 6.14 (Bruker AXS, Inc. 2000) package of programs. Neutral-atom scattering factors and terms for anomalous dispersion were employed throughout the solution and refinement. The structure was refined on F<sup>2</sup> with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms in hughesite were easily located using difference-Fourier maps. Atom parameters are listed in Table 4, and selected interatomic distances along with bond valences, in Table 5. Anisotropic thermal parameters for all non-hydrogen atoms are listed in Table 6. Powder X-ray diffraction data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized MoK $\alpha$  radiation. Observed values of  $d$  and intensities were derived by profile fitting using JADE 9.3 software (Materials Data, Inc.). The measured powder X-ray-diffraction pattern as well as calculated peaks from the refined structure are given in Table 7. The strongest four measured lines in the powder diffraction pattern [ $d$  in Å( $hkl$ )] are: 12.24(100)00 $\bar{1}$ , 8.25(38)100, 9.50(30)0 $\bar{1}$ 0, and 8.99(28)0 $\bar{1}$ 1. A table of structure factors and a cif file are available from the Depository of Unpublished Data on the MAC website [document Hughesite CM49\_1253].

#### ATOMIC ARRANGEMENT OF HUGHESITE

Hughesite is triclinic with space group  $P\bar{1}$  and a cell having the dimensions  $a$  8.668(4),  $b$  10.295(4),  $c$  12.908(5) Å,  $\alpha$  105.826(9),  $\beta$  97.899(9) and  $\gamma$  103.385(9)°. The atomic arrangement of minerals

TABLE 3. HUGHESITE: DETAILS CONCERNING DATA COLLECTION AND STRUCTURE-REFINEMENT PARAMETERS

Diffractometer	Bruker APEX
X-ray radiation, power	MoK $\alpha$ ( $\lambda = 0.71075$ Å), 45 kV, 35 mA
Crystal size	0.12 × 0.10 × 0.08 mm
Structural formula	Na <sub>3</sub> Al(V <sub>10</sub> O <sub>28</sub> )•22 H <sub>2</sub> O
Space group	$P\bar{1}$
Unit-cell parameters	
$a, b, c$ (Å)	8.668(4), 10.295(4), 12.908(5) Å
$\alpha, \beta, \gamma$ (°)	105.826(9), 97.899(9), 103.385(9)
$a : b : c$	0.842:1:1.254
$V$ (Å <sup>3</sup> )	1053.0(8)
$Z$	1
Frame width, scan time, number of frames:	0.20°, 30 s, 4500
Values of $h, k, l$	$-11 \leq h \leq 11, -13 \leq k \leq 13, -17 \leq l \leq 17$
Temperature	20 °C
Detector distance	5 cm
Effective transmission	0.901461 – 1.000
$R_{int}$ (before, after SADABS absorption correction)	0.0628 – 0.0424
Measured reflections, unique reflections, full sphere	16,777, 5,238
Refined parameters	384, refined on F <sup>2</sup>

$R1 = 0.0496$  for 3244  $F_o > 4\text{sig}(F_o)$  and 0.0966 for all 5234 data  
 $wR2 = 0.0974, \text{Goof} = S = 0.908$   
 Largest difference peaks: +0.77, -0.51 e<sup>-3</sup>

containing the decavanadate polyanion ( $V_{10}O_{28}^{6-}$ , as noted by Hughes *et al.* (2005), definitely illustrates the bipartite nature of mineral structures, as described by Hawthorne (1983). In his work, Hawthorne recognized two parts of complex mineral structures: 1) the *structural unit*, the anionic portion of the structure that contains higher-valence bonds, and 2) the *interstitial complex*, the cationic portion of the structure, which contains lower-valence bonds, typically between alkaline and alkaline earth cations and ( $H_2O$ ), (OH), and Cl groups. Using Hawthorne's (1983) observations,

TABLE 4. FRACTIONAL COORDINATES AND EQUIVALENT DISPLACEMENT PARAMETERS OF ATOMS IN HUGHESITE

Site	x	y	z	$U_{eq}$
V1	0.19664(7)	0.07252(7)	0.53427(5)	0.0125(2)
V2	0.00684(8)	-0.01910(7)	0.70657(5)	0.0140(2)
V3	0.05702(8)	-0.24605(7)	0.51040(5)	0.0130(2)
V4	0.13793(8)	0.29976(7)	0.72602(6)	0.0159(2)
V5	0.23092(8)	-0.15303(7)	0.33568(6)	0.015(2)
O1	0.0777(3)	-0.3380(3)	0.5906(2)	0.0205(7)
O2	0.0306(3)	-0.1114(3)	0.7861(2)	0.0218(7)
O3	0.2935(3)	0.2256(3)	0.6399(2)	0.0152(6)
O4	0.1426(3)	0.1546(3)	0.7872(2)	0.0160(6)
O5	0.0639(3)	-0.3000(3)	0.2426(2)	0.0164(6)
O6	0.3388(3)	0.0267(3)	0.4679(2)	0.0163(6)
O7	0.1205(3)	0.1691(3)	0.4334(2)	0.0116(6)
O8	0.3853(3)	-0.1811(3)	0.2887(2)	0.0239(7)
O9	0.1756(3)	-0.0537(3)	0.6175(2)	0.0119(6)
O10	0.2318(3)	-0.2436(3)	0.4451(2)	0.0155(6)
O11	-0.0937(3)	-0.3713(3)	0.3912(2)	0.0153(6)
O12	-0.1796(3)	0.0251(3)	0.7324(2)	0.0164(6)
O13	0.0236(3)	-0.0972(3)	0.4164(2)	0.0123(6)
O14	0.2603(3)	0.4354(3)	0.8177(2)	0.0273(7)
Na1	1/2	0	0	0.0138(6)
Na2	0.0840(2)	-0.23409(19)	0.91567(14)	0.045(1)
Al1	1/2	1/2	1/2	0.0308(7)
O15	0.3401(6)	-0.2340(5)	0.8678(4)	0.047(1)
O16	-0.1577(5)	-0.2284(4)	0.9817(3)	0.0361(9)
O17	0.2394(5)	-0.0098(4)	1.0568(3)	0.0343(9)
O18	0.1335(6)	-0.3768(5)	1.0298(3)	0.042(1)
O19	0.3240(4)	0.3649(4)	0.3938(3)	0.0219(7)
O20	0.3641(4)	0.5526(4)	0.5967(3)	0.0225(7)
O21	0.4653(4)	0.6348(3)	0.4336(3)	0.0221(7)
O22	-0.0907(5)	-0.4258(4)	0.7443(3)	0.0314(9)
O23	0.4448(6)	0.1295(6)	0.8839(4)	0.054(1)
O24	0.3910(6)	-0.4946(6)	1.0844(5)	0.097(2)
O25	0.4448(6)	0.8361(4)	0.6853(3)	0.0339(9)
H15A	0.365(9)	-0.234(8)	0.816(6)	0.09(3)
H15B	0.395(11)	-0.276(10)	0.891(7)	0.14(4)
H16A	-0.229(6)	-0.292(5)	0.954(4)	0.02(1)
H16B	-0.147(5)	-0.209(5)	1.048(4)	0.02(1)
H17A	0.222(6)	-0.007(5)	1.119(4)	0.03(1)
H17B	0.209(6)	0.053(5)	1.054(4)	0.02(1)
H18A	0.117(8)	-0.347(7)	1.085(5)	0.06(2)
H18B	0.209(6)	-0.411(7)	1.042(6)	0.11(3)
H19A	0.264(6)	0.308(6)	0.404(4)	0.04(2)
H19B	0.269(5)	0.394(4)	0.353(3)	0.01(1)
H20A	0.289(5)	0.514(5)	0.590(3)	0.01(1)
H20B	0.385(6)	0.646(6)	0.638(4)	0.05(1)
H21A	0.531(6)	0.672(5)	0.408(4)	0.02(1)
H21B	0.385(6)	0.667(5)	0.433(4)	0.02(1)
H22A	-0.093(6)	-0.486(5)	0.754(4)	0.02(2)
H22B	0.018(11)	-0.409(9)	0.693(7)	0.17(4)
H23A	0.369(7)	0.140(7)	0.851(5)	0.07(3)
H23B	0.492(6)	0.131(5)	0.848(4)	0.02(2)
H24A	0.443(7)	-0.413(6)	1.054(5)	0.06(2)
H24B	0.414(7)	-0.554(6)	1.160(5)	0.08(2)
H25A	0.544(8)	0.873(7)	0.690(5)	0.07(2)
H25B	0.404(7)	0.877(6)	0.675(5)	0.03(2)

Schindler *et al.* (2000a, 2000b) described the nature of bonding between the two distinct parts of the structure. In the pascoite family of minerals (Table 1), the ( $V_{10}O_{28}^{6-}$ ) structural units are very similar. However, in rakovanite and gunterite, like many other decavanadates (Duraisamy *et al.* 2000), the ( $V_{10}O_{28}^{6-}$ ) groups are protonated. Minerals of the pascoite family vary more significantly in the composition and arrangement of the interstitial complexes. In all cases, the charge of the decavanadate polyanion is balanced by that of the interstitial complex. Below are the descriptions of the anhydrous, polyanion structural unit and the hydrated interstitial complex in hughesite. Bond-valence calculations, performed for each cation site, are presented in Table 5.

### Structural unit in hughesite

The decavanadate polyanion complex in hughesite is shown in Figure 6. As found in all pascoite-family minerals (Swallow *et al.* 1966) and numerous synthetic vanadate compounds (Ferreira da Silva *et al.* 2002, Hughes *et al.* 2005), the complex is formed of ten distorted, edge-sharing octahedra. The vanadyl bond, defined by Schindler *et al.* (2000a), is a  $V^{5+}-O$  bond less

TABLE 5. SELECTED BOND-LENGTHS (Å), BOND VALENCE\* OF EACH BOND (vu) AND BOND-VALENCE SUMS

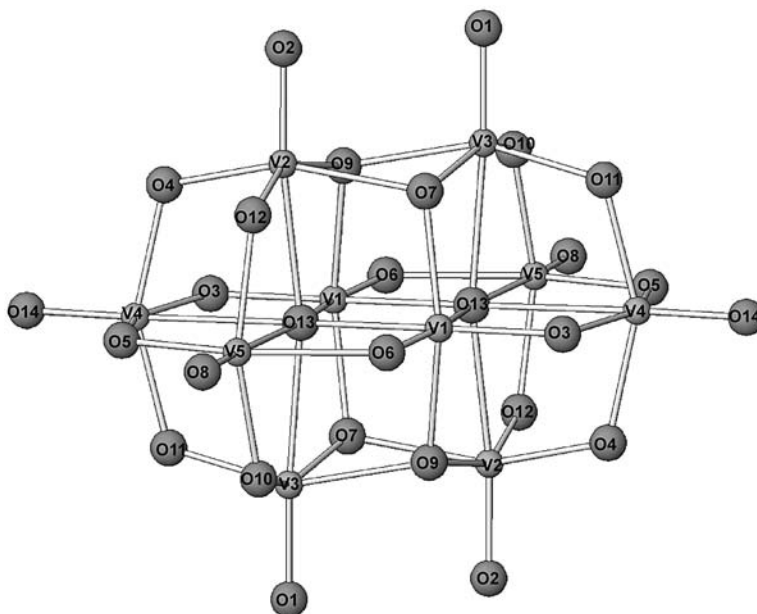
V1-	O3	1.717(3)	1.261	V3-	O1	1.601(3)	1.731
	O6	1.677(3)	1.405		O7	2.020(3)	0.558
	O7	1.973(3)	0.631		O9	2.015(3)	0.564
	O9	1.893(3)	0.784		O10	1.831(3)	0.928
	O13	2.080(3)	0.474		O11	1.822(3)	0.949
	O13	2.141(3)	0.401		O13	2.242(3)	0.306
Mean		1.9136	0.826	Mean		1.9215	0.839
Sum			4.956	Sum			5.035
V2-	O2	1.602(3)	1.721	V4-	O3	2.016(3)	0.563
	O4	1.823(3)	0.938		O4	1.876(3)	0.821
	O7	2.002(3)	0.583		O5	1.850(3)	0.881
	O9	2.017(3)	0.560		O11	1.887(3)	0.798
	O12	1.828(3)	0.936		O13	2.354(3)	0.226
	O13	2.256(3)	0.293		O14	1.595(3)	1.753
Mean		1.9222	0.839	Mean		1.9295	0.840
Sum			5.031	Sum			5.042
V5-	O5	1.828(3)	0.933	Al-	O19	1.882(3)	0.483
	O6	2.061(3)	0.498		O19	1.882(3)	0.483
	O8	1.597(3)	1.747		O20	1.889(3)	0.492
	O10	1.893(3)	0.785		O20	1.889(3)	0.492
	O12	1.871(3)	0.832		O21	1.876(3)	0.500
	O13	2.305(3)	0.257		O21	1.876(3)	0.500
Mean		1.9258	0.842	Mean		1.8827	0.492
Sum			5.052	Sum			2.95
Na1-	O15	2.489(5)	0.170	Na2-	O2	2.411(3)	0.214
	O15	2.489(5)	0.170		O15	2.384(5)	0.193
	O17	2.458(4)	0.240		O16	2.375(4)	0.208
	O17	2.458(4)	0.240		O17	2.461(4)	0.193
	O23	2.332(5)	0.158		O18	2.410(4)	0.140
	O23	2.332(5)	0.158		O22	2.529(4)	0.169
Mean		2.4251	0.189	Mean		2.4287	0.186
Sum			1.136	Sum			1.117

\* Bond-valence parameters from Brown & Altermatt (1985).



TABLE 6. ANISOTROPIC THERMAL PARAMETERS ( $\text{\AA}^2$ ) FOR NON-HYDROGEN ATOMS

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
V1	0.0099(3)	0.0133(4)	0.0161(4)	0.003(3)	0.0031(3)	0.0072(3)
V2	0.0185(4)	0.0141(4)	0.0123(4)	0.0059(3)	0.0045(3)	0.0073(3)
V3	0.0148(3)	0.0124(4)	0.0161(4)	0.0061(3)	0.0056(3)	0.0082(3)
V4	0.0174(4)	0.0141(4)	0.0157(4)	0.0045(3)	0.0034(3)	0.0039(3)
V5	0.0151(3)	0.0182(4)	0.0177(4)	0.0077(3)	0.0077(3)	0.0085(3)
O1	0.023(2)	0.021(2)	0.024(2)	0.009(1)	0.008(1)	0.014(1)
O2	0.030(2)	0.020(2)	0.022(2)	0.010(1)	0.009(1)	0.014(1)
O3	0.011(1)	0.015(2)	0.019(1)	0.002(1)	0.002(1)	0.008(1)
O4	0.020(1)	0.014(2)	0.014(1)	0.005(1)	0.003(1)	0.005(1)
O5	0.021(1)	0.014(2)	0.015(1)	0.008(1)	0.005(1)	0.005(1)
O6	0.010(1)	0.018(2)	0.020(2)	0.004(1)	0.004(1)	0.007(1)
O7	0.012(1)	0.010(1)	0.013(1)	0.003(1)	0.005(1)	0.005(1)
O8	0.025(2)	0.029(2)	0.026(2)	0.015(1)	0.012(1)	0.014(1)
O9	0.013(1)	0.011(1)	0.013(1)	0.003(1)	0.001(1)	0.007(1)
O10	0.017(1)	0.015(2)	0.017(1)	0.008(1)	0.007(1)	0.007(1)
O11	0.014(1)	0.014(2)	0.019(2)	0.005(1)	0.004(1)	0.006(1)
O12	0.017(1)	0.019(2)	0.016(1)	0.006(1)	0.007(1)	0.011(1)
O13	0.009(1)	0.015(2)	0.015(1)	0.003(1)	0.003(1)	0.009(1)
O14	0.027(2)	0.022(2)	0.026(2)	0.002(1)	0.001(1)	0.003(1)
Al1	0.0117(9)	0.011(1)	0.021(1)	0.0039(7)	0.0063(7)	0.0093(8)
Na1	0.031(2)	0.066(2)	0.042(2)	0.010(1)	0.008(1)	0.024(2)
Na2	0.036(1)	0.033(1)	0.027(1)	0.0100(9)	0.0066(8)	0.0149(9)
O15	0.054(3)	0.054(3)	0.044(3)	0.023(2)	0.021(2)	0.019(2)
O16	0.045(2)	0.040(3)	0.020(2)	0.009(2)	0.011(2)	0.007(2)
O17	0.044(2)	0.039(2)	0.029(2)	0.021(2)	0.017(2)	0.015(2)
O18	0.061(3)	0.049(3)	0.028(2)	0.029(2)	0.015(2)	0.017(2)
O19	0.016(2)	0.020(2)	0.029(2)	-0.001(1)	0.001(1)	0.015(2)
O20	0.015(2)	0.018(2)	0.033(2)	0.001(1)	0.012(1)	0.007(2)
O21	0.018(2)	0.020(2)	0.038(2)	0.008(1)	0.012(1)	0.021(2)
O22	0.040(2)	0.024(2)	0.036(2)	0.011(2)	0.011(2)	0.018(2)
O23	0.037(2)	0.102(4)	0.050(3)	0.034(3)	0.019(2)	0.048(3)
O24	0.057(3)	0.077(4)	0.147(6)	0.009(3)	-0.004(3)	0.041(4)
O25	0.032(2)	0.027(2)	0.041(2)	0.008(2)	0.005(2)	0.011(2)

FIG. 6. The  $(V_{10}O_{28})^{6-}$  decavanadate group in hughesite.

than 1.74 Å in length. Each vanadium-bearing octahedron in hughesite contains one vanadyl bond except for the V1 octahedron, which contains two. In the V2–V5 octahedra, the vanadyl bond is *trans* to the long V–O bond, and the remaining four bonds are approximately equal in length. This bond topology is characteristic of the decavanadate group observed in pascoite-family minerals (Hughes *et al.* 2008).

In hughesite, O2, an exterior atom of the polyanion complex bonds to Na2 of the interstitial complex, whereas the other exterior oxygen atoms of the decavanadate complex bond to the interstitial complex through hydrogen bonding. Of particular interest in the decavanadate group is the presence of one “interior” oxygen atom that exhibits a six-coordinated bonded geometry, as noted by Hughes *et al.* (2002). Oxygen

atom O13 bonds to six vanadium atoms, which is a curious coordination for oxygen in general, even more unusual where bonded to a pentavalent cation. Table 8 presents a bond-valence analysis of the O13 atom of the decavanadate complex. As observed in each V-bearing octahedron, the O13–V bond is the longest bond in the polyhedra, and as such it has the lowest valence in the polyhedra. The bond-valence sum for O13 is 1.957 *vu*. Thus, although O13 has an atypical coordination, the applicability of the valence-matching principle is maintained.

#### The interstitial complex in hughesite

The interstitial complex, the hydrated portion of the atomic arrangement, is composed of two separate components. First is the Na<sub>3</sub>(OH<sub>2</sub>)<sub>12</sub>O<sub>2</sub> trimer (Fig. 7b). The trimer consists of two separate cation sites: M1 and M2. Both sites are occupied by Na. The second part of the interstitial complex is the Al(OH<sub>2</sub>)<sub>6</sub> monomer (Fig. 7a), which resides at the center of the unit cell. The monomer sits roughly in the *a*–*b* plane and is surrounded by four decavanadate groups, bonding solely to terminal oxygen atoms of the decavanadate groups through hydrogen bonding. Hughesite is unique in the pascoite family, and atypical among complex bipartite mineral structures (Hawthorne 1983), in that the interstitial complex contains Al as well as an alkali, Na. The arrangement of the anhydrous structural units, linked by components of the interstitial complex in hughesite, is shown in Figure 8. The two components of the interstitial complex are separated and not directly bonded to each other, but the sum of the charges on the two balances the 6<sup>−</sup> charge of that structural unit. All of the oxygen atoms in the interstitial complex form parts of H<sub>2</sub>O molecules; thus the interstitial complex is fully hydrated. Atoms O24 and O25 are connected to the remainder of the structure solely through hydrogen bonding.

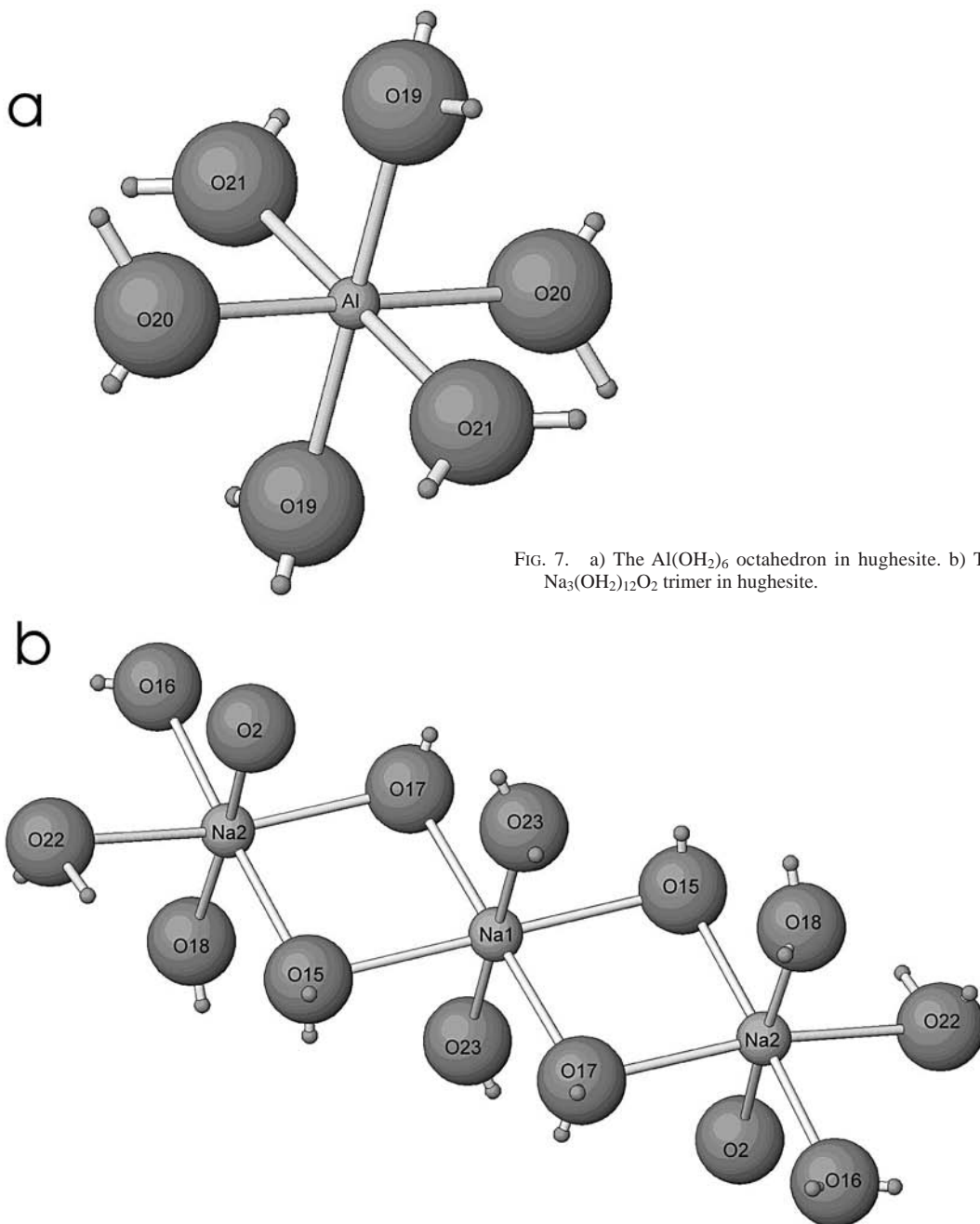
TABLE 7. POWDER X-RAY-DIFFRACTION PATTERN OF HUGHESITE

<i>l</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>l</i> <sub>rel</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>l</i> <sub>obs</sub>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>calc</sub>	<i>l</i> <sub>rel</sub>	<i>h</i>	<i>k</i>	<i>l</i>
100	12.243	12.130	100	0	0	0	11	2.7721	2.7731	3	2	3	1
30	9.408	9.502	25	0	0	0			2.7611	8	1	2	2
28	8.994	8.984	28	0	0	1			2.7511	1	1	1	4
38	8.246	8.237	36	1	0	0			2.7380	1	2	0	4
15	7.561	7.615	9	1	0	0	23	2.7244	2.7266	3	3	1	2
		7.332	4	1	0	0			2.7216	1	1	3	3
		6.543	1	0	0	1			2.7089	2	3	1	1
14	6.450	6.428	9	1	0	1			2.6479	1	0	3	4
		6.223	1	1	0	1			2.5627	1	1	4	1
		6.065	1	0	0	2			2.5575	1	1	3	4
3	6.093	6.053	1	0	0	2	8	2.5461	2.5518	1	0	1	5
		5.769	2	1	1	1			2.5232	1	3	2	2
7	5.722	5.502	4	1	1	0			2.4914	1	3	1	3
5	5.491	5.476	2	1	0	2	3	2.3569	2.3543	2	1	2	3
		4.7341	3	1	2	0			2.3188	1	2	0	5
5	4.7355	4.5559	1	1	1	2			2.2993	1	3	2	3
		4.5069	2	0	0	2	6	2.2994	2.2946	1	3	0	4
		4.4922	1	0	0	2			2.2461	1	0	4	4
5	4.5067	4.4902	2	1	1	1	10	2.2271	2.2290	1	1	4	4
		4.2336	3	0	0	3			2.2256	2	1	3	5
6	4.2422	3.9220	1	1	2	1			2.2101	2	1	3	2
		3.9073	4	2	0	1			2.1811	1	0	3	3
4	3.7645	3.7758	4	1	2	2	1	2.1212	2.1228	1	4	1	2
		3.6229	1	1	0	3			2.0682	1	2	4	4
		3.6130	2	2	0	2			2.0530	1	4	2	2
7	3.5993	3.5992	3	2	1	1	9	2.0487	2.0522	3	0	4	5
		3.4636	2	1	0	3			2.0276	1	1	2	4
		3.3545	2	1	2	3			2.0236	6	4	1	3
18	3.3535	3.3523	6	2	1	2	14	2.0195	2.0212	5	1	4	5
		3.2829	3	1	0	3			1.9923	1	2	2	3
		3.2622	1	0	0	3			1.9632	2	1	3	3
5	3.2456	3.2355	1	1	2	1	12	1.9548	1.9424	2	4	2	3
		3.2334	1	1	0	3			1.9043	1	4	1	0
		3.2138	1	2	2	2	6	1.8903	1.8926	2	2	3	2
10	3.0722	3.0668	5	1	0	4			1.8894	1	4	1	4
		3.0500	1	2	0	3	4	1.8323	1.7965	1	1	5	5
		3.0325	1	0	0	4	1	1.7176	1.7196	1	2	3	3
		2.9948	1	0	0	3	4	1.6619	1.6777	1	3	3	5
		2.9914	2	1	0	3			1.6673	1	2	3	7
7	2.9179	2.9177	4	1	3	3			1.6633	1	1	5	6
		2.8944	1	2	2	1	1	1.6298	1.6327	1	4	5	2
8	2.8774	2.8842	3	2	2	2	2	1.6041	1.5901	1	5	1	1
		2.8688	1	3	1	1			1.5626	1	1	6	2
		2.8106	1	3	0	1			1.5612	1	2	1	7
		2.7906	2	2	2	3	7	1.5589	1.5520	1	2	4	5
									1.5511	1	5	1	0

TABLE 8. BOND VALENCE OF EACH BOND (*vu*) AND BOND-VALENCE SUM OF THE SIX-COORDINATED O13 ATOM OF THE DECAVANADATE COMPLEX

O13	Bond length (Å)	Valence ( <i>vu</i> )
V1	2.080(3)	0.474
V1_1	2.141(3)	0.401
V2	2.256(3)	0.293
V3	2.242(3)	0.306
V4	2.354(3)	0.226
V5	2.305(3)	0.257
Sum		1.957
Average	2.2297	0.326

Bond-valence parameters from Brown & Altermatt (1985).



## ACKNOWLEDGEMENTS

We thank Jim Fisher, general mine superintendent, Denison mines, for allowing us to obtain specimens for study, and Dr. Andy Sommer of Miami University for

use of the Raman microscope. We also thank Michael Schindler and Bob Martin for their careful reviews of this manuscript. This work was partially supported by NSF grants EAR-0409435 and EAR-0952298 and by the John Jago Trelawney Endowment to the Mineral

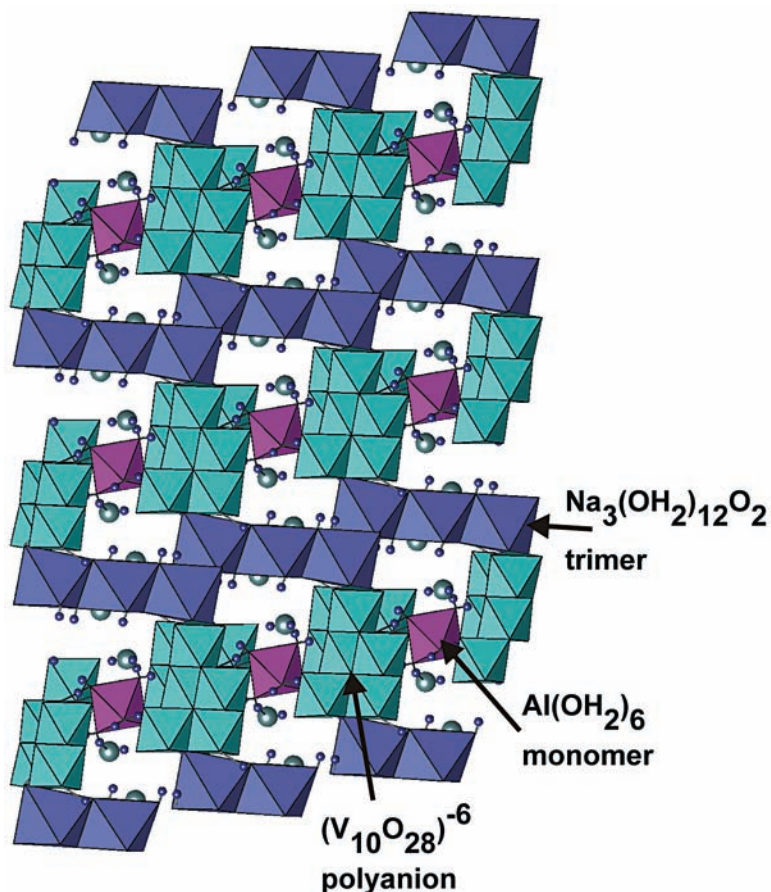


FIG. 8. Polyhedral representation of the hughesite structure viewed along [010].

Sciences Department of the Natural History Museum of Los Angeles County.

#### REFERENCES

- 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.
- BRUKER AXS, INC. (2000): SHELXTL v.6.14 Software Package. Madison, Wisconsin, U.S.A.
- BRUKER AXS, INC. (2003): SaintPlus v.6.45 Software Package. Madison, Wisconsin, U.S.A.
- COLOMBO, F., BAGGIO, R. & KAMPF, A.R. (2011): The crystal structure of the elusive huemulite. *Can. Mineral.* **49**, 849-864.
- DURASAMY, T., RAMANAN, A. & VITTAL, J.J. (2000): Novel self-assembled decavanadate clusters forming 1D molecular chains and 2D molecular arrays:  $[\text{HMTA}-\text{H}\dots\text{H}_2\text{O}][\text{HMTA}-\text{CH}_2\text{OH}][\text{H}_3\text{V}_{10}\text{O}_{28}\{\text{NaH}_2\text{O}\}_4]\cdot 4\text{H}_2\text{O}$  and  $[\text{Na}_2(\text{H}_2\text{O})_{10}][\text{H}_3\text{V}_{10}\text{O}_{28}\{\text{Na}(\text{H}_2\text{O})_2\}]\cdot 3\text{H}_2\text{O}$ . *Crystal Engineering* **3**, 237-250.
- FERREIRA DA SILVA, J.L., MINAS DA PIEDADE, F.M. & DUARTE, T.M. (2002): Decavanadates: a building-block for supramolecular assemblies. *Inorganica Chimica Acta* **356**, 222-242.
- FISCHER, R.P. & HILPERT, L.S. (1952): Geology of the Uravan mineral belt. *U.S. Geol. Surv., Bull.* **988-A**, 1-13.
- HAWTHORNE, F.C. (1983): Graphical enumeration of polyhedral clusters. *Acta Crystallogr.* **A39**, 724-736.
- HUGHES, J.M., SCHINDLER, M. & FRANCIS, C.A. (2005): The  $C2/m$  disordered structure of pascoite,  $\text{Ca}_3[\text{V}_{10}\text{O}_{28}]\cdot 17\text{H}_2\text{O}$ : bonding between structural units and interstitial complexes

- in compounds containing the  $[V_{10}O_{28}]^{6-}$  decavanadate polyanion. *Can. Mineral.* **43**, 1379-1386.
- HUGHES, J.M., SCHINDLER, M., RAKOVAN, J. & CURETON, F.E. (2002): The crystal structure of hummerite,  $KMg(V_5O_{14}) \cdot 8H_2O$ : bonding between the  $[V_{10}O_{28}]$  structural units and the  $\{K_2Mg_2(H_2O)_{16}\}$  interstitial complex. *Can. Mineral.* **40**, 1429-1435.
- HUGHES, J.M., WISE, W.S., GUNTER, M.E., MORTON, J.P. & RAKOVAN, J. (2008): Lasalite,  $Na_2Mg_2[V_{10}O_{28}] \cdot 20H_2O$ , a new decavanadate mineral species from the Vanadium Queen mine, La Sal district, Utah: description, atomic arrangement, and relationship to the pascoite group of minerals. *Can. Mineral.* **46**, 1365-1372.
- KAMPF, A.R., HUGHES, J.M., MARTY, J., GUNTER, M.E. & NASH, B. (2011): Rakovanite,  $Na_3\{H_3[V_{10}O_{28}]\} \cdot 15H_2O$ , a new pascoite family mineral with a protonated decavanadate polyanion: crystal structure and descriptive mineralogy. *Can. Mineral.* **49**, 889-898.
- KAMPF, A.R., HUGHES, J.M., MARTY, J. & NASH, B. (2011): Gunterite,  $Na_4(H_2O)_{16}(H_2V_{10}O_{28}) \cdot 6H_2O$ , a new mineral with a doubly-protonated decavanadate polyanion: crystal structure and descriptive mineralogy. *Can. Mineral.* **49**, 1243-1251.
- KAMPF, A.R. & STEELE, I.M. (2008): Magnesioascoite, a new member of the pascoite group: description and crystal structure. *Can. Mineral.* **46**, 679-686.
- PAAR, W.H., COOPER, M.A., HAWTHORNE, F.C., MOFFATT, E., GUNTER, M.E., ROBERTS, A.C. & DUNN, P.J. (2009): Braithwaiteite,  $NaCu_5(TiSb)O_2(AsO_4)_4[AsO_3(OH)]_2(H_2O)_8$ , a new mineral species from Laurani, Bolivia. *Can. Mineral.* **47**, 947-952.
- POUCHOU, J.-L. & PICOIR, F. (1991): Quantitative analysis of homogeneous or stratified microvolumes applying the model "PAP." In *Electron Probe Quantitation* (K.F.J. Heinrich & D.E. Newbury, eds.). Plenum Press, New York, N.Y. (31-75).
- SCHINDLER, M., HAWTHORNE, F.C. & BAUR, W.H. (2000a): A crystal chemical approach to the composition and occurrence of vanadium minerals. *Can. Mineral.* **38**, 1443-1456.
- SCHINDLER, M., HAWTHORNE, F.C. & BAUR, W.H. (2000b): Crystal-chemical aspects of vanadium: polyhedral geometries, characteristic bond valences, and polymerization of  $(VO_n)$  polyhedra. *Chem. Mater.* **12**, 1248-1259.
- SHAWE, D.R. (2011): Uranium–vanadium deposits of the Slick Rock district, Colorado. *U.S. Geol. Surv., Prof. Pap.* **576-F**.
- SWALLOW, A.G., AHMED, F.R. & BARNES, W.H. (1966): The crystal structure of pascoite,  $Ca_3V_{10}O_{28} \cdot 17H_2O$ . *Acta Crystallogr.* **21**, 397-405.
- WEEKS, A.D. (1956): Mineralogy and oxidation of the Colorado Plateau uranium ores. In *Contributions to the Geology of Uranium and Thorium* (L.R. Page, ed.). *U.S. Geol. Surv., Prof. Pap.* **300**, 181-193.

Received May 26, 2011, revised manuscript accepted November 19, 2011.

