HYDROPASCOITE, Ca₃(V₁₀O₂₈)·24H₂O, A NEW DECAVANADATE MINERAL FROM THE PACKRAT MINE, MESA COUNTY, COLORADO

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Abstract

Hydropascoite, Ca₃(V₁₀O₂₈)-24H₂O, is a new mineral species (IMA2016-032) discovered in the Packrat mine, near Gateway, Mesa County, Colorado. It occurs as blades up to 2 mm in length on asphaltum associated with montroseite- and corvusite-bearing sandstone. Hydropascoite is dark yellow green, with a pistachio green streak, vitreous luster, Mohs hardness of ca. 1½, brittle tenacity, irregular fracture, and one perfect cleavage on {001}. Density (meas.) is 2.38(2) g/cm³. Hydropascoite is biaxial (-), with α 1.730(5), β 1.780(5), γ 1.790(5) (white light); 2V (meas.) = 54.1(6)°, and extreme dispersion. The optical orientation is $X \wedge \mathbf{a} \approx 10^\circ$, $Z \wedge \mathbf{c}^* \approx 20^\circ$. Hydropascoite is pleochroic, with X=bluish green, Y=orange, Z = yellowish green; X > Z > Y. Electron probe microanalysis gave the empirical formula $(Ca_{2.69}Na_{0.30})_{\Sigma_2.99}$ $(H_{0.31}V^{5+}_{10}O_{28})$ ·24H₂O, based on O = 52. Hydropascoite is triclinic, $P\overline{I}$, a 10.08700(19), b 11.0708(2), c 21.8112(15) Å, α 94.112(7)°, β 96.053(7)°, γ 116.398(8)°, V 2150.2(2) Å³, and Z=2. The strongest four lines in the diffraction pattern are [d in $\text{\AA}(I)(hkl)$]: 8.92(100)(110), 10.70(31)(002), 9.77(28)(010), and 7.4539(22)(102). The atomic arrangement of hydropascoite was solved and refined to $R_1 = 0.0488$ for 8187 independent reflections with $F > 4\sigma F$. The structural unit in hydropascoite is the $[V_{10}O_{28}]^{6-}$ decavanadate group; charge balance in the structure is maintained by the $[Ca_3 \cdot 24H_2O]^{6+}$ interstitial complex. The three Ca polyhedra in the interstitial complex are not polymerized. Linkage between the structural unit and the components of the interstitial complex is principally by hydrogen bonding. In addition to the extensive hydrogen bonding, three oxygen atoms of the structural unit bond directly to calcium atoms of the interstitial complex. The mineral is named to recognize its chemical and structural similarity to pascoite, Ca₃(V₁₀O₂₈)·17H₂O, and its higher H₂O content.

Keywords: hydropascoite, new mineral species, decavanadate, crystal structure, Packrat mine, Mesa County, Colorado, USA.

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INTRODUCTION

The Uravan mineral belt (Fischer & Hilpert 1952, Chenoweth 1981) sits astride the Colorado-Utah border. The mineralized belt consists of bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter & Gualtieri 1965, Shawe 2011). In the formation of these deposits, uranium and vanadium were transported as oxyanions of U^{6+} and V^{4+} in weakly alkaline, moderately reducing, CO2-rich ground water, and deposited largely as uraninite, $U^{4+}O_2$, and montroseite, $V^{3+}O(OH)$, where the solutions encountered more reducing conditions by contacting carbonaceous material and H₂S (Evans & Garrels 1958, Hostetler & Garrels 1962). Later exposure of these deposits to more oxidizing near-surface aqueous solutions, which in turn reacted with sulfides to make the solutions more acidic, resulted in a variety of secondary phases. One group of secondary phases of particular interest are those that contain the $[V_{10}O_{28}]^{6-}$ decavanadate cluster as a structural unit.

Pascoite, $Ca_3(V_{10}O_{28})\cdot 17H_2O$, contains the $[V_{10}O_{28}]^{6-}$ decavanadate cluster, and until recently was one of only a few known minerals containing that structural unit. However, the recent exploration of uranium-vanadium mines of the Colorado Plateau has revealed many new minerals that contain the decavanadate cluster and variants of that cluster. The complete list of pascoite-group minerals and their

literature references is given in Table 1, which illustrates that 11 new decavanadate minerals have been described since 2008, all coming from the Colorado Plateau. In addition to the previously known $[V_{10}O_{28}]^{6-}$ decavanadate cluster, new phases have been discovered that contain protonated decavanadate groups, $[H_x V_{10}O_{28}]^{(6-x)-}$, and mixed-valence decavanadate groups, $[(V^{4+}_x V^{5+}_{10-x})O_{28}]^{(6+x)-}$, the latter two variants of the decavanadate cluster being previously unknown in nature.

To these previously discovered pascoite-group minerals, we now add the new mineral hydropascoite, $Ca_3(V_{10}O_{28})\cdot 24H_2O$. The name hydropascoite is based upon the compositional and structural similarity of the mineral to pascoite, $Ca_3(V_{10}O_{28})\cdot 17H_2O$, and the fact that it has 41% more H_2O groups. Hydropascoite was approved by the Commission on New Minerals, Nomenclature, and Classification of the International Mineralogical Association (IMA 2016–032). The holotype specimen of hydropascoite is deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, USA; catalogue number 66267.

OCCURRENCE

Hydropascoite was found in the main tunnel level of the Packrat mine, near Gateway, Mesa County, Colorado, USA (38°38′51.28′′N 109°02′49.77′′W). The Packrat mine is near the northern end of the Uravan mineral belt. The original claims, Packrat #1

Mineral species	Ideal formula*	First reference; best structure reference
	Decavanadates: [V1	0 ₀ O ₂₈] ⁶⁻
Huemulite	[Na ₄ Mg(H ₂ O) ₂₄] [V ₁₀ O ₂₈]	Gordillo et al. (1966), Colombo et al. (2011)
Hughesite	[Na ₃ Al(H ₂ O) ₂₂] [V ₁₀ O ₂₈]	Rakovan <i>et al.</i> (2011)
Hummerite	[K ₂ Mg ₂ (H ₂ O) ₁₆] [V ₁₀ O ₂₈]	Weeks <i>et al</i> . (1951), Hughes <i>et al</i> . (2002)
Hydropascoite	[Ca ₃ (H ₂ O) ₂₄] [V ₁₀ O ₂₈]	This work
Kokinosite	[Na ₂ Ca ₂ (H ₂ O) ₂₄] [V ₁₀ O ₂₈]	Kampf <i>et al</i> . (2014a)
Lasalite	[Na ₂ Mg ₂ (H ₂ O) ₂₀] [V ₁₀ O ₂₈]	Hughes <i>et al</i> . (2008)
Magnesiopascoite	[MgCa ₂ (H ₂ O) ₁₆] [V ₁₀ O ₂₈]	Kampf & Steele (2008)
Pascoite	[Ca ₃ (H ₂ O) ₁₇] [V ₁₀ O ₂₈]	Hillebrand et al. (1914), Hughes et al. (2005)
Postite	[MgAl ₂ (OH) ₂ (H ₂ O) ₂₇] [V ₁₀ O ₂₈]	Kampf <i>et al</i> . (2012)
Schindlerite	[Na ₂ (NH ₄) ₄ (H ₂ O) ₁₀] [V ₁₀ O ₂₈]	Kampf et al. (2013a), Kampf et al. (2016b)
Wernerbaurite	[Ca ₂ (NH ₄) ₂ (H ₂ O) ₁₆] [V ₁₀ O ₂₈]	Kampf <i>et al</i> . (2013a), Kampf <i>et al</i> . (2016b)
	Protonated Decavanadates:	[H _x V ₁₀ O ₂₈] ^{(6-x)-}
Gunterite	[Na ₄ (H ₂ O) ₂₂] [H ₂ V ₁₀ O ₂₈]	Kampf <i>et al</i> . (2011a)
Rakovanite	[Na ₃ (H ₂ O) ₁₅] [H ₃ V ₁₀ O ₂₈]	Kampf <i>et al.</i> (2011b)
	Mixed-Valence Decavanadates: [(\	V ⁴⁺ _x V ⁵⁺ _{10-x})O ₂₈] ^{(6+x)-}
Nashite	[Na ₃ Ca ₂ (H ₂ O) ₂₄] [(V ⁴⁺ V ⁵⁺ ₉)O ₂₈]	Kampf <i>et al.</i> (2013b)
Bluestreakite	$[K_4Mg_2(H_2O)_{14}] [V^{4+}_2V^{5+}_8O_{28}]$	Kampf <i>et al</i> . (2014b)

TABLE 1. DECAVANADATE FAMILY OF MINERALS

* Expressed as the interstitial complex and the structural unit.



FIG. 1. Hydropascoite crystals (green) with pascoite (orange); FOV 0.85 mm across.

and #2, were filed in 1943, but mining apparently did not commence until the early 1950s. The mine remained in operation until 1990 and consists of several miles of drifts and numerous stopes. The mine site was reclaimed in 2002 and was reopened in 2007 for further exploration. It is currently inactive. The sample of the new mineral was collected by two of the authors (JM and TPR) on October 1, 2015.

The mineral is very rare. It has so far been found on only one specimen. It occurs on asphaltum associated with montroseite- and corvusite-bearing sandstone. Other secondary minerals found in close association with hydropascoite are pascoite, rossite/metarossite, and sherwoodite. Other secondary minerals found in the mine include andersonite, ansermetite, calcite, dickthomssenite, gatewayite (Kampf *et al.* 2016a), gypsum, hewettite, hummerite, kegginite (Kampf *et al.* 2017a), lasalite, magnesiopascoite, martyite, mesaite (Kampf *et al.* 2017b), morrisonite (Kampf *et al.* 2016a), munirite, navajoite, packratite (Kampf *et al.* 2016a), pharmacolite, picropharmacolite, postite, rösslerite, selenium, uranopilite, vanarsite (Kampf *et al.* 2016a), and other potentially new minerals, currently under study.

The new mineral forms from the oxidation of montroseite-corvusite assemblages in a moist environment. Mining operations have exposed unoxidized and



FIG. 2. Crystal drawing of hydropascoite, clinographic projection in non-standard orientation (a vertical).

oxidized phases. Under ambient temperatures and generally oxidizing near-surface conditions, water reacts with pyrite and an unknown As-bearing phase (perhaps arsenopyrite) to form aqueous solutions with relatively low pH. The various secondary vanadate phases that form depend upon prevailing Eh-pH conditions and the presence of other cations (*e.g.*, Na⁺, Ca²⁺, Mn²⁺, Pb²⁺).

PHYSICAL AND OPTICAL PROPERTIES

Hydropascoite crystals form as blades, flattened on {001} and elongated on [100], up to 2 mm in length, exhibiting the forms {001}, {010}, {011}, {101}, $\{10\overline{1}\}$, and $\{1\overline{1}0\}$ (Figs. 1 and 2). The megascopic color is dark yellow-green and the streak is pistachio green. The mineral is non-fluorescent. Crystals are transparent with a vitreous luster and exhibit brittle tenacity, perfect cleavage on {001}, and irregular fracture. The mineral has a Mohs hardness of about 1½, based upon scratch tests. The density measured by flotation in a mixture of methylene iodide and toluene is 2.38(2) g/cm³; the density calculated using the empirical formula is 2.324 g/cm³, and using the ideal formula is 2.332 g/cm³. At room temperature, hydropascoite is very slowly soluble in H₂O and immediately soluble in dilute HCl.

Hydropascoite is biaxial (–), with α 1.730(5), β 1.780(5), γ 1.790(5), determined in white light; the 2*V* determined from extinction data collected with a spindle stage and analyzed with the program EX-

Constituent	Mean	Range	S.D.	Normalized	Standard
Na₂O (wt.%)	0.78	0.17-2.20	0.44	0.62	albite
CaO	12.62	9.10-13.90	1.28	10.02	diopside
V ₂ O ₅	76.10	66.25-82.63	3.68	60.44	V metal
H ₂ O	10.50*			28.92 [†]	
Total	100.00			100.00	

TABLE 2. CHEMICAL ANALYSES OF HYDROPASCOITE

* By difference

⁺ Based upon the crystal structure with V = 10 and O = 52 *apfu*.

CALIBR (Gunter *et al.* 2004) is 54.1(6)°; the calculated 2V is 47.1°. Dispersion is extreme based on anomalous extinction colors, but the sense could not be determined because the unfavorable orientation of the acute bisectrix, nearly parallel to the direction of elongation of the blades, prevented conoscopic observation. The partially determined optical orientation is $X \wedge \mathbf{a} \approx 10^\circ$, $Z \wedge \mathbf{c}^* \approx 20^\circ$. Hydropascoite is pleochroic, with X = bluish green, Y = orange, Z = yellowish green; X > Z > Y.

CHEMICAL COMPOSITION OF HYDROPASCOITE

Analyses (26 points from 11 crystals) were performed at the University of Utah using a Cameca SX-50 electron microprobe with four wavelengthdispersive spectrometers and Probe for EPMA software. Analytical conditions were 15 keV accelerating voltage, 10 nA beam current, and a beam diameter of $10-15 \mu$ m. Counting times were 20 s on peak and 20 s on background for each element. Some analytical spots had a variable time-dependent increase in Ca and V that was monitored and corrected by fitting a loglinear curve to the data and extrapolating back to the "time-zero" intensity. Raw X-ray intensities were corrected for matrix effects with a $\phi p(Z)$ algorithm (Pouchou & Pichoir 1991).

Partial dehydration of the very H₂O-rich crystals occurs when they are subjected to an ultimate vacuum of 2×10^{-5} torr for approximately five minutes during vacuum deposition of the conductive carbon coat. This also results in a change in megascopic color of the crystals from green to orange. The H₂O loss results in higher concentrations for the remaining constituents than is to be expected for the fully hydrated phase. The crystals dehydrated to a formula of (ideally) Ca₃(V₁₀ O₂₈)·7H₂O (Table 2); a search of data bases revealed no such known compound. Garrels & Larsen (1959), in a study of the geochemistry and mineralogy of ores from the Colorado Plateau, noted that the pascoite minerals tend to dehydrate to a powder ("after some weeks"), and we posit that hydropascoite dehydrates to a powder under vacuum as well. Indeed, we have observed such dehydration in natural samples of hydropascoite; our experience suggests that dehydration in decavanadates results in a general degradation of the crystal structures and not in a rearrangement of structural units to yield a structure with long-range order.

Additional loss of H₂O from the sample evidently did not occur in the high vacuum of the electron microprobe chamber, as there were no systematic increases in concentration of constituents measured over the two-hour analytical session. Repeated analyses (five) of the same spot on one sample also produced no changes in elemental concentrations other than a 50% decrease in Na. There was also no observed damage from the electron beam. Based upon the difference from the measured oxide total and 100%, the sample lost approximately 60% of its structural water under vacuum. Because insufficient material was available for a direct determination of H₂O, it was calculated based upon the structure determination. The analyzed constituents were then normalized to provide a total of 100% when combined with the calculated H₂O. Analytical data are given in Table 2. From those data, the empirical formula (based on 52 O *apfu*) is $(Ca_{2.69}Na_{0.30})_{\Sigma_{2.99}}(H_{0.31}V^{5+}_{10}O_{28})$. $24H_2O$. The simplified structural formula is $Ca_3(V_{10})$ O₂₈)·24H₂O, which requires CaO 11.14, V₂O₅ 60.23, H₂O 28.63, total 100.00 wt.%.

The Gladstone-Dale compatibility index $1 - (K_P/K_C)$ for the empirical formula is -0.012, in the superior range (Mandarino 2007).

CRYSTAL STRUCTURE: EXPERIMENTAL

Single-crystal X-ray studies were carried out using a Rigaku R-Axis Rapid II curved imaging-plate microdiffractometer with monochromatized MoK α radiation. X-ray powder diffraction data were recorded using the same diffractometer and radiation. A Gandolfi-like motion on the φ and ω axes was used to randomize the sample for the powder measurements. Observed *d* values and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). Data (in Å) are given in Table 3. TABLE 3. CALCULATED POWDER X-RAY DIFFRACTION PATTERN (d in Å) FOR HYDROPASCOITE

I _{obs}	$d_{\rm obs}$		$d_{\rm calc}$	I _{calc}	hkl	I _{obs}	$d_{ m obs}$		$d_{\rm calc}$	I _{calc}	hkl
31	10.70		10.7483	49	002			(2.9142	4	1 3 5
28	9.77		9.8281	46	010	10	2 000		2.8953	7	1 1 7
100	8.92		8.9415	100	110	12	2.090		2.8881	2	301
			8.7343	4	101				2.8831	6	205
			7.8297	2	101				2.8417	3	226
20	7.75		7.7878	25	0 1 2	5	2.794		2.7911	2	116
22	7.41		7.4539	26	102				2.7778	4	$\overline{2}$ $\overline{2}$ 1
00	0.04	5	6.9875	27	112				2.7757	2	107
20	6.91	Ì	6.7656	12	1 1 2	0	0 700	6	2.7339	3	207
7	0.44	6	6.1960	4	0 1 3	9	2.732	ĺ	2.7238	4	1 3 2
(6.11	Ì	6.0615	8	103				2.7181	3	1 4 1
			5.6833	2	113				2.6950	3	242
8	5.496		5.4903	6	120			(2.6880	2	1 4 2
			5.4546	2	013	8	2.675	{	2.6770	6	135
		(5.1087	5	111				2.6641	2	3 1 4
10	5.030	{	5.0154	3	$\overline{2}$ 10	4	0 500	5	2.5930	2	316
		l	4.9354	5	0 2 1	4	2.583	Ì	2.5710	4	$\overline{2}$ 27
			4.7748	3	2 1 1				2.5047	2	2 1 7
0	4 700	5	4.7576	2	<u>1</u> <u>1</u> 3	4	0.405	5	2.5020	3	028
8	4.729	Ì	4.7391	3	$\bar{2}$ 12	4	2.495	Ì	2.4791	3	218
			4.5801	4	112	F	0 460	5	2.4699	2	3 1 5
10	1 100	5	4.5408	6	1 1 4	5	2.403)	2.4531	3	035
10	4.402)	4.4713	5	014				2.2865	2	3 1 6
			4.3274	2	213			(2.2718	2	036
			3.6625	2	130	5	2.263	{	2.2597	2	137
			3.5613	2	132				2.2554	5	4 02
			3.5574	2	$\overline{2}$ $\overline{1}$ 1	4	2.228		2.2281	4	038
			3.5497	2	114				2.1708	2	328
10	2 5 2 4	5	3.5171	2	106	7	0.450	5	2.1616	3	327
13	3.324	Ì	3.5134	11	230	1	2.156	Ì	2.1560	2	1 4 2
			3.3825	2	2 1 3				2.1389	3	1 4 7
8	3.355		3.3612	6	232				2.1337	2	306
			3.2570	2	032			(2.0096	4	1 4 8
			3.1073	2	2 1 5	8	2.0039	{	2.0050	2	328
		(3.0715	3	216				2.0026	3	4 1 5
7	3.069	{	3.0490	3	0 1 7				1.9808	2	052
		l	3.0413	5	025			(1.9731	3	4 37
			3.0308	2	206	8	1.9668	ł	1.9635	4	0 5 3
		(2.9886	2	302				1.9602	2	426
14	2.988	ł	2.9805	6	330			1	1.9374	2	4 28
		l	2.9759	5	300				1.9362	2	147
						9	1.9310	ł	1.9345	2	512
									1.9336	3	511
									1.9308	3	$0\bar{5}4$

Chemical formula Crystal size Crystal system	$\begin{array}{l} Ca_{3}H_{48}O_{52}V_{10}\\ 30\times90\times130~\mu\text{m}\\ \text{triclinic} \end{array}$	
Space group	P1	
Unit cell dimensions	a = 10.08700(19) Å b = 11.0708(2) Å	$\alpha = 94.112(7)^{\circ}$ $\beta = 96.053(7)^{\circ}$
	c = 21.8112(15) Å	$\gamma = 116.398(8)^{\circ}$
Volume	2150.2(2) Å ³	/ = 110.000(0)
Ζ	2	
Density (calculated)	2.332 g/cm ³	
Absorption coefficient	2.566 mm ⁻¹	
<i>F</i> (000)	1508	
Theta range	2.99 to 27.44°	
Index ranges	$-13 \le h \le 13, -14 \le k \le 13$	\leq 12, –28 \leq ℓ \leq 28
Reflections collected	36754	
Independent reflections	9782 [<i>R</i> _{int} = 0.039]	
Completeness to 27.44°	99.5%	
Max. and min. transmission	0.9270 and 0.7310	
Refinement method	Full-matrix least-squares	on F ²
Function minimized	$\Sigma w (F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9782 / 72 / 730	
Goodness-of-fit on F ²	1.069	
Final R indices	8187 data; $F_{o} > 4\sigma F$ all data	$R_1 = 0.0488, wR_2 = 0.1383$ $R_1 = 0.0583, wR_2 = 0.1438$
Largest diff. peak and hole	2.275 and –1.094 eÅ ^{–3}	

TABLE 4. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR HYDROPASCOITE

TABLE 5. ATOM COORDINATES AND EQUIVALENT ISOTROPIC ATOMIC DISPLACEMENT PARAMETERS (Å²) FOR HYDROPASCOITE

Atom	x/a	y/b	z/c	$U_{\rm eq}$	Atom	x/a	y/b	z/c	$U_{\rm eq}$
V1	0.16388(8)	0.49631(7)	0.00189(3)	0.01382(15)	OW6	0.5785(4)	0.5361(4)	0.25920(19)	0.0332(9)
V2	0.85498(8)	0.24079(7)	0.94275(3)	0.01585(16)	H6A	0.491(4)	0.483(6)	0.266(3)	0.04
V3	0.92766(8)	0.32503(7)	0.08574(3)	0.01542(16)	H6B	0.569(7)	0.518(7)	0.2217(14)	0.04
V4	0.21973(8)	0.58107(8)	0.14479(3)	0.01813(17)	OW7	0.4851(5)	0.5677(5)	0.38018(19)	0.0353(9)
V5	0.91531(9)	0.58628(8)	0.14078(4)	0.01859(17)	H7A	0.549(6)	0.542(7)	0.388(3)	0.042
V6	0.10026(8)	0.44718(8)	0.46174(4)	0.01800(17)	H7B	0.448(7)	0.563(7)	0.412(2)	0.042
V7	0.84736(9)	0.24654(9)	0.53196(4)	0.02327(18)	OW8	0.5461(5)	0.8688(4)	0.4006(2)	0.0403(10)
V8	0.13397(9)	0.47523(9)	0.60958(4)	0.02138(18)	H8A	0.483(6)	0.841(6)	0.424(3)	0.048
V9	0.80603(9)	0.22238(9)	0.38815(4)	0.02408(19)	H8B	0.597(7)	0.950(3)	0.414(3)	0.048
V10	0.38144(9)	0.67560(9)	0.54033(4)	0.02555(19)	OW9	0.6899(5)	0.8189(4)	0.21966(19)	0.0352(9)
Ca1	0.71772(10)	0.92913(9)	0.03622(4)	0.0208(2)	H9A	0.718(8)	0.767(6)	0.203(3)	0.042
Ca2	0.52033(11)	0.72454(11)	0.30301(5)	0.0245(2)	H9B	0.662(8)	0.849(6)	0.191(2)	0.042
Ca3	0.21419(11)	0.11006(10)	0.27334(5)	0.0241(2)	OW10	0.4822(5)	0.9072(5)	0.2639(2)	0.0399(10)
01	0.0323(3)	0.5368(3)	0.06272(13)	0.0147(6)	H10A	0.573(3)	0.960(6)	0.279(3)	0.048
02	0.0302(3)	0.3141(3)	0.01215(14)	0.0157(6)	H10B	0.438(6)	0.938(7)	0.284(3)	0.048
O3	0.2129(3)	0.6789(3)	0.98862(13)	0.0146(6)	OW11	0.2603(4)	0.6503(5)	0.31414(18)	0.0396(10)
O4	0.8387(3)	0.3948(3)	0.13598(15)	0.0198(6)	H11A	0.218(7)	0.645(7)	0.3460(18)	0.047
O5	0.2310(3)	0.4566(3)	0.93896(15)	0.0193(6)	H11B	0.198(6)	0.644(8)	0.287(2)	0.047
O6	0.9771(4)	0.2411(3)	0.88789(14)	0.0196(6)	OW12	0.7834(5)	0.8314(5)	0.3541(2)	0.0416(10)
07	0.1032(3)	0.3896(3)	0.13661(14)	0.0167(6)	H12A	0.744(8)	0.800(7)	0.384(2)	0.05
O8	0.7147(3)	0.2498(3)	0.88650(14)	0.0191(6)	H12B	0.811(8)	0.782(6)	0.339(3)	0.05
O9	0.0935(4)	0.6114(3)	0.18974(14)	0.0191(6)	OW13	0.2768(6)	-0.0092(5)	0.1938(2)	0.0467(11)

TABLE 5. CONTINU	JED
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Atom	x/a	y/b	z/c	$U_{\rm eq}$	Atom	x/a	y/b	z/c	$U_{\rm eq}$
O10	0.2957(3)	0.5301(3)	0.06378(15)	0.0208(7)	H13A	0.250(8)	-0.087(3)	0.181(4)	0.056
011	0.8257(4)	0.6244(4)	0.18981(16)	0.0277(8)	H13B	0.352(6)	0.042(5)	0.183(4)	0.056
O12	0.7764(4)	0.0833(3)	0.95643(16)	0.0226(7)	OW14	0.3458(4)	0.0202(4)	0.34168(18)	0.0313(8)
O13	0.3604(4)	0.6095(4)	0.19671(16)	0.0254(7)	H14A	0.295(6)	-0.036(5)	0.362(2)	0.038
014	0.8437(4)	0.1632(3)	0.09119(15)	0.0213(7)	H14B	0.416(5)	0.080(5)	0.366(2)	0.038
O15	0.1255(3)	0.5987(3)	0.53320(15)	0.0195(6)	OW15	0.9635(4)	0.0765(4)	0.2299(2)	0.0337(9)
O16	0.0681(4)	0.3434(3)	0.53045(16)	0.0217(7)	H15A	0.897(6)	0.015(4)	0.243(3)	0.04
017	0.0836(4)	0.5769(3)	0.41116(15)	0.0213(7)	H15B	0.957(7)	0.146(4)	0.238(3)	0.04
O18	0.0328(4)	0.3126(4)	0.40469(15)	0.0244(7)	OW16	0.2331(6)	0.2230(6)	0.1774(2)	0.0517(12)
O19	0.2897(4)	0.5143(4)	0.47163(16)	0.0238(7)	H16A	0.199(9)	0.224(8)	0.211(2)	0.062
O20	0.6178(4)	0.2007(4)	0.39829(17)	0.0281(8)	H16B	0.201(9)	0.266(8)	0.157(3)	0.062
O21	0.1656(4)	0.6299(4)	0.65632(15)	0.0255(7)	OW17	0.4886(4)	0.2601(4)	0.28010(19)	0.0328(8)
O22	0.8203(4)	0.1411(4)	0.45897(17)	0.0270(7)	H17A	0.537(7)	0.271(6)	0.3142(18)	0.039
O23	0.3271(4)	0.5414(4)	0.59389(16)	0.0267(8)	H17B	0.505(7)	0.335(4)	0.272(3)	0.039
O24	0.6594(4)	0.2315(4)	0.52193(17)	0.0271(8)	OW18	0.0897(6)	0.0880(5)	0.3687(2)	0.0488(12)
O25	0.8435(4)	0.1485(4)	0.58355(18)	0.0326(8)	H18A	0.045(8)	0.013(4)	0.348(3)	0.059
O26	0.7757(5)	0.1050(4)	0.33277(19)	0.0370(9)	H18B	0.091(9)	0.071(7)	0.4051(15)	0.059
O27	0.5555(4)	0.7183(5)	0.5400(2)	0.0388(10)	OW19	0.0484(6)	-0.1383(5)	0.2747(2)	0.0532(13)
O28	0.1267(4)	0.3747(4)	0.66096(17)	0.0328(8)	H19A	0.088(8)	-0.096(7)	0.248(3)	0.064
OW1	0.8392(5)	0.8522(5)	0.9676(2)	0.0362(9)	H19B	-0.032(5)	-0.200(6)	0.258(3)	0.064
H1A	0.876(7)	0.870(7)	0.935(2)	0.043	OW20	0.2418(6)	0.3299(5)	0.3079(3)	0.0539(13)
H1B	0.866(8)	0.798(6)	0.981(3)	0.043	H20A	0.316(5)	0.401(5)	0.322(4)	0.065
OW2	0.9283(5)	0.9520(4)	0.10571(19)	0.0381(10)	H20B	0.176(6)	0.346(7)	0.294(4)	0.065
H2A	0.941(8)	0.884(5)	0.109(3)	0.046	OW21	0.9818(6)	0.3319(5)	0.2525(2)	0.0433(11)
H2B	0.928(8)	0.978(6)	0.1420(17)	0.046	H21A	0.996(8)	0.379(7)	0.225(2)	0.052
OW3	0.5775(4)	0.9284(4)	0.1199(2)	0.0354(9)	H21B	0.940(8)	0.359(7)	0.275(3)	0.052
НЗА	0.545(7)	0.969(6)	0.097(3)	0.043	OW22	0.4798(8)	0.4093(8)	0.1278(3)	0.0739(17)
H3B	0.498(5)	0.865(5)	0.125(3)	0.043	H22A	0.450(11)	0.426(10)	0.093(2)	0.089
OW4	0.6108(5)	0.6978(5)	0.0573(3)	0.0618(16)	H22B	0.511(11)	0.355(9)	0.116(4)	0.089
H4A	0.656(7)	0.657(7)	0.065(4)	0.074	OW23	0.5982(6)	0.1749(6)	0.1691(3)	0.0617(15)
H4B	0.523(4)	0.652(7)	0.059(4)	0.074	H23A	0.657(8)	0.170(10)	0.199(3)	0.074
OW5	0.4918(5)	0.8416(6)	0.9670(2)	0.0564(15)	H23B	0.537(7)	0.183(9)	0.190(3)	0.074
H5A	0.408(5)	0.793(7)	0.972(3)	0.068	OW24	0.1645(11)	0.1424(12)	0.5121(4)	0.134(4)
H5B	0.495(8)	0.860(8)	0.9319(19)	0.068	H24A	0.192(14)	0.126(14)	0.481(4)	0.161
					H24B	0.084(9)	0.081(11)	0.513(7)	0.161

Note: U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

The Rigaku CrystalClear software package was used for processing the single-crystal structure data, including the application of numerical and empirical absorption corrections, the latter with a multi-scan approach using ABSCOR (Higashi 2001). The structure was solved by direct methods using SIR2011 (Burla *et al.* 2012). SHELXL-2013 (Sheldrick 2015) was used for refinement of the structure. All nonhydrogen atoms were refined with anisotropic displacement parameters. Difference Fourier syntheses located all H-atom positions, which were then refined with soft restraints of 0.82(3) Å on the O–H distances and 1.30(3) Å on the H–H distances and with the U_{eq} of each H set to 1.2 times that of the donor O atom. Data collection and refinement details are given in Table 4, atom coordinates and displacement parameters in Table 5, and selected bond distances and bondvalence sums in Table 6. A table of structure factors, a CIF file, and a table of anisotropic displacement parameters are available from the Depository of Unpublished Data on the MAC website [document Hydropascoite CM54-2 10.3749/canmin.1600069].

Atomic Arrangement of Hydropascoite

In decavanadate-bearing minerals, the structure consists of two distinct parts, a rigid structural unit (the decavanadate group) and an interstitial complex, as suggested by Schindler & Hawthorne (2001) for minerals with structural units of higher bond valence. The interstitial complex acts as the cationic portion of

TABLE 6. SELECTED BOND DISTANCES (Å) AND BOND VALENCES (vu) IN HYDROPASCOITE

Bond	Distance	BV	Bond	Distance	BV	Bond	Distance	BV
V1–O10	1.684(3)	1.38	V6–O19	1.696(3)	1.34	Ca1–OW5	2.348(4)	0.36
V1–O5	1.706(3)	1.30	V6–O18	1.699(3)	1.32	Ca1–OW1	2.366(4)	0.34
V1–O3	1.908(3)	0.75	V6–O16	1.921(3)	0.73	Ca1–OW2	2.379(4)	0.33
V1–O2	1.910(3)	0.75	V6–O17	1.926(3)	0.72	Ca1–OW4	2.398(5)	0.31
V1–O1	2.131(3)	0.41	V6–O15	2.114(3)	0.43	Ca1–OW3	2.423(4)	0.29
V1–O1	2.174(3)	0.37	V6–O15	2.119(3)	0.43	Ca1–O12	2.457(3)	0.27
Mean, sum	1.919	4.96	Mean, sum	1.913	4.97	Ca1–O14	2.464(3)	0.26
						Mean, sum	2.405	2.16
V2–O12	1.629(3)	1.60	V7–O25	1.610(4)	1.68			
V2–O6	1.805(3)	0.99	V7–O24	1.815(4)	0.97	Ca2–OW10	2.415(4)	0.30
V2–O8	1.815(3)	0.97	V7–O22	1.825(4)	0.94	Ca2–OW11	2.421(4)	0.29
V2–O2	2.014(3)	0.57	V7–O16	2.002(3)	0.58	Ca2–OW7	2.443(4)	0.28
V2–O3	2.016(3)	0.56	V7–O17	2.026(3)	0.55	Ca2–OW12	2.466(4)	0.26
V2–O1	2.225(3)	0.32	V7–O15	2.246(3)	0.30	Ca2–OW8	2.486(4)	0.25
Mean, sum	1.917	5.01	Mean, sum	1.921	5.02	Ca2–OW6	2.555(4)	0.20
						Ca2–O13	2.561(3)	0.20
V3–O14	1.626(3)	1.61	V8–O28	1.620(4)	1.64	Ca2–OW9	2.581(4)	0.19
V3–07	1.795(3)	1.02	V8–O21	1.808(4)	0.99	Mean, sum	2.491	1.97
V3–O4	1.818(3)	0.96	V8–O23	1.832(3)	0.92			
V3–O2	2.023(3)	0.55	V8–O17	1.995(3)	0.60	Ca3–OW20	2.379(5)	0.33
V3–O3	2.023(3)	0.55	V8–O16	2.021(3)	0.55	Ca3–OW13	2.407(4)	0.30
V3–O1	2.224(3)	0.32	V8–O15	2.247(3)	0.30	Ca3–OW14	2.438(4)	0.28
Mean, sum	1.918	5.01	Mean, sum	1.921	5.00	Ca3–OW15	2.457(4)	0.27
						Ca3–OW16	2.496(5)	0.24
V4–O13	1.615(3)	1.66	V9–O26	1.608(4)	1.69	Ca3–OW17	2.497(4)	0.24
V4–O9	1.815(3)	0.97	V9–O20	1.844(4)	0.90	Ca3–OW19	2.508(5)	0.23
V4–O8	1.894(3)	0.78	V9–022	1.866(4)	0.84	Ca3–OW18	2.513(5)	0.23
V4–07	1.895(3)	0.78	V9–O21	1.888(4)	0.79	Mean, sum	2.462	2.12
V4–O10	2.134(3)	0.41	V9–O18	2.025(4)	0.55			
V4–O1	2.314(3)	0.25	V9–O15	2.322(3)	0.25			
Mean, sum	1.945	4.85	Mean, sum	1.926	5.02			
V5–O11	1.617(3)	1.65	V10-027	1.603(4)	1.72			
V5–O9	1.886(3)	0.80	V10–O20	1.842(4)	0.90			
V5–O4	1.897(3)	0.78	V10-024	1.879(4)	0.81			
V5–O6	1.921(3)	0.73	V10-023	1.879(4)	0.81			
V5–O5	2.036(3)	0.53	V10–O19	2.036(4)	0.53			
V5–O1	2.335(3)	0.24	V10–O15	2.314(3)	0.25			
Mean, sum	1.949	4.73	Mean, sum	1.926	5.02			

Bond-valence parameters from Brese & O'Keeffe (1991).

the structure, and must balance the anionic charge of the decavanadate group. The interstitial complex invariably contains H₂O molecules in addition to the cations necessary to achieve the charge balance; in the decavanadate minerals discovered to date, those cations or cationic complexes are Na, Mg, Al, K, Ca, and NH₄ (Table 1). In the decavanadate group *sensu stricto*, $[V_{10}O_{28}]^{6-}$, the interstitial complex must provide six positive charges to balance that anionic charge; in the case of hydropascoite, that charge is balanced by the interstitial complex of $[Ca_3(H_2O)_{24}]^{6+}$. In the protonated decavanadates, with a structural unit of $[H_xV_{10}O_{28}]^{(6-x)-}$, the charge requirement of the interstitial complex is modified by the protonation of the decavanadate group, and thus that group must supply (6 - x) positive charges, with x equal to the number of H atoms in the decavanadate group. Finally, in the mixed-valence decavanadates, $[(V^{4+}_xV^{5+}_{10-x})O_{28}]^{(6+x)-}$, the charge of the interstitial complex is modified by the amount of reduced V^{5+} , and thus the interstitial complex must supply (6 + x) positive charges, with x equal to the amount of decavanadate V^{5+} reduced to V^{4+} . The three groups of decavanadates are summarized in Table 1.



FIG. 3. Crystal structure of hydropascoite viewed along [010]. The unit is cell shown by dashed lines. VO_6 octahedra are orange, Ca atoms are light blue spheres, O atoms of H_2O groups are large white spheres, and H atoms are small white spheres.

The atomic arrangement of hydropascoite is depicted in Figure 3. As shown there, the decavanadate group is linked to the [Ca₃(H₂O)₂₄]⁶⁺ interstitial complex predominantly by hydrogen bonding between the oxygen atoms of the decavanadate group and the hydrogen atoms of the interstitial H₂O. As noted in Table 6, the [Ca1O₂(H₂O)₅] polyhedron shares two oxygen atoms with the decavanadate group (O12, O14) and the central Ca1 cation also bonds to five independent H_2O molecules. The $[Ca2O(H_2O)_7]$ polyhedron shares one oxygen atom with the structural unit (O13) and Ca2 also bonds to seven H₂O molecules, and in the $[Ca3(H_2O)_8]$ polyhedron all the bonds are to H₂O molecules, and there are no direct linkages to the decavanadate group. There are no shared H₂O molecules or oxygen atoms between Ca polyhedra and thus no polymerization of the Ca polyhedra in the interstitial complex.

The ideal formula of hydropascoite is $Ca_3(V_{10} O_{28})$ ·24H₂O, which is consistent with all V being 5+. Phases containing the (V⁵⁺₁₀O₂₈) unit are typically orange. The green color of hydropascoite suggests that intervalence charge transfer (IVCT) between V⁴⁺ and V⁵⁺ in the decavanadate structural unit is occurring. Indeed, examination of the bond-valence sums for hydropascoite (Table 5) suggests that the adjacent vanadium sites V4 and V5 may contain 15–25% V⁴⁺. As noted above, mixed-valence decavanadates typically have interstitial units with total positive charge >6 in order to balance the charge of the mixedvalence decavanadate clusters, which have a negative charge >6. The most likely mechanism for attaining charge balance in hydropascoite is to protonate (add some H to) the decavanadate group, $[H_r V_{10} O_{28}]^{(6-x)-}$. Samples of pascoite, typically vellow-orange in color and putatively with all V in the 5+ valence state, are known that are green in color, suggesting reduction of even a small amount of V⁵⁺ to V⁴⁺ in the decavanadate group can change the color. As noted above, hydropascoite changes from green to orange under vacuum, suggesting that the small amount of V4+ in the decavanadate cluster is oxidized to V⁵⁺ and the H bound to the decavanadate cluster is lost to balance that oxidation. Note that H in the protonated decavanadate units typically cannot be located in structure refinements.

In summary, hydropascoite is added to the growing list of decavanadate minerals found in the Uravan mineral belt. With the $[V_{10}O_{28}]^{6-}$ structural unit as the anion portion of the structure, the anionic charge is balanced, as in pascoite, with three Ca ions in the interstitial complex, but differing from pascoite in the extent of hydration of the interstitial group.

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References

- BRESE, N.E. & O'KEEFFE, M. (1991) Bond-valence parameters for solids. Acta Crystallographica B47, 192–197.
- BURLA, M.C., CALIANDRO, R., CAMALLI, M., CARROZZINI, B., CASCARANO, G.L., GIACOVAZZO, C., MALLAMO, M., MAZZONE, A., POLIDORI, G., & SPAGNA, R. (2012) *SIR2011*: a new package for crystal structure determination and refinement. *Journal of Applied Crystallography* 45, 357–361.
- CARTER, W.D. & GUALTIERI, J.L. (1965) Geology and uranium–vanadium deposits of the La Sal quadrangle, San Juan County, Utah, and Montrose County, Colorado. United States Geological Survey Professional Paper 508, 82 pp.
- CHENOWETH, W.L. (1981) The uranium-vanadium deposits of the Uravan mineral belt and adjacent areas, Colorado and Utah. *In* Western Slope Colorado, New Mexico Geological Society Guidebook (R.C. Epis & J.F. Callender, eds.). 32nd Field Conference, October 1981 (165–170).
- COLOMBO, F., BAGGIO, R., & KAMPF, A.R. (2011) The crystal structure of the elusive huemulite. *Canadian Mineralogist* **49**, 849–864.
- EVANS, H.T., JR. & GARRELS, R.M. (1958) Vanadium in aqueous solution as applied to the interpretation of the Colorado Plateau ore deposits. *Geochimica et Cosmochimica Acta* 15, 131–149.
- FISCHER, R.P. & HILPERT, L.S. (1952) Geology of the Uravan mineral belt. *United States Geological Survey Bulletin* **988-A**, 13 pp.
- GARRELS, R.M. & LARSEN, E.S., III. (1959) Geochemistry and Mineralogy of the Colorado Plateau Uranium Ores. United States Geological Survey Professional Paper 320, 102 pp.
- GORDILLO, C.E., LINARES, E., TOUBES, R.O., & WINCHELL, H. (1966) Huemulite, $Na_4MgV_{10}O_{28}$ ·24H₂O, a new hydrous sodium and magnesium vanadate from Huemul mine, Mendoza Province, Argentina. *American Mineralogist* **51**, 1–13.

- GUNTER, M.E., BANDLI, B.R., BLOSS, F.D., EVANS, S.H., SU, S.C., & WEAVER, R. (2004) Results from a McCrone spindle stage short course, a new version of EXCALIBR, and how to build a spindle stage. *Microscope* 52, 23–39.
- HIGASHI, T. (2001) ABSCOR. Rigaku Corporation, Tokyo, Japan.
- HILLEBRAND, W.F., MERWIN, H.E., & WRIGHT, F.E. (1914) Hewettite, metahewettite and pascoite, hydrous calcium vanadates. *Proceedings of the American Philosophical Society* 53(213), 31–54.
- HOSTETLER, P.B. & GARRELS, R.M. (1962) Transportation and Precipitation of uranium and vanadium at low temperatures, with special reference to sandstone-type uranium deposits. *Economic Geology* 57, 137–167.
- HUGHES, J.M., SCHINDLER, M., RAKOVAN, J., & CURETON, F.E. (2002) The crystal structure of hummerite, $KMg(V_5O_{14})^{\bullet}8H_2O$: bonding between the $[V_{10}O_{28}]^{6-}$ structural unit and the $\{K_2Mg_2(H_2O)_{16}\}^{6+}$ interstitial complex. *Canadian Mineralogist* **40**, 1429–1435.
- HUGHES, J.M., SCHINDLER, M., & FRANCIS, C.A. (2005) The C2/ m disordered structure of pascoite, Ca₃(V₁₀O₂₈)·17H₂O. Canadian Mineralogist 43, 1379–1386.
- HUGHES, J.M., WISE, W.S., GUNTER, M.E., MORTON, J.P., & RAKOVAN, J. (2008) Lasalite, Na₂Mg₂[V₁₀O₂₈]·20H₂O, 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. *Canadian Mineralogist* **46**, 1365–1372.
- KAMPF, A.R. & STEELE, I.M. (2008) Magnesiopascoite, a new member of the pascoite group: Description and crystal structure. *Canadian Mineralogist* 46, 679–686.
- KAMPF, A.R., HUGHES, J.M., MARTY, J., & NASH, B. (2011a) Gunterite, Na4(H₂O)₁₆(H₂V₁₀O₂₈)·6H₂O, a new mineral with a doubly-protonated decavanadate polyanion: Crystal structure and descriptive mineralogy. *Canadian Mineralogist* **49**, 1243–1251.
- KAMPF, A.R., HUGHES, J.M., MARTY, J., GUNTER, M.E., & NASH, B. (2011b) Rakovanite, Na₃{H₃[V₁₀O₂₈]}·15H₂O, a new species of the pascoite family with a protonated decvanadate polyanion. *Canadian Mineralogist* **49**, 889– 898.
- KAMPF, A.R., HUGHES, J.M., MARTY, J., & NASH, B.P. (2012) Postite, $Mg(H_2O)_6Al_2(OH)_2(H_2O)_8(V_{10}O_{28}) \cdot 13H_2O$, a new mineral species from the La Sal mining district, Utah: Crystal structure and descriptive mineralogy. *Canadian Mineralogist* **50**, 45–53.
- $\begin{array}{l} {\rm KAMPF, A.R., Hughes, J.M., MARTY, J., \& NASH, B.P. (2013a) \\ {\rm Wernerbaurite, } {[Ca(H_2O)_7]_2(H_2O)_2(H_3O)_2} \{V_{10}O_{28}\}, \\ {\rm and \ schindlerite, } {[Na_2(H_2O)_{10}](H_3O)_4} \{V_{10}O_{28}\}, \ the \\ {\rm first \ hydronium-bearing \ decavanadate \ minerals. \ Canadian \ Mineralogist \ 51, \ 297-312. \end{array} }$
- Kampf, A.R., Hughes, J.M., Marty, J., & Brown, F.H. (2013b) Nashite, Na_3Ca_2([V^{5+}_9V^{4+}_1]O_{28})\cdot 24H_2O, a new

mineral species from the Yellow Cat Mining District, Utah and the Slick Rock Mining District, Colorado: Crystal structure and descriptive mineralogy. *Canadian Mineralogist* **51**, 27–37.

- KAMPF, A.R., HUGHES, J.M., NASH, B.P., & MARTY, J. (2014a) Kokinosite, Na₂Ca₂(V₁₀O₂₈)·24H₂O, a new decavanadate mineral species from the St. Jude mine, Colorado: crystal structure and descriptive mineralogy. *Canadian Mineral*ogist 52, 15–25.
- KAMPF, A.R., HUGHES, J.M., MARTY, J., NASH, B.P., CHEN, Y.-S., & STEELE, I.M. (2014b) Bluestreakite, K₄Mg₂ (V⁴⁺₂V⁵⁺₈O₂₈)·14H₂O, a new mixed-valence decavanadate mineral from the Blue Streak Mine, Montrose County, Colorado: Crystal structure and descriptive mineralogy. *Canadian Mineralogist* **52**, 1007–1018.
- KAMPF, A.R., HUGHES, J.M., NASH, B.P., & MARTY, J. (2016a) Vanarsite, packratite, morrisonite, and gatewayite: Four new minerals containing the [As³⁺V^{4+,5+}₁₂As⁵⁺₆O₅₁] heteropolyanion, a novel polyoxometalate cluster. *Canadian Mineralogist* 54,145–162.
- KAMPF, A.R., HUGHES, J.M., NASH, B.P., MARTY, J., COOPER, M.A., HAWTHORNE, F.C., KARPENKO, V.Y., PAUTOV, L.A., & AGAKHANOV, A.A. (2016b) Revision of the formulas of wernerbaurite and schindlerite: Ammonium- rather than hydronium-bearing decavanadate minerals. *Canadian Mineralogist* 54, 555–558.
- KAMPF, A.R., HUGHES, J.M., NASH, B.P., & MARTY, J. (2017a) Kegginite, Pb₃Ca₃[AsV₁₂O₄₀(VO)]·20H₂O, a new mineral with an ε-isomer of the Keggin anion. *American Mineralogist* 102, 461–465.
- KAMPF, A.R., HUGHES, J.M., NASH, B.P., & MARTY, J. (2017b) Mesaite, CaMn²⁺₅(V₂O₇)₃·12H₂O, a new vanadate mineral from the Packrat mine, near Gateway, Mesa County, Colorado, USA. *Mineralogical Magazine* **81**, 319–327.

- MANDARINO, J.A. (2007) The Gladstone–Dale compatibility of minerals and its use in selecting mineral species for further study. *Canadian Mineralogist* 45, 1307–1324.
- POUCHOU, J.-L. & PICHOIR, 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 City, New York (31–75).
- RAKOVAN, J., SCHMIDT, G.R., GUNTER, M., NASH, B., KAMPF, A.R., MARTY, J., & WISE, W.S. (2011) Hughesite, Na₃Al(V₁₀O₂₈)·22H₂O, a new member of the pascoite family of minerals from the Sunday mine, San Miguel County, Colorado. *Canadian Mineralogist* **49**, 1253– 1265.
- SCHINDLER, M. & HAWTHORNE, F.C. (2001) A bond-valence approach to the structure, chemistry, and paragenesis of hydroxyl-hydrated oxysalt minerals. I. Theory. *Canadian Mineralogist* 39, 1225–1242.
- SHAWE, D.R. (2011) Uranium-vanadium deposits of the Slick Rock district, Colorado. United States Geological Survey, Professional Paper 576-F, 80 pp., 20 plates.
- SHELDRICK, G.M. (2015) Crystal structure refinement with SHELXL. Acta Crystallographica C71, 3–8.
- WEEKS, A.D., CISNEY, E.A., & SHERWOOD, A.M. (1951) Hummerite and montroseite, two vanadium minerals from Montrose County, Colorado. Proceedings of the 31st Annual Meeting. *American Mineralogist* 36, 326– 327.
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