

## MARTYITE, A NEW MINERAL SPECIES RELATED TO VOLBORTHITE: DESCRIPTION AND CRYSTAL STRUCTURE

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### ABSTRACT

Martyite,  $Zn_3(V_2O_7)(OH)_2 \cdot 2H_2O$ , a new mineral species from the Blue Cap mine, near La Sal, San Juan County, Utah, U.S.A., is named for its discoverer, Joe Marty, of Salt Lake City, Utah, who is also responsible for the discovery of three other new minerals from the same area. Martyite formed from post-mining leaching and oxidation of V–U oxide replacements of organic matter. It occurs as thin yellow-orange to red-orange plates and flakes with a rounded or irregular outline, up to 0.01 mm thick and 1 mm long, typically in irregularly intergrown mats and rosette-like clusters. The mineral has a pale yellow-orange streak, an adamantine luster, a Mohs hardness of about 3, and two cleavages, {001} perfect and {110} good. The measured density is 3.37(3) g/cm<sup>3</sup>, and the calculated density is 3.375 g/cm<sup>3</sup>. It is optically uniaxial (+),  $\omega$  1.797(3),  $\epsilon$  1.806(3), and distinctly pleochroic: O >> E. Electron-microprobe analyses provided: ZnO 46.93, CoO 2.39, CaO 0.58, MgO 0.03, V<sub>2</sub>O<sub>5</sub> 39.47, H<sub>2</sub>O 12.06 (calc.), total 101.46% which, based on V = 2 apfu and sufficient H for charge balance, yields  $(Zn_{2.66}Co_{0.15}Ca_{0.05})(V_2O_7)(OH)_{1.72} \cdot 2.23H_2O$ . Martyite is hexagonal,  $P\bar{3}m1$ ,  $a$  6.0818(4),  $c$  7.1793(10) Å,  $V$  229.97(4) Å<sup>3</sup>,  $Z$  = 1. Its atomic structure [ $R_1$  = 1.84% for  $F_o > 4\sigma(F_o)$ ] consists of edge-sharing sheets of Zn–O octahedra parallel to (001) linked in the  $c$  direction by divanadate ( $V_2O_7$ ) groups. The open space in the resulting framework is occupied by H<sub>2</sub>O molecules. The structure of martyite is topologically identical to that of volborthite,  $Cu_3(V_2O_7)(OH)_2 \cdot 2H_2O$ . The Jahn–Teller distortion of one of the two non-equivalent Cu–O octahedra in volborthite results in a monoclinic symmetry. These minerals may have applications as molecular sieve materials.

*Keywords:* martyite, new mineral species, crystal structure, divanadate, volborthite group, Blue Cap mine, Utah.

### SOMMAIRE

La martyite,  $Zn_3(V_2O_7)(OH)_2 \cdot 2H_2O$ , nouvelle espèce minérale découverte à la mine Blue Cap, près de La Sal, comté de San Juan, au Utah, est nommée en l'honneur Joe Marty, de Salt Lake City, qui est aussi responsable de la découverte de trois autres espèces dans la même région. La martyite est apparue tardivement, après les exploitations minières, comme résultat de lessivage et de l'oxydation d'assemblages d'oxydes V–U remplaçant la matière organique. Elle se présente en minces plaquettes et flocons jaune-orange ou rouge-orange ayant un contour arrondi ou irrégulier, atteignant une épaisseur de 0.01 mm et une longueur de 1 mm, typiquement en nattes intercroisées et en groupements en rosette. Le minéral possède une rayure jaune-orange pâle, un éclat adamantin, une dureté de Mohs d'environ 3, et deux clivages, {001} parfait et {110} bon. La dureté mesurée est 3.37(3) g/cm<sup>3</sup>, et la densité calculée est 3.375 g/cm<sup>3</sup>. La martyite est optiquement uniaxe (+),  $\omega$  1.797(3),  $\epsilon$  1.806(3), et distinctement pléochroïque: O >> E. Les analyses avec une microsonde électronique ont donné: ZnO 46.93, CoO 2.39, CaO 0.58, MgO 0.03, V<sub>2</sub>O<sub>5</sub> 39.47, H<sub>2</sub>O 12.06 (calc.), pour un total de 101.46%, ce qui a mené à  $(Zn_{2.66}Co_{0.15}Ca_{0.05})(V_2O_7)(OH)_{1.72} \cdot 2.23H_2O$  en supposant deux atomes de V par formule unitaire et assez de H pour assurer l'électronneutralité. La martyite est hexagonale,  $P\bar{3}m1$ ,  $a$  6.0818(4),  $c$  7.1793(10) Å,  $V$  229.97(4) Å<sup>3</sup>,  $Z$  = 1. Sa structure atomique [ $R_1$  = 1.84% pour  $F_o > 4\sigma(F_o)$ ] contient des feuillettes d'octaèdres Zn–O à arêtes partagées parallèles à (001), liés dans la direction  $c$  par des groupes de divanadate ( $V_2O_7$ ). Les trous dans la trame qui en résulte sont les sites de molécules de H<sub>2</sub>O. La structure de la martyite est topologiquement identique à celle de la volborthite,  $Cu_3(V_2O_7)(OH)_2 \cdot 2H_2O$ . La distorsion Jahn–Teller d'un des deux octaèdres Cu–O non-équivalents de la volborthite est la cause de sa symétrie monoclinique. Ces minéraux pourraient bien avoir des applications dans le domaine de tamis moléculaires.

(Traduit par la Rédaction)

*Mots-clés:* martyite, nouvelle espèce minérale, structure cristalline, divanadate, groupe de la volborthite, mine Blue Cap, Utah.

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## INTRODUCTION

Thanks to the recent collecting efforts of Joe Marty of Salt Lake City, Utah, several new vanadium minerals have been identified and described from the U–V deposits east of La Sal, Utah: dickthomssenite,  $\text{Mg}(\text{V}_2\text{O}_6) \cdot 7\text{H}_2\text{O}$  (Hughes *et al.* 2001), from the Firefly–Pigmy mine; lasalite,  $\text{Na}_2\text{Mg}_2(\text{V}_{10}\text{O}_{28}) \cdot 20\text{H}_2\text{O}$  (Hughes *et al.* 2008), from the Vanadium Queen mine; magnesiopascoite,  $\text{Ca}_2\text{Mg}(\text{V}_{10}\text{O}_{28}) \cdot 16\text{H}_2\text{O}$  (Kampf & Steele 2008), from the Blue Cap mine, and martyite,  $\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  (this study), also from the Blue Cap mine. Martyite is named for Joe Marty (born 1945), in recognition of his contributions to mineralogy. The new mineral and name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007–026). The two cotype specimens are housed in the mineral collection of the Natural History Museum of Los Angeles County (catalogue numbers 58610 and 58611).

## OCCURRENCE

Martyite occurs in the Blue Cap mine, about 15 km east of La Sal, San Juan County, Utah, U.S.A. ( $38^\circ 21' 14''\text{N}$ ,  $109^\circ 03' 39''\text{W}$ ), in association with gypsum, rossite, pyrite, montroseite and another new mineral species, magnesiopascoite (Kampf & Steele 2008) on a V–U oxide-replacement assemblage developed at the expense of organic material. All samples of martyite were recovered from a single isolated pillar in the mine. Other minerals identified from the mine are brochantite, calcite, coffinite, devilline, dickthomssenite, dolomite, lasalite, navajoite, sherwoodite, uraninite, uranopilite and zeunerite.

Uranium–vanadium mineralization in the mines of the area occurs in certain layers of the sandstone paleochannels in the Salt Wash and Brushy Basin members of the Morrison Formation (Carter & Gualtieri 1965). Carbonaceous material in these layers is considered to have created a reducing environment, which caused the precipitation of uranium and vanadium oxides (*e.g.*, uraninite, corvusite and montroseite) from solution. Martyite, magnesiopascoite and rossite appear to have formed from post-mining leaching and oxidation of vanadium oxides by circulating groundwater.

## PHYSICAL AND OPTICAL PROPERTIES

The mineral forms thin plates and flakes with the {001} form prominent. A poorly developed {110} form is in some cases observed; however, the plates usually exhibit a rounded or irregular outline. Thickness ranges from exceedingly thin to 0.01 mm, and maximum dimensions reach 1 mm. Thin flakes and plates typically form irregularly intergrown mats and rosette-like clus-

ters. Thicker plates are in some cases intergrown with the mats of flakes and may extend out from these mats as individuals. The mats of very thin flakes are bright yellow-orange, whereas coarser plates are red-orange if viewed on edge (Fig. 1).

The streak is pale yellow-orange. Crystals are transparent with an adamantine luster. Very thin flakes are slightly flexible, but coarser plates are brittle with a curved fracture. The Mohs hardness is about 3. There is one perfect cleavage on {001}, and one good cleavage on {110}. Crystals exhibit a curved fracture. The density measured by sink–float in Clerici solution is  $3.37(3) \text{ g/cm}^3$ , and that calculated from the empirical formula is  $3.375 \text{ g/cm}^3$ . Crystals rapidly dissolve in cold dilute HCl.

The mineral is optically uniaxial (+), with the following optical constants measured in sodium light (589 nm):  $\omega$  1.797(3),  $\epsilon$  1.806(3). The pleochroism is strong: O (red-orange)  $\gg$  E (yellow).

The Gladstone–Dale compatibility index,  $1 - (K_p/K_c)$  as defined by Mandarino (1981), provides a measure of the consistency among the average index of refraction, calculated density and chemical composition. For martyite, the compatibility index is 0.057, indicating good agreement among these data.

## CHEMICAL COMPOSITION

Quantitative chemical analyses were performed with an electron microprobe (wavelength-dispersive spectrometry, 15 kV, 25 nA, focused beam). Four analyses gave the following averages (and ranges): ZnO 46.93 (45.5–48.4), CoO 2.39 (1.26–2.97), CaO 0.58 (0.42–1.06), MgO 0.03 (0.01–0.03),  $\text{V}_2\text{O}_5$  39.47 (38.5–40.0),  $\text{H}_2\text{O}$  12.06 (calc.), total 101.46%. The  $\text{H}_2\text{O}$  calculated from the crystal-structure analysis is in close agreement with the value obtained by thermogravimetric analysis of synthetic material (Hoyos *et al.* 2001), approximately 12 wt.%.

The empirical formula (based on  $V = 2$  apfu and sufficient H for charge balance) is:  $(\text{Zn}_{2.66}\text{Co}_{0.15}\text{Ca}_{0.05})(\text{V}_2\text{O}_7)(\text{OH})_{1.72} \cdot 2.23\text{H}_2\text{O}$ . The end-member formula is  $\text{Zn}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , which requires: ZnO 50.85,  $\text{V}_2\text{O}_5$  37.89,  $\text{H}_2\text{O}$  11.26, total 100.00 wt.%.

X-RAY CRYSTALLOGRAPHY  
AND DETERMINATION OF THE STRUCTURE

X-ray powder-diffraction data (Table 1) were obtained using a Gandolfi camera (114.6 mm diameter, Ni-filtered  $\text{CuK}\alpha$  radiation). The data show good agreement with the pattern calculated from the structure.

The collection of structure data was performed on a Bruker PLATFORM three-circle goniometer equipped with a 1K SMART CCD detector. A full sphere of three-dimensional data was collected. Fifty duplicate frames, acquired at the end of the data collection,

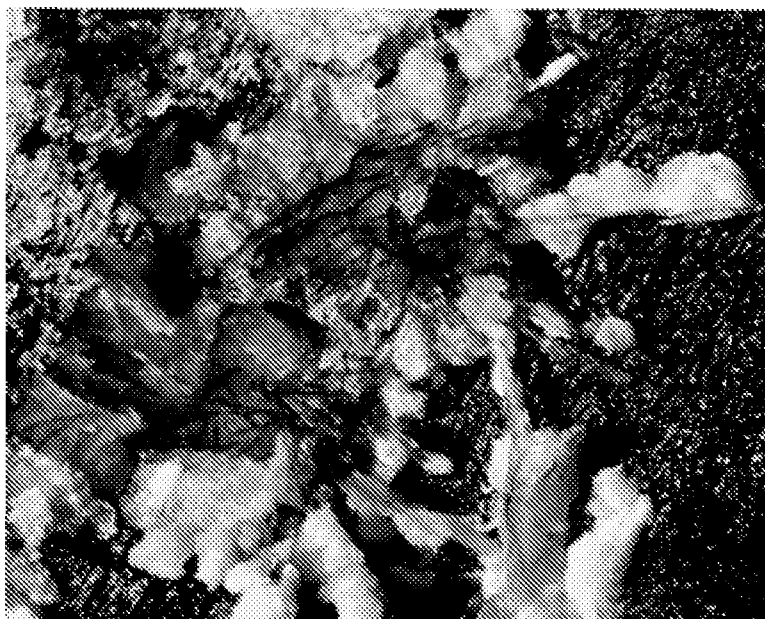


FIG. 1. Clusters of yellow flakes and coarser red-orange plates of martyite on V-U replacement of organic material. Field of view is 1.4 mm across. Image by Joe Marty.

TABLE 1. OBSERVED AND CALCULATED X-RAY POWDER-DIFFRACTION PATTERN OF MARTYITE

$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l_{\text{calc}}$	$hkl$
100	7.211	7.179	100	001	5	1.912	1.918	5	121,211
10	5.267	5.267	4	010	5	1.881	1.881	3	113
20	4.252	4.247	17	011,101	5	1.802	1.795	4	004
5	3.590	3.590	4	002	20	1.773	1.771	17	023,203
10	3.037	3.041	6	110	15	1.737	1.741	14	122,212
50	2.968	2.966	49	012,102	5	1.702	1.705	1	031
20	2.796	2.800	14	111	5	1.574	1.577	3	032,302
35	2.628	2.634	30	200	20	1.513	1.520	14	220
40	2.470	2.472	32	021,201	5	1.485	1.488	7	221
10	2.316	2.320	8	112	25	1.485	1.488	15	024,204
5	2.184	2.179	4	013,103	10	1.347	1.353	5	132,312
15	2.123	2.123	13	202					

indicated that no significant decay had taken place. The measured intensities were corrected for Lorentz and polarization effects using the program SAINT and an empirical absorption correction was applied using the program SADABS (Bruker 1997). The SHELXL97 software (Sheldrick 1997) was used for the refinement of the structure.

The structure of martyite was solved by direct methods. The location of Zn, V and O atoms was straightforward. With all non-hydrogen atoms located and refined anisotropically at full occupancies, the  $R_1$  (conventional  $R$  factor) converged to 2.78% for 290

reflections with  $F_o > 4\sigma(F_o)$ . Because the chemical analyses indicated significant Co at the Zn site, the site was refined accordingly, yielding an improved  $R_1$  of 2.00%. The difference map showed peaks assignable to all likely H atom positions. These positions were refined with O (donor) – H distances restrained to 0.9 Å with standard deviations of 0.03. Because OW is located on a three-fold axis, three H atoms, each with 2/3 occupancy, were assigned to it. In the final refinement,  $R_1$  converged to 1.84%. Table 2 gives the details of the data collection and structure refinement, Table 3, the final fractional coordinates and displacement parameters, Table 4, selected interatomic distances and angles, Table 5, hydrogen bond distances and angles, and Table 6, bond valences. Tables of observed and calculated structure-factors are available from the Depository of Unpublished Data on the MAC website [document Martyite CM46\_687].

#### ATOMIC ARRANGEMENT

The structure of martyite consists of defect brucite-like sheets of edge-sharing Zn–O octahedra parallel to (001) linked in the  $c$  direction by divanadate ( $V_2O_7$ ) groups consisting of two tetrahedra sharing a common corner. The open space in the resulting sheet-and-pillar framework is occupied by  $H_2O$  molecules. Figure 2

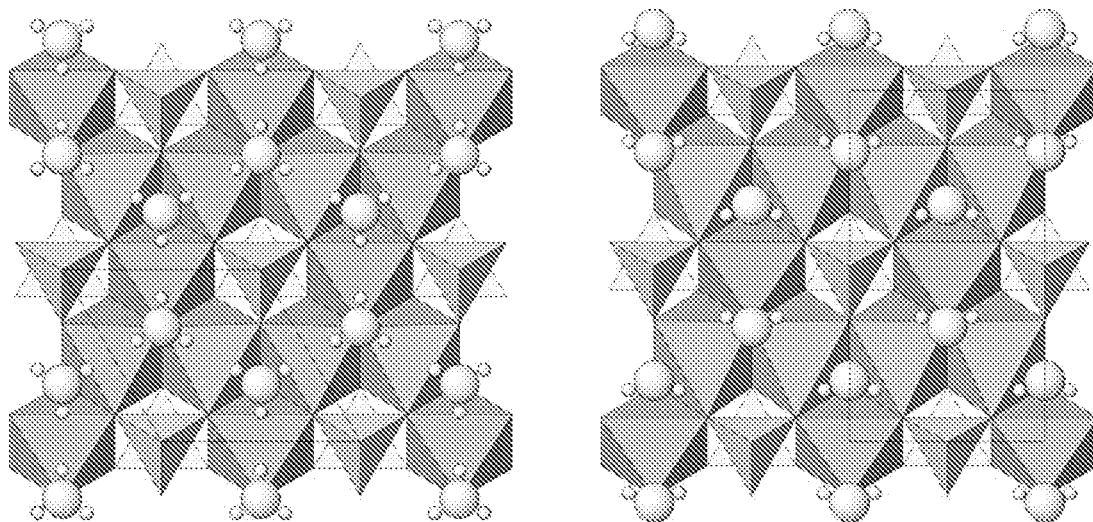


FIG. 2. The crystal structures of martyite (left) and volborthite (right) viewed down the  $c$  axis.

TABLE 2. MARTYITE: DATA COLLECTION AND STRUCTURE-REFINEMENT DETAILS

Diffractometer	Bruker SMART Platform CCD		
X-radiation / power	MoK $\alpha$ ( $\lambda = 0.71073$ Å) / 50 kV, 45 mA		
Temperature	298(2) K	Space group	$P\bar{3}m1$
Unit-cell dimensions		Absorption coefficient	9.578 mm $^{-1}$
$a$ (Å)	6.0818(4)	$F(000)$	229
$c$ (Å)	7.1793(10)	Crystal size ( $a \times b \times c$ )	0.14 $\times$ 0.13 $\times$ 0.01 mm
$V$ (Å $^3$ )	229.97(4)	Index ranges	$-8 \leq h \leq 8,$ $-8 \leq k \leq 8,$ $-10 \leq l \leq 10$
$Z$	1	Independent reflections	295
$\theta$ range	3.87 to 30.46 $^\circ$	Completeness to $\theta =$	99.0%
		$2\theta$	28.26 $^\circ$
Reflections collected	2310	Goof	0.721
Reflections, $F_o > 4\sigma(F_o)$	290		
Parameters refined	26		
Refinement method	Full-matrix least-squares on $F^2$		
$R$ indices [ $F_o > 4\sigma(F_o)$ ]	$R_1 = 1.84\%$ , $wR_2 = 4.81\%$		
$R$ indices (all data)	$R_1 = 1.91\%$ , $wR_2 = 4.86\%$		
Largest diff. peak / hole	+0.62 / -0.57 e/Å $^3$		

Notes:  $R_w = \sum |F_o^2 - F_c^2(\text{mean})| / \sum |F_o^2|$ .  $\text{Goof} = S = (\sum [w(F_o^2 - F_c^2)]^2 / (n-p))^{1/2}$ .  
 $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ .  $wR_2 = (\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2)^{1/2}$ .  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $a$  is 0,  $b$  is 12.994, and  $P$  is  $(2F_o^2 + \text{Max}(F_o^2, 0)) / 3$ .

shows the structure of martyite viewed down the  $c$  axis compared to the structure of volborthite. Figure 3 shows the structure of martyite viewed down  $a$ .

#### Relationship to volborthite

Neglecting the hydrogen atoms, the structure of martyite is topologically identical to that of volborthite,  $\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . The structure of volborthite, determined by Lafontaine *et al.* (1990) using powder data, is monoclinic. The deviation from hexagonal symmetry is attributable to the Jahn–Teller distortion (elongation) of one of the two non-equivalent Cu–O octahedra, which has Cu–O bonds of 1.901 ( $\times 2$ ), 2.049 ( $\times 2$ ) and 2.380 ( $\times 2$ ) Å. In contrast, the other Cu–O octahedron, with Cu–O bonds of 1.906 ( $\times 2$ ) and 2.159 ( $\times 4$ ) Å, is somewhat squat and similar to the Zn–O octahedron in martyite.

TABLE 3. MARTYITE: COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS

atom	$x$	$y$	$z$	occ	$U_{eq}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Zn	½	0	½	0.88	0.0185(2)	0.0157(2)	-0.0113(2)	0.0270(3)	0.0050(2)	0.0025(1)	0.0056(1)
Co	½	0	½	0.05	0.0185(2)	0.0157(2)	0.0113(2)	0.0270(3)	0.0050(2)	0.0025(1)	0.0056(1)
V	0	0	0.24954(9)		0.0101(2)	0.0102(2)	0.0102(2)	0.0100(3)	0	0	0.0051(1)
O1	0.1568(2)	-0.1568(2)	0.3267(3)		0.0225(4)	0.0205(7)	0.0205(7)	0.0225(9)	0.0016(4)	-0.0016(4)	0.0072(8)
O2	0	0	0		0.0306(12)	0.0348(19)	0.0348(19)	0.0223(24)	0	0	0.0174(10)
OH	¾	½	0.3753(4)		0.0152(6)	0.0137(9)	0.0137(9)	0.0182(14)	0	0	0.0068(4)
OW	¾	½	0.0013(9)		0.0789(22)	0.1011(36)	0.1011(36)	0.0346(28)	0	0	0.0506(18)
HOH	¾	½	0.247(4)		0.0500						
HW	0.831(6)	0.415(3)	-0.029(10)	0.67	0.0500						

The vanadate tetrahedra in the structures of both martyite and volborthite exhibit one very long V–O bond corresponding to the O shared between two V atoms. The average length of the V–O bonds in both minerals is unusually large, 1.740 Å in volborthite and 1.755 Å in martyite, resulting in very low bond-valence sums for V, 4.763 and 4.568 *vu*, respectively. The reason for this is not clear; it seems unlikely that the oxidation state of V is lower than +5 for tetrahedral coordination (Schindler *et al.* 2000).

TABLE 4. SELECTED BOND-DISTANCES (Å) AND ANGLES (°) IN MARTYITE

Zn octahedron			
Zn–OH (×2)	1.971(1)	OH–Zn–OH	180.00
Zn–O1 (×4)	2.196(1)	OH–Zn–O1 (×4)	85.54(7)
<Zn–O>	2.151	OH–Zn–O1 (×4)	94.46(7)
		O1–Zn–O1 (×2)	180.00
		O1–Zn–O1 (×2)	85.66(11)
		O1–Zn–O1 (×2)	94.34(11)
V tetrahedron			
V–O1 (×3)	1.742(2)	O1–V–O1 (×3)	110.38(7)
V–O2	1.792(1)	O1–V–O2 (×3)	108.55(7)
<V–O>	1.755		

TABLE 5. HYDROGEN-BOND DISTANCES (Å) AND ANGLES (°) IN MARTYITE

D–H	<i>d</i> (D–H)	<i>d</i> (H–A)	∠D–H–A	<i>d</i> (D–A)	A	∠H–D–H
OH–HOH	0.92(3)	1.76(3)	180(3)	2.685(6)	OW	
OW–HW*	0.89(3)	2.68(3)	103(3)	3.001(3)	O1	114(5)

D = donor O; A = acceptor O. \* Each of three H atoms associated with OW are 2/3 occupied, and each of these H atoms forms split H-bonds to two O1 atoms.

The H<sub>2</sub>O molecules in both the martyite and volborthite structures are bound to the framework only by H bonds to framework O atoms. The H bond schemes are somewhat different in the two structures. In both structures, the OH is a hydrogen-bond donor to the O of the H<sub>2</sub>O molecule. In volborthite, the H atoms of the H<sub>2</sub>O are directed toward two of the three O atoms shared between V and Cu. In martyite, the three two-thirds-occupied H atom sites associated with the H<sub>2</sub>O are positioned between pairs of O atoms shared between V and Zn, forming bifurcated hydrogen bonds.

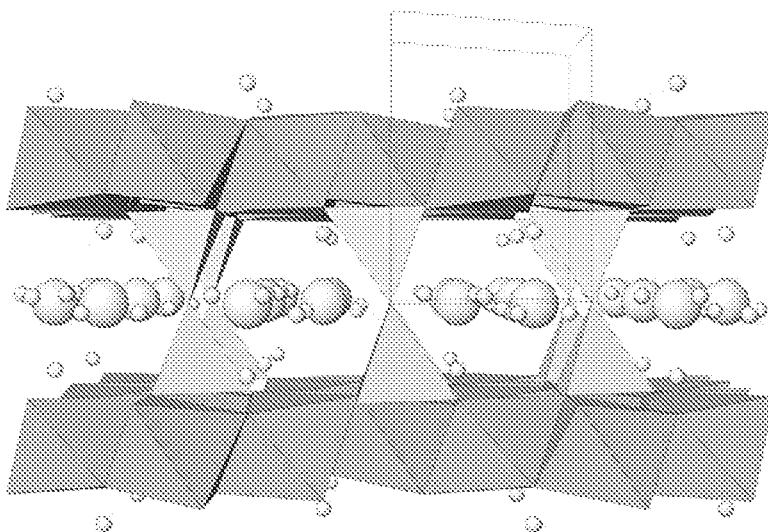
### The structure of synthetic Zn<sub>3</sub>(V<sub>2</sub>O<sub>7</sub>)(OH)<sub>2</sub>•2H<sub>2</sub>O

Interest in open-framework vanadium oxide phases for a variety of molecular sieve applications has led to numerous efforts to synthesize and determine the structures of such compounds. In 1997, Zavalij *et al.* determined the structure of synthetic Zn<sub>3</sub>(V<sub>2</sub>O<sub>7</sub>)(OH)<sub>2</sub>•2H<sub>2</sub>O using the Rietveld method. They reported a structure

TABLE 6. BOND-VALENCE SUMMATIONS FOR MARTYITE

	O1	O2	OH	OW	Σcv
Zn	0.265 <sup>x2</sup> · x4 <sup>·</sup>		0.486 <sup>x3</sup> · x2 <sup>·</sup>		2.030
V	1.179 <sup>x3</sup> · x3 <sup>·</sup>	1.030 <sup>x2</sup>			4.568
HOH			0.795	0.205	1.000
HW	0.040 <sup>x3</sup> · x3 <sup>·</sup>			0.880 <sup>x2</sup> · x2 <sup>·</sup>	1.000
Σav	1.748	2.060	2.253	1.965	

Non-hydrogen bond-strengths from Brese & O'Keeffe (1991); hydrogen bond-strengths from Ferraris & Ivaldi (1988), based on O–O distances; valence summations are expressed in valence units.

FIG. 3. The crystal structure of martyite in perspective viewed down the *a* axis.

with  $a$  6.05098(5),  $c$  7.19498(9) Å,  $P\bar{3}m1$ , identical to that reported here in most essential details. Unlike the structure of martyite, they noted the O atom bridging the divanadate (pyrovanadate) group and the O atom of the H<sub>2</sub>O molecule to be slightly shifted off their threefold axes and disordered. They also reported significantly more distorted polyhedra. Their ZnO<sub>6</sub> octahedron has two short Zn–O bonds at 1.941 Å and four long bonds at 2.226 Å. Their VO<sub>4</sub> tetrahedron has three short V–O bonds at 1.695 Å and one long one at 1.781 Å.

In 2001, Hoyos *et al.* reported on the synthesis and Rietveld structure determination of a compound of the same composition and similar cell,  $a$  6.07877(8) and  $c$  7.1827(2) Å, but provided the space group  $P\bar{1}$ . The structure they reported is similar to that of martyite and that reported by Zavalij *et al.* (1997); however, in their structure, the Zn coordination is trigonal prismatic, rather than octahedral. Published graphs of the Rietveld data for the Hoyos *et al.* and the Zavalij *et al.* studies are virtually identical, leading to the conclusion that Hoyos *et al.* simply made an incorrect choice of space group.

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