The Canadian Mineralogist
Vol. 49, pp. 849-864 (2011)
DOI: 10.3749/canmin.49.3.849

THE CRYSTAL STRUCTURE OF THE ELUSIVE HUEMULITE

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ABSTRACT

The crystal structures of natural huemulite from the West Sunday mine, Utah, USA, and synthetic huemulite, $Na_4Mg(V_{10}O_{28})•24H_2O$, have been solved and refined to $R_1 = 0.0313$ (for 3535 unique $F_o > 4\sigma F$ reflections) and 0.0246 (for 3672 unique $F_o > 4\sigma F$ reflections), respectively. Huemulite is triclinic, space group $P\overline{1}$, $Z = 1$; unit-cell dimensions of the natural sample are *a* 9.0453(2), *b* 11.3337(3), *c* 11.7372(8) Å, α 105.223(7), β 97.383(7), γ 100.790(7)°, *V* 1120.30(9) Å^3, whereas those of the synthetic sample are *a* 9.0425(2), *b* 11.3303(2), *c* 11.7353(8) Å, α 105.222(7), β 97.377(7), γ 100.791(7)°, *V* 1119.47(8) Å^3. The structure consists of decavanadate oxyanions $(V_{10}O_{28})^{6-}$ linked *via* an interstitial complex composed of isolated $[Mg(H_2O)_6]^{2+}$ octahedra and an $[Na_4(H_2O)_{14}]^{4+}$ cationic group (defining an infinite zigzag chain). There are also four isolated H_2O groups, two of them positionally disordered. All except four H atoms have been located, showing a network of hydrogen bonds that further links the interstitial complex and the structural unit, stabilizing the atomic arrangement. The Lewis acidity of the interstitial complex (0.18) is almost coincident with the upper limit of basicity of the structural unit (0.17), thus showing that the valence-matching principle is maintained in this structure. It is probable that the X-ray pattern and the unit-cell dimensions in the original description of huemulite were measured using a mixture that included fully hydrated and partially dehydrated material. Huemulite is a member of the pascoite group, which is closely related to a synthetic family of general formula $Na_4M(V_{10}O_{28})•23H_2O$ (*M*: Ni, Mg). The unit cell and atomic positions of huemulite are related to those of the synthetic family by the transformation matrix $M = [100 / 011 / 01\overline{1}]$. However, some of the symmetry restrictions (*e.g.*, inversion centers, cell centering) present in huemulite are relaxed, with the consequence that fewer atoms are symmetry-related in the synthetic materials.

Keywords: huemulite, decavanadate, hydrogen bonding, valence-matching principle, pascoite family.

SOMMAIRE

Nous avons résolu la structure cristalline de la huémulite, $Na_4Mg(V_{10}O_{28})•24H_2O$, provenant de la mine West Sunday, au Utah, et de son équivalent synthétique, et nous l'avons affiné jusqu'à un résidu R_1 de 0.0313 (pour 3535 réflexions uniques, $F_o > 4\sigma F$) et de 0.0246 (pour 3672 réflexions uniques, $F_o > 4\sigma F$), respectivement. La huémulite est triclinique, groupe spatial $P\overline{1}$, $Z = 1$; les paramètres réticulaires de l'échantillon naturel sont *a* 9.0453(2), *b* 11.3337(3), *c* 11.7372(8) Å, α 105.223(7), β 97.383(7), γ 100.790(7)°, *V* 1120.30(9) Å^3, tandis que ceux de l'échantillon synthétique sont *a* 9.0425(2), *b* 11.3303(2), *c* 11.7353(8) Å, α 105.222(7), β 97.377(7), γ 100.791(7)°, *V* 1119.47(8) Å^3. La structure contient des oxyanions de décavanadate $(V_{10}O_{28})^{6-}$ en liaison grâce à un complexe interstitiel contenant des octaèdres $[Mg(H_2O)_6]^{2+}$ isolés et un groupe cationique $[Na_4(H_2O)_{14}]^{4+}$ dans un agencement en chaînes en zigzag infinies. Il y a de plus quatre groupes H_2O isolés, dont deux montrent un désordre de position. Tous les atomes d'hydrogène sauf quatre ont été localisés; ce réseau de liaisons hydrogène assure un supplément de liaisons entre le complexe interstitiel et l'unité structurale, ce qui stabilise l'agencement des atomes. L'acidité de Lewis du complexe interstitiel (0.18) coïncide presque avec la valeur limite supérieure de la basicité de l'unité structurale (0.17), ce qui démontre que le principe de la concordance des valences est respecté dans cette structure. Il est probable que le spectre

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de diffraction X et les dimensions de la maille dans la description originale de la huémulite ont été mesurés sur un mélange de matériaux pleinement hydraté et partiellement déshydraté. La huémulite fait partie du groupe de la pascoïte, et est étroitement liée à une famille de produits de synthèse répondant à la formule générale $Na_4M(V_{10}O_{28})•23H_2O$ (*M*: Ni, Mg). La maille élémentaire et les positions des atomes de la huémulite sont liés à celles des produits de synthèse selon la matrice de transformation M = [100 / 011 / 01$\bar{1}$]. Toutefois, certaines des restrictions en matière de symétrie présentes dans la huémulite, par exemple les centres d'inversion et le centrage de la maille, sont relachées, ce qui se traduit par des positions d'atomes dans ces produits de synthèse moins strictement régies par la symétrie.

(Traduit par la Rédaction)

Most-clés: huémulite, décavanadate, liaisons hydrogène, principe de la concordance des valences, groupe de la pascoïte.

Introduction

In natural systems, vanadium can exhibit three different oxidation states (V^{3+}, V^{4+}, V^{5+}), resulting in complicated chemical systems, a characteristic enhanced by the broad range of possible Eh and pH values in the environments where V-bearing minerals precipitate. In particular, V^{5+}, most commonly present as $(VO_4)^{3-}$ in solids, can give rise to several types of complex anions, depending on the pH and the concentration of V of the solution, the electrolytic medium and temperature (Evans & Garrels 1958, Wanty & Goldhaber 1992); at 25°C, V^{5+} occurs as pyrovanadates [$(V_2O_7)^{4-}$, $(HV_2O_7)^{3-}$, $(H_2V_2O_7)^{2-}$] for pH values above 8, metavanadates [$(V_3O_9)^{3-}$, $(V_4O_{12})^{4-}$, $(H_2V_3O_{10})^{3-}$, $(HV_3O_{10})^{4-}$, $(V_5O_{15})^{5-}$] in the pH range 8 to 6, and decavanadates [$(V_{10}O_{28})^{6-}$] as solutions become more acidic (Marvin & Magin 1959).

Huemulite, ideally $Na_4Mg(V_{10}O_{28})•24H_2O$, is a phase whose oxyanion belongs to the latter group. The mineral was first found as a post-mining product in the Agua Botada, Agua Botada Sur and Huemul uranium orebodies of the Malargüe area, Mendoza Province, Argentina, in association with thenardite, gypsum, epsomite, and two other vanadium-bearing minerals, rossite, $Ca(V_2O_6)•4H_2O$, and hummerite, $K_2Mg_2(V_{10}O_{28})•16H_2O$. The chemical and physical properties of huemulite were thoroughly described by Gordillo *et al.* (1966), but its crystal structure was not solved, despite the fact that they apparently had grown recrystallized and synthetic crystals of suitable quality. Crystals of synthetic huemulite were deposited by Gordillo in the collection of the Museo de Mineralogía of the Universidad Nacional de Córdoba (Argentina).

Recently, excellent crystals of a mineral considered to correspond to huemulite were collected by Joe Marty at the West Sunday mine, Slick Rock District, San Miguel County, Colorado, USA, and were submitted to one of the authors (ARK) for identification. Semiquantitative analyses of these crystals by energy-dispersion spectrometry (EDS) indicated the presence of Na, Mg, V and O in a stoichiometry consistent with huemulite; however, powder X-ray diffraction (PXRD) data exhibited some significant differences from those reported for huemulite by Gordillo *et al.* (1966). The PXRD data closely matched those of $Na_4Mg(V_{10}O_{28})•23H_2O$, which had been sythesized by Miras *et al.* (2005), who also determined its crystal structure.

Herein, we present crystal-structure determinations for the natural crystals from the West Sunday mine and for the synthetic crystals deposited by Gordillo, and the results of an investigation to determine whether these phases and that synthesized by Miras *et al.* (2005) are equivalent to huemulite.

Background Information: the Bond-Valence Theory

The structures of hydrated oxysalt minerals can be described in terms of two well-differentiated parts: a *structural unit* (the anionic part of the structure) consisting of polyhedra of higher bond-valence, and an *interstitial complex* (the cationic part), which may contain alkali or alkaline-earth cations, (H_2O) and $(OH)^-$ groups. This approach, which takes into account bond-valence theory, coordination geometry and polyhedron linkage, was first proposed by Hawthorne (1983) and has been successfully applied to most groups of hydrated oxysalts, *e.g.*, sulfates (Hawthorne 1992), phosphates (Hawthorne 1992, 1998), borates (Schindler & Hawthorne 2001a, 2001b), uranyl oxide hydroxyhydrates (Schindler & Hawthorne 2004), V-bearing minerals (Schindler *et al.* 2000a, Hughes *et al.* 2002, 2005, Kampf & Steele 2008) and organic minerals (Echigo & Kimata 2010). For a detailed analysis of the subject, we refer the interested reader to Schindler & Hawthorne (2001c) and Hawthorne & Schindler (2008). The most important points are summarized here:

1) The Lewis basicity of the structural unit is defined as the effective charge of the anion divided by the maximum and minimum observed number of accepted bonds, thus obtaining a range.

2) The Lewis acidity of the interstitial complex is defined as its effective charge divided by the number of bonds emanating from the interstitial complex.

3) The valence-matching principle applies, requiring that the Lewis acidity of the interstitial complex must closely match the range in Lewis basicity of the structural unit for a compound to be stable.

Schindler *et al*. (2000b) analyzed the role of H_2O groups in vanadium minerals, and predicted the range in Lewis basicity for various structural units; their results show the validity of the valence-matching principle in evaluating the structures of complex vanadium hydrate minerals. They also showed that there is a positive covariation of average basicities of structural units and the pH values at which those units are most concentrated.

Experimental: X-Ray Diffraction and SEM–EDS Characterization

During the course of this investigation, powder and single-crystal X-ray-diffraction data were collected on a Rigaku R-AXIS Rapid II curved-imaging-plate microdiffractometer with monochromatized Mo$K\alpha$ X-radiation. Rigaku Rint Rapid software was used for recording PXRD patterns. The Rigaku 2DP software was used for integrating PXRD images and obtaining intensity *versus* 2θ plots. The JADE 9.1 software was used for interpreting PXRD patterns and data. The structures of both natural (from the West Sunday mine, Utah, USA) and synthetic crystals (using a cleaved fragment from C.E. Gordillo) were solved and refined using data collected with the equipment mentioned above.

Semiquantitative energy-dispersive spectrometry was performed on a Hitachi S–3000N scanning electron microscope using an Oxford SEMEDX200 detector. Images were taken with a FEG SEM Sigma.

The Rigaku CrystalClear software package was used for processing of the structure data; the structure was solved by direct methods using SIR92 (Altomare *et al*. 1994). The SHELXL–97 software (Sheldrick 2008) was used for the refinement of the structure; neutral-atom scattering factors were employed throughout the process. Refinement was performed with anisotropic atomic displacement parameters for all non-hydrogen atoms. Isotropic atomic displacement parameters equal to 1.2 times that of the nearest oxygen atom were used for hydrogen. Full use of PLATON (Spek 2003) was made for the final verification of the model. An EDS analysis of the synthetic material showed only the peaks corresponding to O, Na, Mg, and V.

Crystallographic and structure-refinement details for natural and synthetic huemulite are given in Table 1; coordinates and displacement parameters appear in Tables 2a (synthetic) and 2b (natural), whereas selected interatomic distances are listed in Table 3. Table 4 displays all relevant H-bonding interactions in the structure. A list of structure factors is available from the

TABLE 1. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS

Sample	Synthetic (code 1686)	Natural (West Sunday mine)
Diffractometer	Rigaku R-Axis Rapid II	Rigaku R-Axis Rapid II
X-ray radiation / power	Mo$K\alpha$ / 50 kV, 40 mA	Mo$K\alpha$ / 50 kV, 40 mA
Temperature	298(2) K	298(2) K
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.0425(2)	9.0453(2)
b (Å)	11.3303(2)	11.3337(3)
c (Å)	11.7353(8)	11.7372(8)
α ( )	105.222(7)	105.223(7)
β ( )	97.377(7)	97.383(7)
γ ( )	100.791(7)	100.790(7)
V (Å^3)	1119.47(8)	1120.30(9)
Density (g/cm^3)	2.234	2.232
Absorption coefficient (mm^{-1})	2.17	2.170
F(000)	750	750
Crystal size (μm)	140 × 110 × 70	90 × 80 × 70
θ range (°)	3.01 to 25.68	3.01 to 25.68
Index ranges	$-11 \le h \le 11$	$-11 \le h \le 11$
	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-14 \le l \le 14$	$-14 \le l \le 14$
Reflections coll. / unique	30150 / 4223 [R_{int} = 0.0259]	30329 / 4231 [R_{int} = 0.0361]
Reflections with ($F_o^2 > 2\sigma$ (F_o^2)	3672	3535
Completeness to θ = 25.68°	99.9%	99.9%
Max. / min. transmission	0.860 / 0.750	0.859 / 0.822
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters refined	385	385
GoF	1.061	1.078
Final *R* indices [$F_o > 4sF$]	R_1 = 0.0246, wR_2 = 0.0676	R_1 = 0.0313, wR_2 = 0.0990
R indices (all data)	R_1 = 0.0298, wR_2 = 0.0730	R_1 = 0.0389, wR_2 = 0.1040
Largest diff. peak / hole	+0.54 / -0.33 *e*/A^3	+0.439 / –0.442 *e*/A^3

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$; for synthetic huemulite, *a* is 0.0397 and *b* is 0.6771; for the West Sunday huemulite, *a* is 0.0712 and *b* is 0.

TABLE 2a. COORDINATES AND DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN SYNTHETIC HUEMULITE§

	x/a	*y/b*	*z/c*	U_{iso}/U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V1	0.83596(4)	0.74497(4)	0.75465(3)	0.02424(11)	0.0280(2)	0.01904(19)	0.0197(2)	-0.0024(2)	0.00178(16)	0.00230(15)
V2	1.18295(5)	0.84113(4)	0.79384(4)	0.02460(11)	0.0282(2)	0.0215(2)	0.0283(2)	0.00811(16)	0.01661(17)	0.00740(16)
V3	1.03857(4)	0.76811(3)	0.99849(3)	0.01924(10)	0.0222(2)	0.01564(18)	0.0230(2)	0.00569(14)	0.00724(15)	0.00847(15)
V4	0.81256(4)	0.94733(3)	0.97807(3)	0.01611(10)	0.01277(18)	0.01633(18)	0.02017(19)	0.00198(14)	0.00407(14)	0.00745(14)
V5	0.97200(4)	1.02589(3)	0.77571(3)	0.01931(10)	0.0228(2)	0.01971(19)	0.01627(19)	0.00284(15)	0.00428(15)	0.00785(15)
Na1	0.5000	0.5000	0.5000	0.0408(4)	0.0358(8)	0.0473(9)	0.0275(7)	-0.0074(7)	0.0042(6)	0.0037(7)
Na2	0.28638(13)	0.40537(11)	0.70452(10)	0.0428(3)	0.0494(7)	0.0471(6)	0.0401(6)	0.0157(5)	0.0180(5)	0.0187(5)
Na3	0.5000	0.5000	1.0000	0.0335(3)	0.0322(7)	0.0330(7)	0.0358(8)	0.0052(6)	0.0061(6)	0.0129(6)
Mg1	0.5000	0.0000	0.5000	0.0263(2)	0.0246(6)	0.0293(6)	0.0312(6)	0.0093(5)	0.0109(5)	0.0145(5)
O1	0.7036(2)	0.63652(17)	0.66035(16)	0.0397(5)	0.0448(11)	0.0289(9)	0.0304(10)	-0.0090(8)	-0.0027(8)	0.0002(8)
O2	0.70196(17)	0.82217(14)	0.86861(14)	0.0236(3)	0.0183(8)	0.0224(8)	0.0274(8)	-0.0016(6)	0.0015(6)	0.0086(7)
O3	0.82631(18)	0.88103(14)	0.69383(13)	0.0252(3)	0.0278(8)	0.0248(8)	0.0182(8)	-0.0018(7)	-0.0009(6)	0.0061(6)
O4	1.0129(2)	0.72617(15)	0.69917(14)	0.0297(4)	0.0399(10)	0.0220(8)	0.0245(8)	0.0034(7)	0.0137(7)	0.0014(7)
O5	0.88645(18)	0.67025(14)	0.87581(14)	0.0239(3)	0.0284(8)	0.0159(7)	0.0264(8)	0.0016(6)	0.0075(7)	0.0059(6)
O6	0.83030(16)	1.06848(13)	0.89225(13)	0.0187(3)	0.0149(7)	0.0203(7)	0.0228(8)	0.0031(6)	0.0029(6)	0.0108(6)
O7	1.13044(18)	0.96593(14)	0.72610(14)	0.0248(3)	0.0305(9)	0.0244(8)	0.0230(8)	0.0060(7)	0.0130(7)	0.0095(7)
O8	1.18995(18)	0.75544(14)	0.90835(15)	0.0257(3)	0.0264(8)	0.0220(8)	0.0361(9)	0.0114(7)	0.0161(7)	0.0121(7)
O9	0.89011(16)	0.85207(13)	1.07876(13)	0.0169(3)	0.0162(7)	0.0159(7)	0.0199(7)	0.0024(6)	0.0052(6)	0.0074(6)
O10	0.94441(19)	1.11931(16)	0.69616(15)	0.0291(4)	0.0320(9)	0.0313(9)	0.0279(9)	0.0049(7)	0.0054(7)	0.0170(7)
O11	1.3220(2)	0.80842(17)	0.72721(17)	0.0374(4)	0.0408(10)	0.0341(10)	0.0466(11)	0.0143(8)	0.0297(9)	0.0135(8)
O12	1.06696(19)	0.67647(15)	1.07938(16)	0.0304(4)	0.0349(9)	0.0267(8)	0.0395(10)	0.0130(7)	0.0121(8)	0.0196(8)
O13	1.00329(15)	0.90959(13)	0.90089(12)	0.0170(3)	0.0165(7)	0.0162(7)	0.0190(7)	0.0029(6)	0.0052(6)	0.0064(6)
O14	1.30389(17)	0.99325(14)	0.93135(14)	0.0235(3)	0.0185(8)	0.0241(8)	0.0314(9)	0.0056(6)	0.0104(6)	0.0108(7)
OW1	0.5134(2)	0.37056(19)	0.6329(2)	0.0448(5)	0.0476(12)	0.0316(10)	0.0555(13)	0.0091(9)	0.0156(10)	0.0104(10)
H1A	0.521(4)	0.2968(14)	0.603(3)	0.054*						
H1B	0.578(3)	0.397(3)	0.6976(18)	0.054*						
OW2	0.3009(3)	0.5503(2)	0.5917(2)	0.0553(6)	0.0779(17)	0.0447(13)	0.0498(14)	0.0226(13)	0.0269(12)	0.0117(11)
H2A	0.219(3)	0.535(4)	0.539(3)	0.066*						
H2B	0.306(4)	0.6200(19)	0.643(3)	0.066*						
OW3	0.1431(2)	0.2115(2)	0.55469(17)	0.0437(5)	0.0503(12)	0.0529(12)	0.0312(10)	0.0096(10)	0.0161(9)	0.0153(10)
H3A	0.120(4)	0.193(3)	0.4791(10)	0.052*						
H3B	0.064(2)	0.182(3)	0.579(3)	0.052*						
OW4	0.0645(3)	0.4593(2)	0.7686(2)	0.0577(6)	0.0755(16)	0.0465(13)	0.0735(16)	0.0283(12)	0.0491(13)	0.0291(12)
H4A	0.023(4)	0.419(3)	0.812(3)	0.069*						
H4B	0.052(4)	0.5324(16)	0.797(3)	0.069*						
OW5	0.4297(2)	0.61851(18)	0.86666(18)	0.0368(4)	0.0343(10)	0.0350(10)	0.0459(11)	0.0111(8)	0.0109(9)	0.0164(9)
H5A	0.365(3)	0.661(2)	0.884(3)	0.044*						
H5B	0.505(2)	0.674(2)	0.866(3)	0.044*						
OW6	0.3393(2)	0.30988(17)	0.85774(18)	0.0349(4)	0.0308(10)	0.0312(10)	0.0464(11)	0.0026(8)	0.0130(8)	0.0184(9)
H6A	0.267(2)	0.264(2)	0.875(3)	0.042*						
H6B	0.399(3)	0.262(2)	0.848(3)	0.042*						
OW7	0.6897(2)	0.45484(18)	0.8785(2)	0.0415(5)	0.0301(10)	0.0318(10)	0.0704(14)	0.0074(8)	0.0144(10)	0.0255(10)
H7A	0.748(3)	0.5233(17)	0.883(3)	0.050*						
H7B	0.747(3)	0.415(3)	0.907(3)	0.050*						
OW8	0.6347(2)	0.14362(19)	0.64575(18)	0.0404(4)	0.0336(10)	0.0431(11)	0.0443(12)	0.0115(9)	0.0076(9)	0.0107(10)
H8A	0.605(3)	0.144(3)	0.7117(16)	0.048*						
H8B	0.7297(14)	0.155(3)	0.645(3)	0.048*						
OW9	0.3120(2)	0.0307(2)	0.57329(19)	0.0428(5)	0.0432(11)	0.0565(13)	0.0527(12)	0.0259(10)	0.0313(10)	0.0361(11)
H9A	0.267(3)	0.003(3)	0.623(2)	0.051*						
H9B	0.274(3)	0.093(2)	0.576(3)	0.051*						
OW10	0.4647(2)	0.13222(18)	0.41227(17)	0.0339(4)	0.0276(9)	0.0468(11)	0.0400(10)	0.0135(8)	0.0132(8)	0.0275(9)
H10A	0.523(3)	0.142(3)	0.364(2)	0.041*						
H10B	0.3753(16)	0.123(3)	0.376(2)	0.041*						
OW11	0.5428(2)	0.1401(2)	0.86016(19)	0.0401(5)	0.0244(10)	0.0518(12)	0.0507(12)	0.0060(9)	0.0047(8)	0.0294(10)
H11A	0.473(3)	0.090(2)	0.877(3)	0.048*						
H11B	0.623(2)	0.132(3)	0.898(3)	0.048*						
OW12A	0.8775(10)	0.3473(11)	0.5385(5)	0.102(4)	0.082(5)	0.146(9)	0.087(4)	0.059(6)	0.009(3)	0.031(4)
OW12B	0.9643(19)	0.4380(17)	0.5229(13)	0.090(7)	0.073(10)	0.087(10)	0.093(9)	0.031(8)	-0.009(7)	-0.001(7)

*: $U_{iso} = 1.2U_{eq}$ (host). Full occupancy for all atoms except OW12A [0.26(2)] and OW12B [0.65(2)]. § Code1686.

TABLE 2b. COORDINATES AND DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN HUEMULITE FROM THE WEST SUNDAY MINE

	x/a	*y/b*	*z/c*	U_{iso}/U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V1	0.83583(6)	0.74493(4)	0.75461(4)	0.02819(15)	0.0332(3)	0.0215(3)	0.0246(3)	-0.0016(2)	0.0030(2)	0.0044(2)
V2	1.18297(6)	0.84107(4)	0.79391(5)	0.02845(15)	0.0334(3)	0.0245(3)	0.0327(3)	0.0091(2)	0.0179(2)	0.0099(2)
V3	1.03858(5)	0.76814(4)	0.99854(4)	0.02289(14)	0.0266(3)	0.0183(2)	0.0275(3)	0.00639(19)	0.0087(2)	0.0106(2)
V4	0.81258(5)	0.94732(4)	0.97815(4)	0.01973(14)	0.0175(2)	0.0188(2)	0.0244(3)	0.00257(18)	0.00524(19)	0.00930(19)
V5	0.97184(5)	1.02587(4)	0.77563(4)	0.02316(14)	0.0274(3)	0.0226(3)	0.0210(3)	0.00336(19)	0.0059(2)	0.0100(2)
Na1	0.5000	0.5000	0.5000	0.0443(5)	0.0406(10)	0.0500(11)	0.0306(9)	-0.0071(8)	0.0053(8)	0.0051(8)
Na2	0.28622(15)	0.40535(13)	0.70437(12)	0.0469(3)	0.0549(8)	0.0493(8)	0.0452(8)	0.0167(6)	0.0194(6)	0.0209(6)
Na3	0.5000	0.5000	1.0000	0.0372(4)	0.0374(9)	0.0357(9)	0.0397(10)	0.0059(7)	0.0068(8)	0.0152(8)
Mg1	0.5000	0.0000	0.5000	0.0295(3)	0.0278(7)	0.0317(7)	0.0361(8)	0.0099(6)	0.0112(6)	0.0173(6)
O1	0.7034(3)	0.6365(2)	0.6604(2)	0.0437(6)	0.0480(13)	0.0323(12)	0.0350(12)	-0.0100(10)	-0.0028(10)	0.0018(10)
O2	0.7021(2)	0.82217(17)	0.86874(17)	0.0266(4)	0.0211(9)	0.0261(10)	0.0294(11)	-0.0017(8)	0.0011(8)	0.0095(8)
O3	0.8264(2)	0.88089(18)	0.69397(16)	0.0282(4)	0.0315(10)	0.0282(10)	0.0200(10)	-0.0014(8)	-0.0013(8)	0.0077(8)
O4	1.0134(2)	0.72612(18)	0.69966(18)	0.0329(5)	0.0441(12)	0.0245(10)	0.0288(11)	0.0054(9)	0.0146(9)	0.0038(9)
O5	0.8866(2)	0.67004(17)	0.87591(18)	0.0294(4)	0.0338(11)	0.0192(9)	0.0356(11)	0.0018(8)	0.0111(9)	0.0096(8)
O6	0.83062(19)	1.06803(16)	0.89220(17)	0.0220(4)	0.0185(9)	0.0229(9)	0.0270(10)	0.0035(7)	0.0039(7)	0.0121(8)
O7	1.1305(2)	0.96598(17)	0.72635(17)	0.0282(4)	0.0354(11)	0.0267(10)	0.0266(10)	0.0060(8)	0.0151(9)	0.0114(8)
O8	1.1896(2)	0.75564(17)	0.90795(19)	0.0296(5)	0.0306(10)	0.0230(10)	0.0418(12)	0.0103(8)	0.0161(9)	0.0135(9)
O9	0.89051(19)	0.85238(16)	1.07903(16)	0.0212(4)	0.0216(9)	0.0177(9)	0.0266(10)	0.0025(7)	0.0083(8)	0.0098(8)
O10	0.9448(2)	1.11888(19)	0.69620(18)	0.0327(5)	0.0358(11)	0.0352(11)	0.0311(11)	0.0050(9)	0.0059(9)	0.0187(9)
O11	1.3218(2)	0.8082(2)	0.7272(2)	0.0404(5)	0.0451(13)	0.0369(12)	0.0504(14)	0.0166(10)	0.0308(11)	0.0163(11)
O12	1.0670(2)	0.67687(18)	1.07928(19)	0.0332(5)	0.0390(12)	0.0285(10)	0.0411(12)	0.0121(9)	0.0113(10)	0.0208(9)
O13	1.00340(19)	0.90933(15)	0.90088(16)	0.0220(4)	0.0253(10)	0.0184(9)	0.0249(10)	0.0047(8)	0.0090(8)	0.0088(8)
O14	1.3036(2)	0.99306(17)	0.93123(18)	0.0261(4)	0.0229(10)	0.0268(10)	0.0337(11)	0.0068(8)	0.0120(8)	0.0134(9)
OW1	0.5128(3)	0.3704(2)	0.6328(3)	0.0488(6)	0.0563(16)	0.0342(13)	0.0595(17)	0.0127(12)	0.0189(13)	0.0143(13)
H1A	0.522(4)	0.2976(17)	0.600(3)	0.059*						
H1B	0.573(4)	0.388(4)	0.699(2)	0.059*						
OW2	0.3005(4)	0.5502(3)	0.5913(3)	0.0601(7)	0.087(2)	0.0466(15)	0.0550(18)	0.0260(16)	0.0302(15)	0.0138(14)
H2A	0.220(3)	0.537(4)	0.538(3)	0.072*						
H2B	0.296(5)	0.619(2)	0.640(3)	0.072*						
OW3	0.1424(3)	0.2114(2)	0.5546(2)	0.0483(6)	0.0559(16)	0.0532(15)	0.0393(14)	0.0097(12)	0.0189(12)	0.0167(12)
H3A	0.126(4)	0.189(4)	0.4786(10)	0.058*						
H3B	0.065(3)	0.178(3)	0.577(3)	0.058*						
OW4	0.0641(3)	0.4596(3)	0.7690(3)	0.0609(8)	0.0793(19)	0.0494(16)	0.078(2)	0.0301(14)	0.0518(16)	0.0321(15)
H4A	0.030(5)	0.420(4)	0.815(3)	0.073*						
H4B	0.038(5)	0.528(2)	0.793(4)	0.073*						
OW5	0.4289(3)	0.6185(2)	0.8664(2)	0.0406(5)	0.0381(13)	0.0381(13)	0.0505(14)	0.0111(10)	0.0128(11)	0.0179(11)
H5A	0.362(3)	0.659(3)	0.885(3)	0.049*						
H5B	0.508(3)	0.674(2)	0.875(3)	0.049*						
OW6	0.3394(3)	0.3095(2)	0.8575(2)	0.0382(5)	0.0361(13)	0.0321(12)	0.0508(14)	0.0041(9)	0.0144(11)	0.0194(11)
H6A	0.266(3)	0.264(3)	0.875(3)	0.046*						
H6B	0.402(3)	0.263(3)	0.855(3)	0.046*						
OW7	0.6896(3)	0.4551(2)	0.8786(3)	0.0459(6)	0.0347(13)	0.0350(13)	0.0758(18)	0.0085(10)	0.0149(12)	0.0270(13)
H7A	0.748(4)	0.5255(18)	0.889(3)	0.055*						
H7B	0.748(3)	0.413(3)	0.903(3)	0.055*						
OW8	0.6348(3)	0.1433(2)	0.6461(2)	0.0447(6)	0.0453(14)	0.0444(14)	0.0453(15)	0.0132(11)	0.0126(12)	0.0108(12)
H8A	0.626(4)	0.165(3)	0.7189(13)	0.054*						
H8B	0.700(3)	0.154(4)	0.601(3)	0.054*						
OW9	0.3124(3)	0.0304(3)	0.5729(2)	0.0468(6)	0.0465(14)	0.0582(16)	0.0595(16)	0.0263(12)	0.0315(12)	0.0377(13)
H9A	0.270(4)	0.005(3)	0.625(3)	0.056*						
H9B	0.271(4)	0.091(2)	0.581(3)	0.056*						
OW10	0.4644(2)	0.1323(2)	0.4127(2)	0.0373(5)	0.0302(12)	0.0500(13)	0.0437(13)	0.0135(10)	0.0136(10)	0.0278(11)
H10A	0.514(3)	0.135(3)	0.357(2)	0.045*						
H10B	0.3733(18)	0.123(3)	0.378(3)	0.045*						
OW11	0.5427(2)	0.1398(2)	0.8601(2)	0.0437(6)	0.0305(12)	0.0547(15)	0.0540(15)	0.0086(11)	0.0065(11)	0.0313(12)
H11A	0.481(3)	0.096(3)	0.890(3)	0.052*						
H11B	0.625(2)	0.133(3)	0.898(3)	0.052*						
O12WA	0.8766(11)	0.3447(13)	0.5397(6)	0.111(5)	0.090(6)	0.156(10)	0.100(5)	0.058(7)	0.015(4)	0.042(5)
O12WB	0.965(2)	0.437(2)	0.5225(15)	0.100(8)	0.085(13)	0.105(14)	0.115(12)	0.057(11)	0.011(9)	0.020(9)

*: $U_{iso} = 1.2U_{eq}$(host). Full occupancy for all atoms except for OW12A [0.29(2)] and for OW12B [0.57(1)]

TABLE 3. SELECTED BOND-LENGTHS (Å)
FOR SYNTHETIC AND WEST SUNDAY HUEMULITE

	Synthetic	W. Sunday		Synthetic		W. Sunday	
V1–O1	1.6005(17)	1.601(2)	Na1–OW2	2.298(2)	2×	2.301(3)	2×
V1–O4	1.8309(17)	1.834(2)	Na1–OW1	2.411(2)	2×	2.413(3)	2×
V1–O3	1.8724(16)	1.8703(19)	Na1–O1	2.4165(17)	2×	2.416(2)	2×
V1–O5	1.8859(16)	1.890(2)	<Na1–O>	2.375		2.377	
V1–O2	2.0544(16)	2.054(2)					
V1–O13	2.3041(14)	2.3045(18)	Na2–OW2	2.360(3)		2.362(3)	
<V1–O>	1.925	1.926	Na2–OW4	2.360(2)		2.366(3)	
			Na2–OW6	2.372(2)		2.375(3)	
V2–O11	1.6136(16)	1.613(2)	Na2–OW1	2.376(2)		2.374(3)	
V2–O4	1.8293(17)	1.826(2)	Na2–OW3	2.432(2)		2.435(3)	
V2–O8	1.8543(16)	1.848(2)	Na2–OW5	2.629(2)		2.629(3)	
V2–O7	1.8978(16)	1.8979(19)	<Na2–O>	2.421		2.423	
V2–O14	2.0375(16)	2.035(2)					
V2–O13	2.3029(14)	2.3017(18)	Na3–OW7	2.411(2)	2×	2.410(2)	2×
<V2–O>	1.922	1.923	Na3–OW6	2.4198(19)	2×	2.423(2)	2×
			Na3–OW5	2.4132(19)	2×	2.418(2)	2×
V3–O12	1.6125(16)	1.6080(19)	<Na3–O>	2.415		2.417	
V3–O5	1.8100(16)	1.810(2)					
V3–O8	1.8382(15)	1.8396(19)	Mg1–OW8	2.078(2)	2×	2.080(3)	2×
V3–O9	1.9816(14)	1.9820(18)	Mg1–OW9	2.0468(18)	2×	2.041(2)	2×
V3–O6^{i}	2.0047(15)	2.0072(19)	Mg1–OW10	2.0762(17)	2×	2.075(2)	2×
V3–O13	2.2461(14)	2.2442(17)	<Mg–O>	2.067		2.065	
<V3–O>	1.916	1.915					
			V5–O10	1.6161(16)		1.6108(19)	
V4–O2	1.6863(15)	1.6859(19)	V5–O7	1.7956(16)		1.7965(19)	
V4–O14^{i}	1.6938(15)	1.6938(18)	V5–O3	1.8411(15)		1.8411(19)	
V4–O6	1.8998(14)	1.8972(18)	V5–O9^{i}	1.9877(15)		1.9847(19)	
V4–O9	1.9476(14)	1.9482(18)	V5–O6	2.0199(15)		2.0165(18)	
V4–O13	2.1099(14)	2.1125(18)	V5–O13	2.2414(14)		2.2450(17)	
V4–O13^{i}	2.1427(14)	2.1436(18)	<V–O>	1.917		1.916	
<V4–O>	1.913	1.913					

Symmetry code: (i) $-x + 2, -y + 2, -z + 2$.

Depository of Unpublished Data on the MAC website [document Huemulite CM49_849].

Even if well-behaved under the rather short duration of CCD exposures (a few hours), the compound does not seem to be stable under long-term radiation conditions: a previous attempt to collect the data using a four-circle diffractometer showed significant changes in the diffraction pattern of the sample after the first day of irradiation, suggesting either a polymorphic change or simply decomposition. No attempt was made to further study the resulting product.

The products of a new synthesis and structural changes caused by aging of this material were investigated using PXRD patterns measured with a PANalytical X'PERT Pro diffractometer, using Cu$K\alpha$ X-radiation and a secondary graphite monochromator. The tube was operated at 40 mA and 40 kV. In order to examine sample stability, eight patterns (from 5° to 65° 2θ, step size 0.02° 2θ, 0.7 s/step) were taken successively.

The Synthesis of Huemulite

We synthesized huemulite using a modified version of the method described by Gordillo *et al.* (1966). Stoichiometric amounts of reagent-grade $Mg(CO_3)$, V_2O_5 and $Na_2(CO_3)$ were mixed in water and heated to 80°C. The pH was adjusted to 5 by adding HCl. The solution was stirred for 24 hours keeping the temperature at 80°C and then filtered. The powder was allowed to dry at room temperature. The synthesis product was mostly an unidentified brown powder of poor crystallinity. In addition, a few large (up to 6 mm on edge) tabular bright reddish orange crystals of huemulite crystallized from the remaining liquid that was trapped in the moist powder.

Examination of the Type Material

During the early stages of our crystallographic analysis, both using synthetic and natural materials, we noted that the unit-cell parameters of the samples under study differed from those reported by Gordillo *et al.* (1966) for huemulite, either natural or synthetic.

These differences, even if slight, were far beyond the limits of experimental error, and were confirmed by the (also slight, but nonetheless clear) mismatch of the corresponding PXRD diagrams (Fig. 1).

Gordillo *et al*. (1966) did not designate any type specimens in their original description of huemulite; however, we located a specimen designated as a type for the species in the U.S. National Museum of Natural History (Smithsonian Institution). This specimen is recorded as having been donated by E. Linares, one of the authors of the original description of huemulite. Unfortunately, the only phase similar to huemulite that could be found on this specimen provided PXRD data matching lasalite, $Na_2Mg_2(V_{10}O_{28})\bullet 20H_2O$ (Hughes *et al*. 2008). Semiquantitative EDS analyses corroborated this identification. We also dissolved some of this phase in water and allowed the water to slowly evaporate, resulting in well-formed orange crystals, which also yielded PXRD data matching lasalite.

Noting that some of the descriptive work on huemulite was conducted at Yale University, we next sought original samples of huemulite from the Peabody Museum of Natural History at Yale. We were successful in obtaining material from the powder-diffraction slides used by Horace Winchell (one of the authors of the original description) in recording the original PXRD data for natural, recrystallized and synthetic huemulite. New PXRD data obtained on these samples exhibited some similarity with the published data on huemulite, but also distinct differences. The samples clearly appeared dessicated, leading us to conclude that the discrepancies in the PXRD data probably were the result of modification of the structure due to H_2O loss. Furthermore, we suspected that the grinding of the original samples would very likely have resulted in partial dehydration prior to the recording of the PXRD data reported in the original description.

To test this hypothesis, we mildly to moderately heated natural crystals from the West Sunday mine to obtain material in varying stages of dehydration. The PXRD patterns recorded on this material, although not exactly duplicating the published pattern for huemulite or those obtained from the dessicated Yale samples, exhibited close similarities. On the basis of these results, it appears likely that Horace Winchell recorded his PXRD data from partially dehydrated samples, and that the fully hydrated huemulite starting material is identical to the West Sunday mine crystals.

As a final test, we dissolved in water some of Winchell's PXRD sample corresponding to recrystallized huemulite and allowed the solution to slowly evaporate. Well-formed orange crystals resulted and these provided a PXRD pattern identical to those of the West Sunday mine crystals and the synthetic material deposited by Gordillo *et al*. in the museum at Córdoba.

One remaining discrepancy is a mismatch between the unit cell of Gordillo *et al*. (1966) and those obtained in our structure studies of the West Sunday and synthetic crystals (Table 5). Although the cell of Gordillo *et al*. does show some similarities to those of the other phases, we were unable to transform it to match. Furthermore, efforts to force the Rigaku software to index the recorded reflections for the West Sunday and synthetic crystals based upon the cell of Gordillo *et al*. failed.

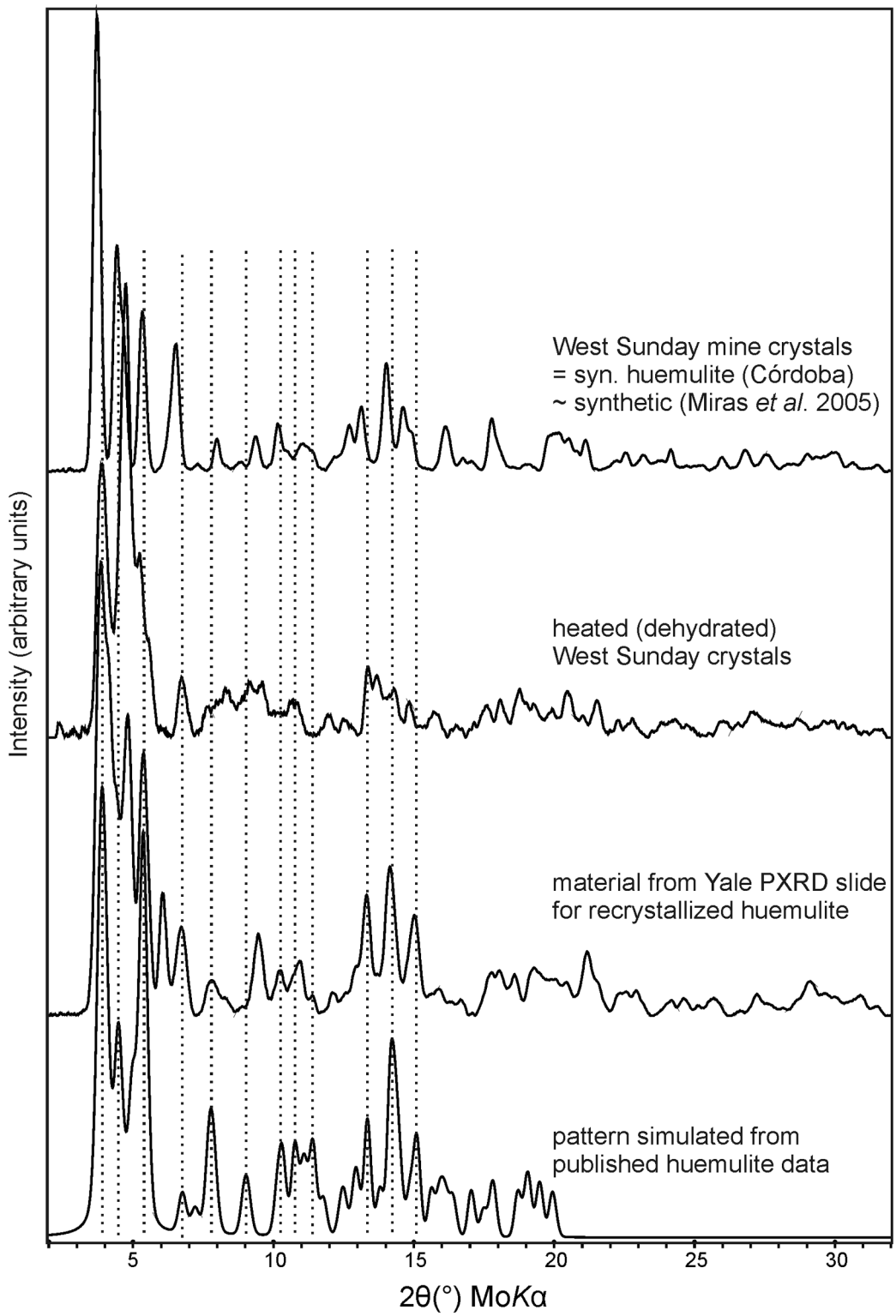
The discrepancy between the cells cannot be fully explained; one possibility, given their similarity and the PXRD evidence, is that Gordillo *et al*. simply misinterpreted their rotation, Weissenberg and precession films. Another possibility is that the material studied by Gordillo *et al*., being so sensitive to H_2O loss with concomitant structural changes, is indeed different from the one we have studied in this contribution. This perplexing fact poses an obvious quota of intrigue regarding the elusiveness of the huemulite mineral as reported in the original work.

The material synthesized by us provides a PXRD pattern with an excellent match to the pattern calculated from the structure herein reported for huemulite. However, crystals become opaque and duller after a few weeks of exposure to air. The PXRD pattern of this material shows, in addition to the previous peaks, some that have been reported for huemulite in the original description (most notably a peak at 10.14 Å) and which are absent in the freshly synthesized mate-

TABLE 4. HYDROGEN-BONDING INTERACTIONS IN THE STRUCTURE OF HUEMULITE

D–H···A	D–H (Å)		H···A (Å)		D···A (Å)		D–H···A (°)	
	Syn	WSM	Syn	WSM	Syn	WSM	Syn	WSM
O12WB···O4^{v}	–	–	–	–	2.819	2.826	–	–
O12WA···OW4^{x}	–	–	–	–	2.837	2.824	–	–
OW11–H11*B*···O8^{vi}	0.84	0.84	2.52	2.51	3.190	3.196	138	139
OW11–H11*B*···O6^{vii}	0.84	0.84	2.13	2.13	2.874	2.879	148	148
OW11–H11*A*···O14^{viii}	0.84	0.84	1.99	2.00	2.825	2.826	172	168
OW10–H10*B*···O3^{ii}	0.84	0.85	1.89	1.88	2.722	2.723	174	175
OW10–H10*A*···O11^{v}	0.84	0.84	1.96	1.99	2.785	2.793	170	159
OW9–H9*B*···OW3	0.84	0.84	1.99	2.00	2.810	2.819	167	165
OW9–H9*A*···O7^{viii}	0.85	0.85	1.90	1.91	2.729	2.736	165	165
OW8–H8*B*···O10^{vii}	0.85	0.85	2.10	2.50	2.867	2.869	150	107
OW8–H8*A*···OW11	0.85	0.84	1.91	1.97	2.757	2.754	178	154
OW7–H7*B*···O12^{vi}	0.84	0.84	2.15	2.14	2.938	2.944	157	161
OW7–H7*A*···O5	0.83	0.84	1.92	1.93	2.748	2.746	173	166
OW6–H6*B*···OW11	0.84	0.84	2.08	2.06	2.903	2.902	168	174
OW6–H6*A*···O9^{iii}	0.84	0.85	1.98	1.97	2.813	2.817	174	174
OW5–H5*B*···O2	0.84	0.84	2.20	2.21	3.036	3.041	179	171
OW5–H5*A*···O8^{ix}	0.84	0.84	2.08	2.07	2.912	2.911	173	173
OW4–H4*B*···O8^{ix}	0.84	0.85	2.51	2.59	3.231	3.230	144	133
OW4–H4*B*···O5^{ix}	0.84	0.85	2.45	2.39	3.204	3.197	149	159
OW4–H4*A*···O12^{iii}	0.85	0.85	2.03	2.03	2.875	2.876	178	176
OW3–H3*B*···O10^{viii}	0.84	0.84	2.05	2.05	2.837	2.835	156	156
OW3–H3*A*···O3^{ii}	0.84	0.85	2.14	2.10	2.897	2.899	150	156
OW2–H2*B*···O11^{ix}	0.85	0.85	2.07	2.07	2.897	2.897	164	163
OW2–H2*A*···OW12*A*^{ii}	0.86	0.86	2.06	2.07	2.699	2.719	131	132
OW2–H2*A*···OW12B^{ii}	0.86	0.86	1.84	1.84	2.639	2.640	155	155
OW1–H1*B*···OW7	0.84	0.84	2.10	2.10	2.927	2.930	165	168
OW1–H1*A*···OW8	0.84	0.84	2.31	2.33	3.009	3.016	142	140
OW1–H1*A*···OW10	0.84	0.84	2.43	2.41	3.127	3.123	142	144

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$; (v) $-x + 2, -y + 1, -z + 1$; (vi) $-x + 2, -y + 1, -z + 2$; (vii) $x, y - 1, z$; (viii) $x - 1, y - 1, z$; (ix) $x - 1, y, z$; (x): $x + 1, y, z$.


West Sunday mine crystals
= syn. huemulite (Córdoba)
~ synthetic (Miras et al. 2005)
heated (dehydrated)
West Sunday crystals
material from Yale PXRD slide
for recrystallized huemulite
pattern simulated from
published huemulite data
Intensity (arbitrary units)
5
10
15
20
25
30
2θ(°) MoKα

rial. In addition, a sequence of PXRD pattern measured on powdered material (crystallized a few hours before) shows a structural change between the first scan and the others (2^{nd} to 8^{th}). All this proves the marked sensitivity of the material to dehydration, grinding and X-ray exposure.

Based upon our investigation, we conclude that the West Sunday mine crystals are indeed huemulite and that Gordillo's synthetic material, noted above, is the synthetic equivalent of huemulite. It is likely that Gordillo *et al*. (1966) determined the composition of huemulite using the fully hydrated phase, but recorded their PXRD data using partially dehydrated material, which was probably unavoidable, considering that the material had to be ground and spread on glass slides.

The Material Studied

The sample of synthetic huemulite is from the collection of the Museo de Mineralogía of the Universidad Nacional de Córdoba (Argentina), catalogue number 1686. The material is readily soluble in water; recrystallized huemulite (Figs. 2A, B) forms dark orange crystals tabular on {001}; other major forms are possibly {100}, {010} and {110}. There are in addition other smaller, non-indexed forms that can be seen in SEM images. There are two cleavage directions, one much better than the other, that intersect at a high angle. Only V, O, Na and Mg were detected in EDS analyses.

The samples of natural huemulite were collected at the West Sunday mine, Utah (USA) by Joe Marty, who provide them for study. They are now deposited in the collections of the Natural History Museum of Los Angeles County, catalogue numbers 63555 to 63557. Huemulite from the West Sunday mine occurs as groups of euhedral transparent bright orange crystals (Fig. 2C), with individuals reaching *ca*. 400 μm.

Description of the Structure

Huemulite is triclinic, space group $P\bar{1}$, with $Z = 1$; cell dimensions appear in Table 1. The structure consists of decavanadate oxyanions $(V_{10}O_{28})^{6-}$, two cationic groups, $[Mg(H_2O)_6]^{2+}$ and $[Na_4(H_2O)_{14}]^{4+}$, the latter defining an infinite zigzag chain, and four uncoordinated H_2O groups, two of them disordered. As the structures of synthetic and natural huemulite are virtually the same, numerical values given in the following sections correspond to those of synthetic huemulite. The equivalent values for natural huemulite can be found in the respective tables.

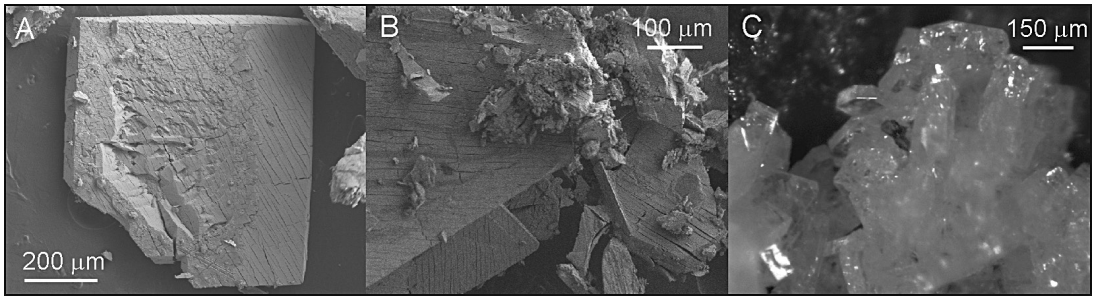


FIG. 2. A and B. SEM images of recrystallized huemulite. The two cleavage directions are clearly seen. C. Photograph of natural huemulite from the West Sunday mine.

FIG. 1. Comparison of the X-ray powder-diffraction diagrams of huemulite measured in this work using synthetic and natural (both untreated and dehydrated), as well as recrystallized material used by Gordillo *et al*. (1966) for the original description. Patterns simulated using data reported by Gordillo *et al*. (1966) for huemulite and by Miras *et al*. (2005) for $Na_4Mg(V_{10}O_{28})•23H_2O$ are also included.

TABLE 5. COMPARISON OF THE UNIT CELLS OF HUEMULITE

	(a)	(b)	(c)	(d)	(e)
a (Å)	11.770(19)	9.0425(17)	9.0453(2)	8.954(2)	8.954(2)
b (Å)	11.838(8)	11.3303(2)	11.3337(3)	13.854(3)	11.339(2)
c (Å)	9.018(9)	11.7353(8)	11.7372(8)	18.356(4)	11.656(2)
α (°)	107.217(83)	105.222(7)	105.223(7)	91.643(4)	105.920(17)
β (°)	112.167(67)	97.377(7)	97.383(7)	91.815(4)	97.081(4)
γ .(°)	101.500(83)	100.791(7)	100.790(7)	104.442(4)	100.253(4)
V (Å³)	1041(3)	1119.47(8)	1120.30(9)	2202.6(8)	1101.3(7)
Z	1	1	1	2	1

Column headings: (a): recrystallized huemulite (original description), (b) synthetic huemulite, (c) West Sunday mine material, (d) synthetic $Na_4Mg(V_{10}O_{28})•23H_2O$ (Miras *et al.* 2005) and (e) synthetic huemulite transformed according to the transformation matrix: 100 / 0½½ / 0½$\bar{½}$.

The structural unit ($[V_{10}O_{28}]^{6-}$)

The decavanadate group present in huemulite has a well-known and documented geometry (Schindler *et al*. 2000b, Hughes *et al*. 2002, 2005, 2008), with very little variation among different structures. It is centrosymmetric (Fig. 3) and consists of ten V atoms [V1 to V5 + (i), (i) being those related to the previous ones by the $-x + 2, -y + 2, -z + 2$ operation], and 28 atoms of oxygen, eight of them terminal [O1, O10–O12 + (i)], 14 μ_2-bridging [O2 to O5; O7, O8, O14 + (i)], four μ_3-bridging [O6, O9 + (i)] and two μ_6-bridging [O13 + (i)], linking the V atoms into an hexa-anionic species with D_{2h} point symmetry. There are no H atoms present in this structural unit.

The compact array can be described as formed by ten edge-sharing octahedra, each of which contains a single vanadyl bond [defined by Schindler *et al*. (2000b) as a V^{5+}–O bond shorter than 1.74 Å], save for V4, which contains two vanadyl bonds. In the remaining octahedra, the vanadyl bond is *trans* with respect to a long V–O bond, with four equatorial bonds of intermediate length approximately perpendicular to this O–V–O direction. In addition to binding to the vanadium atoms of the structural unit, some of these O^{2-} anions are bound to the Na atom. Hydrogen bonding to the H atoms of the (H_2O) groups of the interstitial complex is also possible.

The central atom O13 is special in that it binds to six V^{5+} atoms, an unusual coordination for oxygen, the more so considering that it is bound to such a highly charged cation. Bond-valence oversaturation is avoided by an elongation of the V–O bonds, so as to give a total of 1.96 valence units (*vu*), even lower than the expected 2.00 *vu*. Very similar values can be calculated for the central O atom in similar structures: 1.98 *vu* in hummerite (Hughes *et al*. 2002) and 1.96 *vu* in pascoite (Hughes *et al*. 2005), lasalite (Hughes *et al*. 2008) and magnesiopascoite (Kampf & Steele 2008).

The interstitial complex $\{Na_4Mg(H_2O)_{20}{\bullet}4H_2O\}^{6+}$

The symmetry-equivalent structural units in huemulite are connected by the interstitial complex; all oxygen atoms occur in the latter as (H_2O) groups, in contrast to the structural unit.

The Mg1 atom is coordinated by six H_2O groups [O8w to O10w + (ii), (ii): $-x + 1, -y, -z + 1$] determining an almost ideal $[Mg(H_2O)_6]^{2+}$ octahedron [Mg–O range: 2.0468(18)–2.0762(17) Å; O–Mg–O range: 93.26(7)–86.74(7)°] (Fig. 4). This group interacts with the structural unit only through hydrogen bonding. There are three independent Na atoms in the structure (Na1 and Na3 located at inversion centers and Na2 in a general position, Fig. 5), linked into an infinite zigzag chain by four μ_2-bridging H_2O (O1w and O7w; O5w and O6w), three μ_1 H_2O (O2w, O3w and O4w), and an oxygen belonging also to the decavanadate group (O1), which complete the octahedral environments around

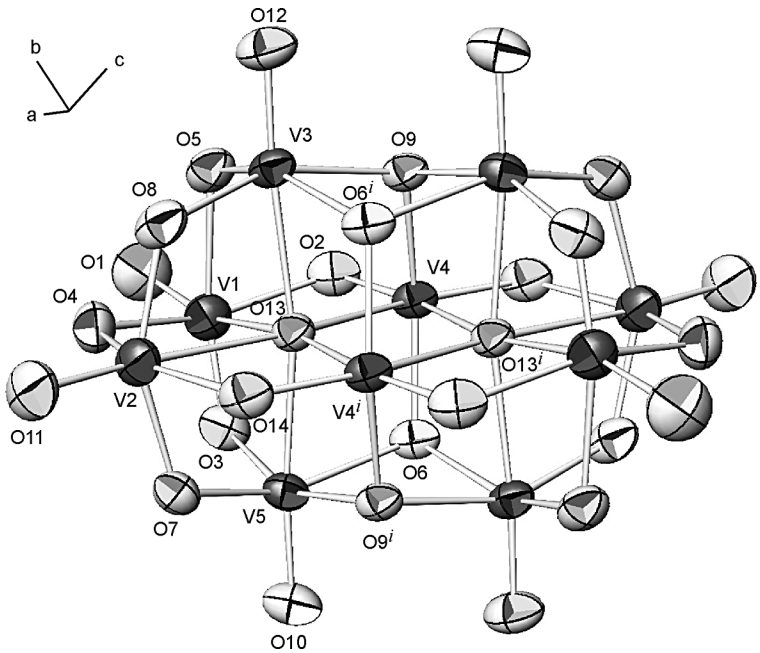


FIG. 3. Ellipsoid plots of the centrosymmetric decavanadate anion $[V_{10}O_{28}]^{6-}$. Unlabeled atoms are related to labeled ones by the symmetry operation (i) $-x + 2, -y + 2, -z + 2$.

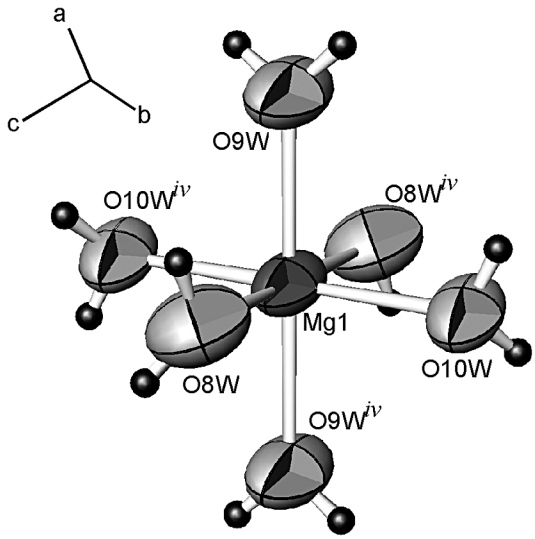


FIG. 4. Ellipsoid plots of the centrosymmetric Mg octahedron $[Mg(H_2O)_6]^{2+}$. For reasons of clarity, the labels of the hydrogen atoms have been omitted. Symmetry code (iv) $-x + 1, -y, -z + 1$.

each Na. The following ranges in Na–O distances and O–Na–O angles are found: Na1: 2.298(2)–2.4165(17) Å, 79.60(7)–100.40(7)°; Na2: 2.360(3)–2.629(2) Å, 84.10(8)–94.21(8)°; Na3: 2.411(2)–2.4132(19) Å, 83.38(8)–96.62(8)°. As seen in Figure 5, the consecutive pairs of (parallel) rhomboidal Na_2O_2 loops joining at Na1 and Na3 break their common line at Na2 by a zigzag linear angle of 112.6(1)°, and a dihedral angle of 60.1(1)°.

In addition to the direct bonding between the structural unit and the interstitial complex through two oxygen atoms [O1 and O1(i)], there is an extensive network of hydrogen bonds linking the two structural components. Schindler *et al*. (2000a) used the valence-matching principle to analyze the role and types of hydrogen bonds in vanadium minerals, and here we apply their method to the interaction between the structural unit and the interstitial complex in huemulite.

Bonding between the structural unit and interstitial complex in huemulite: bond-valence parameters and new values for Na^+, Mg^{2+} and V^{5+}

The interaction between the structural unit and interstitial complex can be understood by the capacity of each component to accept or to donate electrons, *i.e*., by their Lewis basicity and acidity (Brown 1981). In Table 6, we report the bond-valence sums of all atoms

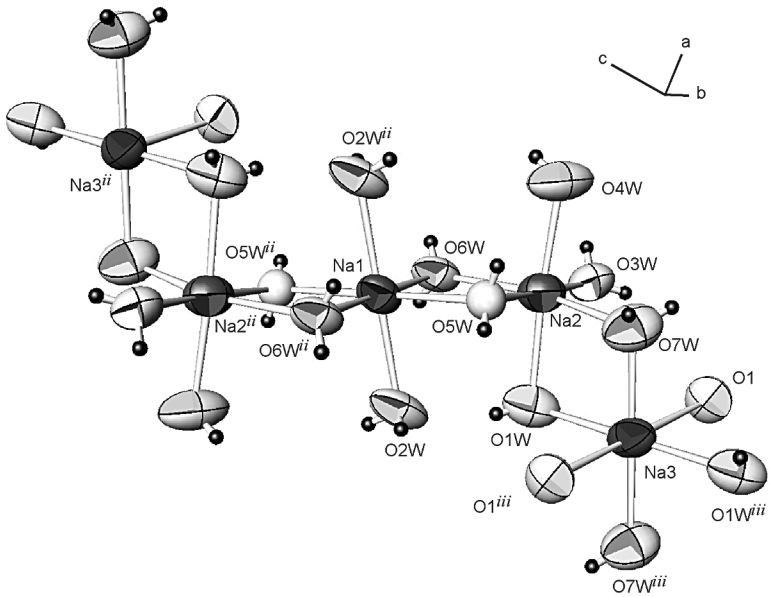


FIG. 5. Ellipsoid plots of the centrosymmetric sodium chain $[Na_4(H_2O)_{14}]^{4+}$. For reasons of clarity, the labels of the hydrogen atoms have been omitted. Unlabeled atoms are related to the labeled ones by the symmetry operations (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 2$.

TABLE 6. BOND-VALENCE SUMS IN SYNTHETIC HUEMULITE

	Na1	Na2	Na3	Mg1	V1	V2	V3	V4	(V4)	V5	H bonds	VB	
OW1		0.18	0.16								-0.11;-0.13;-0.15	-0.05	OW1
(OW1)			0.16										
OW2	0.16										-0.14;-0.21;+0.15	-0.04	OW2
(OW2)	0.16												
OW3		0.15									-0.16;-0.17;+0.18	0	OW3
OW4		0.18									-0.10;-0.10;-0.16;+0.16	-0.02	OW4
OW5	0.16	0.09									-0.12;-0.15	-0.02	OW5
(OW5)	0.16												
OW6	0.16	0.18									-0.15;-0.18	0.01	OW6
(OW6)	0.16												
OW7		0.19	0.22								-0.16;-0.06;-0.16	0.03	OW7
(OW7)			0.22										
OW8				0.33							--0.16;-0.20;+0.13	0.10	OW8
(OW8)				0.33									
OW9				0.36							-0.18,-0.22	-0.04	OW9
(OW9)				0.36									
OW10				0.33							-0.19; -0.21;+0.10	0.03	OW10
(OW10)				0.33									
OW11											-0.13;-0.18;+0.15;+0.20	0.04	OW11
OW12A											-0.04;+0.06	0.02	OW12A
OW12B											-0.12;+0.16	0.04	OW12B
O1			0.16		1.73							1.89	O1
(O1)			0.16										
O2					0.51			1.38			+0.12	2.01	O2
O3					0.84					0.91	+0.16;+0.21	2.12	O3
O4					0.92	0.93					+0.04	1.89	O4
O5					0.8		0.98				+0.10;+0.21	2.09	O5
O6							0.58	0.78		0.56	+0.13	2.05	O6
O7						0.77				1.01	+0.22	2.00	O7
O8						0.88	0.91				+0.10;+0.15	2.04	O8
O9							0.61	0.68		0.61	+0.18	2.08	O9
O10										1.66	+16;+0.17	1.99	O10
O11						1.65					+0.16;+0.19	2.00	O11
O12							1.69				+0.14;+0.16	1.99	O12
O13					0.26	0.26	0.3	0.43	0.43	0.31		1.99	O13
(O13)								0.43	0.43				
O14						0.53		1.34			+0.18	2.05	O14
VB	0.96	0.97	1.08	2.04	5.06	5.02	5.07	5.01		5.06			

Notes: Non-hydrogen bond strengths have been specifically calculated for this work (see Table 7 for details). Hydrogen bond strengths were based on O…O distances following Ferraris & Ivaldi (1988). Valence summations are expressed in valence units.

in huemulite (the synthetic sample), calculated with improved bond-valence parameters as explained below.

At this stage, a brief consideration regarding the bond-valence (B.V.) calculation is in order. Because bond-valence parameters are dependent not only on the cation–anion pair involved, but also on second-order factors such as oxidation states and coordination numbers [Brown (2009) provided an illuminating review on the subject], the confidence in a particular B.V. calculation strongly depends upon having an accurate set of parameters to describe the situation under study. As it is not easy to have a suitable set of parameters at hand, the most convenient way is to generate them by selecting a particular subset of reported structures with adequate geometry, similar to the one of interest (I.D. Brown, pers. commun. 2008). This has been our approach, and we have obtained the $\mathbf{R_0}$ parameters used in this work through a very simple least-squares calculation performed on a selected group of cases, taken both from the CSD (Allen 2002) and the ICSD (ICSD 2008) and having the ***S*** parameter constant at its usual value of 0.37. Table 7 gives details of the procedures used for these calculations and the results obtained, as well as a comparison with similar results in the literature. For our group of interest, $[V_{10}O_{28}]^{6-}$, the calculated range in Lewis basicity is 0.15–0.17 *vu* (Schindler *et al*. 2000a).

Huemulite contains the interstitial complex $\{Na_4Mg(H_2O)_{20}(H_2O)_4\}^{6+}$ and the structural unit $[V_{10}O_{28}]^{6-}$. In order to test whether the Lewis acidity of the interstitial complex matches the range in Lewis basicity of the structural unit, we must calculate the number of bonds emanating from the complex. This step requires detailed information of the types of (H_2O) groups in the interstitial complex accepting bonds from interstitial cations and other H_2O groups, including: (a) transformer (H_2O) groups, defined as those which accept one bond, (b) non-transformer (H_2O) groups, and (c) reverse transformer (H_2O) groups, which accept three bonds. Further details about these arrangements are given by Schindler & Hawthorne (2001c).

Inspection of the bond-valence table for huemulite (Table 6) shows that O9W is the only transformer H_2O group, accepting one bond from Mg1 with hydrogen bonds to O3W and O7; the disordered O12WA,B H_2O groups behave in a similar fashion, acting as hydrogen-bond acceptors toward H2WA,B and as donors toward O4 and O4W (see Table 4). All remaining H_2O groups accept two bonds, while providing another two. Thus, the interstitial complex can be described in detail as: $\{^{[6]}Na_4\ ^{[6]}Mg\ (H_2O)_4\ (H_2O)_{20}\ (H_2O)_0\}^{6+}$, in which the different H_2O groups are listed in the sequence transformer, non-transformer and reverse-transformer (H_2O) groups. Neither the second group nor the third

TABLE 7. CALCULATION OF BOND-VALENCE PARAMETERS FOR Na^+, Mg^{2+} AND V^{5+}

Cation	R_0	S	Final valence	Comments	Ref.
V^{5+}	1.799(6)	0.37	4.997(117) *vu*	From a VO_6 group in decavanadate, using 1212 bonds, in 202 octahedra	(vii)
V^{5+}	1.803	0.37			(i, vi)
V^{5+}	1.799	0.37			(ii)
Na^+	1.737(16)	0.37	0.975(15) *vu*	From a NaO_6 group, (no further restriction) using 7944 bonds in 1324 octahedra	(vii)
Na^+	1.800	0.37			(vi)
Na^+	1.803	0.37			(I)
Na^+	1.756	0.37			(iii)
Na^+	1.5766	0.475		Including second neighbors	(iv)
Na^+	1.661	0.44			(v)
Mg^{2+}	1.665(8)	0.37	1.993(121) *vu*	From a MgO_6 group (no further restrictions) using 4386 bonds in 731 octahedra	(vii)
Mg^{2+}	1.693	0.37			(i, vi)
Mg^{2+}	1.636	0.42			(v)

References: (i) Brown & Altermatt (1985), (ii) Tytko *et al.* (1999), (iii) Wood & Palenik (1999), (iv) Adams (2001), (v) Allmann (1975), (vi) Brese & O'Keeffe (1991), (vii) this work. Values obtained by a least-squares fit to the formula. Expected cation valence: = Σ exp [(R_0 – R)/S], where the sum is taken over a coordination polyhedron, and where R stands for the coordination distance.

(no groups of this type available in this particular case) contribute to the final equation. The total number of bonds from this complex is provided by: 4 × 6 (Na) + 1 × 6 (Mg) + 4 [transformer (H_2O) groups] – 0 [reverse transformer (H_2O) groups] = 34 bonds. This number of bonds results in a Lewis acidity of 6 / 34 = 0.176 *vu*, just slightly in excess of the upper limit of the Lewis basicity of the structural unit $[V_{10}O_{28}]^{6-}$ (0.15–0.17 *vu*). Hewettite, $Ca(V_6O_{16})(H_2O)_6$, with a Lewis acidity of 0.15 and a Lewis basicity of 0.14 (Schindler *et al.* 2000a), is another example where there is a small difference between the bond valences of the structural unit and the interstitial complex, yet it is also a stable structure.

It should be mentioned that the $(V_{10}O_{28})^{6-}$ anion achieves its maximum concentration at a pH value of 5.8 (Schindler *et al.* 2000a). Interestingly, Gordillo *et al.* (1966) reported that after dissolution of huemulite in cold water, the pH of the solution is between 5.5 and 6.5. A mildly acidic environment of crystallization can be expected at the type locality, where Cu–Fe–(Zn–Pb) sulfides have been reported (Gordillo *et al.* 1966), which upon oxidation would lower the pH.

The crystal-structure refinement of huemulite confirms that it can be included in the pascoite family, defined by Hughes *et al.* (2008) as those minerals formed by a structural unit $[V_{10}O_{28}]^{6-}$ balanced by interstitial groups composed of mono- and divalent cations plus Al^{3+} (up to now, only Na, K, Mg, Ca, and Al are known) fully coordinated by H_2O groups. Other species belonging to this family are pascoite, $Ca_3[V_{10}O_{28}]•17H_2O$, magnesiopascoite, $Ca_2Mg[V_{10}O_{28}]•17H_2O$, hummerite, $K_2Mg_2[V_{10}O_{28}]•16H_2O$, lasalite, $Na_2Mg_2[V_{10}O_{28}]•20H_2O$, rakovanite, $Na_3\{H_3[V_{10}O_{28}]\}•15H_2O$, and hughesite, $Na_3Al(V_{10}O_{28})•22H_2O$. It should be mentioned that a number of synthetic compounds (see list in Hughes *et al.* 2005, page 1384, for a long, but not exhaustive list) are known whose structural unit is also the $[V_{10}O_{28}]^{6-}$ polyanion.

Structurally Related Compounds

When analyzing the literature in search of candidates for comparison, we found that huemulite (labelled I) is chemically and structurally related to a family of synthetic materials formulated as $Na_4MV_{10}O_{28}•23H_2O$ (M = Ni^{2+}, Mg), described by Sun *et al.* (2002, M = Ni^{2+}, labeled IIa in this work) and Miras *et al.* (2005, M = Mg, labeled IIb in this work). The transformation matrix M = [100 / 011 / 01$\bar{1}$] applied to the structure of huemulite not only transformed its unit-cell parameters into a different set with values very similar to those of (IIa,b) (Table 8), but also brought the atoms to almost the same coordinates (Fig. 6).

The transformation modifies the initial primitive cell of huemulite ($P\bar{1}$, Z = 1) into a doubled one, centered at *a* and thus describable as *A*. Inspection of Figure 7 provides an understanding of some of the basic differences in the two structures from a crystallographic point of view. The small shaded triclinic cell at the top corresponds to the primitive unit-cell of (I), space group $P\bar{1}$, as used throughout this analysis. All the heavy dots on the cell axis represent centers of symmetry in this cell, where some of the centrosymmetric groups reside, either $V_{10}O_{28}$, $Na_3(H_2O)_{14}$ or $Mg(H_2O)_6$. If the structure is described instead by the double cell derived from the

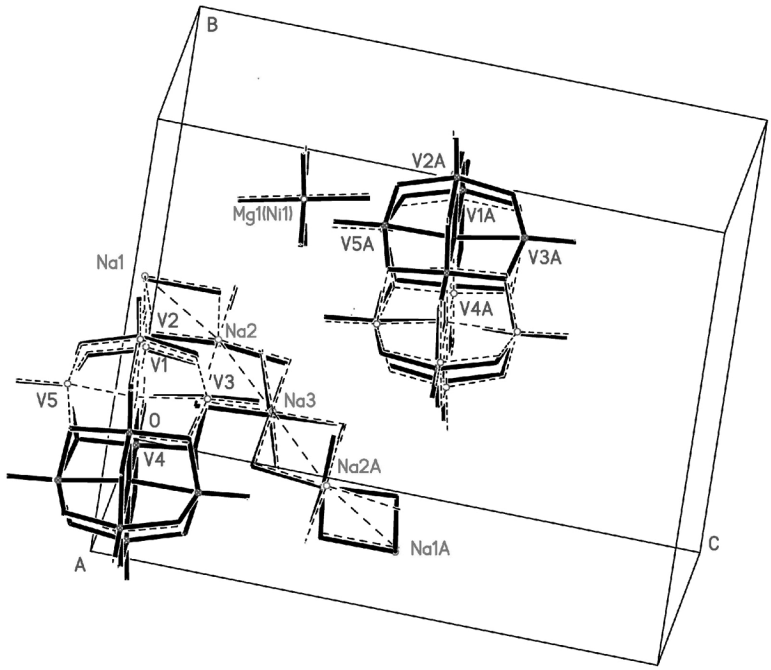


FIG. 6. Structural superposition of I (full line) and IIa,b (dashed lines), showing the almost perfect match, in spite of the crystallographic differences.

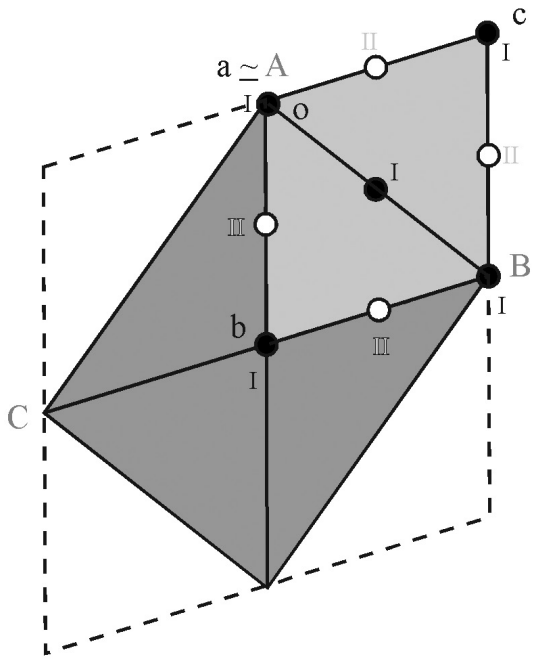


FIG. 7. Cell transformation relating I to I_T and IIa,b (see text for details).

TABLE 8. COMPARISON AMONG THE ISOTYPIC COMPOUNDS

	synthetic huemulite (this study, I_T)	IIa $Na_4Ni(V_{10}O_{28})$ $\cdot 23H_2O$ (Sun *et al.* 2005)	IIb $Na_4Mg(V_{10}O_{28})$ $\cdot 23H_2O$ (Miras *et al.* 2005)
a (Å)	9.0369(8)	8.925(2)	8.924(2)
b (Å)	13.9692(14)	13.862(3)	13.854(3)
c (Å)	18.2825(13)	18.341(4)	18.356(4)
α (°)	92.116(7)	91.81(3)	91.643(4)
β (°)	91.994(6)	91.85(3)	91.815(4)
γ (°)	105.027(8)	104.32(3)	104.442(4)
V (Å^3)	2225.2(3)	2195.5(8)	2202.6(8)
Z	2	2	2
Space group	$A\bar{1}$	$P\bar{1}$	$P\bar{1}$

M transformation already discussed, the space group is now $A\bar{1}$, with the centers of symmetry, of course, still present. This is the cell (hereafter I_T) that is metrically and structurally equivalent to those of IIa and b. The latter, however, even if sharing the same external "cage", is internally described by a primitive space-group $P\bar{1}$, having in common with I_T only the centers of symmetry marked as black dots in Figure 7, but not the white ones, which become general positions. As a consequence, some of the symmetry restrictions present in the constitutive groups in I_T, *e.g.*, inversion centers

and cell centering, are relaxed. There is in addition a different state of hydration (four H_2O per formula in I_T, two in IIa,b).

However, there remains the very real possibility that Miras *et al*. (2005) based the structure of their synthetic phase on the *A*-centered unit cell, but mistakenly assigned it the $P\bar{1}$ space group. It is also possible that Miras *et al*. failed to locate the partially occupied H_2O sites (O12W and O13W) and that their phase is, in fact, chemically and structurally identical to huemulite.

Acknowledgements

We are grateful to Raúl Lira and Hebe D. Gay for providing the sample of synthetic huemulite donated by C.E. Gordillo. Joe Marty graciously made available the samples of natural huemulite. Francisco Locati and Silvina Marfil kindly measured an EDS spectrum. The manuscript benefitted from the very detailed criticism by Uwe Kolitsch, Associate Editor Olga Yakubovich, Editor Robert Martin and an anonymous reviewer; all of them are gratefully acknowledged. This study was funded, in part, by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

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Received April 19, 2010, revised manuscript accepted June 6, 2011.