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HUEMULITE,¹ Na₄MgV₁₀O₂₈·24H₂O, A NEW HYDROUS SODIUM AND MAGNESIUM VANADATE FROM HUEMUL MINE, MENDOZA PROVINCE, ARGENTINA

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ABSTRACT

Huemulite, a new mineral with the formula Na₄MgV₁₀O₂₈·24H₂O, was found in several uraniferous ore-bodies of the "sandstone-type deposits", in the southwestern part of Mendoza province, Argentina. Huemulite appears in botryoidal masses, thin films, or as interstitial filling in the sandstone that is the host rock. It is soft, yellowish orange to orange in color, with a dull luster and specific gravity of 2.39 g/cm³. It is not fluorescent.

The mineral is easily soluble in cold water, giving an orange solution of pH 5.5 to 6.5. From this solution the mineral recrystallizes giving tabular crystals elongated parallel to (010), with a perfect cleavage parallel to (001) and less perfect parallel to (010). The optical properties determined in the recrystallized material show that the mineral is biaxial negative, 2V=25°–30°, pleochroic with X light yellow, Y golden yellow, and Z yellowish orange. The indices of refraction measured with sodium light are $\alpha=1.679$, $\beta=1.734$, and $\gamma=1.742$. The dispersion is strong with $r > v$.

Chemical analyses were performed on both natural and recrystallized material. A synthetic compound was prepared which gives a *x*-ray powder, and single crystal data similar to those of huemulite.

Huemulite is triclinic, space group P1 or P $\bar{1}$. Unit cell data obtained on the recrystallized material are: $a=11.770 \text{ \AA} \pm .019$, $b=11.838 \pm .008$, $c=9.018 \pm .009 \text{ \AA}$, $\alpha=107^\circ 13' \pm 05'$, $\beta=112^\circ 10' \pm 06'$, $\gamma=101^\circ 30' \pm 05'$; $a:b:c=0.9943:1:0.7618$, $V=1040.67 \text{ \AA}^3 \pm 2.70$. Cell contents Na₄MgV₁₀O₂₈·24H₂O gives a calculated density of 2.40 g/cm³. The strongest lines of the *x*-ray powder diffraction pattern are: 7.6 (100), 10.6 (90), 9.1 (60), 10.2 (55), 8.2 (35), 3.05 (30), 5.26 (25).

The name huemulite comes from the Huemul mine, the most important uranium deposit of the area where the mineral was discovered.

INTRODUCTION

This paper presents the study of a new hydrous sodium and magnesium vanadate that was found in some of the uraniferous deposits of the Malargüe area, Mendoza province, Argentina. The discovery of this

¹ Approved by the Commission on New Minerals and Mineral Names, IMA, May 19, 1965.

species adds a new natural member to the salts of the isopolycomplex ion $(V_{10}O_{28})^{6-}$, described by Evans *et al.* (1955; 1964).

V. Angelelli of the Geology Department of the Argentina Atomic Energy Commission (C.N.E.A.) first collected huemulite in 1959, in the underground level -18 of the ore-body known as Agua Botada. The sample was given to Linares for identification as a possible secondary mineral of uranium or vanadium. Optical and *x*-ray determinations showed that it did not correspond with any of the uranium or vanadium minerals known, thus starting an investigation of its physical and chemical properties.

More material was collected during other visits to the area and it was also identified in the ore bodies Huemul, and Agua Botada Sur (Brodtkorb, 1963), which are adjacent to the original site of discovery.

Preliminary chemical tests showed that the mineral is a hydrous sodium vanadate with uranium present only as impurity. The tests also showed that it is easily soluble in water and that it can be readily recrystallized from the solution by slow evaporation of the water. The optical and other physical properties were investigated mainly in recrystallized material whose identity with natural material was checked by *x*-ray data. Chemical analyses were performed in both natural and recrystallized mineral; similar or identical synthetic compound was also prepared and studied.

A preliminary report with all the data obtained was presented to the II Argentine Geological Congress in 1963 (Linares *et al.*, 1963). The following year the unit cell was measured by Linares and Winchell at Yale University and the data thus obtained refined using the facilities of the Yale Computer Center. During the same year the chemical and physical properties were more elaborately checked by Gordillo and Toubes in the laboratories of the C. N. E. A.

The new mineral is named huemulite from the most important uranium mine of the Malargüe area.

ACKNOWLEDGEMENTS

Thanks are due by Linares, Gordillo and Toubes to our colleagues of the Servicio Laboratorios (C.N.E.A.), and to V. Angelelli who encouraged us in the study of this mineral, and also to Angelelli and P. N. Stipanovic for many helpful suggestions.

Linares is also indebted to the Division of Raw Materials of the U. S. Atomic Energy Commission and to Dr. M. L. Jensen of Yale University, since the last part of this investigation was carried out during his post-doctoral research year at Yale University, under a grant AT(30-1) 2261 of the U.S.A.E.C.

OCCURRENCE

Huemulite was found the first time in the level -18 of the ore-body Agua Botada. It was later found elsewhere in the same mine and also in the Huemul and Agua Botada Sur mines.

The uraniferous district known as "Malargüe area," where these mines are located is in the southwestern part of Mendoza province, about 450 km southwest of the city of Mendoza, Argentina (Fig. 1). The area is generally one of continental sediments of Middle Cretaceous age, called locally Diamantino, with a total thickness of 900 m. Overlying it are marine and continental sediments of Upper Cretaceous and Tertiary age. Middle Tertiary (Oligocene) basic volcanic bodies, predominantly hornblendiferous andesites, cut through the sediments in the entire area. There are some outcrops of small flat bodies of ignimbrite. The complex is covered by Pleistocene and Recent sediments.

The uraniferous ore-bodies are located in conglomerates, arkosic conglomerates, and arkosic sandstone beds of the lower portion of the Diamantino. The sandstones are generally enclosed between beds of siltstone and claystone; they are always associated with an asphaltic material originating, it is thought, from the oil in the adjacent small oil field of Pampa Amarilla. The average dip of these beds is 35° W., with a mean thickness of 1.2 m and a grade of 0.25% U_3O_8 , 2.0% of Cu and 0.2% V_2O_5 .

Uraninite is the principal uranium mineral; it occurs with copper and iron sulfides such as chalcopyrite, chalcocite, covellite, bornite, idaite, pyrite, marcasite, and small amount of galena and sphalerite (Brodtkorb, 1963). No primary vanadium minerals are known yet. It is thought that the probable source of this element is the asphaltic material.

In the alteration zone above the water-table, many hydrated yellow minerals like tyuyamunite, sengierite, carnotite, cuprosklodowskite, autunite, bayleyite, andersonite, etc. are found in close association with copper minerals such as malachite, azurite and chalcantite.

The three principal ore-bodies of the area shown in Fig. 1 are Huemul, Agua Botada and Agua Botada Sur.

PHYSICAL AND OPTICAL PROPERTIES OF HUEMULITE

Huemulite is yellowish orange to orange in color. It occurs as an aggregate of microscopic fibers, rounded masses forming thin films, and as interstitial filling in the sandstone. It is associated with the vanadates hummerite and rossite, and also with thenardite, gypsum and epsomite. The mineral is formed shortly after the levels and underground works are opened and is easily recognized by its bright color.



FIG 1 General geology and uraniumiferous deposits of the Malarqué district, Mendoza province, Argentina. (After Stipanovic, P. N. *et al.*, 1962).

Natural huemulite is too fine-grained to permit the accurate determination of its properties. However, it may be recrystallized very easily by evaporating a water solution made from it. The product gives the same x-ray powder pattern, and to the extent that other measurements can be made on the fine-grained material, both recrystallized and wholly-synthetic huemulite thus obtained have properties identical with the natural mineral.

The habit of the recrystallized material and also of the synthetic product is tabular, similar to rossite (Palache *et al.*, 1951), elongated parallel to the *c*-axis with perfect cleavage parallel to (001) and less perfect parallel to (010). The physical properties of the natural and recrystallized material are the following:

	Natural	Recrystallized
Color	Yellowish orange to orange	Yellowish orange to reddish orange, depending on the thickness of the crystals obtained.
Streak	Yellow	Yellowish orange
Fluorescence	None	None
Luster	Dull	Vitreous to subadamantine
Hardness		2.5 to 3. Brittle
Density	2.39 g/cm ³	

The optical properties were determined in the recrystallized mineral and in the synthetic material, with very good agreement between both sets of data (Table 1). Under the microscope, thin crystals of huemulite are yellow, pleochroic, biaxial negative with 2V near 25° to 30°. The birefringence is high, with colors that range from blue to green.

TABLE 1. OPTICAL PROPERTIES OF HUEMULITE

		Recrystallized	Synthetic
Pleochroism	X	light yellow	light yellow
	Y	golden yellow	yellowish orange
	Z	yellowish orange	yellowish orange
Refractive indices ¹	α	1.679 ± .003	1.680 ± .002
	β	1.734 ± .003	1.734 ± .002
	γ	1.742 ± .003	1.738 ± .002
2V _x		20° to 25°	25° to 28°
Dispersion		<i>r</i> > <i>v</i> , strong	<i>r</i> > <i>v</i> , strong

¹ The indices of refraction were measured by R. O. Toubes in the recrystallized mineral by C. E. Gordillo in the synthetic material, both using sodium light at 20° C.

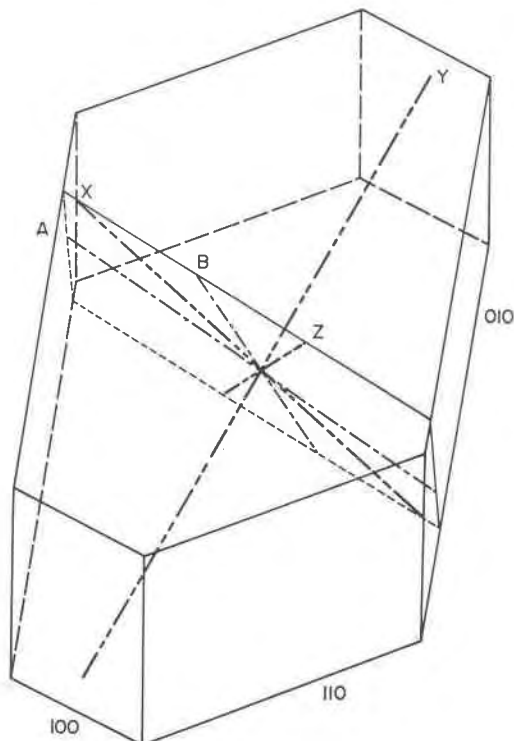


FIG. 2. Preliminary optical orientation of huemulite.

X-RAY CRYSTALLOGRAPHY

Single crystals of the recrystallized mineral were studied using rotation, Weissenberg, and precession methods to determine the dimensions of the unit cell. These data were then refined by using the powder data obtained on both natural and recrystallized material on a Norelco wide-range diffractometer. Zero-point corrections were applied to each diffractometer chart by reference to quartz peaks (100) and (101) at $2\theta = 20.840$ and 26.640 respectively ($\text{CuK}\alpha = 1.54050$; angle calculated from d-data of Swanson *et al.*, 1953). The quartz was present in the natural material as a minor impurity, and was added to the synthetic powders before making the charts used for refinement. The single-crystal data permitted unequivocal indexing of eight lines in the powder patterns; a least-squares solution using the 2θ values for these eight lines permitted indexing several more lines and further refinement of the lattice constants. The final refinement gave an unreliability number $S_Q = 0.00012$, where S_Q^2 is the sum of the squared differences between observed and calculated

TABLE 2. CRYSTALLOGRAPHIC DATA OF HUEMULITE AND SYNTHETIC COMPOUND

	Huemulite	Synthetic
Symmetry	Triclinic	Triclinic
<i>a</i>	11.770 Å ± .019 ¹	11.694 Å ± .123 ¹
<i>b</i>	11.838 ± .008	11.869 ± .053
<i>c</i>	9.018 ± .009	9.049 ± .061
α	107° 13' ± 05'	107° 28' ± 35'
β	112° 10' ± 06'	111° 52' ± 40'
γ	101° 30' ± 05'	101° 27' ± 31'
<i>a</i> : <i>b</i> : <i>c</i>	0.9943:1:0.7618	0.9853:1:0.7624
Volume	1040.67 Å ³ ± 2.70	1041.26 Å ³ ± 17.56
Space group	<i>P</i> 1 or <i>P</i> $\bar{1}$	<i>P</i> 1 or <i>P</i> $\bar{1}$
Unit cell contents	Na ₄ MgV ₁₀ O ₂₈ · 24H ₂ O	Na ₄ MgV ₁₀ O ₂₈ · 24H ₂ O
Density:		
Calculated from		
Na ₄ MgV ₁₀ O ₂₈ · 24H ₂ O	2.404	2.403
Observed	2.39 ± .05	

¹ Standard error from least-squares solution; these estimates measure precision on the basis of internal consistency only.

The least-squares refinement program is one written by C. W. Burnham of the Geophysical Laboratory, Washington, D. C., to whom our thanks are due for a Fortran deck for compiling the program.

Q-values for the lines used, divided by 14 (6 parameters were calculated using 20 lines measured on two diffractometer charts made with natural and with recrystallized huemulite).

Parallel runs on data from the same charts and from these charts plus one made with wholly-synthetic material, with and without correction terms to allow for specimen displacement from the diffractometer axis (Kasper and Lonsdale, 1959, p. 221), showed

(a) that the systematic correction-term parameters were much smaller (*t* = .38 to .59) than their own estimated standard errors, (b) that the unreliability number *S*_Q was greater with than without correction-terms, and (c) that the wholly-synthetic powder, either alone or with the others, yields poorer results for reasons still unknown.

All of the lattice constants thus calculated agree within their respective standard errors, with the data in Table 2.

In Table 3, the x-ray powder diffraction data for natural, recrystallized, and synthetic huemulites are compared with calculated values obtained from the least-squares refinement.

DIFFERENTIAL THERMAL ANALYSES

Samples of natural huemulite and of the synthetic compound were analyzed in a Deltatherm apparatus, model D-200, using chromel-alumel

TABLE 3. X-RAY POWER DATA FOR HUEMULITE NATURAL, RECRYSTALLIZED, AND SYNTHETIC ($\text{CuK}\alpha=1.54050$)

N°	hkl	Calculated d Å	Film Natural		Natural		Diffractometer Recrystallized		Synthetic	
			I	d Å	I	d Å	I	d Å	I	d Å
1	010	10.586	Sb	10.77	90	10.59	85	10.61	100	10.65
2	100	10.205			55	10.20	50	10.20	65	10.12
3	110	9.122	S	9.11	60	9.12	50	9.11	40	9.05
4	101	8.211	M	8.22	35	8.22	35	8.20	10	8.19
5	001	7.622	VS	7.62	100	7.62	100	7.61	65	7.62
6	111	6.043	w	6.07	15	6.07	10	6.04	20	6.08
7	{111 201}	{5.673 5.620}	w	5.62	7	5.63	5	5.66	10	5.65
8	210	5.398			9	5.41			8	5.45
9	020	5.293			11	5.32	9	5.32	11	5.34
10	011	5.250			25	5.26	16	5.25	10	5.29
11	211	5.150	w	5.13	10	5.18	10	5.17	5	5.18
12	220	4.561	w	4.57	14	4.567	8	4.559	6	4.562
13	112	4.488			13	4.485	8	4.491	5	4.502
14	{221 122}	{4.030 3.995}	w	4.022	15	4.000	9	4.024	4	4.015
15	022	3.953			20	3.956	15	3.952	15	3.973
16	{221 131}	{3.808 3.802}	w	3.793	25	3.795	20	3.792	10	3.798
17	{221 021}	{3.698 3.696}	w	3.681	20	3.696	15	3.681	8	3.699
18	112	3.600	w	3.581	20	3.580	20	3.580	11	3.566
19	{320 302}	{3.470 3.463}			15	3.469	7	3.467	15	3.450
20	312	3.305			7	3.305	4	3.300	6	3.298
21	{312 132}	{3.278 3.270}	w	3.276	15	3.268	7	3.264	20	3.259
22	012	3.193			20	3.182	6	3.175	15	3.173
23	220	3.160			15	3.147	10	3.148	15	3.153
24	{131 330}	{3.071 3.046}	M	3.064	30	3.054	25	3.060	12	3.062
25	113	2.967			11	2.963	10	2.961	10	2.964
26			M	2.905	35	2.833	35	2.882	10	2.886
27					25	2.843	20	2.843	12	2.849
28			w	2.817	10	2.813	7	2.812	11	2.817
29					25	2.750	10	2.748	8	2.753
30			M	2.714	25	2.703	20	2.704	6	2.696
31					17	2.617	11	2.616	15	2.612
32			w	2.569	15	2.570	10	2.566	9	2.569
33					10	2.532	7	2.533	6	2.529
34			vw	2.489	13	2.489	7	2.493	8	2.496
35					9	2.399	9	2.399	10	2.396
36					9	2.339	5	2.339	7	2.339
37			M	2.293	15	2.296	13	2.296	7	2.294
38			vw	2.196			9	2.187		
39			vw	2.132			14	2.147		
40			w	2.094			12	2.101		
41			w	2.045			10	2.053		

thermocouples, kaolin calcined at 950° C. as inert material, with a rate of heating of 10° C./min \pm 10%, in an air atmosphere.

For the DTA analyses, 300 mg of pure samples of both huemulite and synthetic were ground to 30 microns to avoid any error attributable to particle size and also permit the comparison between different curves. The samples were left in a desiccator, with a humidity of about 50%, for 48 hours to attain equilibrium.

The curves obtained (Fig. 3) are similar for both huemulite and synthetic, with endothermic peaks at 85° C., 133° C., and 169° C. The areas

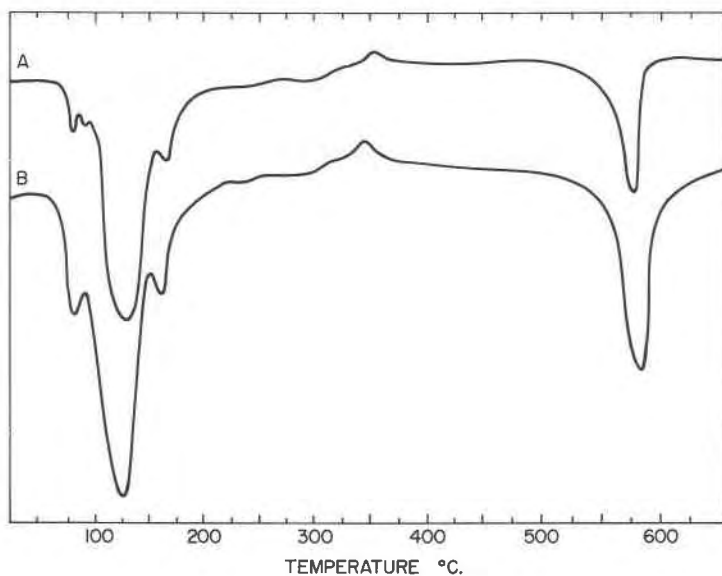


FIG. 3. Differential thermal analysis curves of: A—natural huemulite; B—synthetic huemulite.

corresponding to these peaks, measured with a Coradi polar planimeter showed that of the total 24 molecules of water, 2 are given off to produce the first peak, 20 for the middle one and 2 for the third one. The small endothermic peak that appears in the curve of the natural material at 97° C. and not detected in the synthetic, corresponds to gypsum present as impurity.

The small exothermic peak between 340° C. and 360° C., corresponds to recrystallization of the anhydrous molecule with evolution of heat. The endothermic peak at 580° C. corresponds to the melting of the mineral.

The thermogravimeter curve was performed in a Chevenard thermobalance, with photographic register and a rate of heating of 300° C./hour.

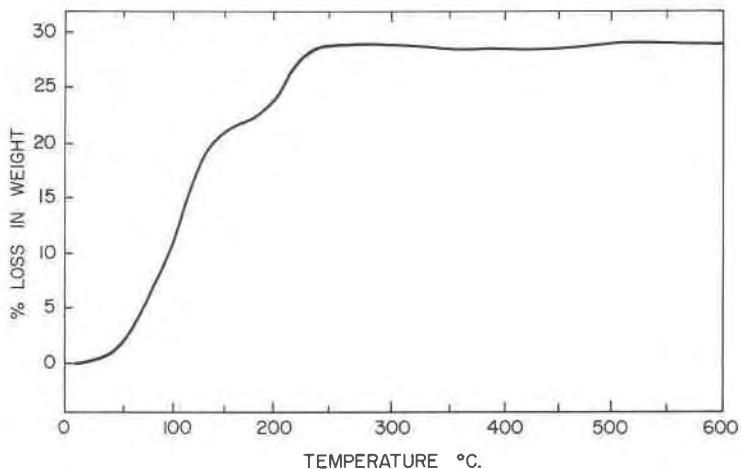


FIG. 4. Chevenard thermobalance curve of huemulite.

Samples weighing 200 mg of both natural and synthetic huemulite were used. The curve obtained is shown in Fig. 4 and is the same for both. The loss of weight took place in three steps. The total loss corresponds exactly with the 24 molecules of water and is complete at 255° C. The weight loss up to 150° C. corresponds only to 17 molecules.

The poor coincidence between the data obtained with these methods

TABLE 4. CHEMICAL ANALYSES OF HUEMULITE (NATURAL MATERIAL)

	Sample 1	Sample 2
I. Insoluble in cold water	25.8%	25.43%
II. Soluble in cold water		
V ₂ O ₅	35.5	40.21
CaO ¹	5.6	3.53
SO ₃ ¹	7.2	4.45
K ₂ O	0.4	0.52
Na ₂ O	4.2	3.94
MgO	n.d.	1.18
MnO	n.d.	0.02
UO ₃	<10 ppm	<10 ppm
III. Water on natural sample		
H ₂ O—	11.5	12.00
H ₂ O+	8.0	8.80
Totals	98.2	100.08

¹ The content of CaO and SO₃ corresponds to gypsum as an impurity which was easily checked by optical and x-ray determinations.

TABLE 5. CHEMICAL COMPOSITION OF RECRYSTALLIZED AND SYNTHETIC MATERIALS AND THEORETICAL COMPOSITION OF HUEMULITE

	Recrystallized			Synthetic H/5			Synthetic H/7			Theoretical composition %			
	Analys. %	Ratios	Metal equiv.	Oxygen equiv.	Analys. %	Ratios	Metal equiv.	Oxygen equiv.	Analys. %		Ratios	Metal equiv.	Oxygen equiv.
V ₂ O ₅	59.8	.329	.658	1.645	60.06	.330	.660	1.650	60.46	.332	.664	1.660	60.39
Na ₂ O	8.4	.135	.270	.135	8.52	.137	.274	.137	8.33	.134	.268	.134	8.24
MgO	3.0	.075	.075	.075	2.90	.072	.072	.072	2.91	.072	.072	.072	2.68
H ₂ O	29.2	1.622	3.244	1.622	28.60	1.589	3.178	1.589	28.45	1.580	3.160	1.580	28.69
Total	100.4	—	—	—	100.08	—	—	—	100.15	—	—	—	100.00
	Tot. Oxygen equivalent			3.477	Tot. Oxygen equivalent			3.448	Tot. Oxygen equivalent			3.446	

Atoms per unit cell.¹

Element	Recrystallized	Synthetic H/5	Synthetic H/7
V	9.9	9.9	9.9
Na	4.0	4.1	4.0
Mg	1.1	1.1	1.1
H	48.6	47.6	47.4
O	52.0	51.7	51.6

¹ Atoms per unit cell calculated multiplying the metal and oxygen equivalent by 0.01 (to convert to a fractional scale) and by 1.498 gram-formula weight, derived from the unit cell volume (1040.7 Å³), observed density (2.39 g/cm³) and Avogadro's number (6.02×10²³).

should be attributed to the poor precision of the thermobalance and to the different rates of heating.

CHEMICAL PROPERTIES AND COMPOSITION

Huemulite is easily soluble in cold water; the solution obtained is orange yellow and the pH is 5.5 to 6.5, with no reducing power. Thus all the vanadium must be as V^{5+} . The mineral melts at 500° C. to a red liquid.

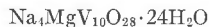
The water solution of the natural material recrystallizes if evaporated slowly, giving the crystals that were used for the single-crystal study and for the final determination of the optical properties. In this case we obtained crystals as big as 5 mm, weighing 15 to 20 mg. If the recrystallization is made in a more humid environment (by putting the Petri dish with the solution inside a larger container filled with water), instead of obtaining well formed crystals, we got fibrous or radial aggregates of acicular or needle-like crystals.

Huemulite is easily synthesized in a humid environment by putting the stoichiometric quantities of vanadium pentoxide, basic magnesium carbonate and sodium carbonate in cold water. The mixture is heated in a water bath until the components dissolve and react with each other, and CO_2 is eliminated. The solution is concentrated and the excess vanadic acid separated by filtration. After this, the solution is allowed to cool and crystallize.

Chemical composition. The chemical analyses made on two impure samples of huemulite are given in Table 4.

The first chemical analyses performed on recrystallized material (Table 5) showed a deficit in the total; in the beginning of our study it was impossible to synthesize a compound that would give the same x -ray diffraction data as the original. After several runs and tests, we supposed that the deficit might correspond to magnesium. A new chemical analysis was performed and a synthetic prepared introducing magnesium in the composition. At this time we obtained triclinic crystals similar to huemulite and the x -ray data and optical properties of these last crops (H/5 and H/7) agree very well with those of huemulite (Tables 2 and 3).

The chemical analyses of the two different crops of synthetic crystals, of the recrystallized material, and the theoretical composition of huemulite are given in Table 5, which shows that the unit-cell content is:



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