

THE CRYSTAL STRUCTURE OF HEWETTITE

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ABSTRACT

Crystals of hewettite ($\text{CaV}_6\text{O}_{16}\cdot 9\text{H}_2\text{O}$) from Colorado are monoclinic, space group $P2_1/m$, a 12.290(1), b 3.590(1), c 11.174(2) Å, β 97.24(1)°. As predicted previously, the V_6O_{16} layer structure is similar to that of $\text{Li}_3\text{V}_6\text{O}_{16}$. The published structure for the latter (trial-and-error) is further refined by least-squares analysis to $R = 0.069$. The hewettite structure was analyzed using 187 F data for $h0l$ and $h1l$ reflections measured by microdensitometry from two precession patterns, in which the nets are very diffuse but well resolved. Least-squares refinement of this limited number of poor data converged to an R of 0.17, but the result is not conclusive. The best interpretation of the resulting V positions and the electron-density distribution was found to be based on the incorporation of the layer from $\text{Li}_3\text{V}_6\text{O}_{16}$ directly with little change in dimensions. Interlayer electron-density maxima indicate the presence of Ca in a half-occupied site, and $8\text{H}_2\text{O}$ in the unit cell, consistent with the cell volume. Structures previously proposed for presumed $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{V}_6\text{O}_{16}$ are criticized for the gross distortions of the layer structure, and inconsistency with the cell volumes.

Keywords: hewettite, crystal structure, layer, vanadium bronze.

SOMMAIRE

Les cristaux de hewettite $\text{CaV}_6\text{O}_{16}\cdot 9\text{H}_2\text{O}$ provenant du Colorado sont monocliniques, groupe spatial $P2_1/m$, a 12.290(1), b 3.590(1), c 11.174(2) Å, β 97.24(1)°. Tel qu'anticipé, la structure en feuillets de V_6O_{16} ressemble à celle du $\text{Li}_3\text{V}_6\text{O}_{16}$. La structure de ce dernier, connue seulement à la suite d'une ébauche par approximations successives, a été affinée par moindres carrés jusqu'à un résidu R de 0.069. La structure de la hewettite a été examinée en utilisant 187 données de F pour des réflexions $h0l$ et $h1l$ mesurées au microdensitomètre sur deux clichés de précession, sur lesquels les taches sont très diffuses mais bien résolues. Un affinement de cette faible quantité de données inférieures a donné une convergence, avec un R de 0.17, mais le résultat n'est pas considéré définitif. La position des atomes de vanadium et la distribution de la densité des électrons s'expliquent par l'incorporation directe d'un feuillet de

$\text{Li}_3\text{V}_6\text{O}_{16}$ sans changement important dans ses dimensions. Des maxima de densité des électrons entre les feuillets seraient l'expression de la présence de Ca dans une position à moitié occupée, et de $8\text{H}_2\text{O}$ par maille élémentaire, ce qui concorde avec le volume de la maille. Les structures proposées pour les composés $\text{Na}_2\text{V}_6\text{O}_{16}\cdot 2\text{H}_2\text{O}$ et $\text{Na}_2\text{V}_6\text{O}_{16}$ contiennent des distortions jugées inacceptables dans la structure du feuillet et des violations du volume de la maille élémentaire.

(Traduit par la Rédaction)

Mots-clés: hewettite, structure cristalline, feuillets, bronze de vanadium.

INTRODUCTION

Hewettite was first described by Hillebrand *et al.* (1914) from Minasragra in Peru and Paradox Valley in Colorado. Their study defined the characteristic physical and chemical properties of this hydrated calcium vanadate mineral: fibrous and lath-like crystal habit, deep red color, and tendency to lose or regain water according to conditions of temperature and humidity. The composition of fresh material was found to be $\text{CaV}_6\text{O}_{16}\cdot 9\text{H}_2\text{O}$. In a careful X-ray crystallographic study of hewettite from Colorado, Qurashi (1961) found three distinct phases, containing 9, 6, and 3 H_2O , respectively. Subsequently, the term "hewettite" became associated with the fully hydrated form ($9\text{H}_2\text{O}$) and "metahewettite" with the dehydrated form ($3\text{H}_2\text{O}$; Fleischer 1987).

The study of the structure of hewettite has always been hampered by the extreme softness and fibrous texture of the crystals. The integrity of the crystals is damaged by any loss of water or rehydration. Therefore, no well-defined structure has heretofore been determined for hewettite. Bachmann (1962) first recognized that hewettite is based on a V_6O_{16} -type layer structure analogous to that found by Wadsley (1957) for the synthetic vanadium bronze $\text{Li}_{1+x}\text{V}_3\text{O}_8$ ($x=0.5$; $\text{Li}_3\text{V}_6\text{O}_{16}$). Bachmann & Barnes (1962) attempted to determine the crystal structure of a

TABLE 1. REFINED STRUCTURE PARAMETERS FOR $\text{Li}_3\text{V}_6\text{O}_{16}$

Atom	x	z	u, Å
Li	0.685(3) (0.690)	0.508(5) (0.494)	0.15(3)
V(1)	0.5365(2) (0.5360)	0.8424(4) (0.8392)	0.074(4)
V(2)	0.0777(2) (0.0778)	0.2040(4) (0.2042)	0.071(4)
V(3)	0.8036(2) (0.8022)	0.0695(4) (0.0696)	0.080(4)
O(1)	0.4572(10) (0.458)	0.0667(20) (0.075)	0.12(1)
O(2)	0.9284(10) (0.928)	0.8789(21) (0.879)	0.13(1)
O(3)	0.6718(9) (0.675)	0.7971(18) (0.796)	0.10(1)
O(4)	0.1857(9) (0.188)	0.4170(18) (0.422)	0.10(1)
O(5)	0.4401(9) (0.438)	0.6140(17) (0.616)	0.10(1)
O(6)	0.9551(9) (0.956)	0.2909(18) (0.286)	0.10(1)
O(7)	0.7238(11) (0.725)	0.2230(21) (0.225)	0.13(1)
O(8)	0.1742(9) (0.175)	0.9864(18) (.992)	0.10(1)

All atoms located in 2(e), with $y=1/4$.
Wadsley's (1957) parameters in parentheses.

sodium-calcium analog of hewettite (later named *barnesite* by Weeks *et al.* 1963), but their result is of doubtful validity, as will be shown here. This paper describes the structure analysis of a hewettite crystal from Colorado and gives a more secure understanding of the crystal chemistry of this mineral and its analogs. Up to now, no structural investigation of

TABLE 2. UNIT-CELL DATA FOR HEWETTITE AND METAHEWETTITE

Specimen	a	b	c	β	Ref.
Synthetic $\text{Li}_3\text{V}_6\text{O}_{16}$	12.03	3.60	6.68	107.8	1.
Hewettite $\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$	12.56	3.615	11.47	97.0	2.
Reconstituted hewettite	12.250(2)	3.497(1)	11.174(2)	97.25(2)	3.
Weeks AW-220-54	12.290(1)	3.590(1)	11.174(2)	97.24(1)	4.
Metaheawettite $\text{CaV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$	12.15(1)	3.607(3)	18.44(1)	118.03(3)	5.

References: 1. Wadsley (1957), 2. Qurashi (1961), 3. Bayliss (1982), 4. This work, 5. Bayliss & Warne (1979). Units: cell edges in Å, β in degrees.

synthetic vanadium bronzes of this type, other than $\text{Li}_3\text{V}_6\text{O}_{16}$, has been carried out.

Many years ago the author received from Alice Weeks a fine section of petrified wood about $8 \times 5 \times 5$ cm (Weeks no. W-220-54). The specimen was donated to her by Hans Adler and is known to have originated from the Colorado Plateau, but unfortunately its locality is otherwise unknown. On the fracture surface are fine, radiating groups of hewettite crystals, as well as crusts of a soft, fibrous, black mineral tentatively identified as corvusite. The hewettite crystals have remained fully hydrated, unlike most other samples of hewettite, which generally lose water rapidly when exposed to the atmosphere. These crystals yielded single-crystal (precession) X-ray data that, although of very poor quality, are much better than any previously available. Thus it has been possible to obtain more reliable structural information than has previously been available.

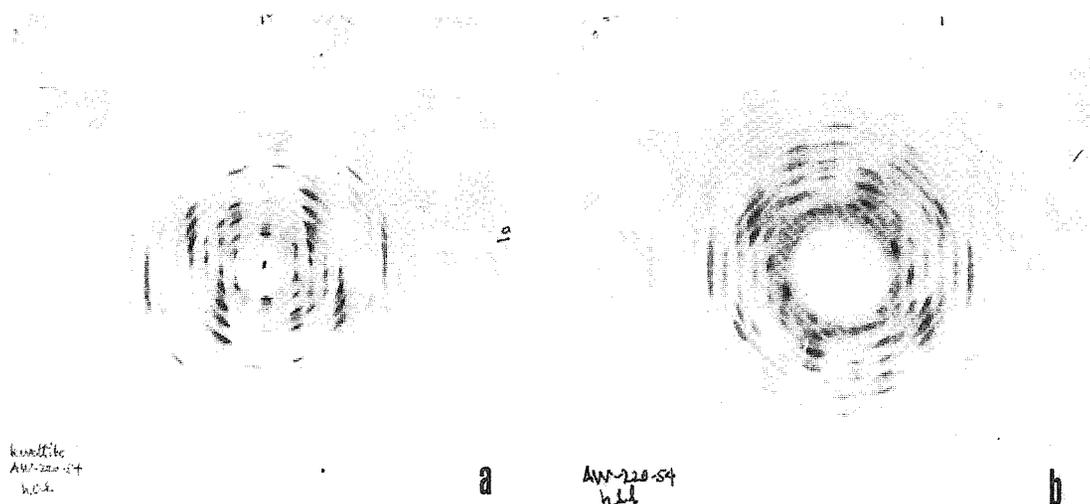


FIG. 1. Precession photographs of hewettite: (a) $h0l$ net; (b) $h1l$ net. These photographs are the source of the intensity data for the structure analysis.

TABLE 3. STRUCTURE PARAMETERS FOR WEEKS' HEWETTITE

Atom	x	z	$U, \text{\AA}^2$
Layer atoms:			
V(1)	0.554(1)	-0.088(1)	0.029(7)
V(2)	0.055(1)	0.120(2)	0.040(7)
V(3)	0.796(1)	0.036(2)	0.026(6)
0(1)	0.446(4) (0.457)	0.019(5) (0.043)	0.07(3)
0(2)	0.940(4) (0.944)	-0.058(5) (-0.067)	0.03(2)
0(3)	0.688(3) (0.692)	-0.118(4) (-0.119)	0.00(1)
0(4)	0.123(5) (0.134)	0.236(6) (0.244)	0.07(3)
0(5)	0.500(4) (0.482)	-0.211(5) (-0.219)	0.05(2)
0(6)	0.936(5) (0.919)	0.170(6) (0.166)	0.07(3)
0(7)	0.703(4) (0.703)	0.120(4) (0.125)	0.01(2)
0(8)	0.170(4) (0.171)	0.011(4) (-0.002)	0.02(2)
Interlayer atoms:			
Ca*	0.228(4)	0.470(4)	0.07(2)
O(9)	0.681(6)	0.657(7)	0.08(3)
O(10)	0.147(8)	0.646(10)	0.15(5)
O(11)	0.67(6)	0.368(7)	0.08(3)
O(12)*	0.071(11) (0.035)	0.409(13) (0.434)	0.08(6)

*Occupancy 0.5. All atoms located in 2(e), with $y = 1/4$. Parameters in parentheses adjusted to normalize the structure to that of $\text{Li}_3\text{V}_6\text{O}_{16}$.

Hewettite is a member of a group of minerals referred to by chemists as "vanadium bronzes"; these minerals have been classified and briefly characterized by Evans & White (1987). A review of past studies of hewettite-type minerals is not made in this report, except for studies that pertain to the crystal-structure problem. The principal results of the present work are a clearer understanding of the role of the V_6O_{16} layer in such mineral phases, and the structure of the cation-water interlayer material.

THE STRUCTURE OF THE HOLOTYPE BRONZE, $\text{Li}_3\text{V}_6\text{O}_{16}$

Wadsley (1957) determined the structure of a phase which he designated as $\text{Li}_{1+x}\text{V}_3\text{O}_8$ with $x = 0.5$, analogous to the γ -phase in the $\text{LiVO}_3\text{-V}_2\text{O}_5$ system found by Flood *et al.* (1946). Wadsley refined the monoclinic structure in space group $P2_1/m$ by trial and error using only the $h0l$ reflections. His final conventional reliability indices R were 0.12 for the $h0l$ data and 0.14 for the $h1l$ data. Wadsley's published data seemed suitable for a least-squares analysis, which would be equivalent to a full three-dimensional treatment assuming that there are no variable y coordinates. When this was done in this laboratory using all 328 nonzero data (assuming isotropic thermal parameters and separate scale-factors for the $h0l$ and $h1l$ data sets), a reliability index R of 0.069 (R_w 0.070) was reached. Thus Wadsley's

TABLE 4. OBSERVED AND CALCULATED STRUCTURE-FACTORS FOR WEEKS' HEWETTITE

H	K	L	FREL	FCAL	H	K	L	FREL	FCAL	H	K	L	FREL	FCAL	
0	0	1*	141	141	4	0	-5	8	-6	8	0	0	0	82	-45
0	0	2	70	71	4	0	-4	27	26	8	0	1	70	-42	
0	0	4	35	-35	4	0	-3	8	-8	10	0	1	46	-32	
0	0	7	23	-22	4	0	-2	40	46	8	0	3	8	-1	
0	0	6	16	-7	4	0	-1	34	36	8	0	4	19	29	
0	0	7	20	-7	4	0	0	31	33	9	0	-3	8	26	
0	0	8	23	24	4	0	1	23	24	7	0	-2**	78	23	
0	0	9	23	22	4	0	2	21	20	9	0	-1	8	1	
1	0	-11	26	-9	4	0	3	31	-17	9	0	0	8	9	
1	0	-10	8	-14	4	0	4	8	-7	10	0	-1	8	4	
1	0	-9	32	-10	4	0	5	8	-6	10	0	0	8	-4	
1	0	-8	22	-14	4	0	6	8	-8	11	0	-1	8	-4	
1	0	-7	8	3	5	0	-6	11	-6	11	0	0	35	-5	
1	0	-6	22	-14	5	0	-5	25	25	11	0	1	32	21	
1	0	-5	8	7	5	0	-4	73	84	12	0	-2	22	-10	
1	0	-4	17	-8	5	0	-3	118	111	12	0	-1	37	-17	
1	0	-3	13	-9	5	0	-2	113	95	12	0	0	28	-14	
1	0	-2	16	16	5	0	-1	64	41	0	1	1*	8	-19	
1	0	-1	14	14	5	0	0	31	-8	0	1	2*	8	-12	
1	0	1*	-3	-3	5	0	2	17	12	0	1	3*	8	-10	
1	0	2	17	-4	5	0	3	34	-22	0	1	4	21	21	
1	0	3	22	-7	5	0	4	8	-4	0	1	5	8	-4	
1	0	4	8	11	5	0	5	8	12	0	1	6	8	6	
1	0	5	8	8	6	0	-6	30	-13	0	1	7	16	-14	
1	0	6	53	62	6	0	-5	8	-5	0	1	8	32	-23	
1	0	7	45	37	6	0	-4	33	-16	0	1	9	35	-27	
1	0	8	42	30	6	0	-3	30	-12	0	1	10	17	-14	
2	0	-6	39	-40	6	0	-2	33	-14	0	1	11	16	-10	
2	0	-5	20	-22	6	0	-1	27	-8	1	1	-9	23	-6	
2	0	-4	60	-43	6	0	0	8	4	1	1	-8	26	-16	
2	0	-3	31	-44	6	0	1	6	-6	1	1	-7	21	-21	
2	0	-2	44	-18	6	0	2	8	2	1	1	-6	29	-19	
2	0	-1	31	42	6	0	3	8	4	1	1	-5	8	-6	
2	0	0	14	11	6	0	4	41	48	1	1	-4	31	-20	
2	0	1	53	64	6	0	5	32	36	1	1	-3	36	34	
2	0	2	14	-11	6	0	6	40	43	1	1	-2*	8	84	
2	0	3	27	-9	6	0	7	34	18	1	1	-1*	11	114	
2	0	4	8	0	7	0	-7	25	-19	1	1	0*	8	42	
2	0	5	8	11	7	0	-6	32	-20	1	1	1*	8	10	
2	0	6	21	-10	7	0	-5	29	-15	1	1	2*	8	-29	
3	0	-7	8	-3	7	0	-4	22	4	1	1	3*	8	-19	
3	0	-6	8	8	7	0	-3	28	17	1	1	4	33	-14	
3	0	-5	8	4	7	0	-2	22	12	1	1	5	8	-2	
3	0	-4	27	-8	7	0	-1	6	3	1	1	6	24	19	
3	0	-3	53	30	7	0	0	25	-11	1	1	7	8	17	
3	0	-2	45	49	7	0	1	23	-16	1	1	-7	8	-12	
3	0	-1	16	0	7	0	2	44	-28	2	1	-6	8	-10	
3	0	0	3	11	7	0	3	17	17	2	1	-5	21	-10	
3	0	1	87	-47	7	0	4	30	-18	2	1	-4	28	23	
3	0	2	103	-64	8	0	-6	27	25	2	1	-3	8	-5	
3	0	3	102	-61	8	0	-5	34	33	2	1	-2*	8	-1	
3	0	4	112	-76	8	0	-4	35	39	2	1	-1*	8	-3	
3	0	5	32	-31	8	0	-3	8	-4	2	1	0*	8	-40	
3	0	6	8	2	8	0	-2	41	-16	2	1	1*	8	9	
4	0	-6	8	2	8	0	-1	73	-36	2	1	2*	8	28	
H	K	L	FREL	FCAL	H	K	L	FREL	FCAL	H	K	L	FREL	FCAL	
2	2	3	21	26	3	1	-2	73	6	8	1	-5	5	7	
2	1	5	80	79	3	1	0	8	4	8	1	-3	8	-10	
2	1	6	45	40	3	1	1	25	23	8	1	-2	26	-11	
2	1	7	13	13	3	1	2	8	-2	8	1	-1	36	-15	
2	1	8	21	-19	3	1	3	8	9	8	1	0	23	-14	
2	1	9	15	-17	3	1	4	8	-2	8	1	1	23	-13	
2	1	10	18	-15	3	1	5	27	-14	9	1	-7	28	28	
3	1	-9	25	-15	3	1	6	34	-20	9	1	-6	29	26	
3	1	-8	45	-26	3	1	7	34	-20	9	1	-5	24	21	
3	1	-7	47	-32	3	1	8	32	-12	9	1	-4	8	-3	
3	1	-6	39	-20	4	1	-10	26	-18	9	1	-3	24	-11	
3	1	-5	56	-27	4	1	-9	28	-20	9	1	-2	36	-21	
3	1	-4	8	-8	4	1	-8	2	-12	9	1	-1**	43	-19	
3	1	-3	13	-3	4	1	-7	8	-6	9	1	0**	61	-28	
3	1	-2*	16	6	4	1	-6	22	29	9	1	1	8	14	
3	1	-1*	4	-4	4	1	-5	86	56	9	1	2	24	-6	
3	1	0*	-14	6	4	1	-4	90	74	9	1	3	23	13	
3	1	1*	-25	6	4	1	-3	71	50	9	1	4	8	4	
3	1	2	8	0	4	1	-2	8	0	9	1	5	8	-10	
3	1	3	24	-12	6	1	-1	18	-7	10	1	6	23	-14	
3	1	4	8	11	6	1	0	-11	9	10	1	7	24	26	
3	1	5	8	16	6	1	1	8	11	10	1	-6	27	20	
3	1	6	8	9	6	1	2	8	7	10	1	-5	22	22	
4	1	-7	8	22	6	1	3	37	36	10	1	-4	29	17	
4	1	-6	25	22	6	1	4	34	37	10	1	-3	24	26	
4	1	-5	23	27	6	1	5	31	30	10	1	-2	8	14	
4	1	-4	8	16	7	1	-4	35	-19	10	1	-1	8	17	
4	1	-3	25	34	7	1	-3	43	-21	10	1	0	8	15	
4	1	-2	21	-18	7	1	-2	28	-9	10	1	1	22	14	
4	1	-1	20	-29	7	1	-1	8	-9	10	1	2	8	-2	
4	1	0	8	-1	7	1	0	29	23	10	1	3	8	-4	
4	1	1	27	-21	7	1	1**	51	19	10	1	4	24	-14	
4	1	2	8	12	7	1	2	74	24	10	1	5	8	-9	
4	1	3	25	-14	7	1	3**	20	41	10	1	6	23	-9	
4	1	4	12	0	7	1	4	8	10	11	1	-6	26	19	
4	1	5	22	18	7	1	5	17	-6	11	1	-5	31	0	
4	1	6	35	27	7	1	-6	23	-11	11	1	-4	8	-3	
5	1	-6	8	4	8	1	-9	21	-12	11	1	-3	8	-3	
5	1	-5	26	29	8	1	-8	18	-14	11	1	-2	8	4	
5	1	-4	22	27	8	1	-7	15	-7	11	1	-1	21	8	
5	1	-3	39	35	8	1	-6	8	-3	11	1	0	23	14	

* Single asterisk indicates reflections hidden in the blind region. F(calc) values for these reflections were included in the Fourier synthesis shown in Figure 2.

** Double asterisk indicates reflections omitted from least-squares analysis.

data proved to be of very good quality and the accuracy of the structure determination was substantially improved, although little change from Wadsley's structure was found. The refined parameters are given in Table 1.

TABLE 5. INTERATOMIC DISTANCES IN THE LAYER STRUCTURES OF $\text{Li}_3\text{V}_6\text{O}_{16}$ AND HEWETTITE

Atoms	W	E	B
V(3)-V(1)	3.105(3) Å	3.12(2) Å	4.13 Å
V(3)-V(2)	3.141(3)	3.20(2)	3.01
V(3)-V(2') (x2)	3.196(2)	3.24(2)	3.34
V(2)-V(2') (x2)	3.323(2)	3.37(2)	3.62
V(1)-V(1') (x2)	3.095(2)	3.09(2)	3.47
Angle V(1)-V(3)-V(2)	168.1(4)°	171(1)°	153°
V(1)-0(5)	1.61(1)	1.43(5)	1.67
-0(3)	1.74(2)	1.72(5)	1.74
-0(1') (x2)	1.89(1)	1.97(2)	1.86
-0(1)	2.01(2)	1.90(6)	2.48
-0(7)	2.83(1)	2.79(5)	3.22
V(2)-0(4)	1.61(1)	1.46(6)	1.67
-0(6)	1.74(2)	1.62(7)	1.80
-0(2') (x2)	1.88(1)	1.94(2)	1.85
-0(8)	2.12(2)	1.99(5)	2.46
-0(2)	2.36(2)	2.28(5)	3.06
V(3)-0(7)	1.60(2)	1.56(5)	1.56
-0(8) (x2)	1.87(1)	1.94(2)	1.85
-0(6)	1.96(1)	2.14(6)	2.02
-0(3)	2.01(1)	2.03(6)	2.38
-0(2)	2.25(2)	2.18(6)	2.38
0(1)-0(1') (x2)	2.38(2)	2.31(5)	2.68
-0(5)	2.97(3)	2.73(8)	3.62
-0(3) (x2)	2.71(2)	2.77(5)	2.73
-0(5) (x2)	2.78(2)	2.82(6)	2.70
-0(7) (x2)	3.02(2)	2.88(5)	2.89
0(2)-0(8) (x2)	2.50(2)	2.35(5)	2.72
-0(6)	2.67(3)	2.58(9)	3.38
-0(2) (x2)	2.67(2)	2.58(5)	3.54
-0(4) (x2)	2.71(2)	2.72(6)	2.34
-0(6) (x2)	2.73(2)	2.76(7)	2.78
-0(8)	2.82(3)	2.83(7)	2.85
0(3)-0(5)	2.68(3)	2.42(6)	2.65
-0(7)	2.72(3)	2.64(7)	2.61
-0(8) (x2)	2.67(2)	2.69(4)	4.33
0(4)-0(6)	2.64(3)	2.33(9)	3.32
-0(8)	2.83(3)	2.65(9)	2.42
0(6)-0(7)	2.68(3)	2.84(8)	3.80
-0(8)	2.71(3)	2.89(6)	3.96
0(7)-0(8) (x2)	2.78(2)	2.90(6)	2.85

W: $\text{Li}_3\text{V}_6\text{O}_{16}$ (Wadsley 1957) refined. E: Weeks' hewettite refined (this work). B: "Hydrated" hewettite, Bachmann & Barnes (1962).

THE CRYSTALLOGRAPHY OF HEWETTITE

All previous crystallographic measurements of hewettite agree on the space group $P2_1/m$, and all find unit-cell dimensions a 12.3 ± 0.2 Å and b 3.61 ± 0.01 Å (fiber axis). The c and β parameters vary freely to accommodate a variety of cations and number of water molecules. A fairly consistent set of parameters has been reported for the lowest hydrate (metahewettite, $\text{CaV}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$; see Table 2). Measurements of the higher hydrates show more variation, doubtless because of variations in vacant and disordered water sites. The crystals used in this study gave single-crystal patterns of unusually good resolution, although the reflections are greatly broadened and diffuse. Figure 1 shows precession photographs of the $h0l$ and $h1l$ nets produced by one crystal; in these the monoclinic net is clearly discernible. Some scattering from a minor amount of metahewettite is present. The unit cell of the hewettite used in this study was best measured from a fiber pattern made with $\text{CrK}\alpha$ radiation (corrected for film shrinkage). Least-squares analysis of 2θ values for 42 $h0l$ reflections provided a , c , and β parameters. A Guinier-Hägg pattern gave a sharp

measurement of the b axis (from the 020 reflection), but was otherwise unsuitable for analysis. The resulting unit-cell parameters agree well with those of Bayliss (1982) and are listed in Table 2 with various unit-cell dimensions of hewettite and metahewettite previously reported.

Density measurements are of little value because of the inevitable admixture of various hydrates, and rupture of the structure by dehydration. The best values were reported by Hillebrand *et al.* (1914): 2.511 g/cm³ for the 9-hydrate, and 2.942 for the 3-hydrate. Based on the unit-cell data given in Table 2, the calculated densities are 2.59 (Weeks cell) and 3.05 g/cm³ (Bayliss & Warne 1979), respectively.

To check the composition, a carefully controlled energy-dispersion test for cations was made on a broad, flat crystal surface using a JEOL scanning electron microscope by Dr. C. A. Lawson of the U.S. Geological Survey. Only Ca and V were detected. The measured Ca/V ratio, calibrated against anhydrous $\text{Ca}_2\text{V}_2\text{O}_7$, was found to be 0.167.

STRUCTURE ANALYSIS OF HEWETTITE

Figure 1 represents the sole record (two films made with $\text{MoK}\alpha$ radiation) from which the intensity data were measured in an attempt to refine the structure of hewettite. Intensities were measured by means of a Nonius Model II microdensitometer. The intensity scale was calibrated against a strip of linearly scaled density marks on the same type of film. The I values were taken at peak maximum, and relative F values obtained by graphical estimation of the Lorentz-polarization correction but without absorption or other corrections.

A Patterson map was calculated to obtain the initial vanadium positions. The eight oxygen atoms of the layer structure (after $\text{Li}_3\text{V}_6\text{O}_{16}$) were introduced geometrically to complete the initial model (Wadsley's numbering of atoms is retained in this model). An electron-density map gave a clear image of the V_6O_{16} layer structure, and also some information about the interlayer material. Least-squares refinement of x and z parameters for the layer atoms, 3 water molecules, and one Ca atom split between two sites, together with the corresponding U values, converged at R 0.25. By this means, bond lengths are determined with an estimated standard deviation (esd) of approximately 0.15 Å.

A more satisfactory refinement (in terms of the thermal parameters) was obtained by including the nonobserved reflections at half of an estimated threshold value (about 8, as suggested by a referee), but excluding the $h1l$ reflections in the blind region (266 reflections total). With 6 reflections omitted because of outlying ΔF values (> 30), refinement converged to an R of 0.24; at this point, for the observed reflections only (175), R was 0.17. The

parameters so obtained are listed in Table 3, and the $F(\text{obs})$ and $F(\text{calc})$ data are listed in Table 4.

INTERPRETATION OF THE HEWETTITE STRUCTURE

The resulting structure contains several unsatisfactory interatomic distances (see Table 5). The V–O terminal bonds to O(4) and O(5) are unacceptably short: 1.43 and 1.46 Å, respectively. In $\text{Li}_3\text{V}_6\text{O}_{16}$ these bonds are both 1.61 Å. The shortest O–O distance in the layer in $\text{Li}_3\text{V}_6\text{O}_{16}$ is 2.38 Å for O(1)–O(1'); two others are 2.50 Å, and all others are greater than 2.64 Å. In the refined hewettite structure the O(1)–O(1') distance is 2.31 Å, 4 are less than 2.4 Å, and 6 more are less 2.6 Å. The structure so defined for hewettite is far too crowded. On the other hand, the positions refined for the vanadium atoms are close in dimensions to those of $\text{Li}_3\text{V}_6\text{O}_{16}$, differing by less than 0.015 Å (Table 5). It seems reasonable to assume that the oxygen dimensions in the layer also should be similar; that is, the layer should be rather rigid and not change appreciably from one structure to another as the cations and water

molecules vary. Oxygen coordinates for such a layer structure were therefore constructed around the vanadium atoms guided as far as possible by the electron-density mapping, and these coordinates are given in parentheses in Table 4. Structure factors for this adjusted structure [all U s and Ca parameters refined, O(9), O(10), O(11) fixed from previous refinement; O(12) adjusted to a Ca–O distance of 2.35 Å, occupancy 0.5] gave an R of 0.20. In spite of the higher reliability index for this structure, this model is probably closer to the true structure.

The thermal parameters for vanadium obtained from the refinement are reasonable ($U = 0.028 \text{ \AA}^2$), but for the layer oxygen atoms these parameters run unrealistically from $U = 0$ to 0.06 \AA^2 (Table 3). In comparison, all the thermal parameters for the refined $\text{Li}_3\text{V}_6\text{O}_{16}$ structure are entirely reasonable and internally consistent (Table 1). The thermal parameters for the refined Ca and H_2O molecules in hewettite are larger, as expected, but reasonable, including that for O(12) at half occupancy.

Because of the large esd values of the H_2O positions the location of hydrogen bonds is somewhat

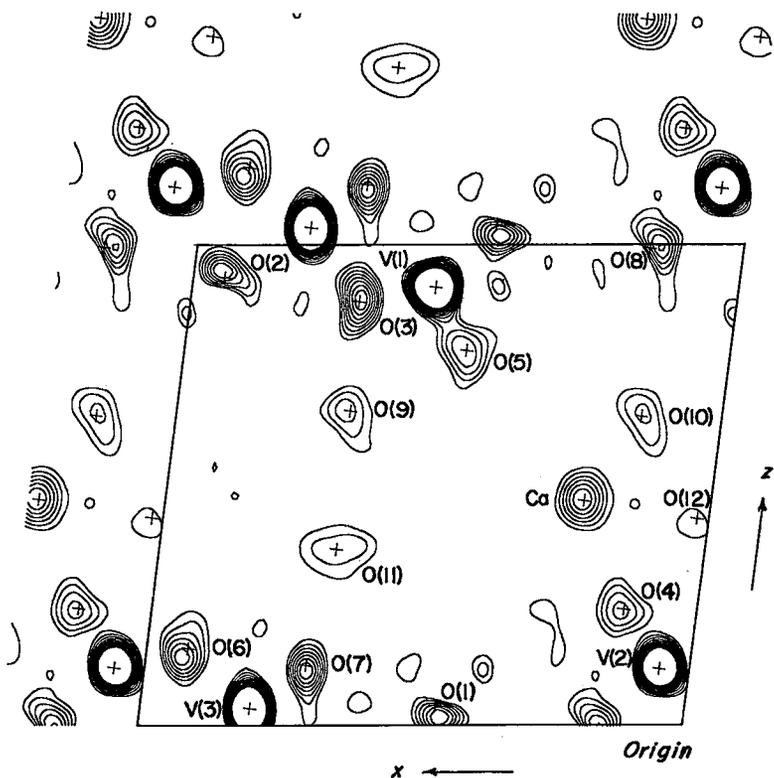


FIG 2. Electron-density projection of hewettite from $y = 0$ to $y = \frac{1}{2}$. Position of atoms in the adjusted structure are indicated.

TABLE 6. INTERATOMIC DISTANCES IN INTERLAYER STRUCTURE OF WEEKS' HEWETTITE

Atoms	Refined	Adjusted
Ca-O(12)	1.96(14) Å	2.36 Å
-O(10)	2.35(12)	2.35
-O(9) (2x)	2.63(7)	2.65
-(11) (2x)	2.69(6)	2.69
-O(4)	2.76(8)	2.62
O(9)-O(3)	2.51(9)	2.49
-O(5)	2.83(10)	3.02
-O(4) (2x)	3.12(8)	3.00
-O(11)	3.20(12)	3.20
O(10)-O(12)	2.71(18)	2.56
-O(11) (2x)	2.85(10)	2.85
-O(6) (2x)	2.98(11)	2.98
-O(12) (2x)	3.20(14)	2.92
O(11)-O(10) (2x)	2.85(10)	2.85
-O(7)	2.85(10)	2.80
-O(9)	3.20(12)	3.20
-O(5)	3.20(7)	2.96
O(12)-O(4)	2.11(17)	2.62
-O(6)	2.96(15)	3.12
-O(10) (2x)	3.20(14)	2.92
-O(10)	2.71(18)	2.56
-O(12') (2x)	3.37(18)	2.57

uncertain, but no interoxygen distances are less than 2.64 Å (Table 5). The electron density found (Fig. 2) accounts for 7H₂O in the unit cell. The Ca site is half occupied, and O(12), also half occupied, is probably associated with the Ca atom. In the absence of Ca + O(12), a water molecule is likely present in an ill-defined position that does not appear in the electron-density map. In this way, 8H₂O are ac-

counted for. There is generous room for one more oxygen atom at 0.53, ¼, 0.45. This site, which is too diffuse to be resolved, may be only half occupied because of its proximity to a center of symmetry at ½, 0, ½. Thus, 9 water molecules all fit comfortably in the structure, and Ca has a normal coordination of 7 or 8.

A view of the structure is shown projected along the *b* axis in Figure 3, which shows how the *c* axis is expanded to accommodate the Ca²⁺ ions and water molecules. The final electron-density projection of the lower half of the unit cell in this view (*y* from 0 to ½), corresponding to the adjusted structure, is shown in Figure 2.

THE PROBLEM OF THE BACHMANN - BARNES STRUCTURE

As mentioned above, the only other attempt to determine the structure of hewettite was made by Bachmann & Barnes (1962). They studied crystals from the Cactus Rat mine, Utah, which they assumed to be (Na,Ca)V₆O₁₆•2H₂O. Their data for this "hydrated" form were measured for 63 nonzero *h0l* reflections by visual estimate from oscillation photographs rotated about the fiber axis, and precession photographs about [001] for 18 nonzero *hko*

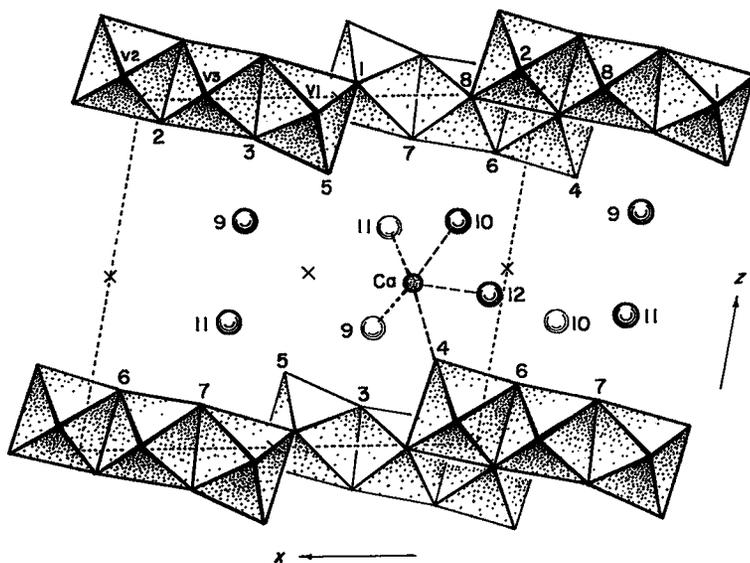


FIG. 3. Schematic view of the structure of hewettite projected along the *b* axis. VO₆ groups are shown as octahedra; light interlayer atoms are located at *y* = -¼, and heavy atoms are located at *y* = +¼. Crosses indicate centers of symmetry at *y* = 0 and *y* = ½.

reflections. For another crystal, presumed to be dehydrated by heating to 140°C, 59 $h0l$ reflection intensities were measured. Vanadium positions for each were estimated from a b -axis Patterson projection, and the V-phased electron-density maps were used to find oxygen and Na(Ca) positions. Bachmann & Barnes (1962) refined the structures by trial-and-error methods, making use of ΔF maps. For the $h0l$ reflections their final R values were 0.19 for the dehydrated form and 0.17 for the hydrated form.

The structures found by Bachmann & Barnes are based primarily on the V_6O_{16} layer structure of Wadsley's $Li_3V_6O_{16}$, as predicted by Bachmann (1962), but are grossly distorted with respect to the latter. The dimensions of the V(1)–V(3)–V(2) backbone [V(3)–V(2)–V(1) in Bachmann & Barnes] are compared in Table 5. These dimensions, especially the backbone angle, are clearly inconsistent with any idea of structural rigidity of the layer.

Another difficulty is raised by the unit-cell volumes, which are 352 Å³ for the dehydrated form and 356 Å³ for the hydrated form. A loss of 2H₂O would require a difference of about 50 Å³ between these two values. The volume of the Weeks hewettite analyzed above is 489 Å³. Allowing 275 Å³ for the V_6O_{16} layer (from $Li_3V_6O_{16}$), H₂O plus Ca occupies 214 Å³, which, by assuming 10 Å³ for Ca, leads to a reasonable 23–25 Å³ for each of 8 or 9H₂O. This reasoning suggests that both crystals of Bachmann & Barnes contain 3H₂O, which is the amount for the closely analogous minerals barnesite (Weeks *et al.* 1963) and metaheawettite (Qurashi 1961). The cell volume found by Bayliss & Warne (1979) for metaheawettite is 356.7 Å³ (Table 2).

A least-squares analysis of the data of Bachmann & Barnes for the dehydrated form lowered the reliability index appreciably, but did not change their structure significantly. In view of the problems outlined above, it is difficult to accept the structure of Bachmann & Barnes at face value. It seems likely that the principal source of distortion in their data lies in the method of intensity measurement. Hewettite crystals are usually greatly twisted about the fiber axis, by 10° or more, and the effect of such distortion (as well as tilting of the fiber elements) on oscillation photographs is difficult to predict. Serious overlap may occur where complete resolution would be expected for well-formed crystals. In the crystals from the Weeks specimen twinning has been observed on 001, giving the $h0l$ patterns a pseudo-orthorhombic appearance, thus indicating another possible source of confusion.

CONCLUSIONS

In this paper the results of three investigations are reported: (1) The crystal structure of $Li_3V_6O_{16}$ was

significantly refined using the data of Wadsley (1957). (2) The structure of a hewettite crystal from Colorado was analyzed, using data from $h0l$ and $h1l$ precession photographs. The diffuseness of the patterns is severe, so that a normal least-squares refinement of the structure ($R = 0.17$) did not lead to conclusive results. Assuming that the layer structure of $Li_3V_6O_{16}$ is rigidly incorporated into the hewettite structure, an adjusted structure is proposed, which is considered to be more realistic than the least-squares structure. (3) The structure analyses of Bachmann & Barnes (1962) were re-examined. It is found that their structures, although based on the layer structure of $Li_3V_6O_{16}$, contain gross distortions of this structure. The quality of their data, and the supposed degree of hydration of the two crystals studied, are called into question.

These studies have led to the conclusion that: (i) the dimensions of the V_6O_{16} vanadium bronze layer are well defined by a refinement of $Li_3V_6O_{16}$ using the data of Wadsley, and (ii) that this layer is probably rigid and is only slightly distorted by incorporation into other bronzes with variable amounts of low-charge cations and water molecules. The present study of hewettite, although based on data of poor quality, strongly supports the latter conclusion, and throws light on the structure analysis of Bachmann & Barnes, whose experimental difficulties were much more serious. It has been shown (Evans & Hughes, in prep.) that the V_6O_{16} layer forms the basis of several vanadium bronze minerals in addition to hewettite and metaheawettite, namely: barnesite (Weeks *et al.* 1963), hendersonite (Lindberg *et al.* 1962), and grantsite (Weeks *et al.* 1964). Clearly, a more detailed structure-analysis of another member of this group, especially a trihydrate, is needed to support the results reported here, but the extreme softness of these minerals makes such a study difficult.

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