

THE STRUCTURE OF VANADINITE

J. TROTTER¹ AND W. H. BARNES

Division of Pure Physics, National Research Council, Ottawa, Canada

ABSTRACT

Two-dimensional Fourier and difference syntheses have been used to solve and refine the structure of vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$. The isostructural relationship of vanadinite to other apatite-like minerals has been confirmed. The chlorine ion is surrounded by six divalent lead ions at the corners of a regular octahedron; the co-ordination of oxygen around vanadium is tetrahedral. Interatomic distances are given and the accuracy of the results is assessed in terms of the standard deviations of atomic positions and of interatomic distances.

INTRODUCTION

Thirty-five years ago, Hentschel (1923) established the space group of apatite and measured the unit cell dimensions. Some years later Náray-Szabó (1930), Mehmel (1930, 1932), and Hendricks, Jefferson & Mosley (1932) (see also *Strukturbericht*, vol. II, and Wyckoff, 1931, 1935, 1951) published the results of investigations of the crystal structure of apatite and certain other apparently isostructural minerals which have the space group $P6_3/m$, with two formula units of $A_5(XO_4)_3Z$ per cell, where A , X , and Z may be various divalent metal ions (A), pentavalent atoms (X), and monovalent anions (Z). There has been much discussion about the admissibility of some of these compounds into the list of apatite-type structures (see *Strukturbericht*, vols. II-VII, and *Structure Reports*, vols. 9-13), but there is no doubt about the eligibility of fluor-apatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, chlor-apatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$, and vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$. Although more exact data are required to fix unequivocally the two-fold sites of the F atoms in fluor-apatite (compare Náray-Szabó, Mehmel, Hendricks *et al.*, *loc. cit.*, and Bale (1940)), there seems to be no question about the locations of the Cl atoms in chlor-apatite and in other apatite-like compounds containing Cl. Although Náray-Szabó (1930) confined his attention to fluor-apatite, Mehmel (1932) and Hendricks, Jefferson & Mosley (1932) extended their studies and speculations to other minerals of the apatite type. No complete determination of the structure of vanadinite, $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$, however, was carried out, although Mehmel reports unit cell dimensions of $a = 10.47 \text{ \AA}$, $c = 7.43 \text{ \AA}$, and Hendricks, Jefferson & Mosley report $a = 10.31 \text{ \AA}$, $c = 7.34 \text{ \AA}$ (where Å probably

¹National Research Laboratories Postdoctorate Fellow.

should be read as kX units). Since the accuracy claimed in both papers is ± 0.02 the difference of about 1.5% between the two sets of parameters may arise from calibration of the cameras used.

Hendricks, Jefferson & Mosley (1931, p. 361) state that "Extensive observations were not made upon vanadinite. It is probable, however, that its structure closely simulates that of mimetite since the units of structure for the two substances differ but slightly in dimensions. The presence of the larger V^{+5} , in comparison with As^{+5} , results in a slight increase in the value of a ." A direct determination of the crystal structure of vanadinite, therefore, has been long overdue. It is a fairly widespread vanadium mineral and is also of interest as an orthovanadate in which tetrahedral co-ordination of O around V is to be expected as in pucherite, $BiVO_4$ (Qurashi & Barnes, 1953), descloizite, $Pb(Zn,Cu)(VO_4)(OH)$ (Qurashi & Barnes, 1954), pyrobelonite, $PbMn(VO_4)(OH)$ and brackebuschite, $Pb_2(Mn,Fe)(VO_4)_2 \cdot H_2O$ (Donaldson & Barnes, 1955).

EXPERIMENTAL, AND CRYSTAL DATA

Translucent, deep orange-red prisms of vanadinite from the Apache Mine, near Globe, Arizona were available for the present investigation. The crystal employed for the collection of intensity data was reduced to a sphere of radius 0.25 mm. in a Bond (1951) Sphere Grinder in order to facilitate the determination of absorption corrections which are large even for $MoK\alpha$ radiation. No difficulty was experienced in grinding the vanadinite crystals into excellent spheres.

The space group was established by inspection of zero and upper level precession photographs ($\mu = 30^\circ$; $MoK\alpha$ radiation). The unit cell dimensions were determined from back-reflection oscillation photographs ($CuK\alpha_1$, $\lambda = 1.5405 \text{ \AA}$; $CuK\alpha_2$, $\lambda = 1.5443 \text{ \AA}$) by the method of Farquhar & Lipson (1947).

Vanadinite is hexagonal, space group $P6_3/m (C_{6h}^{2})$ with $a = 10.331 \pm 0.001 \text{ \AA}$, and $c = 7.343 \pm 0.001 \text{ \AA}$. The density was measured with a Berman balance using two separate crystals of 19.26 mgm. and 18.30 mgm., and toluene. The observed values were 6.862 gm. per ml. and 6.859 gm. per ml.; mean, 6.861 gm. per ml. The calculated value, assuming 2 formula units of $Pb_5(VO_4)_3Cl$ per cell, is 6.887 gm. per ml. The absorption coefficient for $MoK\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) is 726 cm.^{-1}

The intensities of the reflections in the $\{hk0\}$ and $\{h0l\}$ zones were estimated visually from precession photographs: the multiple exposure technique was employed. The usual corrections for Lorentz and polarization factors (Waser, 1951), and the appropriate absorption corrections for a spherical crystal (Evans & Ekstein, 1952), were applied. The relative

values of the structure amplitudes were derived from the usual formulae for a mosaic crystal, and the absolute scale was established by comparison with the F -values calculated from the final atomic co-ordinates.

STRUCTURE ANALYSIS

The $\{hk.0\}$ Zone

According to Hendricks, Jefferson & Mosley (1931) the sets of equivalent positions in space group $P6_3/m$ occupied by the various atoms of pyromorphite and of mimetite are

$$(b) 000; 00\frac{1}{2}$$

$$(f) \pm(\frac{1}{3}, \frac{2}{3}, z; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}-z)$$

$$(h) \pm(x, y, \frac{1}{4}; \bar{y}, x-y, \frac{1}{4}; y-x, x, \frac{1}{4})$$

(i) $\pm(x, y, z; \bar{y}, x-y, z; y-x, \bar{x}, z; x, y, \frac{1}{2}-z; \bar{y}, x-y, \frac{1}{2}-z; y-x, \bar{x}, \frac{1}{2}-z)$
with 2 Cl in (b), 4 Pb_I in (f), 6 Pb_{II} in (h), 6 P (pyromorphite) in (h), 6 As (mimetite) in (h), 6 O_I in (h), 6 O_{II} in (h), and 12 O_{III} in (i).

For the $\{hk.0\}$ zone of vanadinite, 80 of a possible 93 independent reflections in the range $\sin \theta \leq 0.5$ (MoK α radiation) were observed. Although a Patterson synthesis would certainly have shown the locations of the lead atoms, the observed intensity distribution indicated that they probably occupy virtually the same sites as in mimetite, namely, 4 Pb_I in (f) with $z = 0$ and 6 Pb_{II} in (h) with $x = \frac{1}{4}$, $y = 0$ (Hendricks, Jefferson & Mosley, 1931, p. 360). A trial Fourier synthesis, therefore, was calculated with the observed structure amplitudes and with signs calculated on the basis of these co-ordinates for the lead atoms. Well resolved peaks corresponding to the Cl and V atoms, in addition to those due to the Pb atoms, appeared in the electron density map at sites consistent with equipoints (b) for the 2 chlorine ions (superimposed at the origin as in mimetite) and with (h) for the 6 vanadium atoms (as for the 6 As in mimetite). A small shift ($\sim 0.1 \text{ \AA}$) in the position of Pb_{II} was indicated. A peak consistent with the superposition of 2 atoms of O_{III} with equipoints (i) was clearly resolved. To complete the mimetite structure there should also be peaks representing O_I and O_{II} in separate sets of (h) positions; small ones in fact were observed but the co-ordinates of these two atoms could not be fixed accurately at this stage because the peaks were only of about the same height as the diffraction ripples around the Pb atoms. This electron density map, however, showed no features which might cast doubt on the predicted structural similarity of vanadinite with chlor-apatite, pyromorphite, and mimetite. It provided x, y co-ordinates for all atoms. Positional and temperature parameters were refined by successive difference syntheses.

Scattering factor curves for the various atoms were derived as follows.

Lead. The atomic scattering curve for Pb in the *Internationale Tabellen* (1935) was adjusted to that of Pb^{+2} by reducing the value at $\sin \theta/\lambda = 0$ from 82 to 80, leaving those at $\sin \theta/\lambda \geq 0.4$ unchanged, and drawing a smooth curve from 80 at $\sin \theta/\lambda = 0$ to join that representing these higher values.

Vanadium. Because the vanadium-oxygen bonds have some covalent character V^{+3} was chosen as a compromise between unionized V and fully ionized V^{+5} . The corresponding scattering curve was calculated from the atomic scattering data for vanadium (Qurashi, 1954) by deducting the contributions of one 4s and two 3d electrons, utilizing the screening parameters and individual electron contributions given by Viervoll & Ögrim (1949).

Chlorine. The scattering curve for Cl^{-1} was taken directly from the *Internationale Tabellen* (1935).

Oxygen. To balance the ionic charges in the crystal, each oxygen atom was considered to have gained $1\frac{1}{2}$ electrons. McWeeny's (1951) scattering curve for O was adjusted to that of $\text{O}^{-1.5}$ by increasing the value at $\sin \theta/\lambda = 0$ to 9.5, leaving those values at $\sin \theta/\lambda \geq 0.4$ unchanged, and drawing a smooth curve from 9.5 at $\sin \theta/\lambda = 0$ to join that representing these higher values.

Temperature factor corrections of the usual form, $\exp[-B(\sin \theta/\lambda)^2]$ were applied to the scattering curves with an initial value of $B = 2.6 \text{ \AA}^2$ for all atoms.

The final F_o and $(F_o - F_{c(h)})$ maps for the $\{hk.0\}$ zone are reproduced in Fig. 1, where the symbols representing the two superimposed atoms of O_{III} have been displaced slightly from each other for clarity, and where $F_{c(h)}$ is the structure factor calculated for the heavier atoms only (i.e., omitting the contributions of the oxygen atoms). The complete difference $(F_o - F_o)$ map exhibited no unusual features and, therefore, is not shown.

The $\{h0.l\}$ Zone

Of 104 possible independent reflections within the range $\sin \theta \leq 0.5$ ($\text{MoK}\alpha$ radiation), 81 were observed. Because of the hexagonal symmetry the structure factor expression for this zone includes all three atomic co-ordinates x , y , z . The final values of x and y for all atoms derived from refinement of the $\{hk.0\}$ zone were employed in calculating structure factors preparatory to the first Fourier synthesis for the $\{h0.l\}$ zone. Values of z are fixed by the space group symmetry at 0 and $\frac{1}{2}$ for Cl (equipoints b), and at $\pm\frac{1}{4}$ for Pb_{II} , V, O_{I} , and O_{II} (equipoints h); for Pb_{I} and O_{III} the values of Hendricks, Jefferson & Mosley (1931) for mimetite were adopted provisionally, although that for O_{III} could,

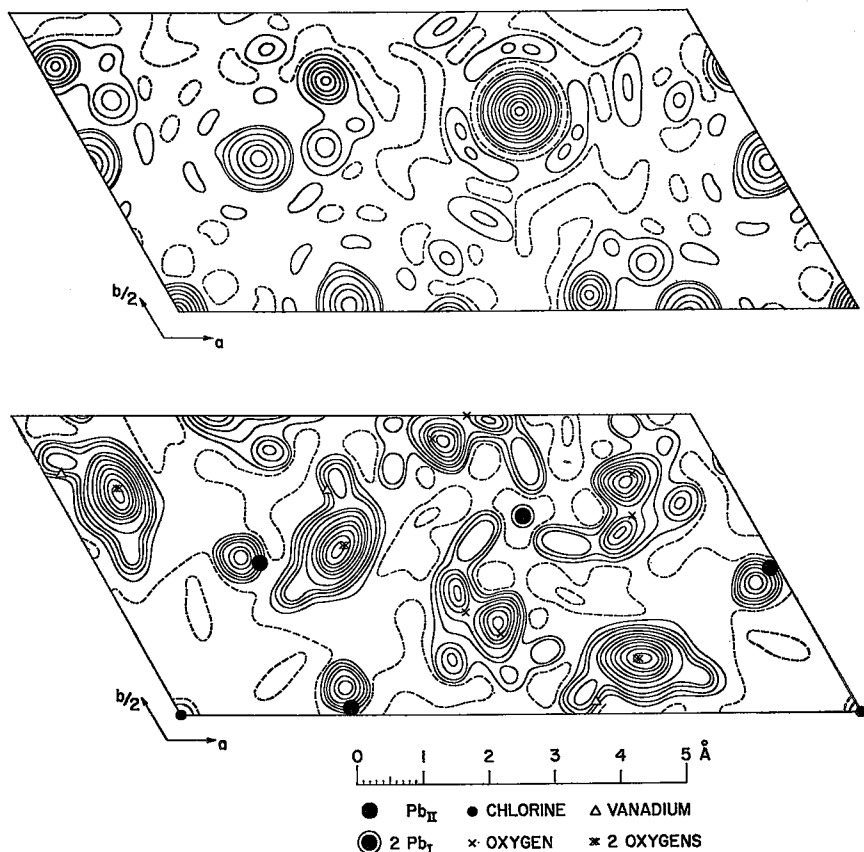


FIG. 1. The $\{hk.0\}$ zone of vanadinite; *top*, final F_o map with contours at intervals of $10e.\text{\AA}^{-2}$ except for Pb where the 30 and $40e.\text{\AA}^{-2}$ contours have been omitted and the intervals are of $50e.\text{\AA}^{-2}$ above the $50e.\text{\AA}^{-2}$ contour; *bottom*, final $(F_o - F_{c(h)})$ map with contours at intervals of $2e.\text{\AA}^{-2}$. (In both maps the zero contour lines are broken, and negative contours have been omitted.)

of course, have been omitted. The first electron density map was very satisfactory and refinement was effected by successive difference syntheses. A small shift of Pb_I from its reported position in mimetite at $z = 0$ was required, a slightly different value for the x co-ordinate of O_{III} from that found in the analysis of the $\{hk.0\}$ zone was indicated, and the value of the z co-ordinate of O_{III} was established, otherwise the x and y co-ordinates derived from the data for the $\{hk.0\}$ zone were confirmed as were the fixed z co-ordinates required if Cl, Pb_{II}, V, O_I, and O_{II} are indeed in the expected sites.

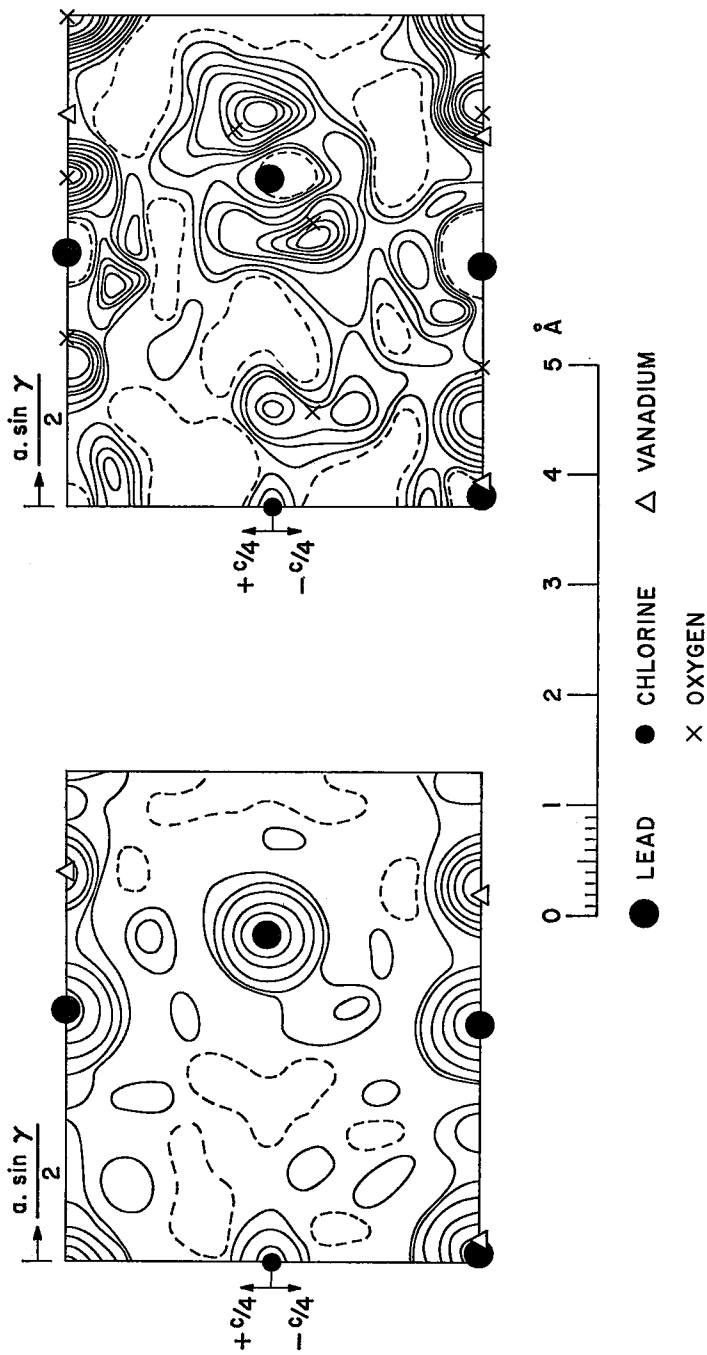


FIG. 2. The $\{h0l\}$ zone of vanadinite; *left*, final F_o map with contours as in the corresponding map of fig. 1; *right*, $(F_o - F_c(h))$ map with contours as in the corresponding map of fig. 1. (Zero contours broken, negative contours omitted.)

The final F_o and $(F_o - F_{c(h)})$ maps for this zone are reproduced in Fig. 2, where $F_{c(h)}$ has the same significance as before. The complete difference $(F_o - F_c)$ map for this zone also exhibited no unusual features and is not shown.

Results and Accuracy

The fractional co-ordinates are listed in Table 1. The value (0.3812) shown for the x co-ordinate of O_{III} is the weighted mean of those obtained from the separate analyses of the $\{hk.0\}$ zone (0.3807) and the $\{h0.l\}$ zone (0.3825).

TABLE I. FRACTIONAL CO-ORDINATES OF THE ATOMS

Atom	x	y	z
Pb _I	$\frac{1}{3}$	$\frac{2}{3}$	0.0054
Pb _{II}	0.2558	0.0107	$\frac{1}{4}$
V	0.4046	0.3787	$\frac{1}{4}$
Cl	0	0	0
O _I	0.3309	0.5005	$\frac{1}{4}$
O _{II}	0.6006	0.4604	$\frac{1}{4}$
O _{III}	0.3812	0.2873	0.0463

The structure factors calculated, with the co-ordinates of Table 1, for the heavier atoms (Pb, V, Cl) only ($F_{c(h)}$), and for all the atoms (F_c), together with the observed structure amplitudes, are given in Table 2. For the final temperature factor corrections the value of B was 1.5 for Pb, V, and Cl, and 2.6 for O. The discrepancy factor, R , for the $\{hk.0\}$ zone is 0.13 when the metal and chlorine atoms only are considered, and 0.11 when the contributions of the oxygen atoms are included. For the $\{h0.l\}$ zone, the corresponding values of R are 0.16 and 0.12.²

Standard deviations of the co-ordinates, calculated with Cruickshank's formula (1949), are given in Table 3, and standard deviations of inter-atomic distances, calculated with expressions of the form $\sigma_{\text{Pb-V}} = [\sigma^2_{\text{Pb}} + \sigma^2_{\text{V}}]^{\frac{1}{2}}$, are presented in Table 4.

DESCRIPTION OF THE STRUCTURE, AND DISCUSSION

A projection of the structure of vanadinite down the c -axis is shown in Fig. 3. The most important features are the octahedral co-ordination of Pb_{II}⁺² around Cl⁻¹ and the tetrahedral co-ordination of oxygen atoms around V.

Each Cl⁻¹ ion is surrounded by six Pb_{II}⁺² at the corners of a regular octahedron in which the Pb_{II}-Cl distance is 3.17 Å and the shortest

²Values for the unobserved reflections were included in the calculations of R only when F_c was greater than the threshold value of F_o .

TABLE 2. STRUCTURE AMPLITUDES OBSERVED, $|F_o|$; STRUCTURE FACTORS CALCULATED FOR Pb, V, Cl only, $F_{c(h)}$, AND FOR ALL ATOMS, F_c .

$h\bar{k}0$	$ F_o $	F_c	$F_{c(h)}$	$h\bar{k}0$	$ F_o $	F_c	$F_{c(h)}$
00.0	—	+1184	+992	34.0	55	+59	+58
10.0	<37	-33	+10	44.0	415	+413	+412
20.0	242	-214	-215	54.0	<35	-18	-38
30.0	471	+475	+477	64.0	90	-104	-100
40.0	213	+191	+225	74.0	169	+182	+181
50.0	40	+43	+65	84.0	109	+104	+102
60.0	66	+96	+95	94.0	<24	-18	-15
70.0	<30	+15	+14	15.0	139	-156	-182
80.0	165	+165	+160	25.0	158	+165	+147
90.0	155	+157	+166	35.0	110	+105	+122
10,0.0	73	-92	-98	45.0	<35	+21	+14
11,0.0	<20	-6	-9	55.0	98	+90	+94
12,0.0	171	+179	+179	65.0	55	-62	-60
11.0	80	+112	+133	75.0	51	+50	+57
21.0	266	-244	-251	85.0	182	+176	+175
31.0	<46	+11	+42	95.0	90	-76	-76
41.0	397	+401	+367	16.0	216	-215	-202
51.0	178	-201	-195	26.0	122	-150	-152
61.0	147	-158	-144	36.0	83	+90	+100
71.0	294	+301	+281	46.0	131	-134	-133
81.0	75	+53	+48	56.0	161	-146	-142
91.0	83	-100	-98	66.0	83	+83	+73
10,1.0	35	+70	+69	76.0	33	-57	-53
11,1.0	63	+60	+60	86.0	85	-77	-78
12.0	223	-209	-247	17.0	198	+201	+212
22.0	115	+101	+137	27.0	161	-161	-173
32.0	72	-84	-109	37.0	53	-70	-75
42.0	179	-180	-205	47.0	133	+151	+154
52.0	112	+115	+108	57.0	31	-41	-46
62.0	105	-121	-110	67.0	54	-74	-77
72.0	58	-91	-92	77.0	<16	+36	+39
82.0	105	+102	+113	18.0	55	-58	-53
92.0	143	-126	-126	28.0	54	+79	+71
10,2.0	36	-62	-58	38.0	45	+54	+54
11,2.0	112	+103	+101	48.0	61	+71	+75
13.0	<45	+31	-63	58.0	72	+92	+95
23.0	253	-273	-226	68.0	93	-78	-75
33.0	83	+117	+124	19.0	90	-108	-107
43.0	60	-76	-52	29.0	53	-84	-75
53.0	39	-41	-45	39.0	240	+218	+215
63.0	<35	+33	+41	49.0	<24	+7	+7
73.0	128	-132	-131	59.0	84	-79	-81
83.0	43	-35	-45	1,10.0	43	+68	+64
93.0	77	+85	+84	2,10.0	58	-80	-79
10,3.0	108	-99	-97	3,10.0	<23	-28	-34
14.0	296	+285	+306	1,11.0	41	-56	-52
24.0	238	-206	-218	2,11.0	<19	+19	+18

$h0l$	$ F_o $	F_c	$F_{c(h)}$	$h0l$	$ F_o $	F_c	$F_{c(h)}$
10.0	<37	-33	+10	80.0	165	+164	+158
20.0	242	-215	-216	90.0	155	+156	+164
30.0	471	+474	+477	10,0.0	73	-86	-93
40.0	213	+198	+232	11,0.0	<20	-7	-9
50.0	40	+44	+65	12,0.0	171	+179	+179
60.0	66	+95	+95	10.1	<37	+17	+11
70.0	<30	+15	+13	20.1	65	+61	+55

TABLE 2 (continued)

$h0.l$	$ F_o $	F_c	$F_{c(h)}$	$h0.l$	$ F_o $	F_c	$F_{c(h)}$
30.1	57	+58	+35	10.5	<30	-7	-15
40.1	<35	+17	+25	20.5	66	+68	+56
50.1	61	+57	+41	30.5	29	+27	+22
60.1	93	+89	+103	40.5	<28	+3	-3
70.1	32	+40	+48	50.5	58	+57	+45
80.1	<28	+7	+5	60.5	53	+57	+41
90.1	51	+67	+66	70.5	<25	+17	+21
10,0.1	51	+65	+65	80.5	23	+17	+17
11,0.1	65	+51	+48	90.5	40	+48	+50
00.2	321	-226	-212	10,0.5	31	+41	+41
10.2	237	-203	-230	00.6	142	-147	-120
20.2	51	-39	-18	10.6	105	-126	-134
30.2	128	+135	+92	20.6	<28	-11	-8
40.2	406	-400	-393	30.6	63	+61	+55
50.2	223	-235	-228	40.6	201	-242	-246
60.2	228	+266	+291	50.6	134	-140	-142
70.2	107	-146	-145	60.6	173	+185	+190
80.2	247	-263	-265	70.6	77	-98	-97
90.2	82	+97	+99	80.6	157	-185	-184
10,0.2	<22	+8	+2	90.6	63	+70	+68
11,0.2	30	-61	-67	10.7	40	-32	-36
12,0.2	16	-11	-8	20.7	<26	+13	+5
10.3	<34	-22	-38	30.7	26	-24	-16
20.3	<33	+8	-19	40.7	43	-28	-38
30.3	57	-56	-29	50.7	<24	+4	+3
40.3	<32	-16	-45	60.7	49	-61	-56
50.3	<30	-15	-15	70.7	46	-46	-49
60.3	99	-101	-91	80.7	18	+15	+17
70.3	56	-53	-60	90.7	31	-43	-39
80.3	<26	+6	+10	00.8	308	+324	+320
90.3	52	-67	-60	10.8	<24	0	+4
10,0.3	71	-71	-71	20.8	55	-81	-84
11,0.3	44	-36	-34	30.8	165	+174	+180
00.4	693	+695	+627	40.8	52	+99	+98
10.4	<32	-14	+4	50.8	23	+28	+27
20.4	117	-154	-158	60.8	44	+46	+41
30.4	342	+332	+341	70.8	<16	+8	+8
40.4	155	+162	+172	10.9	26	-17	-18
50.4	54	+43	+49	20.9	43	+40	+39
60.4	62	+80	+74	30.9	<20	+13	+11
70.4	<27	+13	+12	40.9	19	-12	-12
80.4	124	+131	+129	50.9	62	+38	+35
90.4	125	+133	+137	00.10	30	-71	-60
10,0.4	49	-77	-79	10.10	48	-62	-64
11,0.4	18	-7	-7	20.10	11	-2	-2

Pb_{II} - Pb_{II} distance (along an edge of the octahedron) is 4.48 Å. The octahedron around the Cl^- at $z = 0$ shares one face with that around the Cl^- at $z = \frac{1}{2}$ and the opposite face with that around Cl^- at $z = -\frac{1}{2}$ so that each Pb_{II} is equidistant from 2 Cl^- and the Pb_{II} octahedra form a continuous chain along the direction of the z axis. Outside the octahedra the nearest neighbours of each Pb_{II} are six atoms of oxygen distributed as follows: O_I at 3.17 Å, 2 O_{III} at 2.89 Å, O_{II} at 2.54 Å, 2 O_{III} at 2.52 Å.

TABLE 3. STANDARD DEVIATIONS (IN Å) OF ATOMIC CO-ORDINATES
(Separately for Each Zone; Standard Deviations of Weighted Means, s.d.w.m.)

Atom	x			y			z
	{hk.0}	{h0.l}	s.d.w.m.	{hk.0}	{h0.l}	s.d.w.m.	{h0.l}
Pb _I	0	0	0	0	0	0	0.008
Pb _{II}	0.004	0.006	0.003	0.004	0.006	0.003	0
V	0.024	0.049	0.022	0.024	0.049	0.022	0
Cl	0	0	0	0	0	0	0
O _I	0.053	0.051	0.037	0.054	0.051	0.037	0
O _{II}	0.053	0.051	0.037	0.054	0.051	0.037	0
O _{III}	0.040	0.068	0.034	0.040	0.068	0.034	0.088

TABLE 4. STANDARD DEVIATIONS (IN Å) OF INTERATOMIC DISTANCES

Pb-Cl, 0.004	Pb-V, 0.018	Pb-O, 0.04
Pb-Pb 0.006	V-V, 0.025	V-O, 0.05
		O-O, 0.06

The VO₄ groups appear as isolated tetrahedra with V at distances of 1.76 Å from O_I and from O_{II}, and 1.72 Å from each of two O_{III}. These V-O bonds are equal in length within the limits of experimental error but the tetrahedra are not regular ones because the O-O distances vary from 2.56 Å to 3.01 Å and the O-V-O angles from 94° to 121°.

Each Pb_I is surrounded by nine atoms of oxygen, 3 O_I at 2.47 Å and 3 O_{II} at 2.57 Å (from six separate VO₄ tetrahedra), and 3 O_{III} at 2.76 Å. It has three equidistant Pb_{II} neighbours at 4.29 Å and three others at 4.39 Å.

The shortest distances between Pb_{II} and V are 3.31 Å, 3.69 Å, 3.79 Å, and 3.96 Å; those between Pb_I and V are 3.51 Å and 4.06 Å. The shortest V-V distance is 4.32 Å between atoms related by a centre of symmetry.

The dimensions of the unit cell of vanadinite presented in this paper are in very much better agreement with those found by Hendricks, Jefferson & Mosley (1932, p. 355) than they are with those reported by Mehmel (1932, p. 236), and the structure investigation has confirmed the close relationship between vanadinite and mimetite predicted by the former. The differences among the fractional atomic co-ordinates in vanadinite and the corresponding ones published by Hendricks, Jefferson & Mosley (1932, p. 360) for pyromorphite and for mimetite do not exceed approximately 0.04 for x and y, and 0.02 for z in the case of the oxygen atoms, and 0.01 for x, y, and z in the case of the heavier atoms.

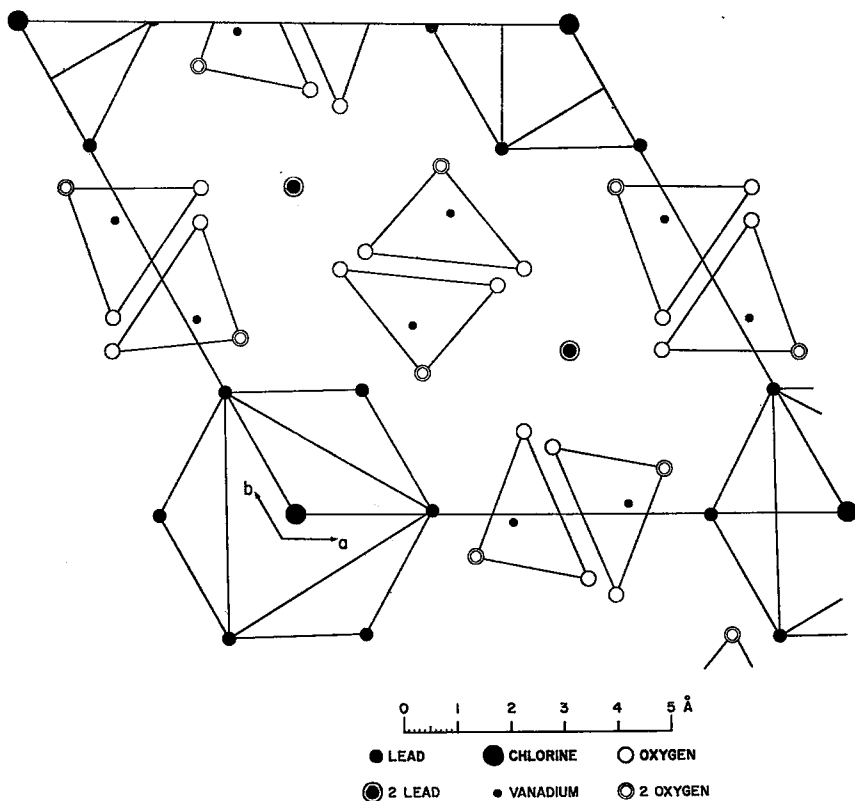


FIG. 3. Projection of the structure of vanadinite on (00.1).

It is of interest to compare some of the interatomic distances in vanadinite with those in pyrobelonite and brackebuschite (Donaldson & Barnes, 1955), in spite of the structural differences among these minerals. Thus, although the VO_4 tetrahedra show various degrees of distortion in the different structures, the V-O bonds in vanadinite are essentially the same length (1.72 Å, 1.76 Å) as two of those in pyrobelonite (range, 1.62–1.83 Å) and the shorter ones in brackebuschite (range, 1.71–1.90 Å), and, although two of the O-O distances (each 2.56 Å) in vanadinite are shorter than any of those in pyrobelonite (2.75–2.99 Å) or in brackebuschite (2.75–3.02 Å), they are comparable with one of those (2.50 Å) in pucherite (Qurashi & Barnes, 1952).

There is, however, no regularity in the number or distribution of electronegative elements around the lead cations in the three minerals; in vanadinite there are 9 O at 2.47–2.76 Å from Pb_{I} , and 6 O at 2.52–3.17 Å plus 2 Cl at 3.17 Å each from Pb_{II} ; in pyrobelonite there are

7 O at 2.28–2.89 Å from Pb; in brackebuschite there are 8 O at 2.54–2.95 Å from Pb(1), and 10 O at 2.58–3.02 Å from Pb(2).

The lowest values of the Pb–Pb and V–V separations in vanadinite (4.29 Å and 4.32 Å, respectively) are larger than those in pyrobelonite (4.07 Å and 4.01 Å) and in brackebuschite (4.04 Å and 3.80 Å), while the shortest Pb–V distance is smaller (3.31 Å in vanadinite, 3.47 Å in pyrobelonite, 3.48 Å in brackebuschite).

Grateful acknowledgment is made to Mrs. M. E. Pippy for assistance with the calculations, and to Dr. F. R. Ahmed for computing the final Fourier syntheses on FERUT.

REFERENCES

- BALE, W. F. (1940): A comparative roentgen-ray diffraction study of several natural apatites and the apatite-like constituent of bone and tooth substance, *Amer. J. Roentgenol. & Rad. Therapy*, **43**, 735–747. (This author appears to have been unaware of Mehmel's second (1932) paper.)
- BOND, W. L. (1951): Making small spheres, *Rev. Sci. Instr.*, **22**, 344–345.
- CRUICKSHANK, D. W. J. (1949): The accuracy of electron-density maps in X-ray analysis with special reference to dibenzyl, *Acta Cryst.*, **2**, 65–82.
- DONALDSON, D. M., & BARNES, W. H. (1955): The structures of the minerals of the descloizite and adelite groups: II—pyrobelonite, *Am. Mineral.*, **40**, 580–596; III—brackebuschite, *Am. Mineral.*, **40**, 597–613.
- EVANS, H. T. & EKSTEIN, M. G. (1952): Tables of absorption factors for spherical crystals, *Acta Cryst.*, **5**, 540–542.
- FARQUHAR, M. C. M., & LIPSON, H. (1946): The accurate determination of cell dimensions from single-crystal X-ray photographs, *Proc. Phys. Soc.*, **58**, 200–206.
- HENDRICKS, S. B., JEFFERSON, M. E., & MOSLEY, V. M. (1932): The crystal structures of some natural and synthetic apatite-like substances, *Zeit. Krist.*, (A) **81**, 352–369.
- HENTSCHEL, H. (1923): Röntgenographische Untersuchungen am Apatit, *Centralbl. f. Min., Geol., Palaeont.*, 609–626. (This paper is incorrectly ascribed to Leonardt by Nàray-Szabó (1930).)
- Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935), Borntraeger, Berlin.
- MCWEENY, R. (1951): X-ray scattering by aggregates of bonded atoms. I. Analytical approximations in single-atom scattering, *Acta Cryst.*, **4**, 513–519.
- MEHMEL, M. (1930): Über die Struktur des Apatits. I., *Zeit. Krist.*, (A) **75**, 323–331.
- (1932): Beziehungen zwischen Kristallstruktur und chemischer Formel des Apatits, *Zeit. physik. Chem.*, (B) **15**, 223–241.
- NÀRAY-SZABÓ, ST. (1930): The structure of apatite (CaF) $Ca_4(PO_4)_6$, *Zeit. Krist.*, (A) **75**, 387–398.
- QURASHI, M. M. (1954): On the completion and extension of the table of atomic scattering factors published by Viervoll & Ögrim, *Acta Cryst.*, **7**, 310–312.
- & BARNES, W. H. (1953): The structure of pucherite, $BiVO_4$, *Am. Mineral.*, **38**, 489–500.
- (1954): The structures of the minerals of the descloizite and adelite groups: I—descloizite and conichalcite (part 1), *Am. Mineral.*, **39**, 416–435.
- Structure Reports*, Oosthoek, Utrecht.
- Strukturbericht*, Akad. Verlag, M. B. H., Leipzig.
- VIERVOLL, H. & ÖGRIM, O. (1949): An extended table of atomic scattering factors, *Acta Cryst.*, **2**, 277–279.

- WASER, J. (1951): Lorentz and polarization correction for the Buerger precession method, *Rev. Sci. Instr.*, **22**, 567-568.
- WYCKOFF, R. W. G. (1931): *The Structure of Crystals*, 2 ed., pp. 300, 301, Chem. Cat., New York.
- (1935): *The Structure of Crystals*, 2 ed., supplement, pp. 68, 69, Reinhold, New York.
- (1951): *Crystal Structures*, vol. II, Chap. VII, text pp. 43, 44; table p. 85; illus. p. 22, Interscience, New York.