

Crystallography of psilomelane, $A_3X_6Mn_8O_{16}$

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Summary. Psilomelane has been redefined from single crystal study to be of orthorhombic symmetry with the space group $P222$, the dimensions a 9.45, b 13.90, c 5.72 Å, and two molecules of $A_3X_6Mn_8^{4+}O_{16}$ per unit cell, where A represents Ba^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Si^{4+} etc., and X_6 stands for $(O,OH)_6$ with OH about 5. This formula is very closely followed by 14 analyses of psilomelane, and the calculated density agrees fairly well with the observed density. The powder data of psilomelane cannot be indexed with Wadsley's monoclinic cell and the conditions for the space group $A2/m$, proposed by Wadsley for his crystal, are not satisfied by the indexing. Wadsley's crystal was not psilomelane but probably an altered phase of Vaux's neotype specimen.

The electron micrograph of shining platy crystals of psilomelane shows some almost square-faced crystals whereas that of the botryoidal material consists only of particles with irregular edges. The dehydration product of psilomelane shows gradual shrinkage of the orthorhombic cell up to 500° C, marked structural changes at 600° C, and transformation at 800° C to a monoclinic phase, similar to hollandite.

PSILOMELANE, a hydrated barium manganese oxide, was first named and described by Haidinger (1831) for the 'smooth, black, uniform and botryoidal' mineral from Schneeberg, Saxony, but his description accompanying Turner's chemical analysis (1831) did not adequately define psilomelane as a single species with a definite chemical formula. Vaux (1937) defined psilomelane from Schneeberg and Cornwall as a distinct mineral with the formula $H_4(Ba,Mn)_2Mn_3^{4+}O_{20}$, derived from five chemical analyses (although Turner's analysis showed wide discrepancy); from X-ray study 'by both crystal and powder photographs' of psilomelane (specimens BM. 69160 and BM. 32687 from Schneeberg and Spitzleite, Saxony) Vaux proposed an orthorhombic symmetry with the dimensions, a 9.1, b 13.7, c 2.86 Å, without giving his method of derivation. Based on the same analyses of psilomelane two modified formulae were suggested by Fleischer and Richmond (1943) and by Palache, Berman, and Frondel (1944).

Wadsley (1953) studied the same specimens of psilomelane as Vaux (BM. 69160 and BM. 32687) and found monoclinic symmetry with the dimensions, a 9.56, b 2.88, c 13.85 Å, β 92° 30', Z 2 for $(Ba,H_2O)_2Mn_5O_{10}$

and space group $A2/m$. Wadsley determined these values from single-crystal study about the b -axis of a tiny plate ($0.1 \times 0.06 \times 0.02$ mm) with ridged faces, separated from the outer crust of the botryoidal material of the specimen BM. 69160, and he observed that even this tiny plate was not a single crystal but a multiple one. Vaux (*loc. cit.*) as well as Wadsley (*loc. cit.*) stated that the powder photographs of the botryoidal core-material and the encrusted platy crystals of psilomelane were identical, but their powder data were not available. Fleischer and Richmond (1943) and Gruner (1943) reported powder data for psilomelane from Schneeberg. Fleischer (1960) derived the unit-cell contents per 20 oxygen atoms from 14 analyses of psilomelane and showed that with the unit-cell dimensions of Wadsley his formula is better than those proposed earlier:

Vaux (1937)	$H_4(Ba, Mn)_2Mn_8^{4+}O_{20}$
Fleischer and Richmond (1943)	$Ba(Mn^{4+}, Mn^{2+})_9O_{18} \cdot 2H_2O$
Palache, Berman, and Frondel (1944)	$BaMn^{2+}Mn_8^{4+}O_{16}(OH)_4$
Wadsley (1953)	$(Ba, H_2O)_4Mn_{10}O_{20}$

Mukherjee (1959) studied two specimens of 'psilomelane' from Madhya Pradesh, India, and proposed a space group $P2_12_12(D_2^3)$ for the orthorhombic cell with the dimensions, a 8.254, b 13.40, c 2.864 Å, using Lipson's method (1949) of derivation for the orthorhombic system from powder-spacing data. Mukherjee assumed Vaux's formula without reporting the chemical analysis of his specimen, but his powder data are somewhat different from those reported by Gruner (1943).

Vaux's psilomelane

The two specimens of psilomelane, BM. 69160 and BM. 32687, studied by Vaux were obtained from the British Museum through the courtesy of Dr. M. H. Hey. The specimen BM. 69160 consisted of shining minute platy crystals encrusted on the dull botryoidal core associated with quartz; specimen BM. 32687 was only of dull botryoidal material with quartz. The shining crystals showed the same powder pattern (taken with Fe- $K\alpha$ radiation) as the dull botryoidal material (fig. 1), but the powder photograph of the crystals was more distinct with enhanced intensity for weak and diffuse lines. The powder photograph of the same specimen BM. 69160 of psilomelane, taken at the British Museum by Dr. R. J. Davis (using Fe- $K\alpha$ radiation), is exactly identical with that taken by the author (fig. 1).

Single crystal data. A tiny crystal about $0.02 \times 0.03 \times 0.1$ mm (off BM. 69160) having smooth shining faces and a ridged face on one side was selected for obtaining rotation and Weissenberg photographs about [001] using Fe- $K\alpha$ radiation. The c -axis from the layer-line spacings

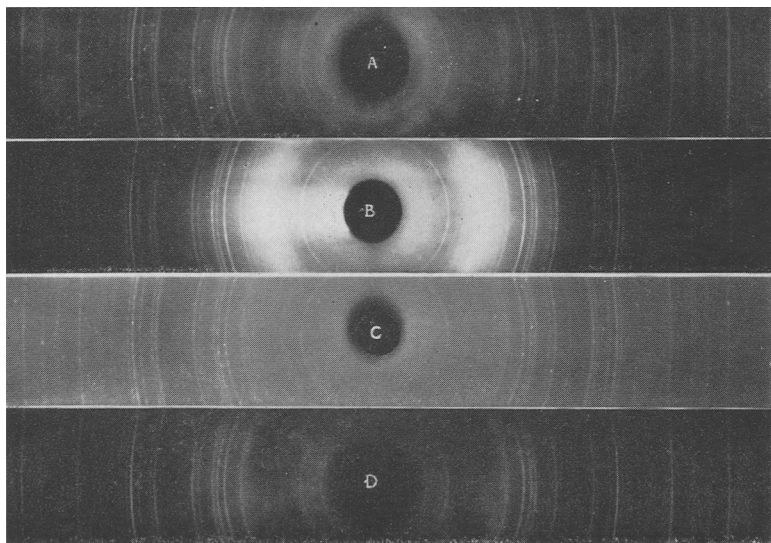


FIG. 1. X-ray powder photographs of psilomelane (taken with Fe- $K\alpha$ radiation): A. dull botryoidal material of BM. 69160; B. type material of BM. 69160, taken at the British Museum by Dr. R. J. Davis (using powder camera of 114.6 mm diameter); C. shining crystals of BM. 69160; D. dull botryoidal material of BM. 32687.

and the a and b axes from the zero-layer Weissenberg photograph about [001] were determined as $a 9.45 \pm 0.02$, $b 13.90 \pm 0.02$, $c 5.72 \pm 0.02$ Å. The angle between the a and b axes (a and c axes of Wadsley) was found to be 90° in the zero-layer Weissenberg photograph about the c -axis (b -axis of Wadsley). The reflexions on the Weissenberg photographs appeared as elongated streaks, and the intensities satisfied the conditions for orthorhombic symmetry. The conditions limiting possible reflexions indicated that the space group is one of $P222$, $Pmm2$, $Pmmm$. The dimensions a and b are similar to those determined by Vaux but the c axial length is double. Vaux's data were probably obtained from oscillation photographs.

Powder spacing data. The indexing of all the powder lines of psilomelane (off BM. 69160) with the orthorhombic axes $a 9.45$, $b 13.90$,

TABLE I. Powder spacing data of psilomelane, BM. 69160, indexed on an orthorhombic cell with a 9.45, b 13.90, c 5.72 Å, together with an attempted indexing on Wadsley's monoclinic cell

I/I_1	$d(\text{Å})$	$\sin^2\theta_{\text{obs}}$	Author's orthorhombic cell		Wadsley's monoclinic cell			
			hkl	$\sin^2\theta_{\text{calc}}$	hkl	$\sin^2\theta_{\text{calc}}$	F_{obs}	I_p
10	9.50	0.0104	100	0.0105	100	0.0103	9	2
30	6.93	0.0195	020	0.0194	002	0.0196	26	13
7	5.74	0.0285	001	0.0286	$\bar{1}02$	0.0286	18	5
10	5.58	0.0301	120	0.0299	102	0.0311	22	8
7	4.73	0.0419	200	0.0420	200	0.0411	26	9
10	4.01	0.0583	121	0.0585	$\bar{2}02$	0.0582	30	10
40	3.885	0.0620	220	0.0614	202	0.0631	50	26
70	3.465	0.0780	040	0.0776	004	0.0783	61	34
40	3.320	0.0851	230	0.0856	$\bar{1}04$	0.0861	60	31
50	3.240	0.0892	{ 140 221	{ 0.0881 0.0900	203	0.0888	0	0
30	2.970	0.1062	041	0.1062	(?)			
70	2.875	0.1134	{ 320 231 002	{ 0.1138 0.1142 0.1145	{ 010 $\bar{2}04$	{ 0.1130 0.1144	0 52	0 19
7	2.750	0.1239	{ 301 102	{ 0.1231 0.1250	{ 110 204	{ 0.1232 0.1243	0 27	0 5
15	2.660	0.1326	{ 150 022	{ 0.1318 0.1339	012	0.1325	0	0
70	2.415	0.1607	{ 151 212	{ 0.1604 0.1613	211	0.1602	86	83
50	2.360	0.1683	{ 400 132	{ 0.1679 0.1687	{ 113 205	{ 0.1691 0.1696	37 0	15 0
10	2.313	0.1751	{ 060 222	{ 0.1746 0.1759	{ 006 212	{ 0.1762 0.1762	11 0	1 0
50	2.254	0.1845	160	0.1851	(?)			
100	2.190	0.1955	401	0.1964	$\bar{2}13$	0.1945	101	100
50	2.150	0.2026	{ 411 142 061	{ 0.2013 0.2026 0.2032	213	0.2018	46	20
10	2.118	0.2089	302	0.2089	{ $\bar{3}11$ $\bar{2}06$	{ 0.2084 0.2097	40 33	15 5

F_{obs} Observed structure amplitudes of diffracted spots in single crystal zero-layer and 1st-layer Weissenberg photographs about the b -axis (Wadsley, 1953, p. 436).

I_p Intensity of Debye-Scherrer lines, calculated from Wadsley's F_{obs} .

TABLE I (cont.)

I/I_1	$d(\text{\AA})$	$\sin^2\theta_{\text{obs}}$	Author's		Wadsley's monoclinic cell			
			orthorhombic cell		hkl	$\sin^2\theta_{\text{calc}}$	F_{obs}	I_p
7	2.093	0.2139	{ 161 312	{ 0.2137 0.2138	(?)			
15	2.021	0.2292	{ 322 440	{ 0.2284 0.2455	312 107	0.2288 0.2457	0 0	0 0
10	1.950	0.2465	{ 152 360	{ 0.2463 0.2691	{ $\bar{5}$ 02 $\bar{2}$ 15	0.2702 0.2702	12 43	< 1 14
70	1.820	0.2828	{ 520 402	{ 0.2817 0.2824	{ 502 215	0.2825 0.2826	29 87	3 57
15	1.735	0.3111	{ 521 080 133	{ 0.3103 0.3104 0.3118	503	0.3100	0	0
25	1.709	0.3208	{ 180 303	{ 0.3209 0.3520	(?)			
40	1.634	0.3511	{ 072 362	{ 0.3521 0.3837	(?)			
70	1.560	0.3848	{ 550 190	{ 0.3836 0.4034	$\bar{2}$ 17	0.3851	100	61
15	1.523	0.4040	{ 452 380	{ 0.4036 0.4048	{ 217 $\bar{5}$ 13	0.4025 0.4044	49 48	15 14
15	1.495	0.4194	{ 532 014	{ 0.4204 0.4630	308	0.4205	22	< 2
60	1.422	0.4634	{ 291 024	{ 0.4635 0.4775	{ 120 604	0.4623 0.4628	— 14	— < 1
70	1.399	0.4785	{ 480 622	{ 0.4783 0.5116	218	0.4771	0	0
10	1.353	0.5119	{ 134 503	{ 0.5122 0.5199	{ 605 701	0.5105 0.5124	0 0	0 0
10	1.341	0.5208	{ 472 701	{ 0.5200 0.5427	(?)			
7	1.314	0.5427	{ 234 314	{ 0.5437 0.5574	{ 2.0.10 124	0.5428 0.5430	30 —	3 —
20	1.296	0.5578	{ 730 244	{ 0.5577 0.5777	(?)			
7	1.273	0.5782	{ 183 054	{ 0.5786 0.5793	(?)			

TABLE II. Chemical analyses of psilomelane,

	1	2	3	4	5	6	7
Mn ⁴⁺	8.20	8.21	8.48	8.32	8.34	8.14	8.24
Mn ²⁺	1.07	1.07	1.17	1.61	1.55	1.78	1.04
Ba	1.22	1.22	0.85	1.09	1.16	1.16	1.02
Si	0.09	0.09	0.01	0.11	0.05	0.17	0.02
Al	0.08	0.07	0.15	—	—	—	0.03
Fe	0.02	0.03	0.02	0.04	—	—	0.02
Ca	0.04	0.05	0.12	—	—	—	0.14
Mg	0.04	0.04	0.03	0.08	—	—	—
Na	—	—	—	0.01	—	—	0.16
K	—	—	0.09	0.02	—	—	0.13
Cu	0.07	0.04	0.05	—	—	—	<0.01
Co	0.13	0.14	0.07	—	—	—	—
W	0.04	0.03	—	0.01	—	—	—
As	—	—	—	—	—	—	0.20
H	5.17	5.20	4.87	4.50	5.01	4.87	5.11
Mn + A	11.00	10.99	11.04	11.29	11.10	11.25	11.01
<i>D</i> _{calc}	4.70	4.69	4.53	4.69	4.69	4.71	4.59
<i>D</i> _{obs}	4.71	4.70*	—	4.697	—	—	4.45
<i>D</i> _F †	{ 4.77 4.82‡	4.76	4.49	4.69	—	—	4.64

* Determined by the author on the Berman density balance, using bromoform.

† Calculated by Fleischer from Wadsley's formula and cell-dimensions.

‡ Wadsley's calculated value.

1. Vaux's 1 from Schneeberg, Saxony; British Museum No. BM. 69160. Analyst, H. Bennett.

2. Vaux's 2 from Spitzleite, Eibenstock, Saxony; British Museum No. BM. 32687. Analyst, H. Bennett.

3. Vaux's 3 from Restormel mine, Lostwithiel, Cornwall; British Museum No. BM. 27214. Analyst, H. Bennett.

4. Vaux's 4 from Schneeberg, Saxony; specimen in the Academy of Natural Sciences, Philadelphia. Analyst, H. J. Hallowell.

5. Vaux's 5 from Schneeberg, Saxony. Analyst, E. Turner. (H₂O+ is taken as 4.2, the average value of the other three samples from the same locality.)

6. Fleischer's B from Romanèche, France. Analyst, E. Turner.

7. Fleischer's 3 from Romanèche, France. U.S. National Museum No. R 2232. Analyst, M. Fleischer.

recalculated as ratios to 22 oxygen

	8	9	10	11	12	13	14
Mn ⁴⁺	7.91	8.37	8.70	8.45	8.04	8.46	8.19
Mn ²⁺	1.16	1.04	0.88	1.01	1.10	0.90	1.13
Ba	0.96	1.23	0.90	1.01	0.99	0.92	0.93
Si	0.07	0.08	—	0.14	0.08	0.07	0.03
Al	—	0.09	{ 0.10	0.06	—	0.05	—
Fe	0.11	0.02	{	0.01	0.04	0.15	0.03
Ca	0.07	—	—	—	0.34	0.05	0.01
Mg	0.44	—	—	0.06	0.07	0.05	0.03
Na	0.06	0.02	—	0.04	0.12	0.10	—
K	0.02	0.02	0.18	0.06	0.11	0.08	0.10
Cu	—	—	—	{ 0.01	—	—	0.01
Co	—	—	—	{	0.03	—	0.01
W	0.22	0.03	—	0.02	—	0.06	0.13
As	—	—	—	—	—	—	0.03
V	—	—	—	—	0.13	—	—
Zn	—	—	—	0.01	—	—	0.02
Sr	—	—	—	—	—	0.12	—
H	5.08	5.12	5.15	5.02	5.45	4.65	5.72
Mn + A	11.02	10.90	10.76	10.88	11.05	11.01	10.65
<i>D</i> _{calc}	4.65	4.67	4.50	4.56	4.55	4.58	4.57
<i>D</i> _{obs}	—	4.74	4.61	4.56	4.41	4.44	4.43
<i>D</i> _F †	4.72	4.73	4.56	4.67	4.66	4.60	4.70

† Calculated by Fleischer from Wadsley's formula and cell-dimensions.

8. Fleischer's 1 from Sodaville, Nevada; P. F. Kerr's sample. Analyst, F. A. Gonyer. (H₂O+ is taken as 4.38; on the basis of 100 % of the formula weight the excess value of 0.31 is assumed to be due to H₂O—.)

9. Fleischer's 2 from Mayfield prospect, Chispa Siding, Jeff Davis Co., Texas; S. G. Lasky's sample. Analyst, W. T. Schaller.

10. Fleischer's J from Pilbara, W. Australia; A. D. Wadsley's sample. (H₂O+ is taken as 4.65; on the basis of 100 % of the formula weight the excess value of 0.49 is assumed to be due to H₂O—.)

11. Fleischer's 4 from Tolbard mine, Paymaster Dt., Imperial Co., California; J. B. Hadley's sample. Analyst, M. Fleischer.

12. Fleischer's 5 from Manila, Utah (exact locality unknown); U.S. National Museum No. 94341. Analyst, M. Fleischer.

13. Fleischer's 6 from Hoggett manganese group, Hidalgo Co., New Mexico; S. K. Neuscher's sample. Analyst, M. Fleischer.

14. Fleischer's 7 from Talamantes mine near Parral, Chihuahua, Mexico; P. D. Trask's sample. Analyst, M. Fleischer.

c 5.72 Å is most satisfactory (table I). The powder-spacing data are identical with those reported by Gruner (1943) for psilomelane from Schneeberg, Saxony. The data of C. Frondel, quoted by Fleischer and Richmond (1943), are slightly different from those of Gruner.

Unit-cell contents. Vaux (1937) derived the number of oxygen atoms per unit cell of psilomelane (BM. 69160) as 20.5 ± 0.7 , and the atomic proportions per 20 oxygen atoms as the most probable integral value; the value of H, computed from H_2O +, comes out at 4.73 per 20 oxygen atoms (for BM. 69160 and BM. 32687), much higher than corresponds to H_4O_{20} in the formula unit. With the new cell-dimensions and density (below) we find 44 oxygen per unit cell, and the number of atoms per 22 oxygen atoms (table II) was calculated from the chemical analyses, quoted by Vaux, for the two specimens of psilomelane. The formula comes out as $(Ba, Mn, R)_3 Mn_8^{4+} H_5 O_{22}$ where R represents the remaining cations. The ideal formula may be taken as $A_3 X_6 Mn_8^{4+} O_{16}$ where A represents Ba^{2+} , Mn^{2+} , $R^{+2+3+4+}$ etc., and X_6 stands for $(O, OH)_6$ with OH about 5. The manganese in different valency states is partly replaced by other cations and the excess Mn^{4+} may be partly distributed in the position for Mn^{2+} . The positions of Ba^{2+} , Mn^{2+} , and other cations in A are ambiguous, but Mn^{2+} is much nearer to Ba^{2+} than Mn^{4+} as regards ionic charge as well as ionic potential and ionic size. The exclusion of SiO_2 , Al_2O_3 , Fe_2O_3 , WO_3 , and alkalis by Vaux in his calculation of atomic proportions, while including CaO, MgO, CuO, CoO, is probably not justified.

The density, determined on a number of small fragments of psilomelane (BM. 69160) by the Berman density balance using bromoform, is 4.70 ± 0.02 g. cm^{-3} , similar to Vaux's value of 4.71 g. cm^{-3} . With the new values of the axial lengths ($V = 751.3$ Å³), the molecular weight ($M = 1063$, calculated from the atomic weights of all the constituents in actual proportions), and density, the number of formula units per unit cell comes out as 2 ($Z = 2.001$), and the calculated density is 4.70 g. cm^{-3} .

There are accordingly 6 (Ba, Mn, R), 16 Mn^{4+} , 10 H, 44 O, and in all 76 atoms in the unit cell of psilomelane.

The *electron micrograph* of psilomelane was taken in the usual way (Mukherjee, 1963) by Siemens Elmiskop I, using an accelerating potential of 60 KV and at low instrumental magnification ($\times 5000$) in order to avoid undue rise of temperature and retain the original character of the mineral. The electron micrograph of the shining crystal (off BM. 69160) shows some almost square-faced crystals of 0.2μ - 0.5μ dimensions

(arrow in fig. 2*a*) and particles of irregular edges of sizes in the range 0.1–2 μ . The electron micrograph of the botryoidal material (off BM. 69160 as well as off BM. 32687) shows only the particles with irregular edges, of which the larger units are 1–2 μ across (fig. 2*b*). The micrograph of a very small shining crystal shows some square-faced crystals,

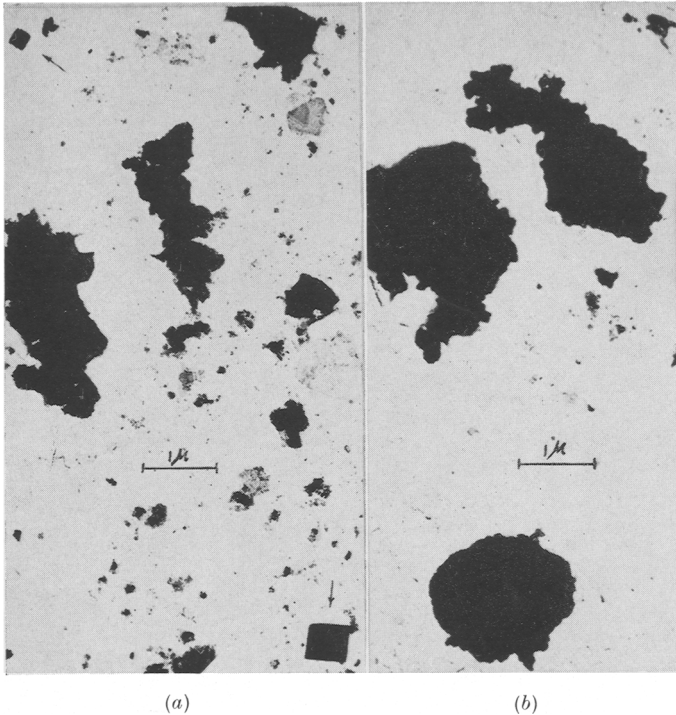


FIG. 2. Electron micrographs of psilomelane: *a*, shining crystal of BM. 69160; *b*, dull botryoidal material of BM. 32687.

invariably associated with the irregular particles of the botryoidal material. This possibly suggests that the smallest shining crystal that could be selected for X-ray study will always be admixed with multiple crystals, and only one axis, around which the crystals are similarly oriented, could be set for Weissenberg photographs. The difficulty in isolating a good single crystal from the botryoidal material is a great hindrance for the determination of the structure of psilomelane.

Wadsley's psilomelane

Wadsley (1953) obtained single-crystal data from the study of a tiny plate, separated from the outer crust of the botryoidal core of Vaux's psilomelane (BM. 69160). The structure amplitudes for reflexions ('streaks with lengths of 2-3 mm.') in the Weissenberg photographs were determined by him, using the 'strongest reflexion (406)' as reference. The $\sin^2\theta$ values, corresponding to the strong reflexions in his Weissenberg photographs, such as (302, 302, $\bar{1}13$, 402, $\bar{4}06$, 406, 513, $\bar{6}11$), were found to be different from those of the strong powder lines of psilomelane and the intensity relations of many reflexions appeared quite different from those of the powder lines reported by Gruner and the author. Therefore powder data for Wadsley's crystal were computed for his monoclinic cell.

The $\sin^2\theta$ and d values were calculated from Wadsley's cell dimensions, and the powder intensities from his observed single crystal F values, using the formula $I = (Lp).(F)^2.p.A$. The intensity of Debye-Scherrer lines on a cylindrical film depends on $(1 + \cos^2 2\theta)/(\sin^2\theta \cos\theta) = 4 Lp/\sin\theta$. The Lorenz-polarization factor for powder photographs (Lp) was obtained from the function, tabulated in *International Tables for X-ray Crystallography*, 1959, vol. II, no. 5.2.5B. The structure amplitudes (F) were taken from Wadsley's observed F values (listed in his table 2, p. 436, *loc. cit.*). The multiplicity factor (p) was taken as 2 for ($0k0$) and ($h0l$) reflexions and 4 for (hkl) reflexions. The absorption factor (A) was omitted because it did not very much affect the conclusion in the present case. It could, however, be estimated as that for a sphere or cylinder of psilomelane of about 0.2 mm diameter, the absorption coefficient being available from Wadsley's cell dimensions and contents $2[\text{Ba}_{0.64}(1.36\text{H}_2\text{O})\text{Mn}_5\text{O}_{10}]$ using atomic absorption factors from tables. The powder intensities from Wadsley's data along with his observed single-crystal F values are included in table I for comparison. The intensities of the powder lines are expressed on the basis of 100 for the strongest reflexion ($\bar{2}13$).

Comparing the powder data of Wadsley's crystal with those of Gruner, Fleischer and Richmond, and the author, it is quite evident that Wadsley's single-crystal data produce a distinctly different powder pattern from that of psilomelane. The d values of many strong powder lines of Wadsley's material, corresponding to the reflexions 302, 302, $\bar{1}13$, 402, $\bar{4}06$, 406, 513, $\bar{6}11$, are very different from those of the powder lines of psilomelane, though the d values of four strongest lines, 211,

213, 215, $\bar{2}17$, are similar to those of the powder lines of psilomelane. Some of the powder lines of psilomelane cannot be indexed at all with Wadsley's cell (indicated by (?) in table I), and the powder intensities from Wadsley's data are different for many lines. Moreover, the indexing of the powder lines of psilomelane indicates that reflexions with $k+l \neq 2n$ are also present, which rules out the possibility of the space group $A2/m$ proposed by Wadsley.

Unit cell contents of psilomelane

Fleischer (1960) showed that the four formulae of psilomelane, suggested by Vaux (1937), Fleischer and Richmond (1943), Palache, Berman, and Frondel (1944), and Wadsley (1953), are all fairly good approximations but that of Wadsley is best when they are based on a unit-cell (that of Wadsley) containing 20 oxygen atoms. But as we have seen above, Wadsley's material cannot have been true psilomelane.

Since the new unit cell contains 22 oxygen atoms, atomic ratios have been calculated on this basis for 5 chemical analyses quoted by Vaux and 9 analyses quoted by Fleischer (table II); the average value for the sum of cations is 11 ($Mn+A = 11.00$) and H is about 5 (5.07). The formula for psilomelane, $A_3X_6Mn_8^{4+}O_{16}$ where A represents Ba^{2+} , Mn^{2+} , Fe^{3+} , Si^{4+} etc., and X_6 stands for $(O,OH)_6$ with OH about 5, is very closely followed by most of the 14 analyses. The major deviations are for those analyses where the adsorbed water and constitutional water were not separately determined. Moreover, the uncertainty in the determination of constitutional water is an important factor; Fleischer (1960) observed from dehydration study of psilomelane that some of the water determined as H_2O+ may be considered as adsorbed. The calculated values of specific gravity are almost the same as the observed values for 5 samples (within 0.01 for 4 samples and 0.07 for 1 sample) and are higher than the observed values for 5 samples (within 0.14) but are lower than the values calculated by Fleischer. According to Vaux and Fleischer (*loc. cit.*) the possibility of pyrolusite and cryptomelane admixtures in psilomelane samples (bulk material analysed) may account for the discrepancies.

For the two original samples of Haidinger from Schneeberg and Romanèche (nos. 5 and 6 in table II) the procedure followed by Turner (1831) for the determination of 'oxygen and red-oxide' and the evaluation of MnO_2 and MnO by Vaux and Fleischer (*loc. cit.*) from those data are not quite justified. The calculation of specific gravity from unit-cell contents and molecular weight, derived from such analytical data, is

liable to give inaccurate values. Moreover, no check on the purity of this material is possible (Fleischer suggested probable contamination by pyrolusite).

Definition of psilomelane

The definition of psilomelane by Wadsley is different from that by Vaux. The powder data of Gruner, and of Fleischer and Richmond (*loc. cit.*) adequately describe the typical material from the type locality and this, with the chemical data, properly defines psilomelane; Vaux's analysed specimen BM. 69160 may properly be taken as the neotype specimen. The indexing of the powder lines of psilomelane is not possible on the basis of Wadsley's monoclinic cell or on Vaux's orthorhombic cell, but the indexing is ideal with author's orthorhombic cell. Moreover, the density, calculated from author's formula, unit-cell contents, and volume of the unit cell, agrees fairly well with the observed density.

Considering Wadsley's evidence on the nature of the crystal he examined, the only question is about the 'tiny plate' Wadsley separated from the outer crust of the botryoidal core; this may represent a material of the formula $A_2B_5O_{10}$ for which there is good structural evidence. It is almost certainly an oxide for which both A and B have about the weight of Mn (the difference in weight may be evaluated from detailed examination of his intensity data). Although B is mainly Mn there is very little evidence as to A , and the discussion of the structure about $Ba_{0.64}(1.36H_2O)$ is speculative. It is quite evident that Wadsley's crystal was not psilomelane, but may be an altered phase of Vaux's neotype specimen.

Mukherjee's powder data for the material from Madhya Pradesh, India (1959) should be reconsidered in the light of the new cell, since the cell dimensions derived from powder data are of much lower reliability than those from single crystal data. This will be discussed as soon as the chemical analysis of the specimen is available.

Dehydration of psilomelane

Fleischer and Richmond (1943) reported that the 'dehydration of psilomelane at 500–600° C gives hollandite as the chief product', and Fleischer (1960) observed that 'psilomelane is converted to hollandite at about 550° C'. An analogy of the structure of psilomelane heated to 600° C with that of hollandite (Byström and Byström, 1950) was drawn by Wadsley (1953).

The powder-spacing data of psilomelane (BM. 32687), heated at 400° C for 2 hours, were not significantly altered except slight shifting of reflexions towards higher angles. When heated at 600° C for 2 hours, the angles for all the reflexions were further increased, the intensity relations were significantly altered, and a new line at 3.13 Å was faintly recorded indicating marked structural changes in the orthorhombic cell. On heating at 700° C for 2 hours, the reflexion at 3.13 Å appeared as the most intense line with a broad diffuse halo at 3.10 Å which may be attributed to the disordered state and a period of marked structural changes initiating a phase transformation. The transformation to the monoclinic phase, very similar to hollandite, was confirmed at 800° C when the two reflexions at 3.14 Å and 3.11 Å (corresponding to 10 $\bar{3}$ and 103 reflexions of hollandite) appeared as two sharply separated lines of strong intensity, and the powder-spacing data for most of the reflexions were almost identical to those of hollandite (Mukherjee, 1960) but the intensity relations were not exactly the same.

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