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The Crystal Structure of Psilomelane, $(Ba, H_2O)_2Mn_5O_{10}$

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Psilomelane crystallizes in the monoclinic system, space group $A2/m$, with $a = 9{\cdot}56$, $b = 2{\cdot}88$, $c = 13{\cdot}85$ Å, $\beta = 92^\circ\ 30'$. The formula is $(Ba, H_2O)_2Mn_5O_{10}$ with the ratio $Ba:H_2O \simeq 1:2$. The structure consists of treble strings of MnO_6 octahedra joined by double strings to form a series of tunnels or tubes running in the direction of the b axis. The tunnels are occupied by a double row of barium ions and water molecules which are crystallographically indistinguishable. It is considered probable that each tunnel contains an ordered sequence of barium ions and water molecules which, however, are disordered in the structure as a whole. The relationship between psilomelane and its dehydration product, identical with the mineral hollandite, is considered briefly.

Psilomelane was the name given by Haidinger (1831) to a hydrated oxide mineral containing both manganese and barium. Unfortunately, the name has been applied to any massive sub-crystalline manganiferous ore possessing no distinguishing petrographic features. That psilomelane is a distinct species was shown from chemical and X-ray evidence by Vaux (1937), who examined crystals from several sources. The present structure analysis fully confirms Vaux's results, and it is clear that the term should refer only to this particular mineral. An abbreviated account of the structure has been published (Wadsley, 1952*b*).

Experimental

Although the mineral is of widespread occurrence, crystals of psilomelane are rare. We have been fortunate in obtaining portions of three specimens examined by Vaux, BM 69,160 from Schneeberg, Saxony, BM 32,687 from Spitzleite, Saxony, both by the courtesy of Dr F. A. Bannister, British Museum (Natural History), and also No. 3692, Platten, Bohemia from the Brooke Collection, University of Cambridge, by courtesy of Dr S. O. Agrell, who stated in a letter that this was originally No. 4182 used by Vaux. Each of these specimens consisted of a botryoidal core encrusted with minute platy crystals, powder photographs of which confirmed their common identity. The largest crystal which could be found for detailed X-ray examination, a tiny plate $0{\cdot}1 \times 0{\cdot}06 \times 0{\cdot}02$ mm. with ridged faces (from specimen BM 69,160), proved to have monoclinic symmetry, not orthorhombic as proposed by Vaux, and with the dimensions

$$a = 9{\cdot}56 \pm 0{\cdot}02,\ b = 2{\cdot}88 \pm 0{\cdot}02,\ c = 13{\cdot}85 \pm 0{\cdot}02\ \text{Å}\,,\quad \beta = 92^\circ\ 30' \pm 20'\,.$$

These figures were determined from a single setting of the crystal, the b axis from layer line spacings, and a, c and β from a zero-level Weissenberg photograph taken with unfiltered copper radiation. The reflexions absent on zero- and first-level equi-inclination Weissenberg records were for $k+l \neq 2n$. The space group was therefore limited to $A2/m$, $A2$ or Am.

The formula computed from the analysis quoted by Vaux for this specimen was $Ba_{0.64}Mn^{4+}_{4{\cdot}28}Mn^{2+}_{0{\cdot}56}R_{0{\cdot}18}O_{10}$. $1{\cdot}36\,H_2O$, giving $d_{\text{calc.}} = 4{\cdot}82$ g.cm.$^{-3}$, $d_{\text{obs.}} = 4{\cdot}71$ g.cm.$^{-3}$ and $z = 2$. Assuming that Mn^{2+} together with the minor elements R substitute for Mn^{4+} as they do in hollandite (Byström & Byström, 1950), a mineral of similar composition, the formula simplifies to $Ba_{0{\cdot}64}(Mn, R)_{5{\cdot}02}O_{10}\,.\,1{\cdot}36\ H_2O$. Being based upon an integral number of oxygen atoms, this formula involves no assumptions about the nature of the 'combined' water. The agreement between the observed and calculated densities is superior to that found by adopting Vaux's formula $H_4BaR_2Mn_8O_{20}$, or $BaMn^{2+}Mn^{4+}_8O_{16}(OH)_4$ given by the editors of the new *Dana's System of Mineralogy* (1944).

The reflexions on the rotation photograph taken about the b axis were elongated in the directions of the powder arcs, showing that the crystal was a multiple one. The corresponding zero- and first-level moving films were streaks with a uniform length of 2–3 mm. in general clearly resolved. Intensity data for these levels were recorded with filtered molybdenum radiation using the multiple-film technique, the films being separated from each other with tinfoil to increase the interfilm factor. Intensities were measured by comparison with a series of standards prepared by oscillating the crystal and film carriage 5° on either side of the strongest reflexion (406) during appropriate time intervals.

The intensities were corrected for Lorentz and polarization factors in the usual manner, and were subsequently placed on an absolute scale by comparing with the computed structure amplitudes. The measured F's were weighted with a temperature factor $B = 0{\cdot}8 \times 10^{-16}$ cm.^{2} obtained experimentally by plotting the mean values of F_o/F_c within limited ranges of $\sin\theta$ against $\sin\theta$, and obtaining the best fit to this curve with selected Debye–Waller values.

It was a matter of extreme difficulty to provide diffraction data about another axis. Because of the spread of the spots on the layer lines, the crystal could not be set on either a or c to give zero-layer moving films free from overlapping n-level normal-beam Weissenberg records. The structure was therefore determined from the $(h0l)$ and $(h1l)$ data, involving the uncertainties mentioned below.

Structure determination

There was no evidence to distinguish between the space groups $A2/m$, $A2$ or Am. A piezoelectric test proved negative, a statistical examination of intensities by the method of Howells, Phillips & Rogers (1950) to detect a centre of symmetry was indeterminate, and the crystals were too small and poorly formed to provide morphological point-group data. The structure was assumed to be centrosymmetric with the space group $A2/m$, and the final close correlation between observed and calculated structure amplitudes was sufficient to justify this selection.

Since the length of b is only 2·88 Å, the atoms should be clearly resolved in a projection down this axis, provided that all the manganese atoms have their usual sixfold grouping of oxygen ions. The ten manganese atoms in the unit cell may be arranged in one of two ways. Two atoms will be in a twofold position with the remainder either in an eightfold position or in two sets of fourfold sites. The barium and 'combined' water do not offer such straightforward alternatives. Chemical analysis does not distinguish between hydrogen ions, hydroxyl ions or discrete water molecules, and although the fractional quantity of water in the unit cell may be due to analytical uncertainty, a temperature–weight-loss curve showed no significant loss of water below 110° C., the temperature at which non-lattice water is usually estimated. Barium must definitely be non-stoichiometric if treated as an individual constituent of the structure.

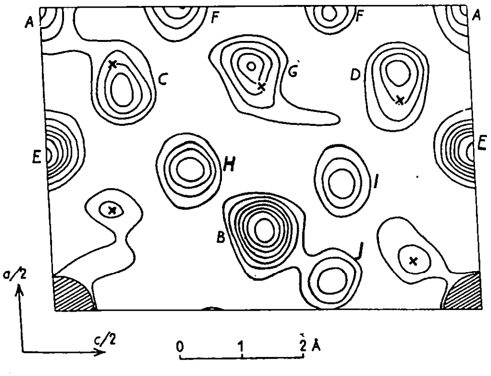


Fig. 1. Patterson projection on the b axis. Only positive regions are drawn. The crosses indicate the positions chosen for the oxygen atoms in the preliminary F_c calculations.

The Patterson function $P(x, z)$ is shown in Fig. 1. If fractional quantities of Ba atoms occupy lattice sites, they will most probably be present in the twofold positions $2(c)$ or $2(d)$ given in the *Internationale Tabellen* for the space group $A2/m$, i.e. at $(\frac{1}{2}, 0)$ for this projection. The presence of 2 Mn_1 which can be arbitrarily placed at the origin would provide a double vector peak in Patterson space at $(\frac{1}{2}, 0)$. There is, however, a single peak only at this point (A in Fig. 1) and it is therefore improbable that the Ba ion occupies a twofold site.

It was considered unlikely that both the barium ions and water would each only partly fill independent fourfold sites in the structure. Together, however, these components provided an integral formula $(Ba, H_2O)_{2\cdot0}(Mn, R)_5O_{10}$ which, although possibly fortuitous, offered few real objections provided that water molecules rather than H^+ or $(OH)'$ were present. The radii of the barium ion and the water molecule are sufficiently alike to permit isomorphous replacement to occur. As a single unit, $\frac{1}{2}(Ba_{0\cdot64}H_2O_{1\cdot36})$ would occupy a fourfold position and would have approximately the same scattering power as a manganese atom.

From an analysis of hollandite $Ba_{2-y}Mn_8O_{16}$ $(y \simeq 1)$, a mineral of similar chemical composition, Byström & Byström (1950) found Ba–Mn and Mn–Mn distances of 4·1 and 2·9 Å respectively. Accepting these values provisionally for psilomelane, the Mn_1–(Ba, H_2O) vector would be either B, C or D, and Mn_1–Mn_2 either E or J, in the Patterson projection (Fig. 1) since Mn_1 occupying a twofold site must be placed at the origin. The most probable combination appeared to result from the peak B being identified with Mn_1–Ba, E with Mn_1–Mn_2 and the remaining manganese atom located by the peaks F as Mn_1–Mn_3 vectors. The main features of Fig. 1 could then be explained in a satisfactory manner. Ba–Ba provided a vector coinciding with the Mn_1–Mn_2 vector at E, and Mn_2–Ba together with Mn_1–Ba falling on B, each peak of greater height than the others in the figure. Ba–Mn_3 gave C and D, a second Ba–Mn_2 vector would be identified with G, Mn_2–Mn_3 with H and I, Mn_2–Mn_2 with A and Mn_3–Mn_3 with J.

By considering the appropriate symmetry elements, this grouping provided a model in which ten approximately equidistant manganese atoms were arranged in a roughly rectangular manner about two (Ba, H_2O) groups, so that each of these latter was at a distance of 3·9–4·2 Å from six Mn atoms. The atoms Mn_2 and Mn_3 would therefore occupy general fourfold positions $4(i)$ for the space group $A2/m$. The oxygen atoms, so far not considered, were each likewise placed in the general positions $4(i)$. The parameters could not be selected with any precision from the Patterson data, but were placed in the positions marked by crosses in Fig. 1 to give a mean Mn–O distance of 1·95 Å.

Structure factors calculated for this model agreed reasonably well with the observed values, and a Fourier projection on the *b* axis was computed to refine the parameters. The electron-density diagram showed regular peaks at the positions proposed for the metal atoms with some slight changes of position. The oxygen peaks were poorly defined, obscured as they were by diffraction ripple. Further structure factors computed with the revised metal-atom parameters gave no changes of sign. An F_o-F_c synthesis was prepared by subtracting the Mn and Ba contributions from the observed structure amplitudes. The oxygen atom peaks were resolved but slightly irregular in shape, and the water peak appeared in the Ba position to confirm the association of these units. A further F_o-F_c synthesis was calculated, the terms including approximate computed oxygen-atom contributions for reflexions whose intensities lay below the observable limit. This is shown in Fig. 2 from which the parameters of the oxygen atoms in Table 1 were measured. The discrepancy factor for the calculated and observed structure amplitudes in Table 2 is 16%.

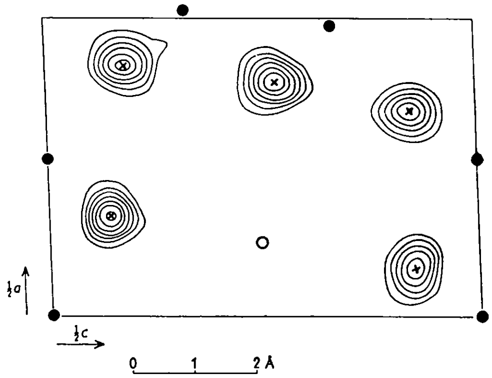


Fig. 2. Final F_o-F_c Fourier projection on the *b* axis, showing the resolution of the oxygen atoms. Contours are drawn at equal but arbitrary intervals. The dots represent the manganese atoms, the open small circle the (Ba, H_2O) group, found in the F_o synthesis.

Table 1. *Parameters of the atoms in psilomelane*

Space group *A*2/*m*. (0, 0, 0; 0, ½, ½)+

Atom	No. of equivalent atoms	*x*	*y*	*z*
Mn_1	2 in 2(*b*)	0	½	0
Mn_2	4 in 4(*i*)	0·265	0	0
Mn_3	4 in 4(*i*)	0·488	0	0·335
(Ba, H_2O)	4 in 4(*i*)	0·124	0	0·246
O_1	4 in 4(*i*)	0·168	0	−0·072
O_2	4 in 4(*i*)	0·421	0	0·092
O_3	4 in 4(*i*)	0·394	0	−0·232
O_4	4 in 4(*i*)	0·346	0	0·422
O_5	4 in 4(*i*)	0·080	0	−0·075

It has been pointed out that it was a matter of great difficulty to obtain diffraction data about another axis. By placing Mn_1 in 2(*b*) for the space group *A*2/*m*, and the remaining atoms in 4(*i*), all fall in special positions parallel to the *b* axis. Structure factors calculated on this basis for the ($\bar{h}ll$) reflexions agreed well with the observed values, those for the non-observed reflexions being invariably less than the limiting values (Table 2). It must be pointed out, however, that only fourteen observable terms were available for comparison even after an exposure of 300 hr. Thus, although the good agreement between F_o and F_c for the *h*0*l* zone must rule out *Am* as the space group, it is possible there may be some small deviations from zero in the *y* parameters of the oxygen ions which would remain undetected with the limited diffraction evidence.

Discussion

The structure of psilomelane is built up of manganese–oxygen octahedra, the mean Mn–O distance being 1·93±0·06 Å. These are joined by sharing edges to form double and treble units which are elongated in the *b*-axis direction as continuous strings of octahedra. The treble strings are linked by double strings in a near rectangular group by sharing corners to form a series of tubes or tunnels parallel to the *b* axis. The tunnels are occupied by a double row of barium ions and water molecules (Fig. 3).

It will be noted that the octahedra associated with each manganese atom are of two kinds. That of Mn_1 shares six edges with adjacent octahedra, the only other case in which a tetravalent positive ion has such a grouping being lithiophorite, a mixed layer mineral (Wadsley, 1952*a*). The remaining octahedra each share four edges with their neighbours as in the manganese minerals ramsdellite (Byström, 1949) and hollandite (Byström & Byström, 1950) the structures of which are based upon double strings of coordinated octahedra. The interatomic distances are listed in Table 3. The O–O distances vary from 2·92 to 2·63 Å for unshared edges and from 2·55 to 2·73 Å for the shared edges.

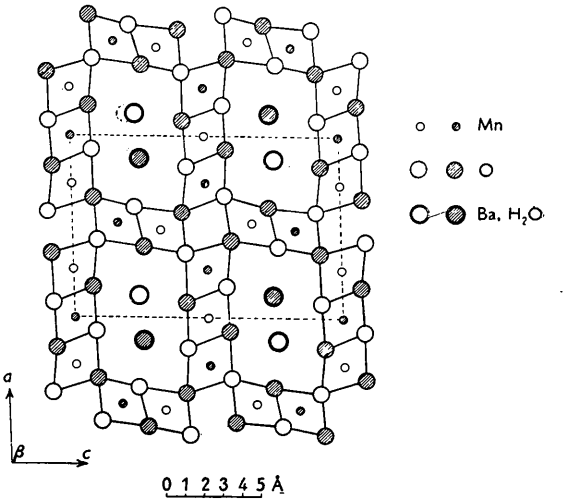


Fig. 3. The structure of psilomelane projected on the *b* axis showing four linked tunnels. The unit cell is shown by broken lines. Open circles indicate atoms at $y = 0$, shaded circles at $y = \frac{1}{2}$.

Table 2. *Observed and calculated F's for psilomelane*

(Filtered molybdenum radiation)

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
100	9	−9	904	< 18	6	$\bar{4},0,12$	21	25
200	26	28	$\overline{10},0,6$	< 19	10	$\bar{3},0,12$	< 16	−12
300	26	−28	$\bar{9}06$	18	−25	$\bar{2},0,12$	< 16	−3
400	33	16	$\bar{8}06$	21	25	$\bar{1},0,12$	< 16	−1
500	35	−39	$\overline{70}6$	< 16	−4	1,0,12	< 16	2
600	< 13	9	$\bar{6}06$	< 15	11	2,0,12	23	26
700	25	21	$\bar{5}06$	17	−16	3,0,12	24	−20
800	53	61	$\bar{4}06$	102	114	4,0,12	21	20
900	< 17	−9	$\bar{3}06$	< 12	−19	5,0,12	31	−34
10,0,0	< 18	13	$\bar{2}06$	33	28	6,0,12	< 19	1
11,0,0	< 19	3	$\bar{1}06$	44	−38	7,0,12	< 19	13
12,0,0	21	21	106	36	−35	8,0,12	38	40
002	26	22	206	< 12	−3	9,0,12	< 22	0
004	61	66	306	19	18	$\bar{5},0,14$	< 19	6
006	< 11	4	406	110	113	$\bar{4},0,14$	35	30
008	55	45	506	< 14	−6	$\bar{3},0,14$	18	33
0,0,10	< 14	1	606	15	24	$\bar{2},0,14$	< 18	−5
0,0,12	77	77	706	< 16	−9	$\bar{1},0,14$	< 18	8
0,0,14	18	12	806	24	25	1,0,14	< 18	5
0,0,16	37	27	906	26	−33	2,0,14	20	−27
0,0,18	< 21	17	10,0,6	< 19	7	3,0,14	18	31
$\overline{13},0,2$	< 22	−3	11,0,6	20	16	4,0,14	30	27
$\overline{12},0,2$	30	35	$\bar{9}08$	< 19	3	5,0,14	24	22
$\overline{11},0,2$	24	29	$\bar{8}08$	43	43	6,0,14	< 20	−5
$\overline{10},0,2$	< 18	1	$\bar{7}08$	31	38	7,0,14	21	18
$\bar{9}02$	21	−22	$\bar{6}08$	< 16	−3	8,0,14	< 22	−9
$\bar{8}02$	16	13	$\bar{5}08$	21	−11			
$\bar{7}02$	18	10	$\bar{4}08$	32	23	011	< 36	−34
$\bar{6}02$	14	−10	$\bar{3}08$	< 14	11	013	37	53
$\bar{5}02$	< 12	21	$\bar{2}08$	16	−28	015	< 41	7
$\bar{4}02$	57	45	$\bar{1}08$	18	33	017	< 46	−8
$\bar{3}02$	63	57	108	24	40	019	51	51
$\bar{2}02$	30	−31	208	< 13	−17	$\bar{6}11$	101	−101
$\bar{1}02$	18	20	308	22	23	$\bar{5}11$	< 48	−24
102	22	25	408	15	−12	$\bar{4}11$	< 44	5
202	50	−52	508	< 15	5	$\bar{3}11$	< 40	33
302	77	76	608	36	−39	$\bar{2}11$	< 37	−27
402	88	81	708	50	54	$\bar{1}11$	< 36	18
502	29	40	808	29	33	111	< 36	−23
602	19	−19	908	19	22	211	86	−72
702	33	28	10,0,8	< 20	−4	311	< 40	−15
802	30	−33	11,0,8	22	19	411	< 44	4
902	< 17	3	$\bar{9},0,10$	< 20	6	511	< 48	−7
10,0,2	18	−27	$\bar{8},0,10$	23	−25	611	< 51	−25
11,0,2	46	49	$\bar{7},0,10$	33	25	$\bar{5}13$	< 48	−36
12,0,2	< 21	17	$\bar{6},0,10$	30	−29	$\bar{4}13$	45	38
$\overline{12},0,4$	30	−19	$\bar{5},0,10$	30	31	$\bar{3}13$	41	−48
$\overline{11},0,4$	24	25	$\bar{4},0,10$	45	51	$\bar{2}13$	101	−92
$\overline{10},0,4$	< 19	−14	$\bar{3},0,10$	69	56	$\bar{1}13$	69	−70
$\bar{9}04$	18	20	$\bar{2},0,10$	23	−18	113	< 37	−34
$\bar{8}04$	31	47	$\bar{1},0,10$	< 14	8	213	46	60
$\bar{7}04$	72	64	1,0,10	< 14	0	313	< 43	−21
$\bar{6}04$	28	−32	2,0,10	30	−28	413	53	50
$\bar{5}04$	18	9	3,0,10	41	38	513	80	−74
$\bar{4}04$	51	−39	4,0,10	28	31	$\bar{4}15$	< 48	4
$\bar{3}04$	43	28	5,0,10	24	22	$\bar{3}15$	< 44	14
$\bar{2}04$	52	−48	6,0,10	< 17	−5	$\bar{2}15$	43	−46
$\bar{1}04$	60	62	7,0,10	18	14	$\bar{1}15$	< 41	8
104	49	55	8,0,10	19	13	115	< 43	−15
204	27	−26	9,0,10	25	−17	215	87	−93
304	19	20	10,0,10	< 22	−4	315	< 46	0
404	28	33	$\bar{9},0,12$	< 21	−9	415	< 49	−20
504	< 13	−13	$\bar{8},0,12$	24	40	$\bar{2}17$	100	−94
604	< 14	−15	$\bar{7},0,12$	< 19	19	$\bar{1}17$	46	−51
704	34	38	$\bar{6},0,12$	< 18	15	117	< 46	−36
804	35	38	$\bar{5},0,12$	18	−21	217	< 49	14

Table 3. *Interatomic distances*

Mn_1–O_1	1·85 Å	O_5–O_4	*u*	2·92 Å	(H_2O, Ba)–O_1	2·85 Å
Mn_1–O_5	1·95	O_5–O_1	*u*	2·77	(H_2O, Ba)–O_3	2·96
Mn_2–O_1	2·02	O_1–O_2	*u*	2·82	(H_2O, Ba)–O_5	2·91
Mn_2–O_4	1·98	O_4–O_2	*u*	2·83	(H_2O, Ba)–(H_2O, Ba)	2·78
Mn_2–O_5	2·01	O_2–O_3	*u*	2·85	(H_2O, Ba)–O_2	3·62
Mn_2–O_2	1·92	O_2–O_4	*u*	2·67	(H_2O, Ba)–O_1	3·84
Mn_3–O_3	1·86	O_3–O_4	*u*	2·63	(H_2O, Ba)–O_4	3·16
Mn_3–O_3	1·92	O_5–O_1	*s*	2·60	(H_2O, Ba)–O_5	3·00
Mn_3–O_4	1·85	O_5–O_5	*s*	2·63		
Mn_3–O_2	1·94	O_4–O_1	*s*	2·73		
		O_2–O_3	*s*	2·57		
		O_3–O_3	*s*	2·55		

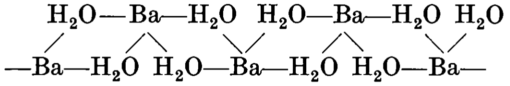
u = unshared; *s* = shared.

The normal length of a shared edge for the Mn–O octahedron is 2·5–2·6 Å (Byström, 1949; Wadsley, 1952*a*) and the value 2·73 Å for O_4–O_1 seems rather large. By changing the *x* parameter of O_4 from 0·346 to 0·330, an improvement of this value and also of the rather low values of O_2–O_4 and of O_3–O_4 can be effected (Table 4). There is no evidence of this shift in any of the Fourier projections, and structure factors including the revised parameter gave no significant change in the discrepancy factor. If this new value is correct, it is probable that the diffraction data are inadequate for precise atomic positions, although the more general aspects of the structure are quite clear.

Table 4. *Changes in interatomic distances by altering the x parameter of* O_4 *from* 0·346 *to* 0·330

	Distances computed from the Fourier parameters	Distances computed from revised parameters of O_4
Mn_2–O_4	1·98 Å	1·90 Å
Mn_3–O_4	1·85	2·00
O_4–O_1 (shared)	2·73	2·52
O_3–O_4 (unshared)	2·63	2·79
O_2–O_4 (unshared)	2·67	2·79
O_4–O_5 (unshared)	2·92	2·79
(H_2O, Ba)–O_4	3·16	3·10

The association of the (Ba, H_2O) groups with their neighbours is unusual. Each is situated at the centre of fourteen oxygen atoms and equivalent (Ba, H_2O) units, forming an irregular tetrahexahedron. The double row consists of interpenetrating tetrahexahedra. It is, however, more convenient for the purposes of this discussion to ignore the more distant atoms O_1, O_2, O_4 and O_5 coplanar with the central atom, and to describe the coordination in terms of the polyhedron formed by the ten nearer neighbours, a prism and pyramid. The double row is then seen to consist of a staggered string formed by each prism and pyramid sharing one edge with the adjacent members (Fig. 4). The shared edge corresponding to the linkage (Ba, H_2O)–(Ba, H_2O) is shorter than the other edges of the unit polyhedron (Table 3). Since two adjacent positive ions would tend to repel one another, it is unlikely that two Ba ions would occupy each site on a shared edge which is here equal in length to the diameter of the Ba ion. For this reason, the disposition of the double row would be since the ratio Ba:H_2O is almost equal to 1:2. The unit prism and pyramid, therefore, will have Ba as the central coordinating cation, and the water molecules will be common to each unit of the staggered string (Fig. 4) forming a continuum.



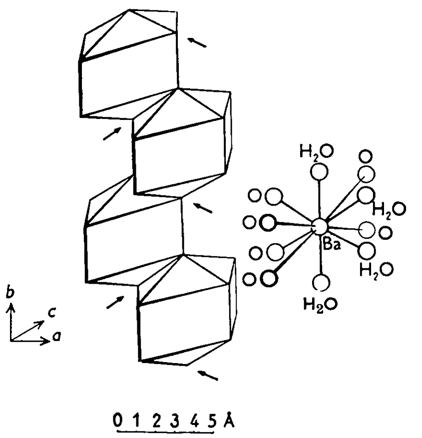


Fig. 4. A staggered string of polyhedra. The shared edges (indicated by arrows) link two water molecules. The atoms comprising a single polyhedron (a prism and pyramid) are shown in the smaller figure.

In any one tunnel it is most probable that this arrangement is preserved. The length of the *b* axis would then be 3×2·88 Å = 8·64 Å, but for this there is no diffraction evidence. It is concluded that the double rows of Ba atoms and water molecules, perfect for each tube, do not possess mutual periodicity, and consequently the X-ray data, presenting an averaged picture of the structure, fails to distinguish between the two scattering units. The chemical formula for any one unit cell would be $Ba_2Mn_{15}O_{30}4\,H_2O$, but since there is disorder giving the *b* axis only one-third its true value, the formula in the title is preferred.

Some confusion has existed in the past concerning the substantial amount of lower-valency manganese invariably present in psilomelane, and the tendency to regard Mn^{2+} as a separate constituent has led to difficulties of formulation. The Ba ions which are

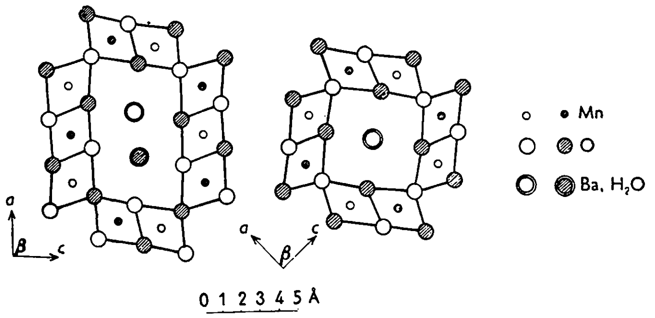


Fig. 5. The structure of psilomelane (left) compared with that of hollandite (right). Open circles indicate atoms at $y = 0$, shaded circles at $y = \frac{1}{2}$.

coordinated to the oxygen ions of the stable $Mn^{4+}O_6$ cotahedra will upset the charge distribution, and for the structure to exist at all an equivalent number of the Mn^{4+} ions must be reduced to Mn^{2+} ions. These will remain in the Mn^{4+} sites as charge deficiencies.

The dehydration of psilomelane

There is a marked resemblance between the chemical composition of psilomelane and hollandite $Ba_{2-y}Mn_8O_{16}$ ($y \simeq 1$), the only significant difference being the water present in the former.

The structure of hollandite has recently been determined (Byström & Byström, 1950) and the similarity to psilomelane is evident from Fig. 5. Here the Ba ions are situated in a single row in tunnels formed by double strings of MnO_6 octahedra linked in a square array by sharing corners, and elongated in the b-axis direction.* The Ba positions are only half filled. In order to avoid placing two Ba ions in adjacent sites in a row, Byström & Byström (1951) suggested that these ions together with vacant sites may be ordered

—vac.—Ba—vac.—Ba—vac.— etc.

The rows, themselves perfect, possess no periodicity in the structure as a whole.

It has been pointed out (Fleischer & Richmond, 1943) that psilomelane is converted to hollandite on heating to 550° C. Since most of the water is expelled at this temperature, the double rows in the tunnels will now consist mainly of Ba ions. The creation of so many vacant sites will doubtless lead to structural instability, and the formation of a single hollandite-type row of Ba ions and vacant sites for each tunnel may readily be visualized. The tunnels of linked MnO_6 octahedra would then collapse to those of hollandite by the rearrangement of the treble strings into double strings. It is evident from a powder photograph of psilomelane heated to 550° C. that this structural change is accompanied by a period of marked crystal disorder.

A temperature v. weight curve recorded for the writer by Mr A. J. Gaskin, Geology Department, University of Melbourne, showed no abrupt transition which would be expected if the loss of water occurred at a definite temperature, as in a hydrate. After heating to 400° C., the water expelled may be readmitted by leaving the specimen exposed to the atmosphere for several days at room temperature. Powder photographs have shown that psilomelane can be heated to 400° C. without changing, despite the fact that at least 60% of the water is lost. It has been seen (Fig. 4) that the water molecules, lying on the shared edges of the polyhedra coordinated to each Ba atom, may well be a continuum for each tunnel, terminating only at the surfaces of the crystal. The loss of water at these boundaries will cause further molecules to diffuse and escape, since they are unimpeded by strong ionic forces within the crystal. Consequently the loss of water from psilomelane when heated is unlikely to cause drastic structural changes until such a time as the reorientation of the rows af Ba ions and of the MnO_6 octahedra can be effected.

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* Hollandite may be either tetragonal, or monoclinic pseudotetragonal. The b axis here refers to the monoclinic symmetry axis.