X-ray study of psilomelane and cryptomelane.

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Summary. Psilomelane has been shown to be orthorhombic with *a* 8·254, *b* 13·40, *c* 2·864 Å. by the application of Lipson's method. The indexing of powder photographs of psilomelane ($R''_2\,\mathrm{Mn}^{\mathrm{iv}}_8\,\mathrm{O}_{16}(\mathrm{OH})_4$, where R'' includes the bivalent metals Mn, Ba, Ca, Mg, Co) indicates the space-group $P2_12_12$ (D_2^3) with one molecule per unit cell. Indexing of powder photographs of psilomelane is not satisfactory with Vaux's axes. Fermor's 'psilomelane' is cryptomelane, which is tetragonal with *a* 9·822, *c* 2·858 Å. Cryptomelane ($\mathrm{K}R_8\mathrm{O}_{16}$, where R stands for Mn in different valency states, partly replaced by other cations) is body-centred tetragonal with one molecule per unit cell. Fermor's stalactitic 'psilomelane' has an inner dull core of cryptomelane and an outer fine-grained crust of pyrolusite in each needle-shaped body.

Psilomelane.

PSILOMELANE, a botryoidal material from Schneeberg, Saxony, was first described by Haidinger (1831). The chemical and X-ray study by Vaux (1937) of the original psilomelane from Schneeberg indicates that the name belongs to an orthorhombic species with the composition $\mathrm{H_4BaMnMn_8O_{20}}$ having 10 to 17 % BaO. Vaux reported the cell-dimensions of psilomelane, $a = 9·1$ Å., $b = 13·7$ Å., $c = 2·86$ Å. as new data without detailed information on the method of derivation. Fleischer and Richmond (1943) gave X-ray powder spacing data of psilomelane for a sample from Vaux's collection. Wadsley (1953) studied a minute platy crystal (0·1 × 0·06 × 0·02 mm.) separated from the outer crust of the botryoidal core of a psilomelane from Vaux's collection and showed that the crystals have monoclinic symmetry with the dimensions, $a = 9·56$ Å., $b = 2·88$ Å., $c = 13·85$ Å., $\beta = 92° 30'$, $Z = 2$ for $\mathrm{(Ba,H_2O)_2Mn_5O_{10}}$ and the space-group $A2/m$. The *b*-axial length was determined from a single setting of the crystal about the *b*-axis and *a*, *c*, and β from a zero-level Weissenberg photograph. Fermor (1909) described psilomelane from manganese ores of Indian deposits and named manganites with 5 to 15 % BaO from Tekrasai, Singhbhum, and Kajlidongri, Jhabua, 'baryta-psilomelane'.

Orthorhombic psilomelane (massive) containing 10 to 15 % aO has been detected in manganese ores from the Jhabua and Ratanp eposits

(Bilaspur, Madhya Pradesh) by X-ray powder diffraction methods. The powder spacing data of this psilomelane are in good agreement with those reported by Fleischer *et al.* for Vaux's psilomelane. Lipson's method (1949) for orthorhombic systems has been successfully applied to index the powder data of psilomelane. For orthorhombic crystals,

$$q_{hkl} = \sin^2\theta_{hkl} = h^2A+k^2B+l^2C,$$

where $A = \lambda^2/4a^2$, $B = \lambda^2/4b^2$, $C = \lambda^2/4c^2$. Lipson's method is to examine systematically the differences between the observed values of q in order to get relationship such as $q_{0kl}-q_{1kl} = A$ &c.; A occurs as differences between q values, where h values differ by unity and the kl values for the two lines are the same. Such differences are found in the powder spacing data of psilomelane by the diagrammatic method of Lipson. The possible values deduced from difference diagram are: $A = 0{\cdot}01375$, $B = 0{\cdot}00522$, $C = 0{\cdot}1142$; Fe-$K\alpha$-radiation was used for the powder photograph. The cell-dimensions are: $a = 8{\cdot}254$ Å., $b = 13{\cdot}40$ Å., $c = 2{\cdot}864$ Å.; $a:b:c = 0{\cdot}616:1:0{\cdot}214$. After indexing of all the powder lines (table I), it is found that the only systematic absences are the odd orders of $h00$ and $0k0$ indicating the space-group $P2_12_12$ (D_2^3).

Vaux's values for the cell-dimensions give $A = 0{\cdot}01132$, $B = 0{\cdot}00499$, $C = 0{\cdot}1145$, according to the above calculation. Indexing of all the powder lines of psilomelane (Fleischer's data) is not satisfactory with these values; the error of q_{hkl} values for some of the intense lines is quite high. It is, however, possible to index the powder photograph on the basis of Wadsley's (loc. cit.) monoclinic cell; but the space group suggested by the powder lines so indexed differs from that ($A2/m$) proposed by Wadsley. On the other hand, the agreement in indexing on the basis of an orthorhombic cell is better than that obtained on the assumption of monoclinic symmetry. The present specimen studied is, therefore, distinctly different from that described by Wadsley.

The chemical analyses of a number of psilomelanes by Vaux and Fermor show that the number of atoms in the unit cell per 20 oxygen atoms comes out at $\mathrm{Mn^{iv}} \approx 7{\cdot}6$ to $7{\cdot}9$, $\mathrm{Mn''} \approx 0{\cdot}9$ to $1{\cdot}0$, $\mathrm{Ba} \approx 0{\cdot}8$ to $1{\cdot}1$, $\mathrm{Ca+Mg+Co} \approx 0{\cdot}2$ to $0{\cdot}3$, and $\mathrm{H} \approx 4$. The ideal formula is

$$R''\mathrm{Mn_8O_{16}(OH)_4},$$

where R'' includes the bivalent metals Mn, Ba, Ca, Mg, Co, &c. The molecular weight is calculated with the atomic weight of R'' as the weighted mean value of the atomic weights of all the bivalent metals

Table I. X-ray powder data for psilomelane from Jhabua (VV-S 17/1, contains 11 % BaO; specimen collected by Mr. V. Venkatesh of the Geological Survey of India) and from Ratanpur (BNS–9(X), contains 13 % BaO; specimen collected by Dr. B. N. Sinha of the Geological Survey of India). *B*, broad and diffuse.

d.	I/I_0.	$\sin^2\theta$ (obs.).	*hkl.*	$\sin^2\theta$ (calc.).
6·95 Å.	20	0·0194	110	0·0190
4·14	10	0·0547	200	0·0550
3·93 *B*	10	0·0606	210 130	0·0602 0·0607
3·49	80	0·0769	220	0·0759
3·33 *B*	20	0·0844	040	0·0835
3·11	20	0·0968	140	0·0973
3·02 *B*	15	0·1026	230	0·1020
2·86 *B*	15	0·1145	001	0·1142
2·81	10	0·1187	011	0·1194
2·66	20	0·1326	111	0·1332
2·63	5	0·1355	021	0·1351
2·405	100	0·1620	031	0·1612
2·36	20	0·1683	201	0·1692
2·315	5	0·1747	131 211	0·1749 0·1744
2·25	15	0·1851	250	0·1855
2·24	40	0·1869	060	0·1879
2·215	10	0·1909	221	0·1901
2·18	100	0·1971	041	0·1977
2·15	30	0·2026	160	0·2017
2·13	5	0·2065	340	0·2073
2·065	10	0·2197	400	0·2200
2·035	15	0·2262	410	0·2252
1·925	10	0·2529	241	0·2527
1·865	10	0·2695	170	0·2695
1·815	50	0·2845	331	0·2849
1·735	15	0·3113	360 270	0·3117 0·3108
1·71	20	0·3205	341	0·3215
1·675	5	0·3339	080	0·3341
1·64	25	0·3483	180 510	0·3478 0·3490
1·563	40	0·3835	171	0·3837
1·515	10	0·4082	460	0·4079
1·483	5	0·4259	271 361	0·4250 0·4259
1·425	40	0·4615	012 181	0·4620 0·4620
1·403	25	0·4759	112 470	0·4758 0·4758
1·375	5	0·4955	600	0·4950
1·363	5	0·5044	032 531	0·5038 0·5049
1·353	10	0·5119	202	0·5118
1·340	5	0·5218	0.10.0 461	0·5220 0·5221

Mn, Ba, Ca, Mg, and Co in the proportions stated above, when with the above values of axial lengths and a density 4·6±0·1 g./cm.^{3} for psilomelane, the number of molecules per unit-cell comes out to be $Z \approx 1$.

A spectrum analysis of psilomelane (VV-S 17/1) shows Mn and Ba as major constituents, Mg, Al, Fe, Si, Ca, K, Na, Co, Ni, Cu as minor, and V, Ag, Pb, W, As, Ti, Ge, Ga, Sn, Sb, Li as traces. Spectrum analysis was carried out using a Hilger 'Large Quartz Spectrograph' with a direct current arc between 'Spec-pure' carbon rods at 9 amps, 220 volts.

Cryptomelane.

Fermor (1909) described psilomelane as a manganite containing potassium, barium, and sodium in different proportions. Richmond and Fleischer (1942) first proposed the name cryptomelane for the commonest variety of crystalline 'psilomelane', which is a distinct mineral species characterized by the presence of potassium, with little or no barium. Ramsdell (1942) determined the cell-dimensions of cryptomelane as a = 9·82 Å., c = 2·86 Å. (body-centred tetragonal).

The X-ray study of a number of specimens of Fermor's 'psilomelane' (registered collection in the Indian Museum) shows that the powder pattern corresponds exactly with that of Ramsdell's cryptomelane. Fermor's psilomelane (A. 680) from Chikhli, Satara, Bombay, containing about 2 % potassium with small amounts of barium and sodium, is considered as an ideal cryptomelane (table II). The cell-dimensions determined after indexing of all the powder lines by Hesse's method (1948), are a = 9·822 Å., c = 2·858 Å. (±0·003 Å.), and the axial ratio c/a 0·291. The conditions limiting possible reflections are: hkl only with $h+k+l = 2n$, $00l$ only with $l = 2n$, $h00$ only with $h = 2n$. These conditions indicate one of the space-groups $I4/mmm$, $I\bar{4}2m$, $I\bar{4}m2$, $I4mm$, $I422$, $I4/m$, $I\bar{4}$, or $I4$, in agreement with Ramsdell. The recorded chemical analyses of a number of cryptomelanes by Fleischer and Fermor indicate that the ideal formula is KR_8O_{16}, where R stands for Mn in different valency states (predominantly Mn^{iv}), partly replaced by other cations. With the above values of axial lengths and density 4·4±0·1 g./cm.^{3} for cryptomelane the number of formula units per unit-cell comes out to be $Z \approx 1$. The spectrum analysis of cryptomelane (A. 680) shows Mn as the major constituent, K, Mg, Al, Fe, Si, Ca, Na, Ba, Co, Ni, Cu, Ti, Li as minor, and V, Ag, Pb, Sn, As, Mo, W, Ga, Ge, Zn, Zr, Pt, Sb as traces.

TABLE II. X-ray powder data for cryptomelane from Chikhli, Satara, Bombay, India (Fermor's No. A. 680).

d.	I/I_0.	$\sin^2\theta$ (obs.).	hkl.	$\sin^2\theta$ (calc.).
6·94	70	0·0195	110	0·0194
4·91	60	0·0388	200	0·0388
3·475	20	0·0776	220	0·0777
3·108	100	0·0970	130	0·0971
2·455	10	0·1555	400	0·1554
2·395	70	0·1633	121	0·1633
2·198	20	0·1939	240	0·1942
2·153	50	0·2022	301	0·2022
1·830	30	0·2797	141	0·2799
1·638	10	0·3493	600	0·3496
1·538	50	0·3962	251	0·3964
1·428	20	0·4594	002	0·4592
1·352	20	0·5127	451	0·5130
1·290	10	0·5632	370	0·5633
1·235	5	0·6144	402	0·6146
1·216	5	0·6338	332	0·6340
1·148	5	0·7111	152	0·7117

Fermor's 'baryta-psilomelane' from Tekrasai, Singhbhum (A. 380), containing 15 % BaO was not available. Two specimens of psilomelane of Fermor (A. 377 and A. 385) from Tekrasai containing small amounts of barium, potassium, and sodium give similar powder patterns to that of cryptomelane. Fermor's stalactitic psilomelane (A. 268) from Garbham, Vizagapatam, reveals an interesting example of the pseudomorphous changes that occur in manganites. The outer fine-grained crust, scraped from one of the constituent needle-shaped bodies, gives a powder pattern of pyrolusite (MnO_2, tetragonal, $a = 4{\cdot}382$ Å., $c = 2{\cdot}855$ Å.) whereas the inner dull core gives a powder pattern of cryptomelane. The deposition of pyrolusite on cryptomelane suggests that the alkali ions which are loosely bound to the cryptomelane structure along the a-direction are displaced from the lattice as a result of which an outer crust of pyrolusite is formed, the c-axial length remaining the same for both minerals. The nature of the transformation seems to imply that pyrolusite was formed by a shifting and re-stacking of the structure already existing in cryptomelane, due to the displacement of alkalis, and not by *de novo* recrystallization of the oxide (Bernal *et al.*, 1957).

Mathieson and Wadsley (1950) studied a crystalline specimen of 'hollandite' (No. 4199, Geological Survey of India collection) from Sitapar, Chhindwara, India, and found it to be 'monoclinic cryptomelane' with cell-dimensions, $a = 9{\cdot}79$ Å., $b = 2{\cdot}88$ Å., $c = 9{\cdot}94$ Å., and $\beta = 90^\circ\,37'$. Byström and Byström (1950) observed that Weissenberg photographs of the prismatic crystals of 'hollandite' showed tetragonal Laue symmetry C_{4h} with $a \approx 9{\cdot}9$ Å. In order to index the powder pattern of hollandite, a small monoclinic deformation with the tetragonal c-axis as b-axis in the monoclinic cell was assumed with the dimensions, $a = 9{\cdot}91$ Å., $b = 2{\cdot}87$ Å., $c = 9{\cdot}75$ Å., and $\beta = 90{\cdot}6^\circ$, but the structure was derived on the tetragonal basis. An X-ray study of a hollandite crystal with well-developed crystal faces from Fermor's original collection has been made in this laboratory. The zero-layer and equi-inclination Weissenberg photographs about the a and b crystallographic axes of hollandite showed the monoclinic symmetry of the crystal, and the results will be published shortly.

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