Psilomelane from India

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Summary. Mukherjee's definition of psilomelane, $A_3X_6Mn_8O_{16}$ of orthorhombic symmetry with the space group $P222$ and the dimensions determined for a single crystal of the Schneeberg sample, is found true for the psilomelane from Ratanpur, India. The indexing of powder data of the Ratanpur sample with the orthorhombic axes a 9·45, b 13·90, c 5·72 Å is most satisfactory.

MUKHERJEE (1965) showed from single crystal study of Vaux's psilomelane from Schneeberg that the mineral has 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+}, etc., and X_6 stands for $(O, OH)_6$ with OH about 5. Moreover, the study of 14 analyses of psilomelane showed that the calculated density, based on O_{22} and the unit-cell dimensions of the Schneeberg sample, agrees fairly well with the observed density for all the samples.

Earlier Mukherjee (1959*a*) proposed for psilomelane, from the powder data of two specimens (VV–S17/1 and BNS–9(X)/53) from India, the space group $P2_12_12$ for the orthorhombic cell with a 8·254, b 13·40, c 2·864 Å, by the application of Lipson's method (1949) for the orthorhombic system. The indexing of the powder data of psilomelane from India has been reconsidered in the light of the orthorhombic cell obtained for the Schneeberg sample, and the recently available chemical analysis of the Ratanpur sample has been used for verification of the formula of psilomelane.

The specimen of psilomelane, BNS–9(X)/53, collected by B. N. Sinha from Ratanpur area in Bilaspur district, Madhya Pradesh, has compact texture (in massive form, Sinha, 1963), submetallic lustre, and dark-grey colour, and is associated with pyrolusite. The powder-spacing data of this psilomelane are slightly different from those of the Schneeberg sample, and the intensities of powder lines have distinct differences (fig. 1). The broad and diffuse nature of the powder lines indicates the poor state of crystallinity of this material compared to that of the Schneeberg sample

(cf. fig. 1, Mukherjee, 1965). The indexing of the powder lines (table I) with the orthorhombic axes a 9·45, b 13·90, c 5·72 Å is most satisfactory. The chemical analysis of the sample (table II) shows higher amounts of Fe_2O_3, Al_2O_3, CaO, MgO, Na_2O, and K_2O compared to the Schneeberg sample. The cell contents per 22 oxygen atoms show that the sum of

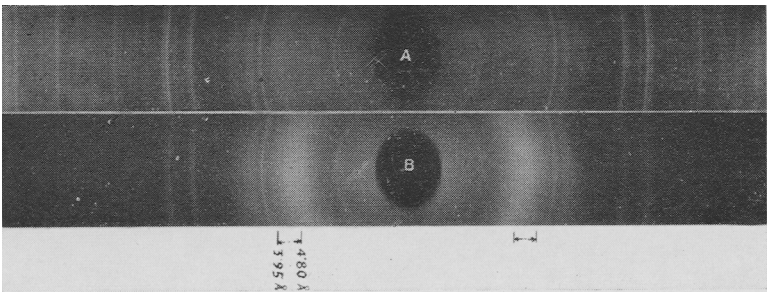

FIG. 1. X-ray powder photographs of psilomelane (taken with Fe-Kα radiation).
A. Specimen No. BNS–9(X)/53 from Ratanpur, M.P.
B. Specimen No. VV–S17/1 from Amliamal, M.P.

cations is 11 ($Mn+A = 11{\cdot}22$) and H is about 5 ($H = 5{\cdot}01$). The formula comes out as $A_3Mn_8^{4+}H_5O_{22}$ where A represents the remaining cations Mn^{2+}, Ba^{2+}, Fe^{3+}, Al^{3+}, Si^{4+} etc., and in simplified form as $A_3X_6Mn_8^{4+}O_{16}$ where X_6 stands for $(O, OH)_6$ with OH about 5. The density of the sample, determined on a number of small fragments by the Berman density balance using bromoform, is $4{\cdot}52 \pm 0{\cdot}02$ g cm^{-3}. With the values of axial lengths ($V = 751{\cdot}3$ Å^3), molecular weight ($M = 1020$, calculated from the atomic weights of all the constituents in actual proportions), and observed density, the number of formula units per unit cell is 2 ($Z = 2{\cdot}005$), and the calculated density is about 4·51 g cm^{-3}. The electron micrograph of this psilomelane, taken by Siemens Elmiskop I at a magnification of X 5000, shows particles with irregular edges of sizes in the range 0·5–5 μ, almost similar in shape but larger in size compared to those of the botryoidal material of the Schneeberg sample (Mukherjee, 1965, *vide* fig. 2).

The specimen of psilomelane, VV–S17/1, collected by V. Venkatesh from Amliamal area, Jhabua district, Madhya Pradesh, was found to be contaminated with pyrolusite and amorphous admixture, revealed by a broad halo at 4·80–3·95 Å in the powder photograph (Mukherjee, 1959*b*), and by the powder line at 3·11 Å (Mukherjee, 1959*a*, *vide* table I), which

TABLE I. Powder data for psilomelane, BNS–9(X)/53 (indexed with a 9·45, b 13·90, c 5·72 Å)

I/I_1	d	$\sin^2\theta_{obs.}$	hkl	$\sin^2\theta_{calc.}$	I/I_1	d	$\sin^2\theta_{obs.}$	hkl	$\sin^2\theta_{calc.}$
30	6·95Å	0·0194	020	0·0194	5*	1·925 d	0·2528	332	0·2526
7	5·60 d	0·0299	120	0·0299	7	1·865 b	0·2694	360	0·2690
7*	4·15 d	0·0544	130	0·0542	40	1·820 } b	0·2828	402	0·2824
10	3·92 b	0·0610	220	0·0614		1·810 }	0·2860	342	0·2865
80	3·48	0·0774	040	0·0776	10	1·735 b	0·3111	080	0·3104
25	3·32 b	0·0851	230	0·0856	20	1·710 b	0·3205	180	0·3209
20	3·25 b	0·0886	140	0·0881	5*	1·673 d	0·3348	043	0·3352
7*	3·07 d	0·0994	310	0·0993	7*	1·653 d	0·3430	460	0·3425
15	2·98 b	0·1056	041	0·1062	20	1·633 b	0·3515	303	0·3520
15	2·86 b	0·1145	320	0·1138				072	0·3521
			002	0·1145	40	1·563 b	0·3835	550	0·3835
7*	2·80 d	0·1194	012	0·1194				362	0·3836
			240	0·1196	7	1·520 b	0·4055	380	0·4048
15	2·66 b	0·1325	150	0·1318				470	0·4055
5*	2·64 d	0·1344	022	0·1339	7	1·493 b	0·4204	532	0·4204
90	2·407	0·1617	212	0·1614				630	0·4213
30	2·360	0·1683	400	0·1679	5*	1·484 d	0·4252	082	0·4249
			132	0·1687				403	0·4255
7	2·313	0·1751	060	0·1746	40	1·423 b	0·4627	014	0·4629
			222	0·1759	25	1·400 b	0·4780	024	0·4775
30	2·250 } b	0·1851	160	0·1851				480	0·4783
	2·240 }	0·1867	420	0·1872	5*	1·372 d	0·4978	552	0·4980
5*	2·210 d	0·1919	042	0·1921	5*	1·363 d	0·5044	214	0·5049
100	2·185	0·1963	401	0·1964	10	1·353 b	0·5119	622	0·5116
40	2·150	0·2027	142	0·2026				134	0·5122
			061	0·2032	5	1·342 d	0·5202	503	0·5199
5	2·120 d	0·2085	302	0·2089				472	0·5200
5*	2·080 d	0·2167	260	0·2166	7	1·297 d	0·5572	314	0·5574
10	2·030 b	0·2274	322	0·2283				730	0·5577

b stands for broad and d for diffuse powder line.

* The diffuseness and spread of the reflexions indicate that these lines may be omitted from the powder data because of the uncertainties involved.

is due to pyrolusite. The density of the separated fragments of pure mineral was determined as $4{\cdot}50 \pm 0{\cdot}02$ g cm^{-3}. The available sample being small the complete chemical analysis of the separated pure mineral was

TABLE II. Chemical analysis of psilomelane*, recalculated as ratios to 22 oxygen

MnO_2	68·92	Mn^{+4}	8·18
MnO	6·40	Mn^{+2}	0·93
BaO	12·98	Ba	0·87
SiO_2	0·78	Si	0·13
Al_2O_3	0·86	Al	0·17
Fe_2O_3	0·95	Fe	0·12
CaO	0·75	Ca	0·14
MgO	0·98	Mg	0·25
CuO	0·07	Cu	0·01
CoO	0·22	Co	0·03
NiO	0·15	Ni	0·02
Na_2O	0·65	Na	0·21
K_2O	0·75	K	0·16
H_2O+	4·40	H	5·01
H_2O-	0·95	$(Mn+A)$	11·22
	99·81	$D_{calc.}$	4·51
		$D_{obs.}$	4·52

* Specimen No. BNS–9(X)/53, collected from Ratanpur, Bilaspur district, Madhya Pradesh, by Dr. B. N. Sinha, Senior Geologist of G.S.I.; Analyst, Dr. B. D. Sarma, Senior Chemist of G.S.I.

not possible; H_2O+ was determined by B. D. Sarma as 4·08, H_2O- as 0·75, and BaO as 11·15 %. The spectrum analysis of the pure mineral, carried out by the Hilger large quartz-spectrograph using carbon-arc cathode-layer method at 9 amps, 220 volts d.c., shows similar elemental composition to that of the Ratanpur sample. The samples, BNS–9(X)/53 and VV–S17/1, contain Mn, Ba as major constituents, Mg, Al, Fe, Si, Ca, Na, K, Co, Ni, Cu as minor, Ti, V, Ag, P as traces, and Pb, Zn, Zr, Sn, Cr, Ga, Li as minute traces; W, Ge, As, Sb are other trace elements present only in VV–S17/1.

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