An X-ray study of manganese minerals.

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Summary. Rhodonite, rhodochrosite, spandite, psilomelane, beldongrite, braunite, sitaparite, and vredenburgite from a collection by Fermor have been studied by the X-ray powder diffraction method. The cell dimensions of all forms of cryptomelane—massive, horny, botryoidal, reniform, mamillated, and stalactitic—are $a = 9.82$ Å., $c = 2.86$ Å., whereas the cell dimensions of shiny pitch-like beldongrite are $a = 9{\cdot}85$ Å., $c = 2{\cdot}87$ Å. The amorphous admixture associated with cryptomelane is revealed by a broad halo, 4·60 Å. to 3·90 Å., in the powder pattern. Aminoff's crystal data for braunite are discussed with a different orientation, and a new space group, $I\,4/mmm$ (D_{4h}^{17}), is assigned after indexing the powder pattern. Fermor's sitaparite (bixbyite) is assigned a new space group $I\,m3$ (T_h^5), different from that proposed by Pauling *et al.*, on the basis of a fresh indexing of the powder pattern. Manganese-garnet from the gondite series has a cell-size of the order of spessartine, whereas the cell-size of manganese-garnet from the kodurite series varies from 11·72 to 11·95 Å. Fermor's spandite from the kodurite series is a mixture of spessartine, grossular, and andradite garnet-molecules with almandine and pyrope as minor components. Ramsdellite and γ-MnO_2 or β-MnO_2 are found in a number of samples of manganese ores.

FERMOR (1909) classified manganese-ore deposits in India into three main groups: deposits interbedded with the Archeans, including the gondites; deposits associated with the kodurites; and lateritoid deposits or surface enrichments of a lateritic nature. Fermor's 'gondite series' of Central Provinces is characterized by the presence of various manganiferous silicates, chiefly spessartine and rhodonite. The ore body consists mainly of a banded quartzite–manganese-oxide–braunite rock. Associated manganese minerals are sitaparite, hollandite, jacobsite, hausmannite, psilomelane, and pyrolusite. Fermor's 'kodurite series' of Vizagapatam is characterized by spandite (a garnet intermediate in composition between spessartine and andradite), rhodonite, psilomelane, and pyrolusite with some braunite, manganmagnetite, and, in one locality, 'vredenburgite'. Other manganese ore deposits associated with Archean rocks, and the lateritoid deposits in parts of Orissa, Bombay, and Mysore, contain psilomelane and pyrolusite, with braunite and spessartine in a few localities.

The space-group and cell-dimensions of cryptomelane and psilomelane were previously reported by the author (Mukherjee, 1959).

Results and discussion.

The original type minerals from the collection in the Indian Museum made by Fermor were used for the X-ray study, and most of the specimens studied are described in the Memoirs of the Geological Survey of

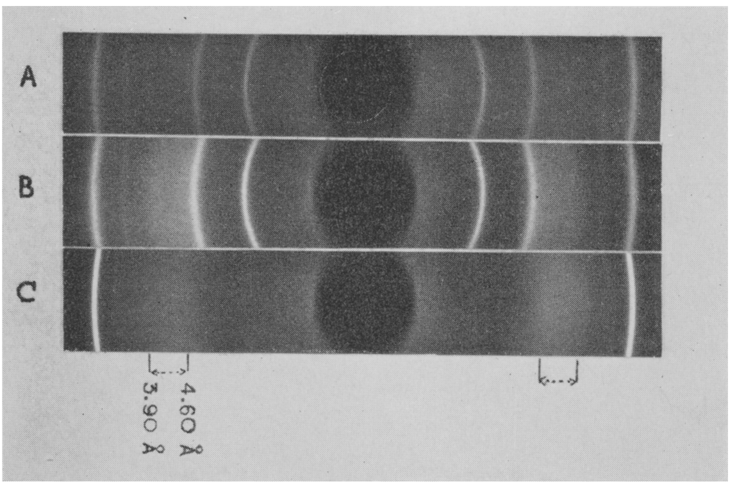

Fig. 1. X-ray powder diffraction photograph of Fermor's psilomelane. A, Cryptomelane (A385). B, Cryptomelane (1158) with amorphous admixture. C, Pyrolusite (A268, outer crust) with amorphous admixture.

India (1909, vol. 37, pts. i–iii) by Fermor. The powder photographs were obtained using Fe-$K\alpha$ radiation, and the relative intensities of powder lines were determined on a Moll recording microphotometer.

Cryptomelane and beldongrite. Almost all manganese ores of Indian deposits contain cryptomelane with more or less amorphous admixture. But the X-ray powder diffraction method gives practically no information concerning amorphous phases, which may sometimes be present as a major constituent along with the cryptomelane. Fleischer and Richmond (1943) pointed out that in an intergrowth of 50 % cryptomelane and 50 % amorphous material, the X-ray powder pattern would only be that of pure cryptomelane. In the present investigation the presence of amorphous admixture with cryptomelane was clearly revealed by a broad halo (4·60 Å. to 3·90 Å.) in the powder pattern (fig. 1).

The cell-dimensions of tetragonal cryptomelane (Fermor's 'psilomelane'—massive, horny, botryoidal, reniform, mamillated, pisolitic, and stalactitic[1]) are *a* 9·82 Å., *c* 2·86 Å., and *c*/*a* 0·291. Beldongrite, the smooth shiny pitch-like mineral from Beldongri quarry, Madhya Pradesh, described by Fermor (no. 1079, Indian Museum no. 18/922), was shown to be tetragonal on indexing the powder pattern by Hesse's method (1948) and the cell-dimensions are *a* 9·855 Å., *c* 2·869 Å. (±0·003), and *c*/*a* 0·291. Two samples of beldongrite from Mansar mine, Chargaon, Madhya Pradesh (Fermor's nos. 1026 and 1035), showed identical powder patterns. Beldongrite is isostructural with cryptomelane, and detailed work, including a chemical analysis, is in progress.

Monoclinic hollandite with well-developed crystal faces was found on a matrix of massive cryptomelane in Kajlidongri, Chhindwara, and Balaghat manganese ores. Ramsdellite was detected in Dongri Buzurg and Sandur manganese ores. γ-MnO_2 or β-MnO_2 of McMurdie[2] was found in Sandur and Belgaum ores in intimate association with pyrolusite.

Braunite. The powder spacing data of braunite from Kacharwahi, Nagpur (Fermor's no. B 1259), are similar to those reported by Harcourt (1942) for braunite (Harvard Museum no. 83692) from Vizagapatam, India. The cell-dimensions of tetragonal braunite were determined after indexing the powder pattern (table I) by Hesse's method as *a* 9·402 Å., *c* 18·740 Å. (*c*/*a* 1·994). The systematic absences indicate a space-group $I\,4/mmm$ (D_{4h}^{17}). With the above axial lengths and sp. gr. 4·8 for braunite the unit-cell contents are $8(3Mn_2O_3.MnSiO_3)$.

Aminoff (1931) determined the cell-dimensions of tetragonal braunite from Långban as *a* 13·28 Å., *c* 18·58 Å. from single crystal measurements. This cell is face-centred, and gives on conversion to the body-centred lattice *a* 9·39 Å., *c* 18·58 Å., *z* 8. Aminoff suggested a space-group D_{4h}^{20} on the basis of indexing of his photographs, but the conditions limiting possible reflections for the space-group D_{4h}^{20} are not satisfied by his index-

[1] The following specimens were examined (both Fermor's and the Indian Museum numbers are given, the latter in parentheses): A680 (J903) and A682 (J904) from Chikhli, Satara, Bombay; A705 (J905) from Yeruli, Satara, Bombay; A376 (J917), A377 (J918), and A385 (J921) from Tekrasai, Singhbum, Bihar; A267 (18/425) and A268 (18/426) from the Garbham mine, Vizagapatam; and 1158 (18/986) from Sonegaon, Guguldoho, Nagpur. A268 has an inner dull core of cryptomelane and an outer crust of pyrolusite.

[2] Byström (1950) concluded that the γ-MnO_2 of McMurdie and Golovato (1948) is not identical with the oxide called γ-MnO_2 by Cole *et al.* (1947) and by Byström (1949), but is a rather poor β-MnO_2 preparation.

ing; the definite existence of the powder line 130 excludes the space-group D_{4h}^{20}, and the possible presence of reflections 150, 053, and 039 cannot be ruled out.

Sitaparite. The powder spacing data of sitaparite (Fermor's no. B 322) from Sitapar, Chhindwara, are similar[1] to those of bixbyite from Simson, Utah, reported by Zachariasen (1928). The cell-size of sitaparite

TABLE I. X-ray powder data for braunite, Kacharwahi, Nagpur (Fermor's no. B1259).

d, Å.	I/I_0	$Sin^2 \theta$ obs.	*hkl*	$Sin^2 \theta$ calc.	*d*, Å.	I/I_0	$Sin^2 \theta$ obs.	*hkl*	$Sin^2 \theta$ calc.
5·360	10	0·0326	112	0·0319	1·681	5	0·3314	345	0·3317
4·655	20	0·0432	004	0·0427	1·659	80	0·3405	440	0·3392
3·470	30	0·0778	123	0·0770				048	0·3405
3·320	10	0·0850	024	0·0851	1.537	20	0·3965	347	0·3958
2·960	10	0·1069	130	0·1060				149	0·3965
2·830	5	0·1170	132	0·1167	1·501	25	0·4158	163	0·4162
2·710	100	0·1276	224	0·1275	1·464	20	0·4370	451	0·4373
2·508	15	0·1489	134	0·1487	1·418	60	0·4660	264	0·4667
2·405	5	0·1620	233	0·1618	1·412	30	0·4698	2·2·12	0·4693
2·345	40	0·1704	040	0·1696	1·368	15	0·5007	363	0·5010
			008	0·1709	1·355	25	0·5102	448	0·5101
2·141	45	0·2044	235	0·2045	1·265	20	0·5856	273	0·5858
1·915	10	0·2555	244	0·2547	1·175	20	0·6786	080	0·6784
			228	0·2557	1·164	20	0·6913	471	0·6917
1·871	20	0·2676	341	0·2677				181	0·6917
1·841	10	0·2764	150	0·2756	1·146	10	0·7134	565	0·7133
			138	0·2769	1·078	50	0·8062	664	0·8059
1·803	15	0·2883	053	0·2890	1·051	40	0·8483	480	0·8480
			343	0·2890				088	0·8493
1·735	20	0·3113	147	0·3110					
			039	0·3117					

was determined as *a* 9·40 ±0·01 Å. Three original type samples of sitaparite from Fermor's collection showed identical powder patterns. After indexing all the powder lines of sitaparite (table II), the conditions limiting possible reflections are found to be those of a body-centred cubic lattice. These systematic absences indicate a space-group *Im*3 (T_h^5). The definite existence of the powder lines 310 and 510 excludes the possibility of the space-group *Ia*3 (T_h^7) for bixbyite, suggested by Pauling and Shappell (1930) from the study of Laue photographs.

With *a* 9·40 Å. and sp. gr. 5·0 for sitaparite, the unit-cell content is 16 ($FeMnO_3$), as found by Zachariasen (1928). Fleischer and Richmond (1943) reported in the powder data for bixbyite the spacings 4·204 (10), 1·075 (40), and 1·048 (20), but these lines could not be indexed on the

[1] Mason (1942) has also found sitaparite to be identical with bixbyite.

basis of a body-centred cubic lattice (table II); these lines, which are moderately intense in Fleischer's data, are not, however, present in the data of Zachariasen or of the present author. Evidently, they were due to some impurity in Fleischer's sample.

TABLE II. X-ray powder data for sitaparite, Sitapar, Chhindwara (Fermor's no. B322).

d, Å.	$h^2+k^2+l^2$	hkl	I/I_0	d, Å.	$h^2+k^2+l^2$	khl	I/I_0
4·700	4	200	10	1·257	56	642	10
3·837	6	211	60	1·195	62	732, 651	10
3·327	8	220	5	1·176	64	800	25
2·976	10	310	5	1·158	66	811, 741, 554	25
2·716	12	222	100	1·141	68	820, 644	20
2·513	14	321	20	1·125	70	653	15
2·354	16	400	40	1·109	72	822, 660	10
2·215	18	411	5	1·094	74	831, 750, 743	10
2·105	20	420	5	1·079	76	662	60
2·006	22	332	40	1·065	78	752	5
1·921	24	422	10	1·052	80	840	50
1·846	26	510	40	1·039	82	910, 833	10
1·718	30	521	20	1·026	84	842	10
1·662	32	440	90	1·015	86	921, 761, 655	30
1·614	34	530, 433	10	1·003	88	664	20
1·567	36	600, 442	5	0·9917	90	930, 851, 754	20
1·527	38	611, 532	20				
1·488	40	620	5				
1·452	42	541	30				
1·419	44	622	70				
1·387	46	631	30				
1·358	48	444	20				
1·330	50	710, 550, 543	5				
1·305	52	640	10				
1·280	54	721, 633, 552	25				

Manganese-garnet. The cell-size of manganese-garnet was determined with an accuracy of ±0·003 Å. The manganese-garnet of Fermor's gondite series has a cell-size (11·615 Å.–11·642 Å.) near that of spessartine. In Fermor's kodurite series the cell-size of the manganese-garnet lies between 11·72 Å. and 11·95 Å. for different samples. The molecular percentage composition of four constituents in Fermor's spandite from Kotakarra, kodurite series (A233), was derived from the recorded chemical analysis[1] as: spessartine 37·65, grossular 34·87, almandine 16·82, andradite 10·66 %, and the cell-size was determined as 11·723 Å. from the powder pattern. The recorded chemical analysis[1] of Fermor's spandite from Garbham, kodurite series (A219), shows that the spandite is a mixture of spessartine (39.26 %) and andradite (46·23 %) with pyrope (14·51 %) as a minor constituent, and the cell-size was determined as 11·915 Å. from the powder pattern. The analytical data of Fe''' and Al''' for spandite, A219, are probably anomalous.

Jacobsite, hausmannite, and vredenburgite. Jacobsite was found as a major constituent in almost all specimens of ores from Tirodi, Dongri Buzurg, Balaghat, and Beldongri (Madhya Pradesh) and from Kodur, Devada, Garividi, and Avagudem (Vizagapatam). The cell-size of jacobsite lies between 8·42 Å. and 8·52 Å. for different samples from Tirodi and Kodur.[2] A pure sample of hausmannite was separated from the ore of Sitapar, Chhindwara. The cell-dimensions of the tetragonal mineral were determined after indexing the powder pattern by Hesse's method (1948) as *a* 5·75 Å., *c* 9·41 Å. (±0·01). Hausmannite was found associated with almost all specimens of jacobsite as a minor constituent.

Vredenburgite (Fermor's no. B1257) from Beldongri contains mainly jacobsite with a considerable amount of hausmannite.[3] The feebly magnetic fraction contains braunite, cryptomelane, and hausmannite, and the strongly magnetic fraction contains jacobsite and hausmannite. Vredenburgite from Garividi, Vizagapatam (Fermor's no. A346), contains jacobsite and a small amount of hausmannite.

Rhodonite and rhodochrosite. Rhodonites, of pink, greenish grey, and brown, were found in rocks of the gondite series associated with spessartine and quartz. The powder spacing data of pink rhodonite are similar to those reported by Mikheev and Dubinina (1948) for a sample from Sverdlovsk, Ural. The pink material of rhodonite rock (no. 23/364) from Bhandara, Madhya Pradesh, contains rhodonite, spessartine, and rhodochrosite, and the associated yellowish-white material contains quartz, feldspars, and fluorapatite. The dark brown (partly blackened) material of the rhodonite rock contains rhodonite, rhodochrosite, cryptomelane, and hematite. Fermor's pinkish-white rhodochrosite (no. B325) from Gaimukh, Chhindwara, is associated with rhodonite, braunite, and barite.

[1] Chemical analyses by Mr. T. R. Blyth, reported by Fermor in Mem. Geol. Surv. India, 1909, vol. 37, p. 168.

[2] Johansson (1928) found *a* 8·42 Å., and Passerini (1930) *a* 8·515 Å.

[3] Orcel and Pavlovitch, 1932; cf. Fermor, 1938, and Mason, 1947.

Various manganese ores. Nearly three hundred specimens of manganese ores from various deposits, collected by geologists of the Geological Survey of India and from Fermor's collection, were studied. An isodynamic separator was used to concentrate the minerals in a number of magnetic fractions, and the mineralogical composition of the ore was determined from the minerals identified in each fraction. In the manganese ores of Madhya Pradesh and Bombay (Jhabua, Kajlidongri, Sitapar, Chhindwara, Balaghat, Beldongri, Chargaon, Tirodi, Jagantola, Bharweli, Ramrama, Suteli, Bhandara, Chikhla, Sitasaongi, and Dongri Buzurg) the most common manganese minerals are braunite, spessartine, jacobsite, cryptomelane, pyrolusite, hausmannite, bixbyite, hollandite, and psilomelane. In the Vizagapatam deposits (Devada, Kodur, Garbham, Avagudem, Garividi, and Chipurupalli) jacobsite, spandite, pyrolusite, cryptomelane, braunite, and hausmannite occur in most specimens of ore. In Mysore (Sandur, Ramandrug, Shimoga, Belgaum, and North Kanara), Bombay (Panchmahals, Sivarajpur, Bamankua, Pani, Baria, Satara, Jambughoda, Chota Udaipur, and Baroda), Rajasthan (Banswara), and Orissa (Keonjhar, Koraput, Kalahandi, Bonai, and Bamra) deposits, pyrolusite and cryptomelane with amorphous admixture are the major constituents of ore; braunite, spessartine, and jacobsite are sometimes associated as minor constituents. Manganese-amphibole and -pyroxene are not included in the present investigation.

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