

*X-ray studies on pyrolusite (including polianite)
and psilomelane.*

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ONE of the most promising uses of X-ray diffraction methods in mineralogy is the study of those minerals which are opaque and whose crystals are extremely minute. Although recent methods of ore examination by reflected polarized light have given valuable information about these substances, their application to soft, powdery materials is extremely difficult, an objection which does not apply to X-ray methods.

Pyrolusite (including polianite).—The present study had for its main objective an attempt to settle, by X-ray examination, the uncertainty existing as to the relationship between polianite and pyrolusite. Work already carried out by St. Johns¹ has suggested that polianite and pyrolusite are identical, since they have the same cell sides as found from powder photographs. Breithaupt² himself, who first gave the name polianite to the mineral from Platten, insisted that polianite and pyrolusite are not independent species, reserving the latter name for pseudomorphous powdery specimens.

Single-crystal photographs were taken about the *c*-axis from specimens of polianite from Platten, Bohemia, and of pyrolusite from Elgersburg, Thuringia. These photographs are absolutely identical, the corresponding spots being the same in position, characteristics, and relative intensity. However, the spots are not sharp and are always quite broad, indicating that what are, to the eye, single crystals are in reality groups of fibres. In most specimens of pyrolusite the fibres are oriented parallel to the *c*-axis only. This fact would lead to the conclusion that the material consists of very small crystals with large surface area, hence accounting for the high catalytic activity exhibited by preparations of manganese dioxide. Crystals

¹ A. St. Johns, *Physical Rev.*, 1923, vol. 21, p. 389.

² A. Breithaupt, *Ann. Phys. Chem. (Poggendorff)*, 1844, vol. 61, p. 191.

of polianite also give broad spots, but otherwise behave as single crystals. It was quite fortunate that for the present work material was available from the original specimens, both polianite described by Dana and Penfield¹ from Platten, Bohemia, and the Elgersburg material originally described and named pyrolusite by Haidinger² in 1827. In this way it was possible to establish definitely the above-mentioned identity of these two minerals.

Hitherto it has been customary to use two mineral names for crystallized MnO_2 : polianite for the well-formed tetragonal crystals, isomorphous with minerals of the rutile group; and pyrolusite for the fibrous material, some of which is definitely pseudomorphous after manganite. In the writer's view polianite should no longer be used, since pyrolusite is the older and better name. The fact that fibrous specimens do not conform accurately to the formula MnO_2 , and hence are possibly mixed with small quantities of other minerals, does not in itself constitute a sufficient reason for employing two mineral names. Pyrolusite should be retained as the name both for single crystals and for fibrous material of tetragonal MnO_2 , isomorphous with rutile.

It was also found that many specimens of compact manganese ore, originally labelled psilomelane, give powder photographs identical with that of pyrolusite. A specimen (B.M. 91116) labelled varvicite from Ilfeld, Harz, was also examined and proved to be pyrolusite; and the partial analyses made by Phillips and Turner³ suggest an impure pyrolusite.

Psilomelane.—This mineral was also first described by Haidinger,⁴ who gave the name to the botryoidal material from Schneeberg, Saxony. He was of the opinion that Turner's chemical analysis of this material corresponded to a mixture and not to one mineral; and it was not until Fermor's⁵ discovery and description of hollandite in 1906 that

¹ E. S. Dana and S. L. Penfield, Amer. Journ. Sci., 1888, ser. 3, vol. 35, p. 243. X-ray photographs were obtained from the specimen, a crystal from which is figured in Dana, Syst. Min., 6th edit., 1892, p. 236, fig. 1. In addition, identical X-ray photographs were obtained from B.M. 21987, also from Platten, in the British Museum collection.

² W. Haidinger, Trans. Roy. Soc. Edinburgh. 1831, vol. 11, p. 136. A portion of the type specimen, B.M. 91106, was fortunately available in the British Museum collection, and was photographed.

³ R. Phillips and E. Turner, Phil. Mag., 1829, vol. 6, p. 281; 1830, vol. 7, p. 284.

⁴ W. Haidinger, Trans. Roy. Soc. Edinburgh, 1831, vol. 11, p. 129.

⁵ L. L. Fermor, Trans. Mining and Geol. Inst. India, 1906, vol. 1, p. 76; Records Geol. Surv. India, 1917, vol. 48, p. 103. [M.A. 1-45.]

any certain evidence existed that both barium and manganese are present in one and the same mineral. During the early period of the present investigation a specimen (no. 4181) was found in the Brooke collection at Cambridge which was labelled polianite from Platten. This material consists of small plates encrusted over a botryoidal matrix, differing considerably from the material labelled polianite in the British Museum. Upon examination by X-rays it was found not only to be orthorhombic, but also to have an entirely different cell size. At a later date a similar specimen was discovered in the collections of the Academy of Natural Sciences of Philadelphia, and an examination of a polished section of the latter specimen showed that there is no apparent difference between the crystalline crust and internal compact material. This specimen was labelled as having come from Schneeberg, Saxony. Further X-ray examination of both of these specimens, both by crystal and powder photographs, showed them to be identical, as well as being distinct from pyrolusite. By means of powder methods these specimens were then compared with several compact specimens in the British Museum labelled psilomelane (analyses 1, 2, and 3 in table I), and were found to be in perfect agreement.

In endeavouring to discover why these specimens were labelled polianite an interesting point suggests itself. Apparently these two specimens in reality came from Schneeberg, but the label of the one which went to Cambridge was altered owing to the fact that some one determined the mineral as being polianite, and hence came to the conclusion that if it were polianite it must have come from Platten. The specimen in the Academy of Natural Sciences, whilst being called polianite, still kept its true locality of Schneeberg. A specimen labelled leptonematite from Schneeberg, in the British Museum, has been found to be the same material, and adds corroborative evidence to the view that this material did really come originally from that locality.

Chemical analysis of this material establishes its identity with the psilomelane originally described by Haidinger and analysed by Turner. Moreover, chemical analyses by Gorgeu,¹ Zambonini,² and others suggest that psilomelane from Romanèche is identical with the Schneeberg material, and this assumption has been proved to

¹ A. Gorgeu, *Bull. Soc. Franç. Min.*, 1890, vol. 13, p. 21.

² F. Zambonini and V. Caglioti, *Periodico Min. Roma*, 1931, vol. 2, p. 73. [M.A. 4-520.]

be correct by powder photographs of psilomelanes from the former locality (B.M. 1906, 249), showing perfect agreement with those of

TABLE I. Chemical analyses of Psilomelane.

	1.	2.	3.	4.	5.
MnO ₂ ...	66.62	66.73	70.38	68.00	66.98
MnO ...	7.09	7.12	7.90	10.70	10.18
BaO ...	17.46	17.48	12.38	15.73	16.36
SiO ₂ ...	0.52	0.51	0.09	0.59	0.26
TiO ₂ ...	nil	nil	nil	—	—
Al ₂ O ₃ ...	0.37	0.35	0.73	—	—
Fe ₂ O ₃ ...	0.15	0.20	0.18	0.30	—
CaO ...	0.19	0.26	0.66	—	—
MgO ...	0.15	0.13	0.13	0.30	—
Na ₂ O ...	trace	trace	trace	0.02	—
K ₂ O ...	trace	trace	0.42	0.08	—
Li ₂ O ...	trace	trace	trace	—	—
CuO ...	0.48	0.31	0.38	trace	—
NiO ...	trace	trace	0.03	trace	—
CoO ...	0.90	1.00	0.48	—	—
WO ₃ ...	0.89	0.68	—	0.28	—
H ₂ O+ ...	4.38	4.41	4.18	3.82	6.22
H ₂ O- ...	0.48	0.50	1.88	0.48	
	99.68	99.68	99.82	100.30	100.00
Sp. gr. ...	4.71	—	—	4.697	—

Number of atoms in the unit cell per 20 oxygen atoms.

Mn ^{iv} ...	7.60	7.60	7.83	7.69	7.21
Mn ⁱⁱ ...	0.99	0.99	1.08	1.48	1.35
Ba ...	1.13	1.13	0.78	1.01	1.00
Ca ...	0.03	0.05	0.11	—	—
Mg ...	0.04	0.03	0.03	0.07	—
Cu ...	0.06	0.04	0.05	—	—
Co ...	0.12	0.13	0.06	—	—
H ₂ O ...	2.41	2.42	2.24	2.08	3.22
ΣRO ...	2.37	2.37	2.11	2.56	2.35

1. 'Leptonematite', Schneeberg, Saxony. (B.M. 69160.)

2. 'Leptonematite', Spitzleite, Eibenstock, Saxony. (B.M. 32687.)

3. Psilomelane, Restormel iron mine, Lostwithiel, Cornwall. (B.M. 27214.)
Analyses 1-3 by Miss H. Bennett.

4. 'Polianite', Schneeberg, Saxony. Specimen in the Academy of Natural Sciences, Philadelphia. Analyst, H. J. Hallowell. The analysis as reported gives MnO₂ 62.80, MnO 10.70, oxygen 5.20%. Since 5.20% oxygen corresponds closely to 62.80% Mn₂O₃, it has been assumed that the figures should be MnO₂ 62.80 + 5.20 = 68.00, MnO 10.70%.

5. Psilomelane, Schneeberg, Saxony. Analyst, E. Turner, Trans. Roy. Soc. Edinburgh, 1831, vol. 11, p. 172.

specimens from the latter. Sufficient evidence is therefore available to retain the name psilomelane for this material.

An interesting feature of various published analyses of psilomelanes is the fact that they contain varying amounts of barium, but the amount present never exceeds about 17 % BaO. This fact bears out the original theory of Haidinger, as expressed above, that there are many impurities present in many of the psilomelanes, thus accounting for the wide variation in the BaO content; but the fact which Haidinger overlooked was that psilomelane in its pure form has a definite chemical formula. In view of these facts it would seem proper to apply the name psilomelane to manganese minerals which contain 17 % BaO.

For the density of psilomelane, only values obtained on analysed material can be accepted. Apart from Haidinger's original value of 4.004–4.079, three figures are available: Turner found 4.365 for Romanèche material; E. E. Schmid¹ 4.31 for material from Elgersburg; and L. L. Fermor² 4.54 for material from Tekrasai, Bengal. For the material of analysis 4, H. J. Hallowell reports a density of 4.697; a careful determination on the specimen B.M. 69160 (analysis 1) gave D_4^{20} 4.71 ± 0.01. From this value, the analysis, and the unit cell size, the number of oxygen atoms per unit cell is found to be 20.53 ± 0.7. Accepting this as an approximation to 20, the atomic proportions per 20 oxygen for the four new analyses and for Turner's original analysis have been calculated, omitting SiO₂, Al₂O₃, Fe₂O₃, WO₃, and alkalis, and are included in table I. The ideal formula is evidently H₄R₂Mn₈O₂₀, where R includes the divalent metals Mn, Mg, Ca, Ni, Co, and Cu; but there is a noticeable excess of RO and a corresponding deficiency of Mn^{IV}.

One of the Cambridge specimens of this material also carries small crystals of pyrolusite which can be distinguished readily from the true psilomelane by X-ray photographs. This might lead to the conclusion that there is frequently a varying amount of pyrolusite material included in any specimen from these localities, and its presence would obviously account for the discrepancies in the analyses, as varying amounts of pyrolusite would cause the barium oxide content of the whole to differ radically. This gives a very good example of the importance of carrying out X-ray examinations, along with other means of identification, for material which has only been

¹ E. E. Schmid, Ann. Phys. Chem. (Poggendorff), 1865, vol. 126, p. 154.

² L. L. Fermor, Mem. Geol. Surv. India, 1909, vol. 37, p. 100.

analysed, as any impurities present can be detected with great ease.

Table II gives a comparison of the symmetry and cell dimensions of the minerals discussed above, together with those of other manganese minerals which have been determined by other workers. An interesting feature of this comparison is the fact, first noticed by J. D. Bernal, that a simple relation exists between the cell dimensions of psilomelane, pyrolusite, and manganite. In the table this idea

TABLE II. X-ray data for manganese oxide minerals.

Mineral.	System.	Cell-sides:			Ratios.
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
1. Pyrolusite	Tetragonal ...	4.38	4.38	2.86	1 1 1
2. Psilomelane	Orthorhombic ...	9.1	13.7	2.86	2 3 1
3. Manganite	Orthorhombic ...	8.84	5.23	5.74	2 1 2
4. Braunite	Tetragonal ...	13.28	13.28	18.58	3 3 6
5. Artif. Mn ₂ O ₃	Cubic ...	9.41	9.41	9.41	2 2 3
6. Hausmannite	Tetragonal ...	8.14	8.14	9.42	2 2 3

1, 2. New data.

3. J. Garrido, Bull. Soc. Franç. Min., 1935, vol. 58, p. 224. [M.A. 6-176.]

4. G. Aminoff, Kungl. Svenska Vetenskapsakad. Handl., 1931, ser. 3, vol. 9, no. 5, p. 14. [M.A. 4-461.]

5. R. W. G. Wyckoff, The structure of crystals, 2nd edit., 1931, p. 254.

6. G. Aminoff, Zeits. Krist., 1926, vol. 64, pp. 475-490. [M.A. 3-342.]

has been carried further so as to include other manganese minerals, which have been added for comparison. These figures present an obvious explanation for the intimate intergrowth of the manganese oxides. As the values for the *c*-axis are in some cases the same, this seems to be the most permanent value for these minerals, and the variations in cell size have taken place along the other two axes. The fact that dimensions along the *a*- and *b*-axes consist of simple multiples is also interesting in the light of the many pseudomorphous changes which occur in these minerals.

This work has been carried on in the laboratory of the Imperial College of Science, London, and in the Mineral Department of the British Museum, under the direction of Mr. F. A. Bannister. The author is also deeply indebted to Dr. G. F. Herbert Smith, Keeper of Minerals in the British Museum, and Prof. P. G. H. Boswell. The samples of polianite described by Dana were made available through the courtesy of Prof. W. E. Ford of Yale University.