## CRYPTOMELANE, A NEW NAME FOR THE COMMONEST OF THE "PSILOMELANE" MINERALS\*

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#### Abstract

The name cryptomelane is proposed for a distinct mineral species, hitherto included in the so-called psilomelanes. It is characterized by its distinctive x-ray powder diffraction photograph, the presence of essential  $K_2O$  and the low percentage of BaO.

### INTRODUCTION

A comprehensive and integrated study of the manganese oxide minerals has been undertaken by the Chemical Laboratory of the Federal Geological Survey. The results to date are sufficient to characterize these minerals, but the work is still in progress and some time necessarily will elapse before publication in detail of the chemical, optical, and x-ray data, as well as data on thermal behavior and on paragenesis. The present paper summarizes briefly our results for the so-called psilomelanes, the commonest one of which has not hitherto been given a specific name.

The term "psilomelane" has come to be a mineralogical waste-basket; as generally used, it denotes a hard, compact manganese oxide, too fine grained to be determined accurately. "Wad" has a similar connotation, but is generally applied to soft material of low apparent specific gravity. This use of "psilomelane" as a general descriptive term is doubtless convenient in the field, but it has led to much confusion. X-ray study by Ramsdell<sup>1</sup> some years ago showed that most "psilomelanes" are crystalline and that several distinct minerals, which were not characterized chemically by him, had been grouped together under this name. Later, x-ray and chemical study of type specimens by Vaux<sup>2</sup> proved that the material named psilomelane by Haidinger<sup>3</sup> is essentially a hydrous barium manganate. X-ray study and new chemical analyses by us confirm Vaux's findings. Ramsdell<sup>4</sup> also recognized psilomelane to be a distinct mineral (his Group II). The name psilomelane should therefore be restricted to this single mineral species, essentially a hydrous bariummanganese manganate.

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<sup>1</sup> Ramsdell, L. S., An x-ray study of psilomelane and wad: Am. Mineral., 17, 143-149 (1932).

<sup>2</sup> Vaux, George., X-ray studies on pyrolusite (including polianite) and psilomelane: Mineralog. Mag., 24, 521-526 (1937).

<sup>3</sup> Haidinger, William, Mineralogical account of the ores of manganese: Trans. Royal Soc. Edinburgh, 11, 119 (1831).

<sup>4</sup> Ramsdell, L. S., op. cit., p. 145.

Some so-called "psilomelanes" have proved to be braunite, hausmannite, or pyrolusite. In addition to these, the following minerals have been identified among the "psilomelanes" studied, the new name cryptomelane being applied to the commonest of these crystalline "psilomelanes," which is characterized by the presence of  $K_2O$  with little or no barium.

- 1. Cryptomelane, about 60% of the samples.
- 2. Psilomelane, about 30% of the samples.
- 3. Hollandite,
- 4. Coronadite, about 10% of the samples.
- 5. Ranciéite,
  6. Lithiophorite,

The new name cryptomelane here given for the most abundant of these minerals is derived from the Greek words meaning hidden and black, and seems appropriate, as the identity of this common black manganese mineral has been lost within the group of such minerals. Ramsdell<sup>5</sup> also found this mineral to be the most common of the "psilomelane" minerals, and therefore referred to it as "true psilomelane." On the basis of priority, however, the name psilomelane should be restricted to the mineral so named by Haidinger; Ramsdell's term "true psilomelane" should be dropped.

### DESCRIPTION OF CRYPTOMELANE

X-ray Crystallography. Ramsdell<sup>6</sup> recognized that a "barium-free psilomelane" was a distinct mineral species on the basis of x-ray photographs. He<sup>7</sup> has determined the cell size and tabulated the powder diffraction data in his table.

The x-ray data obtained by Richmond agree closely with those of Ramsdell. These data were derived from Weissenberg photographs taken on a cleavage fragment of the mineral from Tombstone, Arizona. Richmond's results are:

 $a_0 = 9.82$   $c_0 = 2.83$  $c_0/a_0 = 0.288$ 

It was not possible to determine the space group although the extinctions definitely indicate a body centered lattice.

The powder and Weissenberg photographs of cryptomelane are nearly identical with those of the triclinic, pseudotetragonal hollandite. Frondel and Heinrich<sup>8</sup> have already shown that hollandite and coronadite are

<sup>5</sup> Ramsdell, L. S., op. cit., pp. 144-145.

6 Ramsdell, L. S., op. cit., p. 145.

<sup>7</sup> See this issue, page 611.

<sup>8</sup> Frondel, Clifford, and Heinrich, E. W., New data on hetaerolite, hydrohetaerolite, coronadite and hollandite: *Am. Mineral.*, **27**, 48–56 (1942).

isostructural. Cryptomelane, therefore, must be isostructural with both hollandite and coronadite.

The content of the unit cell, on the basis of the analyses given below and the x-ray data is, at the present time, undetermined. This is due primarily to our lack of knowledge of the valencies of the manganese in these minerals. Additional information must be obtained before any definite composition can be given for cryptomelane.

Chemical Composition. Four of the analyses of cryptomelane made in the course of our work are given in Table 1. ZnO is present in appreciable amounts in two samples. A little cobalt and copper are also present; other analyses indicate several per cent of cobalt. The water content is variable. X-ray powder pictures of the residues from the water determination (Penfield method) are identical with those of the original samples. The water is therefore regarded as non-essential. The literature contains many analyses close to those given in Table 1.

*Physical Properties.* The appearance of cryptomelane shows the bewildering diversity that has made identification of the members of this group of minerals so difficult. Most commonly it occurs as fine-grained masses with noticeable conchoidal fracture. Less commonly it is botryoidal. Massive cleavable varieties are not common, but have been found, as have radial fibrous varieties that grade into distinct individual fibers. The fine-grained, cleavable, and fibrous varieties are all shown on a single specimen from Tombstone. All three give identical *x*-ray patterns.

The color on fresh fracture is usually steel-gray to bluish-gray, varying to dull black, and it tarnishes to a dull grayish-black. The streak of the mineral is brownish-black, the shade varying somewhat, but distinctly blacker than that of manganite or braunite, and distinctly browner than that of pyrolusite or psilomelane. The hardness is 6 to  $6\frac{1}{2}$ , but the apparent hardness, particularly of massive or fibrous varieties, may be much lower, even 1.

Identification. X-ray powder pictures are the only certain means of identification of the "manganese oxide" minerals. The streak is helpful, but must be used with caution. A flame test, made by introducing the powdered mineral directly into the flame on a platinum or nichrome wire, may give useful information. A strong potassium flame (use of a blue glass or Merwin screen may be necessary) is a fairly good indication of cryptomelane.

The barium manganates give little or no barium flame when tested in this way. If the powdered mineral on the wire is dipped into dilute HCl and held in the flame, a strong green flame (caused by manganese chloride is observed which disappears in a few seconds and is followed by the more persistent barium flame. The presence of barium is best confirmed by precipitation as sulfate.

	1.	2.	3.	4.
$MnO_2^*$	83.13	86.54	81.75	87.09
MnO	2.08	3.92	3.50	2.49
CuO	0.12	0.44	0.06	None
NiO	None	None	0.02	None
CoO	None	0.21	0.21	0.08
ZnO	5.23	None	None	1.69
MgO	0.05	None	0.02	0.07
BaO	0.13	1.04	None	None
SrO	None	0.21	None	None
CaO	0.27	0.30	0.28	None
$Na_2O$	0.44	0.47	0.56	0.48
K <sub>2</sub> O	3.50	3.88	3.84	3.10
$H_2O-$	0.81	0.21	0.38	0.60
$H_2O+$	2.58	1.62	3.45	3.58
$Al_2O_3$	0.37	None	1.37	0.39
$Fe_2O_3$	0.46	0.36	4.00	0.19
$SiO_2$	0.58	0.03	0.35	0.18
$TiO_2$	0.01	None	None	None
$P_2O_5$	0.07	0.19	None	None
	99.83	99.42	99.79	99.94
G.	4.33	4.32	4.41	4.17

TABLE 1. ANALYSES OF CRYPTOMELANE (M. Fleischer, analyst)

\* Arbitrarily stated as  $MnO_2$  as calculated from the analytically determined "available oxygen."

- 1. Massive cleavable, from Tombstone, Arizona, collected by A. E. Granger, Survey Laboratory, No. D-1237.
- 2. Massive cleavable, from Deming, New Mexico, collected by J. B. Hadley No. D-1331.
- 3. Fine grained, steel-gray, from the Sugar Stick prospect near Mena, Arkansas, collected by H. D. Miser, No. D-1331.
- Extremely fine grained, black, from Philipsburg, Montana, collected by E. N. Goddard, No. D-1331.