THE AMERICAN MINERALOGIST, VOL. 46, MARCH-APRIL, 1961

A POORLY CRYSTALLIZED, LOW BARIUM, PSILOMELANE-TYPE MINERAL

A. A. LEVINSON, *The Dow Chemical Company, Freeport, Texas.*

ABSTRACT

A poorly crystallized manganese mineral from Zacatecas, Mexico is described. Its *x*-ray diffraction pattern gives only three distinct lines in addition to a few extremely weak bands and lines. The *x*-ray data indicate the specimen is a psilimelane-type mineral. Chemical analysis shows the mineral to be similar to psilomelane except that barium is low ($BaO = 4.5$ per cent). Significant substitution of potassium, sodium, calcium, and strontium takes place for barium.

The nomenclature of psilomelane and psilomelane-type (Fleischer and Richmond, 1943) is reviewed. It is suggested that the term manganomelane be used as the general name for all hard manganese oxide minerals not specifically identified. Wad should continue to be used for soft manganese minerals not specifically identified.

INTRODUCTION

The mineral psilomelane has only recently reached the status of a well defined species. Highlights in this elucidation have been the redefinition of psilomelane as a single species by Vaux (1937), the detailed crystal structure investigation of Wadsley (1952, 1953), and the general review and verification of Fleischer (1960A). These studies have been concerned with well-crystallized psilomelanes which have the formula $(Ba,H_2O)_2Mn_5O_{10}$, or approximate it closely, with $Ba:H_2O$ approximately 1:2, and Mn including Mn^{+4}, Mn^{+2}, as well as various other elements.

This paper is concerned with poorly crystallized psilomelanes and psilomelane-type minerals which have received essentially no recent consideration although they have been recognized by Ramsdell (1932), and others subsequently. One such psilomelane-type mineral is described in detail and it is shown that this particular specimen (1) is very poorly crystallized as determined by its *x*-ray diffraction pattern and (2) has extensive isomorphous substitution of potassium, sodium, calcium, and strontium for barium. Because of these variations from the accepted chemical and structural definition of psilomelane, the term psilomelane-type is used to refer to the specimen being described. Throughout this paper the term psilomelane-type refers to a variant of true psilomelane as defined by Vaux (1937), Wadsley (1952, 1953), and Fleischer (1960A). It is not used in the general sense as suggested by Fleischer and Richmond (1943). Further comment on this terminology is presented below.

OCCURRENCE AND PREVIOUS STUDIES

The specimen described in this report is from the La Abundancia mine, Zacatecas, Mexico. This deposit has been most recently described by Wilson and Rocha (1956A); they also give older references. According to

Wilson and Rocha (1956A) the deposit is in the form of mantos and chimneys enclosed in shales and is believed to have formed by replacement by hydrothermal solutions. They also report that by *x*-ray diffraction J. M. Axelrod has identified pyrolusite (dominant mineral), cryptomelane, and two unidentified manganese minerals, as well as quartz, opal, calcite and other gangue minerals. Fleischer (1960B) states that one of Axelrod's unidentified minerals is now recognized to be the so-called "gamma MnO_2"; the other is still unidentified but is not the same as the material described in this paper. The reported presence of pyrochroite by Wilson and Rocha (1956A) was apparently in error according to Fleischer (1960B).

Wilson and Rocha (1956A) note that part of the ore is soft and has been selectively mined, whereas a hard ore has been left in the form of pillars. The mineral described below is undoubtedly an example of the hard ore.

PHYSICAL PROPERTIES

Form = massive, compact
Color = black; Streak = black
Fracture = conchoidal
Hardness = 6
Specific Gravity = 3.98 (at 25° C). Lower than true psilomelane (Fleischer, 1960A); probably due to adsorbed water and isomorphous substitutions for Ba described below.
Luster = Dull, submetallic in hand specimen. Takes excellent polish giving metallic luster in reflected light.

OBSERVATIONS IN REFLECTED LIGHT

The study of several polished sections of the La Abundancia manganese mineral indicates that it is essentially one phase. Several of the sections are homogeneous whereas a few, under high magnification, appear to contain a small number of very minute needles which show some variation in reflectivity upon rotation. Their exact nature could not be determined.

CHEMISTRY

In Table 1 a chemical analysis is presented of the psilomelane-type mineral from the La Abundancia mine. The most noticeable differences between this material and normal psilomelane are its low BaO content and higher than usual contents of CaO, K_2O, and Na_2O; the SrO content is probably normal for psilomelane. Calculations show that if Sr, Ca, K and Na are placed in the (Ba,H_2O) positions, the mineral under discussion fits the chemical requirements of psilomelane. In Table 2 these calculations are summarized and compared with the 14 authenticated psilomelanes described by Fleischer (1960A). For comparison with Fleischer's results, the data are based on $O = 20.00$.

TABLE 1. CHEMICAL ANALYSIS OF PSILOMELANE-TYPE MINERAL, LA ABUNDANCIA MINE, ZACATECAS, MEXICO

MnO_2	70.4	Fe_2O_3	2.6
MnO	9.3	MgO	0.9
BaO	4.5	H_2O^+	5.3
SrO	1.4	SiO_2	0.9
CaO	1.6	CO_2	0.3
K_2O	1.5	Others	0.3
Na_2O	0.7	Total	99.7

Notes on Analysis:

1. Wet Analyst: J. A. Greear.
2. Specimen oven dried at 110° C. for 2 hours before analysis. Ignition loss = 1.9%.
3. "Others" are remaining mixed oxides (chiefly Al_2O_3) from ammonium hydroxide precipitate after deduction of Fe_2O_3.
4. Barium and strontium determined by emission spectrographic analysis. Analyst: H. Holt.
5. Traces of Mo, Ni, Cu, Cr detected by *x*-ray fluorescence and emission analysis. Li, W, V, As, Pb, Co and Zn specifically looked for but not detected.
6. A specimen of the analyzed material has been deposited at the U. S. National Museum. U.S.N.M. No. 109398.

For the calculations in Table 2 on the La Abundancia mine specimen, all constituents reported in the analysis (Table 1), with the exception of SiO_2 and CO_2, are considered to be part of the mineral. A required amount of CaO (0.3%) was deducted as CO_2 is present as calcite. As pointed out by Fleischer (1960A), some other constituents, such as

TABLE 2. UNIT CELL CONTENTS OF PSILOMELANES, 0 = 20.00

	This Paper La Abundancia	Fleischer (1960A) 14 Psilomelanes
Sum Cations	11.6	11.3 average
Sum Ba Positions	Ba = .30 Sr = .15 K = .33 } 1.23 Na = .22 Ca = .23	1.26 average
Mn^{+4}	8.43	8.18— 9.00 (range)
Mn^{+2}	1.37	0.90— 1.64 (range)
Mn^{+4}/Mn^{+2}	6.16	5.20—10.00 (range)
H_2O^+	3.07	2.31— 3.09 (range) Average = 2.71
Sum Ba, Sr, Ca, K, Na + H_2O	4.30	3.46– 4.51 (range) Average 3.97

Fe_2O_3, may not belong in psilomelane, but no attempt was made to correct for this possibility.

Although the data in Table 2 speak for themselves, there are a few points worth noting.

1. The grouping of Ba, Sr, Ca, K and Na for the purposes of unit cell content calculation in psilomelane is a commonly accepted procedure. For example, it was used by Fleischer (1960A) in his Table 2.
2. The ratio Mn^{+4}/Mn^{+2} for cryptomelane is considerably higher than the largest value (10.00) reported by Fleischer (1960A) for any psilomelane. The specimen under study has a value for the Mn^{+4}/Mn^{+2} ratio so low, that no cryptomelane can be expected and, therefore, the K_2O plus Na_2O cannot represent cryptomelane. This is an important point in view of the fact that the psilomelane-type mineral under discussion contains more potassium and sodium ions than it does barium and strontium. (If all the potassium and sodium were allocated to cryptomelane, the specimen would contain about 50 per cent of that species.) Additionally, the analysis yielded significantly more H_2O^+ (5.3 per cent) than can be accounted for in a cryptomelane plus psilomelane mixture of approximately equal proportions.

X-RAY DIFFRACTION

The literature contains several references to poorly crystallized psilomelanes. Ramsdell (1932), in what is probably the first detailed *x*-ray study of specimens called psilomelane, reported a semi-amorphous type along with at least two other types (one of which was true psilomelane, and the other was later described as the new mineral cryptomelane). He suggested that the semi-amorphous type may represent colloidal material as only very few diffuse *x*-ray lines were recorded. Unfortunately, details of Ramsdell's (1932) *x*-ray spacings were not published nor were any chemical data presented to establish the semi-amorphous specimens studied as being true psilomelane chemically (approx. 16 per cent BaO) as defined by Vaux (1937).

Similar difficulties are encountered with other reported occurrences of poorly crystallized psilomelanes. For example, Wilson and Rocha (1956B) mentioned a possible imperfectly crystallized psilomelane from the Talamantes district, Mexico, but they give neither *x*-ray nor chemical data. Fleischer (1960B) states that this specimen is not as well crystallized as most Talamantes specimens (such as Fleischer's, 1960A, specimen number 7) but it shows perhaps three-fourths of the lines on normal exposure. Ramdohr (1956) described a psilomelane from Schneeberg, Saxony, for which he reports only seven *x*-ray diffraction lines. Although this is obviously a poorly crystallized variety no chemical information is given for this psilomelane. (This writer realizes that additional work may show Ramdohr's specimen may not be true psilomelane.) In Fleischer's (1960A) study of 14 authenticated psilomelanes, we are told that only the identity of the specimens had been proved by *x*-ray diffraction. In personal communication Fleischer (1960B) states that all of the 14 psilomelanes reported by him (Fleischer, 1960A) give more or less "normal" patterns except number 5 from Manila, Utah, which shows perhaps a dozen lines.

TABLE 3. *X*-RAY POWDER DATA FOR LA ABUNDANCIA MINERAL AND SELECTED PSILOMELANES

Psilomelane, Schneeberg Fleischer and Richmond (1943)		La Abundancia Mineral* (This Paper)		Psilomelane, Schneeberg, Ramdohr (1956)	
d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
4.205	1				
3.825	1				
3.488	8				
3.318	2				
3.217	1				
2.972	1				
2.842	4				
2.663	1				
2.402	8	2.41	6 broad	2.38	m
2.364	1				
2.251	3				
2.191	10	2.19	4 broad	2.16	m
2.138	2				
1.816	5	1.82†	very faint	1.81	s
1.734	2				
1.712	2	1.72†	very faint	1.71	ss
1.636	2	1.62–1.64†	very faint band		
1.562	4	1.57†	very faint band	1.55	s
1.524	1	1.52†			
1.424	4	1.42	10	1.42	m
1.403	6			1.39	s/ss
		1.17	1		

* Filtered iron radiation; camera diameter 143.2 mm.

† Seen only on films of long exposure.

Table 3 illustrates the differences between well crystallized and poorly crystallized psilomelanes or psilomelane-type minerals. In Table 3 the *x*-ray powder spacings of the La Abundancia specimen are given. They are compared with those reported by Fleischer and Richmond (1943) for what is considered a well crystallized true psilomelane, as well as the *x*-ray spacings reported by Ramdohr (1956) from the psilomelane for which there has been no chemical verification. It is important to note that the weak, broad, diffuse bands (1.62–1.64 Å and 1.52–1.57 Å) and faint lines (1.82 and 1.72 Å) of the La Abundancia mineral are seen only on films of long exposure and then sometimes only when specifically looked for. For all practical purposes, the La Abundancia mineral gives only three consistent easily recognizable lines: 2.41, 2.19 and 1.42 Å. Unpublished information received from Fleischer (1960B) reports that *x*-ray patterns like those from the La Abundancia mineral have been found at the U. S. Geological Survey on minerals from about 20 localities, including quite a few from Cuba. They range from patterns showing only two lines at 2.41 and 2.19 Å to good psilomelane patterns. Qualitative tests showed barium was always present but no complete analyses have been made.

The specimens of Fleischer and Richmond (1943) and Ramdohr (1956) are both from Schneeberg indicating both well crystallized and poorly crystallized examples occur at that locality. The reader is also referred to *x*-ray powder data on still another specimen from Schneeberg, reported by Gruner (1943), for slight differences in comparison with the Fleischer and Richmond (1943) results. Recently, Mukherjee (1959) has described what appears to be an authentic psilomelane (11–13% BaO) from India for which he has recorded almost twice as many lines as did Fleischer and Richmond (1943) and Gruner (1943).

After being heated to about 550° C. (in air for one hour), the La Abundancia specimen gives an *x*-ray pattern whose chief constituent is identical to that of hausmannite. Also, a few weak extra lines are present and these most probably represent hollandite; there may also be a trace of bixbyite. Fleischer (1960A) has noted that true psilomelane changes to hollandite at about 550° C. sometimes accompanied by hausmannite or bixbyite. The behavior of the La Abundancia specimen, that is, giving a pattern of hausmannite rather than hollandite, is not surprising in view of its low BaO content. Levinson (1960) has reported that todorokite, which has almost identical contents of MnO, MnO_2, SrO and Fe_2O_3 as the La Abundancia mineral, likewise inverts to give a hausmannite pattern at about 550° C.

Discussion

The unusual manganese mineral here described has been shown to be chemically similar to psilomelane, but with significant isomorphous substitution in the structural position normally occupied by barium. It seems highly unlikely that K, Na, Ca, and Sr are adsorbed in exactly the amounts necessary to fit the chemical requirements of psilomelane. Also, it has been shown that the mineral is poorly crystallized and that its *x*-ray pattern is closely related to psilomelane. Throughout the study the writer has been particularly attentive to the possibility that some of the unusual aspects of this mineral may be explained by a mixture of two or more minerals. The evidence, however, overwhelmingly favors the conclusion that the specimen is monomineralic.

The study of the La Abundancia mineral has raised many questions. Some of the more interesting might be:

1. Do poorly crystallized psilomelanes or psilomelane-type minerals commonly have considerable isomorphous substitution of K, Na, Ca, and Sr for Ba as does the La Abundancia mineral?
2. Is there a complete series between well crystallized psilomelane and amorphous material (if it exists) of the same or similar composition?

Unfortunately, the answer to these and other questions are not forthcoming from the present study. Many more poorly crystallized psilomelanes and psilomelane-type minerals will have to be studied completely before an attempt to answer these questions is justified. From the evidence and theory presented by Wadsley (1950), it would appear that significant chemical and structural variations can be expected.

NOMENCLATURE

The mineral psilomelane has been clearly defined by Vaux (1937), Wadsley (1952, 1953), and Fleischer (1960A) as a hydrated manganese oxide mineral with approximately 16 per cent BaO, undoubtedly including some SrO. It is unquestionable but that these writers consider psilomelane to be a well crystallized mineral. Accordingly, the specimen from the La Abundancia mine described in this paper cannot be called psilomelane.

The term psilomelane-type has been suggested by Fleischer and Richmond (1943) as a general name for those manganese oxide minerals which are massive, hard, and heavy and not specifically identified. The term is understood to include several distinct minerals, or mixtures, and no chemical formula should be given. Psilomelane-type has in the past, quite within the definition of Fleischer and Richmond (1943), been used for unidentified material with negligible BaO (such as cryptomelane and todorokite).

It is certainly not the desire of this writer to cause confusion in terminology of the psilomelanes as now exists in minerals and synthetic products essentially MnO_2 in composition. However, this paper contains the description of a mineral which shows structural and chemical similarities to true psilomelane; hence, it is called psilomelane-type. Furthermore, by virtue of its poor crystallization as determined by *x*-ray diffraction, and its low BaO content, the phrases poorly crystallized and low barium have been used in the title of this paper. It must be emphasized that at this time no specific or characteristic formula, or name, is assigned to the mineral described in this paper. It is felt that future work on poorly crystallized psilomelanes and psilomelane-type minerals may find that the La Abundancia specimen is merely a member of a complex chemical and structural mineralogical series.

The reader's attention is called to manganomelane, an infrequently used term, which apparently embodies much of the meaning of psilomelane-type as used by Fleischer and Richmond (1943) and has about 20 years' priority. (Manganomelane was proposed in 1923 by Klockmann, but this writer was not able to obtain the original reference.) Ramdohr (1954) discusses manganomelane briefly, as do others. No less respected authorities than Rankama and Sahama (1950, p. 642) state that manganomelane is a very common mineral. Although the term is currently rather vague in its meaning and extent, perhaps with a modified definition, manganomelane may serve a useful function.

Manganomelane is basically a useful term because it recognizes that all types of structural transitions exist between amorphous material (so-called "wad") and well crystallized specimens called psilomelane, pyrolusite, etc. Further, it recognizes chemical transitions or variations (K, Ba, Pb, etc.), as well as physical variations, from soft "wads" to hard compact materials called psilomelane.

This writer suggests that the definition of manganomelane be modified to be used as a general name for all hard manganese oxide minerals, whether individual minerals or mixtures, not specifically identified. In other words, it would replace psilomelane-type as used by Fleischer and Richmond (1943). It would include: (1) amorphous as well as crystalline specimens and all transitions in between; (2) materials of greatly varying composition; (3) materials of greatly varying physical properties; (4) materials of all environments and conditions of formation—not only of colloidal nature as is required by the original definition. If manganomelane is used in the sense suggested above, it would free the term psilomelane-type to be used for those specimens which are found to have chemical and/or structural characteristics, such as the La Abundancia mineral, similar to true psilomelane. The term wad should continue to be used for soft unidentified manganese oxide minerals. The division between wad and manganomelane, which is based on hardness (sometimes apparent), may be arbitrarily set at $H=3$.

The point may be raised that wad itself is reported in some standard references with hardness up to $H=6$ and, therefore, why not use wad to describe all unidentified manganese oxide minerals regardless of hardness? The answer to this is that the term wad, as well as numerous other terms, has been used so loosely in the past that authorities can be found for anything. The use of wad for soft unidentified manganese oxide minerals follows the general usage of the term for the past 50 years, especially in papers on the economic aspects of manganese minerals.

Fleischer (1960B) states he is in favor of the term psilomelane-type (Fleischer and Richmond, 1943) being replaced by manganomelane as the former led to confusion.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Dr. E. R. Wright and The Dow Chemical Company for their encouragement and permission to publish this study. I am indebted to my colleague Mr. J. A. Greear for the chemical analysis. Professor E. Wm. Heinrich kindly examined several polished sections. I am grateful to Dr. Michael Fleischer for critically reading this paper and making available unpublished data from the U. S. Geological Survey.

REFERENCES

FLEISCHER, M. (1960A), Studies of the manganese oxide minerals. III. Psilomelane: *Am. Mineral.*, **45,** 176–187.

——— (1960B), Personal communication. Letter dated July 7, 1960.

———, AND RICHMOND, W. E. (1943), The manganese oxides: a preliminary report: *Econ. Geol.*, **38,** 269–286.

GRUNER, J. W. (1943), The chemical relationship of cryptomelane (psilomelane), hollandite, and coronadite: *Am. Mineral.*, **28,** 497–506.

LEVINSON, A. A. (1960), Second occurrence of todorokite: *Am. Mineral.*, **45,** 802–807.

MUKHERJEE, B. (1959), *X*-ray study of psilomelane and cryptomelane: *Mineralog. Mag.*, **32,** 166–171.

RAMDOHR, P. (1954), *Klockmann's Lehrbuch der Mineralogie*. Ferdinand Enke, Stuttgart.

——— (1956), Die Manganerze: Symposium Sobre Yacimientos de Manganeso, **Vol. I.** *XX Congreso Geológico Internac., Mexico*, 19–73.

RAMSDELL, L. S. (1932), An *x*-ray study of psilomelane and wad: *Am. Mineral.*, **17,** 143–149.

RANKAMA, K., AND SAHAMA, T. G. (1950), *Geochemistry*. The University of Chicago Press, Chicago.

VAUX, G. (1937), *X*-ray studies on pyrolusite (including polianite) and psilomelane: *Mineralog. Mag.*, **24,** 521–526.

WADSLEY, A. D. (1950), Synthesis of some hydrated manganese minerals: *Am. Mineral.*, **35,** 485–499.

——— (1952), Role of water in the structure of psilomelane, (Ba, $H_2O)_2Mn_5O_{10}$: *Nature*, **170,** 973–974.

———, (1953), The crystal structure of psilomelane, (Ba, $H_2O)_2Mn_5O_{10}$: *Acta Cryst.*, **6,** 433–438.

WILSON, I. F. AND ROCHA, V. S. (1956A), Manganese deposits of La Abundancia and La Esperanza mines, Zacatecas, Mexico: Symposium Sobre Yacimientos de Manganeso, **Vol. III.** *XX Congreso Geológico Internac., Mexico*, 141–149.

——— (1956B), The Talamantes manganese deposits, Chihuahua, Mexico: *ibid.*, 125–132.

Manuscript received June 10, 1960.