AN *X*-RAY STUDY OF PSILOMELANE AND WAD

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Ordinarily the identity of a mineral is established by means of either its crystallographic constants, its optical properties, its chemical composition, or some combination of these. In the case of psilomelane none of these means is sufficient. Psilomelane has never been found in crystals, it is opaque, and the variations in chemical analyses have made it impossible to even assign a formula to it.

The recognition of psilomelane as an independent mineral species depends, to a large extent, upon its possession of a certain combination of physical properties which have been regarded as characteristic. The name psilomelane means "smooth black," and refers to the black color and the smooth rounded surfaces resulting from its frequent occurrence in botryoidal, reniform or stalactitic forms. The hardness is 5–6, the streak black, and the smooth fracture usually reveals a dense fine-grained texture with no definite structure other than an occasional concentric banding.

In the absence of definite crystallographic, optical and chemical data, there are two other means available of defining more specifically the material called psilomelane. One of these is a mineragraphic examination, the other involves the use of *x*-rays. Both of these methods were used by Smitheringale[1] in a study of manganese minerals, which incidentally included two specimens of psilomelane. An etching test[2] has recently been described for distinguishing psilomelane from certain associated minerals in polished sections. However, none of these investigators had in mind the purpose of establishing the identity of psilomelane as an independent mineral species, and did not touch upon this phase of the subject.

This present investigation has been limited to the *x*-ray method, and represents an attempt to answer this question of whether or not the material commonly called psilomelane is in reality a definite mineral. The *x*-ray diffraction patterns obtained by the powder method are especially useful in such a case as this, for if psilomelane is a definite crystalline substance, it must have a characteristic pattern.

Approximately fifty specimens of material, coming from widely scattered localities, and all having to a greater or less extent those

[1] W. V. Smitheringale: *Econ. Geol.*, **24**, (1929), 481–505.

[2] S. R. B. Cooke, Warren Howes and A. H. Emery: *Am. Mineral.*, **16**, (1931), 209–212.

physical properties which are considered typical of psilomelane, have been photographed. There were also included specimens of the closely related material known as wad. In addition, for comparison purposes, powder photographs have been obtained from pyrolusite, polianite, manganosite, bixbyite, braunite, manganite, and hausmannite.

Each of the last named minerals has its own characteristic x-ray pattern, and can be identified readily by this means. But in the case of psilomelane, instead of a single characteristic pattern, a variety of patterns was obtained. In the group of specimens examined, three distinct crystalline types were observed, as well as a semi-amorphous type. The preponderance of the crystalline type is interesting, in view of the many references to psilomelane as an amorphous mineral. In the specimens of wad there was less evidence of crystallinity. Most of the patterns were poorly developed and indicated impure material of a colloidal nature. Such patterns as were observed were rather variable.

The first conclusion to be drawn from the x-ray evidence is that psilomelane is a blanket term, and includes a group of substances with more or less similar physical properties. A second conclusion which was made evident is that the physical properties of psilomelane, even considered as a group, are not distinctive. There is so much overlapping of properties that they alone are insufficient for identification. For example, some specimens which had the normal appearance of psilomelane were found to be pyrolusite or braunite. On the other hand, some which had little or no resemblance to psilomelane, actually proved to be psilomelane.

Since psilomelane has never been precisely defined, in this paper the name has arbitrarily been assigned to the type of material which was most abundant among the specimens studied. This distinction cannot be made on the basis of physical properties, for no consistent difference could be found between these specimens and the others. Its identification is based solely on the diffraction pattern, which is shown in Fig. 1a. To avoid confusion in this paper, this material will be referred to as "true" psilomelane.

For the purposes of description the specimens which were included in this study can be divided into three groups, on the basis of their x-ray patterns.

Group 1

The specimens in this group include the majority of the specimens examined, and represent the material arbitrarily considered as "true" psilomelane. Although they vary considerably in detailed characteristics, all have in common the black color, hardness, and fine even-grained texture, which have been considered typical of psilomelane, and most of them are botryoidal. These specimens are from widely scattered localities, including Bohemia, Hungary, Saxony, Nova Scotia, Vermont, N. Carolina, Wisconsin and Michigan, as well as several specimens from unknown localities.

Group 2

Here are included those specimens whose patterns are different from that of "true" psilomelane, yet which in the past have been identified as psilomelane. First there is a group of five specimens which gave the type of diffraction pattern shown in Fig. 1 b. The localities and brief descriptions of these specimens are as follows: Laramie Co., Wyoming, stalactitic (labelled "manganese fulgerite"); Knapp's Ranch, Calif., rough granular crust; Romanèche, France, smooth botryoidal crust, with radial fibrous structure; two specimens from unknown localities, one with a smooth botryoidal crust, composed of distinct concentric layers; the other a thin dense crust.

Dana lists a psilomelane from Romanèche, France, with a BaO content of 16 per cent. This suggested that the above specimen from the same locality might contain barium. Accordingly it was tested, and considerable barium found. The remaining four specimens were likewise found to contain barium. Five specimens taken at random from Group 1 gave negative results when tested for this element. Definite analyses of these specimens should be made, but the preliminary qualitative results strongly suggest that the so-called psilomelane with an appreciable barium content is in reality a distinct mineral.

In addition to these Ba-containing specimens, there were two specimens labelled "psilomelane, variety lithiophorite," one from Saxony and one from Silesia. It is perhaps doubtful as to whether this material should have been classed as a variety of psilomelane. In appearance it is identical with ordinary psilomelane, but it is softer, and it is supposed to contain lithium and aluminum. No analyses were made, but the diffraction pattern, shown in Fig. 1c,

is distinctly different from that of "true" psilomelane, showing that here too, we are dealing with a distinct crystalline substance. A specimen labelled "psilomelane, variety Kakochlor," also from Silesia, was photographed. Breithaupt used this name for a variety of asbolite. This particular specimen, however, is similar in appearance to the two lithiophorite specimens, and gave an identical diffraction pattern.

Finally, in this group of specimens which have the appearance of psilomelane, but which differ from "true" psilomelane, there are included several specimens which have been designated as semi-amorphous. Powder photographs of extremely fine crystalline material are characterized by diffuse patterns, with relatively few lines. Patterns of this type were secured from some of the psilomelane specimens. In some cases there was partial agreement of the few lines present with the more intense lines of the true psilomelane pattern while in others there was little agreement, and it is doubtful as to whether they represent a minutely crystalline phase of psilomelane or something else. Such material is probably colloidal, and may be rather indefinite in composition. These specimens do not show any consistent differences in appearance from the true psilomelane.

Group 3

In this group are included those specimens which possess the characteristic appearance of psilomelane, but which proved to be either pyrolusite or braunite. Ordinarily pyrolusite and psilomelane are regarded as so distinctly different in physical properties that there would be little possibility of confusing the two. Yet these specimens were found, having the botryoidal structure and hardness of psilomelane, and not distinguishable in appearance from the specimens of group 1, but which give the pyrolusite pattern. The occurrence of pyrolusite with a hardness of 6 is not entirely unexpected, for the mineral polianite, considered as a modification of MnO_2, occurring in tetragonal crystals, has a hardness of 6 to 6.5. This was shown by St. John[3] to have a structure identical with pyrolusite, and this has been verified in this present study. Apparently the relation of polianite to pyrolusite is similar to that of hematite crystals to the softer varieties such as red ocher. In this case we might expect to find MnO_2 with any hardness from 1 to

[3] A. St. John: *Phys. Rev.*, **21**, (1923), 389.

6.5. A specimen from an unknown locality was actually found, with the typical acicular structure of pyrolusite, which had a hardness of about 3.5.

A specimen supposed to be psilomelane, from Santa Clara, Calif., gave the braunite pattern. This specimen is not botryoidal, but it is dense and fine grained, with an even fracture, and would normally

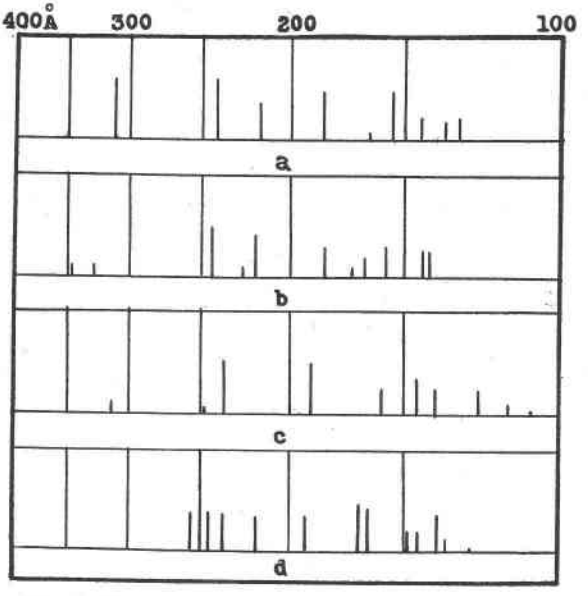

FIG. 1. *X*-ray diffraction patterns of (a) "true" psilomelane, (b) psilomelane containing barium, (c) lithiophorite, and (d) possible dimorphous form of MnO_2.

be identified as psilomelane on the basis of its appearance. Two additional specimens, one from Sheffield, Mass., and the other from Eagle Harbor, Mich., also proved to be braunite. Both were labelled psilomelane, but they have a cellular structure, and would not be classed as having the typical appearance of psilomelane. Braunite was also found as a granular crust on pyrolusite. These specimens indicate that the occurrence of massive braunite may be more common than has been believed.

WAD

No *x*-ray evidence was obtained to indicate the existence of any definite mineral which could be called wad. The *x*-ray patterns re-

vealed that much of the so-called wad is either pyrolusite or true psilomelane, while the rest consists of impure material of a semi-amorphous character.

A specimen from Spain, gray brown in color, soft, earthy, and almost light enough to float on water; together with a very similar material, occurring as a soft brown coating on botryoidal psilomelane from Hurley, Wis., both gave distinct patterns identical with that of "true" psilomelane. On the other hand, a specimen from China,[4] almost indistinguishable from the one from Spain, proved to be practically amorphous.

The soft sooty material frequently associated with pyrolusite was in some cases found to be pyrolusite and in others true psilomelane, but in no case was it amorphous. There was nothing in the appearance of the specimens to give any indication as to which of the two was actually present.

Unusual Specimens

Two of the specimens which were studied seem worthy of special description. The first, from Nassau, Germany, is steel gray in color, and possesses a distinctly radial fibrous structure. Not only is the specimen fibrous, but in places this structure grades into distinct individual needles, which project several millimeters from the surface. Both the needles and the fibrous portion give the "true" psilomelane pattern. The second specimen, from an unknown locality, is soft and black, and to a certain extent resembles ordinary pyrolusite. However, there is a parallel grouping of the needles which gives an almost platy appearance. The x-ray pattern, shown in Fig. 1d, is entirely different from anything else obtained in this investigation. But after heating to a low dull red heat, a normal pyrolusite pattern was secured. This heating was accompanied by a loss of water of only 1 per cent, and the total loss in weight was less than 2 per cent. This would seem to eliminate either dehydration or a change from some other oxide as a cause of the change in pattern. A possible explanation is that this specimen represents an unstable form of MnO_2, which is converted to the normal form by heating.

[4] Collected by F. L. Hess, and made available to the writer through the kindness of E. P. Henderson.

SUMMARY

1. *X*-ray examination of over fifty specimens of psilomelane shows that material included under this name may be any one of several different substances. The term "true" psilomelane has arbitrarily been applied to the type of material which was most abundant among the specimens studied. No identification of "true" psilomelane is possible by means of physical properties alone.

2. Material which in the past has been classified as psilomelane may actually be:

a. "True" psilomelane.

b. Pyrolusite or braunite.

c. A distinct mineral, which has been previously considered as psilomelane containing barium.

d. Lithiophorite, previously considered as a variety of psilomelane containing lithium and aluminum, but which the *x*-ray pattern shows to be a distinct mineral.

e. Semi-amorphous material, which probably can best be classed as wad, but which shows no consistent difference in appearance from true psilomelane.

3. Material which has been classed as wad may actually be:

a. Pyrolusite.

b. "True" psilomelane.

c. Impure material, of semi-amorphous character.