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STUDIES OF THE MANGANESE OXIDE MINERALS.
III. PSILOMELANE*

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ABSTRACT

Study of 14 analyses of psilomelane, including 7 new ones, verifies Wadsley's formula, $(Ba,H_2O)_4Mn_{10}O_{20}$. *X*-ray study of the products of dehydration shows that the water is lost zeolitically up to 500° C. and that the mineral is converted to hollandite at about 550° C. Thermogravimetric and differential thermal analysis curves are given for two analyzed samples.

INTRODUCTION

"The mineralogical determination of those species, the chief constituent of which is Manganese, has been for a long time destitute of that precision at which other species had long arrived, whose chemical constitution was better known." This is the opening sentence of a most remarkable paper by W. Haidinger, read by him on December 17, 1827, and published in 1831 (Haidinger, 1831). In it and the accompanying chemical report by Edward Turner (Turner, 1831), the minerals pyrolusite, manganite, hausmannite, braunite, and psilomelane were named and characterized; the descriptions, with the exception of the chemical composition of braunite, are still valid. When the U. S. Geological Survey began in 1941 a detailed study of the manganese oxide minerals, their determination was still destitute of precision. A preliminary report of our work (Fleischer and Richmond, 1943) partly corrected this, but other commitments have for a long time prevented the publication of the data on which the conclusions of the 1943 report were based.

The name psilomelane was given by Haidinger to the smooth black uniform and botryoidal mineral, which he stated to be "a pretty common species" and for which he lists many localities. He gave the hardness as 5–6, sp. gr. 4.145, 4.079, 4.004. Turner's analysis of a sample from Schneeberg (Table 1, A) gave BaO 16.36%; another sample, from Romanèche, France, sp. gr. 4.365, which he thought contained some pyrolusite (Table 1, B) contained 16.69% BaO.

Later workers, unfortunately, used the name psilomelane to refer to any hard, botryoidal manganese oxide, regardless of composition or density, until the term had practically come to mean any hard, unidentified manganese oxide, soft samples being referred to wad. The data in the literature on psilomelane therefore refer in part to cryptomelane, hollandite, coronadite, and lithiophorite, and probably to other minerals as well. One cannot be sure what mineral was studied unless *x*-ray powder

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data were given for the material described as "psilomelane"; on the other hand, some samples that differ in appearance from the usual hard botryoidal psilomelane have been described under other names. A good example is the "varvacite" of Walker (1888), Table I C, which is soft, fibrous, and radiating and which would be unhesitatingly identified by sight as pyrolusite.

Psilomelane was redefined as a single species by Vaux (1937), who made an *x*-ray study of samples from Schneeberg and Romanèche, reporting it to be orthorhombic with a_0 9.1, b_0 13.7, c_0 2.86 Å, and found from four new analyses that the composition could be expressed as $H_4(Ba, Mn)_2 Mn_8^{+4}O_{20}$ with Ba:Mn close to 1:1. His chemical results were confirmed by Fleischer and Richmond (1943), who followed him in restricting the name psilomelane to this species, the formula of which they gave in the slightly different form $BaR_9O_{18}\cdot 2H_2O$, ($R = Mn^{+4}$, Mn^{+2}, Co, etc.). Palache, Berman, Frondel (1944) likewise restrict the name to this species; they give the formula in a third modification, $BaMn^{+2}Mn_8^{+4}O_{16}(OH)_4$.

Later *x*-ray work by Wadsley (Wadsley 1952, 1953) has shown that psilomelane is monoclinic, space group *A* 2/*m*, with a_0 9.56, b_0 2.88, c_0 13.85 Å, β 92°30′. His structural study showed that Ba and H_2O occupy positions that are crystallographically indistinguishable, although they are very probably in an ordered sequence. On the basis of the structural data, he gave the formula (here doubled for comparison with those above) as $(Ba, H_2O)_4Mn_{10}O_{20}$ with Ba:H_2O approximately 1:2, and Mn including Mn^{+4}, Mn^{+2}, and other elements.

The present paper gives new analyses, dehydration curves, and differential thermal analyses of psilomelane.

CHEMISTRY

In Table 1 are given 17 analyses of psilomelane, 10 from the literature (lettered) and 7 new analyses made in the laboratories of the U. S. Geological Survey (numbered). These include every analyzed sample whose identity has been proved by *x*-ray study. Analyses A, B, and D, included because of their historical interest, are of samples that have not been studied by *x*-rays, although other samples from the same localities have been shown to be psilomelane. Many older analyses, some of which agree closely with those listed here, are given in Doelter's Handbuch der Mineralchemie, Bd. III, Pt. 2, p. 863–881, but these samples as well as one analyzed by Koch and Grasselly (1951) have not been studied by *x*-ray methods.

It will be noted in Table 1 that several of the samples contained large amounts of WO_3, one had a high content of V_2O_5, and three of As_2O_5.

Table 1. Chemical Analyses of Psilomelane

(arrangement chronological)

	A	B	C	D	1	E
MnO_2	66.98	66.40	68.86	66.87	59.65	66.73
MnO	10.18	11.83	7.51	8.23	6.70	7.12
CuO	—	—	—	0.10[a]	0.25	0.31
CoO	—	—	—	—	—	1.00
MgO	—	—	—	0.20	trace	0.13
BaO	16.36	16.69	14.42	16.20	14.40	17.48
CaO	—	—	—	0.40	0.05	0.26
K_2O	—	—	—	0.10	0.11	trace
Na_2O	—	—	—		0.42	trace
H_2O^-	6.22	4.13	5.08	4.65	0.49	0.50
H_2O^+					3.78	4.41
Al_2O_3	—	—	2.23		0.55	0.35
Fe_2O_3	—	—		1.45	3.27	0.20
As_2O_5	—	—	—	1.50	—	—
V_2O_5	—	—	—	—	—	—
WO_3	—	—	—	—	—	0.68
SiO_2	0.26	0.95	1.98	0.40[b]	9.25[c]	0.51
Others	—	—	—	—	0.37[d]	trace[e]
Total	100.00	100.00	100.08	100.10	99.29	99.68
G.	4.004 to 4.079	4.365	3.27	4.21	4.48 (corr. for SiO_2)	

	F	G	H	I	2	3
MnO_2	66.62	68.00	70.38	65.31	69.00	68.40
MnO	7.09	10.70	7.90	7.83	6.99	7.02
CuO	0.48	trace	0.38	—	none	0.03
CoO	0.90	—	0.48	—	—	none
MgO	0.15	0.30	0.13	1.68	trace	none
BaO	17.46	15.73	12.38	14.02	17.84	14.91
CaO	0.19	—	0.66	0.38	none	0.72
K_2O	trace	0.08	0.42	0.11	0.07	0.59
Na_2O	trace	0.02	trace	0.19	0.05	0.48
H_2O^-	0.48	0.48	1.88	4.69	0.07	0.63
H_2O^+	0.48	3.82	4.18		4.46	4.43
Al_2O_3	0.37	—	0.73	—	0.43	0.12
Fe_2O_3	0.15	0.30	0.18	0.84	0.14	0.15
As_2O_5	—	—	—	—	—	2.15
V_2O_5	—	—	—	—	—	—
WO_3	0.89	0.28	—	4.88	0.63	none
SiO_2	0.52	0.59	0.09	0.38	0.85[h]	0.13
Others	trace[f]	trace	0.03[g]	—	—	—
Total	99.68	100.30	99.82	100.31	100.53	99.76
G.	4.71	4.70	—	—	4.74	4.45

TABLE 1 (*continued*)

	4	5	6	7	J
MnO_2	70.85	67.10	70.52	67.91	74.36
MnO	6.87	7.46	6.10	7.62	6.10
CuO	0.03	—	—	0.11	—
CoO	0.03	0.26	0.01	0.07	—
MgO	0.22	0.26	0.22	0.11	—
BaO	14.99	14.59^j	13.56	13.68	13.49
CaO	none	1.84^j	0.27	0.07	—
K_2O	0.27	0.48	0.35	0.43	0.81
Na_2O	0.13	0.35	0.29	none	—
H_2O^-	0.37	0.70	—	0.90	—
H_2O^+	4.39	4.75	4.03^k	5.00	5.14
Al_2O_3	0.29	none	0.27	none	$\left\{\begin{matrix}0.59\\ \end{matrix}\right.$
Fe_2O_3	0.09	0.28	1.12	0.20	
As_2O_5	—	—	—	0.36	—
V_2O_5	—	1.13	—	—	—
WO_3	0.36	—	1.32	2.92	—
SiO_2	0.83	0.48	0.40	0.14	—
Others	0.09^i	—	1.24^l	0.17^m	
Total	99.81	99.68	99.70	99.69	100.49
G.	4.56	4.41	4.44	4.43	4.61

Notes to Table 1—(a) $=CuO+PbO$; (b) $=SiO_2$ 0.25, gangue 0.15; (c) insol. SiO_2 8.35, sol. SiO2 0.90; (d) $=PbO$ 0.32, P_2O_5 0.05; (e) traces NiO and Li_2O; (f) trace NiO; (g) $=NiO$; (h) insol. SiO_2 0.41, sol. SiO_2 0.44; (i) $=ZnO$ 0.07, PbO 0.02; (j) includes some SrO; (k) sample dried at 110° before analysis; (l) $=SrO$ 1.19, P_2O_5 0.05; (m) $=ZnO$ 0.14, PbO 0.01, P_2O_5 0.02.

A-B Turner (1831), A. from Schneeberg, Saxony, B. from Romanèche, France, C. Walker (1888), fibrous, radiating; "varvacite" from near Austinville, Wythe Co., Virgina; *x*-ray identification by U. S. Geological Survey laboratory on type material from U. S. National Museum, G. evidently incorrect. D. Gorgeu (1890), from Romanèche; (1) Analyst-Charles Milton, 1933. Exact locality unknown, sample submitted from Tucson, Arizona; E-H. Quoted by Vaux (1937). (E, F, and H.) Hilda Bennett, analyst; (G) H. J. Hallowell, analyst; E. from Spitzleite, Eibenstock, Saxony; F-G. from Schneeberg; H. from Restormel Mine, Lostwithiel, Cornwall, England. I. Quoted by Kerr (1940); from Sodaville, Nevada; analyst F. A. Gonyer; *x*-ray identification by U. S. Geological Survey laboratory on material supplied by P. F. Kerr. (2) Analyst—W. T. Schaller, 1940. From Mayfield prospect, Chispa Siding, Jeff Davis Co., Texas. Collected by S. G. Lasky. (3) Analyst—M. Fleischer, 1941. From Romanèche, France, U. S. National Museum No. R 2232. (4) Analyst—M. Fleischer, 1941. From Tolbard Mine, Paymaster district, Imperial Co., California, collected by J. B. Hadley. (5) Analyst—M. Fleischer, 1942. Exact locality unknown, sample U. S. National Museum No. 94, 341, sent in from Manila, Utah. (6) Analyst—M. Fleischer, 1943. From Hoggett manganese group, Hidalgo Co., New Mexico, collected by Sherman K. Neuschel. (7) Analyst—M. Fleischer, 1943. From Talamantes Mine near Parral, Chihuahua, Mexico, collected by P. D. Trask; a photograph of this sample is given by Wilson and Rocha (1948), Plate 37 A. (J) Wadsley (1950), massive, from Pilbara, W. Australia.

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

Analysis	C	1	E	F	G	H	I
Mn^{+4}	8.68	8.31	8.54	8.53	8.52	8.67	8.18
Mn^{+2}	1.16	1.14	1.12	1.11	1.64	1.19	1.20
Others[a]	0.31	0.67	0.37	0.38	0.13	0.32	0.79
R	10.15	10.12	10.03	10.02	10.29	10.18	10.17
Ba, etc.[b]	1.03	1.36	1.32	1.31	1.15	1.09	1.17
H_2O	3.09	2.54	2.73	2.71	2.31	2.49	2.84
Ba+H_2O	4.12	3.90	4.05	4.02	3.46	3.58	4.01
G. calcd.	4.66	4.70	4.76	4.77	4.69	4.49	4.72
G. meas.[c]	3.27	4.48[d]	—	4.71	4.70	—	—
Mn^{+4}/Mn^{+2}	7.48	7.29	7.63	7.68	5.20	7.29	6.82

	2	3	4	5	6	7	J
Mn^{+4}	8.69	8.50	8.73	8.42	8.66	9.58	9.00
Mn^{+2}	1.08	1.07	1.05	1.15	0.92	1.18	0.90
Others[a]	0.14	0.25	0.16	0.29	0.33	0.28	0.08
R	9.91	9.82	9.94	9.86	9.91	10.04	9.98
Ba, etc.[b]	1.31	1.50	1.28	1.63	1.29	1.09	1.08
H_2O	2.71	2.66	2.62	2.88	2.39	3.05	2.98
Ba+H_2O	4.02	4.16	3.90	4.51	3.68	4.14	4.06
G. calcd.	4.73	4.64	4.67	4.66	4.60	4.70	4.56
G. meas.[c]	4.74	4.45	4.56	4.41	4.44	4.43	4.61
Mn^{+4}/Mn^{+2}	8.05	7.94	8.31	7.32	9.41	7.27	10.00

[a] Includes Fe, Al, Cu, W, V, As, etc.

[b] Includes Ba, Sr, Ca, Pb, K, Na.

[c] Not corrected for SiO_2 except analysis 1.

[d] Corrected for SiO_2.

The Romanèche sample with 2.15% As_2O_5 (no. 3) and that from Chihuahua with 2.92% WO_3 (no. 7) were of ideal purity, as judged from optical and *x*-ray study, and there can be little doubt that these constituents were present in the manganese oxide mineral and not in any impurity. Tungsten, arsenic, and vanadium are characteristic constituents of manganese oxide minerals, and especially of psilomelane, from many localities in the southwestern United States and Mexico. Their genetic significance is discussed elsewhere by Hewett and Fleischer (1960), who give many additional partial analyses.

In Table 2 are given the calculated unit cell contents, assuming

$O=20.00$, and using the unit cell dimensions of Wadsley (1953). All constituents reported in the analyses, with the exception of SiO_2, have been assumed to be part of the mineral. This is undoubtedly incorrect, especially for at least part of the Al_2O_3 and Fe_2O_3. SrO is reported in only one analysis, but is known to be a characteristic constituent of psilomelanes from many deposits in the southwestern United States and is probably present in some of the other samples of Table 1.

It is interesting to compare the calculations of Table 2 with the requirements of the four formulas that have been suggested in recent years for psilomelane:

1. Vaux	$H_4(Ba, Mn^{+2})_2Mn_8^{+4}O_{20}$
2. Fleischer and Richmond	$Ba(Mn^{+4}, Mn^{+2})_9O_{18}\cdot 2H_2O$
3. Palache, Berman and Frondel	$BaMn^{+2}Mn_8^{+4}O_{16}(OH)_4$
4. Wadsley	$(Ba, H_2O)_4Mn_{10}O_{20}$

All the formulas are fairly good approximations, but that of Wadsley clearly fits the analyses best. The first three formulas give for the sum of the cations 10, whereas Wadsley's formula gives $10+Ba$; the 14 analyses give 11.06 to 11.49, average 11.3. Formulas 2 and 3 require $Ba=1$; the analyses show Ba 1.03 to 1.63, average 1.26. Formula 3 requires $Mn^{+2}=1$ and all but one of the analyses are in the range 0.90 to 1.20; it also requires the ratio $Mn^{+4}/Mn^{+2}=8$; the analyses show the range 5.20 to 10.00, but 11 of the 14 are in the range 6.8–8.4, which may indicate some sort of Eh-pH control of the formation of the mineral. It should be noted, however, that cryptomelane and hollandite, which are commonly associated with psilomelane, show much higher Mn^{+4}/Mn^{+2} ratios.

The first three formulas require $2H_2O$, whereas Wadsley's require $H_2O+Ba=4$. The calculations show H_2O^+ 2.31 to 3.09, average 2.71, but the dehydration studies discussed below show that some of this water is probably adsorbed. The sum of $Ba+H_2O$ ranges from 3.46 to 4.51, average 3.97; 10 of the 14 are between 3.90 and 4.16. Considering the massive nature of most samples and the difficulty of detecting small amounts of opaque admixtures such as pyrolusite, the over-all constancy of composition is surprising.

The calculated specific gravities are in general higher than those determined, as would be expected because the errors in the determination all give low results. They range from 4.49 to 4.77, average 4.67, and only one departs from the average by more than 0.11. There is, however, considerable uncertainty in the calculation because the presence of adsorbed water has not been taken into account; some arbitrary asumption as to how much of the water is adsorbed would have to be made. The data in the next section show that such an assumption would be very uncertain.

STUDY OF DEHYDRATION

Fleischer and Richmond (1943) found that psilomelane was converted to hollandite by heating at 550° C. (this was confirmed on synthetic material by Wadsley (1950)) and concluded that the water was essential. Wadsley (1953) stated that a temperature vs. weight curve recorded by A. J. Gaskin showed no abrupt transition and that powder photographs of material heated to 400° C. showed no change, despite the fact that at least 60% of the water was lost; further that material heated to 400° C. could be dehydrated by exposing the sample to the atmosphere at room temperature. It seemed desirable, therefore, to study the dehydration in more detail. The samples studied were Nos. 6 and 7 of Table 1 from the Hoggett Mine (H_2O^+ 4.03%, sample had been dried at 110° C.), and from Talamantes Mine, Parral, Chihuahua (H_2O^- 0.90, H_2O^+ 5.00%).

TABLE 3. DEHYDRATION OF PSILOMELANE

Temperature ° C.	Loss of Weight—in %			
	Talamantes Mine		Hoggett Mine (sample dried at 110°)	
	M.F.	C.A.K.	M.F.	C.A.K.
400	3.92	2.70	1.09	0.50
500	0.83[a]	1.20	1.15[b]	0.40
600	2.62	1.40	3.53	0.75
700	0.04	0.70	0.00	2.25
800	0.65	1.20	0.47	0.90
900	0.91	1.50	1.29	1.90
Total	8.97	8.70	7.53	6.70
H_2O^+	5.00		4.03	
H_2O^-	0.90		—	

[a] Another sample heated directly and held at 500° C. for 14 days lost 5.12%.

[b] Another sample heated directly and held at 500° C. for 14 days lost 1.90%.

The results are given in Table 3. The losses in weight recorded in the columns headed M.F. were determined by heating weighed samples in platinum dishes at the temperature indicated for 24 hours. The temperatures were held to ±10°. The data marked C.A.K. were determined by C. A. Kinser of the U. S. Geological Survey and are shown in Fig. 1.

The data by Kinser were obtained on a thermogravimetric balance modified from that described by Mauer (1954), which continuously records the weight of a sample as the temperature of the sample is raised at a pre-determined uniform rate.

It will be noted from Table 3 and Fig. 1 that the two samples lost water at very different rates. The total loss in weight exceeds by a good deal the water content; evidently oxygen was driven off above 500° C. in the static dehydrations, and at 700° and above in the rapid heating of the thermogravimetric apparatus.

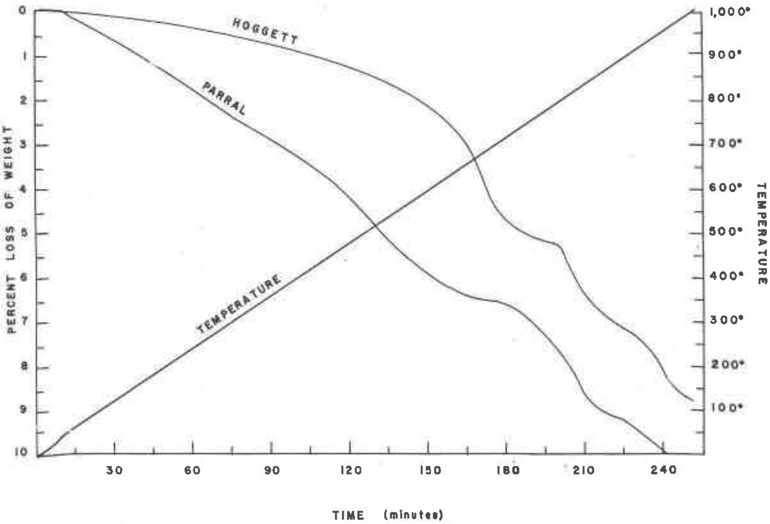

FIG. 1. Thermogravimetric dehydration curves by C. A. Kinser of psilomelanes from the Hoggett Mine, New Mexico, and the Talamantes Mine, Parral, Chihuahua. The loss in weight is read directly from the scale at the left. The temperature for any point on the curves is obtained by drawing a vertical line to the temperature curve and reading from the scale at the right.

X-ray powder patterns were made by E.C.T. Chao of the samples run by Fleischer. For the sample from the Hoggett Mine, the pattern of material heated at 400° was unchanged; the pattern of material heated at 500° C. was still that of psilomelane, but the lines at 3.88, 3.30, 3.21, 2.97, 2.36, and 1.82 had become diffuse and that at 2.25 Å had become markedly weaker; the pattern of samples heated at 600°, 700°, and 800° C. was that of hollandite with perhaps small amounts of bixbyite, as indicated by lines at 2.72 and 1.67 Å; the pattern of material heated at 900° C. was still mainly hollandite, but the broad band at 3.12 Å had changed to a doublet at 3.08 and 3.16 Å, and hausmannite was present in place of bixbyite.

The *x*-ray study of the heated samples from the Talamantes Mine, Parral, showed slightly different behavior. The pattern of material heated at 400° was diffuse with only lines at 6.87, 3.46, 2.40, 2.18, and 2.14, and diffuse bands at 1.82, 1.56, and 1.42 Å; the pattern of material heated at 500° C. was even weaker. The patterns of material heated at 600°, 700°, 800° and 900° C. showed hollandite plus small amounts of hausmannite. The broad band of hollandite at 3.13 changed in the samples heated at 800° and 900° C. to a doublet at 3.10 and 3.18 Å.

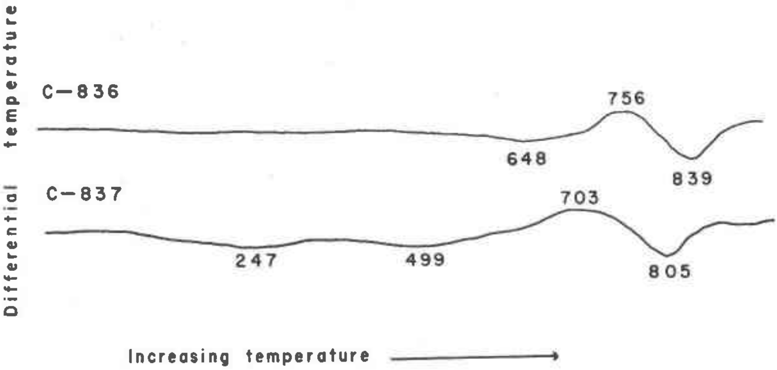

FIG. 2. D.T.A. curves by George T. Faust for psilomelanes from Hoggett Mine, New Mexico (C-836) and from Talamantes Mine, Parral, Chihuahua (C-837).

Thus the results on the two samples confirm Wadsley's findings that heating at 400° C. produced no structural change and the report by Fleischer and Richmond that there is a change at 550° C. to hollandite. Wadsley's statement that the structural change is accompanied by a period of marked crystal disorder is confirmed. The sample from the Talamantes Mine lost its water more readily and showed signs of disorder at lower temperatures than the sample from the Hoggett Mine. We have no explanation for this, nor for the fact that the latter sample gave a small amount of bixbyite first, then hausmannite, whereas the former sample gave hausmannite directly.

DIFFERENTIAL THERMAL ANALYSIS

Figure 2 shows the D.T.A. curves for the same two samples, kindly run by George T. Faust of this laboratory. Each curve shows one exothermal break (at 703° and 756° C.) and one endothermal break (at 805° and 839° C.) for the Parral and Hoggett samples, respectively. The exothermic breaks correspond approximately to the short plateaus on Kinser's thermogravimetric curves, but the endothermal breaks do not correspond closely to decided breaks in Kinser's curves.

Curves have previously been published for "psilomelane" in four papers, but none of these gave *x*-ray data for the samples. Kulp and Perfetti (1950) gave a curve for a sample from Cuba, which showed a broad endothermic peak at 900–1000°. Kauffman and Dilling (1950, p. 229) gave a curve for a sample from California, which showed an endothermic peak at about 840°. Heystek and Schmidt (1953, p. 165) gave a curve for a sample from Frischgewaagd, Waterberg District, South Africa, which showed two large endothermic breaks at 620° and 840° C. There is no way in which one can guess as to what manganese oxide minerals these curves actually represent, in the absence of *x*-ray and chemical data. Rode (1955), on a sample from Schneeberg containing BaO 10.45%, found a sharp exothermic peak at about 750° and an exothermic peak at 1050° C. The analysis indicates that the sample could not have been pure psilomelane.

In view of the differences in behavior of the two samples we have studied, we expect to continue our studies of the thermal behavior of samples for which chemical and *x*-ray data are available.

NOMENCLATURE

The early history of the nomenclature of this mineral was summarized in the Introduction. The name romanèchite was proposed by Lacroix (1910, p. 6) for the same mineral (he quotes Turner's analysis!) and this name has been used, especially in France, up to the present. It has been favored mainly because of the feeling that psilomelane has been used for so many different minerals that the name has ceased to be well-defined. The name romanèchite has, however, also suffered in this way; it has unfortunately also been applied to the potassium manganese oxide cryptomelane by Gruner (1943), who found that the latter occurred at Romanèche and assumed that this was the mineral named by Lacroix. This was unjustified, because it ignored the fact that Lacroix cited six analyses, showing BaO 13.50 to 16.84%.

On the whole, it seems best to retain the name psilomelane for the specific mineral here described and to relegate romanèchite to the synonymy. This nomenclature has been adopted by Palache, Berman, and Frondel (1944), by Hey (1955), and by Strunz (1947).

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