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THERMAL TRANSFORMATIONS AND PROPERTIES OF CRYPTOMELANE

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ABSTRACT

An unusual occurrence of needles of cryptomelane in cavities in a manganese ore from western Australia is described. *X*-ray diffraction data for the acicular crystals are indexed in terms of a body-centered tetragonal unit cell although optical examination of the crystals indicates a pseudotetragonal cell. The powder data are more detailed than those previously reported for cryptomelane. Fiber patterns obtained from the crystals, heat-treated in air at various temperatures and times, establish the following thermal transformations and relative orientations parallel to the [001] axis of cryptomelane.

$$[001] \xrightarrow{\Delta} [110]\,[100] \xrightarrow{\Delta} [100]\,[100] \xrightarrow{\Delta} [110]$$

cryptomelane bixbyite hausmannite spinel

A transformation product of cryptomelane indexed in terms of a spinel structure, $a_0 = 8.42$ Å, is reported.

A correlation of thermogravimetric data with phase determinations shows that on continuous heating at 6° C. per minute, fibered cryptomelane does not transform completely to bixbyite before the formation of hausmannite begins. At this heating rate, the critical temperature for formation of bixbyite from the acicular crystals of cryptomelane is approximately 600° C., for the hausmannite approximately 825° C., and for the spinel approximately 1050° C.

In 1932, Ramsdell (1) showed that the hard, compact manganese oxide, usually known as psilomelane, was actually any one of several distinct minerals, the most common of which he termed "true psilomelane." This mineral was characterized by a distinctive *x*-ray diffraction pattern, the presence of potassium and the virtual absence of barium. In 1942, Richmond and Fleischer (2) determined the chemical composition and physical properties of several specimens of the mineral and gave *x*-ray data which were in close agreement with those given in a second report by Ramsdell (3). They proposed that the term "true psilomelane" be discontinued in favor of a new name "cryptomelane." Although they considered cryptomelane to be isostructural with the manganese minerals hollandite and coronadite, they were unable to determine its space group.

The present authors' interest in cryptomelane arises from studies designed to establish the properties and geochemistry of the different structural types of manganese oxides. During the course of this investigation a manganese ore sample was received from western Australia, which consisted of a dense, dark-gray matrix containing a few small cavities partly

filled with aggregates of acicular crystals, hereafter designated "needles." The needles were shiny and black in reflected light, and frequently oriented toward the centers of the cavities (Fig. 1).

A few of the needles were gently crushed for petrographic examination. Upon crushing, the needles split into fine fibers as shown in Fig. 2. The fragments were dark brown, and nearly opaque except when very thin. They were weakly anisotropic with parallel or nearly parallel extinction. Since the sign of elongation changed as the thin fibers were rotated, it appears that they are biaxial rather than uniaxial in nature.

Chemical Analysis

The limited supply of cryptomelane needles (ca 150 mg.) necessitated the use of micro-analytical techniques and restricted the number of determinations that could be made. The chemical analyses of the needles and the matrix material are compared to those reported by Richmond and Fleischer (2) for various specimens of cryptomelane in Table 1. The relatively large amount of Fe_2O_3 and SiO_2 in the matrix material is due to the presence of hematite and quartz. The calculated chemical formulae in Table 1 are based on similarities of atomic radii and possible substitutions. "*A*" represents large ions (chiefly K^+ with substitution by Ba^{++} and Na^+), and "*R*" represents small ions (chiefly Mn^{+4}, with substitu-

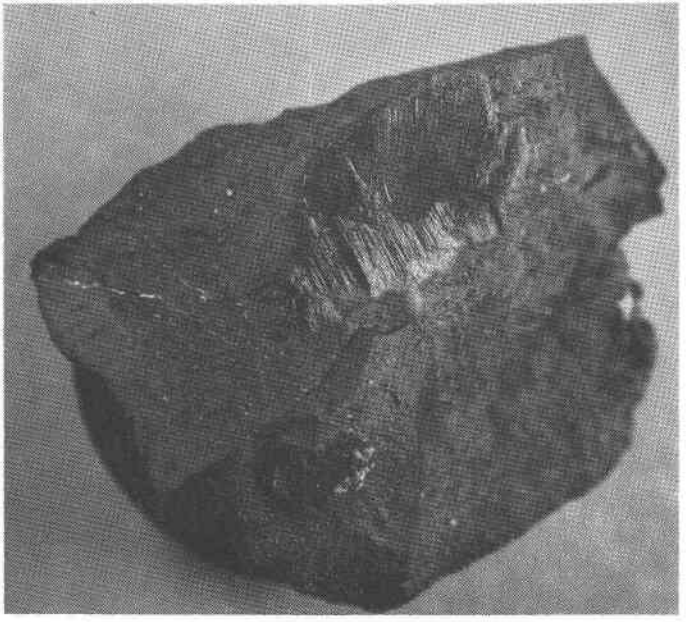

Fig. 1. Needles of cryptomelane in cavity. 5×.

tion of Mn^{+2}, Zn^{+2}, Al^{+3}, Cu^{+2}, Co^{+2}, and Fe^{+3} to maintain electrostatic balance). A chemical formula was not calculated for the matrix material, because of the relatively large amount of Fe_2O_3. Gruner (4) reports the chemical formula, $Mn^{4}_{7.4}(Mn^{2},R^{2})_{0.81}(K,Na)_{0.7}(Ba_{0.0216}\cdot(H_2O))_{1.31}$, and considered that H_2O molecules could also occupy the position of the "A" ions. Bystrom and Bystrom (5) gave the general chemical formula, $A_{(2-y)}B_{(8-z)}X_{16}$,* and suggested that a portion of these "A" positions may be vacancies. Mathieson and Wadsley (6) contend that sodium cannot replace potassium in the cryptomelane structure, but the present investigators consider sodium and potassium are somewhat interchangeable in this structure.

The compositions of the various specimens in Table 1 are similar in many respects. The presence of potassium, the absence of a significant amount of barium, and the fact that lead was not detected, establish that

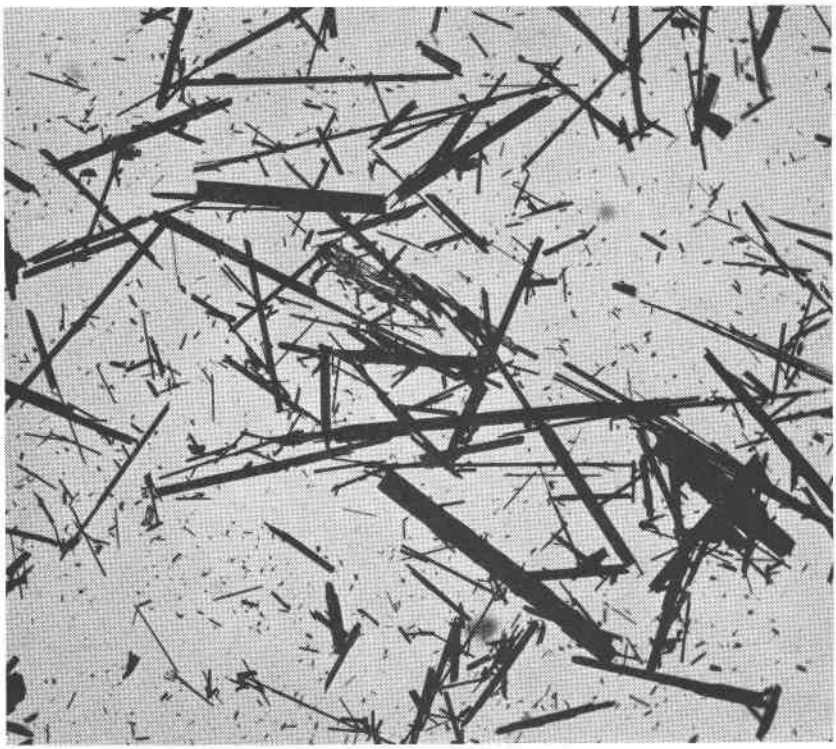

FIG. 2. Isolated fibers of cryptomelane needles. Transmitted light. 100×.

* In this formula y is approximately unity, z falls within the limits 0.1–0.5, A represents large ions, B represents small ions, and X represents O or OH anions.

TABLE 1. CHEMICAL ANALYSES OF CRYPTOMELANE SPECIMENS

	1	2	3	4	5	6
MnO_2	83.13	86.54	81.75	87.09	84.2	73.11
MnO	2.08	3.92	3.50	2.49	3.3	5.16
CuO	0.12	0.44	0.06	None	0.08	0.05
NiO	None	None	0.02	None	++	0.02
CoO	None	0.21	0.21	0.08	0.10	0.06
ZnO	5.23	None	None	1.69	++	None
MgO	0.05	None	0.02	0.07	0.08	0.06
BaO	0.13	1.04	None	None	0.08	0.29
SrO	None	0.21	None	None	++	0.16
CaO	0.27	0.30	0.28	None	0.05	
Na_2O	0.44	0.47	0.56	0.48	0.38	0.84
K_2O	3.5	3.88	3.84	3.10	4.4	2.35
H_2O	0.81	0.21	0.38	0.60	++	3.25
H_2O^+	2.58	1.62	3.45	3.58	++	
Al_2O_3	0.37	None	1.37	0.39	0.77	1.9
Fe_2O_3	0.46	0.36	4.00	0.19	1.86	10.3
SiO_2	0.58	0.03	0.35	0.18	0.30	3.0
TiO_2	0.01	None	None	None	++	0.88
P_2O_5	0.07	0.19	None	None	++	++
Total	99.83	99.42	99.79	99.94	95.6	100.4
Chemical Formula	$A_{0.7}R_8O_{16}$	$A_{0.79}R_8O_{16}$	$A_{0.74}R_8O_{16}$	$A_{0.64}R_8O_{16}$	$A_{0.8}R_8O_{16}$	

1. Tombstone, Arizona—Richmond and Fleischer.
2. Deeming, New Mexico—Richmond and Fleischer
3. Sugar Stick Prospect near Mena, Arkansas—Richmond and Fleischer.
4. Philipsburg, Montana—Richmond and Fleischer.
5. Cryptomelane needles—Western Australia—present investigators.
6. Matrix material—Western Australia—present investigators.

++ = not determined.

both the needles and matrix material are predominantly cryptomelane and not the isostructural minerals, hollandite (barium predominant in "*A*" type ions) or coronadite (lead predominant in "*A*" type ions).

The naturally-occurring mineral cryptomelane has not been reported without potassium, although Dubois (7) and Mathieson and Wadsley (6) report manganese oxides, having *x*-ray diffraction patterns like those of cryptomelane, can be produced in the absence of potassium.

X-RAY DIFFRACTION STUDIES

Fiber photographs revealed that the needles were not single crystals but bundles of acicular crystals all oriented randomly around a common *c* axis. This was confirmed by Weissenberg photographs.

Rotation photographs of needles oriented along the c axis could be indexed with the values reported by Ramsdell as body-centered tetragonal ($a_0=9.82$ Å, $c_0=2.86$ Å, $c/a=0.29$). Richmond and Fleischer (2) reported a body-centered tetragonal unit cell $a_0=9.82$ Å, $c_0=2.83$ Å, $c/a=0.288$. Mathieson and Wadsley (6) reported cryptomelane to be monoclinic ($a_0=9.79$ Å, $b_0=2.88$ Å, $c_0=9.94$ Å, $\beta=90°37$). The present Weissenberg photographs did not show any deviation from tetragonal symmetry, but this is not conclusive, since the needles always consisted of more than one crystal. Powder photographs also failed to reveal any monoclinic deformation of the unit cell. The optical properties of the needles suggest a pseudotetragonal (monoclinic?) symmetry, which would verify Mathieson and Wadsley's results. As Bystrom and Bystrom suggest, however, since the reported deviation of the monoclinic angle from 90° is very small, the monoclinic and tetragonal forms may be considered as essentially the same from an x-ray structural standpoint.

The x-ray diffraction powder patterns, using iron radiation, were obtained from the needles and the matrix material. In Table 2, the observed and calculated interplanar spacings and observed intensities of the x-ray diffraction powder pattern obtained from thoroughly crushed needles are compared to the powder and fiber data for cryptomelane reported by Ramsdell. It may be noted that (1) the powder data reported by Ramsdell account for approximately 50 per cent of the powder data reported by the present investigators, (2) the powder data of the crushed needles may be correlated with those of Ramsdell's, if his powder and fiber data are combined, and (3) the additional very weak reflections, not observed by Ramsdell, may be indexed with the unit cell he reported (body-centered tetragonal $a_0=9.82$ Å, $c_0=2.86$ Å, $c/a=0.29$).

X-ray patterns of the matrix surrounding the cryptomelane needles indicated the presence of cryptomelane, hematite, and quartz. The interplanar spacings and relative intensities of the cryptomelane in this sample and the powder data reported by Ramsdell are shown in Table 3. The lack of correlation of the relative intensities, particularly in the low angle range, is attributed, partially, to a difference in technique. Ramsdell's data were obtained from film measurements (CuKα and MoKα radiation), whereas, the present data were obtained with a diffractometer (iron radiation).

Thermal Transformations

There have been studies made on thermal transformations of various oxides of manganese, some of which include data concerning the thermal transformations of cryptomelane. However, no thermal studies have been made with naturally occurring, fibered cryptomelane. Cole, Wadsley, and

TABLE 2. *X*-RAY DIFFRACTION POWDER DATA FOR CRYPTOMELANE NEEDLES

$d_{(obs.)}$	Relative Intensity	*hkl*	$d_{(calc.)}$	Ramsdell $d_{(obs.)}$
6.94	S	110	6.944	6.92 (F & P)
4.92	S	200	4.910	4.91 (F & P)
3.48	W	220	3.472	3.47 (F & P)
3.10	S	130	3.105	3.11 (F & P)
2.45	W	400	2.455	2.46 (F & P)
2.39	M	121	2.389	2.40 (P)
2.32	VW	330	2.315	2.325 (F)
2.20	W	240	2.196	(2.205) (F)
				(2.210) (P)
2.15	M	301	2.148	2.16 (P)
1.97	VW	321	1.968	—
1.92	W	150	1.926	1.935 (F)
1.83	M	141	1.827	1.835 (P)
1.73	VW	440	1.736	1.74 (F)
1.69	VW	350	1.684	1.69 (F)
1.64	M	600	1.637	1.64 (F & P)
1.61	VW	501	1.617	—
1.54	M	260	1.553	1.55 (F)
		251	1.536	1.54 (P)
1.39	VVW	(170)		
		(550)	1.389	1.39 (F)
1.43	W	002	1.424	1.43 (P)
1.402	VW	611	1.405	—
1.350	VW	451	1.350	1.35 (P)
1.297	VW	370	1.290	1.295 (F & P)
1.232	VW	402	1.2317	1.24 (P)
1.215	VW	332	1.2128	1.22 (P)
1.193	VW	422	1.1947	—
1.158	VW	660	1.1573	(1.16) (F)
		561	1.1502	(1.15) (P)
1.116	VW	811	1.1199	—
1.075	W	190	1.0844	1.09 (F)

P = powder *x*-ray diffraction data.
F = fiber *x*-ray diffraction data.

Walkley (8) report that a cryptomelane, made by ammonia digestion of anodic deposits from the electrolysis of zinc sulfate solutions containing manganese as an impurity, was partially transformed to bixbyite* after heating at 500° C. for 13 hours. McMurdie and Golovato (9) studied the changes of cryptomelane by using differential heating curves and powder

* Bixbyite—chemical formula $(FeMn)_2O_3$—varies in composition from nearly pure Mn_2O_3 to 59% Fe_2O_3, cubic—$a_0 = 9.365$.

diffraction data. They reported that cryptomelane may convert directly to hausmannite* or may go through an intermediate stage of bixbyite, and considered this to be due to the effect of impurities. They also reported that a specimen of massive cryptomelane from Tombstone, Arizona transformed to an unidentified phase upon heating above 1200° C. and that a sample of high-purity pyrolusite (MnO_2) transforms to a Mn_3O_4 phase stable above 1170° C. This Mn_3O_4 phase has a spinel-type structure and an $a_0 = 8.70$ Å. Delano (10) also studied the transformations of natural cryptomelane and found that it converted first to bixbyite and then to hausmannite.

Although changes occurring upon heating cryptomelane powders have been reported, it was of interest to investigate the transformations by rotating crystal and fiber methods. These techniques would not only be expected to reveal changes in structure and crystal orientation, but should also show variations in crystal size. Some of the cryptomelane needles were heated at different temperatures for various times and air-cooled. The single-crystal photographs were made with copper radiation ($\lambda = 1.542$ Å). The long direction or the c axis of the original cryptomelane needle was mounted perpendicular to the x-ray beam.

Rotation photographs of the cryptomelane needles heated at either 500 or 600° C. for 2 hours were identical to those of the cryptomelane needles in their original state (Fig. 3*a*).† Upon heat-treatment at 600° C. for 5 hours the patterns showed the first evidence of the formation of Mn_2O_3.‡ A weak reflection corresponding to the interplanar spacing, $d = 2.72$ ($hkl = 222$), of this phase was evident on the zero layer of the rotation pattern of the cryptomelane. The elongation of this particular reflection in a direction parallel to the c axis of the cryptomelane in a fiber photograph indicated that the Mn_2O_3 phase consisted of small crystallites slightly misoriented perpendicular to the needle axis. It was also concluded from the fiber photograph that the randomness of orientations and crystallite sizes of the cryptomelane phase after this treatment were not different from those of the original cryptomelane needle.

A needle heated at 600° C. for 17 hours showed an increase in the amount of Mn_2O_3. The Mn_2O_3 was polycrystalline and highly orientated

* Hausmannite—chemical formula—

Mn_3O_4—Fe:Mn = 1:23 tetragonal $a_0 = 5.75$

$c_0 = 9.42$

† Cryptomelane is represented by the chemical formula KMn_8O_{16} in Figures 3 and 7 to emphasize the predominance of the K^+ and Mn^{+4} ions in this mineral.

‡ This transformation phase is regarded as Mn_2O_3, not bixbyite, since the original sample contains only 1.86% Fe_2O_3, and the x-ray data agree closely with those of the synthetic Mn_2O_3 reported by Gruner ($a_0 = 9.24$ Å) (11).

TABLE 3. *X*-RAY DIFFRACTION POWDER DATA FOR CRYPTOMELANE IN MATRIX MATERIAL

Matrix Material		Ramsdell's Powder	
$d_{(obs.)}$	$I_{(obs.)}$	$d_{(obs.)}$	$I_{(obs.)}$
6.94	7.6	6.92	W
4.92	7.6	4.91	W
3.48	1.5	3.47	VW
3.10	9.3	3.11	M
2.46	0.2	2.46	VW
2.39	10.0	2.40	S
2.20	3.0	2.21	W
2.15	6.8	2.16	W
1.83	7.0	1.835	M
1.64	3.3	1.64	W
1.54	2.9	1.54	M
1.43	1.2	1.43	W

in both the [100] and the [110] directions which coincided with the original [001] axis of the cryptomelane. No change in the randomness of orientation or crystallite size of the cryptomelane phase in the needles was evident from a fiber photograph. The fiber spots of the Mn_2O_3 phase were more elongated after the 17-hour treatment than after the 5-hour treatment, thus indicating an increase in the amount of randomness of orientations perpendicular to the needle axis with increasing time at this temperature.

After a heat-treatment at 700° C. for 2 hours, there was a definite increase in the amount of Mn_2O_3, and the Mn_2O_3 crystals were oriented slightly more in the [100] direction than in the [110] direction (Fig. 3*b*). Although this figure does not clearly show a difference in intensity corresponding to these orientations, it was quite evident on the original photograph. After 17 hours at 700° C., the amount of Mn_2O_3 increased markedly, and the amount oriented in the [100] and [110] directions appeared to be equal (Fig. 3*c*). When the time at 700° C. was increased to 68 hours, there was again a definite trend toward a preferred orientation in the [100] direction for the Mn_2O_3 phase, and since a fiber photograph showed that the elongated spots of the Mn_2O_3 were discontinuous, it appears that some recrystallization had taken place.

Mn_2O_3 was the only constituent detected in a cryptomelane needle heated at 800° C. for 17 hours. The rotation photograph showed the Mn_2O_3 to consist of small crystals more randomly arranged than in previous heat-treatments but with some preference for the [100] over the

[110] direction. Needles heated for 68 or 110 hours at 850° C. were similar to those heated at 800° C. for 17 hours. A heat-treatment at 875° C. for 24 hours, however, lessened the orientation of the Mn_2O_3 along the [110] axis appreciably (Fig. 4*a*).

Mn_3O_4 appeared as a minor constituent in a cryptomelane needle heated at 900° C. for $1\frac{1}{2}$ hours. The predominant constituent was Mn_2O_3 with the same preferred orientations as in the needles treated at 800° C. for 17 hours. There was a slight increase in the crystal size of the Mn_2O_3 after this heat-treatment as compared to that in the needles heated at lower temperatures. The Mn_3O_4 occurred as a group of crystals randomly oriented with a common [100] axis. The [100] axis of the Mn_3O_4 crystals was parallel to the [001] axis of the original cryptomelane needle.

A rotation photograph of a needle heat-treated to 1000° C. at a rate of 6° C./min., however, showed only Mn_3O_4 with a predominant orientation along the *a* axis, [100] (Fig. 4*b*). This heat-treatment was the only one

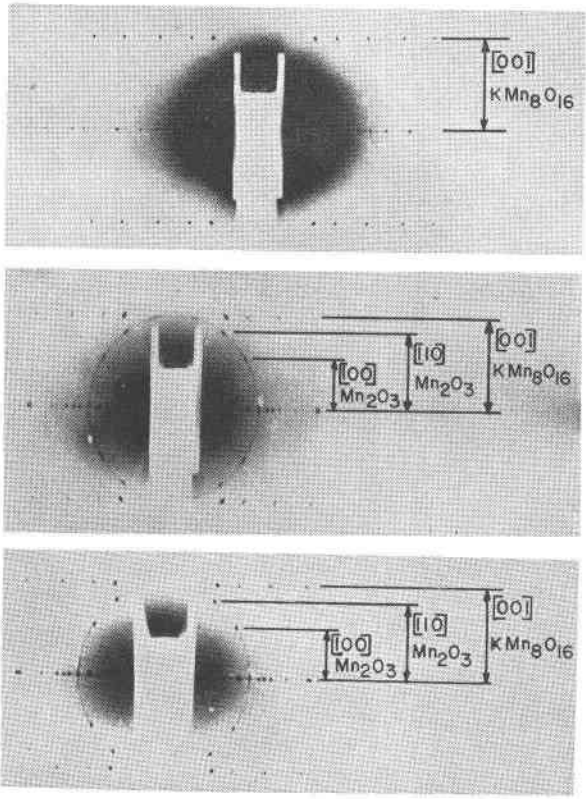

FIG. 3. Rotation patterns of cryptomelane needles. (*a*) As received, Cryptomelane; (*b*) 700° C. for 2 hours, Cryptomelane and Mn_2O_3; (*c*) 700° C. for 17 hours, Cryptomelane and Mn_2O_3.

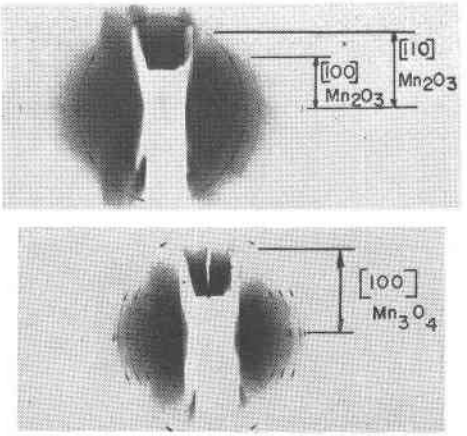

FIG. 4. Rotation patterns of heat-treated cryptomelane needles. (*a*) 875° C. for 24 hours, Mn_2O_3; (*b*) 1000° C. for 6 minutes, Mn_3O_4.

of those used that produced a rotation pattern of only Mn_3O_4. The temperature-time relationship appeared to be more critical for the formation of the Mn_3O_4 than the other thermal products.

Upon heating a cryptomelane needle at 900° C. for 17 hours, a phase with a cubic diffraction pattern similar to that of a spinel was obtained. The [110] axis of the spinel is parallel to the [001] axis of the original cryptomelane needle. The diffraction spots of the spinel are very diffused, indicating a high degree of structural imperfection. The major constituent is again Mn_2O_3 in a polycrystalline state, orientated primarily along its [100] direction.

The only constituent detected after heating the needles at 950° C. for 48 hours is the spinel in a polycrystalline state with a preferred orientation along its [110] axis. With an increase in time at 950° C. to 68 hours, the degree of orientation of the spinel along its [110] axis increases. A heat-treatment at 1000° C. for 92 hours produces a more random orientation of the crystallites of the spinel. The change in degree of orientation of the spinel with increasing time and temperature is shown in Fig. 5. In Table 4 are presented the powder diffraction data (iron radiation) and calculated interplanar spacings of the spinel.

The cell dimensions of the cryptomelane, Mn_2O_3, Mn_3O_4, and spinel remained constant throughout the described thermal treatments. The observed cell diminsions and orientations are represented schematically in Fig. 6.

THERMOGRAVIMETRIC STUDY

Thermogravimetric determinations were made in air with a rate of temperature increase of 6° C. per minute. The graphs obtained by plot-

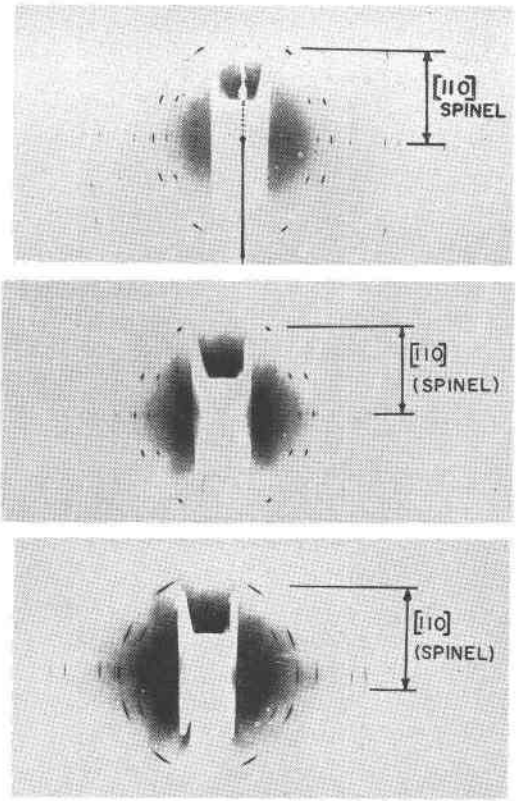

FIG. 5. Rotation patterns of cryptomelane needles heat-treated to produce "Spinel" phase.

ting weight loss versus temperature for the matrix material and the needles were similar. However, the weight loss values for the needles were less accurate because of the limited amount of sample.

A graph of the thermogravimetric results obtained from the matrix material is shown in Fig. 7. The weight loss due to adsorbed water (below 110° C.) is negligible and between 110 and 500° C. the loss of 2.5% is attributed to zeolitic water. (Chemical analysis shows a total water content of 3.25%.) The total weight loss recorded was 11.3%, and 8.8% of this occurred between temperatures of 500 and 1050° C. The theoretical weight loss due to oxygen in this sample for the transformation of MnO_2 and MnO in cryptomelane to Mn_3O_4 is 8.6%.

Cryptomelane needles were heated to 650, 850, 1000 and 1200° C. at the same rate of temperature increase (6° C./min.) used for the thermogravimetric determination. Powder photographs were made of these heat-treated samples. The results of this investigation are included in

TABLE 4. INTERPLANAR SPACINGS AND RELATIVE INTENSITIES FOR SPINEL FORMED BY HEAT-TREATMENT OF CRYPTOMELANE NEEDLES

h k l	$d_{(calc.)}$	$d_{(obs.)}$	$I_{(obs.)}$
111	4.86	4.86	5
220	2.98	2.98	5
311	2.54	2.54	10
222	2.42	2.43	1
400	2.10	2.10	5
422	1.719	1.718	2
511, 333	1.623	1.620	5
440	1.488	1.488	6
533	1.284	1.284	2
444	1.217	1.215	1
642	1.126	1.126	1
731, 553	1.099	1.096	4

Fig. 7. The powder photograph of the cryptomelane needles heated to 1000° C. (6° C./min.) revealed a trace of cryptomelane remaining. As previously noted, the rotation photograph of a needle heated under the same conditions showed only Mn_3O_4 (Fig. 4*b*). This indicates that a small amount of untransformed cryptomelane may be present in the core of the needles. The Mn_2O_3 phase was not detected after this heat-treatment.

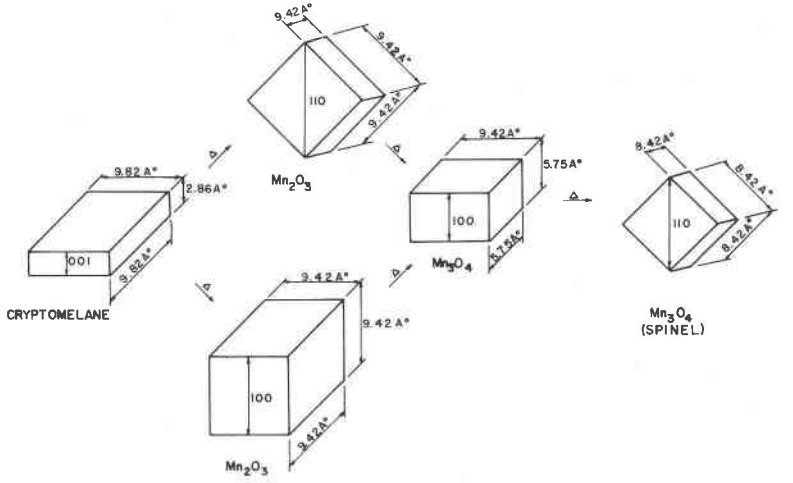

FIG. 6. Relationships of cell dimensions and orientations of thermal transformation products of cryptomelane.

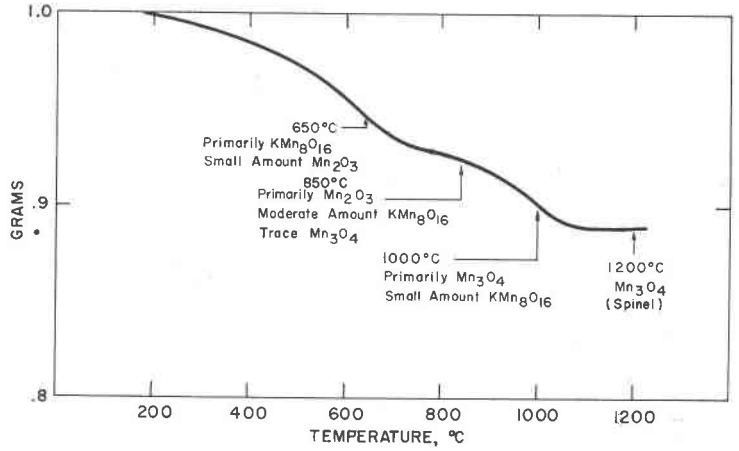

FIG. 7. Thermogravimetric results from matrix material.

probably because of the rapidity with which it transforms to Mn_3O_4 at this temperature.

A minimum rate of weight loss with temperature occurs between approximately 750 and 850° C. and a maximum rate between about 850 and 950° C. The minimum rate may be due to a slow rate of diffusion of oxygen through a relatively thick layer of Mn_2O_3.

The thermogravimetric data in correlation with the phases present indicate that cryptomelane, at a heating rate of 6° C. per min., does not transform completely to Mn_2O_3 before formation of Mn_3O_4 begins, and that Mn_3O_4 forms from the intermediate Mn_2O_3 phase. At this heating rate, the critical temperature for formation of Mn_2O_3 from the needles is approximately 600° C., for the Mn_3O_4 approximately 825° C., and for the spinel approximately 1050° C.

SUMMARY

Cryptomelane needles and their surrounding matrix material were examined. Chemical analyses established that the needles and the principal constituent in the matrix material were cryptomelane. Fiber photographs revealed the needles were bundles of crystals randomly oriented around a common c axis. X-ray diffraction data from powder patterns of the needles are tabulated and indexed in terms of a body-centered tetragonal cell, although optical data indicate a pseudotetragonal cell.

The cryptomelane needles were heat-treated at various temperatures for different times and examined by rotation and fiber methods. A manganese oxide phase with a spinel-type structure, $a_0 = 8.42$ Å, occurs after

heating the needles at temperatures greater than 900° C. for prolonged times. The following representation shows the thermal transformations and relative orientations parallel to the [001] axis of cryptomelane.

$$\underset{\text{cryptomelane}}{[100]} \xrightarrow{\Delta} \underset{Mn_2O_3}{\overset{[110]}{[100]}} \xrightarrow{\Delta} \underset{Mn_3O_4}{[100]} \xrightarrow{\Delta} \underset{\substack{\text{Spinel} \\ (R_3O_4\ \text{type})}}{[110]}$$

Thermogravimetric data, correlated with identified phases, indicate that the Mn_3O_4 phase forms from the Mn_2O_3 phase. At a heating rate of 6° C. per minute, the critical temperature for formation of Mn_2O_3 from the cryptomelane needles is approximately 600° C., for Mn_3O_4, approximately 825° C., and for the spinel, approximately 1050° C.

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