SYNTHESIS OF SOME HYDRATED MANGANESE MINERALS

A. D. WADSLEY, *Commonwealth Scientific & Industrial Research Organisation, Melbourne, Australia.*

ABSTRACT

Attempts have been made to synthesize the minerals psilomelane, cesarolite, ranciéite, chalcophanite, lithiophorite, and lampadite by hydrothermal alteration of the metallic derivatives of a hydrous manganese oxide. The compounds prepared are compared by chemical, x-ray, and electron microscopic methods with mineral specimens, and the conclusions which are drawn offer some evidence for the paragenesis of these minerals.

The term "psilomelane type" has been suggested as a general name for those manganese oxide minerals which are hard, dense, and which generally lack distinctive features (6). Those which are soft and of low apparent specific gravity retain the name "wad" which has been used in a wider sense to describe any manganese material containing much water. It has been realized for many years that these massive materials may contain considerable quantities of other metals, and until x-ray diffraction methods had been applied to their study, it was doubtful whether the metals were present as discrete impurities or as lattice constituents.

Within these groups, several hydrated manganese minerals are regarded as distinct species. These are listed in Table 1 with the formulae and crystalline habits proposed in the literature. It must be emphasized, however, that these formulae, apart from that for psilomelane, are by no means fully established.

TABLE 1. HYDRATED MANGANESE OXIDE MINERALS CONTAINING OTHER METALS

Mineral	Formula	Crystal System
Chalcophanite	$(Mn, Zn)Mn_2O_6 \cdot 2H_2O$	Hexagonal (?)
Lithiophorite	$LiMn_3Al_2O_9 \cdot 3H_2O$	Hexagonal (?)
Ranciéite	$(Mn, Ca)Mn_4O_9 \cdot 3H_2O$	
Cesarolite	$PbMn_3O_7 \cdot H_2O$	
Psilomelane	$MnBaMn_8O_{18} \cdot 2H_2O$	Orthorhombic

The metals other than manganese are major constituents which may be partly replaced by small amounts of other metals. Cobalt is often present in lithiophorite and psilomelane, copper and trivalent iron are common replacement elements, but no acceptable evidence has been produced to show that these metals are major constituents of hydrated manganese minerals.

Very little is known of these minerals. Psilomelane occurrences are common (6) and x-ray work on single crystals has been described (21).

Cesarolite has been reported only from one locality (1) but no x-ray examination is recorded; ranciéite is accredited as a mineral species (18) but no chemical analyses are given; lithiophorite, identified during an examination of psilomelane-type minerals (17) has since been found as well developed crystals (22); while chalcophanite, may be recognized from optical evidence (16).

Although none of these minerals has been synthesized, a group of "metal permanganites" is reported by Mellor (11). The derivatives of calcium, zinc, copper, aluminium and other metals, similar to those prepared originally as chemical precipitates by Sarkar and Dhar (20), have been examined by x-ray powder photographs (4), but little resemblance is borne by these to the appropriate mineral. Gorgeu prepared many hydrated manganese derivatives (8) and noted a chemical similarity to asbolite and lampadite in the cobalt and copper "permanganites," but these two minerals have yet to be accredited.

The writer has recently described a hydrous manganese oxide with the formula $(Na,Mn)Mn_3O_7 \cdot nH_2O$ (23). The powder diffraction data indicated a hexagonal cell with the dimensions $a = 8.41$, $c = 10.1$ Å, and with four molecules in the unit cell. The sodium ions are irreversibly exchanged for those of other metals from solutions of their salts, and this change is usually accompanied by a small decrease in the c axis dimension.

There is a strong chemical resemblance of each of these metal derivatives to the corresponding hydrated mineral listed in Table 1. Recrystallization of the derivatives in some instances may occur, accompanied by structural and minor chemical changes. These experiments will be described in some detail, and compared with mineral specimens on chemical and x-ray evidence.

EXPERIMENTAL

The preparation of the hydrous oxide $(Na,Mn)Mn_3O_7 \cdot nH_2O$ by the oxidation with oxygen of a suspension of manganous hydroxide has been described (23). Metal derivatives are readily formed by agitation with an excess of a 10% solution of the metal salt for 24 hours at room temperature, washing till free from soluble salts, and drying by the aspiration of air. On heating to 200° C. the sodium oxyhydrate and its derivatives lost some water, and the powder pattern of manganous magnanite ($MnO_{1.7-1.8}$) is found. Sarkar and Dhar's (4) preparations also give this pattern.

Recrystallization of some of the derivatives may, however, be readily induced by simple hydrothermal treatment. Sealed glass tubes were found suitable for temperatures up to 200° C. For alkaline solutions or higher temperatures, small stoppered stainless steel cylinders were employed.

X-ray patterns were taken on a General Electric XRD unit with a 14.3 cm. camera using Fe radiation filtered with Mn ($\lambda = 1.937$). Because preparations such as these may contain amorphous oxides which would not be revealed by the powder patterns, electron micrographs where necessary were taken by Mr. J. L. Farrant, Division of Industrial Chemistry, C.S.I.R.O. on an R.C.A. type E.M.U. microscope, to confirm homogeneity. Electron diffraction patterns of the recrystallized barium and lead derivatives were obtained by Mr. J. Spink, Division of Tribophysics, C.S.I.R.O.
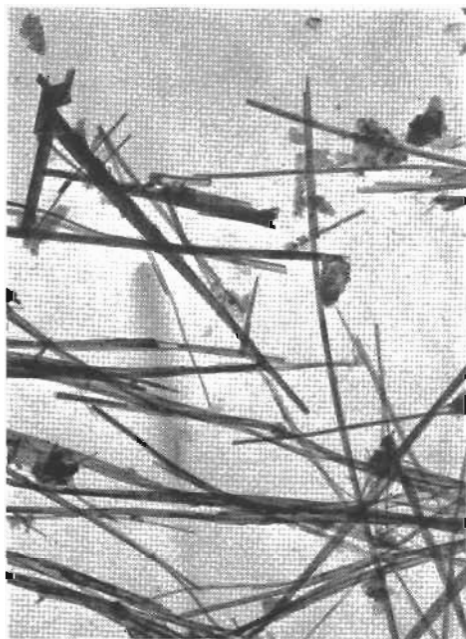

FIG. 1. Electron micrograph of synthetic psilomelane ($\times 20,000$).

BARIUM DERIVATIVE AND PSILOMELANE

Psilomelane is readily synthesized by heating the barium derivative at 160° C. for several weeks with a solution containing 1% of barium and manganese chlorides. Electron micrographs show that the synthetic mineral is mainly composed of needles, occasionally twinned, which although attaining a length of several microns, are not resolved by the ore microscope.

The weak *x*-ray powder photograph was identical with that of the mineral published by Fleischer and Richmond (6), but the electron dif-

fraction pattern was much sharper. This was measured accurately on a recording photometer, and the ring diameters could all be indexed using Vaux's figures for the cell dimensions of orthorhombic psilomelane (21).

$$a = 9.1, \ b = 13.7, \ c = 2.86 \ Å.$$

There was insufficient material for a complete chemical analysis of the synthetic mineral. The determinations made are given in Table 2 together with those for the barium manganate from which it was derived, and a massive psilomelane specimen from Pilbara, Western Australia. The latter was examined optically and found to be homogeneous and fibrous in structure.

TABLE 2. ANALYSIS OF PSILOMELANE

	1	2	3
MnO_2	61.8	62.9	74.36
MnO	11.8	7.6	6.10
BaO	19.6	14.4	13.49
$H_2O_{+120°}$	7.6	N.D.	5.14
K_2O	—		0.81
$(Fe, Al)_2O_3$			0.59
Total	100.8	84.9	100.49
Specific Gravity	4.1	4.4	4.61

1. Barium derivative of $(Na, Mn)Mn_3O_7 \cdot nH_2O$.
2. Recrystallized barium derivative. Contains much loosely held water.
3. Psilomelane, Pilbara, Western Australia.

The atomic ratios $Mn^{4+} : Mn^{2+} : Ba : O$ are $7.90 : 1.16 : 1.02 : 18$ for the synthetic mineral (analysis 2), and $8.14 : 0.82 : 1.00 : 18$ for the Pilbara specimen (analysis 3) assuming that potassium substitutes for barium. These agree reasonably well with the formula $MnBaMn_8O_{18} \cdot 2H_2O$ which has previously been ascribed to this mineral, although the water in analysis 3 is high. The density calculated from this formula and Vaux's dimensions is 4.42, somewhat lower than that measured for this and other mineral specimens. Recrystallization of the barium derivative (analysis 1) is accompanied by the loss of some barium.

When heated to 550°, the synthetic mineral gives a substance with the powder pattern of hollandite. This agrees with Fleischer and Richmond's observation that hollandite $(BaMn_8O_{16})$ is formed as the dehydration product of psilomelane (6).

LEAD DERIVATIVE

The lead derivative was readily recrystallized by heating at 160° C. for six weeks in a 1% solution of lead and manganese nitrates. The chemical composition resembled that of cesarolite.

TABLE 3. ANALYSIS OF CESAROLITE AND SYNTHETIC CORONADITE

	1	2	3	4
MnO_2	53.3	53.11	60.80	51.40
MnO	9.3	5.23	7.12	0.62
PbO	33.3	37.30	28.66	39.09
$H_2O_{+120°}$	3.7	3.56	1.11	3.30
Remainder			2.31	3.66
Total	99.6	99.20	100.00	98.07
Density	5.5	5.94	5.25	5.29

1. Lead derivative of $(Na,Mn)Mn_3O_7 \cdot nH_2O$.
2. Recrystallized lead derivative (synthetic coronadite).
3. Coronadite, Arizona. W. F. Hillebrand analysis (recalc.) in Lindgren and Hillebrand (10). Remainder = Cu, Al, Fe, Zn.
4. Cesarolite, Tunisia. Recalculated from the data of Buttgenbach and Gillet (1). Remainder = Al, Fe, Na, other metals, insoluble.

X-ray powder photographs were very weak, but the electron diffraction pattern of the recrystallized derivative was similar to that of coronadite given by Frondel and Heinrich (7). Although most coronadite specimens contain water, it is considered to be non-essential (6, 7), and a discussion of this preparation is therefore outside the scope of this account.

ZINC DERIVATIVE AND CHALCOPHANITE

Chalcophanite could not be prepared by autoclaving the zinc derivative of $(Mn,Na) Mn_3O_7 \cdot nH_2O$ at 160° with a 1% solution of zinc and manganese chlorides. With this treatment the pattern of hetaerolite with some additional lines (hydrohetaerolite?) is observed. This decomposes to pale brown hetaerolite if the temperature is raised to 300° C. Crystalline chalcophanite loses water readily at 100° C., and is completely dehydrated on heating to 200° C (15); it is thus certain that this recrystallization was attempted at too high a temperature.

A further quantity, autoclaved at 80° with the same solution, showed after six months some additional lines in the diffraction pattern common to the strongest chalcophanite lines. It is considered that complete re-

crystallization would take a much longer period to complete, probably accompanied by further oxidation.

Table 4 gives the analysis of the zinc derivative. An analysis of a crystalline chalcophanite from Buchan, Victoria, which agrees well with the formula $ZnMn_3O_7 \cdot 3H_2O$ is also included. The tentative new formulation of chalcophanite will be discussed in more detail at some future date, when this specimen will be more fully described.

TABLE 4. ANALYSIS OF ZINC DERIVATIVE AND CHALCOPHANITE

	1	2
MnO_2	65.9	65.39
MnO	12.3	0.22
ZnO	14.8	18.19
$H_2O_{\pm 120}{}^{\circ}$	6.0	13.09
Fe_2O_3		0.32
Al_2O_3		0.39
SiO_2		1.88
Total	99.0	99.48
Specific Gravity	4.0	3.70

1. Zinc derivative of $(Mn, Na)Mn_3O_7 \cdot 2H_2O$.
2. Chalcophanite crystals, Buchan, Victoria.

COPPER DERIVATIVE AND LAMPADITE

Lampadite is the name given in a general sense to the cuprian wads (3) but no evidence for the existence of a hydrated copper manganese mineral based on x-ray identification has been recorded.

A cuprian wad of unknown origin, loaned from the University of Adelaide, was found by H. R. Samson on optical examination to consist of a very close intergrowth of two minerals, one black and opaque (manganiferous), the other consisting of transparent green crystals. Separation could not be effected by physical means, but a powder pattern identified the consitutents as dioptase and poorly crystallized lithiophorite. Chemical analysis (Table 5, column 3) gave the $CuO:SiO_2$ ratio as $0.361:0.356$ (very nearly $1:1$), and it seems evident that no significant quantity of copper is present in the manganese mineral. The composition of the lithiophorite (Table 5, column 4) was found by subtracting $CuO \cdot SiO_2 \cdot H_2O$ from the total analysis.

Attempts to synthesize lampadite met with no success. The copper derivative of $(Mn,Na)Mn_3O_7 \cdot nH_2O$ was readily formed, the analysis of which, given in Table 5, is very similar to that of a cuprian wad re-

corded in Dana (3, p. 567). The powder pattern resembled that of manganous manganite. Autoclaving at 160° C. with a mixed solution of copper and manganous sulfates gave copper-free manganite (MnOOH) in close association with small green crystals of a basic copper sulfate. The similarity in appearance of this preparation to that of the dioptase-lithiophorite specimen was most striking, and suggested that the two materials were formed under similar circumstances.

TABLE 5. ANALYSIS OF COPPER DERIVATIVE AND LAMPADITE

	1	2	3	4
MnO_2	65.4	58.77	15.14	34.9
MnO	7.5	9.59	2.65	6.1
CuO	18.8	11.48	28.74	
CoO			1.32	3.0
Fe_2O_3			1.89	4.4
Al_2O_3			8.06	18.6
SiO_2			21.38	
K_2O*			0.37	0.9
$H_2O_{+120}°$	N.D.	21.05	8.19	3.9
$H_2O_{-120}°$	N.D.		11.90	27.4
Total	91.7	100.89	99.64	99.2

* The mixed alkalis in this analysis reported as K_2O–Li present.
1. Copper derivative of $(Na,Mn)Mn_3O_7 \cdot nH_2O$.
2. Lampadite. Dana p. 567 Analysis 6.
3. Dioptase-lithiophorite specimen, South Australia.
4. Analysis 3 corrected for dioptase ($CuO \cdot SiO_2 \cdot H_2O$).

ALUMINIUM DERIVATIVE AND LITHIOPHORITE

The aluminium-lithium derivative was readily recrystallized by heating at 160° for three weeks in a solution containing 1% each of lithium chloride and aluminium sulfate.

Electron micrographs of the derivative were similar to those of the parent hydrous oxide. They consist of series of very thin overlapping films of oxide (Fig. 2), which is characteristic of materials showing a marked c axis development. The recrystallized derivative was made up of large hexagonal prisms with well developed facial angles of approximately 120° (Fig. 3). Figure 4 shows a flake of lithiophorite (Postmasburg, South Africa) from a specimen originally described by deVilliers and van der Walt (22), who generously made some of their material available.

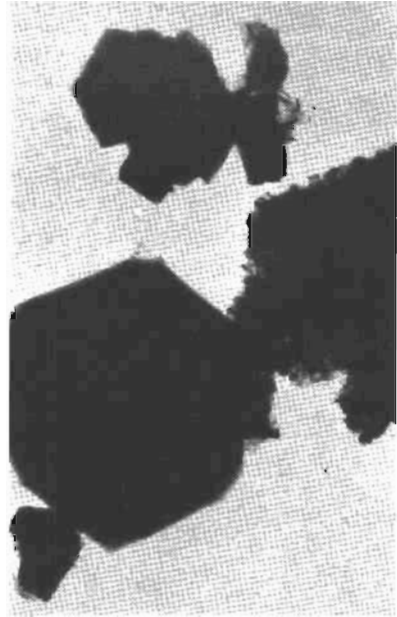The chemical compositions of these derivatives, the Postmasburg
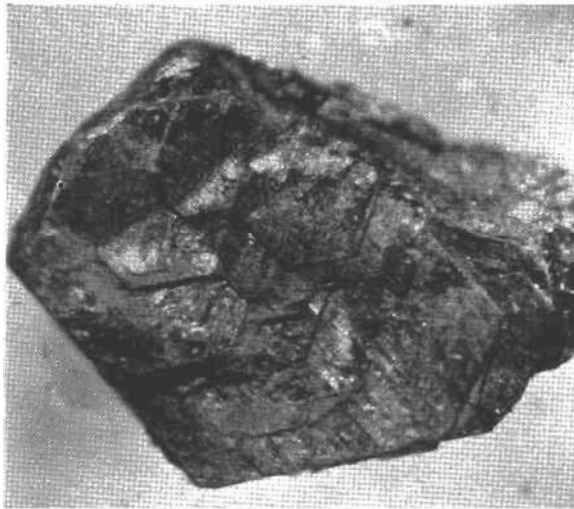
FIG. 2. FIG. 3.

FIG. 4.

FIG. 2. Electron micrograph of the aluminium-lithium deriva-
tive of $(Mn,Na)Mn_3O_7 \cdot nH_2O \cdot$ ($\times$20,000).
FIG. 3. Electron micrograph of the aluminium-lithium deriva-
tive recrystallized under hydrothermal conditions ($\times$12,000).
FIG. 4. Lithiophorite, Postmasburg, South Africa. ($\times$50). (Photograph J. Weymouth.)

specimen, and a new analysis of a cobaltian lithiophorite from New Caledonia containing some free goethite as impurity are given in Table 6.

TABLE 6. ANALYSIS OF ALUMINIUM/LITHIUM DERIVATIVES AND LITHIOPHORITE

	1	2	3	4
MnO_2	57.9	68.18	48.96	35.71
MnO	14.0	7.14	8.20	2.92
Al_2O_3	17.9	15.42	23.84	19.22
Fe_2O_3		—	0.96	15.95
Li_2O	0.22	Present	3.30	0.51
CoO		—	—	6.99
$H_2O_{+120}°$	9.9	8.32	13.15	11.97
$H_2O_{-120}°$		0.73	1.45	4.72
SiO_2		—	0.30	1.63
Total	99.9	99.79	100.16	99.62
Density	3.6	3.95	3.37	N.D.

1. Aluminium/lithium derivative of $(Na,Mn)Mn_3O_7 \cdot nH_2O$. Corrected for $H_2O_{-120}°$.
2. Recrystallized derivative. Insufficient for accurate Li_2O determination.
3. Lithiophorite, Gloucester, South Africa. Analyst C. F. J. van der Walt (22).
4. Lithiophorite, New Caledonia (with some goethite).

The differences in composition between the mineral specimens (including the one associated with dioptase and recorded in Table 5) and the recrystallized derivative is reflected in the x-ray evidence. The powder diffraction patterns of the synthetic materials and the South African specimen are given in Table 7, together with tentative indices, unit cell dimensions and densities calculated from formulae developed from the chemical data.

Laue patterns of the Postmasburg specimen confirmed the hexagonal symmetry suggested by deVilliers and van der Walt, and the powder pattern resembled that of lithiophorite reported by Fleischer and Richmond (6).

It is uncertain whether the c dimension is 9.39 Å or twice this value. The unit cell contents will be either $(Li,Mn,Al)_2O_3 \cdot H_2O$ or $(Li,Mn,-Al)_4O_6 \cdot 2H_2O$ with the possibility that lithium substitutes for aluminium as it may do in the micas.

The axes given for this mineral will not fit the other lithiophorite specimens which have been examined. A complete index of the lines of the New Caledonia and of the dioptase-associated specimens is not possible because of confusion due to the lines of the other minerals present, but the well developed (0001) lines permit the c dimensions to

TABLE 7. X-RAY POWDER DATA FOR ALUMINIUM DERIVATIVE AND LITHIOPHORITE

	1			2			3			4	
I	d	$hkil$	I	d	$hkil$	I	d	$hkil$	I	d	$hkil$
S	10.0	(0001)	S	9.78	(0001)	M	9.66	(0001)	M	9.45	(0001)
W	7.28	(10$\bar{1}$0)	VW	7.46	(10$\bar{1}$0)	M	4.97	(10$\bar{1}$1)	S	4.70	(0002)
M	5.06	(0002)	MW	4.85	(0002)	MS	4.76	(0002)	MW	3.123	(0003)
VW(d)	4.76		VW(d)	3.26	(0003)	W	3.51	(10$\bar{1}$2)	MW	2.385	(0004)
W(d)	3.47	(20$\bar{2}$1)	M	2.458	(0004)	MS	2.988	(11$\bar{2}$1)	M	1.882	(0005)
W	3.372	(0003)	MW	2.071	(31$\bar{4}$0)	M	2.385	(0004)	W	1.508	(10$\bar{1}$5)
W(d)	2.500	{(0004)} {(20$\bar{2}$3)}	MW	2.031	(31$\bar{4}$1)	W	2.255	(11$\bar{2}$3)	VW	1.459	(11$\bar{2}$0)
W	2.429	(30$\bar{3}$0)	W(d)	1.79	(22$\bar{4}$3)	M	1.903	(0005)	VW	1.445	(11$\bar{2}$1)
W(d)	2.38	(10$\bar{1}$4)	VW(d)	1.63	(0006)	M	1.887	(30$\bar{3}$0)	VW	1.396	(11$\bar{2}$2)
VW(d)	2.14	(21$\bar{3}$3)	S	1.421	(31$\bar{4}$5)	MW	1.752	(30$\bar{3}$2)	W	1.229	{(20$\bar{2}$2)} {(11$\bar{2}$4)}
VW(d)	1.85	(21$\bar{3}$4)				VW	1.648	(11$\bar{2}$5)	VW	1.171	(0008)
MW	1.472	(40$\bar{4}$4)				VW	1.582	(20$\bar{2}$5)	VW	1.154	(11$\bar{2}$5)
W	1.420	(0007)				VW	1.489	(31$\bar{4}$2)			
						VW	1.480	(30$\bar{3}$5)			
						W	1.457	(22$\bar{4}$3)			
						VW	1.393	(40$\bar{4}$1)			
						VW	1.373	(0007)			
						VW	1.286	(32$\bar{5}$1)			
						VW	1.241	(22$\bar{4}$5)			
						VW	1.199	(0008)			

	1	2	3	4
Crystal System	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Axial Dimensions (Å)	$a=8.41$ $c=10.1$	$a=8.59$ $c=9.7$	$a=6.52$ $c=9.56$	$a=2.92$ $c=9.39$ or 18.78
Unit cell volume (Å)³	620	624	351	69 or 138
Density (Obs)	3.8	3.6	3.95	3.37
Density (Calc)	3.77	3.86	3.96	3.42
Unit cell contents	$(Na,Mn)_4Mn_{12}O_{28} \cdot 8H_2O$	$Al_5Mn_{13}O_{28} \cdot 8H_2O$	$(Li,Al,Mn)_4Mn_6O_{18} \cdot 4H_2O$	$(Li,Al)MnO_3 \cdot H_2O$ or $(Li,Al)_2Mn_2O_6 \cdot 2H_2O$

S = Strong, MS = Med. strong, M = Medium, MW = Med. weak, W = weak, VW = Very weak, (d) = diffuse.
1. Manganese oxyhydrate.
2. Aluminium lithium derivative of 1.
3. Recrystallized derivative.
4. Lithiophorite, Gloucester, South Africa.

be calculated. The values 9.50 ± 0.04 and 9.68 ± 0.04 Å, respectively, which are found suggest that the structure may be variable, which, in view of the wide variety of composition suggested to the writer by Dr. M. Fleischer (5) is not surprising.

The chemical composition of the recrystallized derivative differs considerably from that of the minerals examined, and consequently both a and c dimensions differ from those of the South African specimen. The unit cell volume is almost exactly five times that of the mineral specimen, and this together with the general similarity of the empirical formulae, suggest that they are members of series capable of considerable variation.

Calcium Derivative and Rancíéite

Although many naturally occurring psilomelane-type and wad minerals have been examined, no rancíéite has been found. The calcium derivative of the parent manganese oxyhydrate may however be given the formula $(Ca,Mn)Mn_4O_9 \cdot 5H_2O$ as can be seen from Table 8.

Table 8. Analysis of Calcium Derivative

	1	2
MnO_2	70.0	69.8
MnO	3.6	3.9
CaO	7.7	8.2
$H_2O_{+120°}$	17.7	18.1
Total	99.0	100.0
Density	3.7	

1. Calcium derivative of $(Na,Mn)Mn_3O_7 \cdot nH_2O$.
2. Calculated from $(Ca,Mn)Mn_4O_9 \cdot 5H_2O$ with $Ca:Mn^{++}=8:3$.

No recrystallization of this material could be effected. When autoclaved with calcium and manganous chlorides at 160° C., a phase change to a calcian manganite identical in most respects with the mineral MnOOH was observed, while heating at a low temperature in air or in a closed tube without additional water resulted in the development of the bixbyite structure. Autoclaving at 80° C. for six months produced very little change in the x-ray data.

The powder pattern differs appreciably from that of the parent oxyhydrate, but most of the lines can be indexed as belonging to a hexagonal cell with the dimensions $a = 8.44$, $c = 9.87$ Å.

The scarcity of $(hk\bar{i}l)$ reflections is characteristic of a very disordered

structure, and it may well be that the formula which has been given assigns too many molecules of water to the material. A lesser degree of hydration would lead to better agreement between the calculated and observed density values.

This pattern differs in many respects from the published data for ranciéite (6). While it would be speculative to say that the powder patterns appear to be derived from similar structures, the similarities in composition between the calcium derivative and corresponding values in the brief reports which have appeared on ranciéite (18) suggest they are closely related.

TABLE 9. X-RAY POWDER DIFFRACTION DATA FOR CALCIUM DERIVATIVE OF
$(Na,Mn)Mn_3O_7 \cdot 2H_2O$

Observed		Calculated	
Intensity	*d* (Å)	*d* (Å)	*hkil*
S	7.17	7.17	(1000)
VW(d)	4.8		
W(d)	3.57	3.59	(2000)
VW	2.57	2.576	(11$\bar{2}$3)
W	2.468	2.468	(0004)
W	2.414	2.426	(20$\bar{2}$3)
VW(d)	2.3		
M	2.069	2.071	(22$\bar{4}$0)
MW	2.029	2.034	(20$\bar{2}$4)
VW	1.804	1.794	(4000)
VW	1.461	1.451	(40$\bar{4}$4)
VW	1.410	1.411	(0007)
VW(d)	1.26		

S = strong, M = medium, MW = Med. weak, W = weak, VW = very weak, (d) = diffuse.

System	Hexagonal
Unit cell dimensions (Å)	$a = 8.44$
	$c = 9.87$
Unit cell volume (Å^3)	609
Density (Calc.)	4.06
Density (Obs.)	3.7
Unit cell contents	$(Mn,Ca)_3Mn_{12}O_{27} \cdot 15H_2O$

THE DERIVATION OF THE HYDRATED MANGANESE MINERALS

From comparisons of the chemistry and mineralogy of the higher manganese oxyhydrates it is possible to deduce how these minerals may have been formed.

The oxyhydrate $(Mn,Na)Mn_3O_7 \cdot nH_2O$ is metastable, losing some

water at a low temperature to form the more stable "manganous manganite" (23). The similarity between this substance and a mineral specimen has recently been demonstrated (19).

On the other hand it will readily form loose hydrous complexes with metals which, while not giving close fitting formulae, may in most cases be represented as $(R,Mn)Mn_3O_7 \cdot nH_2O$, where R is the added metal (23).

Earthy manganese material commonly known as wad may contain considerable amounts of other metals. It is most likely that these substances were formed either by substitution of the "foreign" ion in a hydrous oxide formed naturally by the oxidation of $Mn(OH)_2$ or else by the oxidation with air of mixed sols of $Mn(OH)_2$ with other hydroxides. Although single ionic species in our experiments have been exchanged for sodium in the parent oxide, there is no reason why two or more metals should not be substituted, and the presence of barium, cobalt, tungsten, vanadium, etc., which are common constituents of the wads and other manganese minerals, would be due to this ready substitution.

If the wad so formed is not subjected to further change by heat, pressure, or any violent means of oxidation, then its structure will bear some resemblance to that of the parent hydrous oxide. Although some very soft wads have been examined in this laboratory, x-ray powder patterns show mainly the mineral impurities present, although some additional very diffuse lines similar to those reported by Smitheringale (24) and more recently by McMurdie and Golovato (13) may be observed *if they are sought*. These lines are characteristic of delta-MnO_2 (12), the relationship of which to manganous manganite has been discussed previously (2).
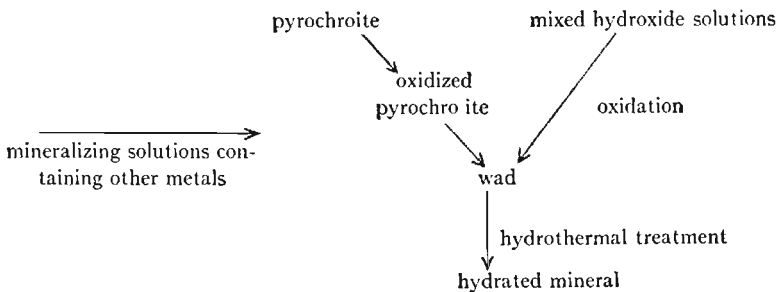
Autoclaving the derivatives at a low temperature in some instances induces rearrangement of the disordered lattice to that of the more stable and sharply defined mineral species, accompanied in some instances by slight changes in composition. Psilomelane can certainly be formed in this way; coronadite and a compound closely resembling lithiophorite may similarly be synthesized; chalcophanite and ranciéite will probably be formed by recrystallization after prolonged autoclaving at a low temperature. The failure of synthesize lampadite does not necessarily mean that this mineral may not exist.

These minerals, seldom found except as massive specimens (i.e. microcrystalline) could well be formed from the hydrous wad with which they are often associated, by hydrothermal alteration, pressure, or perhaps simply by ageing under oxidizing conditions. The rarer crystalline deposits were presumably formed only under conditions where the mangenese and other metals were slowly precipitated from solutions which were saturated with oxygen, perhaps at elevated temperatures.

This theory, derived from chemical experiments, has some support from geological evidence. The crystalline lithiophorite from the Postmasburg deposits was considered by deVillers to be formed directly from solutions of magmatic origin and not by the weathering of an anhydrous mineral. Chalcophanite which may be formed as an alteration product of hetaerolite and franklinite (14) has been reported free of these minerals (9), and has been found by Mr. H. R. Samson and the writer in a manganese deposit in the Buchan District, Victoria, intimately associated with lithiophorite. In this latter case the two minerals undoubtedly crystallized simultaneously, and the conditions for their formation would therefore be identical. The "asbolite" specimen, shown to be an association of dioptase and lithiophorite, most probably was formed by the action of siliceous solutions on a cuprian wad, which removed the copper to form another mineral (dioptase) in much the same way as basic copper sulfate was formed in the laboratory by autoclaving the copper derivative. Psilomelane may be regarded as recrystallized barium wad, and owing to the relative ease with which it is transformed to hollandite, is probably a necessary phase in the paragenesis of this mineral. Little can be said of cesarolite or ranciéite, but their formation as crystalline minerals could occur by the methods which have been suggested.

These minerals are made conspicuous by the presence of metals other than manganese. When there are no substituents, the hydrous oxide $(Mn,Na)Mn_3O_7 \cdot nH_2O$ can be further oxidized at a low temperature only to manganous manganite, or possibly to delta-MnO_2. It is suggested that pyrolusite, cryptomelane, ramsdellite and γ-MnO_2, each of which requires special conditions for its synthesis in the laboratory could be formed on a geological scale at a more elevated temperature, under acid conditions, or perhaps by bacterial oxidation. Consequently the mineral, reported by Samson and Wadsley (19) to resemble manganous manganite may be regarded as a link in the mineralogy of the manganese oxides.

This generic scheme may be represented diagrammatically:

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