

## A MANGANESE OXIDE MINERAL FROM BUCHAN, VICTORIA

H. R. SAMSON\* AND A. D. WADSLEY\*

### ABSTRACT

A manganese mineral occurring as dense nodules intimately associated with hematite is found in Eastern Victoria. The mineral is of the psilomelane type and possesses a colloform texture. X-ray powder patterns and chemical analysis indicate a mineral species corresponding closely to an oxide prepared in the laboratory and previously named manganous manganite.

The manganese ore minerals studied were obtained from the Oxide Mine situated about 4 miles S. E. of Buchan in Eastern Victoria. The ore-body occupies what appears to be a fault in andesitic tuffs of Lower Devonian age and occurs close to the boundary of massive limestones which overlie the volcanic series. The hanging-wall of the fault consists of kaolinized pyroclastic material and the ore-body is composed of soft red earthy hematite in which the manganese ore occurs as dense nodules.

The deposit is apparently supergene in origin, derived from solutions carrying manganese and iron which were precipitated at fairly low temperatures as indicated by the colloform texture. The source of the manganese and iron was probably the overlying limestones and volcanic deposits, the kaolinized tuffs representing part of the leached host rocks. Alternatively, kaolinization may have accompanied oxidation of the previously deposited ore, the fault zone providing channels for circulating waters. There is an extensive development of ochreous iron oxides accompanied by partly weathered nodules which contain numerous pockets of goethite, and possess a distinctive colour and texture. In addition to the fresh unaltered material (specimens 1 and 2) which is a steel-grey colour, a more weathered sample (specimen 3) was examined. This is slightly bluer in colour, more friable owing to the presence of abundant soft goethite, and possesses a distinctive pisolitic texture visible even without polishing.

A polished section of an unaltered nodule is seen under the ore-microscope to consist of an apparently homogeneous mineral, which appears to correspond to the "psilomelane" type of Fleischer and Richmond (4), and is almost completely isotropic, showing pale grey-brown polarization colours. Etching with hydrofluoric acid reveals a zonal texture in massive specimens; occasionally colloform banding is visible without the acid of etch reagents (Figure 1).

\* An officer, Division of Industrial Chemistry, Council for Scientific and Industrial Research, Melbourne, Australia.

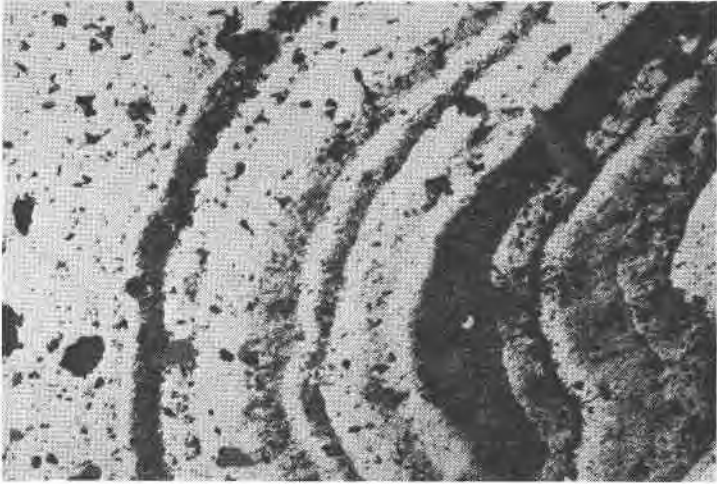


FIG. 1. Colloform texture of Buchan Minerals marked by zones of differing composition, and also by lines of inclusions. Unetched ( $\times 75$ ).

Etching with a nitric acid-hydrogen peroxide mixture, however, reveals the presence of a very finely disseminated phase which remains unaltered after the manganiferous portion has reacted with effervescence. Figure 2 shows the unattacked mineral under oil-immersion appearing as embayed aggregates, and rod-like dendritic growths. The mineral is isotropic and may also take the form of irregular lines, following the colloform banding of the ore. Optical identification is uncertain since the material is so finely divided, but in the light of other evidence (*x*-ray powder photographs) there is no doubt that this mineral is hematite.

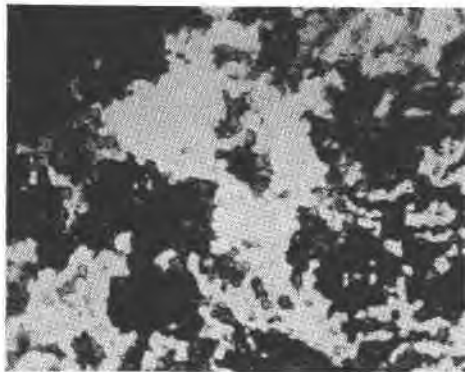


FIG. 2. Etched specimen of manganese ore, Oxide Mine, Buchan. Black = manganese mineral; white = hematite ( $\times 1000$ ).

The intimacy with which the manganese mineral and the hematite are associated makes their separation impossible by the ordinary means. Some specimens contain narrow veinlets of a strongly pleochroic mineral, showing marked anisotropism, and more rarely, small pockets of goethite ringed by needles of the same mineral. Positive identification is uncertain owing to the minute size, but the presence of small percentages of zinc in each specimen, and the occurrence of crystalline chalcophanite associated with goethite in nearby parts of the ore body, suggest that these needles may be chalcophanite and not pyrolusite as might at first be supposed. This view is supported by the fact that specimen 3, the analysis of which shows the highest percentage of zinc, contains more of this mineral than Specimens 1 and 2, and the powder pattern contains the strongest lines of chalcophanite.

Thin sections revealed the presence also of quartz and small amounts of sericite.

The following etch reactions cannot be regarded as being strictly characteristic of the manganese mineral, because of the admixed hematite. Etch reactions of the psilomelane minerals, moreover, are never specific and vary with composition of the mineral except in the case of  $\text{SnCl}_2$ ,  $\text{H}_2\text{O}_2$ , etc., which invariably react vigorously.

*Negative:* HCl, KOH, KCN,  $\text{FeCl}_3$ .

*Positive:*  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2 + \text{HNO}_3$ , blackens with effervescence:  $\text{SnCl}_2$ , stains brown slowly.  $\text{HNO}_3$  conc., darkens slowly.

Specimen 3 has undergone considerable alteration by weathering, containing less disseminated hematite and more goethite and chalcophanite. A transition is noted between the clean unaltered material and areas of extremely fine chalcophanite needles associated with fragments of brown goethite. This appears to represent a partial crystallization or transformation of the gel-like matrix.

The optical examination of the specimens indicates that they possess the properties of a typical member of the psilomelane group, being an isotropic gel mineral, colloform in texture, and with a hardness and reflecting power about equal to that of hematite.

The loosely adherent impurities were removed with a hard scrubbing brush, and each specimen was ground to approximately -60 B.S.S. mesh and then agitated violently with water in order to disperse the earthy material occasionally found in pockets inside the massive specimen. After removal of these impurities, the samples were dried at 60° C. Although physical separation of the major phases is impossible from the finely ground specimens, separation can be effected chemically, as hematite, goethite, sericite and quartz are not appreciably affected by an ice cold 5% nitric acid-hydrogen peroxide mixture by which the manganese mineral is attacked.

A blank was carried out on the earthy materials associated with each specimen, and in each case only traces of iron were dissolved, but not in sufficient quantity to affect the analytical results as expressed. Consequently a complete analysis was made of each specimen by the normal methods, and in addition analyses were made of the material insoluble in this acid mixture.

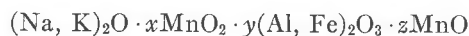
The results are reported in Table 1. The water figure is regarded as uncertain, and in the subsequent treatment of these results will not be considered since the water content of near colloidal materials is of little significance. The distribution of the alkali metals is on the basis that alumina is present in the insoluble portion as sericite.

TABLE 1. MANGANESE ORE, OXIDE MINE. CHEMICAL ANALYSES

Fraction		Specimen 1	Specimen 2	Specimen 3
Acid Soluble	MnO <sub>2</sub>	60.33	56.58	60.15
	MnO	3.93	4.60	4.50
	Al <sub>2</sub> O <sub>3</sub>	4.02	2.56	2.48
	Fe <sub>2</sub> O <sub>3</sub>	1.01	0.38	0.80
	ZnO	1.25	1.08	3.27
	K <sub>2</sub> O	1.05	1.42	0.97
	Na <sub>2</sub> O	0.28	0.31	0.24
Acid Insoluble	SiO <sub>2</sub>	2.70	1.52	3.98
	Al <sub>2</sub> O <sub>3</sub>	—	0.71	1.18
	Fe <sub>2</sub> O <sub>3</sub>	22.19	26.12	15.42
	K <sub>2</sub> O	—	0.22	0.36
Indeterminate	H <sub>2</sub> O-120°	1.07	0.36	1.14
	H <sub>2</sub> O+120°	3.79	3.67	4.31
	Total	101.62	99.53	98.80

All samples contain spectroscopic traces of Co, Ca and Mg. Ba is absent.

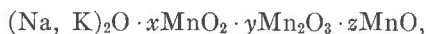
The acid soluble portion of Table 1 corresponds to the manganese phase. Assuming the zinc to be present as chalcophanite, an analysis of these results gives a formula of the type



but  $x$ ,  $y$  and  $z$  differ slightly from specimen to specimen, and as a result precise formulation is not contemplated.

The relatively small amounts of aluminium<sup>3</sup> and iron suggest that they have replaced manganese of a corresponding valency. If this is so, then

the mineral free from these substituted ions will be of the form



and substances of this type are usually simplified to



where  $n$  is the atomic ratio O:Mn.

The analytical results must further be corrected for the presence of chalcophanite in small quantities. The formula of this mineral is usually given as  $\text{ZnO} \cdot 2\text{MnO}_2 \cdot 2\text{H}_2\text{O}$ , and for each analysis two equivalents of  $\text{MnO}_2$  are subtracted for each equivalent of  $\text{ZnO}$ .

Treated in this way, the results in Table 1 lead to values of  $n$  for each specimen of 1.88, 1.88 and 1.87, respectively.\*

The mineral may therefore be regarded as having the formula  $\text{MnO}_{1.88}$  in which the trivalent manganese has been completely replaced by the more stable ions of iron and aluminium.

A more precise formula is not proposed as it is believed that in common with many of the manganese and other metal oxide minerals, this material may exhibit radical departures from stoichiometry due to the reduction of some cations from a high to a low valency with an equivalent number of vacant anionic sites.

X-ray powder patterns were made on each specimen mounted by the wedge method using  $\text{Fe K}\alpha$  radiation. In each case the lines of hematite, silica and the manganese mineral were found and in addition the most prominent lines of goethite for specimens 2 and 3, and of chalcophanite for specimen 3.

The line spacings and intensities are given in Table 2 for the pattern of specimen 1, the lines of the impurities being indicated. The residual pattern which is taken as that of the manganese mineral, appears to be derived from a tetragonal cell having two possible sets of cell dimensions—

$$\begin{array}{ll} a = 6.97 \text{ \AA} & c = 7.12 \text{ \AA} \\ \text{or } a = 9.89 \text{ \AA} & c = 7.12 \text{ \AA} \end{array}$$

Whilst the powder pattern possesses many lines common to that of cryptomelane, a commonly occurring manganese dioxide mineral containing essential potassium, for which the tentative formula  $\text{KR}_3\text{O}_{16}$  ( $\text{R} = \text{Mn}^{\text{iv}}$ , etc.) has been proposed (4), both of these possible sets of dimensions differ considerably from that proposed by Ramsdell (6) for cryptomelane.

Studies in this laboratory have shown that neither the naturally oc-

\* An oxide of this composition reported by Dubois (2) was shown to be identical with  $\gamma\text{-MnO}_2$  (1).

curing mineral nor synthetic cryptomelane possess patterns differing by more than experimental error from Frondel's values (4). These specimens have, however, exhibited a wide variation in composition, both in potassium content and Mn:O ratio, and the possibility that the Buchan specimens are disordered forms of cryptomelane due to lattice imperfec-

TABLE 2. X-RAY DIFFRACTION DATA

Manganese Ore Oxide Mine		Extra Phases	Buchan Mineral	Theoretical Pattern		Manganous Manganite	
<i>I</i>	<i>d</i>		<i>d</i>	<i>hkl</i>	<i>d</i> (calc.)	<i>I</i>	<i>d</i>
W	6.99		6.99	(001)	7.12	MS	7.13
Wd	4.91		4.91	(100)	6.97		
VW	4.24	SiO <sub>2</sub>		(110)	4.93		
VWd	3.99		3.99	(111)	4.06		
M	3.670	Fe <sub>2</sub> O <sub>3</sub>		(002)	3.56	W	3.53
VWd	3.502		3.502	200)	3.48		
MW	3.326	SiO <sub>2</sub>					
Md	3.132		3.132	(201)	3.132		
VW	2.755		2.755				
S	2.700	Fe <sub>2</sub> O <sub>3</sub>					
MS	2.510	Fe <sub>2</sub> O <sub>3</sub>					
MS	2.392		2.392	(003)	2.375	M	2.41
M	2.203	Fe <sub>2</sub> O <sub>3</sub>					
Md	2.152		2.152	(113)	2.140	VWd	2.14
VWd	2.086		2.086	(311)	2.107		
S	1.836	Fe <sub>2</sub> O <sub>3</sub>					
S	1.691	Fe <sub>2</sub> O <sub>3</sub>					
W	1.633		1.633	(411)	1.646		
				(330)	1.643		
				(313)	1.616		
MW	1.597	Fe <sub>2</sub> O <sub>3</sub>					
MWd	1.542		1.542	(214)	1.547		
M	1.482	Fe <sub>2</sub> O <sub>3</sub>					
MS	1.449	Fe <sub>2</sub> O <sub>3</sub>					
MW	1.425		1.425	(005)	1.425	VW	1.42
				(115)	1.369		
Wd	1.368		1.368	(501)	1.369		
				(510)	1.367		
Wd	1.358		1.358	(333)	1.351		
Wd	1.348		1.348	(511)	1.343		

S=strong, MS=medium strong, M=medium, MW=medium weak, W=weak, VW=very weak, d=diffuse.

tions must therefore be rejected. In addition, it is known that variations in composition usually produce slight changes in cell dimensions, whereas the possible values listed above differ very markedly from those calculated by Ramsdell.

Recently Feitknecht and Marti studying the oxidation of manganous hydroxide, reported several new structures which could be distinguished as oxidation proceeded (3). The final oxidation product which they named manganous manganite, had a characteristic powder pattern comprising five distinct lines. In Table 2 the pattern of the manganese mineral is compared with that of manganous manganite prepared by their method. The theoretical pattern obtained from the unit cell values  $a=6.97 \text{ \AA}$ ,  $c=7.12 \text{ \AA}$  is also included.

Although the lines of manganous manganite are few, they agree fairly well with those of the theoretical pattern. By this comparison, four of the five lines in the manganous manganite pattern are seen as reflections from the (00 *l*) planes whilst the remaining line is due to the (113) plane. Although there is insufficient data to reconcile these two powder patterns, it is nevertheless very probable that they are derived from similar crystals in which the *c* axis dimensions would be identical, whilst the *a* and *b* axes are a matter of some doubt.

Feitknecht and Marti in a brief analysis of their oxide, claimed that the pattern of manganous manganite could be derived from a structure of the cadmium iodide type, consisting of layers of  $\text{MnO}_2$  with  $\text{Mn}(\text{OH})_2$  molecules between every fourth and fifth layer giving a formula  $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2$  which is equivalent to  $\text{MnO}_{1.80}$ . Whilst this lends support to the views outlined briefly above the structure of manganous manganite may actually be more complex. A manganese oxide treated with potassium pyrophosphate in neutral ammonium acetate will give a pink solution of the manganese complex if  $\text{Mn}^{+++}$  is present in the lattice (5). By means of this test, it can be shown that manganous manganite contains an appreciable percentage of  $\text{Mn}^{+++}$ . In addition, depending upon the mode of preparation, up to 6% of alkali metal (expressed as the oxide) may be retained by this oxide which cannot be removed by washing with water.

Two preparations of manganous manganite were shaken with an aqueous solution of ferric ammonium sulphate. The sodium is replaced zeolitically, and the  $\text{Mn}^{+++}$  completely, by ferric iron, and in each case the *x*-ray powder patterns were unchanged.

The analytical results, corrected for the ion exchange of Na, are given in Table 3, and are compared with recalculated data for specimen 1.

Structurally the mineral shows similarities to manganous manganite on the one hand and to cryptomelane on the other, but the evidence does

TABLE 3

	Manganous Manganite		Buchan Mineral (1)
	(a)	(b)	
MnO <sub>2</sub>	84.7	86.9	86.5
MnO	8.8	7.6	5.9
Fe <sub>2</sub> O <sub>3</sub>	6.5	5.5	1.5
Al <sub>2</sub> O <sub>3</sub>	—	—	6.0
<i>n</i>	1.86	1.88	1.88

not support the view that the mineral may be classed merely as a disordered form of cryptomelane. It is our belief that the hydrated manganese minerals, chalcophanite, lithiophorite, psilomelane, and rancieite are perhaps closely related, and the purpose of this account is to describe our specimen without assigning to it a new name at this stage. Further work to estimate its significance in a paragenetic scheme of the hydrated manganese mineral is in progress.

## ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. A. B. Edwards of the Mineragraphic Section, C.S.I.R. for his assistance in the microscopical examination; to Mr. J. M. Cowley of the Division of Industrial Chemistry, C.S.I.R. for taking the powder photographs; to Mr. A. J. Gaskin, Geology Department, Melbourne University for assistance in the collection of specimens. The work described in this paper was carried out as part of the research programme of the Division of Industrial Chemistry, Council for Scientific and Industrial Research, Australia.

## REFERENCES

1. COLE, W. F., WADSLEY, A. D., AND WALKLEY, A., *Trans. Electrochem. Soc.* Preprint 92/2 (1947).
2. DUBOIS, P., *Ann. Chimie*, **5**, 411-482 (1936).
3. FEITKNECHT, W., AND MARTI, W., *Helv. Chim. Acta*, **28**, 129-148 (1945).
4. FLEISCHER, M., AND RICHMOND, W. E., *Econ. Geol.*, **38**, 269-286 (1943).
5. LEEPER, G. W., AND JONES, L. H. P., Private communication.
6. RAMSDELL, L. S., *Am. Mineral.*, **27**, 611-613 (1942).