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MINERALOGICAL STUDIES ON MANGANESE DIOXIDE AND HYDROXIDE MINERALS IN HOKKAIDO, JAPAN

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(With 29 Text Figures, 17 Tables and 3 Plates)

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I. Introduction

The element manganese occurs in nature in a great number of different mineralogical forms. The most stable condition of manganese in nature is in the form of oxide, and therefore, when any of the other manganese minerals are decomposed by the influence of surface agencies, they all tend sooner or latter, to assume that form. As a direct result of this, the oxides minerals are the most plentiful of the manganese minerals. They occur in several different forms, varying considerably in the relative proportions of manganese and oxygen, that is, in the degree of oxidation of the manganese, and in the nature of the accompanying chemically or mechanically combined impurities.

Manganese dioxide mineral is one of the most familiar and common minerals found in various manganese deposits, but its mineralogical study has been very indefinite owing to the variability and overlapping of physical properties and chemical compositions. It is obvious, in Hokkaido, that it always occurs in a fine grained massive state, and compares several modifications.

The writer has been interested in the problem of various modifications of manganese dioxide since five years ago, and has studied the problem of persistent minerals in nature, such as manganese dioxide and hydroxide. In as much as minerals should not be dealt with as individual specimens, but must be considered in connection with their crystallization environment, the writer's research has been mainly on the relation between the several modifications of manganese minerals and the differences in the mode of their occurrence.

On the other hand, the utilization of these minerals has increased tremendously in recent years, mainly in the chemical and metallurgical industries, especially in the dry cell industry. The ore is directly used as a basic raw material for a dry cell, so that doubtlessly the mineralogical character of manganese dioxide may greatly influence the electric behaviour of a dry cell. For the increased demands for dry cell as well as new uses, manganese dioxide has been artificially prepared by various chemical or electrochemical methods, and the mineralogical properties of these products have shown that there are several modifications according to the difference of procedures or original reagents used.

In this paper, the writer attempts to identify the various modifications of natural manganese dioxide and hydroxide from the mineralogical standpoint, and a classification of these minerals is attempted.

II. Geotectonic constitution of the island of Hokkaido.

The island of Hokkaido, the northernmost island of Japan, is composed of some contrasted geotectonic units. The axial zone of the island which extends from north and south is the geological backbone of the island made up of Cretaceous and pre-Cretaceous formations with metamorphic and plutonic zones in each tectonic center. It is considered that an orogenic movement of alpine phase predominated over the whole axial zone in the Cretaceous epoch producing the foundation of the island; around it the younger formations are disposed.

In the succeeding Palaeogene epoch, there was no prominent tectonic disturbance in Hokkaido. Only some coal bearing formations were formed around the marginal part of the axial zone. In the Neogene epoch, however, huge volcanic effusions had arose over both flanks of the axial zone. Such activity belongs to the so-called "green tuff activity" that took place along the whole inner side of the Japanese island are keeping pace with the Tertiary circum-Pacific volcanic activity.

In the south-western protruded peninsular area of the island the above mentioned green tuff, and pyroclastic formations with lava and intrusive propylite and liparite are prominently developed. The basement complex of those pyroclastics is composed of a probably Palaeozoic formation which is considered as a northern extension of the Kitakami mountain region, the type locality of the Japanese Palaeozoic.

As to the north-eastern region of the island the Neogene circumstances are similar to those of the south-western region. However, the pyroclastics cover pre-Cretaceous formations which are referred to the

eastern border part of the axial zone.

Such three fold geologic constitution provides the fundamental character of the island of Hokkaido. But by the detailed consideration they are further subdivided into some small sub-provinces.

1. *Geographical distribution of manganese deposits in Hokkaido.*

Several kinds of ore deposits are associated with every igneous activity of each geotectonic unit. Manganese deposits, now under consideration, are also developed as a member of those ore deposits. They are arranged into some metallogenetic controlled by the geotectonic background. Further, their periods of mineralization extend over several epochs, Palaeozoic, Mesozoic, Neogene Tertiary and Quaternary.

They will be summarized as in the following table.

- A. South-western region
 - 1. Western province
 - a) Manganiferous quartz vein in the Palaeozoic formation, Matsumae, Era, etc.
 - b) Epithermal rhodochrosite vein of Neogene epoch, Imai-Ishizaki, Yakumo, Jokoku mine, etc.
 - c) Nodular or bedded sedimentary dioxide deposits of Neogene epoch, Pirika, Kinjo, Daikoku mine, etc.
 - 2. Eastern province
 - a) Epithermal rhodochrosite vein of Neogene epoch
 - b) Nodular or bedded sedimentary dioxide deposit of Neogene epoch
- B. Axial Zone

Manganese oxide deposits developed along the sheared zone running through the pre-Cretaceous formations
- C. North-eastern region

Manganiferous hematite deposits and allied manganese oxide deposits developed among the pre-Cretaceous formation, Tokoro, Kokuriki, Wakasa mine, etc.
- D. Quaternary volcanic zone

Manganese wash deposits of both Nasu and Chishima volcanic chains.
- A. South-western region

Southwestern region of the island is roughly subdivided into two tectonic units by the N-S running line of Hakodate-Suttsu.

 - 1) Western sub-province

In this western sub-province, Palaeozoic horst like massifs surrounded by Miocene pyroclastics and siliceous hard shale are dotted with north-south trend. Each massif is understood as an unheaving horst; in the

Miocene age, its marginal zone of step faults was often an effusive centre of huge pyroclastics. As the effusion is exhausted, in late Miocene, siliceous hard shale developed in the skirts of upheaving massifs.

Although several types of ore deposits are disposed in those terrains; manganese deposits characterize this province.

a) Palaeozoic deposits

Older type of vein formed manganese deposits are occasionally found in the interior region of the Palaeozoic massifs. Main portion of those deposits is formed of oxidized ores. Some rhodonite, magnetite, quartz and rhodochrosite are associated with them. They are considered as one kind of replacement deposit formed in Palaeozoic epoch.

b) Neogene Tertiary deposits

In the Neogene Tertiary deposits were developed with the Neogene effusive activity of the province; there are several epithermal mineral deposits such as gold, silver, base metals, and manganese. Tertiary manganese deposits of South-western Hokkaido, are represented in two different types.

The one is epithermal rhodochrosite veins, the other is a nodular or bedded deposit of sedimentary origin. The former is controlled by a tectonic faulting to similar those of epithermal base metal deposits and especially allied to lead-zinc deposits. In some lead-zinc deposits, rhodochrosite predominates as gangue mineral. A unique type of high concentration of such rhodochrosite is workable for manganese deposits. This type of deposit forms the most important manganese resources in Japan, and has the highest production.

In the western sub-province, this type of deposits is known in the Jokoku, Imai-Ishizaki, Yakumo mine. They occur in Neogene pyroclastic formation and in propylite masses or partly in Palaeozoic formation. The deposits are mainly composed of rhodochrosite and often accompanied by alabandite, sphalerite, galena, chalcopryrite and silver minerals.

The nodular or bedded manganese dioxide deposits are also the important sources manganese. The prominent existence of such type manganese deposits characterizes the western sub-province; moreover, it is a unique metallogenetic province in Japan.

They occur surrounding the Palaeozoic massifs, and are arranged at a distance from the central massif beyond the site of vein type of deposits. Stratified sedimentary regions are the place of such manganese deposits.

The ore is composed of manganese dioxide and hydroxide minerals, such as pyrolusite, manganite, cryptomelane and amorphous manganese dioxide etc. They form some beds or often are concreted in a nodular form

and scattered among sediments. Frequently, they associate with jasper which is called "Toraishi" and soapstone. Pirika and Meppu mine are the typical representatives of this type. Sometime the ore contains shark teeth and other marine fossils, so they are understood to be sedimentary deposits laid under marine water by the accumulation of wad derived from manganese mineral springs. However, some authors postulate them to be of hydrothermal replacement origin.

2) Eastern sub-province

There is no prominent Palaeozoic massif in the eastern sub-province. The greater part of the district is covered by Neogene pyroclastics and propylite masses. Associated base metal deposits are rather more prominent than those of the western province, a) with those deposits, epithermal rhodochrosite veins which have the same character as those of above mentioned are disposed. Inakuraishi, and Ôhe mines work representative deposits. There is no need for additional notes on these rhodochrosite deposits referred to those of the western type. b) Minor sedimentary manganese deposits are also known in the neighbourhood of above mentioned rhodochrosite deposits.

B. Axial Zone.

As already mentioned, the axial zone of Hokkaido is orogenic composed of thick sediments of geosynclinal natures. Along the marginal zone of this supposed geosyncline, there are developed some zones of prominent diabase effusion. Further, allied diabase sheets and dikes are often disposed within the geosynclinal area. Under such geologic circumstances, there were formed cupriferous iron sulphide deposits, the representative ore deposit of the axial zone. Occasional minor manganese deposits are also known with them.

Manganese oxide deposits

Manganese oxide deposits of the axial zone are not very prominent, only sporadic minor occurrences are met with. They developed as lense shaped masses interposed within a sheared zone running through the slate or schalstein. In some cases, manganiferous sediments are associated with them, however, high manganese concentration is always related to the shearing phenomenon. Detailed observation on some sheared zones has revealed that the shearing moment is always accompanied by the permeation of some kinds of solution which caused a prominent wall rock alteration. It is considered that the concentration of manganese has some relationship with such permeation of a solution. With the manganese ore of such deposit braunite and other undeterminable minerals are mentioned. In the neighbourhood of them, manganiferous hematite deposits

of similar occurrence are known. This association is like the same occurrences in the north-eastern region of Hokkaido.

C. North-eastern region

As the basement complex of the green tuff region of north-eastern Hokkaido, pre-Cretaceous formations which are comparable to those of the axial zone are widely developed. With them, prominent manganiferous hematite deposits as well as manganese oxide deposits are developed.

The nature of those deposits is the same as those of the axial zone above described. Tokoro mine works the representative deposits. It develops among the schalstein and red quartzite, as if it were deposited as a member of sedimentary formation. But, high grade ore is always restricted to a sheared zone or brecciated part. The ore is composed of gel-formed hematite and silica mineral. Other undeterminable amorphous components are associated with them. It always contains about 10% of manganese. However, its mineralogical form has not been clearly determined. Another type of manganese deposit is known in the western region distinguished from Tokoro type hematite deposits of the eastern region. Although the circumstances of that deposit are the same as those of the hematite deposits, it is almost free from hematite; a manganese oxide mineral is the main constituent of the ore. Wakasa and Hinode mine etc. are the chief workable deposits of this type.

D. Quaternary volcanic zone

As to the quaternary volcanic activity, associated ore deposits are those of sulphur and limonite. They are restricted to the Nasu volcanic chain in the south-western region and to the Chishima volcanic chain in the north-eastern region respectively. With then, some manganese wad deposits on a minor scale are seldom associated in the same style as limoni-

TABLE 1. Manganese wad deposits by active and extinct springs.

District	Source	Minerals	Mn %
Komaga-dake	Komaga-dake cold spring active	pyrolusite, birnessite	
Iwao	hot spring	pyrolusite, brown manganese	29.77%
Niimi	Niimi hot spring	pyrolusite	30%
Nishitappu	Tarumae volcanic active	black manganese, other mineral calcium carbonate	
Tokati-dake	Tokati volcanic active	amorphous black manganese wad	
Akan	Akan hot spring active	amorphous black manganese wads, other mineral calcium carbonate	

tic deposits derived from mineral springs. They are found in the skirt area around the volcano. There is no difference between the deposits of the Nasu and Chishima chains. (Table 1)

2. *On the respective manganese minerals of the above described deposits*

As above mentioned, the manganese deposits of Hokkaido fall into several divergent types. Some deposits are revealed to possess such characteristic features that no doubt arises concerning their position in the system of ore deposits. However, the situation of many deposits remains undetermined.

a) One of the undoubted types of deposits is hydrothermal, which is represented in the Jokoku, Inakuraishi, Yakumo, mine, and others, the characteristic type of the south-western ore province.

b) Although some objections have been raised, the Tertiary sedimentary deposits of the south-western province are also of undoubted type.

c) Concerning the natures of the manganese hematite and allied deposits in comparatively older formations of the axial zone and the north-eastern region, the precise situation is undeterminable in many respects.

They are treated as sedimentary in origin, but some are considered as metamorphic or replacement deposits.

d) The older deposits which are known in Palaeozoic or pre-Cretaceous formations, Era, Matsumae in the south-western province or in the axial zone are characterized by the replacement features. Almost of all the deposits have been strongly affected by the oxidation of weathering processes. Many of the cryptocrystalline oxide minerals contain minor amounts of extraneous elements of B, K, Fe, Ca and others which are generally determinable by spectrographic and chemical analyses. The explanation usually offered for the presence of these minor elements is that the manganese hydrosol is negatively charged and attracts to it the cations of other elements. The chief types of occurrence of these manganese ores are massive or fibrous, as botryoidal, spongy and banded; as dendritic growths on fracture surfaces or enclosed in chalcedony. Manganese dioxide ores occur frequently in association with a jasperoid called "Toraishi." It is obvious, that they always occur in a fine grained massive state, and that they comprise several modifications. Some members are well crystallized but others are very poorly so.

These manganese ores and their underlying and accompanying beds exhibit many of the characteristic structures and textures of normal sedimentary materials. These deposits are found concordantly or slightly obliquely to the stratification of green tuff, tuff breccia and shale of Miocene. The modes of occurrence of many manganese dioxide deposits

are controlled by geological structure; the deposits are distributed in

TABLE 2. Significant features of layered dioxide of manganese deposits.

	Kokko mine area	Pirika mine area	Kinjo mine area
Larger features stratigraphy lithology	Alluvium Pleistocene Akagawa loam and clay Akagawa & Amemasu etc. volcanics Older volcanics Kuromatsunai formation Otaru agglomerate Miocene Yakumo formation andesitic tuff breccia ore zone upper tuffaceous sand stone shale Kunnui formation Lower tuffaceous sand stone liparite	Alluvium Diluvium Pliocene Setana formation upper muddy sand layer middle sand layer lower volcanics sand gravel layer Kuromatsunai formation agglomerate sand stone & mud stone alt. gray mud stone Miocene Yakumo formation shale mud stone Kunnui formation ore zone basaltic tuff breccia green tuff, green tuf- faceous sand stone gray mud stone liparitic tuff breccia granite border (ore zone) unconformity granite, Palaeozoic formation	Alluvium Diluvium Pliocene two pyroxene andesite hornblende dacite Miocene Yakumo formation tuffaceous shale, basalt Kunnui formation ore zone green tuff
Manganese minerals	cryptomelane	pyrolusite, manganite, groutite	pyrolusite manganite cryptomelane
other minerals	clay, limonite	clay, barite, calcite	clay, calcite, jasper
Relations of dioxides to host rock	syngenetic some redistribution and enrichment	jasper layers syngenetic	syngenetic
post-ore vein minerals		barite, calcite vein	pyrolusite, calcite vein
Supergene enrichment		probable	

such special portions as small basins.

Each of the three areas included in Tertiary formations in Table 2 shows the following two successive episodes: 1) after a period of volcanism that yielded flows and breccias of several varieties of rocks, they were deformed and subjected to great erosion. 2) They were laid down unconformably on the older rocks, and then abruptly there were laid fine-grained tuff and tuff breccia that contain manganese dioxides. In each of the three areas some workers have held the opinion that the manganese dioxides replaced the tuffaceous material after it had been deposited. To the present writers it seems that the similarity of the sequence of episodes in each of the three areas suggests that the mode of genesis should be the same in each area. It is interpreted here that in each area the manganese dioxides were deposited as sediments.

A. Hydrothermal type of deposits

As already mentioned, this type of deposits is fully developed in the Jokoku and Yokumo, mines. The ore minerals of those deposits consist mainly of rhodochrosite, with sphalerite, galena as accessories.

The rhodochrosite usually occurs as pure manganese carbonate. But, in some deposits as of the Ôe and Jokoku mines it contains appreciable amounts of Fe or Mg and Ca replacing manganese. The oxidized ore of surficial weathering zone is generally of low grade one. The universal product of oxidation is pyrolusite (β - MnO_2) or its hydrated derivatives.

B. Sedimentary type of deposit

Although this type of deposit is interbedded with clay and tuff formations and has distinct features of sedimentary origin, prominent alterations of surrounding rocks that are suggestive of igneous affiliation are developed. In these deposits, manganese minerals of hydroxides and dioxide manganese are well represented. They are revealed as pyrolusite, cryptomelane, manganite, groutite, and cryptocrystalline manganese dioxide.

C. Manganese hematite and allied type of deposits

One of the most obscure types of the manganese deposits is this group. As already mentioned, several diverse interpretations are proposed for their origin.

The ore of manganiferous hematite deposit type hematite only is determined as ore mineral, and not as a distinctive mineral of manganese source. But, in manganese oxide deposit of allied type distinctive braunite mineral is well developed, furthermore, undeterminable manganese mineral is also found in company there with.

D. With the older replacement type of manganese deposits

As already mentioned, regarding oxidized ore often associated with



rhodonite, magnetite, quartz and rhodochrosite with respect to the pre-oxidation circumstances, there is not yet available clear information.

III. Mineralogical consideration of manganese dioxide and hydroxide minerals in Hokkaido

Manganese oxide mineral, especially manganese dioxide, is one of the most familiar and common minerals found in various manganese deposits in Hokkaido, but its mineralogical studies of it have been very equivocal owing to the variability and overlapping of physical properties and chemical composition. The material always occurs in a fine-grained massive state, and comprises several modifications. Some members are well crystallized but others are very poorly crystallized. Though loosely known as the "manganese dioxide minerals," many contain additional elements. For example, cryptomelane, which is one of the commonest minerals, has been tentatively ascribed the formula KR_8O_{16} , where R is chiefly Mn^{+4} .

The writer investigated the various modifications of manganese dioxide and hydroxide minerals, mainly from the mineralogical standpoint and classified them on the bases of geological data.

1. *Experimental*

The methods of the mineralogical study have described on manganese dioxides, are optical, chemical, X-ray, thermal, and electron micrography.

The metallographic microscope is the most valuable instrument for identifying opaque minerals and for studying their mutual relationships. The identification of the manganese dioxide minerals in polished sections has made difficulties.

The use of the electron microscope has permitted the precise determination of the shape of the particles of various manganese dioxide minerals.

X-ray diffraction analysis was carried to identify the materials by Philips geiger counter X-ray spectrometer. The conditions of studies in this report are as follows; non filter Fe radiation 35 kv, 7 ma, scan speed 2 per minute, angular aperture 1, receiving slit 0.006 inch, time constant 4 seconds.

Although the thermal methods in current use are fairly numerous most are based upon three fundamental properties; (a) weight changes, (b) energy changes, and (c) dimensional changes. Two or more methods in combination may also be used.

Consequently, since differential thermal analysis is at present the most widely used, and probably the most useful method for identification

and estimation purposes, consideration has been limited to this technique; the results of other methods have been incorporated only where they are necessary to supplement differential thermal data.

Thermobalance curves differ from the above types in being dynamic that is, the change in weight is continuously measured and recorded as the sample heats up.

2. *Cryptomelane*

This alkali-bearing member of MnO_2 was named "cryptomelane" by RICHMOND and FLEISCHER (1942). The formula for cryptomelane is given as KR_8O_{16} . The R is largely Mn^{+4} , but enough is of a lower valence to provide the need of a potassium atom. The composition is not completely uniform, the relative amounts of K and R varying to some slight degree. Also the potassium may be replaced by sodium. Cryptomelane, having a low order symmetry, exists in a much great range of

TABLE 3. X-ray powder data of cryptomelane.

A. S. T. M. No. 6-0547			Kokkô mine		Hollorter Zug Siegen, Deutschland (by Ramdohr)	
d(Å)	I	hkl	d(Å)	I	d(Å)	I
6.92	20	110	6.99	21	6.84	m
4.91	20	200	4.91	16	5.83	ss
3.47	10	220			4.85	m
3.11	60	130	3.10	20	3.47	ss
2.46	10	400			3.09	st
2.40	100	121	1.40	21	2.28	sst
2.21	20	240				
2.16	20	301	2.15	12	2.14	st
					1.99	ss
					1.91	ss
1.84	60	141	1.84	7	1.82	m
1.64	20	600	1.64	6	1.63	s
1.54	60	251	1.54	8	1.53	m
1.43	20	002	1.42	6	1.42	m
					1.39	ss
1.35	60	451	1.35	9	1.35	s
1.30	20	370			1.29	s
1.24	10	402			1.24	ss
1.22	10	332				
1.15	20	561,152	1.18	7	1.15	ss

crystallinity. Its structure is such that other ions such as K, Ba, Pb, and Mn^{+2} often find their way into portions of the lattice, thus causing the Mn : O ratio to be less than 2.00 in most cases. In this formula potassium is lead in coronadite and barium in hollandite. A partially solid solution series exists between hollandite and cryptomelane, but the limit of isomorphous replacement is not known.

Most samples of cryptomelane contain 2-4 percent of non-essential water. Cryptomelane is found as the commonest constituent of manganese dioxide mineral groups. It occurs in a number of habits: 1) most commonly as very fine grained steel gray dense compact masses, showing marked conchoidal fracture, 2) less commonly as botryoidal masses, 3) un-commonly as coarse cleaved masses that would not ordinarily be labelled "psilomelane type."

This name was given by RICHMOND and FLEISCHER (1942) to the potassium-bearing mineral of "psilomelane" type. It differs only slightly from psilomelane; the difference can best be ascertained by X-ray diffraction methods.

The Kokkô mine works manganese ore of syngenetic deposit in the tuff and tuff breccia of Neogene Tertiary. Cryptomelane from the Kokkô mine is general by poor by crystallize (Photo. 1). An X-ray powder diagram was made with unfiltered Fe radiation using a Philips geiger counter X-ray spectrometer. The interplaner spacing and intensities of

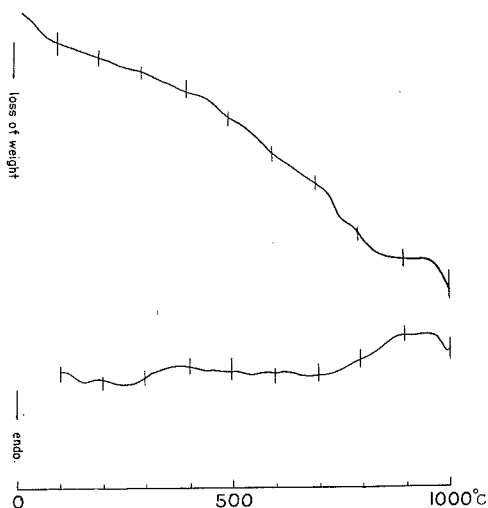


Fig. 2. Differential thermal analysis and thermobalance curves of cryptomelane from the Kokkô mine.

the reflections are listed in Table 3. The result is in good agreement with that obtained by RAMSDELL (1942) and RAMDOHR (1956). Fig. 2 show the differential thermal analysis curve and thermobalance curve of cryptomelane from the Kokkô mine. The irregularity reaction and broad exothermic reaction from 800° to 1000°C appear typical of this group. The reaction is probably of recrystallization type.

3. *Pyrolusite*

Pyrolusite occurs widely distributed in nature and combined with common minerals found in manganese dioxide deposits or oxidized zones in various manganese deposits in Hokkaido.

Pyrolusite, the mineral, is soft and will soil the fingers; it hardness varies from 2 to 2.5; it has a specific gravity of 4.73 to 4.86. It has a metallic luster and varies from grayish-black to black in colour; it shows a black streak. It is formed at or near the surface of the earth under strong oxidizing conditions and usually contains small quantities of silica,

TABLE 4. X-ray powder data of pyrolusite.

A. S. T. M.			No. 4-0591		Fleischer & Richmond		Pirika mine	
d(Å)	I	hkl	d(Å)	I	d(Å)	I	d(Å)	I
			4.08	2				
			3.425	2			3.43	9
			3.346	1				
3.14	100	110	3.096	10			3.12	75
			2.651	0.5				
			2.537	1				
2.42	80	101	2.396	6			2.40	32
2.22	10	200	2.190	3				
2.12	50	111	2.108	4			2.11	18
1.99	10	210	1.964	4			1.97	6
			1.785	1				
			1.708	1				
1.64	80	211	1.618	8			1.62	26
1.57	30	220	1.550	7			1.55	10
			1.434	2			1.43	6
			1.387	3				
			1.356	5			1.34	11
			1.158	1			1.15	5
			1.120	2			1.12	6
			1.098	2				
			1.053	3			1.05	3

lime, iron, and barite.

A typical specimen of pyrolusite can be collected from the manganese dioxide deposits of the Pirika and Hanishi mine (Photo. 2). Orthorhombic pyrolusite is apparently formed by pseudomorphism, based on its manganite formation. On the basis of observation the tetragonal form of MnO_2 , and its properties seem well characterized.

The Pirika mine is working on manganese dioxide ore of sedimentary deposits in the tuff and tuff breccia of Neogene Tertiary. X-ray power reflections of the manganese ore can be grouped with those of pyrolusite (βMnO_2) (Table 4).

The differential thermal analysis curve of pyrolusite and the loss of weight as quantitatively measured by a sensitive thermobalance are shown in Fig. 3. The loss of weight up to 580°C results from deoxidation

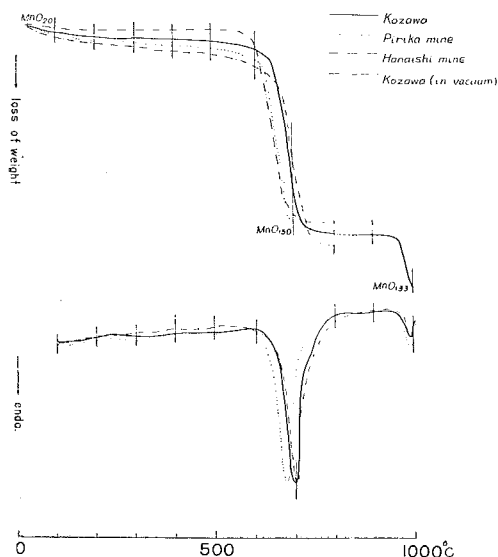


Fig. 3. Differential thermal analysis and thermobalance curves of pyrolusite from the Kozawa, Pirika, and Hanaishi.

alone; it is suddenly increased at about 700°C , amounting to approximately 10.5%. Pyrolusite appears from the thermal behavior of the first endothermic reaction to deoxidize abruptly at about 680°C transforming into $\alpha\text{-Mn}_2\text{O}_3$. The second peak is at about 1000°C . It is also noteworthy that the water content of these specimens is very low and that most of it is released at temperatures lower than 100°C . All oxides and hydroxides of manganese are transformed into Mn_3O_4 at 1000°C .

TABLE 5.

Type of transformation	Activation energy
$\beta\text{-MnO}_3 \rightarrow \alpha\text{-Mn}_2\text{O}_3$ (Pyrolusite)	105 K cal
$\alpha\text{-Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$	270 K cal

TABLE 6. X-ray powder data of ramsdellite.

A. S. T. M. No. 7-222			Tanno mine $2\theta=90^\circ$		Lake valley, New Mexico, U. S. A. (by Ramdohr)	
d(Å)	I	hkl	d(Å)	I	d(Å)	I
4.64	20	020	4.63	8		
4.07	100	110	4.07	41	4.03	sst
3.24	20	120	3.24	4	3.20	ss
2.55	100	130	2.55	22	2.61	ss
					2.53	st
2.44	70	021	2.43	7	2.41	m
2.34	60	111	2.34	5		
2.32	50	040	2.32	10	2.32	ss
2.27	10	200				
2.19	70	121	2.15	9	2.13	m
2.06	40	140	2.06	3	2.05	s
1.907	70	131	1.907	5	1.89	m
1.828	20	230			1.82	s
1.802	10	041				
1.716	10	150			1.70	ss
1.660	80	221	1.658	7	1.65	st
1.621	80	240	1.622	8	1.61	st
1.541	30	231				
1.473	80	151	1.472	7	1.46	st
1.433	50	002	1.434	3	1.43	m
1.360	80	061			1.35	sst
1.352	40	112				
1.337	10	301				
1.323	50	311			1.30	ss
1.272	60	170			1.27	m
1.250	60	132			1.25	m
1.219	30	042				

The product at 700°C denoting the peak in pyrolusite is due to the following endothermic reaction: $4\text{MnO}_2 \rightarrow 2\text{Mn}_2\text{O}_3 + \text{O}_2$

The activation energy of those reactions is shown in Table 5.

4. *Ramsdellite*

The occurrence of ramsdellite, an orthorhombic modification of MnO_2 has not been reported in Japan. But a specimen was collected by Mr. Y. URASHIMA at the Tanno mine, Kitami district in Hokkaido, which was identified by the writer as ramsdellite (Photo 3).

Ramsdellite was first described by L. S. RAMSDELL (1942); the power X-ray pattern has been given by M. FLEISCHER and W. E. RICHMOND (1943); and the crystal structure was determined by A. M. BYSTRÖM (1949). The unit cell dimensions are given $a=4.533 \text{ \AA}$, $b=9.27 \text{ \AA}$, and $c=2.866 \text{ \AA}$, $Z=4$. The crystal lattice is similar to the diaspor.

Ramsdellite from the Tanno mine is usually well crystallized and forms an aggregate of needle-shaped crystal. The small hand specimen received in this laboratory consists of clusters of radiating shiny black crystals (about 8 mm long), embedded in a dull gray matrix. Each portion in specimen gives a black streak.

The X-ray powder pattern obtained with a Phillips Geiger counter X-ray spectrometer with unfiltered Fe radiation is shown in Table 6. The result is in good agreement with that obtained by BYSTRÖM (1949) and RAMDOHR (1956). Differential thermal analysis curves for ramsdellite have been given by J. L. KULP and J. N. PERFETTI (1950). Exothermic phase change from ramsdellite to pyrolusite is shown at 500°C on the differential thermal curve. Subsequent to this reaction the curve is similar to that of pyrolusite as would be expected. The final endothermic peak temperature is reduced. This is probably related to the size of Mn_2O_3 crystallites which form in the pyrolusite decomposition. X-ray diffraction patterns taken at room temperature (ramsdellite), 200°C (ramsdellite), 550°C (pyrolusite), 800°C (Mn_2O_3), and 1000°C (hausmannite) are consistent with the above interpretation.

5. *Birnessite*

Originally $\delta\text{-MnO}_2$ was the name given by MCMURDIE to a synthetic manganese oxide whose X-ray powder pattern consisted of only two lines, at 2.39 and 1.40 Å. Later, MCMURDIE and GOLOVATO (1948) reported two additional lines at 7.0 and 3.64 Å, in the powder pattern of a synthetic $\delta\text{-MnO}_2$. The name "manganous manganite" was applied originally by FETTKNECHT and MARTI (1945) to a manganese oxide that yields a similar powder pattern; it was prepared by oxidizing an alkaline manganous solution with either air or oxygen. Birnessite giving an X-ray powder

TABLE 7. X-ray powder data of birnessite, manganous manganite and δ -MnO₂.

birnessite				manganous manganite						δ -MnO ₂					
(by Jones & Milne)		Todoroki mine		Cole et. al		Feitknecht & Marti		Buser et. al		McMurdie		McMurdie & Golovato		A	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
7.27	s	7.37	37	7.13	ms	6.90	ms	7.4	m			7.0	ms	7.4	vs
		4.69	11												
3.60	w	3.69	9	3.53	w	3.49	w	3.71	w			3.64	vw		
		3.32	5												
		3.27	4												
2.44	m	2.45	5	2.41	m	2.42	m	2.49	m			2.41	mw	2.40	vw
		2.37	7							2.39					
		2.09	5	2.14	vw	1.66	m								
1.412	m	1.41	8	1.419	vw	1.50	w	1.44	m	1.40					

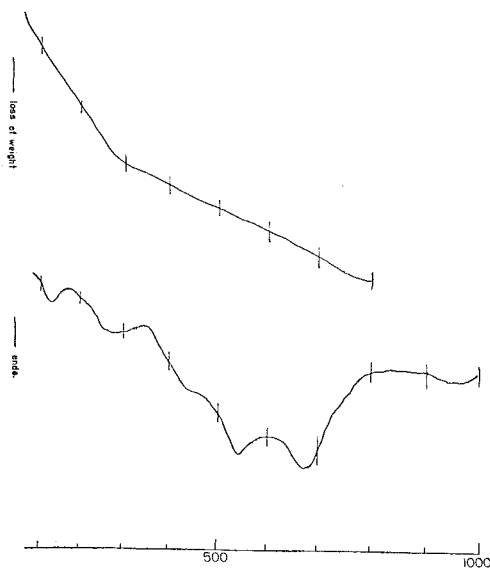


Fig. 4. Differential thermal analysis and thermobalance curves of birnessite from the Todoroki mine.

pattern similar to that of synthetic material is described as “manganous manganite” and δ -MnO₂.

Birnessite in Hokkaido is found at the Todoroki mine. This mineral upon X-ray examination is seem be identical with birnessite ($\text{Na}_{0.7}\text{Ca}_{0.3}$) $\text{Mn}_2\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$, as described by JONES and MILNE (1956). The mineral is usually very soft and varies from blackish-brown to black in colour.

The X-ray powder patterns of birnessite from Todoroki mine is given in the Table 7 together with the patterns of manganous manganite and $\delta\text{-MnO}_2$.

The differential thermal analysis curve of bernessite from Todoroki mine and the loss of weight as quantitatively measured by a sensitive thermobalance are shown in Fig. 4. It shows endothermic peaks at 120° , 260° , 540° , 680°C , and a small broad peak at 930° to 970°C .

Thermobalance curve show a continuous loss of weight, with to bleaks or very prominent flexures but a gradual decrease in amount as the temperature is increased.

6. Todorokite

A certain mineral specimen was found upon X-ray examination to be identical with todorokite (Mn, Ba, Ca, Mg) $\text{Mn}_3\text{O}_7 \cdot \text{H}_2\text{O}$, as described by C. FRONDEL (1953) and T. YOSHIMURA (1934). This mineral occurs

TABLE 8. X-ray powder data of todorokite.

Todoroki mine (by Forndel)		Vermlands Taberg (by Ljunggren)		Todoroki mine	
d(Å)	I	d(Å)	I	d(Å)	I
9.65	10	9.67	vs	9.66	100
7.2	0.5				
4.81	8	4.78	m	4.87	28
4.46	3	4.47	vw		
3.20	4	3.22	vw	3.23	7
2.45	3	2.43	vw		
2.40	4	2.39	vw	2.40	4
2.216	4	2.21	vw		
2.150	1			2.17	4
1.981	1	1.97	vw	1.92	3
		1.74	vw		
		1.68	vw	1.66	3
				1.63	4
1.419	4	1.42	vw		
1.392	1				
1.331	5				

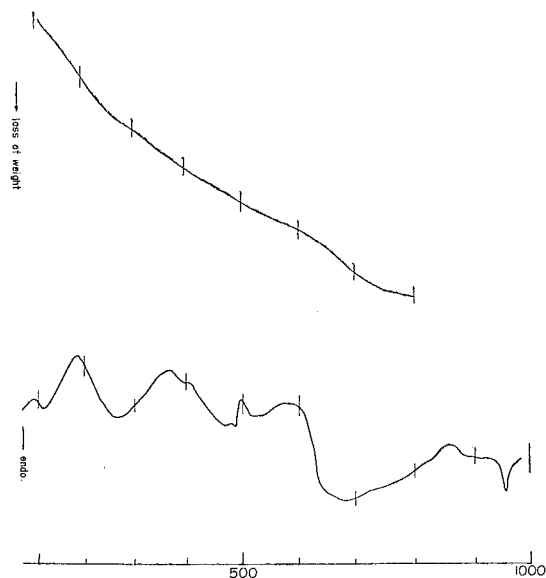


Fig. 5. Differential thermal analysis and thermobalance curves of todorokite from the Todoroki mine.

as an aggregate of very fine fibrous flakes, about 0.05 mm in length at the largest. These flakes are arranged in lamellar layers, the lamellae are vertical to the surface of the layer (Photo. 4). The X-ray powder patterns of todorokite from Todoroki and from Vermlands Toberg are given in Table 8.

The differential thermal analysis curve of todorokite from Vermlands Toberg according to P. LJUNGGREN (1960) is given. It shows endothermic peaks at 105°, 330°, 660°, 730°, 810°C, and a small deflection at 965°C.

The differential thermal analysis curves of these minerals from Todoroki mine obtained by the present writer are given in Fig. 5. The irregularity reaction from 100° to 1000°C appears typical of todorokite from the Todoroki mine. It shows endothermic peaks at 104°, 280°, 480°, 508°, 595°C and broad endothermic reaction from 680° to 880°C and small sharp peak at 980°C. Thermobalance curve show a continuous loss of weight, with no breaks or very prominent flexures but a gradual decrease in amount as the temperature is increased.

7. *Manganese wads*

The Quaternary volcanic activities are often associated with sulphur ore and iron ore, one of the most important mineral resources of Japan. Accompanying these sulphur and iron deposits, manganese wad deposits

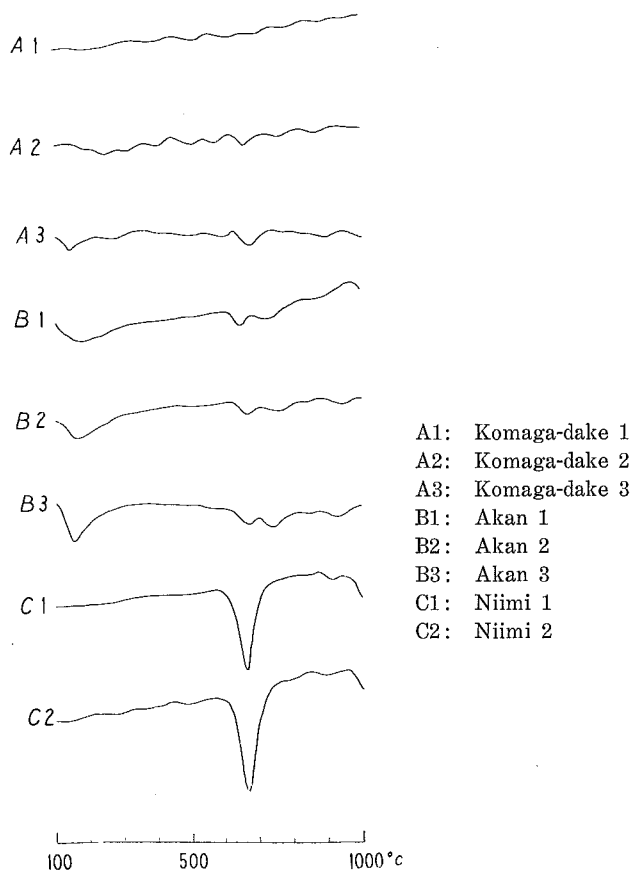


Fig. 6. Differential thermal analysis curves of manganese wad.

are found. Manganese wads are an amorphous, earthy mixture of variable composition, but containing mainly dioxides of manganese and water, with some oxides of iron and other substances. Manganese wads in Hokkaido occur at Akan, Tokachi, Tarumae, Niimi, and Komaga-dake (Fig. 1).

The name is widely applied to a dark-brown earthy oxide of manganese probably in several states of oxidation and combined with diverse amounts of water. It does not possess either a definite atomic structure nor a constant composition; the wad form is probably the first compound resulting from (1) the oxidation of manganous minerals and (2) the precipitation of manganese oxide from surface waters.

Manganese dioxide in noteworthy amounts has been found in the vicinity of active hot and cold springs in several localities in Hokkaido

TABLE 9. X-ray powder data of manganese wads.

Komaga-dake		Niimi		Akan	
d(Å)	I	d(Å)	I	d(Å)	I
				9.66	3
7.59	5				
7.20	5				
		7.02	6		
		4.87	5		
3.12	10	3.11	23		
2.63	3				
2.41	6	2.41	14		
2.11	4	2.11	3		
1.98	2				
1.62	2	1.62	5		
		1.55	3.5		
1.48	2				
1.42	2	1.43	2		

TABLE 10. Chemical composition of manganese wads.

	Komaga-dake	Akan	Niimi
MnO ₂	42.29%	40.29%	85.55%
MnO	24.29	6.21	0.34
SiO ₂	8.10	32.40	0.25
Al ₂ O ₃	0.92	0.62	0.48
Fe ₂ O ₃	0.81	0.49	0.99
CaO	3.31	1.95	0.88
MgO	1.19	2.29	1.63
K ₂ O	0.44	0.49	0.77
Na ₂ O	0.24	0.30	0.30
P ₂ O ₅	0.41	0.54	0.54
BaO	0.13	0.33	0.89
CuO	0.03	0.07	0.03
PbO	0.01	0.03	0.01
ZnO	tr.	tr.	tr.
H ₂ O (+)	13.20	7.80	4.25
H ₂ O (-)	6.39	7.27	1.21
Total	101.76	101.08	98.12

also in the travertine and sinter near extinct springs. In the process of precipitation, it commonly absorbs appreciable amounts of such metals as cobalt, copper, iron, and lead; distinctive names have been given to some of the compounds.

The differential thermal analysis curves of manganese wads in Hokkaido are shown in Fig. 6. Manganese wads are aggregates of certain manganese dioxide minerals. These mineral are pyrolusite, cryptomelane, ranceite and birnessite.

Chemical analysis of manganese wads from Komaga-dake, Akan and Niimi are shown in Table 10. Manganese wads is shown by electron micrographs to occur in single laths and bundles of laths (Photo. 5). There appears to be no evidence of a tubular form like that found for halloysite.

8. *Manganite*

The mineral manganite has received careful study by BUEGER (1936). The crystals are reported to be monoclinic, $a : 8.86 \text{ \AA}$, $b : 5.24 \text{ \AA}$, $c : 5.70 \text{ \AA}$, $\beta = 90$. The unit cell contains $\text{Mn}_5\text{O}_8(\text{OH})_8$. However, it cannot be considered that the structure has been established beyond doubt. There is even some possibility that the substance is orthorhombic rather than monoclinic. Furthermore, the manganite anisotropy studies by KRISHNAN and BANERJEE throw doubt on the equivalent oxidation state of all manganese atoms. They suggest that the manganese is half bivalent and half quadrivalent rather than all trivalent.

In addition to the preparation outlined, FEITKNECHT and MARTI (1945) claim the preparation of MnOOH in two other forms. The preparation given above is called by them " MnOOH " and corresponds to the natural substance. The other forms are designated α and β MnOOH . There is also a supposed manganese manganite.

Manganite occurs widely distributed in nature and common minerals found in manganese hydroxide. It occurs in prismatic crystals and also in stalactite or columnar forms. Manganite frequently alters to pyrolusite, from which it can be distinguished by its hardness and brown streak. Manganite is not so stable under oxidizing conditions as pyrolusite; under such conditions it is generally replaced by the latter. Manganite color varies from steel gray to iron black with a submetallic luster.

The manganite specimens from the Yunosawa mine show typical X-ray diffraction patterns with no extra lines. X-ray powder pattern is shown in Table 11. The specimens were shiny black prismatic crystals. Manganite from Hokkaido is found in both crystalline and massive forms. The crystals are rare, small and much distorted. From the Yunosawa mine short prismatic manganite crystals are found. In those crystal

specimen three faces of $m(110)$, $d(210)$, and $c(001)$ are most frequent in appearing as the dominant face, while $E(205)$, $h(410)$, $e(011)$, $a(100)$, etc. also often appear.

TABLE 11. X-ray powder data of manganite.

A. S. T. M.		Yunosawa mine	
No. 2-0429			
$d(\text{\AA})$	I	$d(\text{\AA})$	I
		4.19	15
		3.75	14
3.40	100	3.40	100
		2.91	11
2.65	80	2.64	100
2.52	40	2.52	5
2.41	80	2.41	18
2.26	60	2.27	52
2.18	60	2.19	15
1.77	80	1.78	16
1.70	70	1.70	45
1.66	80	1.67	26
1.63	70	1.63	41
1.50	70	1.50	11
1.43	70	1.43	6
1.32	70	1.32	6
1.29	20	1.29	5
1.26	20		
1.24	20		
1.21	20		
1.18	40	1.18	5
1.16	40	1.15	4
1.13	60	1.13	19
1.11	20	1.11	2
1.10	20		
1.08	20		

The differential thermal analysis curves of manganite from the Yunosawa mine show a sharp endothermic peak at 395°C followed by a broader endothermic peak at 985°C (Fig. 7). Pure manganite gives a strong peak at about 395°C , corresponding in respect to dehydration to that of $\beta\text{-MnO}_2$. The pattern of $\beta\text{-MnO}_2$ almost disappears at 700°C and that of the second endothermic peak at about 985°C corresponding to the conversion of Mn_2O_3 .

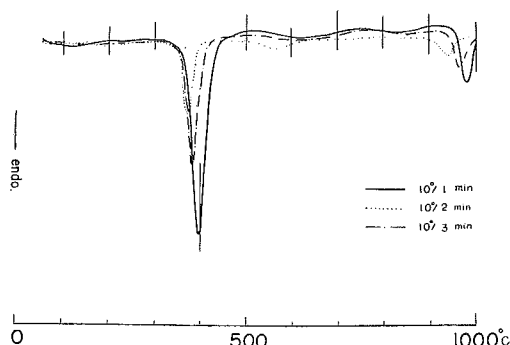


Fig. 7. Differential thermal analysis curves of manganite from the Yunosawa mine.

to Mn_3O_4 . These X-ray powder patterns are shown in Fig. 11-a. The results of PAVLOVITCH (1935) are similar, but be noted that the product after the 370°C peak depended upon the conditions of heating; RODE (1955) has concluded that in vacuum Mn_2O_3 is formed while in air $\beta\text{-MnO}_2$ may be one of the products. Frequently curves for manganite show an additional peak at $550^\circ\sim 600^\circ\text{C}$ which KULP and PERFETTI (1950) have attributed to an unidentified impurity; RODE (1955) however, has considered it to relate to manganite and to represent in vacuum the conversion of Mn_2O_3 to a mixture of α and β hausmannite or in air to represent the decomposition of $\beta\text{-MnO}_2$. The differential thermal analysis curves of manganite from the Yunosawa mine show no additional peak at $550^\circ\sim 600^\circ\text{C}$. This well illustrates the divergence of opinion upon some of the basic processes; the matter of far the products of heating are influenced by factors relating to apparatus and technique to be elucidated.

On the other hand, dehydration curve and thermobalance curve of manganite from the Yunosawa mine are shown in Fig. 8. The loss of weight up to 300°C is effected by dehydration alone, and is suddenly increased at 400°C , amounting to approximately 30%. The secondary loss of about 7% in weight observed at 600°C may be due to deoxidation. Loss of weight up to 580°C does not appear on the differential thermal analysis curve.

9. Groutite

Groutite, HMnO , is a member of the diasporite-goethite group. The writer has recently discovered in the Pirika mine, Hokkaido, the first groutite to be recorded from Japan. The crystallography of groutite, which was first reported by GRUNER (1947), indicated that it is a member of the diasporite-goethite group. The dimensions of the orthorhombic unit

cells are $a : 4.58 \text{ \AA}$, $b : 10.76 \text{ \AA}$, and $c : 2.89 \text{ \AA}$. The atomic arrangement is very nearly identical with that of diaspore.

Groutite is found in the Motoyama deposit of the Pirika mine in Hokkaido. The minute crystals aggregate always in radial form and nearly always are associated with manganite (Photo. 6). The crystal of groutite is thin and platy in habit and forms a radial aggregate. Groutite is associated with manganite, quartz, barite and limonite. The color of

TABLE 12. X-ray powder data groutite.

Cuyuna Range, Minnesota, U. S. A. (by Gruner)			Cuyuna, Range, Minnesota, U. S. A. (by Ramdohr)		Pirika Mine		Manganite A. S. T. M. Card No. 2-0429	
d(Å)	I	(hkl)	d(Å)	I	d(Å)	I	d(Å)	I
5.36	1	020	5.31	s	5.36	10		
4.17	10	110	4.17	sst	4.19	73		
3.462	1-2	120	3.45	s	3.46	9	3.40	100
2.798	6	130	2.79	st	2.79	22		
2.675	6	040	2.66	st	2.67	30	2.65	80
2.524	1	021	2.52	s	2.53	7	2.52	40
2.369	6		2.36	st	2.37	40	2.41	80
2.303	5	140	2.29	st	2.30	20	2.26	60
2.210	2		2.20	m	2.21	13	2.18	60
2.008	1		2.00	s	2.00	2		
1.959	0.5	041	1.95	ss				
1.932	1	150	1.92	s	1.932	7		
1.798	0.5		1.79	ss	1.782	2		
1.763	2		1.75	s	1.763	6	1.77	80
1.732	1		1.73	s	1.735	5		
1.692	5		1.69	st	1.691	16	1.70	70
							1.66	80
							1.63	70
1.603	4		1.60	st	1.604	12		
1.559	0		1.55	s	1.559	3		
1.515	3	061	1.51	m	1.513	7	1.50	70
1.465	1		1.47	ss				
			1.45					
1.448	1		1.44	s	1.446	6		
1.435	2		1.43	s	1.438	7	1.43	70
1.398	1		1.39	s	1.397	3		
1.367	0.5-1		1.36	s	1.361	3		
1.345	1		1.34	s	1.344	2	1.32	70
1.304	0.5		1.30	ss			1.29	20
1.286	1		1.28	s	1.278	3		
1.281	1	180						
1.267	1		1.26	s			1.26	20
1.258	1		1.253	s	1.259	2	1.24	20
1.220	1				1.218	3		
1.212	1		1.217	s/ss			1.21	20
1.202	1		1.208	s/ss				
			1.196	s			1.18	40
1.153	2		1.150	m	1.151	6	1.16	40
1.131	1-2		1.131	m	1.133	5	1.13	60
			1.117	ss			1.11	20
1.107	1		1.105	s			1.10	20

the groutite is dull black and luster submetallic, while manganite is brilliant dark steel gray. Cleavage of groutite is very perfect and yields brilliant reflections. The streak is reddish dark brown like that of manganite. The specific gravity determined on one gram of handpicked material is 4.182 recalculated to 4°C.

X-ray powder diagram was made with unfiltered Fe radiation using a Philips geiger counter X-ray spectrometer. The interplaner spacings and the intensities of reflections are listed in Table 12. Such characters are in agreement with those of the groutite from iron mine of the Cuyuna Range of Minnesota, U. S. A. that obtained Gy GRUNER (1947) and RAMDOHR (1956).

The differential thermal analysis curves for pure manganite have been studied by KULP & PERFETTI (1950); no curve for groutite can be traced. Differential thermal analysis curves and thermobalance curves of groutite from the Pirika mine are as shown in Fig. 8. Groutite gives a curve very similar to that for manganite with two endothermic peaks. These curves each have two remarkable endothermic peaks at approximately 395°C corresponding to dehydration, and an endothermic peak at about 980°C~1020°C.

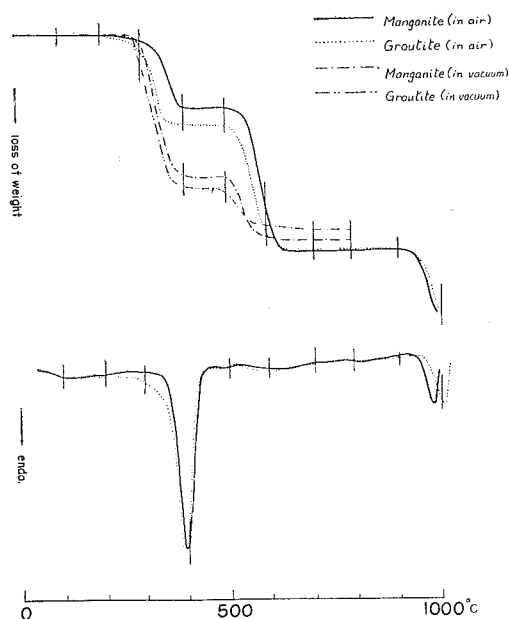


Fig. 8. Differential thermal analysis and thermobalance curves of manganite and groutite.

10. *Thermal behavior of some manganese dioxides and hydroxides*

A. Birnessite and Todorokite

Through a combination of differential thermal analysis and X-ray powder pattern several significant points were brought out which would have otherwise escaped notice. Investigation was made on the effect of heat treatment in air of birnessite and todorokite on X-ray powder pattern. The result are shown in Fig. 9, 10 and summarized:

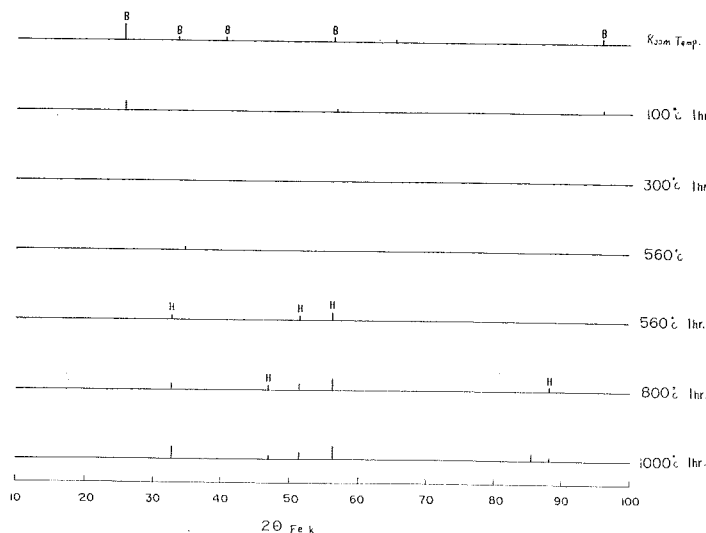


Fig. 9. X-ray powder patterns of heat treatment of birnessite.
B: Birnessite H: Hausmannite

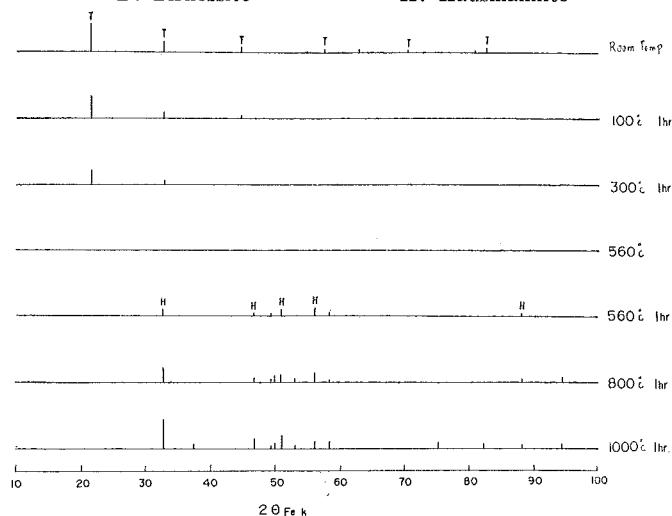


Fig. 10. X-ray powder patterns of heat treatment of todorokite.
T: Todorokite H: Hausmannite

a) Birnessite

X-ray powder patterns of birnessite heated at about 150°C for 1 hr. showed to low intensity patterns. The patterns of this mineral almost disappear at about 300°C for 1 hr. and it goes to amorphous material. X-ray powder patterns of this material upon being heated to 560°C, 800°C and 1000°C for 1 hr. showed Mn_2O_3 patterns.

b) Todorokite

X-ray powder patterns of Todorokite heated at about 300°C for 1 hr.

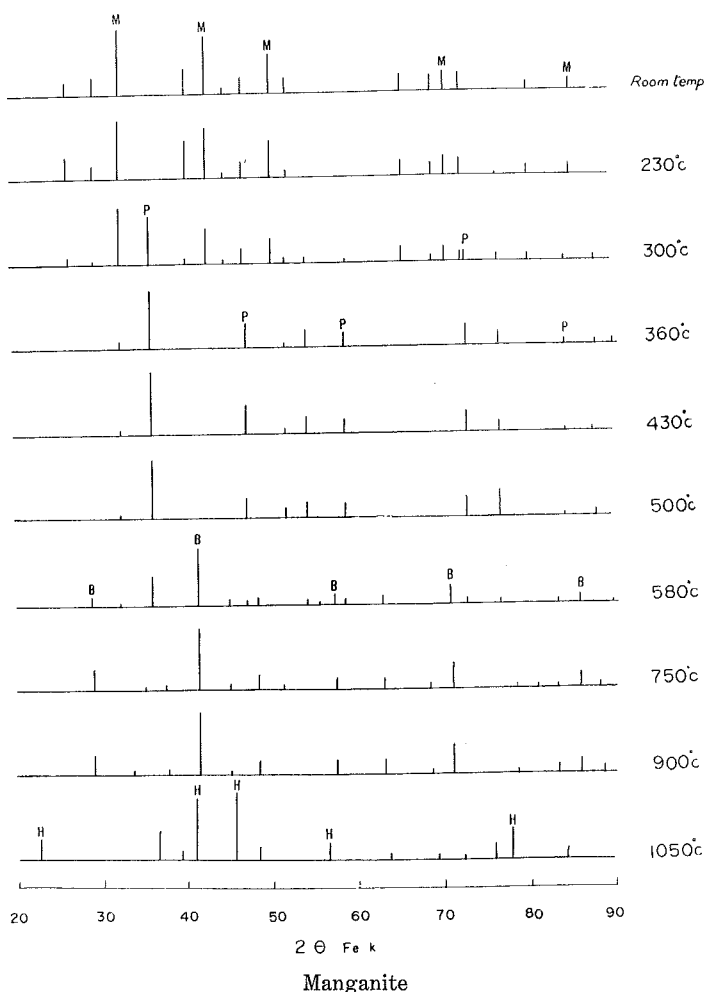
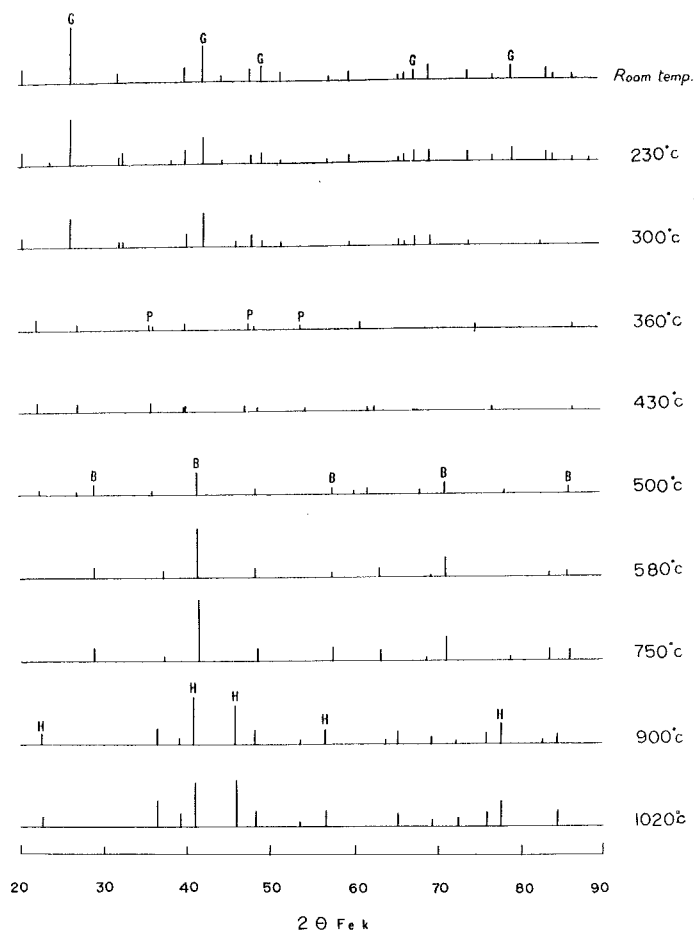


Fig. 11-a. X-ray powder patterns of heat treatment in air.
M: Manganite P: Pyrolusite B: Bixbyite
H: Hausmannite



Groutite

Fig. 11-b. X-ray powder patterns of heat treatment in air.
 G: Groutite P: Pyrolusite B: Bixbyite
 R: Ramsdellite H: Hausmannite

showed to low intensity patterns. The patterns of this mineral almost disappear at about 560°C and it goes to amorphous material. X-ray powder patterns of this material upon being heated to 560°C, 800°C and 1000°C for 1 hr. showed Mn_3O_4 patterns.

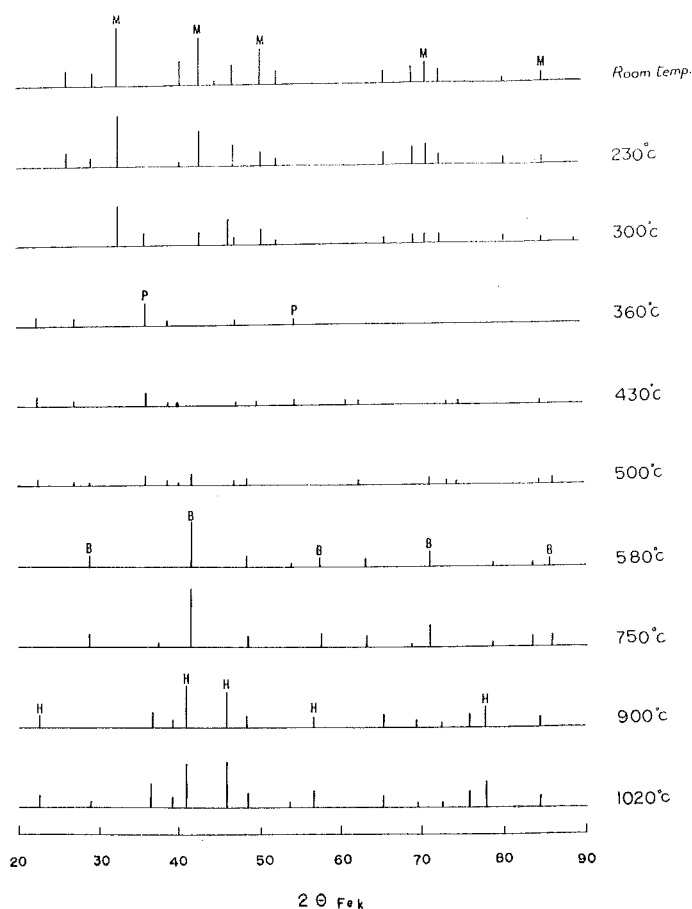
B. $MnO-OH$ system

Investigation was made on the effect of heat treatment in air or in vacuum of manganite and groutite on X-ray powder pattern. The results are shown in Fig. 11, 12 and summarized:

a) Phase conversion in air

X-ray powder patterns of manganite heated at about 300°C showed to some degree β - MnO_2 and manganite patterns. The patterns of manganite almost disappear at the first endothermic reaction, (380°C), corresponding to the dehydration to β - MnO_2 .

According to KULP and PERFETTI (1950), pure manganite gives a strong peak at about 370°C, corresponding to the dehydration to Mn_2O_3 . The results of Pavlovitch (1935) are similar, but he noted that the product after the 370°C peak depended upon the conditions of heating; RÖDE (1955)



Manganite

Fig. 12-a. X-ray powder patterns of heat treatment in vacuum.

M: Manganite

P: Pyrolusite

B: Bixbyite

H: Hausmannite

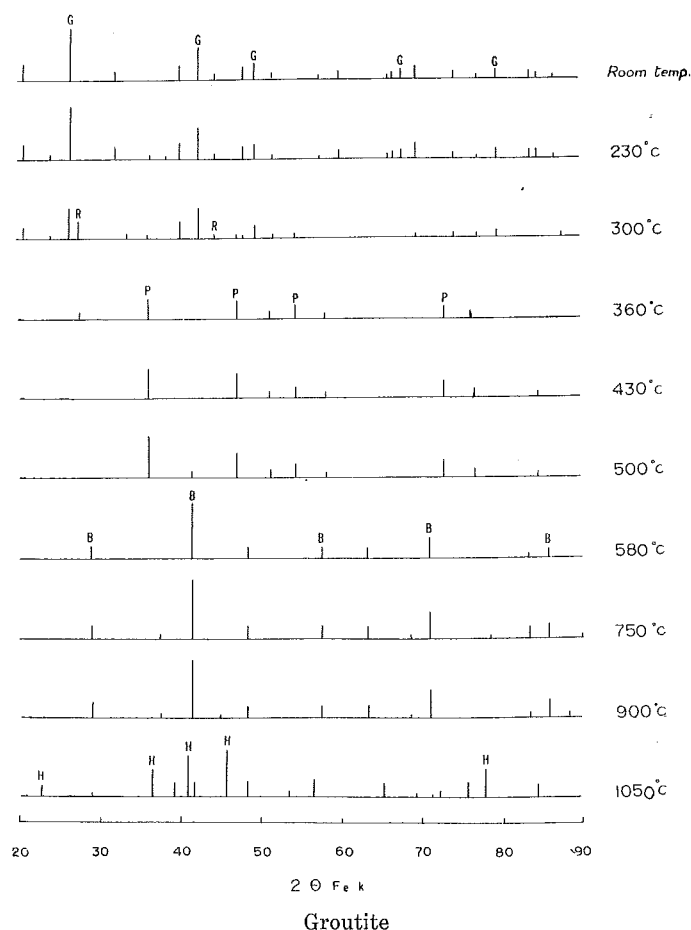


Fig. 12-b. X-ray powder patterns of heat treatment in vacuum.

G: Groutite P: Pyrolusite B: Bixbyite
 H: Hausmannite R: Ramsdellite

has concluded that in vacuum Mn_2O_3 is formed while in air $\beta\text{-MnO}_2$ may be one of the products. Frequently curves for manganite show an additional peak at KULP and PERFETTI (1950) have attributed to an unidentified impurity; RODE (1955), however, has considered it to relate to manganite and to represent in vacuum the conversion of Mn_2O_3 to a mixture of α and β hausmannite or in air to represent the decomposition of $\beta\text{-MnO}_2$. In air, groutite converts to ramsdellite at about 300°C ; it oxidizes partly to ramsdellite. Above 360°C it goes directly to $\beta\text{-MnO}_2$. The patterns of $\beta\text{-MnO}_2$ from groutite almost disappear at 580°C but this temperature

permite patterns to remain of β - MnO_2 from manganite.

Groutite is considerably larger in unit cell volume than is manganite and less stable under pressure and in elevated temperatures. X-ray powder diffraction of manganite and groutite heated to 750°C and 900°C showed good α - Mn_2O_3 patterns, and that of the second endothermic peak at about 985°C corresponding to the conversion of Mn_2O_3 to Mn_3O_4 .

b) Phase conversion in vacuum

The phase changes in vacuum of manganite and groutite could not be followed in the same way as in air.

Usually, the phase changes in vacuum come to pass in low temperature. Two interesting phases were encountered in this study. In the low temperature an unknown phase developed and X-ray powder diffraction of these minerals upon being heated to 360° , 430°C and 500°C showed γ - Mn_2O_3 patterns.

The results obtained are summarized in Table 13.

TABLE 13. Effect of heat treatment of manganite and groutite.

		Original.....1000°C			
		500°			
in air	manganite	→	pyrolusite	→	α - Mn_2O_3 → Mn_3O_4
	groutite	→	ramsdellite pyrolusite	→	α - Mn_2O_3 → Mn_3O_4
in vacuum	manganite	→	unkown phase pyrolusite	→	α - Mn_2O_3 → Mn_3O_4
	groutite	→	ramsdellite unkown phase pyrolusite γ - Mn_2O_3	→	α - Mn_2O_3 → Mn_3O_4

11. Differential thermal analysis of artificial mixture

In the past decade, differential thermal analysis has developed in to a very useful mineralogical technique. Since it provides both qualitative and quantitative data on the presence of thermally active minerals, it is ideally suited to a study of fine-grained natural aggregates which present a difficult problem to other methods of attack. It appeared that the natural occurrence and importance of the manganese oxide minerals would make desirable a preliminary investigation by thermal analysis. In this study it has been the objective to define the thermal curves of the manganese dioxide and hydroxide minerals and to show how the method may be applied to natural mixtures. Some manganese dioxide mineral species under a certain rate of heating show a characteristic type of differential

thermal analysis curve. Natural manganese dioxide ores are aggregates of certain manganese dioxide minerals. A group of natural aggregates has been analysed and concentrations of the various minerals, interpreted in terms of the differential thermal curves of artificial mixture. Since each mineral will ordinarily yield a characteristic set of peaks independent of the foreign constituents, frequently the members of a mixture in a fine-grained aggregate may be defined. Obviously the more complex the mixture the more difficult becomes the interpretation. Usually, however, X-ray, optical, and thermal data together are adequate for definition of the major mineral present in a mixture if the group is thermally reactive. The application of differential thermal analysis to this group of minerals

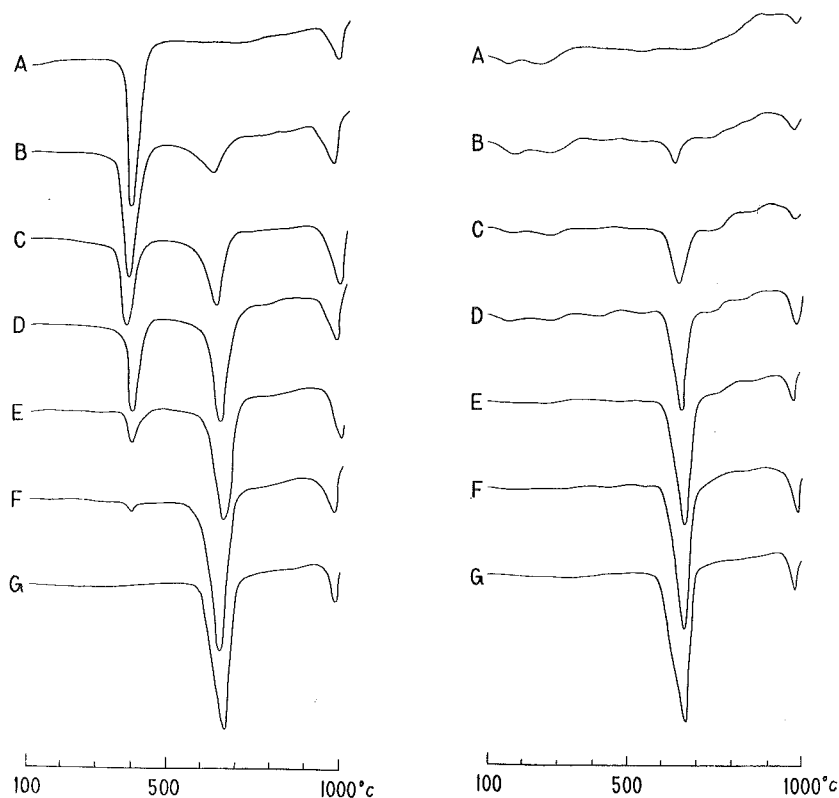


Fig. 13, 14. Differential thermal analysis curves of artificial mixture.

wt. %	A	B	C	D	E	F	G	wt. %	A	B	C	D	E	F	G
Manganite	100	90	70	50	30	10	0	Cryptomelane	100	90	70	50	30	10	0
Pyrolusite	0	10	30	50	70	90	100	Pyrolusite	0	10	30	50	70	90	100

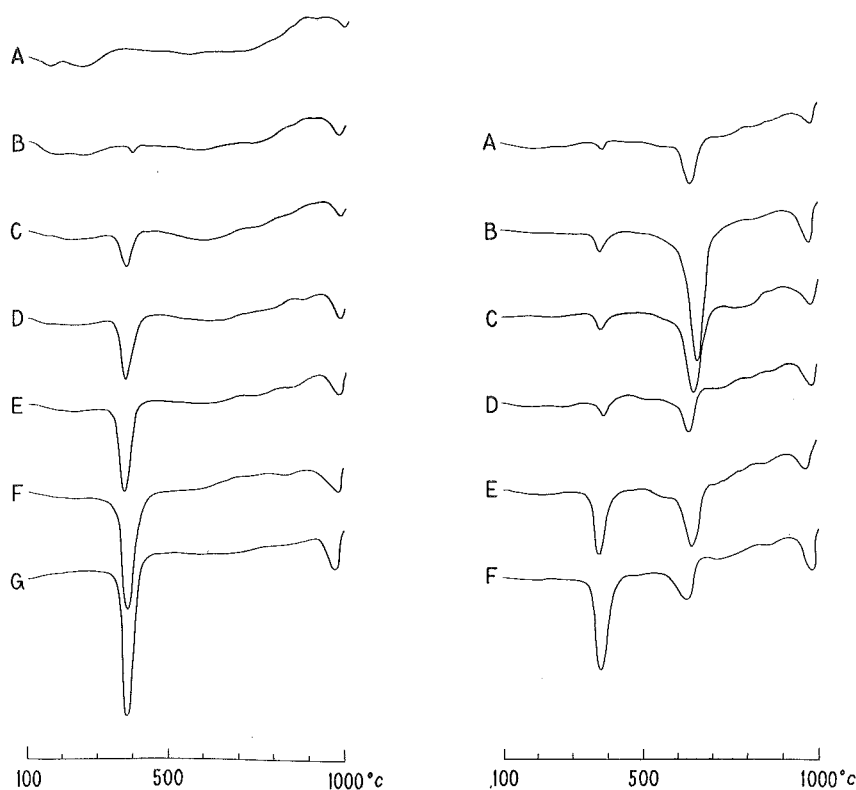


Fig. 15, 16. Differential thermal analysis curves of artificial mixture.

wt. %	A	B	C	D	E	F	G		A	B	C	D	E	F
Cryptomelane	100	90	70	50	30	10	0	Pyrolusite wt. %	20	65	50	25	25	15
Manganite	0	10	30	50	70	90	100	Cryptomelane	65	15	25	50	25	20
								Manganite	15	20	25	25	50	65

provides valuable information unobtainable by other standard techniques.

The analysis of the mineral composition of natural aggregates of manganese dioxide minerals requires a previous knowledge of the size and shape of characteristic peaks as a function of concentration. Artificial mixtures were prepared and thermally analysed. Figs. 13, 14, 15, 16 show the results for mixtures of pyrolusite, manganite and cryptomelane. In general, the variation of peak amplitude or peak area with concentration is well established. These curves are used as a basis for estimating the percentage of these minerals in unknown assemblages.

12. Representative natural aggregates

Figs. 17, 18, 19, and 20 show the differential thermal analysis curves

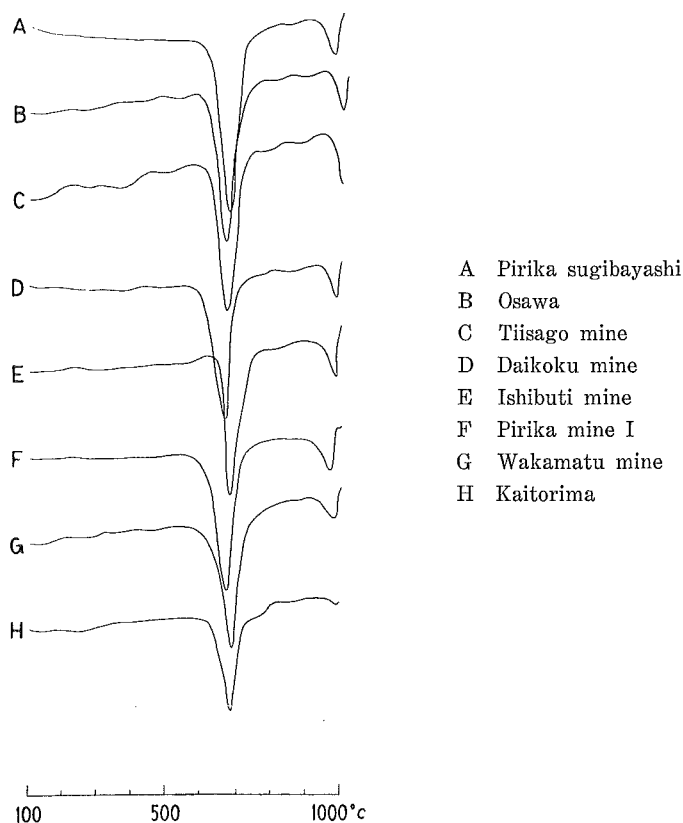


Fig. 17. Differential thermal analysis curves of pyrolusite type ore.

of natural manganese dioxide and hydroxide aggregates. Figs. 17, 18 show those curves of pyrolusite type ores. A sample, shown in Fig. 18-D labelled pyrolusite from Nakauta, contains a small amount of cryptomelane and that in Fig. 18-G labelled pyrolusite from Matsumae, contains manganite and cryptomelane. Differential thermal analysis curves of manganite type ores are shown in Fig. 19. A sample, shown in Fig. 19-B contains pyrolusite and a small amount of cryptomelane. Three specimens, exhibited in Fig. 19-C, -D, and -E contain pyrolusite. Differential thermal analysis curves of several cryptomelane type ores collected from manganese mines in Hokkaido are shown in Fig. 20. These present the presence of colloidal water and a small amount of pyrolusite and clays.

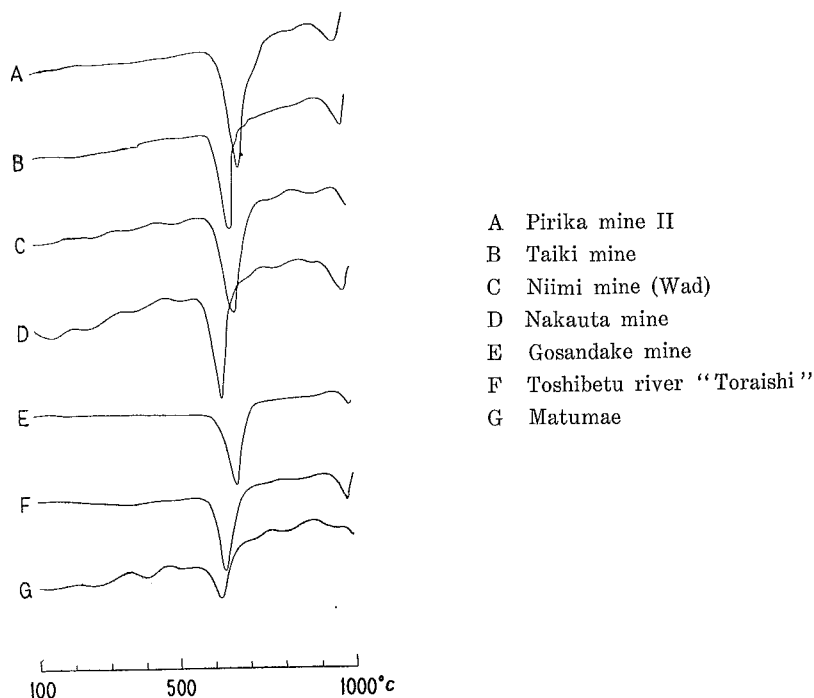


Fig. 18. Differential thermal analysis curves of pyrolusite type ore.

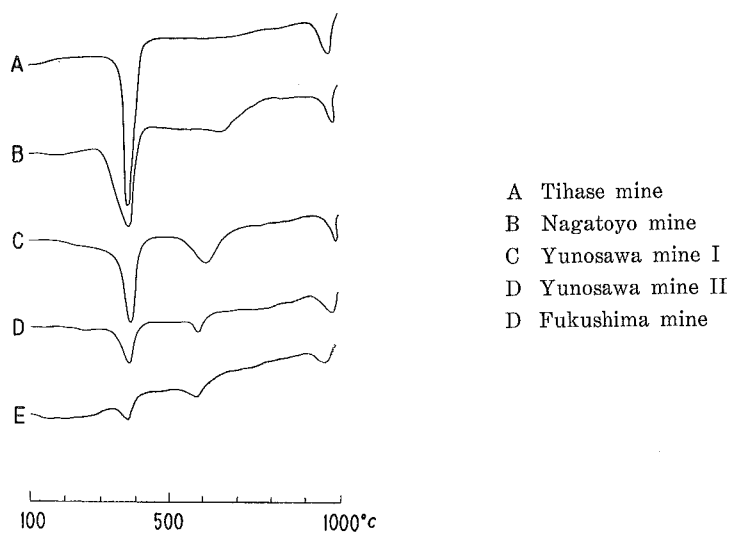


Fig. 19. Differential thermal analysis curves of manganite type ore.

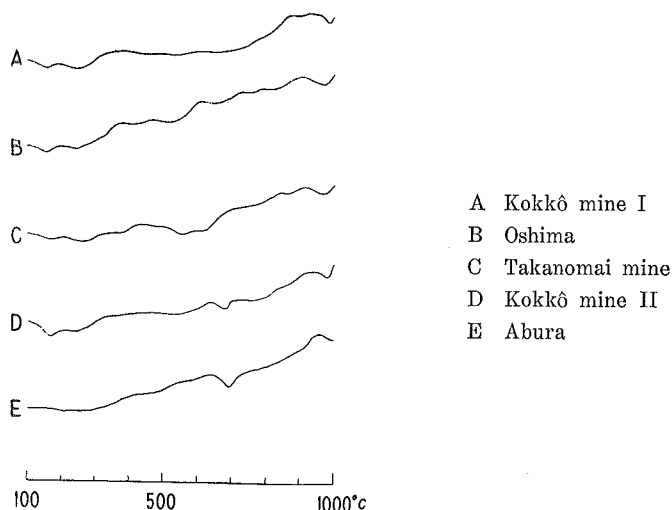


Fig. 20. Differential thermal analysis curves of cryptomelane type ore.

IV. Scheme of classification of manganese dioxide minerals

The method of classification adopted in this work, and the one which can alone claim to be thoroughly scientific, is that which places similar chemical compounds together in a common class and which further arranges the mineral species into groups according to the more minute relation existing between them in respect to chemical composition, crystal-line form and other physical properties.

Manganese dioxide is one of the most familiar and common minerals found in various manganese deposits, but its mineralogical studies of it have been very indeterminate owing to the variability and overlapping of physical properties and chemical composition. Its usual occurrence comprises several modifications which are closely related in their crystal structures. The writer has attempted a classification of various modifications of natural manganese dioxide on the basis of the X-ray analyses of present and previous studies.

1. *Review of previous work*

In their report on the manganese oxide minerals, FLEISCHER and RICHMOND (1943) state that the X-ray method provides the only way of distinguishing many of the minerals, and to this end they list the spacings and intensities of 12 of them. On the other hand, they state that confirmatory chemical tests are required if the minerals cryptomelane, hollandite and coronadite, which GRUNER (1943) showed to be isostructural, are to

be identified with certainty.

Though loosely known as the manganese oxide minerals, many contain additional elements. For example, cryptomelane, which is one of the commonest, has been tentatively given the formula KR_8O_{16} , where R is chiefly Mn^{+4} . Similarly the artificial dioxides often contain important amounts of other elements. These are for the most part adventitious, having been introduced in the reagents or from the manufacturing plant, and may be present as adsorbed ions, or as occupants of lattice position.

While there is doubt about the structure of many of the oxides to be described later, there at least seems general agreement on the dense black oxide produced by heating the nitrate. As early as GEORGEU (1879) prepared MnO_2 by this method and, after an examination of its density, hardness, crystal form and composition, stated it to be an artificial polianite. The identity of polianite and pyrolusite was claimed by ST. JOHN (1923) as a result of X-ray analysis, and was later confirmed by others (FERRARI, 1926, SMITHERINGLE, 1929, VAUX and BENNETT, 1937, STRUNZ, 1943). The first X-ray examination of the oxide formed from the nitrate appears to have been made by FERRARI (1926), who announced that its structure was the same as that of pyrolusite; subsequent X-ray studies confirmed his findings. The recognition that this method of preparation produced the stable modification has led to its adoption when material has been required for precise determination of physical and chemical constants.

Difficulties were soon encountered, however, in trying to establish the nature of the many varieties of MnO_2 produced by other methods, particularly those oxides prepared in the wet way. FERRARI (1926) examined one such oxide (prepared by precipitation with alkali) and stated it to be amorphous. The first serious attempt at a general classification seems to have been made by DUBOIS (1936). He found that several methods of preparation gave an oxide which had a different X-ray pattern from that of pyrolusite. This form, which he called α - MnO_2 , could be produced by the spontaneous decomposition of a solution of permanganic acid, or by the action of H_2O_2 on $KMnO_4$, or by adding a dilute $MnSO_4$ solution to a dilute $KMnO_4$ solution. When the α -form obtained by the decomposition of permanganic acid was heated in a sealed tube at $400^\circ C$ for 48 hours, the product showed a pattern which was different from both the α -form and pyrolusite. The same pattern was obtained from an oxide made by adding $KMnO_4$ to excess $MnSO_4$. He tentatively suggested this third form was a mixture of an unknown oxide and the dioxide. Analysis showed it to have the composition $MnO_{1.88}$. Oxides made by methods such as the above always contain an appreciable amount of potash and of

combined water. They are further characterized by containing considerably less oxygen than corresponds to the formula MnO_2 .

GLEMSER (1939) examined three samples of oxides prepared by: (a) the oxidation of manganous sulfate by ammonium persulfate; (b) the oxidation of the same solution by potassium permanganate; and (c) the decomposition of permanganic acid. These products had identical X-ray diagrams which did not agree with those of DUBOI's third modification. GLEMSER proposed that this new modification be called $\gamma\text{-MnO}_2$. It is of interest to note that although the patterns of GLEMSER's three samples were the same, their composition varied considerably the numerical values of n in the formula MnO_n being 1.93, 1.84 and 1.76. When the samples were boiled with nitric acid, the patterns were sharper but were otherwise unchanged, and n had increased to 1.97 in each instance.

SCHOSSBERGER (1940, 1943) has also reported the existence of GLEMSER's $\gamma\text{-MnO}_2$ in an artificial preparation used for the battery trade. The method of preparation is not stated in the abstracts, and the original paper is not available to the present writer. In their studies on the autoxidation of manganous hydroxide, NICHOLS and WALTON (1942) prepared a number of samples by mean of air and oxygen through alkaline manganous solutions. Apart from one sample which showed the pattern of hausmannite, Mn_3O_4 , they were all reported to be amorphous.

GRUNER (1943) stated that the precipitate obtained on adding HCl to boiling KMnO_4 solution and neutralizing with ammonia was amorphous, but that it gave cryptomelane when heated to 400°C . Exactly the same result was obtained from the amorphous material formed by the addition of KClO_3 to pure $\text{Mn}(\text{NO}_3)_2$ in HNO_3 . On of the latter experiment, however, a pyrolusite was formed in place of the amorphous material, and GRUNER expressed the view that there was no way of predicting which oxide would be produced.

MCMURDIE (1944) has found GLEMSER's γ -modification in oxides produced by electrolytic oxidation, and considered that it might be a very fine-grained pyrolusite. He also described another form which he called $\delta\text{-MnO}_2$ and which he thought might be a fine grained cryptomelane. Most of the samples studied by MCMURDIE were of commercial origin, the methods of preparation not being stated. They consisted chiefly of cryptomelane and $\delta\text{-MnO}_2$ with some $\gamma\text{-MnO}_2$ and pyrolusite. One oxide prepared by the slow addition of HCl to a hot solution of KMnO_4 gave the pattern of $\delta\text{-MnO}_2$. He also examined some natural ores, including some of battery grade from the Gold Coast and from Montana. The conclusions he reached regarding their composition are discussed later.

In addition to X-ray diffraction, MCMURDIE used electron diffraction and electron microscopy as aids in his examination. He was able to show from electron micrographs that within any one crystal species a wide variety of shapes occurred, and that electron diffraction patterns were more informative for some of the finest oxides.

FEITKNECHT and MARTI (1945) have recently described the products obtained by the controlled oxidation of manganous hydroxide. These oxides vary continuously in composition from $\text{MnO}_{1.1}$ to about $\text{MnO}_{1.8}$ and exhibit some five or six different X-ray patterns. They concluded that the structure of the most highly oxidized member of this series (which they called manganous manganite) was derived from the well-marked layer lattice of the parent manganous hydroxide. FEITKNECHT and MARTI suggest that layers of MnO_2 with a cadmium iodide type lattice are interspersed with disordered layers of $\text{Mn}(\text{OH})_2$, such as occur in the α -hydroxides of the divalent metals. Since the average value of n for samples with this pattern is 1.8, they suggest the formula $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2$ for manganous manganite. This presumably means that within the $\text{Mn}(\text{OH})_2$ layers, some Mn^{+2} and $(\text{OH})^-$ ions are replaced by Mn^{+4} and O^{2-} ions.

On the other hand, COLE, WADSLY and WALKLEY (1947) investigated the relationship between γ -phase and ramsdellite and concluded that there were at least three types of γ - MnO_2 characterized by small differences in their X-ray diffraction patterns. The patterns of some samples of γ - MnO_2 met with in this study possess more lines than those given by GLEMSER. One of the three modifications of this mineral has been recognized in some ores including those from the Gold Coast, Africa. The patterns given for cryptomelane, γ - MnO_2 and manganous manganite are the same as those of γ - MnO_2 , $\text{MnO}_{1.88}$ and δ - MnO_2 respectively. And they are suggested that the various forms of γ - MnO_2 discussed above were in perfectly crystallized ramsdellite.

OKADA, UEI and CHIN secured (1947) a new type of the manganese dioxide crystal anodically by electrolysis. The electrolyte is a water solution of the manganese salt and the ammonia salt. This modification was named ϵ - MnO_2 by OKADA and has been investigated by many other workers.

Among the minerals chiefly of manganese dioxide, there are more than twenty species which are reported to be colloidal in character; they are grouped under the name "manganomelane." Their chemical compositions vary to some extent with each specimen, because the strong adsorption of cations by dioxide of manganese does not allow the keeping of constant chemical composition by these minerals. The classification based

on chemical composition alone has therefore only a subordinate meaning. YOSHIMURA (1934) attempts to classify them by the difference of crystallinity and hardness, in the following four division:

1. crystalline manganomelane
2. wad
3. abnormal psilomelane
4. psilomelane

Each division is subdivided into five groups according to chemical composition. MnO_2 , MnO and H_2O are common to all species, so the classification is based on the kind of predominating bases other than MnO . Minerals of group (a) are the purest, containing no bases other than MnO or Mn_2O_3 ; those of group (b) contain plenty of alkalis; those of group (c) alkaline earths and magnesia; those of group (d) iron (Fe^{+3}) and alumina, while minerals of group (e) contain oxides of heavy metals.

SAMSON and WADSLEY (1948) have studied the manganese ore minerals from the oxide mine in Buchan, Victoria. These specimens exhibited a wide variation in composition, both in potassium content and $\text{Mn} : \text{O}$ ratio, therefore the possibility that the Buchan specimens are disordered forms of cryptomelane due to lattice imperfections must be rejected.

DELANO (1950) examined some samples of natural manganese dioxide. These manganese dioxides exist in three crystalline allotropic forms namely, pyrolusite, cryptomelane, and ramsdellite. The term $\gamma\text{-MnO}_2$ should be referred to ramsdellite. The imperfectly crystallized minerals showing a more or less incomplete X-ray pattern which have been generally called $\gamma\text{-MnO}_2$ are really impure varieties of ramsdellite or pyrolusite. There is a series of patterns of infinite gradations between ramsdellite and pyrolusite. Ramsdellite and pyrolusite are known in the form of 100% manganese dioxide crystals but $\gamma\text{-MnO}_2$ and cryptomelane so far have tenaciously retained various impurities. The cryptomelane group comprises a series of alkali compounds between Mn_8O_{16} and $\text{K}_2\text{Mn}_8\text{O}_{16}$. The names $\delta\text{-MnO}_2$ and manganous manganite designate compounds of alkali and manganese oxides in variable proportion and, therefore, are incorrectly chosen.

JONES and MILNE (1956) investigated the relationship between $\delta\text{-MnO}_2$ and manganous manganite and birnessite of natural manganese oxide. Birnessite giving an X-ray powder patterns similar to that of synthetic materials was described as manganous manganite and $\delta\text{-MnO}_2$. The optical, chemical, and X-ray data of birnessite show that it is a naturally occurring $\delta\text{-MnO}_2$.

SREENIVAS (1956) has recently described the $\gamma\text{-MnO}_2$ from Mysore, India. X-ray powder spacings observed and tabulated below agree fairly

well with the values of McMURDIE and GOLOVATO for γ - MnO_2 . That material is unstable at high temperatures. An X-ray powder pattern of the mineral taken after heating 500°C showed a pyrolusite pattern, hence the γ - MnO_2 could be considered as poorly crystallized pyrolusite, but the exact nature of it is still uncertain.

SOREM and CAMERON (1960) have studied the manganese ore mineral from the highly productive deposits of Nsuta, Ghana. The term Nsuta MnO_2 is introduced as a tentative name for the mineral or mineral group most abundant in the ores. An X-ray diffraction data indicate that Nsuta MnO_2 is a discrete mineral or mineral group, with no direct relation to pyrolusite or ramsdellite. Powder patterns given by Nsuta MnO_2 also differ from those reported for the artificial manganese dioxide γ - MnO_2 . One type of Nsuta MnO_2 gives a pattern closely resembling that of ρ - MnO_2 , a chemical product, but the d spacings and relative intensities of certain lines are not identical.

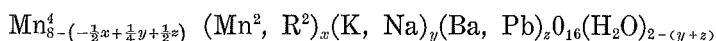
2. α - MnO_2 group

In the course of a study of manganese oxide, precipitates consisting of α - MnO_2 were obtained by the reduction of a KMnO_4 solution by various reagents, for instance, H_2O_2 and HCl . As has been stated previously (COLE, WADSLEY & WALKELY; 1947) and as BYSTROM et al. (1950) could confirm, the X-ray powder photographs of these preparations showed that there must be a close structural similarity between α - MnO_2 and some of the manganese oxide minerals, namely, cryptomelane, hollandite and coronadite. The powder photographs of α - MnO_2 showed the characteristic broadening of the reflections which are caused by very small crystallites. Heat treated samples gave somewhat sharper reflections, but it was impossible to obtain crystals large enough for rotation and WEISSENBERG methods. Hydrothermal syntheses also failed to produce such crystals. As no definite conclusions regarding the composition and structure of α - MnO_2 could be drawn from powder photographs alone, BYSTRÖM determined to investigate also the above-mentioned manganese oxide minerals.

For the nomenclature of the manganese oxide minerals the rules recommended by FLEISCHER and RICHMOND (1943) have been applied. Their description of the chemical and X-ray characteristics of the minerals can be summarized as follows: The general formula is probably AR_8O_{16} with $\text{A}=\text{K}$, Pb and Ba , and $\text{R}=\text{Mn}^{+4}$ chiefly. The minerals contain 0~5% non-essential water. The symmetry is tetragonal (cryptomelane) or pseudotetragonal (coronadite and hollandite), in which case probably triclinic.

The size of the unit cell of cryptomelane has been determined by

RAMSDELL (1942) to be $a : 9.98 \text{ \AA}$, $c : 2.86 \text{ \AA}$, and by RICHMOND and FLEISCHER (1943) to be $a : 9.82 \text{ \AA}$, $c : 2.83 \text{ \AA}$. The reflections indicate a body-centred cell. FRONDEL and HEINRICH (1942) made unsuccessful efforts to index the powder patterns of coronadite and hollandite with this cell. However, they could index nearly all lines in terms of another body-centered tetragonal cell with $a : 6.95 \text{ \AA}$, $c : 5.72 \text{ \AA}$ for coronadite and $a : 6.94 \text{ \AA}$, $c : 5.1 \text{ \AA}$ for hollandite. For coronadite they suggested the formula $\text{MnPbMn}_6\text{O}_{14}$ or $\text{MnPbMn}_6\text{O}_{14}\text{H}_2\text{O}$. Hollandite was looked upon as the barium analogue of coronadite, perhaps $(\text{MnFe})\text{BaMn}_6\text{O}_{14}$. As will be seen, there is a close relationship between the unit cell of cryptomelane and that suggested for hollandite and coronadite: $6.95/\sqrt{2}=9.82$ and $5.72/\sqrt{2}=2.86$. RICHMOND and FLEISCHER (1943), remark that the powder and WEISSENBERG photographs of cryptomelane and hollandite are nearly identical and suggest that the three minerals are isostructural. GRUNER (1943) assumes a complicated general formula for the three minerals, namely,



Evidently from the isostructural relationship between $\alpha\text{-MnO}_2$ and hollandite, it follows that $\alpha\text{-MnO}_2$ must hold some large ions, as for example, potassium, to prevent the structure from collapsing. The necessity of K^+ ions for the formation of $\alpha\text{-MnO}_2$ has been pointed out by COLE et al. (1947).

GRUNER's experiment on the cation exchange of MnO_2 shows that Ag^+ ions enter the structure more readily than the larger Pb^{+2} and Ba^{+2} ions. This is evidently what is to be expected from the structure, as the short A-A distances of about $2.8 \text{ \AA}$ must lead to a certain instability of the structure, because of strong repulsive forces between the cations, and these forces must apparently be less for the smaller ions. In accordance with this the two fold position can be filled to a larger extent with a larger number of adjacent A ions, when these ions are smaller and of less valency, i.e. as is the case for Ag^+ compared with Pb^{+2} and Ba^{+2} . BYSTROM (1950) has recalculated the densities with GRUNER formula. Hollandite, cryptomelane, coronadite and $\alpha\text{-MnO}_2$ form an isostructural series of the general formula. $\text{A}_{2-y} \text{B}_{8-z} \text{X}_{16}$, A being large ions such as Ba^{+2} , Pb^{+2} and K^+ , B small and medium sized ions such as Mn^{+4} , Fe^{+3} , Mn^{+2} and X in the cases investigated O and OH ions. The unit cell, which contains one formula unit, is tetragonal or pseudo-tetragonal, in the latter case monoclinic. Approximate dimensions of the tetragonal unit cell are $a : 9.8 \text{ \AA}$ and $c : 2.86 \text{ \AA}$. In the cases investigated, the variable y in the general formula varies from 0.8 to 1.3 and Z from 0.1 to 0.5. The

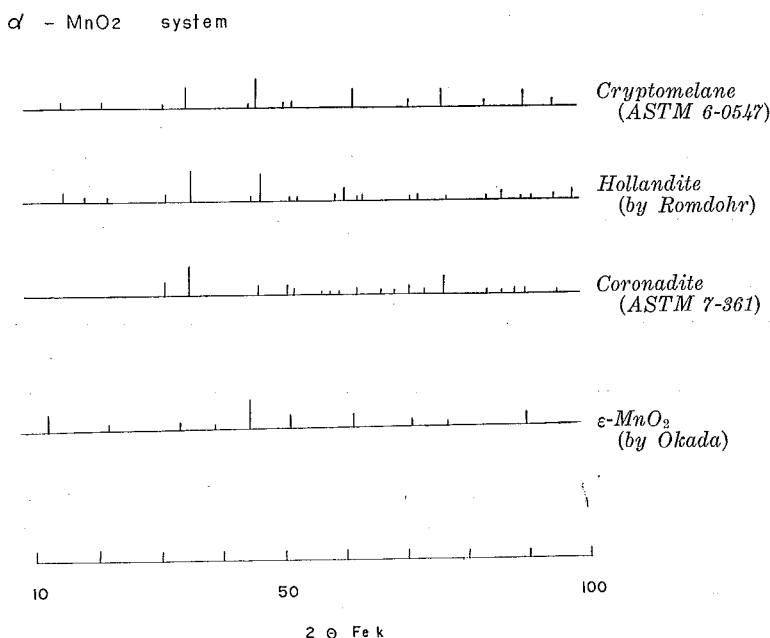


Fig. 21. X-ray powder data of α - MnO_2 group.

spacing and intensities of α - MnO_2 group with data published by other workers are illustrated in Figure 21.

SAMSON and WADSLEY (1948) studied the manganese ore mineral from the oxide mine situated about 4 miles S. E. of Buchan in Eastern Victoria. This mineral polished section is seen under the ore-microscope to consist of an apparently homogeneous mineral, which appears to correspond to the "psilomelane" type and is almost completely isotropic, showing pale grey-brown polarization colours. Studies in his laboratory have shown that neither the naturally occurring mineral nor synthetic cryptomelane possesses patterns differing by more than experimental error from FRONDEL's values. These specimens have, however, exhibited a wide variation in composition, both in potassium content and Mn : O ratio. The possibility that the Buchan specimens are disordered forms of cryptomelane due to lattice imperfections 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.

Structurally the mineral shows similarities to manganous manganite

on the one hand and to cryptomelane on the other, but the evidence does not support the view that the mineral may be classed merely as a disordered form of cryptomelane.

On the other hand, OKADA, UEI and CHIN (1945) have a new type of the manganese dioxide crystal anodically by electrolysis. This modification was named ϵ - MnO_2 by OKADA. This material is show similar patterns and the possibility that the ϵ - MnO_2 are disordered forms of α - MnO_2 due to lattice imperfections must therefore be rejected.

3. β - MnO_2 group

This compound occurs widely in nature. This member of MnO_2 was named pyrolusite. The structure is now well established as tetragonal (rutile group) with $a : 4.38 \text{ \AA}$, $c : 2.86 \text{ \AA}$. The unit cell contains Mn_2O_4 . For a long time it was thought that pyrolusite was an orthorhombic form of manganese dioxide. The tetragonal form was called polianite. Orthorhombic pyrolusite is apparently due to pseudomorphism, based on its formation from manganite. On the basis of these consideration that tetragonal form of MnO_2 , and its properties seem well characterized.

Pyrolusite is the most stable crystalline form of MnO_2 . It possesses a high order symmetry and hence is always found nearly perfectly crystallized. No continuous series exists between perfectly crystallized pyrolusite and amorphous MnO_2 .

Comparison of the spacing and intensities of β - MnO_2 is set out in Figure 22.

4. Ramsdellite

Ramsdellite was first described by RAMSDELL (1942), the powder

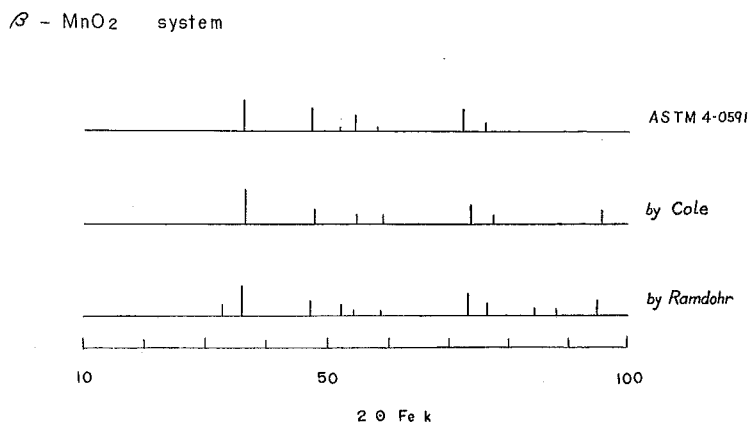


Fig. 22. X-ray powder data of β - MnO_2 group.

X-ray pattern has been given by FLEISCHER and RICHMOND (1943) and the crystal structure was determined by BYSTRÖM. The unit cell dimensions are given $a_0 : 4.533 \text{ \AA}$, $b_0 : 9.27 \text{ \AA}$, and $c_0 : 2.866 \text{ \AA}$, $Z : 4$. The crystal lattice is similar to the diaspore. The network of oxygen octahedra is principally the same in $\beta\text{-MnO}_2$ and ramsdellite. In $\beta\text{-MnO}_2$ every other octahedron is occupied by a Mn ion both in the a and b directions. However, in ramsdellite there are pairs of occupied and

Ramsdellite

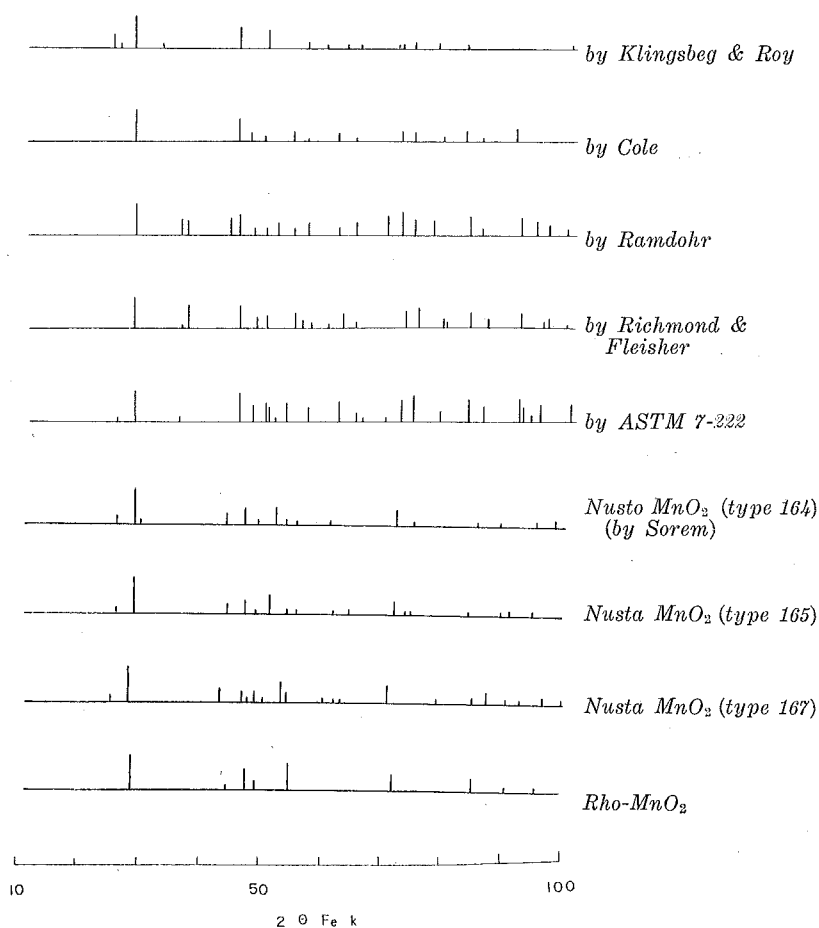


Fig. 23. X-ray powder data of ramsdellite group.

unoccupied octahedra in the b direction, but in the a direction every other octahedron is filled.

Ramsdellite has a still lower order of symmetry than β - MnO_2 . COLE et al. (1947) has studied in all degree of crystallization from nearly perfect to completely amorphous MnO_2 . And he suggested that the various forms γ - MnO_2 discussed above were imperfectly crystallized ramsdellite. But systematic identification of ramsdellite and γ - MnO_2 type is difficult for several reasons. First, under a wide variety of temperature and pressures of water and oxygen, γ - MnO_2 either remained unchanged or converted to β - MnO_2 second, X-ray powder lines γ - MnO_2 are common somewhat diffuse, and contrast is poor because of background fogging, and the d spacings and relative intensities are not identical, reproducible measurements are therefore difficult.

In 1958, NYE wrote that the dominant mineral phase of Gold Coast ore gave an X-ray pattern identical to a chemically prepared MnO_2 termed ρ . NYE remarked that ρ - MnO_2 is clearly different from γ - MnO_2 .

SOREM and CAMERON (1960) has studied the manganese ore mineral from the highly productive deposits of Nusta, Ghana. The term Nusta MnO_2 is introduced as a tentative name for the mineral or mineral group most abundant in the ores. X-ray diffraction data indicate that Nusta MnO_2 is a discrete mineral or mineral group, with so direct relation to pyrolusite or ramsdellite. These patterns are presented graphically in Figure 23, with patterns of ρ - MnO_2 and the mineral ramsdellite. Powder patterns of Nusta MnO_2 and ρ - MnO_2 show certain similarities to the pattern of ramsdellite. These specimens have, however, exhibited a wide variation in character. For example, the structure may be imperfect due to minor impurities, order-disorder phenomena, non-stoichiometric composition, grain size, degree of crystallization and preferred orientation of crystals. The possibility that the Nusta MnO_2 and ρ - MnO_2 are disordered forms of ramsdellite due to lattice imperfections.

5. γ - MnO_2

The samples designated γ - MnO_2 have X-ray patterns similar to those of the oxide $\text{MnO}_{1.88}$ of DUBOIS (prepared by heat treatment of his α - MnO_2) ; of the MnO_2 of GLEMSER made by a preparation similar to the COLE sample; and of the electrolytic sample of γ - MnO_2 described by MCMURDIE (Fig. 24). The diffraction patterns described by these workers are set out in Table 14. It is considered, however, that there are at least three types of γ - MnO_2 characterized by small but nonetheless definite differences in their X-ray diffraction patterns.

The spacings and intensities of the three types of γ - MnO_2 are set out in

TABLE 14. Comparisom of the spacings and intensities of the various forms of γ -MnO₂.

γ -MnO ₂ (by Glemser)		γ -MnO ₂ (by Cole)		γ -MnO ₂ I (by Cole)		γ -MnO ₂ II (by Cole)	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
M	3.89	s(d)	4.02	s	3.94	m	4.38
						ms	3.82
						w	3.10
		vvw	2.53	w	2.57	w	2.68
M	2.42	m	2.41	m	2.41	ms	2.42
				vw	2.33	w	2.34
M	2.09	ms	2.10	ms	2.11	s	2.12
?	1.80					w	2.05
vw	1.614	vs	1.62	vs	1.62	s	1.63
						w	1.59
vw	1.416			vw	1.41	vw	1.43
vw	1.349	w	1.38	vw	1.37	vw	1.35
vw	1.305					vw	1.31
		vvw	1.25				

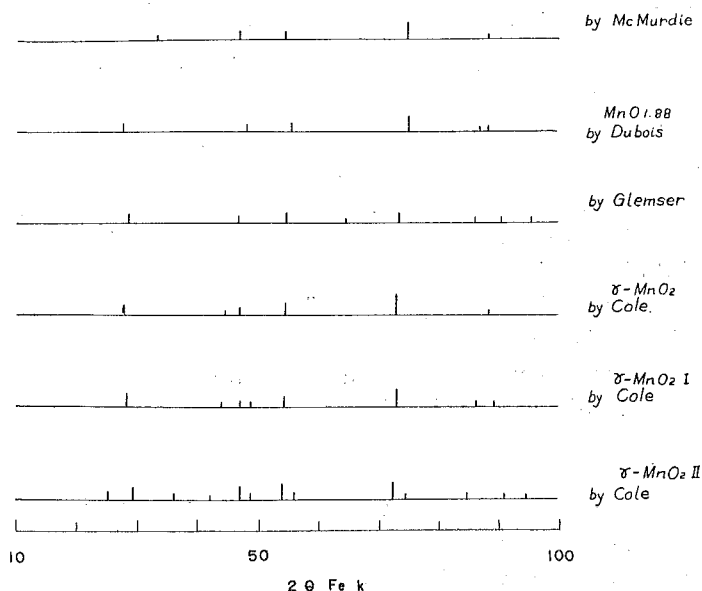
 γ - MnO₂ systemFig. 24. X-ray powder data of γ -MnO₂ group.

Table 14 and the patterns themselves are illustrated in Figure 24. COLE and other consequently suggest that the various forms of γ - MnO_2 discussed above are imperfectly crystallized ramsdellites. Additional evidence is provided by the fact that both γ - MnO_2 and ramsdellite can be converted into pyrolusite upon heat treatment in air at 450°C . Since γ - MnO_2 has been described as a poorly crystalline ramsdellite it was a likely starting material for the synthesis of ramsdellite (many other compounds were used as well). However, under a wide variety of temperatures and pressures of water and oxygen, γ - MnO_2 either remained unchanged or converted to pyrolusite.

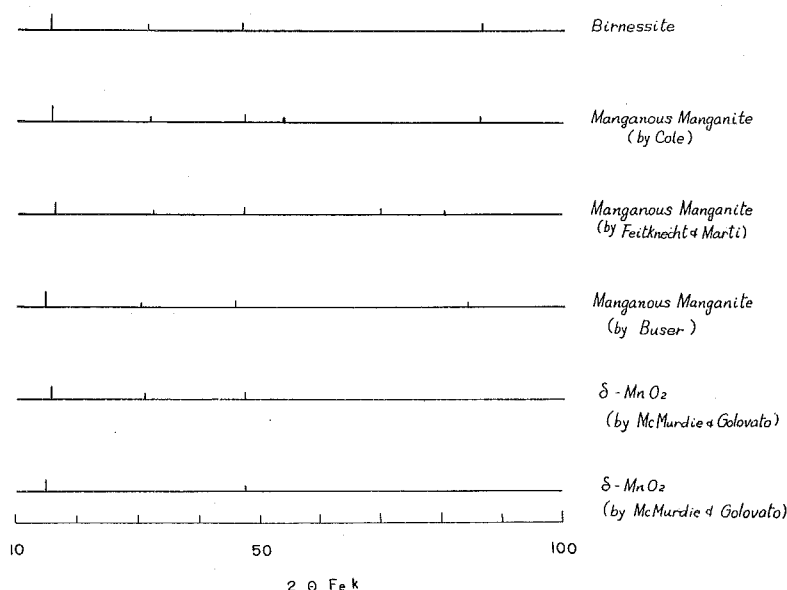
Differences in the patterns of γ - MnO_2 have been noted by other workers. For example, DUBOIS (1936) mentioned that diffraction patterns of $\text{MnO}_{1.88}$ prepared by two methods were not identical, and SCHOSSBERGER (1941) also noted differences in the patterns of γ - MnO_2 , attributing them to lattice distortions brought about by foreign ions. FEITKNECHT and MARTI (1945) also reported modifications of γ - MnO_2 which they designated MnO_2 -a and MnO_2 -b; They could be prepared by heating manganites with nitric acid (a-form), or with water (b-form). They do not give numerical values for the interplaner spacing, but judging from their line diagrams the patterns of γ - MnO_2 -a and γ - MnO_2 -b are in close resemblance to the pattern γ - MnO_2 and γ - MnO_2 forms respectively. None of their diagrams resembles the patterns of γ - MnO_2 II.

It is to be noted that γ - MnO_2 I is the major constituent of Gold Coast and several local ores and can be prepared in the laboratory. γ - MnO_2 II has not been found to occur in an ore.

The evidence that γ - MnO_2 is simply a lower form of ramsdellite seems overwhelming. It is notable that no evidence has been found in the X-ray patterns to support the belief of MCMURDIE and GOLOVATO (1948) that material of the γ - MnO_2 type is poorly crystallized pyrolusite, or that an infinite variety of patterns exists transitional from pyrolusite to ramsdellite, as postulated by BYSTRÖM (1950) and DELANO (1950). I believe that an infinite number of variations exist in this pattern depending upon the degree of crystallization and the impurities such as OH, lower valence Mn, etc., but systematic identification of γ - MnO_2 and ramsdellite is difficult.

6. δ - MnO_2

The X-ray powder patterns of δ - MnO_2 are given in the Table 7 and Figure 25 together with the patterns of manganous manganite and birnesite. Originally δ - MnO_2 was the name given by MCMURDIE (1944) to a synthetic manganese oxide whose X-ray powder pattern consisted of only

δ - MnO₂ systemFig. 25. X-ray powder data of δ -MnO₂ group.

two lines, at 2.39 Å and 2.40 Å. Later, MCMURDIE and GOLOVATO (1948) reported two additional lines at 7.0 Å and 3.64 Å, in the powder pattern of a synthetic δ -MnO₂. The name "manganous manganite" was given originally by FEITKNECHT and MARTI (1945) to a manganese oxide that gives a similar powder pattern and was prepared by oxidizing an alkaline manganous solution with either air or oxygen. Using this and other methods they prepared manganous manganite with the atomic ratio of O : Mn ranging from 1.74 to 1.96 (FEITKNECHT and MARTI, 1945). The most oxidized forms were considered to be disordered because the two inner lines of the X-ray powder patterns disappeared. The X-ray powder pattern of a manganous manganite prepared by COLE, WADSLEY, and WALKLEY (1947) agrees with that of FEITKNECHT. MARTI and COLE et al. were the first to suggest that MCMURDIE's original δ -MnO₂ is similar to manganous manganite. More recently BUSER, GRAF, and FEITKNECHT (1954) have confirmed this suggestion and have clarified the relationship between manganous manganite and δ -MnO₂.

By oxidizing an alkaline manganous solution with oxygen, BUSER, GRAF, and FEITKNECHT obtained a hydrous manganese oxide with formula was similar to an oxide described previously by WADSLEY (1950) with a

formula, computed from his analysis, of $\text{NaMn}_6\text{O}_{12} \cdot 2.5\text{H}_2\text{O}$. It was metastable and it recrystallized, with further oxidation, to a manganous manganite with the formula $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and an equivalent ratio of O : Mn of 1.80. They also prepared a series of poorly crystalline manganous manganites by methods involving the decomposition of permanganate solutions with either HCl or manganous solutions. The O : Mn ratio of these oxides ranged from 1.76 to 1.95 and because the inner lines disappeared from the X-ray powder patterns of the most highly oxidized forms it was concluded that the degree of disorder increased with increasing oxidation. The X-ray powder patterns of the most highly show that manganous manganite and $\delta\text{-MnO}_2$ exhibit the same crystal phase they suggest that both names be retained and that $\delta\text{-MnO}_2$ be used for those oxides with O : Mn 1.90.

FEITKNECHT and MARTI (1945) concluded that the structure of manganous manganite could be derived from the layer lattice of the parent manganous hydroxide, pyrochroite, and suggested that layers of 4MnO_2 are interspersed with layers of $\text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. The similarity of the optics of birnessite and pyrochroite provides some evidence for the first part of this theory. The well-crystallized manganous manganite prepared by BUSTER et al. enabled them to confirm the theory of its structure and they assigned to it a hexagonal unit-cell with $a : 5.82 \text{ \AA}$ and $c : 14.62 \text{ \AA}$. In the more highly oxidized samples the interlayers of 4MnO_2 and $\text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ no longer exist as regular structural units. Instead, there are only individual double layers which are randomly oriented; the result is the basal reflections of $\delta\text{-MnO}_2$ eventually disappear. Thus manganous manganite and $\delta\text{-MnO}_2$ are shown to be variously disordered forms of a distinct crystal phase and are not disordered forms of cryptomelane ($\alpha\text{-MnO}_2$) as has been suggested by MCMURDIE and more recently by BUTLER and THIRSK (1953). Birnessite ($\text{Na}_{0.7}\text{Ca}_{0.3}\text{M}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$) gives an X-ray powder pattern similar to that of synthetic of synthetic materials described as "manganous manganite" and $\delta\text{-MnO}_2$.

The optical and X-ray data of birnessite from the Todoroki mine show it is a naturally occurring $\delta\text{-MnO}_2$. X-ray powder pattern of the same material almost disappears at heat of 700°C , 5 hours and is converted to Mn_3O_4 .

7. Hydrated system

TABLE 15, 16 shows the classification of manganese dioxide in previous results of others workers and in present investigation.

Earthly manganese material commonly known as wad may contain considerable amounts of other metals. Within these groups, several

hydrated manganese minerals are regarded as distinct species. These are listed in Table 17 with the formulae proposed and crystalline habits

TABLE 15. Classification of manganese dioxide by other workers.

name of group	mineral	order ———— disorder
α -MnO ₂	[cryptomelane hollandite coronadite]	[cryptomelane hollandite coronadite] γ -MnO ₂ , birnessite manganous manganite Buchan mineral
β -MnO ₂	pyrolusite	pyrolusite
γ -MnO ₂	ramsdellite	ramsdellite γ -MnO ₂ { γ -MnO ₂ γ -MnO ₂ I γ -MnO ₂ II
ρ -MnO ₂	Nusta MnO ₂	Nusta-MnO ₂ ρ -MnO ₂
ε -MnO ₂		ε -MnO ₂

TABLE 16. Classification of manganese dioxide of present investigation.

name of group	mineral	order ———— disorder
α -MnO ₂	[cryptomelane hollandite coronadite]	[cryptomelane hollandite coronadite] ε -MnO ₂
β -MnO ₂	pyrolusite	pyrolusite
	ramsdellite	ramsdellite Nusta MnO ₂ ρ -MnO ₂
γ -MnO ₂		γ -MnO ₂ { γ -MnO ₂ γ -MnO ₂ I γ -MnO ₂ II } Buchan Mineral
δ -MnO ₂	birnessite	birnessite

TABLE 17. Hydrated manganese oxide minerals containing other metals.

Mineral	Formula	Crystal system
chalcophanite	(Mn, Zn) Mn ₂ O ₅ ·2H ₂ O	Hexagonal (?)
lithiophorite	LiMn ₃ Al ₂ O ₉ ·3H ₂ O	Hexagonal (?)
rancieite	(Mn, Ca)Mn ₄ O ₉ ·3H ₂ O	
cesarolite	PbMn ₃ O ₇ ·H ₂ O	
psilomelane	MnBaMn ₈ O ₁₈ ·2H ₂ O	Monoclinic
todorokite	3(Mn ₂ 3MnO ₂ ·2H ₂ O)2(2ROMnO ₂ ·2H ₂ O) R:Ca, Mg, Ba, Mn etc	

oxidized forms were identical with those given by the original δ - MnO_2 (MCMURDIE). Between this extreme and that represented by the well-crystallized manganous manganite there are intermediate forms giving X-ray powder patterns similar to that of birnessite. While BUSER et al. recorded in the literature.

A. W. WADSLEY (1950) synthesized the minerals by hydrothermal alteration of the metallic derivatives of a hydrous manganese oxide. It will readily form loose hydrous complexes with metals which, while not giving close fitting formulae, may in most cases be represented as $(\text{R}, \text{Mn})\text{Mn}_3\text{O}_7 \cdot n\text{H}_2\text{O}$, where R is the added metal. 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 replacements, 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 and X-ray work on single crystals has been described. Cesarolite has been reported only from one locality but no X-ray examination is recorded; rancieite is accredited as a mineral species but no chemical analyses are given; lithiophorite, identified during an examination of psilomelane-type minerals has since been found as well developed crystals; chalcophanite, may be recognized from optical evidence.

T. YOSHIMURA (1934) investigated a new manganese mineral found in 1934 in the Todoroki mine, Hokkaido, Japan. A classification of the minerals of the manganomelane group was attempted under the YOSHIMURA scheme, and it was shown that the new mineral belonged to the purest species of crystalline manganomelane. As such a mineral had not yet been reported, this mineral was named "todorokite" after the name of the mine where it had first been noticed. X-ray powder pattern of this mineral is in good agreement with that obtained from other groups of hydroxide.

The powder diffraction patterns of the synthetic materials and todorokite are given in Figure 26. The scarcity of (0001) reflections is characteristic about 9.0 Å.

The name psilomelane was given by HAIDINGER (1831) to the smooth black uniform and botryoidal mineral, which he stated to be "a pretty common species" and for which he lists many localities.

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 hydroxide

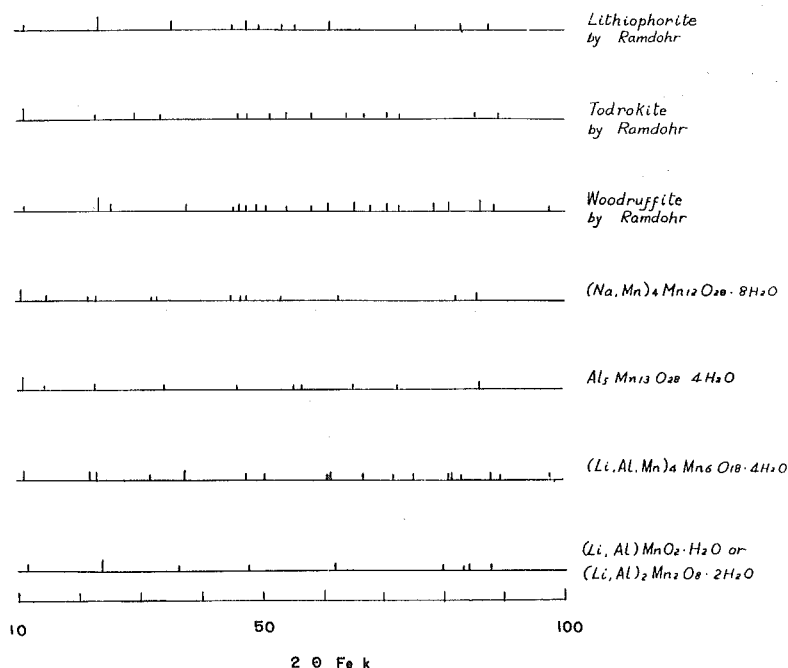


Fig. 26. X-ray powder data of hydrated system.

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 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), 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 ROMANECHÉ, reporting it to be orthorhombic with $a_0 : 9.1 \text{ \AA}$, $b_0 : 13.7 \text{ \AA}$, $c_0 : 2.86 \text{ \AA}$, 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 $\text{BaR}_9\text{O}_{18} \cdot 2\text{H}_2\text{O}$, ($\text{R}=\text{Mn}^{+4}$, Mn^{+2} , Co, etc.). PALACHE, BERMAN, FRONDEL (1944) likewise restrict the name to this species; they give the formula in a third modification, $\text{BaMn}^{+2}\text{Mn}_8^{+4}\text{O}_{16}(\text{OH})_4$.

Later X-ray work by WADSLEY (1953) has shown that psilomelane is monoclinic, space group $A 2/m$, with $a_0 : 9.56 \text{ \AA}$, $b_0 : 2.88 \text{ \AA}$, $c_0 : 13.85 \text{ \AA}$, $\beta : 92^\circ 30'$. 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 as $(\text{Ba}, \text{H}_2\text{O})_4\text{Mn}_{10}\text{O}_{20}$ with Ba : H_2O approximately 1 : 2, and Mn including Mn^{+4} , Mn^{+2} , and other elements. The psilomelane group comprises a series of Ba compound of hydrate system (Fig. 27).

Psilomelane

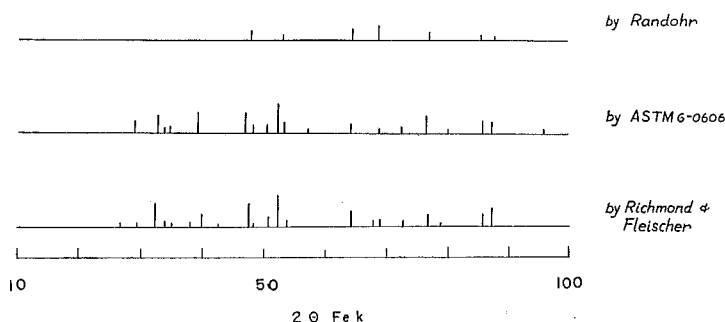


Fig. 27. X-ray powder data of psilomelane.

V. Origin of sedimentary manganese dioxide deposits

Consider sedimentary deposits that apparently are not directly related to igneous processes or to volcanic activities. Many manganese deposits are interlayered with tuffs and are closely related to highly altered reddish or greenish tuffs and clastic sediments of volcanic affiliations.

Bedded manganese dioxide deposits form under either marine or fresh water conditions; they may or may not be associated with volcanic and hydrothermal activities. Assuming an adequate supply of manganese,

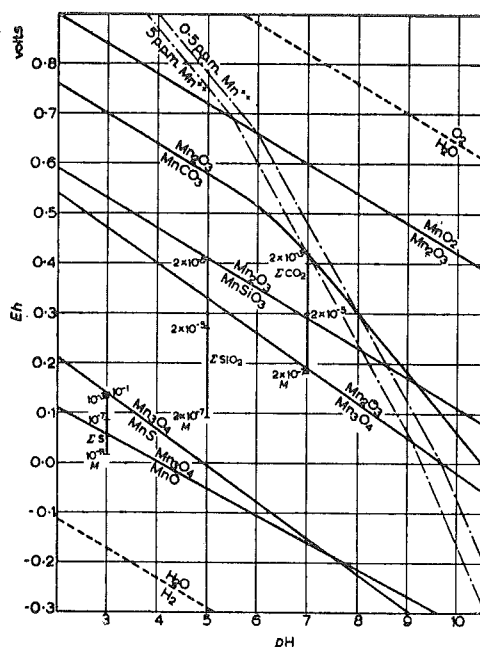


Fig. 28. Eh - pH diagram for anhydrous manganese compounds. Solid lines are boundaries of stability fields, each line separates the field of an oxidized form (above) from that of a reduced form (below). Cross-bars on vertical lines show positions of field boundaries at lower concentrations of carbonate, sulphide, and silica. Dashed lines are limits of possible redox potentials in water solution. Dash-dot lines are "isoconcentration" lines, drawn through points where the concentration of Mn^{+2} in equilibrium with the oxides is 5 p.p.m. and 0.5 p.p.m. respectively. (by Krauskopf)

the place of deposition will depend upon whether or not it is present as a hydrosol or as the Mn^{+2} ion, whether the water is saline or fresh, upon the oxidation-reduction conditions, the pH of the water, and probably many other factors such as currents, bacteria, and temperature of the water.

Eh - pH relations have been applied to sedimentary deposits of manganese by KRAUSKOPF (1957) and by MARCHANDISE (1956). Figure 28, taken from KRAUSKOPF's paper, shows his plot of the stability boundaries among anhydrous manganese compounds. Figure 29 shows his diagram for the manganese hydroxides. Many of the sedimentary deposits are believed to have formed directly as accumulations of manganese

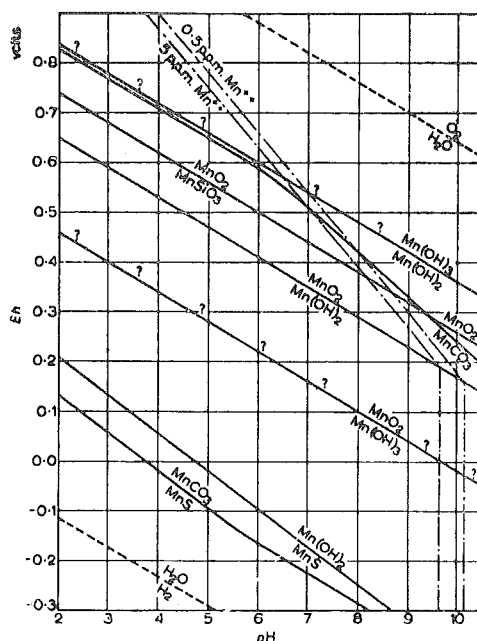


Fig. 29. *Eh*-pH diagram for manganese hydroxides. Symbols same as in Fig. 28. Question marks along stability boundaries for Mn(OH)_3 indicate that under these conditions Mn(OH)_3 is metastable. (by Krauskopf)

oxides. Manganese is precipitated when carbon dioxide is removed from the bicarbonate by the action of bacteria or by oxidation. Bacteria may also utilize the organic substances acting as protective colloids. In these instances manganese is precipitated either as carbonate or as hydroxide.

The Mn(OH)_4 and MnO_2 sols and gels, being negatively charged, readily absorb cations present in solutions, as been shown by laboratory experiments. Owing to its acid character, manganic hydroxide may also form adsorption compounds, such as BaMn_2O_5 , $\text{Mn}^{+2} \text{Mn}^{+4}_4\text{O}_5$, and others. Consequently, the oxidate sediments rich in manganese often contain notable amounts of the following elements: Li, K, Ca, Ba, Ti, Co, Cu, Zn, Pb, as well as others. Manganese-rich bog ores may contain as much as 2.4 percent Zn; 4.88 percent WO_3 is reported in psilomelane and 8 percent Zn in cryptomelane. Manganese wad may contain 2.82 percent NiO, 8.33 percent CoO, 9.53 percent BaO, and up to 14 percent CuO.

An excellent example of an extensive bedded deposit of manganese oxide is that near Setana district, in southwestern Hokkaido. It has been impossible to find any evidence of volcanic activity which many have

occurred during the time of accumulation of the manganese. The writer concluded that the source of the manganese was unknown but probably was ordinary river water that emptied into a nearly closed marine or epicontinental basin. The character of the sediment was controlled closely by oxidation-reduction conditions. Such an explanation might readily be extended to include manganese-bearing zones in the formation. The manganese deposition would then be a function of the oxidation-reduction conditions, and in large basins, this in turn would be somewhat dependent upon distance to the shore and depth of water.

The manganese oxides are associated with tuffs or other fragmental volcanic rocks; a ready source of manganese is available. Hot fragmental volcanic materials ejected under water tend to become more finely and completely fragmented. These materials, agitated by the volcanic activity, are ideally prepared and situated for leaching by either heated sea waters or solutions contributed during the volcanic activity.

The localization of the manganese might have been a function of distance to its source. The depth of the water and the proximity to a shoreline may have played a part in the localization of the manganese at the time of its deposition as suggested by 1) the fact that several of the deposits occur on the high side of pre-ore faults; 2) that most of the deposits are found on the edge of structural basins; and 3) the long axis of most of the ore bodies lie parallel to the edges of the basins.

The sedimentary minerals of manganese are oxides, hydroxides, and carbonates. Manganite, pyrolusite, and cryptomelane, are common in sedimentary deposits of manganese, but braunite and hausmannite are rare. It should be noticed that along with Mn^{+4} there also occurs Mn^{+3} probably derived from Mn^{+2} compounds originally present:



Trippositive manganese occurs in manganite, braunite, and the hausmannite in the weathering zone. Manganite is readily oxidized to the stable pyrolusite by atmospheric oxygen. Some manganous compounds, e.g., szmikite, $Mn(SO_4) \cdot H_2O$; mallardite, $Mn(SO_4) \cdot 7H_2O$; and rhodochrosite, $MnCO_3$, are also found in the oxidation zone. As a rule, they are more stable than the corresponding ferrous compounds. A comparison of the manganese content in the different iron ores of marine origin shows that manganese tends to become concentrated in the siderite ores. The content of manganese in the red clay is considerably in excess of the average content in igneous rocks.

VI. Conclusion

The writer has made systematical and statistical studies on characteristic variations of manganese dioxide and hydroxide from the various occurrences and localities in Hokkaido, Japan.

The mineralogical characteristics of manganese ores are probably of major importance in determining their behavior in several industries. The available data on crystal structure, X-ray diffraction patterns, physical properties and chemical composition of these minerals are summarized. The following minerals were investigated: cryptomelane, pyrolusite, ramsdellite, birnessite, manganite and groutite etc. Identifications based on physical properties are highly uncertain, owing to the variability and overlapping of these properties. X-ray powder pattern and thermal behavior of manganese ores are the best means of identification.

The writer also discussed and attempted the classification of manganese dioxide from the standpoint of mineralogical observations.

On the basis of these observations and considerations, he obtained the following conclusion.

The fundamental cause, controlling the characteristic variations of manganese dioxide and hydroxide minerals, is the difference in the conditions of crystallization environments and weathering situation. Suitable conditions for crystallization are such as moderate temperature, pH or Eh of sedimentary environments, etc.

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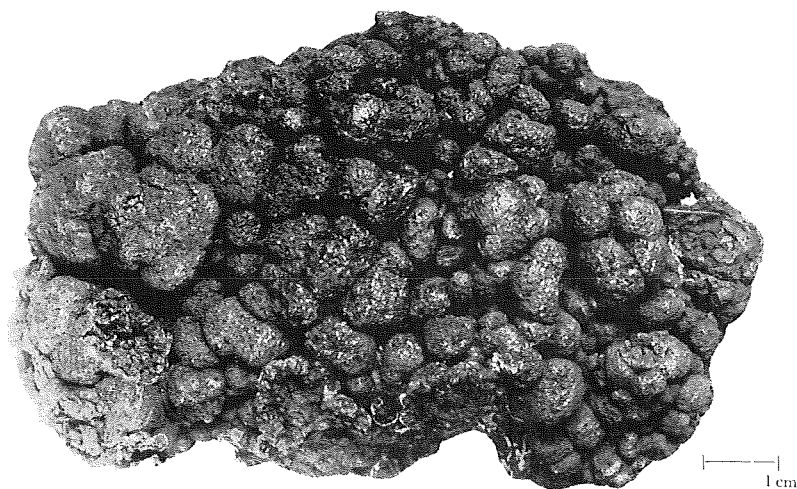


Photo. 1. Cryptomelane from Kokko mine.

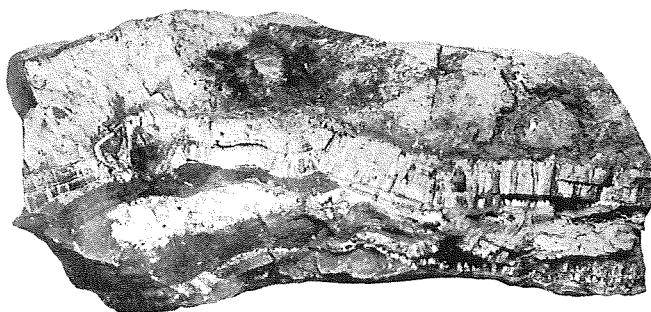


Photo. 2. Banded ore from the Hanaishi mine.



Photo. 3. Ramsdellite from Tanno mine.

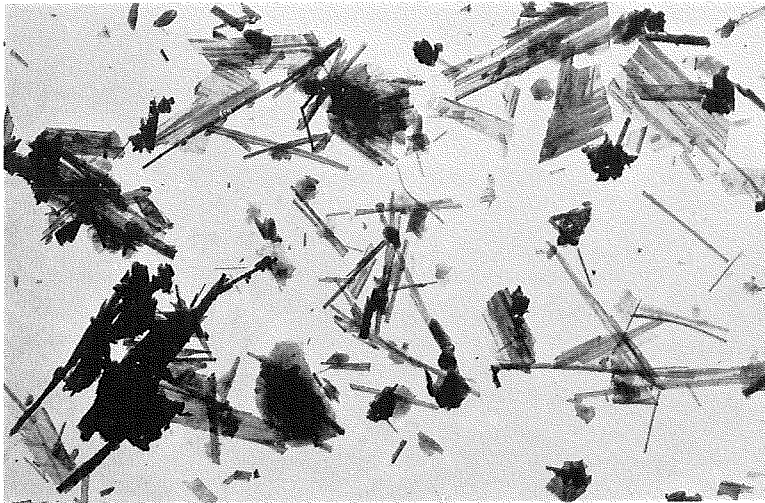


Photo. 4. Electron micrograph of todorokite. ($\times 7,500$)

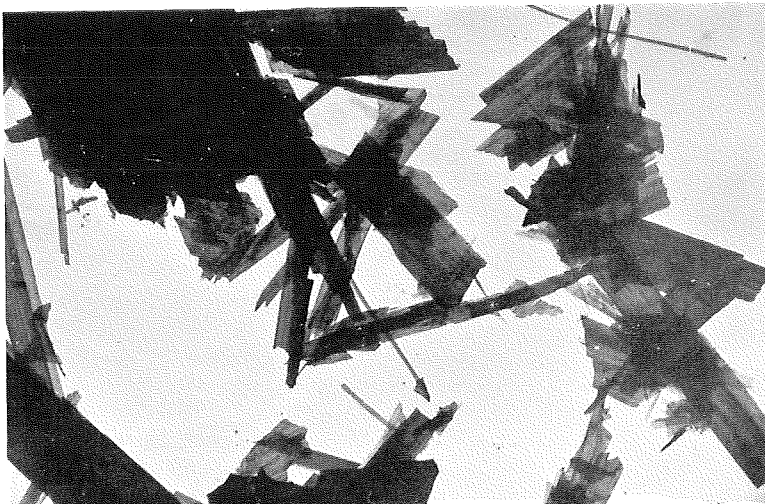
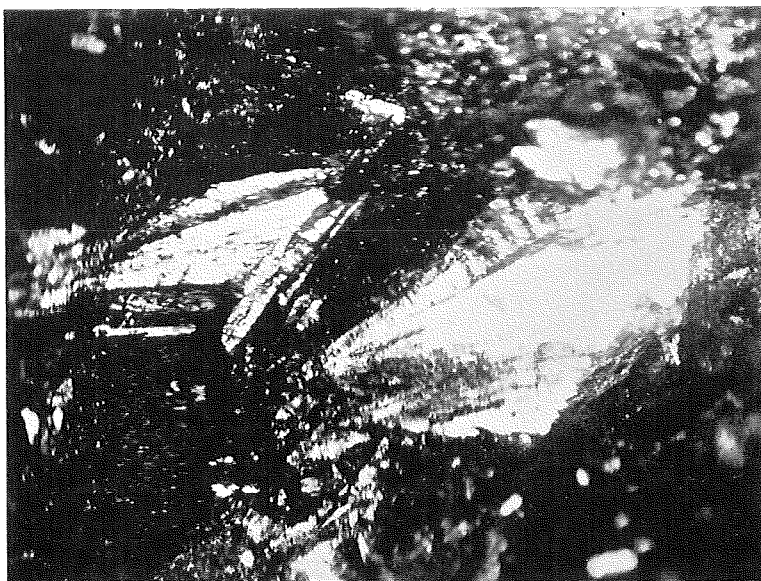


Photo. 5. Electron micrograph of manganese wad from Niimi. ($\times 12,000$)



A. Needle shape crystal



B. Polished section

Photo. 6. Groutite from Pirika mine.