MEMOIRS OF THE COLLEGE OF SCIENCE, UNIVERSITY OF KYOTO, SERIES B,
Vol. XXIII, No. 2, Article 4, 1956.

Mineralogical Study on Manganese Dioxide Mineral

By

Yasuo UKAI, Shin'ichi NISHIMURA and Takashi MAYEDA

Geological and Mineralogical Institute, Universiy of Kyoto

(Received Sept. 30, 1956)

Abstact

The authors investigated the various modifications of manganese dioxide mainly from the mineralogical stand-points. The several experimental results obtained during the investigations came chiefly from X-ray data at room and elevated temperatures, the differential heating curve, the deoxidation curve, the loss of weight by thermobalance and the chemical compositions. These led to the conclusion, that the manganese dioxides are classified to five modifications: 1) well-crystallized pyrolusite which shows numerous distinct diffraction patterns, a remarkable endothermic peak at 650°–680°C. accompanied by another peak at 720°–760°C. (Pirika, Fukaura A and Fukaura B) 2) gamma MnO_2 which shows a few diffused patterns, and a sharp endothermic peak at 568°C. The oxygen evolution occurs most vigorously at 500°C. This member is believed to be a poorly crystallized ramsdellite. (electrolysed MnO_2 from the Mitsui Industrial Chemical Company) 3) cryptomelane containing essential potassium and sodium, which shows the characteristic diffraction patterns at 7.0 Å, 4.9 Å, and gradual broad endothermic peak at 560°–570°C. attended by a double peak at 900°C. (Maruno, Kawai C) 4) delta MnO_2, having a few diffused lines, a characteristic dehydration endothermic peak at 200°C. and a low deoxidation peak at 620°C. This modification has been considered to be a poorly crystallized cryptomelane. The deoxidation begins from 300°C. (Tachiki) 5) a mixture of ramsdellite series mineral and cryptomelane. Half of the numerous diffraction patterns of it corresponds to those of cryptomelane, and others to ramsdellite member. The principal deoxidation of ramsdellite member occurs at 600°–615°C. (Kawai A, Kawai B and Tsujinaka). Furtheremore, the most suitable properties of manganese dioxide for dry cells were experimentally determined as follows; in brief, cryptomelane, γ-phase is superior for continuous discharge, while the former has also excellent properties for intermittent discharge, successively followed by pyrolusite and γ-phase in that order.

Introduction

Manganese dioxide is one of the most familiar and common minerals found in various manganese deposits, but its mineralogical study is very equivocal owing to the variability and overlapping of physical properties and chemical compositions. Furthermore it always occurs in a fine-grained massive state, and comprises several modifications[1, 2, 3] which are closely related in

their crystal structures. Some members are well-crystallized but others are very poorly crystallized. For the above reasons, identifications based on physical properties alone are highly uncertain as well as unreliable. The utilization of these minerals has tremendously increased in recent years, mainly in ceramic, chemical, and metallurgical industries, especially in dry cell industry. The ore is directly used as a basic raw material in 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.

The authors attempted to identify the various modifications of natural manganese dioxides from the mineralogical standpoint, and to determine the species of natural oxides which have superior characteristics for dry cell uses. Some manganese ores were found to be far superior for dry cell purposes, and this knowledge will ultimately lead to the profound improvement of the mineralogical data about the characteristics of natural ore for heavy duty batteries.

The authors hereby wish to express their appreciation to Mr. Yoshio Okada, the vice-president, and Mr. Shigeru Takizawa, the chief of technical-section of the Okada Battery Company. Part of this work is indebted to the scientific research fund of the Ministry of Education.

Specimens

Most of the manganese dioxide specimens under this investigation, were collected by the investigators from various localities throughout Japan, a few specimens however were kindly contributed for our research purposes by the managements of some manganese mines. Out of all these samples, ten representative specimens were selected to perform the various necessary experiments.

The localities these ten selected specimens came from, and their general characteristic physical properties are listed below;

1. Fukaura (A), from the Fukaura Mine, Fukaura Town, Nishi-Tsugaru County, Aomori Pref. Color coal black. Fibrous.
2. Fukaura (B), from the Fukaura Mine. Color bluish black. Massive.

Brittle and easy to grind into fine powder.

3. Tsujinaka, from the Tsujinaka Mine, Nomura Town, Higashi-Ura County, Ehime Pref. Precipitated product, having a botryoidal form.
4. Kawai (A), from the Kawai Mine, Hinozawa, Yamagata Village, Kunoe County, Iwate Pref. Color dull black. Hardness moderate.
5. Kawai (B), from the Kawai Mine. Hardness high. Broken into angular blocks.

Table 1. Chemical composition and specific gravity.

Specimen No.	1	2	3	4	5	6	7	8	9	10
Locality	Fukaura A	Fukaura B	Tsuji-naka	Kawai A	Kawai B	Kawai C	Maruno	Tachiki	Pirika	Electro-lysed MnO_2
Sp. Gr.	3.987	4.809	3.987	4.009	4.314	4.393	3.783	2.774	3.347	——
	%	%	%	%	%	%	%	%	%	%
MnO	70.98	76.45	74.10	76.51	75.26	77.01	73.92	59.39	72.28	70.29
O	14.10	17.12	13.78	14.50	15.74	15.84	14.99	12.43	15.69	17.09
SiO_2	0.73	1.27	1.62	0.38	0.60	0.43	0.14	1.30	10.29	
TiO_2	0.02	0.03	0.04	0.09	0.03	0.05	tr.	0.05	0.03	
Al_2O_3	tr.	0.39	1.71	0.61	0.25	0.46	0.06	1.84	0.27	
Fe_2O_3	0.97	0.42	1.23	1.01	0.86	0.97	1.15	0.51	0.35	
BaO	2.00	tr.	0.10	0.92	1.54	0.97	tr.	0.11	0.32	
CaO	0.59	0.07	0.22	0.27	0.12	tr.	0.64	1.96	1.39	
MgO	1.59	tr.	0.40	0.36	tr.	0.32	0.30	3.46	tr.	
Na_2O	0.32	n. d.	0.25	0.07	0.35	2.30	0.75	tr.	tr.	
K_2O	0.78	n. d.	0.58	0.99	0.50	0.79	1.34	0.79	tr.	
P_2O_5	n. d.	n. d.	n. d.	0.21	0.13	n.d.	n. d.	n. d.	n. d.	
$H_2O(+)$	5.37	4.77	4.66	3.35	3.45	0.89	4.39	4.39	0.53	
$H_2O(-)$	1.79	1.34	0.89	2.07	1.51	0.89	3.38	14.31	0.98	
	%	%	%	%	%	%	%	%	%	
Total	99.24	101.86	99.59	101.34	100.34	100.92	101.06	100.64	102.12	
Sp. Gr. * Corrected	4.22	5.07	4.10	4.28	4.54	4.39	4.19	3.94	4.89	
Mn %	54.97	59.20	57.38	59.25	58.28	59.54	57.24	46.07	55.97	
O % combind with Mn	30.10	34.37	30.50	31.76	32.72	33.21	31.67	25.85	32.00	
O/Mn	1.88	1.99	1.82	1.84	1.93	1.91	1.90	1.93	1.96	

* Corrected specific gravity, excluding the heterogeneously contaminated substance.

6. Kawai (C), from the Kawai Mine. Precipitated product, having a botryoidal or kidney shape.
7. Maruno, from the Maruno Mine, Nomura Town, Higashi-Uwa County, Ehime Pref. Color dull black.
8. Tachiki, from the Tachiki Mine, Tachiki Village, Funai County, Kyoto Pref. Luster resinous. Covering the surface of rhodonite.
9. Pirika, from the Pirika Mine, Imakane Town, Setana County, Hokkaido. Color bluish black. Brittle and easily broken into powder.
10. Electrolysed MnO_2. Synthesized in the Mitsui Industrial Chemical Company. Fine powder.

The chemical compositions[4] and specific gravities of above specimens are represented in table 1.

The specific gravity was precisely determined by the method devised by Yoshida and Takei.[5] The contents of manganese and available oxygen in the chemical composition were analysed according to the analytical process of J. I. S. specifications. As table 1 shows, the principal component of each specimen is naturally consisted of MnO_2 but the atomic ratio Mn : O is not exactly equal to 2, but amounting to 1.82–1.99. This indicates that they were not composed of pure dioxide but included a quantity of low grade oxides, MnO, Mn_2O_3 and Mn_3O_4.

Furtheremore the deficiency of oxygen may be attributed to other factors, such as the defect caused by lattice disorder, or the existence of an OH radical ion which bonds with a Mn ion, but it is impossible to conclude from the chemical data alone to what reason the deficiency of oxygen is due. Above all, it must be pointed out, that the most important problem which controls the mineralogical property of manganese dioxide and consequently the electric behaviour of the dry cell, is that of the existence of alkalis (K, Na) and alkali earths (Ba, Ca) elements, or especially the existence of positive and negative water. These relationships will be discussed in more detail in the succeeding section.

X-ray investigation

Identification of manganese dioxides based on their physical properties alone is highly unreliable, hardness or color is a particulary poor criterion. Optical observation by reflected light makes identification of well-crystallized material possible, but the identification of fine-grained, poorly crystallized material is as yet almost impossible.

On the other hand, X-ray powder methods are the best means of identification. But since the lattice dimensions among the several dioxide modifications differ only very slightly, they must be supplemented by quantitative chemical analyses and other investigation methods in order to distinguish them from each other.

X-ray diffraction patterns were made for each specimen, using a cylindrical camera of 114.6 mm. radius and unfiltered Fe-K_α radiation under the condition of 40 kV, 14 mA. for 2-3 hours. The X-ray data obtained from the above condition, were refered to the results of a Geiger counter X-ray spectrometer applied by the authors.

The X-ray diffraction patterns of various samples were classified into several types as shown in the following tables.

(I) Pyrolusite

There are general good agreements among the specimens from Pirika and Fukaura and they can be correlated with pyrolusite determined by Fleischer, Richmond,[6] and McMurdie.[7]

Table 2. X-ray powder patterns of Pyrolusite

Pyrolusite				Pirika		Fukaura A		Fukaura B	
Fleischer Richmond		McMurdie							
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3.425	2					3.43	vvw	3.43	vvw
3.096	10	3.14	100	3.14	s	3.14	vs	3.14	vs
2.396	6	2.42	80	2.44	w	2.44	m	2.43	m
2.108	4	2.12	50	2.13	w	2.12	m	2.12	m
1.964	4	1.985	70			1.98	vvw	1.98	vvw
1.785	1					1.80	vvw	1.80	vvw
1.618	8	1.635	80	1.64	s	1.64	vs	1.63	vs
1.550	7	1.570	30	1.58	w	1.58	w	1.57	w
1.434	2					1.44	w	1.44	w
1.356	5			1.31	s	1.31	s	1.31	s (d)
1.053	3					1.06	m	1.06	m (d)

(d) diffused pattern

It will be seen that all lines of Fukaura A and B well agree with those of Fleischer and Richmond, and those of Pirika agree with the results

of McMurdie. In the latter case, some of the lines are missing. McMurdie concluded that these extra lines in the former case should be due to impurities, and not be compatible with the pyrolusite structure.

The disappearance of some patterns should be due to the grain size of pyrolusite and not to the contaminating impurities. The diffraction patterns of manganese dioxides generally show very diffused, and only a few lines, but it is a distinctive characteristic of pyrolusite that it always shows numerous sharp lines and has the well-crystallized form. Accordingly the ratio of Mn : O of this group closely approaches to 1 : 2.

(II) γ–phase

This modification was first named in 1936 by O. Glemser[8] and has been investigated by many workers. It has been found to occur in natural ores, and to be a major constituent of the artificial products which have the most favourable characteristic for dry cell use.

It is the characteristic of γ–phase that it is so fine-grained and poorly-crystallized, and that γ–phase shows a few diffused lines. From the X–ray diffraction patterns, McMurdie reported that this modification was related to pyrolusite, but Cole and Byström[9] related this mineral to ramsdellite.

McMurdie neglected a characteristic line at a spacing of about 4 Å of γ–phase and correlated it with the pyrolusite. On the other hand, Cole investigated the relationship between γ–phase and ramsdellite and concluded that there were at least 3 types of γ–MnO_2 characterized by small differences in their X–ray diffraction patterns. And he suggested that the various forms

Table 3. Diffraction patterns of γ–phase

γ–phase				Mitsui Electrolysed product		
Cole		Dubois				
d(Å)	I	d(Å)	I	d(Å)	I	w
4.02	s	4.0	ms	4.0	m	vvd
2.53	vvw					
2.41	m	2.36	m	2.43	m	d
2.10	ms	2.06	m	2.13	s	d
1.62	vs	1.58	s	1.64	vs	vd
1.38	w	1.38	w	1.40	m	vd
1.25	w					

of γ–MnO_2 discussed above were imperfectly crystallized ramsdellite. With this relationship, it is extremely interesting to consider that the δ–phase corresponds to a poorly-crystallized cryptomelane.

The electrolysed manganese dioxide prepared by the Mitsui Industrial Chemical Company shows a few diffused patterns, and generally shows a relatively good agreement to the results of Cole, Dubois[10] on γ–phase. The slight differences in these patterns will be derived from the broadening of each diffraction pattern.

(III) Cryptomelane

This alkali-bearing member of MnO_2 was named as cryptomelane by Richmond and Fleischer.[11] The general formula was given as RMn_8O_{16}. In this formula, R is K or Na in cryptomelane, Pb in coronadite and Ba in hollandite. It is one of the common oxide minerals occurring in natural ores. The specimens from Maruno and Kawai belong to this type.

From the preceding chemical compositions, one sees that these specimens

Table 4. X-ray diffraction patterns of cryptomelane

Cryptomelane				Maruno			Kawai C		
McMurdie		Fleischer, Richmond							
d(Å)	I	d(Å)	I	d(Å)	I	w	d(Å)	I	w
6.92	9	6.863	9	7.0	m	d	7.0	m	d
4.91	5	4.892	8	4.9	mw	d	4.9	m	d
3.47	3	3.445	3						
3.11	10	3.105	10	3.14	m	d	3.14	s	d
2.46	2	2.445	3						
2.40	4	2.387	7	2.40	s	d	2.41	vs	sh
2.27	2	2.183	4						
2.16	3	2.145	5	2.16	s	vd	2.16	ms	d
		1.917	2						
1.835	2	1.820	5	1.83	w	d	1.83	m	d
1.64	3	1.633	4	1.65	w	vvd	1.65	w	vvd
		1.618	4						
1.54	2	1.528	6	1.54	m	vd	1.54	m	d
		1.423	2	1.43	m	d	1.433	m	sh
		1.347	5	1.36	m	vvd	1.36	w	vvd

contain more alkali elements than others, but their potassium contents are lower than those of previously reported cryptomelanes. P. H. Delano[12] stated that the contents of potassium and sodium in cryptomelane were not always constant, and some varieties often contained small amounts of them.

The specimens from Maruno and Kawai which show the characteristic patterns of cryptomelane, such as 7.0 Å, 4.9 Å should belong to the cryptomelane members.

The degree of crystallization of these specimens seems to be very poor since their diffraction patterns are intensely diffused and deprived of some of the weak lines reported by Fleischer[13] and McMurdie.[14]

(IV) δ–phase

Delta MnO_2 is considered to be a poorly crystallized member of cryptomelane, similar to the gamma phase MnO_2 derived from ramsdellite, as was designated by McMurdie. This phase is believed to be the same as the material called "amorphous" by Gruner[15] and "manganous manganite" by Feitknecht and Marti.[16] Reliable knowledge about its crystal structure is almost entirely lacking.

Table 5. X-ray diffraction patterns of δ–phase

McMurdie[2]	Cole[3]		Tachiki		
d (Å)	d (Å)	I	d (Å)	I	w
	7.13	vs	7.0±0.5	vw	vvd
			4.9	w	d
	3.58	w			
			3.1	m	d
2.39	2.41	m	2.39	s	d
	2.14	vw	2.15	w	d
			1.83	vw	d
1.40	1.418	w	1.42	m	vd

The sample from Tachiki belongs to this modification having a few diffused lines. Some diffraction lines, 4.9 Å, 3.1 Å, 1.83 Å are derived from cryptomelane and others generally coincide with those of delta MnO_2 as determined by McMurdie and Cole. It seems to be the characteristic of the delta phase, that a line 2.39 Å appears very intensely notwithstanding the weakness of the other lines belonging to cryptomelane.

The specimen of Tachiki contains a large amount of water, and various thermo-experiments show the peculiar behaviours.

(V) Mixture of ramsdellite series mineral and cryptomelane

The results of powder photograph on specimens from Kawai and Tsujinaka show the numerous diffraction patterns corresponding to ramsdellite reported by M. Fleischer and W. E. Richmond[17] besides the several lines belonging to cryptomelane.

Table 6. X-ray diffraction patterns of mixed ore, ramsdellite series mineral and cryptomelane.

Fleischer Richmond		Cole[3]		Kawai A			Kawai B			Tsujinaka		
d(Å)	I	d(Å)	I	d(Å)	I	w	d(Å)	I	w	d(Å)	I	w
				6.9	vw	vd	7.0	vw	vd	6.9	m	d
				4.9	w	d	4.9	w	d	4.9	vw	d
4.08	10	4.04	vs	4.0	w	vd	4.0	w	vd	4.1	w	d
										3.42	w	d
3.10	9			3.10	vw	vd	3.09	vw	vd	3.10	m	vd
				2.77	s		2.76	m				
2.53	8	2.54	s	2.49	s		2.49	m		2.46	vw	d
2.43	4	2.43	m	2.40	s	vd	2.40	s	vd	2.41	s	
2.32	4	2.33	m									
2.13	5	2.13	ms	2.15	s	vd	2.15	s	vd	2.17	s	d
2.04	2	2.05	vw	2.04	vvw	d				2.14	m	d
1.88	5	1.90	m									
1.82	2	1.82	vvw	1.83	vvw	vd	1.83	vvw	vd			
				1.80	vw	d	1.80	vw	d			
1.64	6	1.65	ms	1.64	vvw	vd	1.64	vvw	vd	1.67	vw	d
1.60	7	1.61	ms	1.58	vw	d	1.58	vw	d			
1.53	3	1.53	vvw	1.54	m	d	1.54	m	d			
1.46	5	1.47	m	1.42	vw	d	1.43	vw	d	1.43	vw	d

These samples differ slightly in their crystallization degree, but show an intimate similarity to each other. About half of the members of the diffraction patterns of Kawai, correspond to those of ramsdellite member and others to cryptomelane. Two lines 2.76 Å, 2.49 Å of Kawai A and B may be correlated to the strongest lines of hausmannite and they perhaps contain hausmannite in small quantity.

Ramsdellite is considered to be the second well-crystallized member after

pyrolusite, but the diffraction patterns mentioned above diffuse very intensely. This fact suggests that ramsdellite is the most crystallized member of γ-phase and that there are various other intermediate members.

Thermal investigation of MnO_2[18, 19]

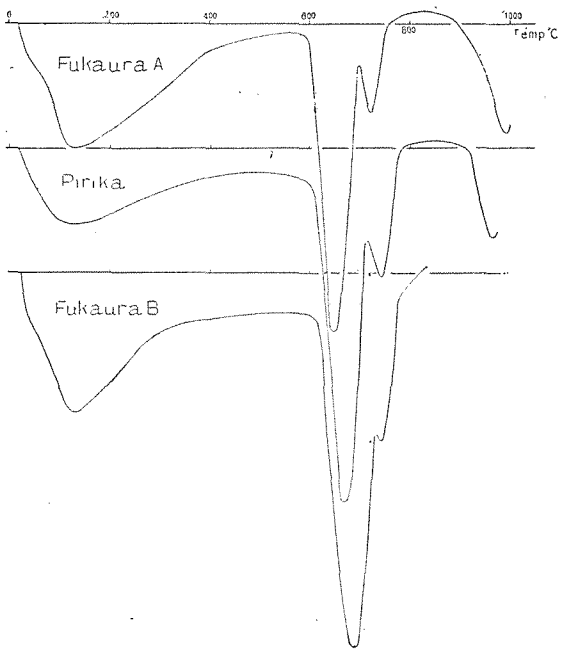

Fig. 1. D. T. A. curve of pyrolusite

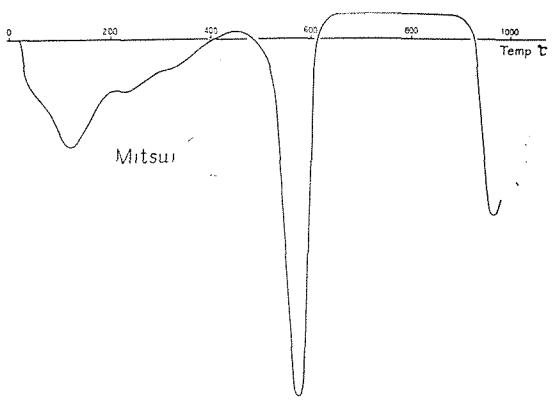

Fig. 2. D. T. A. curve of γ-phase

a) Differential thermal analysis

The authors applied the differential thermal analysis to identify the modification of manganese dioxide. Each specimen (2.0 gr.) ground to fine powder was used. The rate of heating was regulated at 6°C. per minute.

In every experiment, three remarkable endothermic breaks were found, of these, the first peak, at slightly lower temperature than 200°C. corresponds to the dehydration of absorbed water. The second peak, occurring at 500°–700°C. is due to loss of oxygen by the transformation to bixbyite (Mn_2O_3), and the third peak at 950°–1000°C. is due to a further loss in oxygen by the formation of hausmannite (Mn_3O_4). By comparing the differential heating curves in detail, the authors could identify each modification according to their distinct characteristic behaviours.

(I) Pyrolusite

The minerals belonging to this type abruptly deoxidize at 650°–680°C. transforming into Mn_2O_3, and are accompanied by a double endothermic peak at 720°–760°C. Fukaura A, B and Pirika correspond to this group as shown in Fig. 1.

(II) γ–phase

The remarkable appearence of the dehydration peak may be due to the absorbed water and free sulphuric acid occluded during the preparation. The deoxidation reaction to bixbyite occurs instantly as it is in the case of pyrolusite, but its temperature is as relatively low as 568°C.

(III) Cryptomelane and δ–phase

The dehydration peak of cryptomelane is not marked and continues to nearly 300°C. On the other hand, delta phase of Tachiki containing about 18.70 % H_2O (±) shows a most remarkable dehydration peak and this break reappears after the heat treatment at 120°C. for several hours. This fact suggests that a part of this total water must be held in its crystal structure, forming OH' radical combined with Mn ion.

The second peak of deoxidation gradually appears at 560°–570°C. beginning at about 350°C. The third peak is always accompanied by a small peak at about 900°C. The thermal behaviours mentioned above, are the most interesting characteristics of this group.

The temperature of the second peak of Tachiki (δ–phase) is 620°C. The double peak at 608°C, of Kawai C may be attributed to the little contamination of the ramsdellite member.

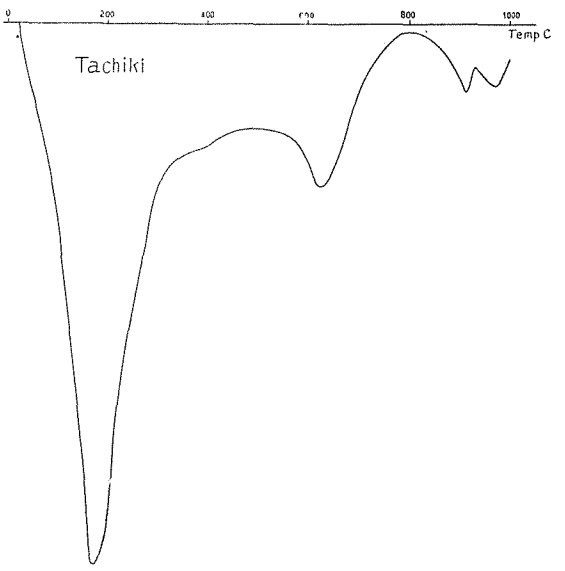

Fig. 3. D. T. A. curve of cryptomelane

(IV) Mixture of ramsdellite series mineral and cryptomelane

The each specimen from Kawai and Tsujinaka shows a principal deoxidation peak at 600°–615°C. beside a double peak at 560°C. The former may be of ramsdellite and the latter may provably be of cryptomelane.

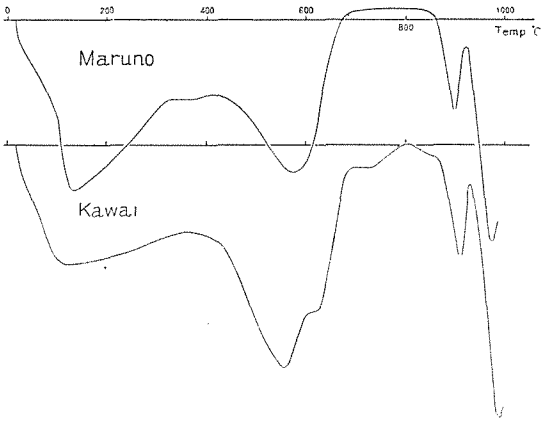

Fig. 4. D. T. A. curve of δ-phase

b) The loss of weight by the thermobalance

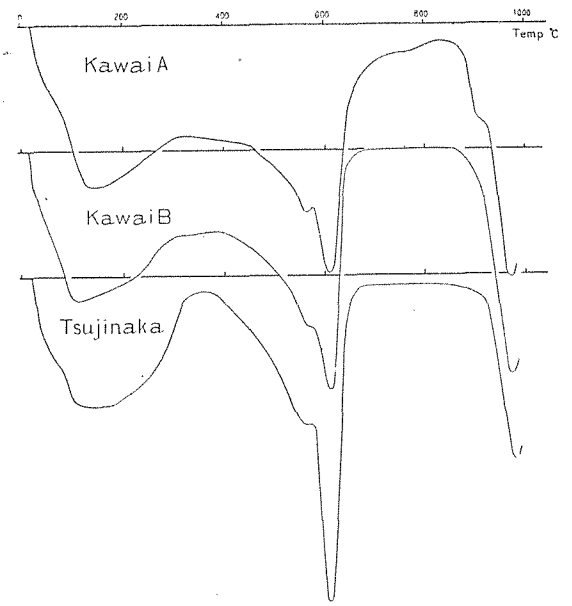

Fig. 5. D. T. A. curve of mixed of ramsdellite member and cryptomelane

To investigate the actual state of the manganese oxide which occurred in the differential heating curve, the loss of weight was quantitatively measured with a sensitive thermobalance. The apparatus used to measure the loss of weight is the Ôshima-Fukuda's thermobalance.

The temperature was stepwisely increased at intervals of 30°–50°C. At each temperature interval, the weight of the sample had been kept constant for 2–3 hours. For this reason, 30–40 hours were required to raise the temperature to over 700°C. This method showed its characteristic loss curve as is depicted in Fig. 6.

(I) Pyrolusite

The loss of weight up to 580°C. is effected by the dehydration alone,

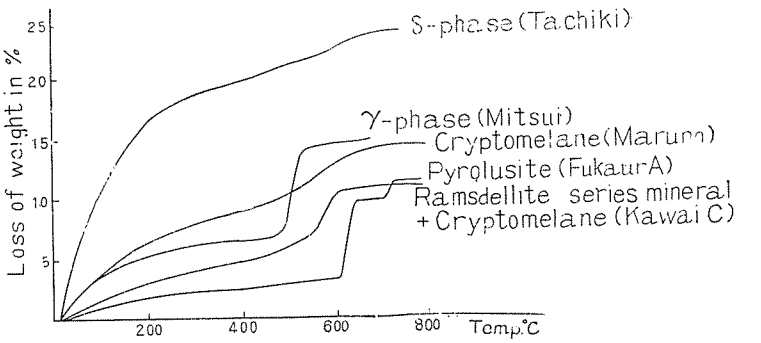

Fig. 6. curve of weight loss, measured by the thermobalance

and is suddenly increased at 600°C., amounting to approximately 6.5 %.

The secondary loss of about 1.5 % in weight observed at 700°C. may be due to the deoxidation, and demonstrate the origin of double peak which appeared on the differential heating curve.

(II) γ-phase

The deoxidation of electrolysed manganese dioxide suddenly occurs at 500°C., and it was found by volumetric analysis that the gradual decrease of weight which continued to that temperature was derived from the water and sulphuric acid occluded during the preparation.

(III) Cryptomelane and δ-phase

The specimens from Maruno and Tachiki dehydrate most of their water up to 300°C., and show the most sluggish loss of weight ranging from 350°C. to 700°C. in the case of Tachiki specimen, and to 600°C. for the Maruno.

(IV) Mixture of ramsdellite series mineral and cryptomelane

The principal loss of weight owing to the deoxidation of ramsdellite was found at 600°–615°C., but it was attended by a gradual decrease of cryptomelane at lower temperature.

c) The volumetric analysis of free oxygen

The loss of weight determined by the thermobalance is frequently influenced to large extent by other factors as well as the deoxidation pheno-

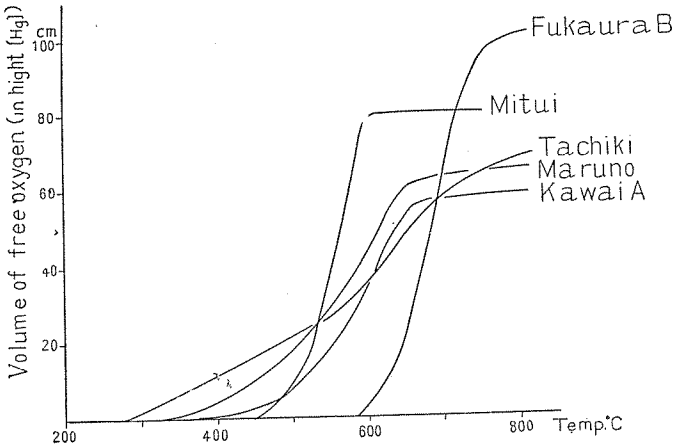

Fig. 7. Volumetric analysis of free oxygen.

mena, thus the volumetric analysis of free oxygen must be performed, in order to investigate the deoxidation mechanism. The authors determined the relative volume of free oxygen by measuring the gas pressure in a capillary tube filled with free oxygen. Before heating the specimen, the capillary tube was conditioned to a vacuum state, in order to introduce the free oxygen. By this means, we could distinguish the oxygen from a dehydrated water.

The results of the various modifications are shown in Fig. 7.

They can easily understand the deoxidation behaviours of various manganese dioxides, that is, pyrolusite deoxidizes at about 600°C., cryptomelane and δ–phase, gradually begin at about 350°C., and γ–phase at about 450°C. and intensely at about 500°C.

The volume of active oxygen

The volume of active free oxygen determined from the above experiments was compared with the calculated volume. The observed volume was higher in some cases than the calculated volume, but the authors could distinguish the various modifications by these data.

(I) Pyrolusite

The observed volume of oxygen isolated at 750°C. was nearly equal to the calculated value. In some specimens the observed volumes exceeded the calculated value, but the difference was always neglisibly small. The heated products were found almost to be α–bixbyite,[20] but the existence of the dif-

Table 7. Volume of active oxygen

Sample	Fukaura A	Fukaura B	Pirika	Mitsui	Tachiki	Maruno	Kawai C	Kawai A	Kawai B	Tsujinaka
Active O_2 of original specimen in %	14.1	17.1	15.7	16.0	12.4	15.0	16.0	14.5	15.7	13.8
Loss of O_2 by heating at 750°C in % (obs.)	5.67	8.96	8.73	7.41	6.12	5.67	5.65	5.15	6.46	5.43
Loss of O_2 by heaing at 750°C in % (calc.)	7.04	8.56	7.85	7.26	6.22	7.50	7.98	7.25	7.87	6.90
Diff. above two values	−1.37	+0.40	+0.88	+0.15	−0.08	−1.83	−2.33	−2.10	−1.41	−1.47
Volume of free O_2 at 750°C in cm^3 (obs.)	51.8	63.4	59.8	54.8	45.3	39.6	39.4	33.7	44.3	40.1
Volume of free O_2 at 750°C in cm^3 (calc.)	49.3	60.0	54.9	56.2	43.5	52.5	55.9	50.8	55.1	48.3
Diff. above two values	+2.5	+3.4	+4.9	−1.4	+1.8	−12.9	−16.8	−17.1	−10.8	−8.2
Volume of free O_2 during 750-1050°C in cm^3 (obs.)	10.0	6.1	9.6	17.6	8.8	28.9	29.9	28.0	28.3	15.6
Volume of free O_2 during 750-1050°C in cm^3 (calc.)	16.4	20.0	18.3	18.7	14.5	17.5	18.6	16.9	18.4	16.1
Diff. above two values	−6.4	−13.9	−8.7	−1.0	−5.7	+11.4	+11.3	+12.9	+9.9	−0.5

fraction patterns 2.76 Å, 2.49 Å corresponding to hausmannite will show a little contamination of hausmannite. The isolated oxygen volume of 1050°C. was remarkably less than the calculated value, and the X-ray investigation also verified the remnants of α-bixbyite. Therefore, more prolonged heating or higher temperature may be required to convert it into hausmannite completely.

(II) γ-phase

This modification could be altered almost completely to α-bixbyite at 750°C., and to hausmannite at 1050°C. almost completely, as X-ray investigations confirmed these facts.

(III) Cryptomelane

The cryptomelane expelled only about two-thirds of its calculated oxygen at 750°C., the remaining oxygen being completely expelled untill 1050°C., with the deoxidation at higher temperature. This characteristic behaviour may be related to the double peak at 900°C. in its differential heating curve. The X-ray patterns showed the existence of α-bixbyite, and no hausmannite pattern at all. It is a characteristic that this mineral does not completely transform to bixbyite, notwithstanding the gradual dissociation from low temperature.

(IV) δ-phase

The volume of expelled oxygen at 750°C. is almost equal to the calculated volume, but the heated product is missing the characteristic patterns at 2.71 Å, 3.85 Å of α-bixbyite and corresponds to γ-bixbyite[21] or hausmannite. The diffraction patterns of γ-bixbyite is so similar to those of hausmannite, that it is difficult to identify these minerals from X-ray data alone. This product may be γ-bixbyite from the chemical standpoint.

(V) Mixture of ramsdellite series mineral and cryptomelane

It resembles to the characteristic of cryptomelane that the amount of active oxygen of this mixture expelled at 750°C. is also insufficient, and the remaining oxygen is fully expelled untill 1050°C.

Indication of the existence of hausmannite was observed in the heated product at 750°C. of Tsujinaka from the examination of the X-ray patterns.

Some characteristics of dry cells manufactured from various manganese dioxides

It is a well-known fact, that the performance of a dry cell depends on the variety of manganese dioxide modifications. Therefore, during the manufacture of dry cells for heavy duty service, it has been customary to add a proper amount of active MnO_2 to the MnO_2 ore. To investigate the suitability of MnO_2 in a dry cell, numerous UM-1 Type experimental dry cells were made according to J. I. S. specifications. The discharge time required until the circuit potential dropped to 0.75 volt, was measured under varying conditions, such as a continuous discharge through a 5-ohm, 10-ohm resistance, and intermittent discharge for 1 hour per day through a 5-ohm resistance.

The experimental results are represented in the following table;

Table 8. Capacity of a dry cell of various MnO_2

5-ohm intermittent discharge				10-ohm continuous discharge				5-ohm continuous discharge and voltage of open circuit			
Sample	mineral	time in min.	relative time	Sample	mineral	time in min.	relative time	Sample	time in min.	relative time	Voltage
Tachiki	delta	533	229	Tachiki	delta	1254	538	Maruno	472	148	1.800
Tsujinaka	R+C	473	164	Maruno	C	1596	499	Kawai A	495	144	1.670
Maruno	C	442	138	Tsujinaka	R+C	1338	473	Kawai B	458	136	1.721
Pirika	P	480	134	Kawai B	R+C	1530	453	Tachiki	303	130	1.819
Fukaura A	P	297	115	Kawai A	R+C	1416	433	Kawai C	448	129	1.743
Fukaura B	P	418	112	Fukaura B	P	1368	428	Fukaura B	390	107	1.661
Kawai A	R+C	325	99.4	Fukaura A	P	1104	417	Tsujinaka	272	94.1	1.567
Kawai B	R+C	318	94.1	Kawai C	C	1458	409	Pirika	240	67.1	1.660
Kawai C	C	325	93.9	Pirika	P	1158	324	Fukaura A	166	62.6	1.545

P: pyrolusite C: Cryptomelane R; ramsdellite series mineral

In order to compare the mutual capacity, it is most reasonable to consider

the active oxygen calculated from the absolute contents and the specific gravities of manganese dioxides.

The corrected values for each specimen were calculated by applying the following formula, and as is also shown in above table.

$$t\,(\text{calc.}) = t/(w-4.4) \times \frac{a}{100}$$

t : discharge time (obs.)
w : total weight in gr.
4.4 : weight of carbon electrode in gr.
a : MnO_2 %

The above table demonstrates that cryptomelane and γ-phase have an excellent quality for continuous discharge, and cryptomelane is also superior for intermittent discharge followed successively by pyrolusite and γ-phase in that order. There are a few exceptions, Tsujinaka, Kawai C which precipitated from the resolved solution.

However the conclusions drawn from the above described experiments should be ascertained on more specimens, practical experiences that the electrolysed MnO_2 is superior for continuous discharge, but inferior for intermittent discharge, and that the manganese dioxide from the northeastern part of Japan which is mainly composed of pyrolusite is generally inferior for dry cell use, showed a good agreement to the above experimental results. The sequence of circuit voltage in each specimen is also represented in the previous table.

Résumé

(1) From the X-ray investigations conducted, the specimens from Pirika and Fukaura have numerous distinct patterns corresponding to those of pyrolusite as determined by McMurdie and Fleischer. On the other hand, the electrolysed manganese dioxide prepared by the Mitsui Industrial Chemical Company shows a few diffused lines that correspond to the γ-phase, which is believed to be a poorly crystallized ramsdellite. Those of Maruno and Kawai C are correlated to cryptomelane and that of Tachiki to a δ-phase, a poorly crystallized cryptomelane. The specimens of Kawai A, B, and Tsujinaka are consisted of a mixture of poorly crystallized ramsdellite series mineral and cryptomelane.

(2) The differential thermal curve of each modification has three essential endothermic breaks; of these, the first peak which appears at a slightly lower temperature than 200°C. corresponds to the dehydration of

absorbed water, and the second peak at 500°–700°C. is due to the transformation to bixbyite (Mn_2O_3). The third peak, at 900°–1,000°C. is due to the second transformation to hausmannite (Mn_3O_4). Some of these essential peaks often appear as double peaks. We could distinctly identify each modification by comparing the differential thermal curves in detail.

(3) To investigate the actual state of the manganese oxide which occurred during the heating process, the loss of weight by thermobalance and the volumetric change of isolated oxygen, were quantitatively determined. From these thermal experiments, some valuable facts to identify the various modifications were found. A small part of water occluded in ore is often held until relatively higher temperature in its crystal structure. Some members begin to deoxidize at low temperature as 350°C.

(4) The volume of active free oxygen determined from the above experiments was compared with the calculated volume. Some members are almost completely transformed to α-bixbyite at 750°C. and to hausmannite at 1050°C., but the others expell only about two-thirds of their calculated oxygen at 750°C., the remaining oxygen being completely expelled untill 1050°C. Thus the deoxidation phenomena of various manganese dioxides are characteristic of their modifications.

(5) The suitability of manganese dioxide for dry cell use depends mostly on the characteristic behaviours of various modifications. To investigate these relationships between the capacity of a dry cell and mineralogical characteristics of various modifications, numerous experimental cells were made according to J. I. S. specifications. The capacity of the dry cell was measured under different conditions, such as continuous discharge and intermittent discharge. Cryptomelane and γ-phase, are excellent for continuous discharge, and cryptomelane is also superior for intermittent discharge successively followed by pyrolusite and γ-phase.

Refferences

1) H. F. McMurdie and F. Golovato: Jour. Res. Nat. Bur. Stand., 41, 589 (1948)
2) H. F. McMurdie: Trans. Electrochem. Soc., 86, 313 (1944).
3) W. F. Cole, A. D. Wadsley and A. Walkley: Trans. Electrochem. Soc., 92, 133 (1950).
4) T. Imai and M. Kaneko: Jour. Mineral. Soc. Japan, 1, 424 (1954).
5) U. Yoshida and T. Takei: Memoir Coll. Sci. Kyoto Imp. Univ., Ser. A, 15, 1 (1932).
6) M. Fleischer and W. E. Richmond: Econ. Geol., 38, 269 (1943).
7) Op. cit. (1)
8) O. Glemser: Ber. Deut. Chem. Ges., (B), 72, 1879 (1939).
9) A. Byström: Acta Cryst., 3, (1950).

10) P. Dubois: Ann. Chimie, 5, 411 (1936).
11) W. E. Richmond and M. Fleischer: Am. Mineral., 27, 607 (1942).
12) P. H. Delano: Ind. Eng. Chem., 42, 523 (1950).
13) Op. cit. (6)
14) Op. cit. (1)
15) J. W. Gruner: Am. Mineral., 28, 497 (1943).
16) W. Feitknecht and W. Marti: Hel. Chem. Acta., 28, 129 (1945).
17) Op. cit. (6)
18) Op. cit. (1)
19) Op. cit. (11)
20) T. E. Moore, M. Ellis and P. W. Selwood: J. Am. Chem. Soc. 72, 856 (1950).
21) Op. cit. (20).