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STUDIES OF THE MANGANESE OXIDES. IV. TODOROKITE*

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ABSTRACT

Todorokite is a very abundant manganese oxide mineral in many deposits in Cuba and has been noted from other localities. Six new analyses are given; they lead to the approximate formula

$$(Na, Ca, K, Mn^{+2})(Mn^{+4}, Mn^{+2}, Mg)_6O_{12}\cdot 3H_2O.$$

Electron diffraction data show the mineral to be orthorhombic, or monoclinic with β near 90°. The x-ray powder pattern is indexed on a cell with $a=0.75$A, $b=2.84_9$A, $c=9.59$A, $\beta=90°$. A differential thermal analysis curve is given.

INTRODUCTION

From 1940 to 1945, the U. S. Geological Survey made a study of the manganese deposits of Cuba and especially those in Oriente Province. Several preliminary reports were published and the results were summarized in papers by Lewis and Straczek (1955) on the geology of south-central Oriente and by Simons and Straczek (1958) on the geology of the manganese deposits of Cuba. The latter paper describes the deposits, but gives only a sketchy account of the mineralogy of the manganese oxides, which was known incompletely although a considerable amount of x-ray data had been accumulated.

The present paper deals with a manganese oxide mineral, whose x-ray pattern was recognized as being distinctive in 1941 and which was designated for some years as "Mineral T." X-ray studies by J. M. Axelrod from 1946 to 1948 showed that this mineral was an abundant constituent of the ores at many localities in Oriente Province, but that it was so intergrown with other minerals that the preparation of samples pure enough to warrant chemical analysis was extremely difficult. The best five samples were finally selected and their analysis was completed in 1952. At that time, it was learned that Arthur Horen, who had made a field study of the manganese ores of the Charco Redondo-Taratana district in 1951–1952, had also identified the same material by x-ray study at Harvard

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University, and it was decided to publish the results jointly. At about this time, the mineral was named delatorreite in honor of Carlos de la Torre y de la Huerta (1858–1950), eminent Cuban paleontologist. The name has frequently been used since within the U. S. Geological Survey and unfortunately appeared in print (Simons and Straczek, 1958, p. 66) without a description of the mineral, before the identity with todorokite (Yoshimura, 1934) had been established by Frondel, Marvin, and Ito. See preceding article, p. 1167. The name delatorreite should now be dropped.

Changes in assignments for several of the authors plus frequent absences abroad for one of us have long delayed publication of our results. We had hoped to do more work on the mineral, but in view of its abundance and widespread distribution, it seemed best to present our data now.

Occurrence and Origin

Todorokite has been found at many mines in Oriente Province, Cuba, and is one of the dominant manganese oxide minerals at the Charco Redondo, Taratana, Ponupo, and Quinto mines; probably many thousands of tons of it have been mined. Commonly associated minerals are pyrolusite, cryptomelane, manganite, psilomelane (including a very poorly crystalline variety), quartz, feldspar, and calcite. A list of localities in Oriente Province is given in Table 1; the page numbers refer to the descriptions of the deposits in Simons and Straczek (1958).

Table 1. Occurrences of Todorokite in Oriente Province, Cuba

Mine	Name of workings, shafts, or pits	Reference Simons and Straczek, 1958 (pages)
Boston mine		158–161
Quinto mine		167–170
Charco Redondo	Socias, Marinez, Unitoria, K-1, K-6, Gutierrez Batey, No. 1, KX	185–191
Lucia mine		192–194
Taratana mine	Canada, Lego	195–198
Guanaba mine		202–204
Sorpresa mine		213
Manacas District		213–215
Fortuna mine		220
New York mine		226–227
Yeya mine		235–237
Abundancia mine		238–240
Ponupo mine	W., Center, and E. Sultana, No. 3, Juanita	243–256
Ponupo de Manacal		264–268

In addition, todorokite has been identified by x-ray study in the laboratories of the U. S. Geological Survey as a constituent of ores from the Embreeville mine, Embreeville, Tennessee; the Lucifer mine, Baja California, Mexico; the Nsuta mine, Ghana, Africa; and the Taxud area, Philippines, also as a constitutent of incrustations from Bikini Atoll and of a deep-sea nodule from the Pacific, from near Cadiz Dry Lake, California, and as a coating on colemanite from Furnace Creek, Death Valley, California.

The manganese ores at the Cuban localities are interbedded with volcanic tuff, now largely altered to montmorillonite clays, and with jasper (bayate), and limestone. At Charco Redondo the "delatorreite" is commonly the matrix for limestone and tuff and in part replaces them. It has commonly crystallized around kernels of tuff. The bayate occurs in lenses ranging in thickness from an inch or two to as much as a foot. It consists of rounded quartz spherulites in a ferruginous matrix; the spherulites range in size from a micron to several tenths of a millimeter and commonly show growth banding with silica alternating with layers of hydrous (?) iron oxides. The contact between the bayate and the massive todorokite is usually, but not always sharp, and there was no definite evidence of either replacing the other. Both were, however, cut by crystalline quartz, commonly amethystine, which lines vugs and contains shreds of bayate and inclusions of manganite or pyrolusite. The last mineral formed was rhombohedral calcite, which occurs in veins and perched on the vuggy quartz.

The todorokite has been altered near the surface and along faults or fissures to pyrolusite, and perhaps to manganite.

The origin of these deposits is discussed at some length by Simons and Straczek (1958, p. 103–110), who conclude that the source of the manganese was probably hot springs. Horen believes the deposits to be of marine sedimentary origin. In contrast, the type todorokite from the Todoroki mine in Hokkaido, Japan, was believed by Yoshimura (1934) to have been formed by late-stage hydrothermal solutions altering inesite.

Physical Properties

Todorokite from Cuba commonly occurs as columnar aggregates, but is also found as fine fibers and as irregular masses. The color and streak are brownish-black to dark brown; comparison by J. J. Fahey with Ridgway's Color Standards of the analyzed samples nos. 1–4 showed two matching dusky purplish gray and two matching sooty black. The apparent hardness is low, the material breaking into fibers; the true hardness is not known. Specific gravity measurements by Horen of six samples on the Berman balance gave an average of 3.49; four pycnometer de-

TABLE 2. ANALYSES OF "DELATORREITE" FROM CUBA AND TODOROKITE FROM JAPAN

	1	2	3	4	5	6	7
MnO_2	72.37	72.15	68.46	71.61	67.86	67.19	65.59
MnO	10.04	8.87	10.70	10.16	11.24	14.56	12.37
CaO	2.57	1.52	2.13	2.66	5.51	2.03	3.28
SrO	0.60	0.24	0.13	0.53	0.92	—	—
BaO	1.05	0.20	0.40	0.18	0.54	0.14	2.05
Na_2O	1.30	1.23	1.44	0.85	1.45	1.34	0.21
K_2O	0.24	0.48	0.75	1.48	0.06	0.43	0.54
MgO	1.04	3.51	3.22	1.58	0.88	3.13	1.01
CoO	—	0.02	0.18	—	—	0.23	—
CuO	tr	tr	0.44	tr	0.02	—	—
Al_2O_3	0.46	0.14	0.19	0.12	0.25	—	0.28
Fe_2O_3	0.06	0.06	0.07	0.06	0.18	—	0.20
SiO_2	0.95	0.24	0.41	0.64	0.64	0.14	1.73[a]
H_2O^-	8.80	10.61	10.99	9.03	9.47	10.69	1.56
H_2O^+							9.72
Others	—	—	—	—	—	—	0.70[b]
	99.48	99.27	99.51	98.90	99.02	99.88	99.24
Active O	13.31[c]	13.25[c]	12.60[c]	13.12[c]	12.49[c]	12.07	—
G	3.82	3.66	3.68	3.78	—	—	3.67

[a] Includes SiO_2 0.45, insol. 1.28%.
[b] Includes P_2O_5 0.42, SO_3 0.28, CO_2 tr., TiO_2 tr.
[c] Average of 2 determinations.

Analyses 1–5 by C. M. Warshaw; SrO in CaO by W. W. Brannock and E. A. Nygaard with flame photometer; SrO in BaO by K. J. Murata and R. S. Harner spectrographically; alkalies by W. W. Brannock with flame photometer; Fe_2O_3 colorimetrically by S. M. Berthold; cobalt by L. E. Reichen polarographically. Analysis 6 by F. A. Gonyer, Harvard University; analysis No. 7 from Yoshimura (1934).

Sample descriptions

Nos. 1–5. Collected by J. A. Straczek; No. 1 from Quinto, shown by x-ray study to contain a trace of pyrolusite; No. 2 from Tarantana; No. 3 from Charco Redondo, contains a trace of calcite; No. 4 from Guanaba, contains a small amount of cryptomelane; No. 5 from Ponupo; the x-ray pattern shows some weak unidentified lines; No. 6 collected by Arthur Horen from Charco Redondo, Batey No. 1 shaft.

terminations by Fahey and one by Yoshimura (Table 2) gave 3.66–3.82; the higher values by pycnometer are to be expected for such fibrous material.

CHEMISTRY

Analyses of six samples from Cuba are given in Table 2 along with the analysis of todorokite from Japan (no. 7). Spectrographic analysis of Nos. 1–5 by K. J. Murata showed the following:

Mo—.0X in samples 1, 2, and 4, 0.00X in 3 and 5
V and B—.0X in samples 1 and 5, .00X in 2 and 3
Ni—.0X in samples 2, 3, and 5, .00X in 4, .000X in 1
Cu—0.X in samples 3, .0X in 5, .00X in 4, .000X in 1 and 2
Co—0.X in samples 3, .0X in 2, .00X in 1, 4, and 5
Ti—.00X in samples 1, 2, and 5, .000X in 3 and 4

Not found—Ag, As, Au, Be, Bi, Cd, Cr, Ga, Ge, In, La, Li, Nb, P, Pb, Pt, Re, Sb, Sc, Sn, Tl, W, Y, Zn.

Analyses 1–7 (Table 2) were recalculated, neglecting SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, and SO_3; it is possible that these are not actually impurities. For analysis 7, H_2O^+ was taken, for the others total H_2O. From the unit cell dimensions obtained by Ross, formulas with O=11 or O=12 (not including H_2O) seemed possible. The results are given in Tables 3 and 4.

TABLE 3. ANALYSES OF TODOROKITE RECALCULATED

No.	Ca[a]	Na	K	ΣX	Mn^{+4}	Mn^{+2}	Mg[b]	ΣY	ΣX+Y	H_2O	Mol. wt.
					For O=11.0						
1	0.33	0.24	0.03	0.60	4.78	0.81	0.15	5.34	5.94	2.81	563
2	0.17	0.23	0.05	0.45	4.74	0.71	0.50	5.95	6.40	3.36	564
3	0.25	0.27	0.09	0.61	4.59	0.88	0.51	5.98	6.59	3.56	576
4	0.31	0.16	0.18	0.65	4.74	0.82	0.23	5.79	6.44	2.88	564
5	0.64	0.27	0.07	0.98	4.56	0.93	0.13	5.62	6.60	3.00	576
6	0.22	0.25	0.05	0.52	4.49	1.19	0.47	6.15	6.67	3.44	579
7	0.44	0.04	0.08	0.55	4.64	1.07	0.15	5.86	6.41	3.32	583
					For O=12.0						
1	0.37	0.26	0.03	0.66	5.22	0.89	0.16	6.27	6.93	3.06	614
2	0.19	0.25	0.06	0.50	5.17	0.78	0.54	6.49	6.99	3.67	615
3	0.27	0.30	0.10	0.67	5.01	0.96	0.57	6.54	7.21	3.88	629
4	0.34	0.17	0.20	0.71	5.17	0.90	0.25	6.32	7.03	3.14	615
5	0.71	0.30	0.08	1.09	4.98	1.01	0.14	6.13	7.22	3.35	628
6	0.24	0.27	0.06	0.57	4.89	1.30	0.51	6.70	7.27	3.76	632
7	0.48	0.05	0.08	0.61	5.06	1.17	0.17	6.40	7.01	3.62	636

[a] Including Sr and Ba.
[b] Including Co and Cu.

The measured specific gravities, as shown in Table 4, do not agree well with those calculated on either assumption. They are lower than those calculated for O=12; because measured specific gravities tend to be low, the formulas in Table 3 calculated on the basis O=12 seem more probable. The formula of the mineral might then be written as

$$(Ca, Na, K)_{0.5-1.1}(Mn^{+4}, Mn^{+2}, Mg)_{6.1-6.7}O_{12}\cdot 3H_2O.$$

TABLE 4. CALCULATED AND MEASURED SPECIFIC GRAVITIES OF TODOROKITE

No.	G (calcd. for O=11)	G (calcd. for O=12)	G (measured)
1	3.49	3.81	3.82
2	3.49	3.81	3.66
3	3.57	3.90	3.68
4	3.49	3.81	3.78
5	3.57	3.89	—
6	3.59	3.91	—
7	3.61	3.94	3.67
Average	3.54	3.87	3.72

It will be noted that the sum of the cations is close to 7; if sufficient Mn^{+2} is taken to occupy Ca positions, the formula might alternatively be written as

$$(Ca, Na, Mn^{+2}, K)(Mn^{+4}, Mn^{+2}, Mg)_6O_{12}\cdot 3H_2O.$$

The Mg might also be placed with the first group. All the analyses, including No. 7 for which H_2O^- was determined, show more than $3H_2O$; presumably some of this in the first six analyses is H_2O^-.

Woodruffite (Frondel, 1953), which is probably isostructural with todorokite, was assigned the formula $(Zn, Mn^{+2})_2 Mn_5^{+4}O_{12}\cdot 4H_2O$; here again the sum of the cations is 7.

ELECTRON MICROSCOPE AND ELECTRON DIFFRACTION DATA ON "DELATORREITE"

Electron micrographs of analyzed samples (Nos. 1–5, Table 2), show the crystals to be thin plates flattened on {001}. Many of the plates are broken into narrow laths or blades which are elongated parallel to the *b* axis (Figs. 1, 2). It appears as though the crystals have two perfect cleavages parallel to {001} and {100}.

All five samples give identical electron diffraction patterns. The electron diffraction single crystal pattern (superimposed on the todorokite powder pattern) shown in Fig. 3, gives the dimensions of the unit cell within the basal plane (within the plane of the plate). The single crystal pattern is indexed as shown in Fig. 4.

Measurement of the electron diffraction patterns of "delatorreite" yield: $a=9.75$ Å, $b=2.84_9$ Å and S=90°. The *x*-ray powder pattern of "delatorreite" shows lines at 9.6 Å, 4.77_1 Å, 3.19 Å, and 2.398 Å suggesting strongly that the spacings in the c-direction (basal reflections) are $0.59/n$ Å, where n is the order. The above data indicate that "delatorreite" is orthorhombic or monoclinic with $a=9.75$ Å, $b=2.84_9$ Å, and $c \sin\beta=9.59$ Å. The *x*-ray powder pattern can be indexed assuming an orthorhombic cell ($\beta=90°$), as shown in Table 5.

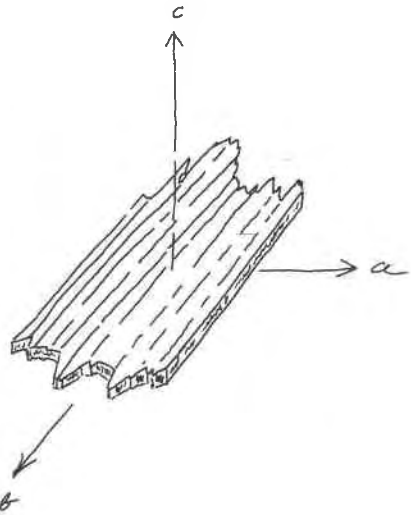

FIG. 1. (Left) Electron micrograph of todorokite.
FIG. 2. (Right) Sketch of a typical crystal of todorokite, showing plate flattened on (001) and broken into thin blades elongated along [010].

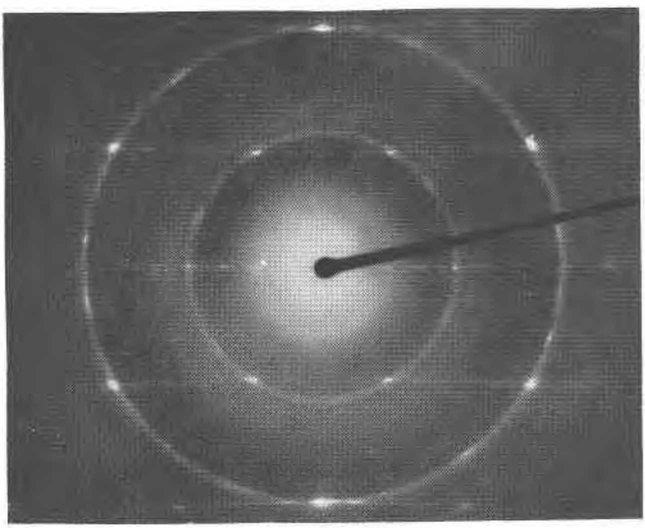

FIG. 3. Electron diffraction spot pattern superimposed on the todorokite powder pattern.

Differential Thermal Analysis

A differential thermal analysis was kindly made by George T. Faust, U. S. Geological Survey, on the analyzed material from the Quinto Pit (Sample no. 1 of Table 2). The curve is given in Fig. 5. Interpretation of this complex curve is deferred; further investigations of this and other manganese oxides are under way at the U. S. Geological Survey.

Acknowledgments

We are indebted to J. M. Axelrod, formerly of the U S. Geological Survey, who made *x*-ray studies of many samples from Oriente; to K. J.

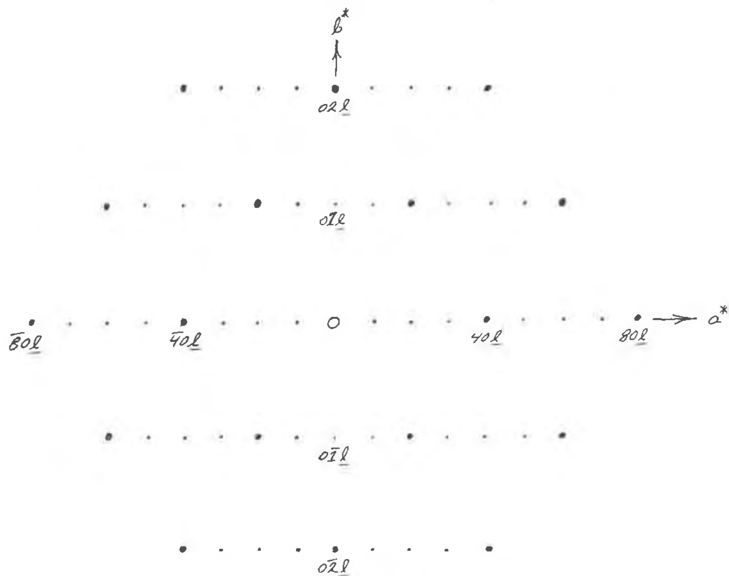

Fig. 4. Method of indexing the spot pattern shown in Fig. 3.

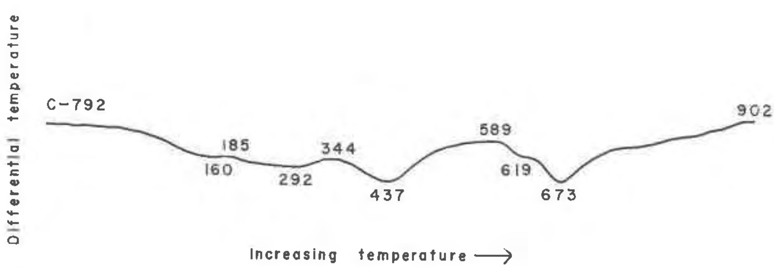

Fig. 5. D T A curve of todorokite, Quinto Pit, Cuba.

TABLE 5. *X*-RAY POWDER DATA FOR "DELATORREITE" AND TODOROKITE, Fe RADIATION, Mn FILTER, 114 MM. DIA. CAMERA

"Delatorreite"				Todorokite†	
I	*d* (meas)	*d* (calc)*	*hkl*	*d* (meas)	I
		9.747	100		
9.6	s	9.592	001	9.65	10
				7.2	½
		6.837	101		
		4.873	200		
4.77	s	4.796	002	4.81	8
				4.46	3
		4.345	201		
		4.303	102		
		3.418	202		
		3.256	300		
3.19	w	3.185	003	3.20	4
3.11–2.95	band	3.077	301		
		3.038	103		
		2.849	010		
		2.734	110		
		2.731	011		
2.7	band	2.690	302		
		2.673	203		
		2.630	111		
		2.460	210		
2.448	m	2.449	012	2.45	3
		2.437	400		
2.398	s	2.398	004	2.40	4
		2.382	211		
		2.376	112		
2.34	m	2.362	401		
		2.329	104		
		2.279	303		
2.21	m	2.189	212	2.216	4
		2.172	402		
2.16	f-b	2.152	204	2.15	1
		2.142	310		
		2.127	013		
2.11	f-b	2.091	311		
		2.078	113		
1.98	m	1.956	312	1.981	1
		1.950	500, 213		
		1.938	403		
		1.930	304		

* Assuming an orthorhombic unit cell with $a=9.75$Å, $b=2.849$Å and $c=9.59$Å.
† From Frondel, *Am. Mineral.*, **38**, p. 766 (1953).

TABLE 5 (*Continued*)

"Delatorreite"			Todorokite†		
I	*d* (meas)	*d* (calc)*	*hkl*	*d* (meas)	I
1.92	w	1.918	005		
		1.910	501		
		1.882	105		
		1.852	410		
		1.834	014		
		1.818	411		
		1.806	502		
		1.803	114		
		1.785	205		
		1.780	313		
1.74	wm	1.728	412		
		1.717	214		
1.69	f-b	1.709	404		
		1.664	503		
		1.652	305		
		1.623	600		
		1.612	510		
		1.605	601		
		1.602	413		
		1.599	006		
		1.597	314		
		1.591	015		
		1.587	511		
		1.578	106		
		1.570	115		
		1.543	512		
1.53	w	1.539	602		
		1.519	206		
		1.513	215, 504		
		1.507	405		
		1.466	414		
		1.448	603		
		1.437	513		
		1.434	306		
		1.429	315		
1.423	m	1.424	020	1.419	4
				1.392	1
				1.331	5

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