

NEW OCCURRENCES OF TODOROKITE*

C. FRONDEL, U. B. MARVIN AND J. ITO, *Harvard University,
Cambridge, Massachusetts.*

ABSTRACT

Chemical, x -ray and other data are given for todorokite, $(\text{Mn}, \text{Mg}, \text{Ca}, \text{Ba}, \text{Na}, \text{K})_2\text{Mn}_3\text{O}_{12}\cdot 3\text{H}_2\text{O}$, from Charco Redondo, Cuba, Farragudo, Portugal, and Hüttenberg, Austria. Additional localities at Romanèche, France, Saipan Island, Bahia, Brazil, and Sterling Hill, New Jersey, are noted. Delatorreite of Simon and Straczek (1958) is identical with todorokite.

INTRODUCTION

We have identified todorokite, a manganese oxide mineral hitherto known only from Japan (Yoshimura, 1934), in manganese ore from the Charco Redondo district, Cuba, and in Museum specimens from six additional localities. Delatorreite, briefly mentioned as a new mineral in a publication by Simon and Straczek (1958) on the Charco Redondo deposit that appeared during the course of our work, is identical with todorokite. Our determination of this material as todorokite is based on a type specimen obtained by W. F. Foshag in 1946 in Japan and now deposited in the U. S. National Museum. Todorokite apparently is a widespread mineral and in the Charco Redondo deposit at least has been an important ore.

LOCALITIES

Charco Redondo, Cuba. The material from Charco Redondo is described in detail in an accompanying paper by Straczek, Horen, Ross and Warsaw (1960). Our specimens were obtained by T. C. Marvin in 1955 during a survey made for the Union Carbide Ore Company. In general they have a slightly divergent or exfoliate fine-columnar to fibrous structure (Fig. 1). The fibers range up to about 10 cm. in length. Fracture surfaces tend to be somewhat curved and show a weak silky sheen. The luster on surfaces broken across the fibrosity is dull. The color of the mineral is dark brownish black. The specific gravity as measured on small grains on the Berman balance varied between 3.1 and 3.4 and undoubtedly is low because of the fibrous structure. The hardness is low but could not be measured accurately. A chemical analysis of the mineral is cited in Table 1, and the x -ray powder data are given in Table 2 and Fig. 2.

Farragudo, Portugal. A stalactitic mass of todorokite (Fig. 1) was found in a small collection of secondary manganese minerals, chiefly crypto-

* Contribution from the Department of Mineralogy, Harvard University, No. 339.

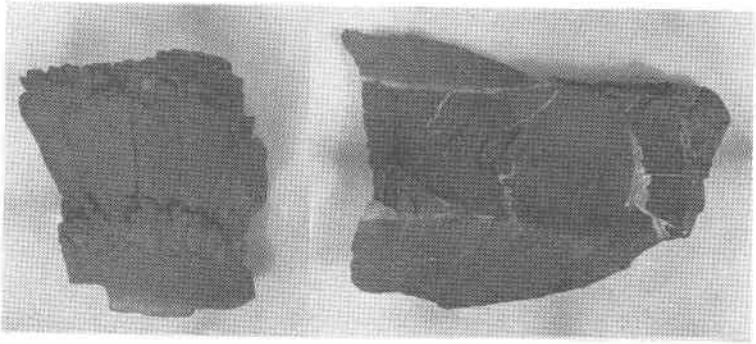


FIG. 1. Todorokite from Charco Redondo, Cuba (right) and from Farragudo, Portugal (left). About $\frac{1}{3}$ natural size.

melane, from this locality. The material is soft and porous, and shows the slightly divergent, long fibrous mode of aggregation and dark brown to brownish black color that appears to be typical of todorokite. A crude concentric layering is present and some of the inner layers have a dense

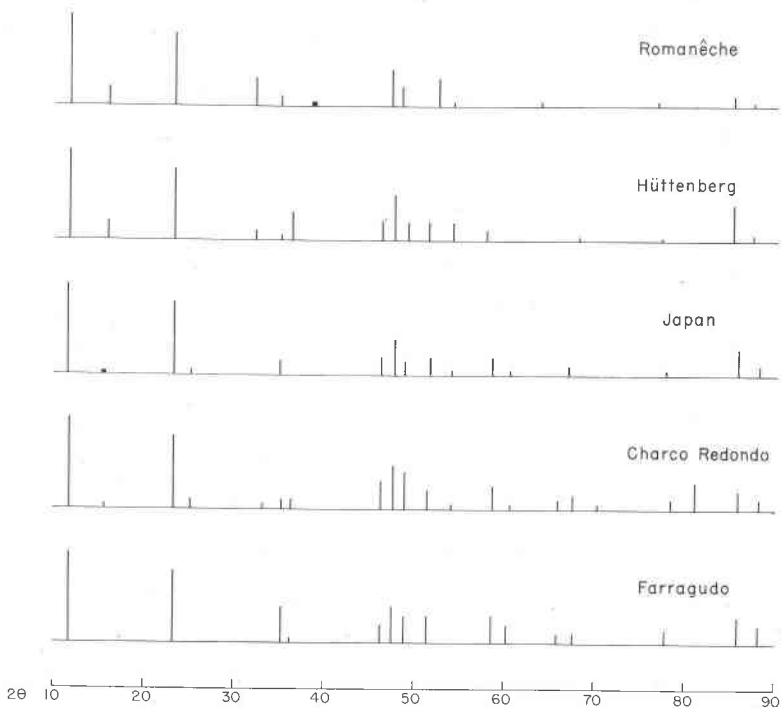


FIG. 2. Powder pattern diagrams.

TABLE 1. CHEMICAL ANALYSES OF TODOROKITE

	Farragudo	Charco Redondo	Hüttenberg	Japan (Yoshimura, 1934)
MnO ₂	70.23	69.57	71.75	65.59
MnO	11.19	11.65	8.62	12.37
CaO	0.96	2.30	1.40	3.28
SrO*	~ 0.01	~ 0.05	~ 0.01	
BaO	0.00x	0.19	4.32	2.05
Li ₂ O*	~ 0.05	~ 0.001	~ 0.01	
Na ₂ O	1.16	1.14	0.17	0.21
K ₂ O	0.61	0.35	0.91	0.54
MgO	3.90	3.25	2.13	1.01
NiO*	~ 0.001	~ 0.05	~ 0.001	
CoO*	~ 0.01	~ 0.05	—	
CuO	0.001	0.01	0.001	
PbO*	~ 0.00x	~ 0.01	0.00x	
Al ₂ O ₃	tr.	tr.	tr.	0.28
Fe ₂ O ₃	0.01	tr.	0.02	0.20
SiO ₂	0.68	0.27	0.23	0.45
SO ₃	0.24	0.14	0.14	0.28
H ₂ O	10.50	10.83	9.95	11.28
Rem.	(Note 1)	(Note 2)	(Note 3)	(Note 4)
Total	99.73	100.16	99.89	99.24
	Molecular Quotients			
MnO ₂	5.12	4.87	6.79	4.30
MnO	1	1	1	1
(Mg, Ca, Ba, Na, K)O	0.89	0.90	0.98	0.61
H ₂ O	3.69	3.66	4.55	3.10

Note 1. Rem. is P₂O₅ 0.13, MoO₃ 0.05, ZnO 0.00x, V₂O₅ 0.00x, TiO₂ 0.00x, Ag tr., As tr.

Note 2. Rem. is MoO₃ 0.05, Sc₂O₃ tr., (Y, Yb)₂O₃ tr., Ag. tr., R₂O₃ 0.26.

Note 3. Rem. is MoO₃ 0.03, ZnO 0.00x, ZrO₂ tr., (Y, Yb)₂O₃ tr., R₂O₃ 0.2.

Note 4. Rem. is P₂O₅ 0.42, TiO₂ tr., insol. 1.28.

* Determinations by optical spectrograph.

structure and earthy luster. A chemical analysis is given in Table 1, and the *x*-ray powder data in Table 2 and Fig. 2.

Hüttenberg, Carinthia, Austria. This material comprised nodular masses about 5 cm. in diameter, without matrix, with an indistinct fibrous structure and coarse concentric layering. The material is very fragile and soft, falling to pieces when handled, and is so light and porous as to float on water. The color is brown, lighter in tone than that from Charco Redondo. The luster of fracture surfaces is dull, as in the other occurrences of todorokite, but the smooth outer surface of the nodules has a

TABLE 2. X-RAY POWDER DATA FOR TODOROKITE
Filtered iron radiation, in Angstroms

Farragudo, Portugal		Charco Redondo, Cuba		Todoroki Mine, Japan		Hüttenberg, Austria		Romanèche, France	
I	d	I	d	I	d	I	d	I	d
10	9.56	10	9.60	10	9.68	10	9.60	10	9.58
		$\frac{1}{2}$ d	7.13	$\frac{1}{2}$ d	7.15	3	7.02	2	6.98
8	4.80	8	4.80	8	4.80	8	4.79	8	4.79
		1 d	4.45	$\frac{1}{2}$ d	4.45				
						1	3.48	3	3.48
		$\frac{1}{2}$ d	3.40						
4	3.19	1	3.20	$1\frac{1}{2}$	3.22	$\frac{1}{2}$	3.21	1	3.22
$\frac{1}{2}$	3.11	1	3.10			3	3.10		
								$\frac{1}{2}$ d	2.98
								$\frac{1}{2}$ d	2.88
2	2.46	3	2.46	2	2.46	2	2.46		
4	2.40	5	2.40	4	2.39	5	2.40	4	2.41
3	2.34	4	2.34	$1\frac{1}{2}$	2.34	2	2.33	2	2.36
3	2.23	2	2.23	2	2.22	2	2.23	3	2.19
		$\frac{1}{2}$ d	2.13	$\frac{1}{2}$ d	2.15	2	2.15	$\frac{1}{4}$	2.15
3	1.98	2	1.98	2	1.98	1	2.00		
2	1.93	$\frac{1}{2}$	1.92	$\frac{1}{2}$	1.92				
								$\frac{1}{2}$	1.83
1	1.78	1	1.78						
1	1.74	1	1.74	1	1.75	$\frac{1}{4}$ d	1.73		
		$\frac{1}{2}$	1.68						
1	1.54	1	1.53	$\frac{1}{2}$	1.54	1	1.55	$\frac{1}{2}$	1.56
		3	1.49						
3	1.42	2	1.42	3	1.42	4	1.43	1	1.43
2	1.39	1	1.39	1	1.39	$\frac{1}{2}$	1.40	$\frac{1}{4}$	1.40

d = diffuse line.

faint bronzy appearance. A few thin intercalated layers of a black dense mineral were identified by *x*-rays as pyrolusite. A chemical analysis of the mineral, cited in Table 1, shows it to be relatively high in Ba. The *x*-ray powder data are given in Table 2 and Fig. 2. Meixner (1957) notes that a soft "wad" occurs at Hüttenberg together with hard, black coatings of secondary manganese minerals that probably include cryptomelane and hollandite.

Saipan, Mariana Islands, Pacific Ocean. This material was identical in form of aggregation and color with that from Charco Redondo. It is relatively brittle and hard, however, because it is intimately admixed with finely divided silica. Although the mineral appears homogeneous to the eye, grains when leached with acid leave a skeleton of silica amounting

in some instances to 50 per cent of the sample or more. Efforts to remove the silica by treatment with heavy liquids were not successful and a chemical analysis was not undertaken. A semi-quantitative spectrographic analysis revealed that Mg was present in amounts greater than Ba and Ca. Small deposits of unidentified manganese oxides have been mined on Saipan and their geology has been described by Cloud, Schmidt and Burke (1956).

Romanèche, France. A Museum specimen from this locality showed a hard, black crust of "romanechite" (=psilomelane) that inwardly was porous and cavernous. Some of the openings were filled with soft brown aggregates of fibrous todorokite. X-ray data for this mineral are given in Table 2 and Fig. 2. The x-ray pattern resembles that of the barium-rich todorokite from Hüttenberg in that it has a definite line rather than a diffuse darkening at about d 7.1 Å. The summary description by Lacroix (1910) of romanechite from Romanèche mentioned soft to porous fibrous varieties that probably refer in part to todorokite.

Sterling Hill, New Jersey. Todorokite was identified in a small collection of secondary manganese oxides from the old surface workings at the south end of the orebody at this place (Palache, 1935). The todorokite forms soft, dark brownish black masses with a confused leafy-fibrous structure. It occurs associated with chalcophanite and secondary calcite crystals in altering franklinite-willemitite ore. Efforts to separate the todorokite from admixed chalcophanite were unsuccessful and a chemical analysis was not made.

Bahia, Brazil. We have also identified todorokite by x-ray means as a rare constituent of the manganese oxide deposits at Saude and at Urandi, Bahia. The deposits of both areas are largely the result of supergene enrichment of metamorphic country rock containing spessartite and other manganese minerals.

OPTICAL PROPERTIES

Under the microscope the mineral is dark brown in color and is not well suited for optical study; all but the thinnest grains are opaque. It appears as irregular, flattened shreds and as minute cleavage flakes, rarely also as irregular laths and then apparently with parallel extinction on both the flattening and perpendicular thereto. Cleavage flakes and laths are not pleochroic; on edge the laths are pleochroic in brown with the long direction dark brown to opaque. The intensity of the pleochroism varies from faint to strong in material from different localities. The indices of refraction were observed to be over 2.00. According to Yoshimura (1934) the mineral from Japan is lath-like, flattened on (010) and elongated [001] with terminal edges inclined ca. 60° and 70° to [001].

Cleavages on (100) and (010). He states that $Y=b$ with Z near or parallel [001] and absorption $Z>X$. Our sample of the Japanese material conformed to the description first given above, although it was relatively dark colored and had a tendency to break into needles rather than into laths or plates.

THERMAL BEHAVIOR

DTA graphs of analyzed material from Charco Redondo, Hüttenberg and Farragudo showed an endothermal peak at about 625° C.; the Hüttenberg material showed an additional endothermal peak at about 980°. X-ray study of samples that had been heated in air to temperatures above and below 625° showed that the mineral breaks down near that temperature to hausmannite, Mn_3O_4 , together with small amounts of unidentified decomposition products that presumably contain the Ba, Mg, and Ca reported in the chemical analyses.

X-RAY POWDER DATA

The x-ray powder spacing data for the original todorokite from Japan and for the three analyzed specimens from Charco Redondo, Farragudo, and Hüttenberg are given in Table 2 and Fig. 2. The patterns were recorded in iron radiation on both film in a 114 mm. diameter camera and by the diffractometer (chart) method. The film data, slightly superior to that obtained from charts, is here given. The x-ray patterns show little variation other than in the relative intensity of certain lines, notably at d 7.1 Å.

CHEMICAL COMPOSITION

Chemical analyses of the todorokite from Charco Redondo, Hüttenberg, and Farragudo are cited in Table 1 together with the original analysis of the Japanese material. These analyses (and those reported in an accompanying paper by Straczek, Horen, Ross and Warshaw (1960)) do not permit a straightforward interpretation. This is often found to be the case with the complex manganese oxides. The crystal chemistry of these minerals generally involves both the coupled substitution of ions of unlike valence in one or more cation positions and valence-coupled omissions, and a satisfactory answer usually is not obtained until the crystal structure is worked out. The ratios of the Charco Redondo and Farragudo material suggest that the idealized formula contains a total of 7 cations and 12 oxygen ions, probably as



The amount of water present does not appear to be less than $3H_2O$ and may be greater. The SiO_2 , Fe_2O_3 , Al_2O_3 , SO_3 , and P_2O_5 reported in the

analyses may be due to admixture. The Hüttenberg material is relatively high in Mn^4 , perhaps due to a small admixture of pyrolusite. The ratios of the analysis of the original todorokite from Japan depart relatively widely from the formula suggested, and the formula $(Mn, Ba, Ca, Mg) Mn_3O_7 \cdot H_2O$ has been proposed, but the sample analyzed evidently was rather impure since it contained a total of 2.43 per cent insoluble, P_2O_5 , SO_3 , and SiO_2 .

The formula suggested here for todorokite is analogous to that earlier obtained for woodruffite, $(Zn, Mn)_2Mn_5O_{12} \cdot 4H_2O$, by Frondel (1953). This mineral appears from *x*-ray study to be isostructural with todorokite.

REFERENCES

- P. E. CLOUD, JR., R. G. SCHMIDT, H. W. BURKE (1956). Geology of Saipan, Mariana Islands. Part 1: General Geology. U. S. Geol. Surv. Prof. Pap. 280-A, 119.
- C. FRONDEL (1953). New manganese oxides: hydrohausmannite and woodruffite. *Am. Min.*, vol. 38, 761.
- A. LACROIX (1910). *Minéralogie de la France*, vol. 4, 6.
- H. MELXNER (1957). Die Minerale Kärntens, Klagenfurt. Part 1, 49.
- C. PALACHE (1935). The minerals of Franklin and Sterling Hill, Sussex County, New Jersey. U. S. Geol. Surv. Prof. Paper 180.
- F. S. SIMONS AND J. A. STRACZEK (1958). Geology of the manganese deposits of Cuba. *U. S. Geol. Surv. Bull.* 1057.
- J. A. STRACZEK, A. HOREN, M. ROSS AND C. M. WARSHAW (1960). Studies of the manganese oxides, IV. Todorokite, *Am. Min.*, 45, 1174.
- T. YOSHIMURA (1934). Todorokite, a new manganese mineral from the Todoroki mine, Hokkaido, Japan. *J. Fac. Sci. Hokkaido Imp. Univ.*, Ser. 4, Vol. 2, 289.

Manuscript received March 3, 1960.