

ZINC-BEARING TODOROKITE FROM PHILIPSBURG, MONTANA

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ABSTRACT

Chemical, physical, optical and x -ray data for zinc-bearing todorokite from Philipsburg, Montana are given. In contrast to other known occurrences, Philipsburg todorokite is of secondary origin and has formed through the processes of cavity filling and replacement of earlier manganese oxides.

INTRODUCTION

A detailed mineralogical study of certain manganese oxide deposits of the Philipsburg District, Montana, has been under way at the University of Wisconsin since 1958. Pyrolusite, manganite, cryptomelane, chalcophanite, hydrohetaerolite, Nsuta (γ) MnO_2 , todorokite, birnessite, and possibly coronadite have been identified in the ores. This paper describes the physical, optical, and x -ray characteristics of Philipsburg todorokite together with its chemical composition. Philipsburg todorokite differs both in composition and in geologic occurrence from todorokite of other known localities.

OCCURRENCE AND ORIGIN

The Philipsburg District is on the west flank of the Flint Creek mountains, Granite County, Montana, approximately 45 miles northwest of Butte on U. S. Highway 10A. The todorokite described in this paper is from the True Fissure mine in the eastern part of the District. The general geology of the Philipsburg District is given by Emmons and Calkins (1913). Goddard (1940) presents a geologic map of the district as well as descriptions and maps of several of the mines active in 1939. No published information is presently available on the True Fissure mine.

The manganese oxide ores of the True Fissure mine are predominantly in the Cambrian Hasmark dolomite. They occur in irregular lenticular to tabular replacement ore bodies adjacent to steeply dipping fissure veins that strike east or northwest. Minerals commonly associated with manganese oxides in the replacement bodies are rhodochrosite, fluorite, quartz, regularly interstratified montmorillonite-illite, goethite, and calcite. Pyrite, sphalerite, tennantite, and locally chalcopyrite and pyrrhgyrite are present but are commonly concentrated within or immediately adjacent to the fissure veins. They are uncommon in the replacement bodies.

The manganese oxide ores have been derived by the oxidation of rhodochrosite. This origin is indicated by the common occurrence of

manganese oxides as microscopic rhombic pseudomorphs after rhodochrosite, the close spatial association within the ore bodies of oxide and rhodochrosite, the similarities in some of the textures of rhodochrosite and the oxides, and the black manganese-rich coating which is presently forming on some mined surfaces.

Pseudomorphs, concretionary banding, cavity filling, and cross-cutting relationships indicate several possible paragenetic sequences of oxide formation. Local variation, repetitions, and reversals of any given sequence are common. Where associated with other oxides, todorokite is neither the first nor last to form. The textural relationships of the todorokite and its common association with cryptomelane, which is clearly secondary and forms rhombic pseudomorphs after rhodochrosite, show that todorokite is secondary and formed through the action of cold meteoric waters. In contrast, todorokite from the Todoroki Mine, Japan, was considered by Yoshimura (1934) to be a hydrothermal alteration product of inosite, and todorokite from Charco Redondo, Cuba, is believed by Simons and Straczek (1958) and by Straczek *et al.* (1960) to be primary and earlier than manganite and pyrolusite. Hot springs are regarded as the source of manganese-rich solutions from which the Charco Redondo todorokite was deposited. Horen, while differing with Straczek, nevertheless regards the Charco Redondo deposits as being of marine sedimentary origin.

PHYSICAL PROPERTIES

Philipsburg todorokite in its most common form is massive, with a gray-black color and submetallic luster. Less commonly it occurs as colloform-banded and botryoidal porous aggregates of acicular fibers oriented normal to discontinuities separating succeeding bands. Hand specimens of this latter material are very light, highly porous and gray to bronze-gray in color. Both textural forms have a distinctly greasy, almost graphitic feel, and soil the fingers. Powder color ranges from brown-black to black. Aggregates of Philipsburg todorokite are soft ($H < 2$), but because of the almost submicroscopic size of the individual fibers the true hardness could not be determined. Ten specific gravity measurements using the Berman balance gave values from 3.28 to 3.51. The average of measurements on both fragments and coarse powder is 3.39. Minor quartz and calcite impurities and the probability of trapped air in the weighed samples make necessary the conclusion that the above value is inaccurate to an unknown degree and should serve only as an approximate minimum.

OPTICAL PROPERTIES

More than 200 polished sections of the Philipsburg ores have been examined. Todorokite is a common although not ubiquitous constituent.

In four sections todorokite is the predominant oxide, and in each it occurs in the gray-black, megascopically massive, less porous form. Attempts to obtain an adequate polish on specimens of the gray, highly porous, colloform-banded material were generally unsuccessful.

Microscopic examination in reflected light shows todorokite to be opaque, light gray, and very weakly bireflectant (Fig. 1). Measured by a method patterned after that of Folinsbee (1949), the maximum reflectivity of an undulose aggregate is 24.5 and a minimum on this same aggregate is 21.0. Bireflectance is therefore 3.5. Examination under crossed polars shows that todorokite occurs as densely packed fan-shaped aggregates of radiating crystallites with undulose extinction (Fig. 2). Polarization colors are white to gray. The maximum angle of rotation of the aggregates is $3.6^\circ \pm 0.1^\circ$ in light with a wavelength of $589 \text{ m}\mu$, and the sign of the phase difference is positive.

X-RAY DIFFRACTION RESULTS

The x-ray powder diffraction data of Columns 1, 2, and 3, Table I were obtained using iron radiation with a manganese filter, on 114.6 mm. diameter Norelco cameras. Column 1 gives data of the gray, highly porous, very light, colloform-banded todorokite from the chemically analyzed sample. Column 2 gives data for the more compact, less porous, gray-black specimen from which the optical properties were obtained. Column



FIG. 1. Todorokite
True Fissure Mine,
Philipsburg, Montana.
Plane light, $\times 172$.



FIG. 2. Todorokite
True Fissure Mine,
Philipsburg, Montana.
Crossed polars $\times 172$.

TABLE I. X-RAY POWDER DIFFRACTION DATA FOR TODOROKITE

Philipsburg Montana		Philipsburg Montana		Charco Redondo Cuba		Todoroki Japan		Huttenberg Austria	
I	d	I	d	I	d	I	d	I	d
10	9.6	10	9.6	10	9.6	10	9.68	10	9.6
1	7.0(d)	$\frac{1}{2}$	7.0(d)	$\frac{1}{2}$	7.0(d)	$\frac{1}{4}$	7.13(d)	3	7.02
6	4.8	6	4.75	8	4.77	8	4.80	8	4.79
1	4.45(d)	$1\frac{1}{2}$	4.45(d)	2	4.4(d)	$\frac{1}{2}$	4.45(d)	-----	
		$1\frac{1}{2}$	3.32					1	3.48
-----		-----		-----		-----		-----	
1	3.20	1	3.17	1	3.18	$1\frac{1}{2}$	3.22	$\frac{1}{2}$	3.21
2	2.46	2	2.45	2	2.45	2	2.46	2	2.46
4	2.405	4	2.395	4	2.395	4	2.39	5	2.40
1	2.34	-----		-----		$1\frac{1}{2}$	2.34	2	2.33
2	2.22	2	2.21	2	2.21	2	2.22	2	2.23
-----		-----		-----		-----		-----	
2	1.99	2	1.975	2	1.98	2	1.98	1	2.00
-----		-----		$\frac{1}{2}$	1.91	$\frac{1}{2}$	1.92	2	1.93
-----		$\frac{1}{2}$	1.81					-----	
$\frac{1}{2}$	1.75	1	1.74	$\frac{1}{2}$	1.73	1	1.75	$\frac{1}{4}$	1.73(d)
-----		-----		$\frac{1}{2}$	1.66			-----	
1	1.54	1	1.54	1	1.53(d)	$\frac{1}{2}$	1.54	1	1.55
3	1.42	4	1.415	4	1.42	2	1.42	4	1.43
				$\frac{1}{2}$	1.405	1	1.39	$\frac{1}{2}$	1.40
				$\frac{1}{2}$	1.385				

3 is a diffraction pattern of Charco Redondo todorokite taken in this laboratory. Columns 4 and 5 are data for todorokite from Todoroki, Japan, and Huttenberg, Austria, given by Frondel, *et al.* (1960). The weak lines at 3.32 Å and 1.81 Å in Column 2 are thought to be due to impurities, the first possibly assignable to quartz.

CHEMICAL COMPOSITION

An analysis of Philipsburg todorokite is given in Column I, Table II. In Column II the analysis is recalculated after allotting all of the CO₂ and some of the CaO to calcite, which is known to be present in the analyzed sample.

Comparison of this analysis with those given for Charco Redondo todorokite by Levinson (1960) and by Straczek *et al.* (1960) and for todorokite from Todoroki, Charco Redondo, and elsewhere by Frondel *et al.* (1960) indicates that there are major differences in MnO and ZnO and lesser differences in CuO and PbO. These differences led the writer to suspect that impurities were present in the analyzed sample of the Philips-

burg todorokite. Although 1.69 per cent ZnO has been reported in cryptomelane from the Philipsburg District (Hewett and Fleischer, 1960) the presence of nearly 5 per cent ZnO in the Philipsburg todorokite was particularly suspect. In particular, chalcophanite, sphalerite, and chalcopyrite, all of which are present elsewhere in the Philipsburg ore bodies, were possible impurities. Polished sections of todorokite showed, however, that the only visible impurities were calcite, quartz, and very minor goethite. After microscopic examination the polished sections were crushed to -250 mesh and a qualitative x-ray spectrographic analysis was made using tungsten radiation and a lithium fluoride analyzing crystal. In every case strong, well defined $ZnK\alpha_1$, $ZnK\alpha_2$ peaks and less well defined but definite $PbL\beta_1$, $PbL\beta_2$ peaks were obtained. Subsequently, four additional polished sections of the analyzed sample of todorokite were prepared. Microscopic examination and x-ray powder photographs indicate that calcite is the only impurity. Microchemical tests with $K_2Hg(CNS)_4$ on both the analyzed sample and on powders of todorokite obtained by scratching small samples from optically monomineralic parts of polished sections all give positive tests for zinc. These results suggest that zinc

TABLE II. ANALYSIS OF TODOROKITE, PHILIPSBURG, MONTANA

	I	II	Molecular proportions
MnO ₂	68.02	72.98	0.8395
MnO	6.35	6.81	0.0960
Fe ₂ O ₃	.55	.59	0.0037
Al ₂ O ₃	.02	.02	0.0002
SiO ₂	.51	.55	0.0091
BaO	.18	.19	0.0012
SrO	.10	.11	0.0011
CaO	5.00	1.24	0.0221
MgO	2.11	2.26	0.0561
Na ₂ O	.15	.16	0.0026
K ₂ O	.86	.92	0.0098
CuO	.72	.77	0.0097
PbO	.52	.55	0.0025
ZnO	4.65	4.99	0.0613
P ₂ O ₅	.05	.05	—
CO ₂	3.02	—	—
H ₂ O	7.77	8.34	0.4633
Insol.	.20	.21	
	100.78	100.76	

Analyst: D. Scott, Union Carbide Nuclear Company. Material dried at 120° C. before analysis. Insolubles determined after boiling 15 minutes in 1:1 HCl.

TABLE III. FORMULAS FOR TODOROKITE

Author	Location	Formula
Levinson (1960)	Charco Redondo	$(\text{Mn}^{2+}, \text{Na}, \text{K}, \text{Mg}, \text{Ba}, \text{Sr}, \text{Ca}, \text{Cu})(\text{Mn}^{3+}, \text{Fe}, \text{Al})_7\text{O}_7 \cdot 2\text{H}_2\text{O}$
Frondel <i>et al.</i> (1960)	Charco Redondo & Farragudo	$(\text{Mn}^{2+}, \text{Mg}, \text{Ca}, \text{Ba}, \text{K}, \text{Na})_2\text{Mn}_5^{4+}\text{O}_{12} \cdot 3\text{H}_2\text{O}$
Straczek <i>et al.</i> (1960)	Charco Redondo	$(\text{Ca}, \text{Na}, \text{K})_{0.6-1.1}(\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mg})_{6.1-6.7}\text{O}_{12} \cdot 3\text{H}_2\text{O}$ or $(\text{Ca}, \text{Na}, \text{Mn}^{2+}, \text{K})(\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mg})_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$
Larson (this paper)	Philipsburg	1) $(\text{Mn}^{2+}, \text{Zn}, \text{Mg}, \text{Ba}, \text{Sr}, \text{Ca}, \text{Na}_2, \text{K}_2, \text{Cu}, \text{Pb})_3\text{Mn}_{10}^{4+}\text{O}_{23} \cdot 9\text{H}_2\text{O}$ or 2) $(\text{Mn}^{2+}, \text{Zn}, \text{Mg}, \text{Ba}, \text{Sr}, \text{Ca}, \text{Na}_2, \text{K}_2, \text{Cu}, \text{Pb})\text{Mn}_3^{4+}\text{O}_7 \cdot 2 \pm \text{XH}_2\text{O}$

and lead are essential components of the Philipsburg todorokite and are not present as impurities.

Table III lists todorokite formulas proposed by Levinson (1960), Frondel *et al.* (1960), Straczek *et al.* (1960) and by the author.

The first of the writer's formulas for Philipsburg todorokite is based on the assumption that Zn substitutes for Mn^{2+} . The total $\text{MnO} + \text{ZnO}$ is given the value 1. The validity of this assignment is open to question but appears justified on the theoretical bases of size and valency equivalence. Furthermore, Philipsburg todorokite is very low in Mn^{2+} and with this assignment the sum $\text{MnO} + \text{ZnO}$ approximates values for MnO given for essentially zinc-free todorokite by previous authors. The resulting formula (Larson, 1 above) is ungainly and shows little similarity to any of the formulas proposed by other authors. Because of this it was felt that some other assumption would perhaps better serve as a basis of calculation.

An examination of published analyses of todorokite given by Levinson (1960), Frondel *et al.* (1960), and Straczek *et al.* (1960) shows that MnO_2 is the component with the least percentage variation. Therefore, rather than using $\text{MnO} + \text{ZnO}$, MnO_2 was placed equal to some integer and used as a base for further calculations.

The Philipsburg analysis was recalculated for $\text{MnO}_2 = 5, 4,$ and 3 . As a check, several of the analyses given by other authors were recalculated on these same bases. The resulting molecular quotients are grouped in Table IV.

An inspection of Table IV shows that on the basis of molecular quotients a formula for todorokite with a $\text{MnO}_2 : (\text{Mn}^{2+} \cdot \cdot \cdot *)\text{O}$ ratio of approximately 3:1 is feasible. Such a ratio is supported by the Philipsburg analysis, Levinson's Charco Redondo analysis, the average of the six analyses given by Straczek *et al.* for Charco Redondo todorokite, the average of the Huttenberg, Farragudo and Charco Redondo analyses given by Frondel *et al.* and the average of all of the analyses given in Table IV.

TABLE IV

Location and author	MnO ₂	(Mn ²⁺ , . . . *)O	H ₂ O
Philipsburg, Mont. (Larson, this paper)	5	1.56	2.76
	4	1.25	2.20
	3	0.94	1.7
Charco Redondo (Levinson, 1960)	5	1.57	2.80
	4	1.26	2.24
	3	0.94	1.7
Charco Redondo (Straczek <i>et al.</i> , 1960) (Avg. of 6 analyses)	5	1.82	3.42
	4	1.46	2.74
	3	1.09	2.05
Charco Redondo (Fron del <i>et al.</i> , 1960)	5	1.93	3.76
	4	1.55	3.01
	3	1.16	2.26
Huttenberg (Fron del <i>et al.</i> , 1960)	5	1.45	3.35
	4	1.16	2.68
	3	0.87	2.01
Farragudo (Fron del <i>et al.</i> , 1960)	5	1.84	3.61
	4	1.47	2.89
	3	1.10	2.17
Average of Charco Redondo, Huttenberg, Farragudo (Fron del <i>et al.</i> , 1960)	5	1.74	3.57
	4	1.39	2.86
	3	1.04	2.14
Average of all of the above analyses	5	1.75	3.35
	4	1.40	2.68
	3	1.05	2.00

* Elements included varied from analysis to analysis:

Philipsburg (Larson)—(Mn²⁺, Zn, Ba, Sr, Ca, Mg, Na₂, K₂, Cu, Pb)

Charco Redondo (Levinson)—(Mn²⁺, Mg, Ca, Ba, Cu, Na₂, K₂, Sr)

Charco Redondo (Straczek *et al.*)—(Mn²⁺, Ca, Sr, Ba, Mg, Co, Cu, Na₂, K₂)

Charco Redondo (Fron del *et al.*)—(Mn²⁺, Mg, Ca, Ba, Na₂, K₂)

Huttenberg (Fron del *et al.*)—(Mn²⁺, Mg, Ca, Ba, Na₂, K₂)

Farragudo (Fron del *et al.*)—(Mn²⁺, Ca, Mg, Na₂, K₂)

It is proposed, therefore, that a logical formula for Philipsburg todorokite is (Mn²⁺, Zn, Mg, Ba, Sr, Ca, Cu, Pb, Na₂, K₂) Mn₃⁴⁺O₇·1.7H₂O or, more briefly, (M²⁺) (M⁴⁺)₃O₇·2 - x H₂O.

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