ZINC-BEARING TODOROKITE FROM PHILIPSBURG, MONTANA

LAWRENCE T. LARSON, Department of Geology and Geography, University of Tennessee, Knoxville, Tenn.

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) MnO₂, 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 pyrrhotite 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 rhodo-
chrosite, 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 se-
quence are common. Where associated with other oxides, todorokite is
neither the first nor last to form. The textural relationships of the todoro-
kite 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 or cold
meteoric waters. In contrast, todorokite from the Todoroki Mine, Japan,
was considered by Yoshimura (1934) to be a hydrothermal alteration
product of inesite, and todorokite from Charco Redondo, Cuba, is be-
lieved by Simons and Straczek (1958) and by Straczek et al. (1960) to be
primary and earlier than manganite and pyrolusite. Hot springs are re-
garded 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 be-
cause 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 ex-
amined. 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 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 chemcially analyzed sample. Column 2 gives data for the more compact, less porous, gray-black specimen from which the optical properties were obtained. Column
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 CO$_2$ 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 cryp-
tomelane from the Philipsburg District (Hewett and Fleischer, 1960) the
presence of nearly 5 per cent ZnO in the Philipsburg todorokite was par-
ticularly suspect. In particular, chalcopyrite, sphalerite, and chalcopy-
rite, 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 ZnKα, ZnKα2 peaks and less well defined
but definite PbLβ1, PbLβ2 peaks were obtained. Subsequently, four addi-
tional polished sections of the analyzed sample of todorokite were pre-
pared. Microscopic examination and x-ray powder photographs indicate
that calcite is the only impurity. Microchemical tests with K₂Hg(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 |
| MnO₂            | 68.02           | 72.98           | 0.8395                |
| MnO             | 6.35            | 6.81            | 0.0960                |
| Fe₂O₃           | 0.55            | 0.59            | 0.0037                |
| Al₂O₃           | 0.02            | 0.02            | 0.0002                |
| SiO₂            | 0.51            | 0.55            | 0.0091                |
| BaO             | 0.18            | 0.19            | 0.0012                |
| SrO             | 0.10            | 0.11            | 0.0011                |
| CaO             | 5.00            | 1.24            | 0.0221                |
| MgO             | 2.11            | 2.26            | 0.0561                |
| Na₂O            | 0.15            | 0.16            | 0.0026                |
| K₂O             | 0.86            | 0.92            | 0.0098                |
| CuO             | 0.72            | 0.77            | 0.0097                |
| PbO             | 0.52            | 0.55            | 0.0025                |
| ZnO             | 4.65            | 4.99            | 0.0613                |
| P₂O₅            | 0.05            | 0.05            | —                     |
| CO₂             | 3.02            | 3.02            | —                     |
| H₂O             | 7.77            | 8.34            | 0.4633                |
| Insol.          | 0.20            | 0.21            | —                     |
|                  | 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.
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 MnO\(_2\)+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 MnO+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 MnO+ZnO, MnO\(_2\) was placed equal to some integer and used as a base for further calculations.

The Philipsburg analysis was recalculated for 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 MnO\(_2\): (Mn\(^{2+}\) ⋅ ⋅ ⋅ *)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.
Elements included varied from analysis to analysis:
- Philipsburg (Larson) — (Mn$^{2+}$, Zn, Ba, Sr, Ca, Mg, Na$_2$, K$_2$, Cu, Pb)
- Charco Redondo (Levinson) — (Mn$^{2+}$, Mg, Ca, Ba, Cu, Na$_2$, K$_2$, Sr)
- Charco Redondo (Straczek et al.) — (Mn$^{2+}$, Ca, Sr, Ba, Mg, Co, Cu, Na$_2$, K$_2$)
- Charco Redondo (Frondel et al.) — (Mn$^{2+}$, Mg, Ca, Ba, Na$_2$, K$_2$)
- Huttenberg (Frondel et al.) — (Mn$^{2+}$, Mg, Ca, Ba, Na$_2$, K$_2$)
- Farragudo (Frondel et al.) — (Mn$^{2+}$, Ca, Mg, Na$_2$, K$_2$)

It is proposed, therefore, that a logical formula for Philipsburg todorokite is
$$(\text{Mn}^{3+}+\text{Zn}, \text{Mg}, \text{Ba}, \text{Sr}, \text{Ca}, \text{Cu}, \text{Pb}, \text{Na}_2, \text{K}_2)\text{Mn}_{3+x}\text{O}_{7+1.7}\text{H}_2\text{O}$$
or, more briefly,$$(\text{M}^{2+}) (\text{M}^{4+})_8\text{O}_{7-2-x}\text{H}_2\text{O}.$$
ACKNOWLEDGMENTS

The author is indebted to Professor E. N. Cameron of the University of Wisconsin for suggesting this study and for a critical reading of the manuscript. The wet analysis was done by Mr. D. Scott of the Union Carbide Nuclear Company through arrangements by Mr. H. R. Spedden of the Union Carbide Ore Company. The author also wishes to thank Professor S. W. Bailey of the University of Wisconsin and Dr. R. K. Sorem of Washington State University who have read parts of the manuscript and have given advice on mineralogical and x-ray techniques. Thanks is extended for the financial support provided by the Union Carbide Fellowship in Economic Geology. The Taylor-Knapp Mining Company of Philipsburg, Montana, is deserving of special thanks for the many kindnesses extended to the author during the summers of 1959 and 1960.

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Manuscript Received May 16, 1961.