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SECOND OCCURRENCE OF TODOROKITE

A. A. LEVINSON, *The Dow Chemical Company, Freeport, Texas.*

ABSTRACT

Todorokite, a hydrated manganese oxide mineral previously reported only from Japan, is described from an occurrence in Cuba. A chemical analysis, *x*-ray powder spacings, data on various physical properties and occurrence are presented and compared with those of the type todorokite from Japan.

INTRODUCTION

During the course of a routine mineralogical study of approximately twenty commercially available manganese ores from various parts of the world, as expected, many different mineral species were encountered. The "manganese ores," as they were designated, were found by *x*-ray diffraction to contain pyrolusite, ramsdellite, braunite, cryptomelane, hausmannite, psilomelane, psilomelane-like minerals, lithiophorite (from South Africa) and todorokite from a Cuban locality. Inasmuch as todorokite has only been reported from the type locality at the Todoroki Mine, Hokkaido, Japan (Yoshimura, 1934), a description is presented of this second occurrence.

The todorokite was first identified as the only manganese mineral in a shipment of ten pounds of "manganese ore" from E. J. Lavino and Company, Philadelphia, Pennsylvania. A second shipment of 500 pounds of what was supposed to be identical ore turned out to be predominantly todorokite with small amounts of pyrolusite.

Representative samples of Cuban todorokite have been deposited with the Smithsonian Institution, U. S. National Museum, Washington, D. C., where they have been given the numbers 113966 and 113967.

MONTENEGRO MINE—LOCATION, DESCRIPTION, MINERALIZATION

The todorokite described in this paper is found at the Montenegro Mine which is located on the northern flank of the Sierra Maestre Mountains twenty kilometers south of Baire, Oriente Province, Cuba. Manganese mineralization at the Montenegro Mine is apparently typical of that in the region. The geology of the area and a description of the Montenegro Mine may be found in Simons and Straczek (1958).

Mr. F. R. Dykstra of the E. J. Lavino Company, from whom the ore was obtained, has supplied the writer with details of the locality, geology and mineralization. His observations and conclusions, which are similar to those of Simons and Straczek (1958), are quoted below:

"Mineralization is confined to the contact between the massive Charco Redondo limestone and underlying volcanic tuffs. The contact is well defined by fault breccia and gouge.

Mineralization is unquestionably related to this interformational movement and to the minor accessory faults in both the limestone and tuff members. This is indicated by the fact that the major ore bodies are typically found at fault intersections.

Unlike most manganese deposits, these would seem to be secondary in nature with the manganese derived from some unknown source but probably related to the regional volcanics. The fact that the most extensive degree of mineralization is found down dip indicates emplacement by ascending solutions.

The mineralized fault zone outcrops at the toe of prominent cliffs formed by the limestone· At the surface the contact dips at about 15° steepening to nearly vertical within four or five hundred feet down dip. Mining has so far proceeded no deeper than six hundred feet down dip. On the up dip extension of the mineralization, the ore bodies tended to be relatively thin, rarely exceeding four or five feet. A good deal of disseminated manganese in the breccia and in the tuff is found here. At depth the ore bodies become much more massive frequently reaching a width of three or four meters. Lateral extension of ore is haphazard particularly up dip where the ore frequently pinches out all together. Down dip this pinching is much less evident and the individual ore bodies are proportionately larger.

In appearance the ore in places varies from a massive kidney form, although relatively soft ore, to a brown ore with a rather unusual fibrous texture."

The todorokite from Cuba is found in an entirely different geological setting from the Japanese material and is of different origin. The Cuban todorokite appears to be a fissure or breccia filling of hypogene origin. Yoshimura (1934) reported todorokite at the type locality to be a hydrothermal alteration product of inesite. Other minerals found in the Todoroki Mine (Syûetu vein) include quartz, rhodochrosite, pyrite, sphalerite and galena as well as several alteration products. The Todoroki Mine consists of workings on gold-bearing quartz veins in Tertiary volcanics.

PHYSICAL AND OPTICAL PROPERTIES OF CUBAN TODOROKITE

The todorokite is black with earthy to submetallic luster. It is found predominantly in massive form but fibrous aggregates are abundant and botryoidal structures are occasionally observed. All types may be porous but particularly the massive variety which disintegrates with evolution of air bubbles when placed in water. The mineral is readily soluble in warm concentrated HCl.

Todorokite is soft ($H=1\frac{1}{2}$ to $2\frac{1}{2}$) and soils the fingers. The hardness will vary slightly with the fibrous aggregates apparently slightly harder.

As far as could be determined, the Cuban todorokite is opaque in crushed fragments. This is distinctly different from the Japanese material which Yoshimura (1934) found to be transparent, pleochroic, show extinction, etc., and on which he was able to measure some optical properties. However, he does report the mineral to be black with metallic luster.

On the bulk sample the specific gravity was measured twice by the pycnometer using n-heptane and found to be 3.24 at 25° C. When this value is corrected for 12.1 per cent $CaCO_3$ and 5.7 per cent acid (HCl) insolubles, assuming an arbitrary average specific gravity of 2.7, the corrected specific gravity of Cuban todorokite is approximately 3.36 which is considerably lower than the 3.67 at 15° C. reported by Yoshimura (1934). Because of the impurities, the value of 3.36 for Cuban todorokite can be considered no more than an order of magnitude.

A polished section was made in an attempt to study todorokite in reflected light. Because the material did not polish well, only a poor section was obtained. Nevertheless, it could be determined that the color in reflected light is various shades of dark gray.

TABLE I. *X*-RAY POWDER SPACING DATA FOR CUBAN TODOROKITE

d(Å)	I	*d*(Å)	I
9.6	10	2.16	1
7.1	½	2.04	½
4.77	8	1.98	2
4.45 4.2	2 broad	1.74	2
3.19	2	1.68 1.64	½ broad
2.46	3	1.53	2
2.40	5	1.42	5
2.35	3 broad	1.38	2
2.22	4		

Fe radiation, Mn filter. Composite pattern from several films obtained on camera of 143.2 mm. diameter and also from several Norelco spectrometer scans.

X-RAY DIFFRACTION

The todorokite from Cuba was first identified by its *x*-ray diffraction pattern the *d*-spacings of which are presented in Table I. The spacings compare favorably with those reported by both Frondel (1953) and Ramdohr (1956) for Japanese todorokite. (These previously published powder *x*-ray spacings show slight variations for presumably identical material.) Good *x*-ray patterns were obtained from examples of the fibrous, botryoidal, and massive types. However, some specimens gave diffuse patterns indicating differences in perfection of crystallization in Cuban todorokite.

The first spacing reported in Table 1 showed some variation from specimen to specimen ranging from 9.50 Å to 9.65 Å. The reflection at 7.1 Å was found on two patterns only and may conceivably represent an impurity, possibly kaolinite from the alteration of the acid insolubles most of which are orthoclase and quartz. Frondel (1953) reports a very weak line for Japanese todorokite at 7.2 Å whereas Ramdohr (1956) does not. Another possibility could be birnessite (delta-MnO_2) which Jones and Milne (1956) found has its strongest line in the range 6.9 Å–7.4 Å.

In addition to calcite, orthoclase and quartz, a very small amount of magnetite may possibly be present in the first (chemically analyzed) todorokite sample. In the second shipment of 500 pounds, pyrolusite and and goethite were identified as additional impurities.

Cuban todorokite was heated at several temperatures in air for an hour and then studied by *x*-ray diffraction. It was found that at approximately 550° C. todorokite inverts to a phase which gives an *x*-ray powder pattern identical to hausmannite. Worthy of note is the fact that hausmannite typically occurs in high-temperature veins.

Little can be said about the crystal structure of todorokite. Yoshimura (1934) suggested monoclinic symmetry on the basis of morphology. Wadsley (1950) has indexed various synthetic hydrated manganese materials on the basis of a hexagonal cell; some of these synthetic materials have *x*-ray spacings and intensities very similar to those of todorokite. Unfortunately, it has been found that even fine fibers of Cuban todorokite are aggregates, and are not amenable to single crystal *x*-ray diffraction studies.

CHEMICAL ANALYSIS

A chemical analysis of the Cuban todorokite is presented in Table II along with the analysis of the type Japanese material. The composition of the todorokite has been recalculated from an analysis of a bulk ore sample (dried at 110° C.) containing 12.1 per cent calcite and 5.7 per cent insolubles from HCl leach; the insolubles are chiefly potash feldspar (orthoclase) and quartz. No pyrolusite was detected on *x*-ray powder patterns of long exposure. Calcium, strontium, barium and magnesium were determined by the emission spectrograph. Mr. J. A. Greear, the wet analyst, has indicated that the H_2O figure may be slightly inaccurate owing to the hydroscopic nature of the todorokite. Furthermore, there seems to be evidence that composition of the todorokite from this Cuban locality is slightly variable.

The original analysis by Yoshimura (1934) reported total Mn as MnO (65.89%) and oxygen (12.07%). The actual valence is not known and the analysis given in Table II reports Mn and O recalculated as MnO and MnO_2 using the figures of Frondel (1953). The weight per cent of the manganese oxides reported in the analysis of Cuban todorokite are calculated in a similar manner.

TABLE II. CHEMICAL ANALYSES OF TODOROKITE

	1. Japan (Yoshimura, 1934)	2. Cuba
Na_2O	0.21	1.3
K_2O	0.54	0.7
CaO	3.28	0.4
BaO	2.05	0.9
SrO	—	1.2
MgO	1.01	2.7
CuO	—	0.5
MnO	12.38	9.2
MnO_2	65.58	70.6
Fe_2O_3	0.20	2.2
Al_2O_3	0.28	1.2
H_2O^+	9.72	8.2
H_2O^-	1.56	Not determined
P_2O_5	0.42	0.2
SiO_2	0.45	Not determined
SO_3	0.28	Not detected
Insol.	1.28	—
	99.24	99.3

Notes on analysis of Cuban todorokite:

1. Wet analyst: J. A. Greear.
2. Emission spectrograph analyst: H. Holt; determined Ca, Ba, Sr, Mg.
3. Material dried at 110° C. before analysis. H_2O^- not determined by J. A. Greear. Another analyst on another portion determined $H_2O^- = 1.58$ per cent.
4. Analysis recalculated on basis of 5.7% HCl insolubles and 12.1% $CaCO_3$.

The ratios of the analysis of the Cuban todorokite are close to the formula:

$$(Mn^2, Na, K, Mg, Ba, Sr, Ca, Cu)\ (Mn^4, Fe, Al)_3O_7 \cdot 2H_2O$$

if the H_2O- (see Note 3, Table II) is included as being essential. Frondel (1953) has shown that the Japanese todorokite has ratios that are between the above formula and $(Mn^2, \text{etc.})_2Mn^4{}_5O_{12} \cdot 4H_2O$. Inasmuch as no other manganese oxide or mineral could be detected in the analyzed material, the high MnO_2 value for Cuban todorokite must be used in the calculation although it is likely that 4–5 per cent of many manganese minerals would not be detected by x-ray techniques.

Frondel (1953) has posed the question of whether or not woodruffite and todorokite are isostructural. On the basis of this new analysis it would appear that they are not. However, because of the uncertainties mentioned above, the problem cannot be unquestionably resolved on the basis of the new analysis.

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