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

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Crystal Data: Monoclinic. *Point Group:* $2/m$. Crystals poor, lathlike, fibrous, elongated ‖ [001] and flattened ‖ {010}, to 15 cm; in banded, reniform, or stalactitic aggregates of crystals; may be very porous. *Twinning:* As contact twins or trillings on an unknown law.

Physical Properties: *Cleavage:* {100} and {010}, perfect. Hardness = Soft.
D(meas.) = 3.66 D(calc.) = 3.67

Optical Properties: Opaque, transparent in thinnest slivers. *Color:* Black to dark brownish black; in transmitted light, brown; in reflected light, gray-white. *Streak:* Black. *Luster:* Metallic to dull; silky in aggregates.
Optical Class: Biaxial; birefringence ∼0.02. *Pleochroism:* Strong to faint; X = dark brown; Z = yellowish brown. *Orientation:* $Y = b$; $Z \simeq c$. *Absorption:* $Z > X$. $n = > 2.00$
2V(meas.) = n.d. *Anisotropism:* Very strong; bluish or brownish.
R_1–R_2: (400) 13.9–24.7, (420) 13.2–24.2, (440) 12.5–23.7, (460) 11.7–22.0, (480) 11.1–20.6, (500) 10.6–19.4, (520) 10.2–18.6, (540) 10.0–17.9, (560) 9.7–17.3, (580) 9.5–16.8, (600) 9.3–16.4, (620) 9.1–16.1, (640) 9.0–15.8, (660) 9.0–15.5, (680) 8.9–15.3, (700) 8.9–15.1

Cell Data: *Space Group:* $P2/m$ (ICDD 38-475). $a = 9.7570(15)$ $b = 2.8419(5)$ $c = 9.5684(14)$ $\beta = 94.074(14)°$ Z = 1

X-ray Powder Pattern: N'Chwaning mine, Kuruman district, South Africa. (ICDD 38-475).
9.555 (100), 2.399 (36), 4.773 (25), 4.462 (25), 2.388 (25), 2.355 (24), 4.860 (17)

Chemistry:	(1)	(2)		(1)	(2)		(1)	(2)
SiO_2	0.45	0.24	CaO	3.28	1.52	H_2O^-	1.56	
MnO_2	65.89	72.15	BaO	2.05	0.20	H_2O		10.61
Al_2O_3	0.28	0.14	SrO		0.24	CO_2	trace	
Fe_2O_3	0.20	0.06	Na_2O	0.21	1.23	P_2O_5	0.42	
MnO		8.87	K_2O	0.54	0.48	SO_3	0.28	
CoO		0.02	O	12.07		insol.	1.28	
MgO	1.01	3.51	H_2O^+	9.72		Total	99.24	99.27

(1) Todoroki mine, Japan; corresponds to $(Ca_{0.48}Mn^{2+}_{0.40}K_{0.08}Na_{0.05})_{\Sigma=1.01}(Mn^{4+}_{5.06}Mn^{2+}_{0.77}Mg_{0.17})_{\Sigma=6.00}O_{12}\cdot 3.62H_2O$. (2) Tarantana mine, Cuba; corresponds to $(Mn^{2+}_{0.49}Na_{0.25}Ca_{0.19}K_{0.06})_{\Sigma=0.99}(Mn^{4+}_{5.17}Mg_{0.54}Mn^{2+}_{0.29})_{\Sigma=6.00}O_{12}\cdot 3.06H_2O$.

Occurrence: A secondary mineral produced from weathering or hydrothermal alteration of other manganese-bearing species; in sedimentary marine fumarolic deposits; the principal manganese oxide in deep-sea manganese nodules.

Association: Pyrolusite, cryptomelane, romanèchite, manganite, rhodochrosite, quartz, "opal".

Distribution: Widespread. Well-characterized material from: the Todoroki mine, south of Ginzan, Hokkaido, Japan. On Groote Eylandt, Northern Territory, Australia. In Cuba, an ore in the Charco Redondo–Taratana district, and elsewhere in Oriente Province. In the USA, at Sterling Hill, Ogdensburg, Sussex Co., New Jersey, and the Tip Top mine, 8.5 km southwest of Custer, Custer Co., South Dakota. From Urandi, Bahia, Brazil. At Nsuta, Ghana. Large crystals from the Smartt mine and elsewhere in the Kuruman district, Cape Province, South Africa. At Romanèche, Saône-et-Loire, France. From Bleiberg and Hüttenberg, Carinthia, Austria.

Name: For its first-noted occurrence in the Todoroki mine, Japan.

Type Material: Harvard University, Cambridge, Massachusetts, 106214; National Museum of Natural History, Washington, D.C., USA.

References: (1) Palache, C., H. Berman, and C. Frondel (1944) Dana's system of mineralogy, (7th edition), v. I, 573–574. (2) Frondel, C., U.B. Marvin, and J. Ito (1960) New occurrences of todorokite. Amer. Mineral., 45, 1167–1173. (3) Straczek, J.A., A. Horen, M. Ross, and C.M. Warshaw (1960) Studies of the manganese oxides. IV. Todorokite. Amer. Mineral., 45, 1174–1184. (4) Post, J.E. and D.L. Bish (1988) Rietveld refinement of the todorokite structure. Amer. Mineral., 73, 861–869.

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