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Some observations on todorokites from marine and terrestrial environments

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ABSTRACT. Manganese nodules from the central Pacific contain poorly crystalline todorokite and also small amounts of a post-depositional recrystallization todorokite. The Cu and Ni of the nodules is preferentially concentrated in the latter. Crystalline todorokite on Groote Eylandt does not contain Cu or Ni, providing further evidence that these elements are not necessary to the development of well-crystalline todorokite.

TODOROKITE is a manganese oxide mineral of widespread occurrence in the weathering zones of manganese orebodies and as such is well known to the economic geologist and mineralogist. A poorly crystalline variety, formerly known as 10 Å manganite, is a major component of marine manganese nodules, where it is commonly the host mineral for the Ni, Cu, and Zn, and sometimes the Co, of the nodules. The relationship between the two forms is not well established, but Burns and Burns (1977) recommend the use of 'todorokite' in place of '10 Å manganite' for the hydrated manganese oxide in marine manganese nodules which gives the *d*-spacings characteristic of terrestrial todorokite. On the other hand, Giovanoli *et al.* (1973) postulate that todorokite is a mixture of sodium manganese (II, III) manganate (IV) hydrate ('buserite') partially dehydrated to birnessite $(Ca,Na)Mn_7O_{14} \cdot 3H_2O$ and altered to manganite $(\gamma MnO \cdot OH)$. These writers suggest that todorokite is therefore not a valid mineral. This concept of complex intergrowths within a single manganese oxide 'mineral' is, however, not confined to todorokite. Coherent lattice intergrowths of hollandite and romanechite have been recently identified by Turner and Buseck (1979) suggesting that manganese oxides classed as discrete minerals when examined by conventional means (microscopy, XRF, EPMA) may prove to be more complex when examined by high-resolution electron microscopy and select-area electron diffraction. No detailed crystal structural studies were attempted in the present investigation, and the nomenclature suggested by Burns and Burns was accepted as a working hypothesis.

The three manganese oxide phases described here are (1) a poorly crystalline marine todorokite characterized by XRD by the presence of two lines at 9.7 Å and 4.8 Å (marine todorokite type A) (fig. 1), (2) a more crystalline marine todorokite with better defined '*d*'-spacings and higher optical reflectivity (marine todorokite type B) (fig. 2), and (3) todorokite of terrestrial origin (fig. 3). The marine todorokite samples type A and type B occur in layers in marine manganese nodules dredged from five locations in the central Pacific Ocean within an area defined by 12° 49′ N to 13° 46′ N and 141° 48′ W to 140° 15′ W. Sample depths are not available. Approximately two hundred nodules from this area were examined mineragraphically, and representative sub-samples analysed by XRD and EPMA. The microanalyses in Table III are for nodules from all locations. Only a limited number of specimens of Type B were observed and analysed but these appear to be randomly distributed through the whole area. The terrestrial todorokite occurred in pisolitic manganese ore from 'G' quarry (14° S, 136° 30′ E) on Groote Eylandt, off the north coast of Australia.

Mineragraphy. The two types of marine todorokite occur in association with δMnO_3 (a poorly crystalline birnessite), amorphous iron oxides, and variable amounts of phillipsite, illite, quartz, feldspar, calcite, and organic remains. The nodules are being described separately (Ostwald, in prep.). The nodules show concentric layering in hand specimen, which under the microscope is revealed as a complex layering of the globular-collomorphic type. Todorokite layers are recognized by their relatively high white-light reflectivity and by confirmatory XRD of powder scrapings (to distinguish from crystalline birnessite). Type B was much rarer,

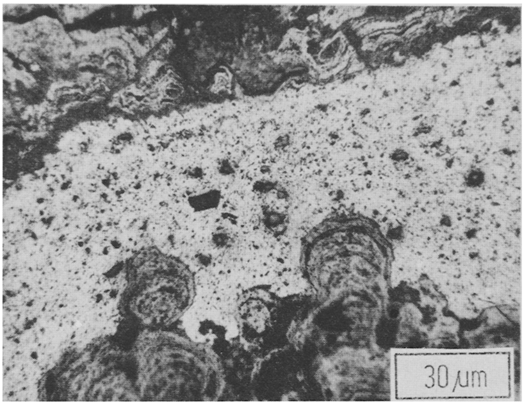

FIG. 1. Polished section of manganese nodule in reflected light, showing zone of marine todorokite type A (white, with abundant micro-inclusions) between zones of dark grey δMnO_2.

and occurred as internally structureless stalactites and globules in cavities in the nodules. In some occurrences this mineral appeared to have formed within gangue components in cavities in the nodules.

The todorokite in the Groote Eylandt ore (Ostwald, 1975) is found as replacement layers in pisoliths and as disseminations in manganiferous clays. In the pisoliths the material is commonly friable and earthy but rare areas of more compact cryptocrystalline material also occur. Data on the reflectivity and microhardness of the todorokites are given in Table I. Very few areas of todorokite are suitable for measurement, and the figures listed are simply ranges for measurable areas in each class.

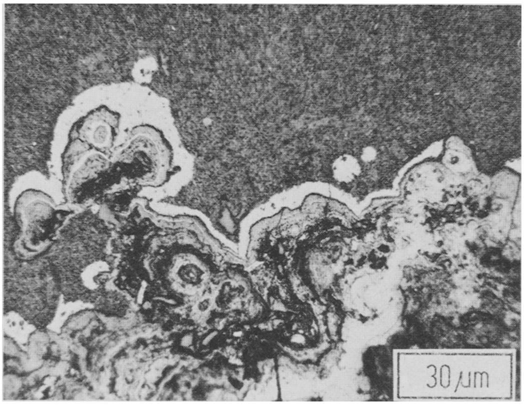

FIG. 2. Polished section of manganese nodule in reflected light, showing thin layer of white marine todorokite type B coating layered collomorphic δMnO_2. The homogeneous grey area is specimen-mounting medium.

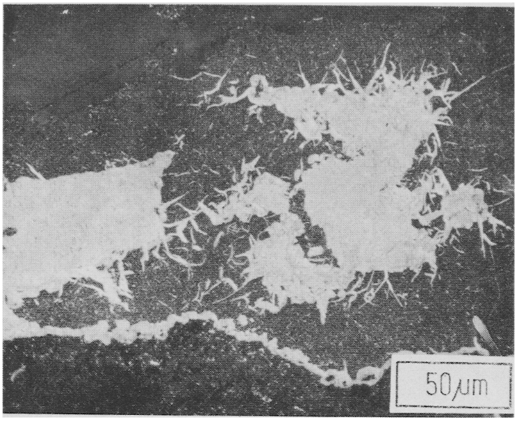

FIG. 3. Polished section of Groote Eylandt ore, showing cryptocrystalline todorokite (white) in clay (dark).

X-ray diffraction. Powder samples of the todorokites were removed by grinding the areas with a diamond-pointed scriber and the powder was examined by standard X-ray diffractometry. The results are listed in Table II. The abundance of *d*-spacings for the terrestrial todorokite is in contrast with the small number of lines recorded for the marine todorokites. Certain *d*-spacings, in particular those at 9.7, 4.8, 2.4, and 2.2 Å, are common to terrestrial todorokite and marine todorokite type B. The lines for the marine todorokites are typically broad while those of the Groote Eylandt mineral are much better defined.

Electron probe microanalysis. EPMA determinations listed in Table III were carried out on areas of the todorokite using an ARL type EMX microprobe, with 52.5° take-off angle. All counting data were fully ZAF corrected by the programme of Wright (1971). All results listed are non-normalized, and totals are less than 100% because the phases are hydrated. In all cases scrapings for XRD analysis were taken from areas adjacent to those analysed by EPMA.

TABLE I. *Reflectivity and microhardness*

	Marine todorokite type A*	Marine todorokite type B†	Terrestrial todorokite‡
R% (589 nm)	12-15	17-19	22
VHN (50 gm)	40-80, mean 55	62-130, mean 86	110-150, mean 135

* Range for samples 1-22 of Table III.
† Range for samples 1-4 of Table III.
‡ Range for samples 1-4 of Table III.

TABLE II. *X-ray diffraction*

Marine todorokite type A*		Marine todorokite type B†		Terrestrial todorokite‡	
d (Å)	I	d (Å)	I	d(Å)	I
9.7	10(b)	9.7	10(b)	9.65	(10)
				7.1	(1)
4.8	5(vb)	4.8	5(b)	4.82	(6)
		4.4	2(vb)	4.45	(1)
				3.22	(1)
		2.4	2(b)	2.41	(4)
				2.34	(2)
		2.2	2(b)	2.22	(3)
				1.41	(1)

* Sample 2, Table III. This pattern is characteristic of the more common todorokite type A in the samples.

† Samples 1-4, Table III.

‡ Sample 1, Table III.

TABLE III. *Electron probe microanalyses (wt. %)*

Sample	Al_2O_3	SiO_2	CaO	MgO	Na_2O	MnO	FeO	Ni	Cu	Co	(Ni+Cu+Co)/Mn
Marine todorokite type A											
1*	0.9	1.4	3.8	1.1	0.2	42.6	1.1	2.1	0.5	0.4	0.09
2	0.5	1.0	3.2	1.6	0.3	51.9	1.2	2.3	0.5	0.3	0.08
3	1.7	0.8	1.7	1.3	0.2	63.3	0.8	1.7	1.2	0.03	0.06
4	2.7	0.8	1.8	1.7	0.1	62.0	0.7	2.2	1.5	0.1	0.08
5	2.6	0.8	1.2	1.4	0.3	58.7	0.6	1.9	1.3	0.1	0.07
6	2.9	1.6	1.9	1.2	0.1	62.9	0.7	2.0	1.5	0.1	0.07
7	6.3	8.4	1.3	0.8	0.3	54.5	1.2	1.6	1.3	0.04	0.07
8	5.3	5.6	1.4	0.9	0.4	52.7	0.8	0.4	1.1	0.05	0.04
9	1.7	2.9	3.2	1.4	0.7	47.7	0.6	0.3	1.2	n.d.	0.04
10	0.8	0.1	3.2	1.2	0.3	57.0	0.2	0.5	1.7	n.d.	0.05
11	4.0	5.4	1.7	0.9	0.5	43.0	1.1	2.2	1.5	0.02	0.11
12	2.6	10.4	2.9	0.6	0.7	39.0	8.2	0.9	0.6	0.2	0.06
13	3.6	9.9	1.9	1.2	0.8	44.8	3.5	1.6	0.8	0.08	0.07
14	3.5	6.9	2.3	0.4	0.5	48.2	3.7	1.9	1.0	0.1	0.08
15	2.6	6.0	2.0	0.1	0.3	53.4	1.0	0.3	1.0	0.1	0.03
16	2.9	3.9	2.1	0.6	0.3	51.7	0.8	1.1	1.3	0.3	0.07
17	1.5	2.5	2.3	0.4	0.4	54.9	0.5	1.0	1.4	0.1	0.06
18	3.0	7.3	2.5	1.2	0.5	53.0	0.8	2.3	1.7	0.05	0.10
19	4.5	8.2	1.7	0.4	0.6	51.8	1.1	1.7	1.8	0.05	0.09
20	1.2	3.0	2.9	1.3	0.7	55.7	1.1	0.8	0.7	0.02	0.04
21	0.4	1.3	1.8	0.7	0.9	58.7	0.4	1.6	1.4	0.04	0.07
22	1.0	3.1	1.8	0.4	0.3	55.4	0.8	1.7	1.5	0.1	0.08
Marine todorokite type B											
1†	3.7	2.2	2.3	0.5	0.8	48.4	0.9	2.4	1.3	0.3	0.11
2	3.7	1.9	2.0	1.2	0.7	48.3	1.6	2.3	1.6	0.1	0.11
3	2.4	1.3	3.4	3.3	0.6	50.2	1.3	2.3	1.4	0.2	0.11
4	0.6	0.3	4.2	2.6	0.9	54.3	0.8	2.7	1.7	0.1	0.11
Terrestrial todorokite											
1‡	0.3	0.6	2.4	2.5	0.8	65.1	0.1	n.d.	n.d.	n.d.	—
2	0.8	0.4	3.1	3.4	0.9	64.3	0.3	0.1	n.d.	n.d.	—
3	1.2	0.8	2.5	2.8	1.1	63.9	0.1	n.d.	n.d.	n.d.	—
4	0.9	1.2	2.3	3.1	0.4	65.2	0.4	n.d.	n.d.	n.d.	—

n.d. = not detected by EPMA.

* Samples 1-11 from 13° 10′ N, 140° 57′ W; Samples 12-16 from 13° 00′ N, 141° 22′ W. Samples 17-18 from 13° 46′ N, 140° 15′ W; Samples 19-20 from 13° 27′ N, 140° 39′ W. Samples 21-22 from 12° 49′ N, 141° 48′ W.

† Samples 1-2 from 12° 49′ N, 141° 48′ W; Sample 3 from 13° 10′ N, 140° 57′ W. Sample 4 from 13° 27′ N, 140° 39′ W.

‡ 'G' quarry, Groote Eylandt.

The elements sought were those which were known to be present in the samples on the basis of total chemistry and qualitative X-ray energy-dispersive spectroscopy. As Al and Si are not constituent elements of todorokite in the formulae given by Straczek *et al.* (1960) and Larson (1962), it is probable that they represent alumino-silicates present within the manganese oxide structures below the resolving power of the EPMA. The other elements listed in Table III appear to be constituent elements of todorokite.

Discussion. The crystal structure of todorokite has been deduced by Burns and Burns (1977) to be a tunnel structure consisting of double and treble chains of edge-shared $[MnO_6]$ octahedra in the *b* axis direction. Within the main framework occur

Mn^{2+} sites in octahedral coordination with oxygen and it is in these that atomic substitution of Mn^{2+} by Ni^{2+} and Cu^{2+} occurs. This basic structural pattern is apparently responsible for X-ray diffraction lines at 2.4 and 1.4 Å. Cations such as Ca^{2+}, Na^+, K^+, and Ba^{2+}, and H_2O molecules probably occur within the tunnels of the structure, and it is this which explains the cation exchange properties and variable chemistry of the mineral. The actual crystallite sizes of polycrystalline todorokite vary considerably, and as a result X-ray patterns show some variability.

The basic crystal morphology is the fibre which may be interpreted as narrow platelets elongate parallel to the *b* axis of the monoclinic system and with cleavages parallel to (001) and (100) (Burns and Burns 1979). The major identifying lines at about 9.6 and 4.8 Å probably represent X-rays diffracted parallel to the fibre axes while the reflections at about 2.4 and 1.42 Å represent X-rays diffracted perpendicular to the fibre axes (Faulring, 1962).

The better defined and more numerous *d*-spacings which characterize marine todorokite B may thus represent a mineral in which the crystallites are either better developed, or more randomly arranged than those of the type A. It is also possible that the globular forms of type B may be equivalent to the post-depositional spherical todorokite clusters depicted by Burns and Burns (1978).

Additional evidence that the globular forms of type B are authigenic or post-depositional recrystallizations is seen from their chemistry. They are enriched in Ni, Cu, and Co, as indicated by their (Ni + Cu + Co)/Mn ratio relative to type A. This is consistent with the observation of Burns and Burns (1978) that nickel and copper were strongly concentrated within such authigenic todorokite areas. Similar observations have been made by Cronan and Tooms (1968).

The question of the significance of copper and nickel in todorokite has received much attention and has been reviewed by Burns and Burns (1977, 1979) and Cronan (1980). Investigations show that Ni^{2+} and Cu^{2+} substitute for Mn^{2+} in todorokite up to about 8 % by weight, and that the presence of these elements stabilizes the todorokite structure, retarding alteration to δMnO_2 (vernadite).

Although some investigations (Usui, 1979) suggest that Cu and Ni are essential to the 10 Å manganite (marine todorokite) crystal structure this is not consistent with the presence of well-crystalline todorokites with little or no Cu and Ni (Corliss *et al.*, 1978; Hoffert *et al.*, 1978). Certainly Cu and Ni are not essential to the structure of terrestrial todorokite, as indicated by the X-ray and EPMA data on the Groote Eylandt todorokite. The specimens examined showed quite reasonable crystallinity but contained no detectable Cu and Ni. The Groote Eylandt ores contain very little Cu, Ni, Co, and Zn, but such as is present is strongly concentrated in lithiophorite (Ostwald, 1975, 1980).

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