

SHORT COMMUNICATION

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An X-ray diffraction investigation of a Marine 10 Å manganate

DURING recent studies on marine ferromanganese crusts from the Manus Is. region of the Western Pacific Ocean one of the authors (JO) noted a todorokite-like mineral, which, when micro-analysed, gave unusually low totals for this mineral, suggesting a high degree of hydration. Micro-analytical totals on apparently dense homogeneous areas of the mineral produced totals of 60-70%, much lower than totals of 85-90% commonly reported for todorokite (Burns and Burns, 1979; Ostwald, 1982a) and lower than that of vernadite 70-85% (Burns and Burns, 1979; Ostwald, 1984a).

The microanalysis and preliminary X-ray diffraction analyses indicated that the phase was chemically and structurally similar to synthetic 10 Å phylломanganate, of formula $\text{Na}_4\text{Mn}_{14}\text{O}_{27} \cdot 21\text{H}_2\text{O}$, reported in JCPDS Card 32-1128. A detailed account of the marine deposit in which the 10 Å manganate mineral occurs is in preparation. This note concentrates on the results of some X-ray diffraction experiments, carried out because recent mineralogical research has suggested that the 10 Å nodule phase commonly considered to be todorokite may show considerable structural variability under heating and liquid intercalation (Paterson, 1981; Arrhenius and Tsai, 1981).

Evidence for a 10 Å phylломanganate in marine deposits. The mineralogy of the marine manganese oxides is complex and poorly understood, in part because of such features of the minerals as fine grain size and poor crystallinity (Glasby, 1977) but also because of difficulties in terminology (Ostwald, 1984b). In the present context it must be recalled that Buser and Grutter (1956) originally defined the nodule phase 10 Å manganite as the component in nodules which gave broad diffraction peaks near 10 Å. Within a few years this phase was equated with todorokite by Levinson (1960), Tooms *et al.* (1969), and Brooke and Prosser (1969), a concept which dominated nodule research for the last decade (Burns and Burns, 1979). This idea was strengthened by the observation of finely-fibrous

structures in transmission electron microscope studies of marine nodules, similar to those in terrestrial todorokite, and by the presence of tunnel structures at higher magnification (Burns and Burns, 1978).

However, evidence that the 10 Å phase in nodules may be more complex than is commonly believed comes from studies such as those of Siegel and Turner (1982) and Ostwald (1982b) that two varieties of the mineral existed in Pacific nodules. At about this time the terminology 'manganite' was changed to 'manganate' chiefly because manganite is a well known terrestrial mineral $\gamma\text{-MnOOH}$. During the 1970-1980 period researchers in Bern, Switzerland, put forward the idea, based largely on mineral synthesis, that the 10 Å phase in nodules was essentially a naturally-occurring layer-lattice structure, a phylломanganate, with 10 Å basal spacings, partially converted into the 7 Å phylломanganate birnessite and further altered into the tunnel structure $\gamma\text{-MnOOH}$.

Giovanoli and Burki (1975) put forward the idea that the fibrous structures seen in nodules under the electron microscope were decomposition products of the 10 Å manganate, and they considered that 'todorokite' was really the alteration product of the 10 Å layer-lattice they termed 'buserite'. The 'buserite' concept aroused considerable debate and recently Giovanoli (1985) has reconsidered his earlier assertions that todorokite is not a valid mineral species. Todorokite is now widely accepted as the important Ni and Cu containing phase in marine nodules and the phase producing diffraction peaks at about 9.8, 4.9 and 2.44 Å (Burns *et al.*, 1983). At about the same time, however, 10 Å manganate nodule phases were reported by Arrhenius and Tsai (1981) from the East Equatorial Pacific, and by Chukhrov *et al.* (1983) from the Pacific. Chukhrov *et al.* (1983) identified three phases, buserite, asbolane (originally described by Chukhrov *et al.* in 1982) and mixed layer hybrid buserite-asbolane. Further studies (Chukhrov *et*

al., 1984) have allowed the distinction between two types of busserite, busserite I, an unstable phyllo-manganate which transforms to birnessite on drying at 100 °C and also during examination in the vacuum of an electron microscope, and busserite II, which does not change its major spacing $d_{001} = 9.7\text{--}9.8$ on heating or dehydration.

Arrhenius and Tsai (1981) distinguished between todorokite, which has fixed diffraction peaks under heating and following intercalation with dodecylammonium ions, and busserite, which contracts to form birnessite ($d_{001} = 7 \text{ \AA}$) on heating and expands to $d_{001} = 25.6 \text{ \AA}$ when intercalated with dodecylammonium ions.

Andreev *et al.* (1984) in a study of Pacific Ocean manganese nodules concluded that these consisted essentially of vernadite, busserite and mixed layer busserite/asbolane, with the Cu and Ni being concentrated in busserite. They claimed that todorokite did not recur in the nodules, and birnessite was very rare.

These recent investigations suggest that a final definition of marine nodule phases has not yet been achieved.

Experimental. The phyllo-manganate sample was suspended on 0.1 M aqueous solution of dodecylammonium chloride for up to 65 hours. At intervals of 20, 40 and finally 65 hours aliquots of the suspension were removed, centrifuged and washed as described by Paterson (1981). The residue was in each case dispersed in water and placed on a glass slide from which the bulk of the liquid was allowed

to evaporate. The moist slide was transferred to a diffractometer and the diffraction pattern recorded.

X-ray diffraction was carried out on a Siemens D500 diffractometer using Cu- $K\alpha$ radiation and graphite monochromator. A 0.3° divergence and 0.15° receiving slit were employed. Data were collected using 0.02° two-theta step size and a counting time of 1 sec/step over the range of 2–70° two-theta for the intercalated manganese oxide, and 5–70° two-theta for the original phyllo-manganate.

Results and discussion. The X-ray experiment indicated:

1. Heating 10 Å phyllo-manganate to 100 °C for 4 hours results in formation of the '7 Å' birnessite structure (Fig. 1a, b). Collapse of the layer structure is irreversible. Neither dispersion in water of 0.1 M dodecylammonium chloride for two days results in re-expansion to the '10 Å' structure. Dehydration via heating appears to be quite harsh and results in permanent collapse of the layer structure.
2. Intercalation of the phyllo-manganate by dodecylammonium chloride results in a diffraction pattern essentially identical to that obtained by Paterson, 1981 (Fig. 2a, b). The observed d -spacings represent the 00 l series consistent with the occurrence of a single-layer/double-layer sequence of alkyl chains that regularly interstratify the layer structure.
3. However, intercalation occurs more slowly than described by Paterson who reported complete

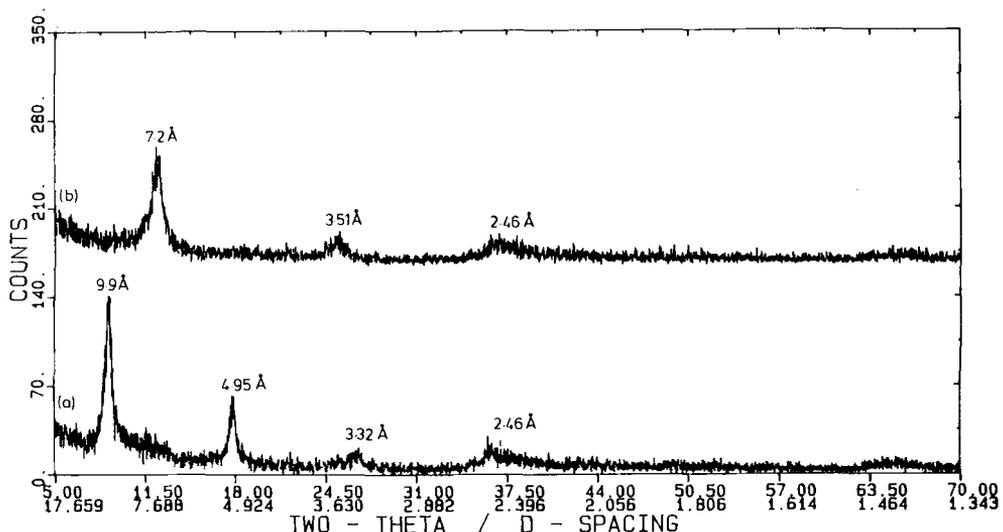


FIG. 1. (a) Powder diffraction pattern of untreated phyllo-manganate. (b) Diffraction pattern of phyllo-manganate heated to 100 °C for 4 hours.

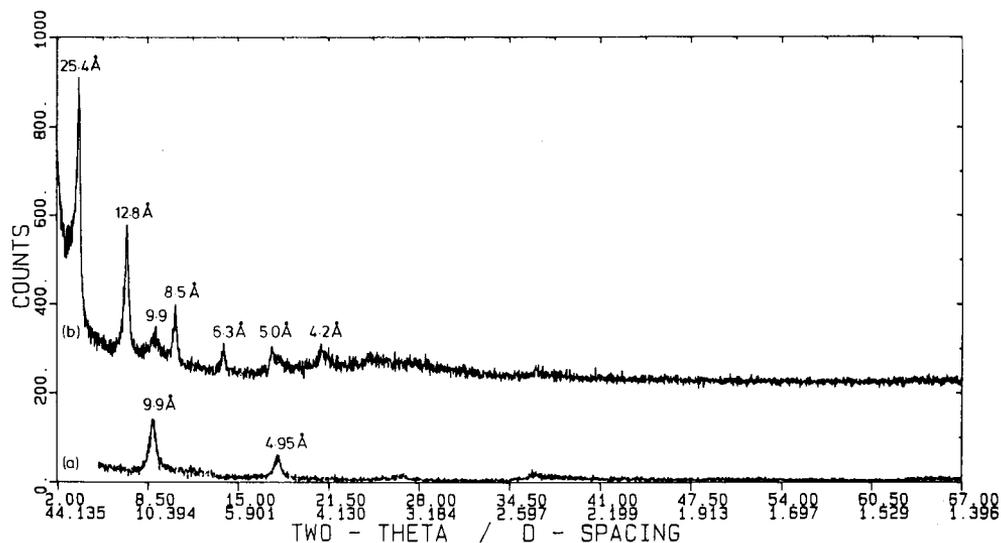


FIG. 2. (a) Powder diffraction pattern of untreated phyllo-manganate. (b) Diffraction pattern of phyllo-manganate intercalated with dodecylammonium chloride (after 40 hrs).

expansion after 16 hours. In our case 60 hours is not sufficient to produce complete expansion, as indicated by the presence of the parent phyllo-manganate in the XRD pattern. About 40 hours appears to be the optimum time for producing the maximum extent of layer expansion.

4. The incomplete expansion suggests that the Manus Is. 10 Å phyllo-manganate is generally unstable but that it also contains domains of more stable structure, possibly producing a hybrid-structured mineral. Similar features were observed in the busserites studied by Chukhrov *et al.* (1984) and Andreev *et al.* (1984).

These results indicate that a layer-lattice manganese oxide occurs in ferromanganese deposits of the Pacific Ocean and confirms the earlier findings of Soviet investigators. The authors feel statements such as those of Andreev *et al.* (1984) that *all* marine manganese oxides giving a major diffraction peak at or near 10 Å are busserite-type layer lattices is extreme, as manganese oxide tunnel structures with major peaks in the region of 9.6–9.8 Å, identified as todorokite, have repeatedly been reported (Turner *et al.*, 1982; Chukhrov *et al.*, 1978). The writers agree with Burns *et al.* (1985) that mineralogical identification of marine manganese oxides required more than just routine X-ray diffraction analysis. The precise mineralogical nature of the phase described here requires further study, and the name 10 Å manganate is used for convenience. No doubt Soviet mineralogists would term it busserite.

The results of the heating and intercalation experiments suggest that marine 10 Å manganate is unstable and the writers suspect that its desiccation to birnessite-type minerals may account for the identification of such in dried ferromanganese nodules and crusts. The numerous identifications of birnessite in marine nodules during the last two decades (Burns and Burns, 1977) may have resulted from such a transformation. Terrestrial occurrences of the 10 Å manganate have not been reported, and this is not surprising as such would be expected to slowly alter to birnessite during geological time. Birnessite, like the other manganese layer-lattices chalcophanite and lithiophorite may be the end products of complex mineral genesis mechanisms (Ostwald, 1984c).

There are suggestions in the literature that the occurrence of birnessite in marine manganese deposits may be a sign of hydrothermal activity, in contrast to normal hydrogenous precipitations which result in nodules and crusts of layered vernadite (δ -MnO₂) and todorokite. The deposits from the Galapagos Hydrothermal Field (Corliss *et al.*, 1978) not only contain vernadite and todorokite (which may be hydrogenous components) but also a 10 Å manganate very similar to the one described in this paper, and well-crystallized birnessite. Lonsdale *et al.* (1980) also identified well-crystallized birnessite (and todorokite) from the region of a young submarine volcano at 8° 48.2' N, 103° 53.8' W, and in this case there was SEM evidence that the birnessite was a recrystallization

product of an older manganese hydroxide. Thus, the association 10 Å manganate and/or birnessite may be a possible indication of marine hydrothermal activity.

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