

XV. MINERALOGY OF MANGANESE NODULES

Masato Nohara

Method

The poor crystallinity of manganese minerals imposes several limitations on the use of X-ray diffraction techniques for analysis of the phase in manganese nodules. For this reason, considerable care was taken for phase analysis under optimum instrumental conditions. The work was carried out by Rigaku Denki diffractometer, using Cu K α radiation at 15–20 mA and 35–40 kV. Cu K α radiation was eliminated by an Ni-filter, and pulse height discrimination was used to reduce fluorescent radiation. Scanning speeds of 1°/min. were used with a time constant of 1–2 sec. The receiving slit was 0.1 mm wide and the divergent and scatter slits were varied depending on the angle scanned with a few exceptions. A proportional counter was used throughout. An iron tube was examined as an alternative source of radiation, but it was found to be only slightly superior to the copper tube. The work was therefore completed using a copper tube.

Results

It is well known that marine manganese nodules consist of an amorphous phase with poorly crystalline todorokite and birnessite (BUSER and GRÜTTER, 1956; BARNES, 1967; CRONAN and TOOMS, 1969; GLASBY, 1972). According to the results of the X-ray powder diffraction patterns for the present nodules, the principal manganese minerals are represented by todorokite and birnessite.

Todorokite, $(\text{Na}, \text{Ca}, \text{K}, \text{Mn}^{2+}) (\text{Mn}^{4+}, \text{Mn}^{2+}, \text{Mg})_6\text{O}_{12} \cdot 3\text{H}_2\text{O}$, from its powder pattern, appears to be identical to a phase termed 10 Å manganite by BUSER and GRÜTTER (1956), and secondly, a phase having a two line powder pattern appears to be identical to the δ - MnO_2 , $(\text{Na}_{0.7}, \text{Ca}_{0.3})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$, of BUSER and GRÜTTER. A third phase, having a powder pattern identical with birnessite of JONES and MILNE (1956) and with 7 Å manganite of BUSER and GRÜTTER, were also observed. However, as BRICKER (1965) has suggested, this phase and the δ - MnO_2 of BUSER and GRÜTTER are the same, differing only in particle size. Therefore, the second and the third phases will be referred to birnessite in this article.

Selected X-ray powder diffraction patterns of those minerals are shown in Fig. XV-1. The results obtained are also summarized in Table XV-1. Birnessite was shown to be the predominant mineral phase present in the majority of nodules from the area surveyed, particularly, in nodules from stations 411, 417, 418, 422, 423, and 431. Todorokite was mainly found in nodules from stations 426, 430, 433, and 407A-2.

In relation to associated sediment-types, todorokite is generally predominant in nodules from deep-sea clay sediments which appear to be older than the silicious clay, according to ARITA (in this report). On the other hand, birnessite seems to be distributed in nodules from both deep-sea clay and siliceous clay sediment-types. However, it is

difficult to find an exact correlation between the mineralogy of the manganese nodules and associated sediment-types.

Nodules from St. 407A-2 contain predominantly todorokite, while those from the adjacent stations 407 and 408, contain weakly-crystalline traces of birnessite and todorokite. 11 nodules from stations 407A-2 (FG32-2) through 407A-2 (FG32-8) were taken from the area of gently rolled topography. From the general consideration of nodule mineralogy particularly in relation with topography throughout the present area, it appears that, contrary to the findings of CRONAN and TOOMS (1969), topography does not play a significant role in controlling nodule mineralogy in this area of the Central Pacific Basin.

Thus there appears to be no obvious correlation between the mineralogy and associated sediment-types or depth of formation or nodule morphology. Also, it is unlikely that the principal factor controlling the mineralogy of marine nodules is the sedimentary characteristic, e.g., the redox potential, as suggested by GLASBY (1972). The kinetics of nucleation or deposition of the iron-manganese oxides seem to play an important role for nodule genesis (NOHARA and NASU, 1977). However, a more detailed study of the mineralogical variations in this area is required to resolve this problem.

In no case could goethite be identified. As minor detrital or authigenic mineral phases, quartz, feldspar, and clay minerals are always recognized in nodules together with the manganese minerals. In this area, manganese nodules commonly have fossil phosphorite cores, and a phosphorite layer is present in a piston core sample, 414A-1 (P67). The association of manganese minerals with phosphorite in all samples may indicate a genetic relationship between these two phases. A more detailed assessment of co-existing manganese and phosphorite deposits is required to establish this point.

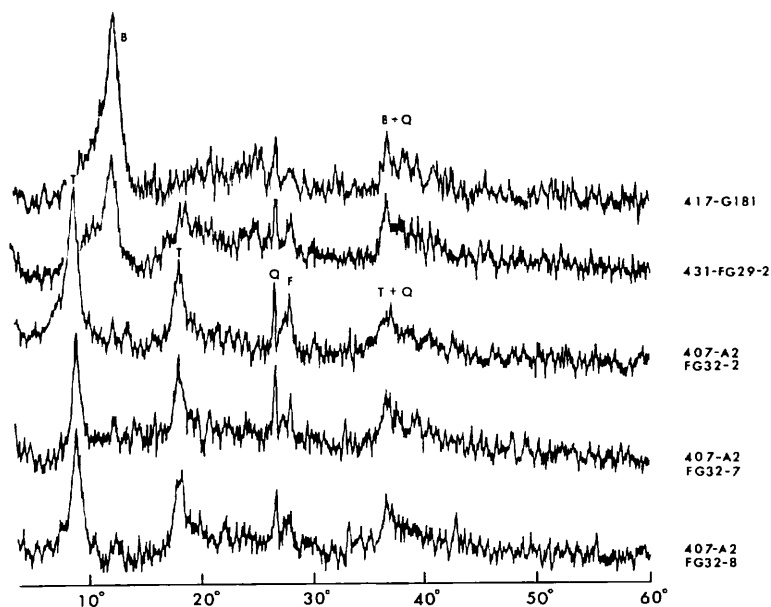


Fig. XV-1 Selected X-ray powder diffraction patterns for manganese nodules from the Central Pacific Ocean. note: B: Birnessite, T: Todorokite, Q: Quartz, F: Feldspar.

Table XV-1 Summary of X-ray diffraction data for manganese nodules from the Central Pacific Basin.

| St. no. | Ob. no. | Opaque mineral | | Gangue mineral | | |
|---------|---------|----------------|------------|----------------|----|---------------|
| | | Todorokite | Birnessite | Q | F | Clay minerals |
| 407 | G171 | t | t | ++ | ++ | + |
| | FG5-2 | + | - | ++ | t | + |
| 408 | G172 | t | t | + | + | t |
| 411 | G175 | t | ++ | ++ | + | t |
| 414 | FG12 | - | + | + | + | t |
| 414A | G193 | + | t | t | t | t |
| 414A-2 | FG25 | t | t | + | + | t |
| 417 | G181 | - | ++ | + | - | + |
| 418 | G182 | t | ++ | + | t | + |
| 419 | G183 | t | t | ++ | + | + |
| 422 | FG18 | t | ++ | t | - | t |
| 423 | G187 | t | ++ | + | t | t |
| | FG19 | t | ++ | + | t | t |
| 424 | G188 | t | + | + | + | + |
| | FG20 | t | + | + | t | + |
| 426 | G190 | + | + | + | t | + |
| | FG22 | ++ | - | t | + | + |
| 430 | G195 | ++ | t | ++ | t | t |
| 431 | FG29 | - | ++ | + | t | - |
| 433 | FG31 | t | + | + | t | t |
| 407A-2 | FG32-2 | ++ | - | + | + | - |
| | 32-3 | ++ | - | - | + | + |
| | 32-4 | ++ | - | ++ | + | + |
| | 32-5 | + | + | ++ | ++ | + |
| | 32-6 | + | + | + | t | + |
| | 32-7 | + | t | + | + | + |
| | 32-8 | ++ | + | ++ | + | - |

note: Q: Quartz, F: Feldspar, ++: predominant, +: dominant, t: trace, -: not detected

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