

**Mineralogical and Geochemical Characteristics of Manganese Nodules
from the Suiko Seamount, Northwestern Pacific Ocean
1-Some Problems Concerning the Mineralogy**

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Abstract

Manganese nodules from the Suiko Seamount exhibit the significant characteristics in mineral compositions. Well-crystallized todorokite and birnessite, which are principal manganese mineral phase in nodules, only occur in the oxide layer directly incasing pebbles and coarse sand.

The preferential formation of todorokite or birnessite phases seem to be principally controlled by the reaction rate of iron-manganese oxides with trace elements such as Cu, Ni, Co, Zn, Pb concentrated in nodules, rather than redox characteristics of sedimentary environment or mineralogical diagenetic process.

1. Introduction

In 1968, geophysical and submarine geological researches were carried out in the northwestern Pacific Ocean by RV "Hakuho Maru" of the Ocean Research Institute, University of Tokyo and dredged hauls were obtained from the east and north crest or small plateau of the Suiko Seamount (Table 1 and Fig. 1). A numerous of manganese nodules were also collected together with various sorts of rock fragments and pebbles by chain dredge (TOMODA ed., 1968).

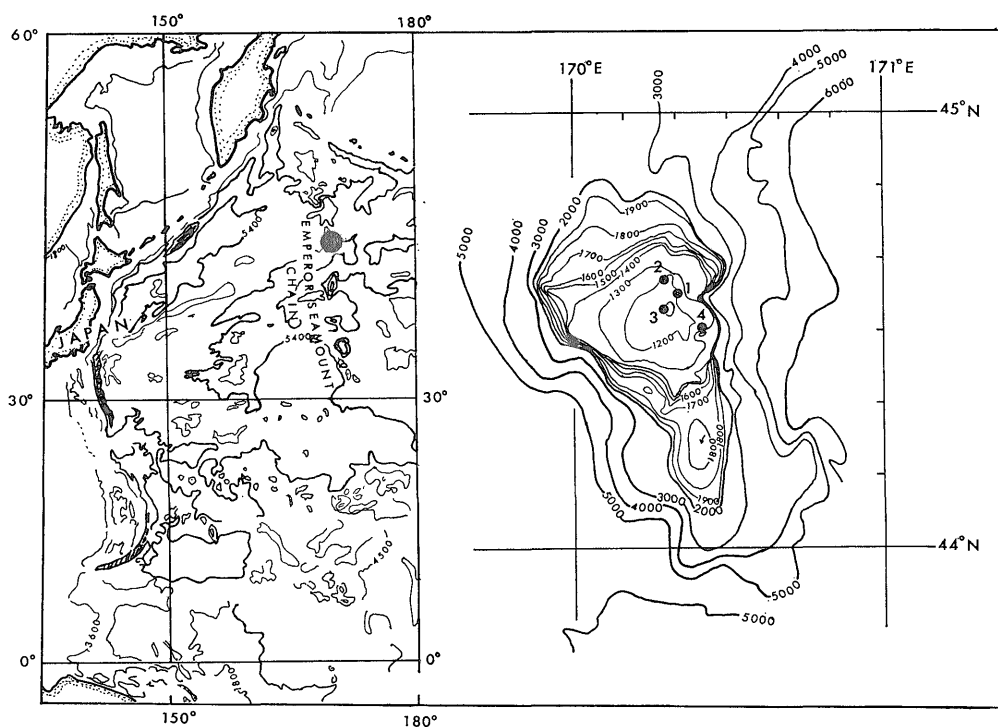
Table 1. Sample locations and water depths.

St. No.	Position	Water depth (m)
68-3-9-6	44° 35'N 170° 20'E	1358-1375
68-3-9-7	44° 37'N 170° 18'E	1365
68-3-9-8	44° 33'N 170° 17'E	1195-1232
68-3-9-9	44° 30'N 170° 25'E	1275-1290

As a part of wider studies of manganese nodules, an initial investigation has been undertaken on the composition of nodules. Works, including accumulation rate studies, are continued on these materials. However, analysis of nodules has revealed variations in both mineral and chemical compositions which are considered to have remarkable significance in terms of the origin of the nodule deposits.

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| 1 : station 68-3-9-6 | 2 : station 68-3-9-7 |
| 3 : station 68-3-9-8 | 4 : station 68-3-9-9 |

Fig. 1 Manganese nodule sample sites in the Suiko Seamount.

2. Description of the nodules

Nodules collected range generally from 14 to 40 cm in diameter and are remarkably large in size compared with those of pelagic nodules. The manganese nodule, which is convex on the upper smooth surface, always macroscopically has a distinct shell-like or parallel laminated layer (Figs. 2 and 3). The thickness of each layer of the crust attains to about 2-5 mm and sometimes to 10 mm. Two or three thick layers can be distinguished within the samples where fine to well sorted coarse sand are imbeded.

Rock fragments and pebbles dredged together with nodules are coated partially to wholly with iron-manganese oxides. Some of them have glacial scratches that appear to be caused by ice-rafting (FUJII *et al.*, 1973). These fragments and pebbles are various sorts of basalt, trachy-andesite, limestone, hornfels and tuffaceous shale (Fig. 4). They are included not only around its center or base but also close to the surface in nodules. Most pebbles and well-sorted coarse sand are completely incased within the iron-manganese nodule or crust.



Fig. 2 Manganese nodules with smooth surface dredged from station 68-3-9-7.

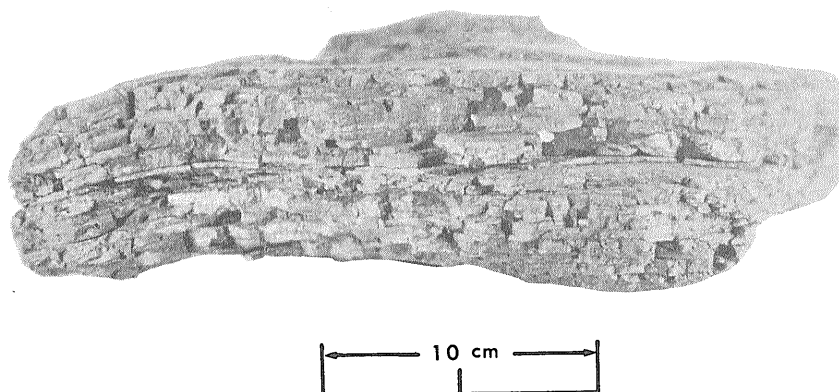


Fig. 3 Laminated manganese oxide layers in variable thickness of manganese encrustation from station 68-3-9-9.

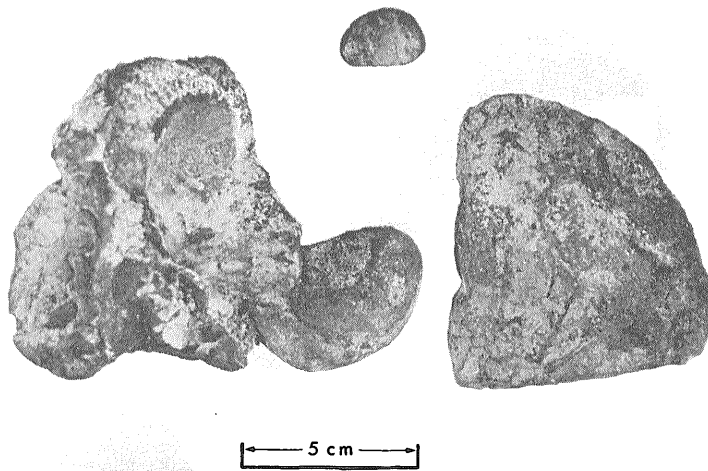


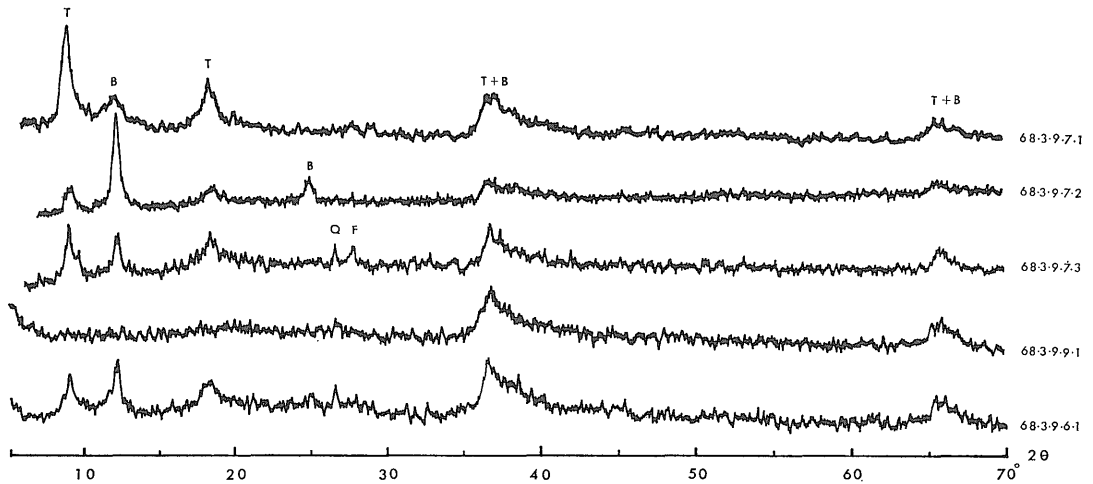
Fig. 4 Ice-rafted pebbles incased in pieces of a thick iron-manganese crust from station 68-3-9-6.

3. Analytical methods

The poor crystallinity of manganese mineral imposes several limitations on the use of X-ray diffraction techniques for the analysis of phases in manganese nodules. For this reason considerable care was taken to ensure that optimum instrumental conditions were used for the phase identification. Works were carried out on Rigaku Denki diffractometer using Cu K α radiation at 15–20 mA and 35–40 KV. The Cu K α radiation was eliminated by means of Ni-filter. Scanning speeds of 1°/min. were used with a time constant of 1–2 sec. The receiving slit was 0.1 mm wide and divergent and scatter slits were varied depending on the angle scanned with a few exceptions.

4. Results and discussion

It is generally known that manganese nodules consist of the amorphous phase with poor crystalline todorokite and birnessite (BUSER and GRÜTTER, 1954; BARNES, 1967; CRONAN and TOOMS, 1969; GLASBY, 1972). According to the results of X-ray powder diffraction patterns for approximately fifty of the our nodules, principal manganese minerals are todorokite and birnessite as well as that which have been reported by other workers. That is, todorokite (Na, Ca, K, Mn²⁺) (Mn⁴⁺, Mn²⁺, Mg)₆O₁₂·3H₂O which, form 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 identical to the δ -MnO₂ (Na_{0.7}, Ca_{0.3}) Mn₇O₁₄·2.8H₂O, of BUSER and GRÜTTER. A third phase having a powder pattern identical with birnessite of JONES and MILNE (1956) and also with 7 Å manganite of BUSER and GRÜTTER was also observed. However, as BRICKER (1965) has suggested, this phase and the δ -MnO₂ of BUSER and GRÜTTER are the same having different particle size. Therefore, both will be referred to in this work as birnessite.



T: todorokite, B: birnessite, Q: quartz, F: feldspar
 Fig. 5 X-ray powder diffraction patterns of selected manganese nodules.

Selected X-ray powder diffraction patterns of these minerals are shown in Fig. 5. It is characteristic that well-crystallized todorokite and birnessite phases occur only in the layer which are directly associated with well-sorted coarse sand. Microscopic observations reveal that these crystalline phases consist of concentrically banded globular structures which suggest its rapid coagulation from colloidal iron-manganese oxides. The marked differences in the mineral compositions in the nodules from the same site, for example, station 68-3-9-7 are observed (see Fig. 5).

There is considerable controversy concerning the environment of deposition and the mechanism of precipitation of manganese oxides of nodules. Using the O:Me ratio as an indicator of phase, MANHEIM (1965) have shown the apparent tendency in appreciably lower oxidation states on nodules from near-shore environments than those from deep-sea environments. PRICE (1967) has also mentioned the preferential formation of todorokite in near-shore environments. BARNES (1967), on the other hand, has concluded from a regional study of the mineralogy of manganese nodules from the Pacific Ocean that todorokite is preferentially formed at greater depths than birnessite. From a consideration of the pressure dependence on the dissolved oxygen contents in sea water, and on the free energy of formation of each mineralogical species, BARNES (1967) concluded that the more-oxidized birnessite should form at a greater depths than does todorokite. Since this is contrary to observation, BARNES (1967) suggested the possible importance of hydrostatic pressure on the mineralogy of nodules, and stressed the need of establish the partial molar volume change by pressure for the formation of manganese oxides.

CRONAN and TOOMS (1969) have found a similar relationship between the manganese mineralogy of nodules and their depth of formation in deep oceans. Todorokite has been found to be enriched in deep water nodules and birnessite to be more abundant at shallower depths. CRONAN and TOOMS (1969) have considered possible oxidation differences between these two minerals and concluded that variations in the mineralogy of nodules with

depth may reflect variations in degree of oxygenation of the environment of deposition.

However, recently GLASBY (1972) has found that todorokite is the principal mineralogical phase in shallow water-continental-margin manganese nodules whereas birnessite is the principal mineralogical phase in deep-sea nodules from the Carlsberg Ridge, Indian Ocean. GLASBY (1972) indicates from a consideration of the thermodynamics of phase conversion that the redox characteristics of the sedimentary environment are the principal factor controlling the mineralogy of marine manganese nodules, rather than the kinetics of nucleation of the manganese oxide phase or the onset of mineralogical ageing with time.

The major criticism against the postulated depth distribution presented by the previous authors is the inadequacy of the numbers of samples studied. From the data presented in this paper, it is apparent that, contrary to the findings of BARNES (1967), CRONAN and TOOMS (1969) and GLASBY (1972), well-crystallized todorokite and birnessite phases co-exist within a single nodule. This suggests that the observed depth distribution of a mineral species depends critically on the sample population considered. For this reason, care must be taken to establish the significance of the sample population in assessing the mineralogical controls of manganese nodules. Also, the co-existence of both mineralogical species within similar depth indicates that depth per se is not a primary parameter controlling nodules mineralogy.

GLASBY (1972) suggested that the mineralogy of manganese nodules was controlled principally by redox conditions at the sediment-water interface. No sediments, however, were obtained from the crest or plateau where they might be essentially swept out by up-welling currents. In addition, all environments in this area appear to be substantially similar conditions. Therefore, the principal factors controlling the mineralogy of manganese nodules from the Suiko Seamount seem not to be the depth of deposition (BARNES, 1967; CRONAN and TOOMS, 1969) or redox characteristics of the sedimentary environment (GLASBY, 1972).

NOHARA (1976) suggested that the heavy trace elements such as Cu, Ni, Co, Zn, Pb, Al and Ti contains in nodules played an important role in the formation of nodules. In their interactions with iron-manganese oxides, these elements themselves give rise to hydrolysis, and thereby are remarkably absorbed onto active surfaces of the oxides. On the other hand, these hydrolyzed elements enhance to rapidly coagulate iron-manganese oxides. Consequently, the preferential formation of todorokite or birnessite phases seems to be primarily ascribed to the kinetics of nucleation of the manganese oxide phases, rather than redox conditions of the environments or mineralogical ageing phenomena.

In addition, as minor mineral composition, groutite $\text{MnO}(\text{OH})_2$, and cryptomelane KM_8O_{16} have been identified by the previous study (NOHARA, 1972).

5. Summary

Manganese nodules from the Suiko Seamount have significant characteristics in mineral compositions. Most of manganese nodules are mineralogically amorphous or

microcryptocrystalline with a few exceptions. Well-crystallized todorokite and birnessite phases occur only in the oxide layer which closely coexist with pebbles and coarse sand to be possibly transported by ice-rafting.

The mineralogy of manganese nodules is controlled principally by the kinetics in interaction of iron-manganese oxides with trace elements such as Cu, Ni, Co and others, rather than redox conditions at the sediment-water interface or mineralogical diagenesis.

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北太平洋, 推古海山より採取されたマンガンノジュールの鉱物学的, 地球化学的特性

—1. 鉱物組成に関するいくつかの問題点—

野原昌人・奈須紀幸

要 旨

推古海山から採取されたマンガンノジュールの鉱物組成について研究した。マンガンノジュールの大部分は鉱物学的には非晶質または隠微晶質である。しかしながら, 非常に結晶質化した todorokite または birnessite が, 氷河によって運ばれてきた礫や荒い砂を含む酸化物層のみに存在し, 同一試料中でも, この 2 つの鉱物の共存が認められる。この結果は, Barnes (1967) や Glasby (1972) の結果と相反するものである。

todorokite や birnessite の生成は, 堆積物—海水境界面での酸化還元条件や鉄, マンガン酸化物の続成作用よりも, Cu, Ni, Co その他の加水分解性元素と鉄—マンガン酸化物との反応速度に支配されているものと解釈される。

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