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Mineralogical and Geochemical Characteristics of Manganese Nodules from the Suiko Seamount, Northwestern Pacific Ocean

2-Geochemical Aspect and Its Origin

Masato NOHARA* and Noriyuki NASU**

Abstract

An initial investigation has been undertaken on the chemical composition of the manganese nodules.

The results of chemical analyses on each layer of single nodules reveal the periodic patterns of distribution for Mn, Fe, Cu, Pb, Zn, Ni and Co contents. The variations strongly suggest that those of the elements in nodules from this region are, at least, climatically controlled.

1. Introduction

In the previous work (NOHARA and NASU, 1977), it was pointed out that well-crystallized todorokite and birnessite phases of manganese nodules from the Suiko Seamount were closely related with oxide layer incasing pebbles and coarse sand transported by ice-bergs. Also, it was suggested that the preferential formation of todorokite or birnessite were controlled by the kinetics in interaction of iron-manganese oxides with hydrolyzable trace elements such as Cu, Ni, Co and others concentrated in nodules, rather than redox characteristics of sedimentary environments or mineralogical ageing with time.

In this paper, their geochemical aspect will be described and discussed in relation to the origin of the nodules.

2. Analytical methods

Nodules were sectioned with a hacksaw blade. Sections, or each oxide layer were then crushed and finally ground in a agate mortar. Before analysis, the samples were dried at 105°C for 4 hours to remove adsorbed water. Samples of about 0.3–0.5 g were used for analysis. The samples were digested in HF-$HClO_4$-HNO_3 and diluted to 100 ml. This stock solution was properly diluted for the analysis using a Perkin-Elmer Atomic Absorption Spectrophotometer.

3. Results and discussion

The analytical results for Mn, Fe, Cu, Pb, Zn, Ni, Co are presented in Table 1. Also presented for comparison are some data on the average abundances of those elements

* Marine Geology Department.
** Ocean Research Institute, University of Tokyo.

Table 1 Average composition of nodules from the Suiko Seamount and different areas within the Pacific Ocean.

	1	2	3	4	5	6	7	8	9	10
Mn	28.14	28.45	26.01	28.47	13.96	16.87	15.51	22.33	19.81	16.61
Fe	18.69	17.57	16.34	17.55	13.10	13.30	9.06	9.44	10.20	13.92
Cu	0.048	0.066	0.050	0.059	0.061	0.393	0.711	0.627	0.311	0.185
Pb	0.228	0.239	0.198	0.218	0.174	0.034	0.049	0.028	0.030	0.073
Ni	0.586	0.882	0.578	0.624	0.393	0.546	0.956	1.080	0.961	0.433
Co	0.581	0.563	0.527	0.619	1.127	0.395	0.213	0.192	0.164	0.595

1: St. 68-3-9-6
2: St. 68-3-9-7
3: St. 68-3-9-8
4: St. 68-3-9-9
5: Mid-Pacific Mountain
6: West Pacific
7: Central Pacific
8: Northeast Pacific
9: Southeast Pacific
10: South Pacific

(5, 6, 7, 8, 9, 10: from Mero (1965) and Cronan and Tooms (1969)).

in nodules from the rest of the Pacific Ocean.

It is known that there are marked differences in chemical compositions between seamounts or the continental borderland and pelagic nodules (Mero, 1965; Cronan and Tooms, 1969; Price and Calvert, 1970; Skornyakova and Andrushchenko, 1970). Pelagic nodules have high Mn/Fe ratio compared with those of the continental borderland or seamount nodules, and also Ni and Cu are relatively enriched in pelagic nodules. Mn contents of present nodules vary from 24% to 35% with 28% in average which is remarkably greater than those of nodules in the rest of the Pacific Ocean. Similarly, the average Fe contents are higher than those of Pacific nodules. Cu and Ni contents are 0.056% and 0.66% in average, respectively. They are approximately same or somewhat lower in comparison with those from the high latitide area in the north Pacific. Although nodules from seamounts or the near-shore are generally rich in Co (Mero, 1965), nodules from this area are markedly depleted in it as compared with that from the Mid-Pacific Mountains (Table 1). Pb contents are a similar value to that from the Mid-Pacific Mountains but approximately several times as great as its average in nodules from the northeastern Pacific (0.028%), south and west Pacific (0.030% and 0.034%) and Indian Oceans (west area: 0.061%, east area, 0.034%).

There is a correlation between the features of layer and chemical compositions in the nodules. The oxide phase, in which well-sorted coarse sand and pebbles are incased, is richer about 1.5–2 fold in Mn than that in the oxide phase including no coarse sand. On the other hand, Fe is markedly low in a phase enriched in Mn. A similar tendency holds for the amount of trace elements. In general, Cu, Ni and Zn are enriched in the Mn-rich oxide phase, while Co and Pb richer in the Fe-rich oxide phase (Fig. 1). Fig. 1 reveals that its contents contained in the nodules vary periodically from its base towards the surface of crust. The cyclic pattern for these elements is closely associated with the nature of oxide phase in which well-sorted coarse sand and pebbles are included or not. Particularly, the oxide phase enriched in Mn, Cu, Ni and Zn is thicker than the others.

Whilist the role of submarine volcanism in determining the mineralogy and chemical compositions of manganese nodules was discussed first by Murray (Murray and Menard, 1891), it has been further polished by several authors as the predominant mechanism con-

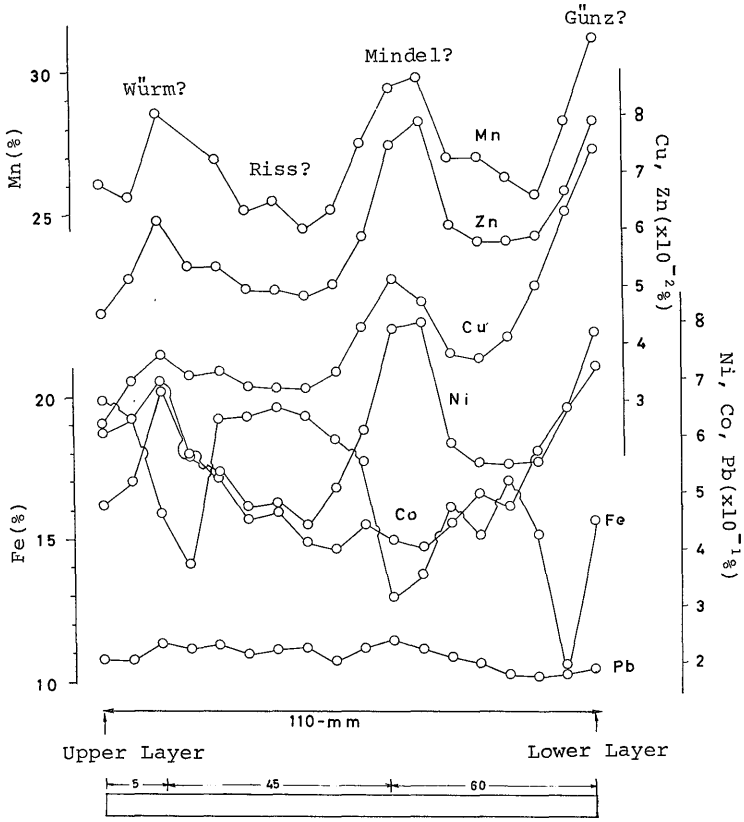

Fig. 1 Periodic variations in Mn, Fe, Cu, Pb, Zn, Ni, Co contents in a single manganese crust from its base to the surface layer. The Mn, Cu, Ni, Zn content peaks coincide with the feature of oxide layers in which fine to well-sorted coarse sand are incased.

trolling nodule genesis in much of the Pacific Ocean (ARRHENIUS *et al.*, 1964; ARRHENIUS and BONATTI, 1965; BONATTI and NAYUDU, 1965; CRONAN and TOOMS, 1967, 1969; SKORNYAKOVA and ANDRUSHCHENKO, 1970).

Most submarine volcanic rocks, including many cores, are more or less weathered, the mafic minerals being more rapidly altered than the felsic minerals. During this weathering, Mn and other elements are leached and either precipitated elsewhere in the rock or removed altogether. NAYUDU (1964) and BONATTI and NAYUDU (1965) have shown from this process that the heighest concentrations of nodules in the Pacific Ocean occur in areas rich in volcanic weathering products such as phillipsite and palagonite, particularly, in the region of the Medoceno Fracture Zone and the Pacific-Antarctic Ridge.

Several authors have interpreted the deposition of marine manganese oxides in terms of a hydrothermal origin. The association of manganese deposits with submarine hydrothermal manganese rich hot springs off the coast of Japan (NIINO, 1959) and the observation of ZELENOV (1964) that hot jets of iron and manganese rich solutions are pouring onto the sea floor around the submarine Banu, Wuhu, volcano, Indonesia would

support a hydrothermal origin for at least some manganese nodules. However, in our example it seems that volcanic activities including submarine hydrothermal hot springs are not principal factor controlling the geochemical characteristics of composition of nodules from the Suiko Seamount. The area is known for the low heat flow and for its inactive volcanic history since Paleogene (SCLATER and FRANCHETEAU, 1970; WATANABE, 1972).

KUNO *et al.* (1956) have studied petrologically rock fragments and pebbles dredged from the base of the Jinmu Seamount that is located in the north of the Suiko Seamount. They have concluded that the rock fragments and pebbles were droped by Pleistocene ice-bergs carried south and east by ocean currents on account of closer affinities with Kuril Island and Kamchtka volcanic rocks than with those of Cenozoic Japanese or Pacific basin types.

It has been well known that in the north Pacific Ocean ice-bergs during Pleistocene were reached from the edge of the continental shelf to the southern limit at approximately 45°N latitude. Very rarely ice-bergs may have floated as far south as 28°N latitude (MENARD, 1953, LISITZIN and TCHERNYSHEVA, 1970).

Manganese nodules collected from high latitude area are generally large in size and associated with erratic pebbles and well-sorted coarse sand (MENARD, 1953; GOODELL *et al.*, 1971; GLASBY, 1972). MENARD (1953) reported on ice-rafted pebbles surrounded by envelopes of well-sorted coarse sand which were incased in pieces of a thick manganese oxide from the Gilbert Seamount, off the Gulf of Alaska. Then MENARD (1953) suggested that the pebbles settled on the relatively smooth surface of the manganese nodule and were incased by slow upward growth of the nodule. The evidence of numerous burried manganese nodules in the north Pacific (SKORNYAKOVA and ANDRUSHCHENKO, 1970) and south Atlantic (GOODELL *et al.*, 1971) suggests that those were once formed during a glacial age in Pleistocene Glacial Epoch and then covered with subsequent glacial deposits.

WANGERSKY and HUCHINSON (1958) found that Caribean sediments from the last four glaciations were rich in manganese. Also, BOSTRÖM (1970) analysed the Caribean core and then found that Mn, Cu and Co were enriched in sediments from most glacial periods. Thus, the data presented in this paper and some reports (ARRHENIUS, 1952; MENARD, 1953; WANGERSKY and HUCHINSON, 1958; BOSTRÖM, 1970) suggest possible that the variations in the content of Mn, Fe, Cu, Pb, Zn, Ni, Co are at least climatically controlled.

The formation of nodules enriched in Mn, Cu and other elements (see Fig. 1) during glacial periods could possibly be the result of an increase in chemical weathering during these periods caused by pluvial conditions which occurred at middle latitudes simultaneously with the glaciations at low latitudes (NILSSON, 1963; BOSTRÖM, 1970, MCGEARY and DAMUTH, 1973). The increase in run off during the glaciations (NILSSON, 1963; TUREKIAN, 1965) could have coincided with an even more accelerated weathering rate. The connection between pluvial and glacial events, however, does not seem to be

fully understood (FLINT, 1959; FAIRBRIDGE, 1964; VAN ANDEL, 1967). An alternative explanation could be that interglacial periods, weathering products enriched in these elements are formed and are brought into this region by ice-rafting. Another explanation could be a more complete removal of Mn, Cu, Ni and others from sea water during cold periods.

The nodules in this region offer also more significant information on its growth rate. The pebbles and well-sorted coarse sand are often observed within 2 mm from surface of nodules. This indicates that these nodules were formed within extremely short range of time and their accumulation rates have been nearly stopped after deposition at a glaciation. The laminated oxide layers in various thickness also suggest that the manganese nodules are intermittently formed and its accumulation rates are remarkably rapid in deposition of them. In view of the argument above, pebbles and well-sorted coarse sand appear to be useful as key-bed to estimate the approximate accumulation rate of nodules in this region. If pebbles and coarse sand near uppersurface of nodules are transported by ice-bergs during last glaciation in Quaternary, and then the four peaks in Mn, Cu, Zn and Ni content-variation in Fig. 1 may be assigned to Günz, Mindel, Riss and Würm, we can deduce approximate accumulation rates on the nodules. The tentative accumulation rates are 2–5 mm/10^3 yrs which suggest that considerably rapid formation of these nodules, as compared with a few mm per million years for pelagic nodules (KU and BROECKER, 1969).

As discussed above, manganese nodules from the Suiko Seamount involve many problems to be solved. Further investigation seems to provide a information as to its origin.

4. Summary

Mn contents of present manganese nodules vary from 24% to 35% with 28% in average which is remarkably greater than it of nodules in the rest of the Pacific Ocean. Their average Fe contents are also relatively high. Ni is present in same or somewhat low concentrations compared with nodules from the rest of the Pacific, while the Cu contents is extremely low. Pb and Co are a similar or slightly low with respect to those in nodules from mountains but approximately several times as great as its average in nodules from deep sea.

Detailed analyses of single nodules reveal the significant periodic patterns for Mn, Fe, Cu, Ni, Zn and Co contents which might be considerably influenced by glaciations in Quaternary.

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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

——2. 地球化学的側面と成因——

野原昌人・奈須紀幸

要　旨

推古海山より採取されたマンガンノジュールの化学組成について検討した．Mn 含有量は 24–35％と変化し，その平均値 28％ は太平洋各域のノジュールのそれに比べて著しく高い．Fe も同様に高含有量，17％を示す．Ni は太平洋各域のノジュールのそれと同程度かいくらか低い傾向を示す．他方，Cu 含有量は著しく低い．Pb と Co は海山性ノジュール中の含有量と同じかわずかに低い．しかし，深海性ノジュールに比べて数倍も高濃度である．

酸化物層の特徴とその化学組成間にはある関係がみられる．すなわち，氷河堆積物である礫や荒い砂を内包する酸化物層には Mn, Cu, Ni, Zn が濃集し，他方 Fe, Pb, Co は著しく減少する．各層毎の分析結果，Mn, Fe, Cu, Co, Zn, Ni の含有量は周期的に変化することが明らかになった．これらの変動性は少なくとも気候的因子の影響を強く受けているものと推定される．

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