

Chemical Composition and the Rate of Accumulation of Ferromanganese Nodules in the Western North Pacific

by

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Abstract

The major and some of the minor constituents and the rate of accumulation of manganese nodules in the western North Pacific were determined. Manganese concentration in the nodules ranged from 20 to 30 per cent in the acid soluble fraction. As to the rare earth concentration, enrichment of cerium was observed in the manganese nodule as compared with that in shales or sea water. Thorium to uranium ratio in the nodule ranged from 9.4 to 14.3, which was very much higher than that in sea water. From the distribution of excess ionium, excess protactinium and Io/Th ratio, a rate of accumulation of 7 mm per million years was obtained with the surface layer of several mm in thickness of the JEDS-4-E4 nodule.

1. Introduction

Since MURRAY and RENARD discovered manganese concretions on the ocean floor during the Challenger Expedition (1873-1876), various hypotheses have been proposed to explain the origin of manganese nodules. Among them, the slow growth hypothesis was suggested by GOLDBERG and ARRHENIUS (1958) and the hypothesis of the rapid formation by submarine volcanic exhalates was presented by BONATTI and NAYUDU (1965).

Recently, by means of the radioactivity method of determination of the growth rate of ferromanganese concretions, evidence for the slow growth has been accumulated (GOLDBERG and KOIDE, 1962; KU and BROECKER, 1967, 1969; BARNES and DYMOND, 1967; BENDER et al., 1966, 1970; SOMAYAJULU and GOLDBERG, 1966; BHAT et al., 1970).

In this paper, the present authors intend to report on the results of their chemical analyses of both major and minor constituents of manganese concretions collected in the western North Pacific. The result of measurement of the growth rate of a manganese nodule by the ionium-thorium and protactinium method of age determination is also reported.

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2. The method of analysis and the samples

During the cruises of the Japanese Expedition to Deep Sea (JEDS-4, 1961; JEDS-5, 1962) aboard the M.S. Ryofu-maru-I (1,200 tons) manganese concretions of two different types were collected in the western North Pacific.

At the station E-4 (38°00'N, 146°00'E) manganese nodules were collected on the southwest slope of the Ryofu Sea Mount with a large rectangular dredge. At the stations E-6 (38°09'N, 148°00'E) and F-27 (34°24'N, 150°28'E), located on the flat plain, manganese concretions of thin plate form and pumices coated with a thin layer of manganese oxide were collected with a beam trawl.

One to two grams of pulverized manganese concretion was dissolved in a hot solution of 6 M HCl. After the residue was separated by centrifuge, the supernatant solution was subjected to spectrophotometric analysis for its manganese, iron, cobalt and nickel content respectively by means of permanganate, o-phenanthroline, dimethyl glyoxime and nitroso-R salt method.

With respect to the determination of rare earth elements, one to two grams of sample was dissolved in 5 ml of concentrated solution of HNO₃, and was diluted to 20 ml, to which 1 ml of H₂O₂ was added drop by drop. The residue was removed by centrifuge. The solution was then diluted to 50 ml which was treated with 5 ml of HF. The precipitate of rare earth fluorides was formed along with the zirconium fluoride precipitate.

The precipitate was removed from the solution by centrifuge, and was washed with distilled water. And it was then dissolved in a small amount of concentrated solution of HNO₃.

The solution was diluted to 20 ml, and the pH of the solution was adjusted to 2.5 with NH₄OH solution. The rare earths were precipitated by adding a saturated solution of oxalic acid. The oxalate precipitate was then subjected to X-ray fluorescence analysis.

In order to study the rate of accumulation of manganese concretions, thorium isotopes, protactinium and uranium were determined as follows.

Thin layers with a known surface area were scraped successively from the surface of a nodule with a dental drill. By the weight of each thin layer and the mean density of a nodule (2.25 g/cm³), the thickness of the layer was estimated.

The method of thorium isotope determination is essentially the same as used in the previous works in our laboratory (MIYAKE et al., 1965, 1968). As to the protactinium determination, the method given by RONA et al (1965) was employed. The content of uranium was determined by radiochemical method (MIYAKE et al., 1970). To know the recoveries of the chemical separations, ²³⁴Th and ²³²U were used respectively as yield tracers.

3. Results and discussions

The result of chemical analyses is shown in Table 1. As seen in the Table, the manganese content in the samples varies from 0.35 to 25% according to the types of concretions. However, so far as the acid soluble fraction is concerned, the manganese

concentration is in the narrow range from 20 to 30% irrespective of the difference of types. The iron to manganese ratio in the concretions varies from 0.2 to 4.4, which is not so low as given by MENARD (1964).

Table 1. Chemical composition of ferromanganese nodules in the western North Pacific.

Sample	Mn %	Fe %	Ni %	Co %	Fe/Mn	Th ppm	Acid soluble	Note
A: JEDS-4-E4; 38°09'N, 148°00'E; 5,650 m								
1.	4.82	1.70	0.02	0.05	0.36	9.7	27.2	Brown thin plate
2.	5.61	3.80	0.03	0.06	0.68	16	24.3	
3.	8.79	2.00	0.04	0.11	0.23	18	28.1	
4.	6.95	6.07	0.03	0.08	0.87	15	44.3	Ferromanganese coated pumice
5.	0.35	1.36	0.02	0.02	3.89	1.7	11.9	
6.	3.45	4.05	0.01	0.04	1.17	5.0	30.8	
7.	13.10	3.32	0.02	0.08	0.25	20	42.8	
B: JEDS-4-E4; 38°00'N, 148°00'E; 3,600—3,800 m								
8.	25.04	18.02	0.18	0.07	0.72	50	88.1	Nodule fragment
9.	14.87	18.53	0.18	0.04	1.24	30	88.3	
10.	21.38	12.01	0.35	0.03	0.55	40	91.4	
C: JEDS-5-F-27; 34°24'N, 150°28'E; 5,880 m								
11.	0.59	2.66	0.01	0.01	4.48	1.7	41.4	Pumice
12.	0.87	2.44	0.02	0.01	2.30	3.0	42.2	
13.	0.77	0.44	0.02	0.01	0.57	3.3	24.9	

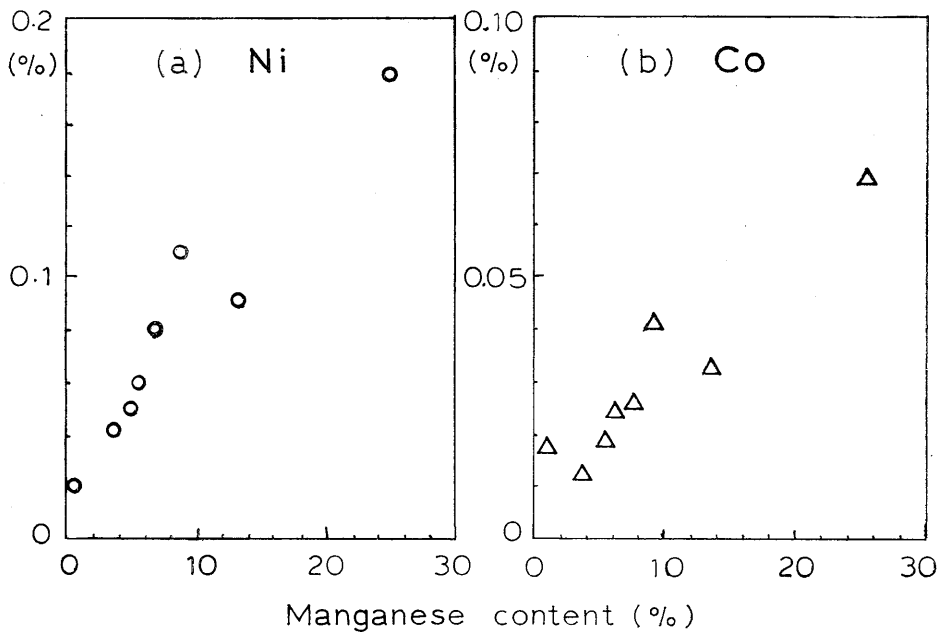


Fig. 1. Relationships between (a) nickel and manganese, (b) cobalt and manganese in manganese nodules.

There are good positive correlations between manganese content and nickel or cobalt content as shown in Figs. 1a and 1b.

Rare earth elements: Table 2 and Fig. 2 give the contents of rare earth elements relative to that of lanthanum (8,000 ppm). A comparison of the rare earth contents in manganese concretions with those in sea water (GOLDBERG et al., 1963), shales (MINAMI, 1935) and sediments (HASKIN, 1962), shows that cerium is much more abundant in relation to lanthanum and praseodymium in the ferromanganese nodules than in other materials. It seems that in sea water cerium is readily oxidized from Ce^{+3} to the higher valence state of Ce^{+4} which is preferentially removed from sea water with manganese oxide.

Radioactive elements: The results of determination of radioactive elements are shown in Table 3.

(a) *Uranium and thorium;* The uranium concentration (3.5 ppm) is lower than the average value of 9 ppm in 48 nodules collected in various parts of the world ocean (KU et al., 1969), but it is close to that of 4–5 ppm given by GOLDBERG (1959) and 2–9.5 ppm given by NIKOLAYEV (1963).

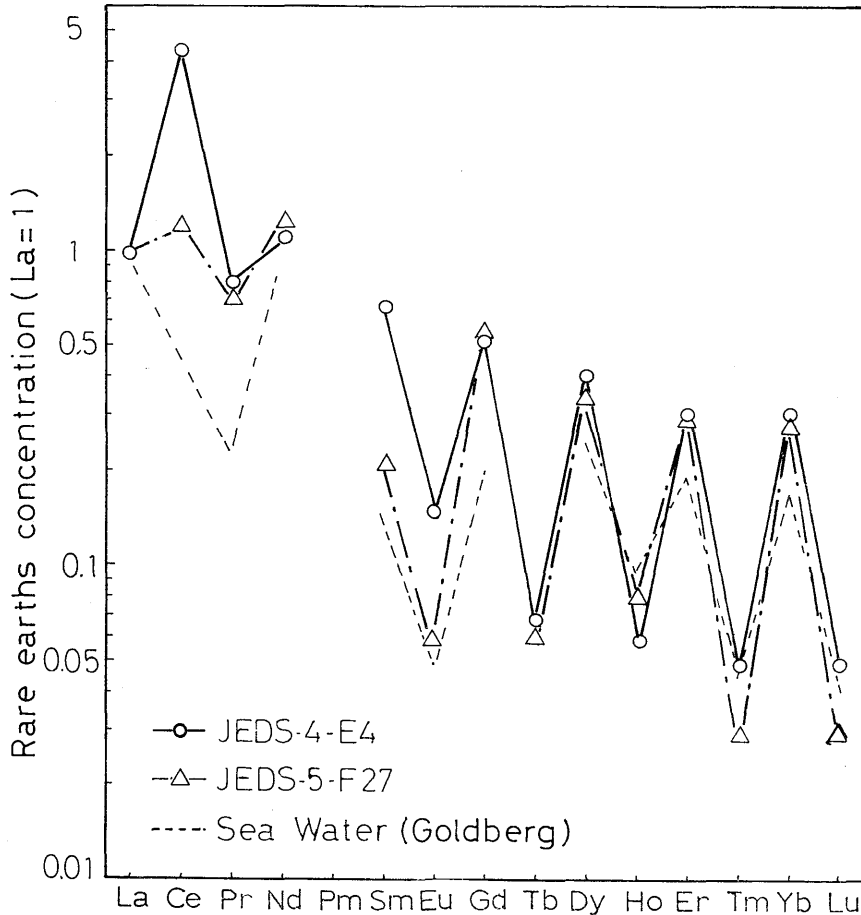


Fig. 2. Rare earth concentration, normalized to lanthanum, in manganese concretions.

Table 2. Content of rare earth elements in manganese nodules (Normalized to La=1)

Element	JEDS-4-E4	JEDS-5-F-27
La	1	1
Ce	4.4	1.2
Pr	0.80	0.72
Nd	1.1	1.30
Pm	—	—
Sm	0.67	0.21
Eu	0.15	0.06
Gd	0.50	0.67
Tb	0.07	0.06
Dy	0.40	0.36
Ho	0.06	0.08
Er	0.30	0.30
Tm	0.05	0.03
Yb	0.30	0.30
Lu	0.05	0.03
Content of La	8 mg/g	6 mg/g

Table 3. Uranium, thorium and protactinium contents in JEDS-4-E4 manganese nodule in the western North Pacific.

Depth (mm)	Residue (%)	U (ppm)	Th (ppm)	Io/Th ratio		²³¹ Pa _{excess} dpm/g
				Measured	Corrected	
0 —0.6	21	3.5±0.2	37±2	11.4	10.7	6.7
0.6—1.4	20	3.5±0.2	33±2	4.40	4.16	0.9
1.4—2.1	19	3.8±0.1	40±2	1.86	1.60	0.1
2.1—2.6	15	3.8±0.2	50±3	0.92	0.70	0.0
2.6—3.2	15	3.5±0.2	50±3	0.51	0.30	0.0
3.2—3.8	16	3.5±0.2	50±3	0.34	0.13	0.0

As to the thorium concentration, a considerably wide range from 1.7 to 50 ppm is observed in the western North Pacific nodules. The Th/U ratio in the JEDS-4-E4 nodule ranges from 9.4 to 14.3. As the Th/U ratio is 6×10^{-4} in sea water, it is obvious that a remarkable fractionation occurs in the precipitation processes between uranium and thorium.

(b) ²³⁰Th/²³²Th ratio, the excess Pa content and the rate of accumulation of manganese nodule; ²³⁰Th and ²³¹Pa are produced from the uranium isotopes ²³⁸U and ²³⁵U in sea water respectively, which are easily hydrolyzed and rapidly precipitated on the ocean floor. In the surface layers of manganese nodules large amounts of excess of ²³⁰Th and ²³¹Pa are contained with respect to the uranium content.

From the decrease of ²³⁰Th and ²³¹Pa contents in a nodule with depth from the surface, the rate of the growth of the nodule can be estimated. As shown in Fig. 3, assuming a constant rate of accumulation for ²³⁰Th, ²³¹Pa and ferromanganese materials during

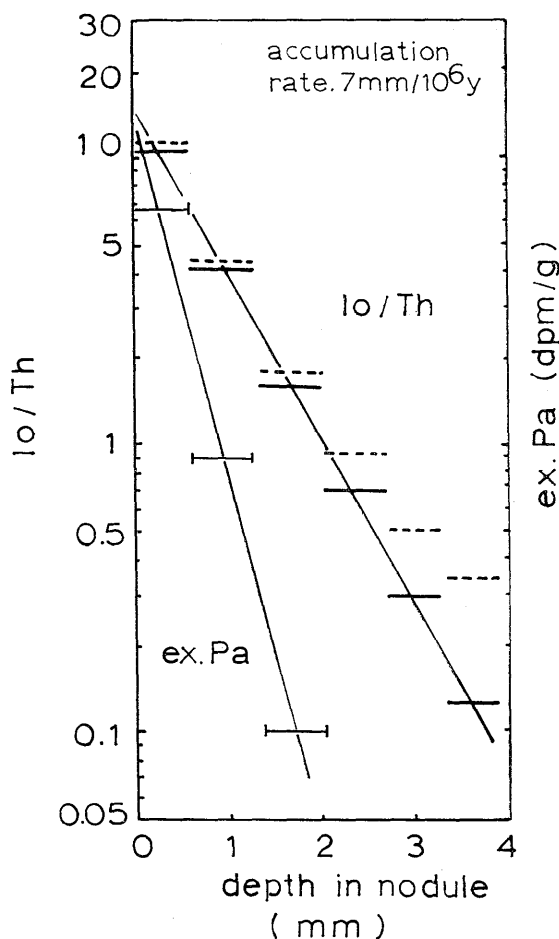


Fig. 3. ^{10}Th and excess protactinium distributions with depth in the manganese nodule, JEDS-4-E4.
 observed ^{10}Th , — excess ^{10}Th , [—] excess Pa

the time interval of several thousand years, it may be said that JEDS-4-E4 nodule has a growth rate of 7.3mm per million years within a surface 4mm. The fact that the ^{10}Th ratio and the excess Pa content in the nodule decrease regularly from the surface clearly indicates a gradual and slow growth.

The above value of accumulation rate by the present authors is in good agreement with those given in the previous studies (BENDER et al., 1966; KU and BROECKER, 1967, 1969; BARNES and DYMOND, 1967; SOMAYAJULU, 1967; BHAT et al., 1970).

The activity ratio of ^{230}Th excess to ^{231}Pa excess was 14.5, which is higher than the ratio of the production rate of these nuclides in the ocean (10).

The content of uranium in the ocean is $3.3 \mu\text{g/l}$ on an average, from which $1.11 \times 10^{-5} \text{ pCi/l} \cdot \text{y}$ and $1.10 \times 10^{-6} \text{ pCi/l} \cdot \text{y}$ respectively of ionium and protactinium are produced. Thus, the activity ratio of the rate of production of two nuclides is 10. Since the rate

of production is equal to the rate of precipitation in the steady state, the activity ratio of ionium and protactinium in the fresh precipitate should be equal to the ratio of the rate of production. However, the ratio increases to about 15 in tens of thousand years, which corresponds to the thickness of only about 0.2mm from the surface. Therefore, the observed ratio of ionium to protactinium of 14.5 near the surface of the nodule may be reasonable.

The source of manganese; GOLDBERG (1958) reported that the residence time of manganese in the ocean is 1.4×10^3 yrs. The average concentration of manganese in sea water is $2 \mu\text{g/l}$. Therefore, in a water column of 4,000m the total amount of manganese is $800 \mu\text{g/cm}^2$. In the steady state, the annual precipitation amount of manganese on the ocean floor is $5.71 \times 10^{-7} \text{g/cm}^2 \cdot \text{y}$.

On the other hand, the annual accumulation rate of manganese in ferromanganese concretion is given as follows:

$$\text{Mn/cm}^2/\text{y} = \text{Growth rate (cm/y)} \cdot \text{cm}^2 \cdot \text{Mn content (g/cm}^3) \cdot \text{Density of nodule (g/cm}^3)/\text{cm}^2$$

Assuming that the growth rate is $7.3 \text{mm}/10^6$ yrs, the manganese content 25% and the density 2.25, then the annual accumulation rate of manganese on the manganese nodule is estimated to be $4.1 \times 10^{-7} \text{g/cm}^2 \cdot \text{y}$, which is in good accord with the calculated annual deposition rate of $5.7 \times 10^{-7} \text{g/cm}^2 \cdot \text{y}$ of manganese in the present environment.

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北太平洋西部海域のマンガン団塊の化学組成と成長速度について

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日本深海研究航海 (JEDS-4, 5) において採取された北太平洋西部海域のマンガン団塊の化学組成 (主成分および、コバルト, ニッケル, 希土類元素などの微量成分) と, イオニウムトリウム法およびプロトアクチニウム法による成長速度の研究を行なった。マンガン含量は, マンガン団塊のタイプにより, 0.35~25% までの大巾な変動を示すが, 酸可溶部分に対する割合は, 20~30% 巾におさまる。希土類元素は濃縮されており, ことに, セリウムの濃縮が著しい。トリウムとウランの重量比は, 9.4~14.3 で, 海水中の値 6×10^{-4} にくらべて, 10^4 倍を示している。イオニウムトリウム法および, プロトアクチニウム法によるこれらのマンガン団塊の表層数 mm の成長速度は, 7 mm/10⁶ 年であることが明らかになった。マンガン団塊を形成するマンガンの原料としては, 海水中のマンガン存在量によって説明できることを示し, 現在のこの部分の深海底におけるマンガン団塊のゆっくりした成長のモデルを, これによって説明できることを明らかにした。

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