

Geochemical characteristics of Antarctic deep-sea ferromanganese nodules from highly oxic deep-sea water

Atsuyuki OHTA¹, Koh NAITO², Yoshihisa OKUDA³ and Iwao KAWABE¹

¹ *Department of Earth and Planetary Sciences, Graduate School of Science,
Nagoya University, Chikusa, Nagoya 464-8602, Japan*

² *Metal Mining Agency of Japan, Toranomon 1-25-5, Minato-ku, Tokyo 105-0001, Japan*

³ *Geological Survey of Japan, 1-3, Higashi-1, Tsukuba 305-0046, Japan*

(Received September 2, 1999 / Accepted October 5, 1999)

ABSTRACT

Six samples of ferromanganese nodules taken from a knoll and a seamount off Wilkes Land, Antarctica, have been analyzed by ICP-AES and their geochemical characteristics have been compared with those of Pacific nodules. The Antarctic nodules have slightly concentric structures with rough surface texture similar to those of early diagenetic Pacific ferromanganese nodules. However, mineralogy, transition metal contents (Mn, Fe, Ni and Cu) and the rare earth element (REE) patterns, suggest that the Antarctic nodules are more similar to hydrogenous Pacific ferromanganese nodules. The Antarctic nodules have higher values of positive Ce anomalies and Co/(Ni+Cu) ratios, but have lower Mn, P, Ni, Cu and V contents than hydrogenous type Pacific nodules. In addition, the Mn content correlates with the Co content in the Antarctic nodules. These features suggest that the Antarctic nodules contain hardly any diagenetic component. This is possibly related to the fact that all Antarctic samples were collected above the CCD. In the Antarctic Ocean, biogenic productivity is generally high, but most of the organic material is decomposed before it reaches the sediment because of the high oxygen content of the water column in the Antarctic Ocean. The Antarctic samples represent more hydrogenous materials even when compared with the hydrogenous nodules from the Pacific Ocean.

INTRODUCTION

Many studies of the mineralogy and chemistry of deep-sea ferromanganese nodules in the Pacific Ocean have been carried out. Calvert and Price (1977) studied the chemical compositions of ferromanganese nodules and associated sediments from the Pacific Ocean. They showed that Ti, P, Co, Pb, Sr, Y and Zr are incorporated into ferromanganese deep-sea nodules with the Fe component, whereas Mg, Ba, Cu, Ni and Zn are incorporated with the Mn component. Pacific deep-sea nodules can be classified into three types; "hydrogenous", "diagenetic" and "sub-oxic diagenetic" type nodules from various view points of mineralogical and chemical compositions and morphology (Halbach et al., 1981; Usui, 1983/84; Dymond et al., 1984). The hydrogenous nodules have smooth surface features and are mainly composed of vernadite (δ -MnO₂). The diagenetic nodules have rough surface textures and are composed mainly of todorokite (10Å manganate). The sub-oxic diagenetic nodules display rough surface textures and are composed mainly of todorokite (10Å manganate) and birnessite

(7Å manganate). The hydrogenous nodules have low Mn/Fe ratios and relatively high contents of Co, Ti, P and rare earth element (REE). In contrast, the diagenetic nodules are characterized by high Mn/Fe ratios and relatively high contents of Ni, Cu and Zn. The sub-oxic diagenetic nodules have much higher Mn/Fe ratios and Mn contents but lower Ni and Cu contents than the diagenetic nodules.

The Pacific hydrogenous nodules show large positive Ce anomalies in their REE patterns, whereas the diagenetic nodules do not (Goldberg et al., 1963; Piper, 1974; Elderfield et al., 1981; Calvert et al., 1987). The Ce anomalies and the Co/(Ni+Cu) ratios display a positive correlation in the three different types of the Pacific deep-sea nodules (Ohta et al., 1999).

In contrast to Pacific nodules, Antarctic ferromanganese nodules have been scarcely studied. Usui et al. (1989) reported the mineralogy and chemical composition from ferromanganese nodules and crusts in the east Antarctic Ocean. They noted that Antarctic nodules are composed mainly of vernadite (δ -MnO₂) and have low Mn/Fe ratios and Cu and Ni contents but high Co contents. Abundant ferromanganese nodules were recovered during cruise TH91 of R/V Hakurei-maru conducted by the Japan National Oil Corporation (JNOC) in 1991. The purpose of this paper is to clarify the differences between Antarctic and Pacific nodules on the basis of their mineralogy and chemical composition.

SAMPLES AND ANALYTICAL METHODS

Six ferromanganese nodules were sampled around an unnamed knoll and the Hakurei Seamount off Wilkes Land, Antarctica during cruise TH91 (Fig. 1). The recovered samples were found to consist of ferromanganese nodules, argillaceous rocks, and pebbles and cobbles of granite, andesite, slate and metamorphic rocks. The pebbles and cobbles were carried from Antarctica by iceberg. Associated sediments consist mainly of foraminiferal ooze containing calcareous shells. The water depth ranges from 3600 to 3800 m on the north-eastern slope of the unnamed knoll and from 3300 to 3400 m on the south-western slope of the Hakurei Seamount. These depths are above the carbonate compensation depth (CCD). Table 1 summarizes the sampling sites and morphologic features of the Antarctic nodules.

All the samples have rough and black-brown surfaces. All samples were cut into round slices, and were divided into three or four parts; core, inside, middle and outside. The outer parts of two samples (AT 1 and AT 3C) were further divided into three or four portions. The cross sections show slightly concentric layered structures, except for AT 1 and AT 3C. The AT 1 sample has the unique feature of a large irregular core with a large amount of phillipsite outside the core. All subsamples were ground and dried in air at room temperature. All the core material was not analyzed chemically or mineralogically, since it is composed mainly of detrital fragments.

Individual subsamples were examined by X-ray powder diffraction using FeK α radiation. Major elements (Mn, Fe, Al, Na, K, Mg, Ca and Ti), minor elements (P, Ba, Sr, V, Co, Cu and Ni) and REE including Y were analyzed by ICP-AES. The details of the analytical method are described elsewhere (Ohta et al., 1999). The chemical data are listed in Table 2a and 2b.

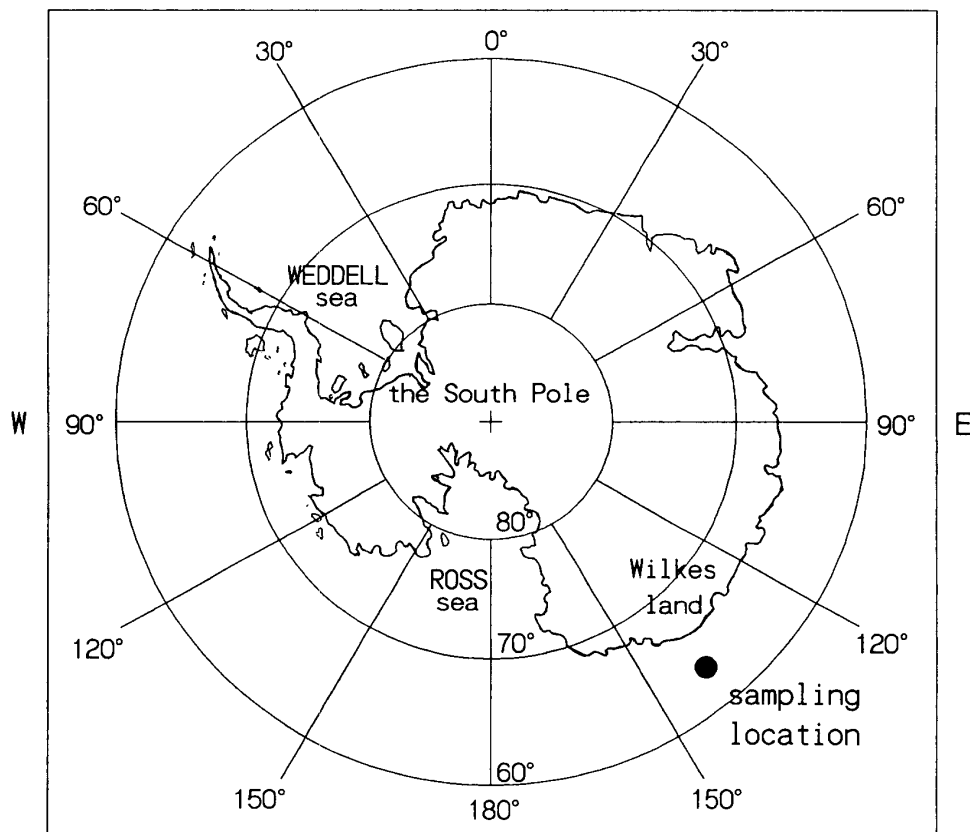


Fig. 1. Schematic map showing the location of the sampling area of the Antarctic nodules in this study.

Table 1. Sampling locations of Antarctic nodules and their superficial features.

sampling site	sample name	location	latitude and longitude	depth (m)	size (mm)	feature
D1202 ST2	AT1	Eastern slope of an unnamed knoll, north of Hakurei Seamount, off Wilkes Land.	62° 19'S and 140° 57~58'E	4090~3956	58.85 × 39.85 × 39.80	Brown and somewhat rough surface texture. Large irregular core and irregular shape.
D1204 ST4	AT2A	North-eastern slope of Hakurei Seamount off Wilkes Land	62° 42'S and 139° 50'E	3845~3770	43.85 × 43.65 × 29.80	Black, ellipse and rough surface texture. Slightly concentric structure.
D1204 ST4	AT2B	North-eastern slope of Hakurei Seamount off Wilkes Land	62° 42'S and 139° 50'E	3845~3770	39.75 × 34.74 × 27.25	Black and rough surface texture, and irregular shape. Slightly concentric structure.
D1206 ST6	AT3A	South-western slope of Hakurei Seamount off Wilkes Land	62° 51'S and 139° 15~16'E	3490~3456	50.10 × 48.85 × 40.75	Black, ellipse and rough surface texture. Slightly concentric structure.
D1206 ST6	AT3B	South-western slope of Hakurei Seamount off Wilkes Land	62° 51'S and 139° 15~16'E	3490~3456	49.45 × 33.15 × 30.20	Black and rough surface texture, and irregular shape. Slightly concentric structure.
D1206 ST6	AT3C	South-western slope of Hakurei Seamount off Wilkes Land	62° 51'S and 139° 15~16'E	3490~3456	43.55 × 35.80 × 34.40	Black and rough surface texture, and irregular shape.

Table 2a. Major and minor element compositions of ferromanganese nodules from the Antarctic Ocean in wt. % of dried nodules substance.

sample name	divided parts	Mn (%)	Fe (%)	Al (%)	Ca (%)	K (%)	Mg (%)	Na (%)	Ti (%)	P (%)	Ba (%)	Co (%)	Cu (%)	Ni (%)	Sr (%)	V (%)
AT101	outside	8.58	10.99	3.54	1.15	1.82	0.802	2.22	1.23	0.167	0.107	0.304	0.088	0.120	0.069	0.024
AT102	inside	7.20	11.19	3.41	1.09	1.67	0.769	1.89	1.23	0.163	0.106	0.210	0.074	0.082	0.064	0.024
AT103	outside	8.74	10.89	3.58	1.19	1.80	0.802	2.21	1.19	0.167	0.104	0.309	0.088	0.118	0.068	0.024
AT104	outside	7.99	10.76	3.60	1.10	1.82	0.790	2.13	1.19	0.164	0.108	0.282	0.088	0.111	0.067	0.024
AT2A1	outside	13.39	14.66	1.74	1.72	0.93	0.894	1.63	1.18	0.243	0.100	0.476	0.079	0.176	0.102	0.038
AT2A2	middle	9.57	13.34	2.13	1.32	0.99	0.776	1.52	1.09	0.192	0.101	0.330	0.062	0.113	0.082	0.031
AT2A3	inside	8.89	14.05	2.58	1.33	1.12	0.776	1.64	1.33	0.199	0.123	0.270	0.067	0.091	0.087	0.032
AT2B1	outside	12.94	14.39	1.74	1.63	0.85	0.900	1.61	1.14	0.243	0.095	0.444	0.070	0.189	0.099	0.038
AT2B2	middle	10.55	14.82	2.15	1.44	0.99	0.827	1.65	1.16	0.219	0.107	0.349	0.065	0.129	0.089	0.035
AT2B3	inside	9.45	14.29	2.39	1.34	1.06	0.807	1.62	1.24	0.194	0.114	0.320	0.065	0.102	0.086	0.033
AT3A1	outside	11.20	14.46	1.93	1.62	0.99	0.906	1.78	1.19	0.209	0.113	0.401	0.102	0.191	0.098	0.035
AT3A2	middle	9.32	14.21	2.34	1.36	1.06	0.810	1.73	1.25	0.174	0.127	0.302	0.096	0.117	0.091	0.031
AT3A3	inside	8.40	14.52	2.48	1.32	1.08	0.713	1.72	1.31	0.169	0.145	0.211	0.086	0.082	0.092	0.032
AT3B1	outside	11.67	13.95	1.99	1.61	0.97	0.872	1.86	1.18	0.191	0.111	0.376	0.079	0.200	0.098	0.032
AT3B2	inside	9.41	14.59	2.42	1.44	1.07	0.801	1.82	1.30	0.174	0.124	0.299	0.070	0.120	0.091	0.029
AT3C1	outside	9.66	12.47	1.99	1.29	0.95	0.754	1.63	1.14	0.138	0.114	0.292	0.096	0.164	0.084	0.024
AT3C2	outside	11.03	14.29	2.20	1.58	1.02	0.854	1.83	1.21	0.208	0.117	0.363	0.071	0.165	0.098	0.033
AT3C3	outside	12.23	14.66	1.92	1.85	0.99	0.928	1.74	1.15	0.254	0.106	0.383	0.068	0.182	0.108	0.044
AT3C4	outside	9.60	13.46	2.36	1.47	1.08	0.784	1.81	1.23	0.198	0.128	0.303	0.074	0.138	0.089	0.028
AT3C5	inside	9.30	14.72	2.41	1.43	1.11	0.829	1.77	1.25	0.150	0.117	0.315	0.066	0.105	0.094	0.034

Table 2b. REE and Y analyses of ferromanganese nodules from the Antarctic Ocean in wt. ppm of dried nodules substance.

sample name	divided parts	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Y (ppm)
AT101	outside	141.0	1156	33.1	129.5	25.9	5.78	24.8	4.24	22.8	4.39	12.1	1.67	11.5	1.67	74.9
AT102	inside	140.3	1150	34.6	132.1	26.6	5.80	25.1	4.38	23.0	4.56	12.3	1.70	11.7	1.68	77.0
AT103	outside	118.5	1078	31.7	122.0	24.6	5.53	22.7	4.11	21.3	4.05	11.6	1.61	10.8	1.55	68.9
AT104	outside	135.1	1135	31.6	124.5	25.2	5.63	23.4	4.13	21.4	4.29	11.8	1.66	10.9	1.62	71.3
AT2A1	outside	197.3	1469	45.6	191.3	36.2	8.62	36.0	5.90	32.2	6.05	17.0	2.22	14.8	2.11	102.5
AT2A2	middle	171.5	1377	40.1	161.8	33.2	7.47	30.9	5.44	28.0	5.33	15.0	1.97	13.3	1.91	89.9
AT2A3	inside	176.8	1457	43.1	172.7	34.8	8.04	32.7	5.54	30.3	5.67	16.1	2.20	14.7	2.12	93.2
AT2B1	outside	185.7	1382	43.4	174.5	34.8	8.26	34.3	5.91	30.3	5.74	16.0	2.04	13.9	2.01	97.1
AT2B2	middle	161.4	1348	39.9	157.6	32.2	7.28	29.9	5.27	27.0	5.28	14.6	1.97	13.1	1.91	86.3
AT2B3	inside	173.7	1416	42.3	164.8	33.3	7.71	32.0	5.67	29.0	5.57	15.5	2.09	13.6	1.97	91.7
AT3A1	outside	171.0	1429	42.9	171.3	34.1	8.15	32.7	5.22	29.2	5.40	15.1	2.01	13.8	2.20	87.0
AT3A2	middle	179.0	1337	41.3	167.3	32.7	7.86	32.0	5.19	27.8	5.11	14.2	1.78	12.4	1.98	84.9
AT3A3	inside	187.5	1358	45.7	180.1	36.0	8.46	33.9	5.43	30.3	5.49	15.3	2.01	14.1	2.24	88.9
AT3B1	outside	186.8	1397	43.2	177.8	34.6	8.37	34.4	5.52	29.7	5.61	15.3	1.90	13.5	2.18	93.7
AT3B2	inside	170.0	1355	40.1	160.8	31.0	7.61	31.0	5.02	27.1	5.02	14.0	1.78	12.7	2.02	83.0
AT3C1	outside	158.0	1300	39.2	159.0	31.1	7.47	30.2	4.92	26.7	4.99	13.9	1.80	12.7	1.89	84.0
AT3C2	outside	159.3	1263	39.2	157.4	31.3	7.70	31.3	5.26	27.4	5.13	14.3	1.92	13.0	1.94	87.2
AT3C3	outside	180.8	1302	43.1	172.1	33.9	8.33	33.8	5.61	29.2	5.47	15.3	1.99	13.6	2.11	94.5
AT3C4	outside	152.8	1282	37.3	150.5	29.2	7.14	29.1	4.87	25.2	4.71	13.2	1.72	12.0	1.83	79.9
AT3C5	inside	178.1	1422	43.3	179.0	36.8	8.21	34.1	5.79	30.8	5.64	16.3	1.99	14.2	2.10	89.4

RESULTS AND DISCUSSION

1. Mineralogical and chemical characteristics of Antarctic deep-sea nodules

X-ray powder diffraction data show that the Antarctic samples contain large amounts of quartz and phillipsite. Subsamples of AT1 exhibit much stronger diffraction peaks of phillipsite than the other samples. Calcite peaks were not recorded in the subsamples, even though the samples were collected above the CCD. In addition, no peaks of todorokite (10Å manganate) or vernadite ($\delta\text{-MnO}_2$) were recorded in X-ray powder diffraction. The strong peak of quartz (2.458Å) interferes with the vernadite peak (2.44Å) and any peaks of quartz or phillipsite interfere with todorokite peaks. The Antarctic nodules are accordingly deduced to be composed mainly of amorphous Fe-Mn materials. Mineralogically, they are similar to Pacific hydrogenous nodules, although they have rough surfaces similar to those of Pacific diagenetic nodules.

The Mn/Fe ratios of nodules and the triangular diagram of the Mn-Fe-(Ni+Cu) $\times 10$ contents are useful tools to classify ferromanganese nodules compositionally (Bonatti et al., 1972; Halbach et al., 1981). Figure 2 shows the Antarctic and Pacific nodules plotted on a three-component diagram of Mn-Fe-(Ni+Cu) $\times 10$. "Hydrogenous", "Diagenetic", and "Intermediate" in Fig. 2 indicate type names of different Pacific ferromanganese nodules. The Antarctic samples have lower (Ni+Cu) $\times 10$ concentrations and lower Mn/Fe ratios (0.736 ± 0.093) than Pacific hydrogenous ones and are

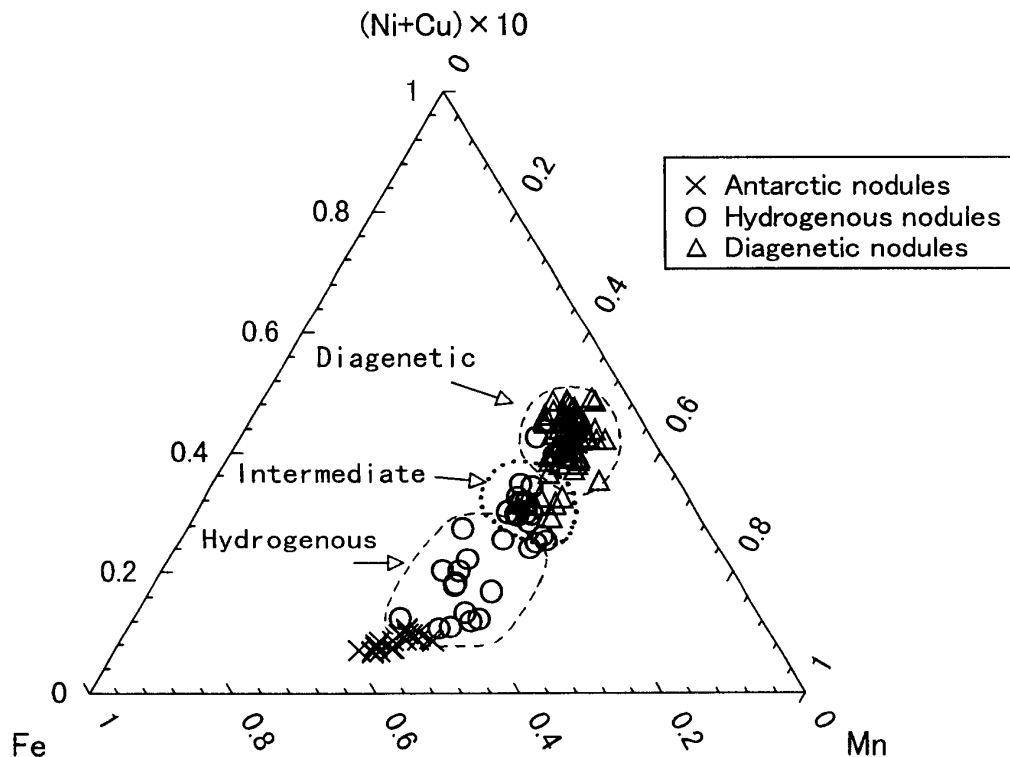


Fig. 2. The three-component diagram of Mn-Fe-(Ni+Cu) $\times 10$. "Hydrogenous", "Intermediate" and "Diagenetic" indicate the types of Pacific ferromanganese nodules, respectively. Data are taken from Calvert and Price (1977), Halbach et al. (1981), Dymond et al. (1984), Calvert et al. (1987), Guo and Sun (1992) and Ohta et al. (1999).

plotted between the Fe apex and the area of typical Pacific hydrogenous nodules. Usui et al. (1989) reported similar compositional data for Antarctic nodules collected from different sites. The Antarctic samples correspond to the hydrogenous type in view of X-ray powder diffraction data and the Mn-Fe-(Ni+Cu) $\times 10$ diagram. However, their slightly lower Mn/Fe ratios and Ni and Cu contents compared to Pacific hydrogenous nodules indicates a greater hydrogenous contribution to these nodules.

2. Characteristics of REE patterns of Antarctic deep-sea nodules compared with Pacific hydrogenous ones

Figure 3 shows REE patterns of the Antarctic samples normalized by C1 Chondrite. Typical Pacific hydrogenous deep-sea nodules for which analytical data are quoted from Ohta et al. (1999) are also plotted in Fig. 3. The REE data of C1 Chondrite values are taken from the mean values of Anders and Grevesse (1992). All the REE abun-

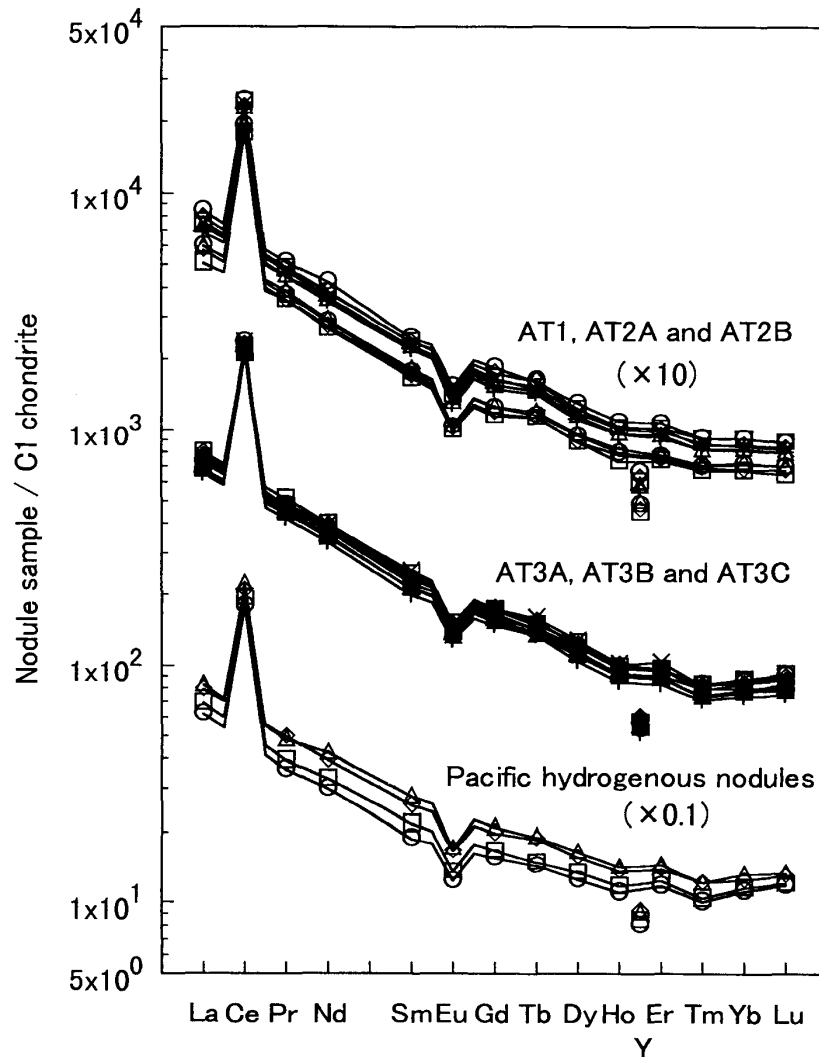


Fig. 3. The REE patterns of the Antarctic samples and Pacific hydrogenous nodules. All samples are normalized by C1 Chondrite (Anders and Grevesse, 1989).

dance patterns of the Antarctic samples are parallel to each other and are very similar to those of Pacific hydrogenous deep-sea nodules (Fig. 3). These patterns show light REE enrichment, fairly large Ce positive anomalies and small negative Eu anomalies.

The Y/Ho ratios of Antarctic samples (16.6 ± 0.4) are significantly smaller than the chondritic ratio (28.0). The Y/Ho ratios of Pacific hydrogenous and diagenetic nodule samples (19.6 ± 1.2 and 19.1 ± 0.9 , respectively, Ohta et al., 1999) and ferromanganese crust samples (20.4 ± 2.2 , Bau et al., 1996) are also smaller than the chondritic ratio. These data show the Y behaves differently from Ho in the marine environment, even though their ionic radii are almost the same. The small Y/Ho ratios of ferromanganese nodules and crusts could be interpreted by the difference of the ground-level electric configurations between Y^{3+} and Ho^{3+} (Kawabe et al., 1991; Ohta et al., 1999). The REE³⁺ ions are characterized by successive addition of fourteen 4f electrons to the Xe core of La^{3+} configuration. By contrast, Y^{3+} has neither 4f electron nor the Xe core.

3. Ce anomaly-Co/(Ni+Cu) diagram for nodules

Recently Ohta et al. (1999) have shown that the Ce anomalies and Co/(Ni+Cu) ratios of Pacific deep-sea nodule samples correlate positively with each other. Three major types of Pacific deep-sea nodules (hydrogenous, diagenetic and sub-oxic diagenetic) can be distinguished in the linear array. The correlation between these elements indicates how efficiently scavenged-type elements (Ce and Co) have been incorporated into ferromanganese nodules relative to nutrient-type elements (REE excepting Ce, Ni and Cu).

The Antarctic nodules are plotted on the diagram of Ce anomaly-Co/(Ni+Cu) ratio

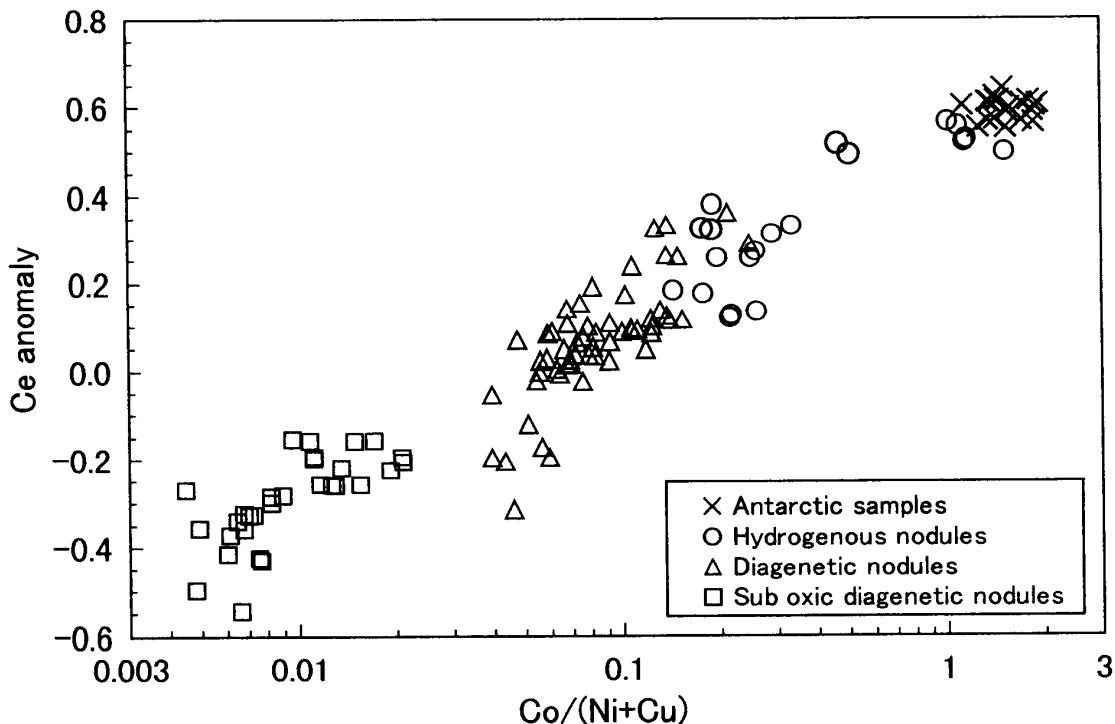


Fig. 4. Diagram shows the Ce anomaly versus the ratio of Co/(Ni+Cu). The data of Pacific ferromanganese nodules are from Ohta et al. (1999) and references therein.

for the Pacific deep-sea nodules (Fig. 4). Our REE data for Antarctic and Pacific nodules include Pr analyses, but most of the literature data of REE analyses for ferromanganese nodules do not include Pr analyses. Ce anomalies shown in Fig. 4 are calculated from the equation: $\log (Ce/Ce^*) = \log Ce_n - \{2\log La_n + \log Nd_n\}/3$. The suffix of “n” denotes the chondrite-normalized REE content.

The Antarctic nodules are plotted on the upper-right end of the array of Pacific nodules (Fig. 4). The Antarctic samples have the largest positive Ce anomalies and the highest ratios of Co/(Ni+Cu) of all the samples plotted. Ohta et al. (1999) inferred that the end-member material of hydrogenous nodules must be the suspended material of amorphous Fe-Mn oxyhydroxides with higher Ce anomalies (about +0.6) and Co/(Ni+Cu) ratios (about 1.5). This diagram indicates that those Antarctic nodules represent “hydrogenous” end-member materials. This geochemical result is related to the fact that Antarctic nodules are composed of amorphous Fe-Mn materials.

4. Some difference between hydrogenous deep-sea nodules from the Antarctic and the Pacific

The Antarctic nodules and Pacific hydrogenous nodules are similar in mineralogy and chemical composition. However, there are some differences between them. Figure 5 shows the average enrichment factors of various elements in the Antarctic nodules relative to Pacific hydrogenous nodules based on the average data for Pacific hydrogenous samples (D535) of Ohta et al. (1999). The chemical analyses of AT 1 samples are not included in calculating the averages, because the AT 1 samples have the relatively higher contents of Na, K and Al than the other subsamples due to large amounts of phillipsite $[(K,Na,Ca)_{2-4}(Al,Si)_{16}O_{32} \cdot 12H_2O]$ in the sample (Table 2a). The Antarctic nodules have higher Ti and K contents and lower V, Mn, Co, Ni, Cu, P, Ca, Mg, Lu and Y contents than the Pacific hydrogenous nodules. The contents of Fe, Al, Na, Sr, Ba, La and Gd of the Antarctic nodules are approximately the same as those of Pacific hydrogenous nodules. The Antarctic nodules are significantly deficient in Lu contents compared with Pacific hydrogenous nodules, whereas the La contents are similar. These differences in the REE patterns will be discussed later.

5. Abundances of P and some first-row transition metals in the Antarctic nodules

The Antarctic nodules show significantly lower concentrations of P and first-row transition metals except Fe and Ti relative to the Pacific hydrogenous ones (Fig. 5). P, Cu, Ni and V are classified as the nutrient-type elements (Chester, 1990). When biogenic materials are decomposed, nutrient-type metals are released into seawater and part of these elements is incorporated into particulate Fe-Mn oxyhydroxide materials. The lower concentrations of P, Cu, Ni and V in Antarctic nodules might imply low biogenic activity in Antarctic shallow water. However, the biogenic productivity around Antarctica is actually as high as in the equatorial Pacific (Tanoue et al., 1982; Chester, 1990). The total concentration of organic material of a sediment sample collected at the D1202 site where nodule sample AT1 was collected was analyzed to be 0.26% (JNOC unpublished data). The total concentration of organic material in the Antarctic sediment is rather high, since those of most oxic pelagic sediments associated with hydrogenous type nodules are less than 0.1% (Chester, 1990).

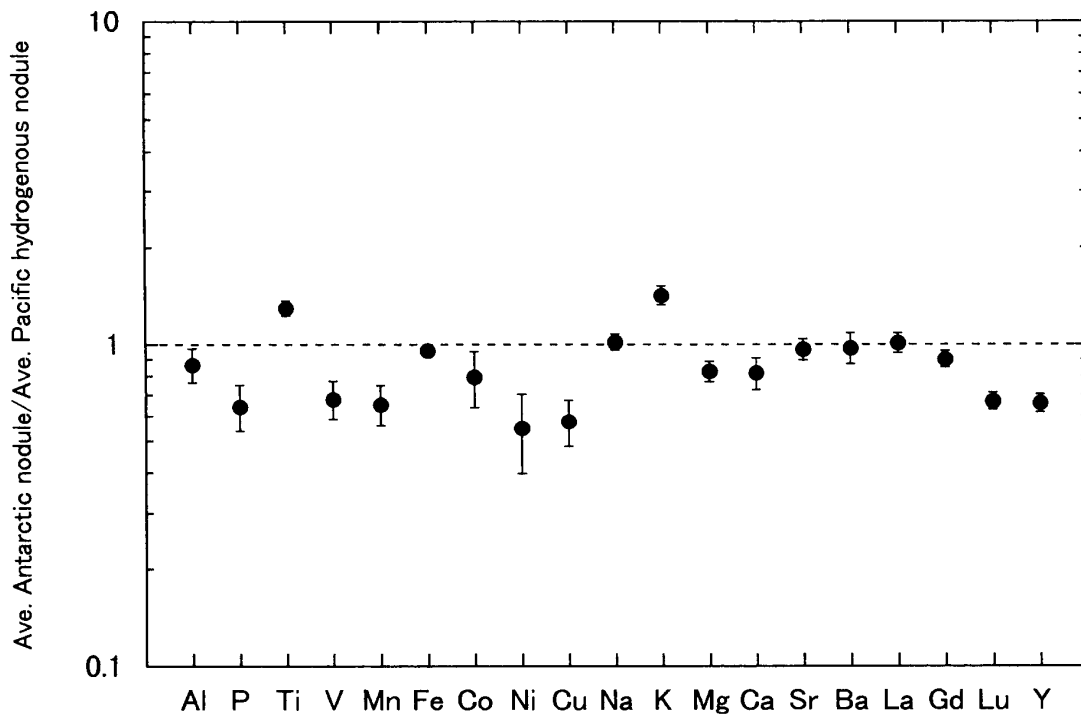


Fig. 5. The ratios of averaged element concentrations in the Antarctic nodules to those in the Pacific hydrogenous ones. Each bar indicates \pm one-sigma variation of each element concentration in the Antarctic samples.

The relatively lower concentrations of P, Cu, Ni and V in Antarctic nodules, therefore, indicate the subtle release of these elements from sediments, that is, there are little contribution of diagenetic materials. These elements once released with decomposition of biogenic materials are effectively recycled by the biogenic activity in water column. The highly oxidic water will form hydrogenous type nodules in Antarctic Ocean, even if the total concentration of organic material in the Antarctic sediments is rather higher than those of most oxidic pelagic sediments in the Pacific Ocean.

Manganese is a scavenged-type element in contrast to P, Cu, Ni and V, so we must consider another reason for Mn depletion in Antarctic ferromanganese nodules. Martin and Knauer (1983) reported that Mn in shallow water is transported with CaCO_3 (biogenic carbonate) into deep water and that the Mn fluxes are nearly constant with depth whereas CaCO_3 fluxes decrease with depth. They inferred that Mn adsorbed on CaCO_3 surface is released to the water column when enough CaCO_3 dissolved, because CaCO_3 surface area becomes insufficient. Although all Antarctic nodule samples lie above the CCD, there are no calcite peaks in X-ray powder diffraction data for these samples. We assume that Mn transported with CaCO_3 into deep water can not be incorporated into ferromanganese nodules but suspended Mn materials without CaCO_3 can be incorporated into ferromanganese nodules. Beneath the CCD, Mn suspended materials without CaCO_3 increase with the consumption of CaCO_3 . Halbach (1986) noted that the Mn/Fe ratios of ferromanganese nodules and crusts collected from a seamount slope beneath the CCD increase with water depth, and he emphasized that the Mn supply to ferromanganese nodules beneath the CCD increases with water depth. Our assumption is consistent with that of Halbach (1986). The lower Mn

contents of the Antarctic nodules compared to that of Pacific hydrogenous nodules may reflect the fact that these nodules were formed above the CCD.

6. The positive correlation between the Mn and Co contents

The Antarctic nodules show a good positive correlation between their Mn and Co contents, but there is no correlation between their Fe and Co contents (Fig. 6). There have previously been reports of similar positive correlations between Mn and Co

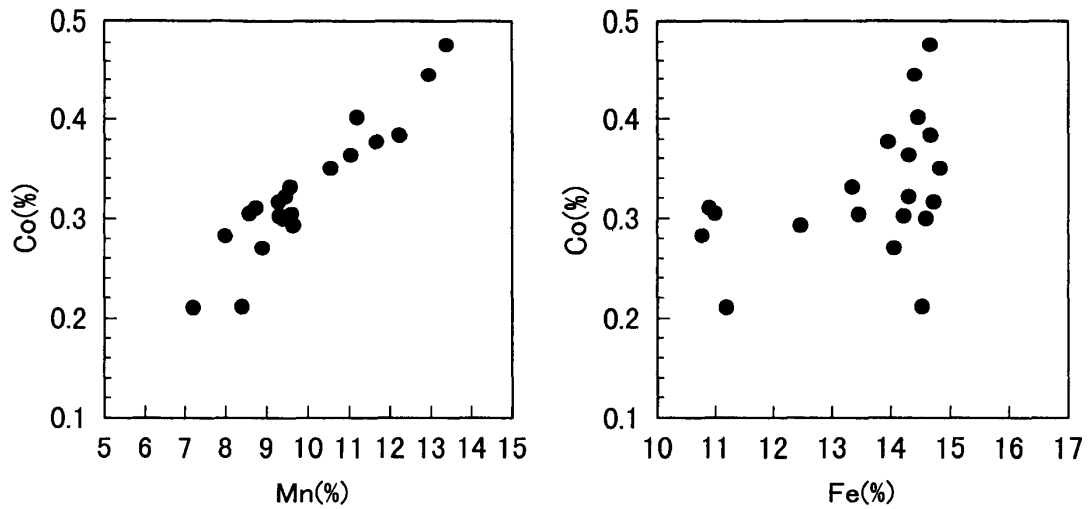


Fig. 6. The relationships between the Co content and the Mn and Fe contents in the Antarctic deep-sea nodules.

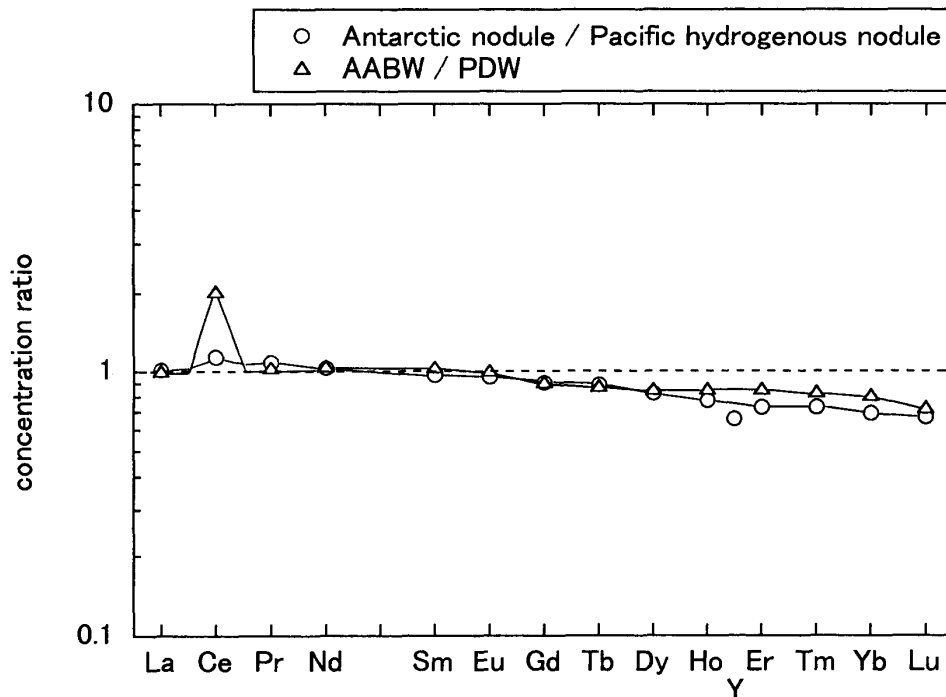


Fig. 7. The REE abundances of the average Antarctic nodules relative to Pacific hydrogenous nodules (open circles). Open triangles show the REE abundances of AABW (Antarctic Bottom Water) relative to PDW (Pacific Deep Water).

contents in ferromanganese crusts (Friedrich and Schmitz-Wiechowski, 1980; Aplin and Cronan, 1985). However, the Co content does not correlate with the Mn content in many Pacific hydrogenous and diagenetic nodules (Halbach et al., 1981; Halbach et al., 1982; Dymond et al., 1984; Glasby et al., 1987; Usui et al., 1987). Murray and Dillard (1979) and Dillard et al. (1982) studied the oxidation states of Co in Pacific ferromanganese hydrogenous nodules by X-ray photoelectron spectroscopy (XPS) and reported that Co(III) is a more dominant species than Co(II). They concluded that Co(II) is oxidized to Co(III) on the surface of δ -MnO₂ based on these data.

Vernadite (δ -MnO₂) is the principal Mn mineral found in ferromanganese crusts just as in hydrogenous nodules (Friedrich and Schmitz-Wiechowski, 1980; Aplin and Cronan, 1985). Ferromanganese crusts are not associated with sediments. The growth condition of such crusts differs from that of Pacific hydrogenous nodules. Even in the case of Pacific hydrogenous nodules, Mn is supplied from the overlying water column and from the water-sediment interface. In the case of the Antarctic nodules, however, Mn must be supplied directly from the overlying water column. The Mn recycled at the water/sediment interface probably contributes little to the Antarctic samples because of the high concentrations of dissolved O₂ in seawater and their formation above the CCD. This possibly explains the positive correlation between the Mn and Co contents in the Antarctic nodules as observed also in ferromanganese crusts.

7. REE patterns of deep-sea nodules reflecting REE characteristics of bottom water

Although REE patterns of the Antarctic nodules resemble those of Pacific hydrogenous nodules, there are some differences. Figure 7 indicates that the REE concentration ratios lie between the average REE analyses of Antarctic samples and Pacific hydrogenous ones. As mentioned above, the REE analyses of AT 1 samples are not included because their samples contain large amounts of phillipsite. The Antarctic nodules have similar average concentrations of light REE but lower average concentrations of heavy REE than the Pacific hydrogenous nodules (Fig. 7). This feature can also be seen between REE analyses of Antarctic Bottom Water (AABW) and Pacific Deep Water (PDW), although AABW have much higher Ce content than PDW (Fig. 7). The REE concentrations of AABW and PDW are taken from Kawabe et al. (1998), but there are no Y data of both AABW and PDW. Figure 7 reveals that the REE abundance patterns for deep-sea nodules reflect the composition of different types of bottom water.

In addition, the average Y/Ho ratio of the Antarctic nodules (16.6 ± 0.4) is slightly smaller than those of Pacific hydrogenous nodules (19.6 ± 1.2). The average Y concentration ratio of deep-sea nodules from the Antarctic to those from the Pacific is 0.66, but the average ratio of Ho in the Antarctic samples to Ho in the Pacific ones is 0.75. It is conceivable that Antarctic deep seawater has a lower Y concentration than Pacific deep seawater.

SUMMARY

(1). Antarctic ferromanganese nodules are similar to Pacific hydrogenous nodules on the basis of their mineralogy and position in the Mn-Fe-(Ni+Cu)×10 ternary dia-

gram, although their morphological features are similar to those of Pacific diagenetic nodules. The chondrite-normalized REE patterns of Antarctic samples indicate light REE enrichment, large positive Ce anomalies, negative Eu anomalies and lower Y/Ho ratios. Their REE patterns resemble those of Pacific hydrogenous nodules. Antarctic nodules have Ce anomalies and Co/(Ni+Cu) ratios even slightly larger than those of Pacific hydrogenous nodules. The Antarctic nodules can represent the hydrogenous end member material.

(2). There are some chemical differences between deep-sea nodules from the Antarctic and Pacific Ocean. The Mn, P, Cu, Ni and V contents of Antarctic nodules are lower than those of Pacific ones. This deficiency of Mn, P, Cu, Ni and V is probably caused by a relatively high decomposition rate of organic materials in the highly oxic water in the Antarctic Ocean and by the formation of the nodules shallower than the CCD. The Antarctic nodules show a good positive correlation between their Mn and Co contents unlike the Pacific hydrogenous nodules. We inferred that Mn components of Antarctic nodules were supplied by the overlying water column, and that they involve little or no regenerated Mn contribution from the sediment/water interface.

(3). The REE concentration ratios between the Antarctic nodules and Pacific hydrogenous ones are almost exactly the same as those between AABW and PDW. Chemical compositions of ferromanganese nodules indeed reflect the REE characteristic of bottom water involving deep-sea nodule formation.

ACKNOWLEDGMENT

Antarctic research cruises of R/V Hakurei-maru were conducted by Japan National Oil Corporation sponsored by Ministry of International Trade and Industry (MITI), Japan. We thank MITI for permitting us to publish this paper. We also thank the on-board scientists and crew members for their works during the TH91 Cruise of R/V Hakurei-maru, and Dr. M. ENAMI who gave advice on X-ray diffractometry.

REFERENCES

- Anders, E. and Grevesse, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta*, **53**, 197–214.
- Aplin, A. C. and Cronan, D. S. (1985) Ferromanganese oxide deposits from the Central Pacific Ocean, I. Encrustations from the Line Islands Archipelago. *Geochim. Cosmochim. Acta*, **49**, 427–436.
- Bau, M., Koschinsky, A., Dulski, P. and Hein, J. R. (1996) Comparison of the partitioning behaviors of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese crusts and seawater. *Geochim. Cosmochim. Acta*, **60**, 1709–1725.
- Bonatti, E., Kraemer, T. and Rydell, H. (1972) Classification and genesis of submarine iron-manganese deposits. In: *Ferromanganese Deposits on the Ocean Floor*, (ed. D. R. Horn), Washington D. C., 149–166.
- Calvert, S. E. and Price, N. B. (1977) Geochemical variation in ferromanganese nodules and associated sediments from the Pacific Ocean. *Mar. Chem.*, **5**, 43–74.
- Calvert, S. E., Piper, D. Z. and Baedeker, P. A. (1987) Geochemistry of the rare earth elements in ferromanganese nodules from DOMES Site A, northern equatorial Pacific. *Geochim. Cosmochim. Acta*, **51**, 2331–2338.
- Chester, R. (1990) *Marine geochemistry*. Unwin Hyman Ltd, 698 pp.

- Dillard, J. G., Crowther, D. L. and Murray, J. W. (1982) The oxidation states of cobalt and selected metals in Pacific ferromanganese nodules. *Geochim. Cosmochim. Acta*, **46**, 755–759.
- Dymond, J., Lyle, M., Finney, B., Piper, D. Z., Murphy, K., Conard, R. and Pisias, N. (1984) Ferromanganese nodules from MANOP Sites H, S, and R—Control of mineralogical and chemical composition by multiple accretionary processes. *Geochim. Cosmochim. Acta*, **48**, 931–949.
- Elderfield, H., Hawkesworth, C. J., Greaves, M. J. and Calvert, S. E. (1981) Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments. *Geochim. Cosmochim. Acta*, **45**, 513–528.
- Friedrich, G. and Schmitz-Wiechowski, A. (1980) Mineralogy and chemistry of a ferromanganese crust from a deep-sea hill, Central Pacific, “VALDIVIA” CRUISE VA 13/2. *Mar. Geol.*, **37**, 71–90.
- Glasby, G. P., Gwozdz, R., Kunzendorf, H., Friedrich, G. and Thijssen, T. (1987) The distribution of rare earth and minor elements in manganese nodules and sediments from the equatorial and S. W. Pacific. *Lithos*, **20**, 97–113.
- Goldberg, E. D., Koide, M., Schmitt, R. A. and Smith, R. H. (1963) Rare-earth distributions in the marine environment. *J. Geophys. Res.*, **68**, 4209–4217.
- Guo, S. and Sun, W. (1992) Rare earth elements in manganese nodules from the Central Pacific Ocean. *Acta Geol. Sinica*, **66**, 135–147.
- Halbach, P., Scherhag, C., Hebisch, U. and Marchig, V. (1981) Geochemical and mineralogical control of different genetic types of deep-sea nodules from the Pacific Ocean. *Mineral. Deposita*, **16**, 59–84.
- Halbach, P., Giovanoli, R. and Borstel, D. V. (1982) Geochemical processes controlling the relationship between Co, Mn, and Fe in early diagenetic deep-sea nodules. *Earth Planet. Sci. Lett.*, **60**, 226–236.
- Halbach, P. (1986) Processes controlling the heavy metal distribution in Pacific ferromanganese nodules and crusts. *Geol. Rund.*, **75**, 235–247.
- Kawabe, I., Kitahara, Y. and Naito, K. (1991) Non-chondritic yttrium/holmium ratio and lanthanide tetrad effect observed in pre-Cenozoic limestone. *Geochem. J.*, **25**, 31–44.
- Kawabe, I., Toriumi, T., Ohta, A. and Miura, N. (1998) Monoisotopic REE abundances in seawater and the origin of seawater tetrad effect. *Geochem. J.*, **32**, 213–229.
- Martin, J. H., and Knauer, G. A. (1983) VERTEX: Manganese transport with CaCO₃. *Deep-Sea Res.*, **30**, 411–425.
- Murray, J. W. and Dillard, J. G. (1979) The oxidation of cobalt(II) adsorbed on manganese dioxide. *Geochim. Cosmochim. Acta*, **43**, 781–787.
- Ohta, A., Ishii, S., Sakakibara, M., Mizuno, A. and Kawabe, I. (1999) Systematic correlation of the Ce anomaly with the Co/(Ni+Cu) ratio and Y fractionation from Ho in distinct types of Pacific deep-sea nodules. *Geochem. J.*, **33**, 399–417.
- Piper, D. Z. (1974) Rare earth elements in ferromanganese nodules and other marine phases. *Geochim. Cosmochim. Acta*, **38**, 1007–1022.
- Tanoue, E., Handa, N. and Kato, M. (1982) Horizontal and vertical distributions of particulate organic matter in the Pacific sector of the Antarctic Ocean. *Trans. Tokyo Univ. Fish.*, **5**, 65–83.
- Usui, A. (1983/84) Regional variation of manganese nodule faces on the WAKE-TAHITI transect: Morphological, chemical and mineralogical study. *Mar. Geol.*, **54**, 27–51.
- Usui, A., Mizuno, A., Moritani, T. and Nakao, S. (1987) Manganese nodules in the northern and central parts of the Central Pacific Basin—Results of the “Basic Study on Exploration of Deep Sea Mineral Resources”. *Bull. Geol. Surv. Japan*, **38**, 539–585.
- Usui, A., Terashima, S., Tokuhashi, S., Kodato, T. and Machihara, S. (1989) Composition of ferromanganese nodules and crusts off the Queen Maud Land and the Wilkes Land, East Antarctica. *Report of the Technology Research Center, J.N.O.C.*, **22**, 15–26.