XVIII. METAL CONTENTS OF MANGANESE NODULES FROM THE GH79-1 AREA

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Mn, Fe, Ni, Cu, Co, Pb, Zn, and H_2O were analysed for 67 samples of manganese nodules obtained during the GH79–1 Cruise, and the chemical characteristics of nodules are discussed on the basis of the analytical data.

Sample preparation and analytical procedure

Sample preparation method applied is the same as the previous ones for the GH77–1 Cruise samples (MORITANI *et al.*, 1979). All nodules were immersed in running water and then ion-free water. After air-dried, samples were ground to under 150 mesh. The ground samples were encased in small paper bags, dried at 20–25°C for 24 hours, and then kept in a desiccator. In most cases an analysis was done for mixed ground sample of two or three different size classes of nodules from each box corer or freefall grab.

Mn, Fe, Ni, Cu, Co, Pb, and Zn were determined by atomic absorption spectrometry (TERASHIMA, 1978). Outline of the procedures is given below.

Sample of 0.1 g was decomposed with a mixture of 5 ml of hydrochloric acid and 5 ml of nitric acid in a covered 50 ml beaker on a boiling water bath for about 30 minutes. After cooling, the solution was filtered into a 100 ml calibrated flask and diluted to the mark with water.

The atomic absorbance of each element in the sample solution was measured by atomic absorption spectrometer using an air-acetylene flame. The concentration of each element was determined from a calibration graph, which was prepared using a series of synthetic standard solutions that has a composition similar to the sample solution.

The total water was analyzed gravimetrically as reported in the previous work (FUJINUKI *et al.*, 1977).

Results and discussion

Results

The contents of Mn, Fe, Ni, Cu, Co, Pb, Zn, and $\pm H_2O$, and the ratio of Mn/Fe in sixty-seven nodule samples are given in Table XVIII-1.

General aspect

Table XVIII-2 presents an average of the contents in the survey area and the reported averaged values for manganese nodules in the Pacific Ocean including the Central Pacific Basin. The average value in the survey area is in nearly same order for Mn, Ni, and Cu, whereas fairly lower for Fe, as compared with the GH77–1 (MORITANI *et al.*, 1979) and GH78–1 (MORITANI *et al.*, preparation) areas. This results in higher Mn/Fe ratio in manganese nodules in the survey area. The GH76–1 area nodules (FUJINUKI *et al.*, 1977)

Table XVIII-1 Chemical composition of manganese nodules from the GH 79-1 cruise.

Analysts: T. Mochizuki and S. Terashima

No.	Station No.	Sample No.	Water Depth (m)	Size	type	Mn (%)	Fe (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	$\pm H_2O$ (%)	Mn/Fe
1	1448	G(B)915	5171	1–2, 2–4, 4–6	DPs	19.58	10.53	0.71	0.41	0.26	630	813	21.80	1.859
2	1449	G(B)916(A)	3957	1–2	Ss	19.10	13.12	0.38	0.40	0.42	848	846	25.01	1.455
3	1451	FG118C-1	5502	2–4, 4–6	IDPs	10.92	7.32	0.37	0.23	0.15	420	451	14.36	1.495
4	1451	FG118C-2	5484	2–4, 4–6	DPs	16.77	9.46	0.58	0.33	0.23	560	711	20.16	1.772
5	1452	FG119-1	5526	2–4	SPs	19.46	10.74	0.62	0.40	0.29	623	660	21.45	1.811
6	1452	FG119-2	5536	1–2, 2–4	IDPs	8.35	9.04	0.65	0.19	0.11	280	479	15.32	0.923
7	1453	G(B)920	5690	2–4, 4–6	DPr	21.43	9.04	0.75	0.58	0.29	469	790	20.85	2.370
8	1453	FG120-1	5729	1–2, 2–4	IDPs	3.10	8.25	0.11	0.10	0.03	112	228	11.40	0.375
9	1454	G(B)921	5350	1–2, 2–4	DPs	19.04	12.02	0.54	0.40	0.28	701	601	23.23	1.584
10	1455	G(B)922	5557	1–2, 2–4, 4–6	DPs	17.97	10.84	0.57	0.40	0.25	630	649	21.32	1.657
11	1456	FG123-2	5407	4–6	Sr(s)	17.73	9.04	0.66	0.54	0.20	504	717	18.76	1.961
12	1456	FG123C-1	5407	1–2, 2–4	Sr(s)	20.77	8.01	0.85	0.73	0.20	434	931	18.62	2.593
13	1457	G(B)924	5380	1–2, 2–4, 4–6	DPs	16.71	10.63	0.56	0.35	0.23	567	629	18.88	1.571
14	1458	G(B)925	5900	2–4, 4–6	DPs	9.25	9.32	0.43	0.32	0.09	119	513	14.46	0.992
15(A)	1459	G(B)926	5630	1–2, 2–4	DPs	17.42	13.12	0.42	0.26	0.29	644	542	20.88	1.327
15(B)	1459	G(B)926	5630	1–2, 2–4	DPs	17.37	12.98	0.42	0.25	0.30	665	532	20.11	1.338
16	1460	G(B)927	5184	2–4, 6–8	DPs	18.68	11.74	0.49	0.33	0.29	701	612	23.14	1.591
17	1461	FG128C-1	5514	2–4, 4–6	Ss/SPs	18.74	13.26	0.39	0.24	0.39	771	522	26.04	1.413
18	1462	G(B)929	4846	1–2	Sr	14.98	8.77	0.64	0.41	0.18	434	708	17.93	1.708
19(A)	1463	G(B)930	5766	2–4, 4–6	SPs	18.94	13.53	0.40	0.24	0.36	806	564	22.84	1.399
19(B)	1463	G(B)930	5766	2–4	SPs	18.64	13.64	0.41	0.27	0.36	841	623	22.64	1.369
19(C)	1463	G(B)930	5766	2–4	SPs	18.50	13.46	0.41	0.25	0.39	841	592	24.45	1.374
20	1464	G(B)931	5775	2–4, 4–6	Ds	19.22	12.78	0.52	0.36	0.34	778	621	21.74	1.503
21	1465	G(B)932	5385	2–4	SPs	18.38	12.26	0.53	0.32	0.31	715	635	21.17	1.499
22	1466	G(B)933	5449	2–4	SPr/Sr	20.41	7.25	0.82	0.73	0.20	420	990	17.30	2.815
23	1467	FG134-1	5227	2–4	Sr	22.68	8.01	0.93	0.76	0.23	504	1004	19.50	2.831
24	1468	FG135C-2	5314	2–4	Sr	23.76	7.59	1.02	0.88	0.21	469	1078	19.09	3.130
25	1469	FG136C-1	5357	1–2	Sr	16.29	6.63	0.68	0.49	0.15	294	869	15.33	2.457
26	1470	G(B)937	5384	2–4, 4–6, 6–8	IDPs(r)	13.61	9.73	0.49	0.32	0.27	567	564	18.40	1.398

Table XVIII-1 (Continued)

No.	Station No.	Sample No.	Water Depth (m)	Size	type	Mn (%)	Fe (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	$\pm H_2O$ (%)	Mn/Fe
27	1471	FG138-1	5205	2–4	SPs	13.67	11.43	0.34	0.24	0.30	708	570	20.03	1.195
28	1472	G(B)939	5366	2–4, 4–6	V	7.99	6.90	0.26	0.11	0.13	399	395	11.83	1.157
29	1473	G(B)940	4992	1–2, 2–4, 4–6	SPr	23.58	7.39	1.02	0.81	0.23	420	1106	20.32	3.190
30	1475	FG142C-1	5195	1–2	Sr	24.41	4.56	1.18	1.05	0.12	280	1213	18.95	5.353
31	1476	FG143C-2	5160	2–4	Sr/SPr	23.82	5.35	1.06	1.01	0.14	336	1134	17.82	4.452
32	1477	G(B)944	5197	1–2	SPr	23.78	4.69	1.06	0.88	0.15	336	1371	17.80	4.963
33	1479	G(B)946	5259	1–2	Dr	25.73	4.69	0.92	0.72	0.17	294	1228	17.10	5.486
34	1480	G(B)947	5256	2–4	SPr	18.26	8.29	0.69	0.62	0.23	518	770	19.73	2.202
35	1481	G(B)948	5287	2–4	DPs(r)	18.20	10.18	0.65	0.46	0.25	630	683	20.13	1.787
36	1482	G(B)949	5222	1–2, 2–4	SPr	22.74	5.21	1.09	0.97	0.15	350	1129	17.40	4.364
37	1483	G(B)950	5211	1–2, 2–4	SPr	23.34	5.62	1.13	0.96	0.18	371	1171	18.26	4.153
38	1484	G(B)951	5244	1–2, 2–4	SPr	23.22	5.87	1.10	0.99	0.18	378	1100	18.31	3.955
39	1486	D315	1609	2–4	IDPs	26.92	9.80	0.69	0.03	1.39	1612	663	25.73	2.746
40	1487	FG159C-1	5608	2–4, 4–6	DPs	19.10	11.25	0.63	0.40	0.30	651	604	21.06	1.697
41	1488	FG160C-2	5538	2–4	IDPs	20.47	11.77	0.61	0.44	0.32	701	646	22.56	1.739
42	1489	G(B)953	5370	4–6, 6–8	Ss	18.50	12.77	0.40	0.22	0.40	848	485	25.22	1.448
43	1490	G(B)954	4877	1–2, 2–4	DPs	22.08	11.39	0.72	0.42	0.37	841	736	22.28	1.938
44	1491	G(B)955	4517	2–4	DPs	20.29	12.43	0.65	0.35	0.40	932	705	22.68	1.632
45	1492	G(B)956	4239	1–2	V	13.97	11.05	0.34	0.19	0.31	693	516	22.31	1.264
46	1452-A	FG158C-2	5291	2–4, 4–6	DPs	15.28	12.26	0.25	0.20	0.32	701	457	21.12	1.246
47	1481-A	FG153C-2	5291	4–6	IDPs	18.92	12.95	0.69	0.48	0.25	581	705	20.70	1.461
48	1481-A-1	FG154C-1	5300	2–4, 4–6	SPs	18.38	11.22	0.61	0.41	0.26	637	649	19.89	1.638
49(A)	1481-A-1	FG154C-2	5293	2–4, 4–6	SPs	20.23	9.87	0.70	0.51	0.25	602	694	19.79	2.049
49(B)	1481-A-1	FG154C-2	5293	2–4	SPs	18.56	10.01	0.66	0.48	0.23	546	691	19.74	1.854
50	1481-A-1	FG154C-3	5301	2–4, 4–6	SPs	14.32	7.97	0.54	0.44	0.16	434	592	17.78	1.796
51	1481-A-1	GF154C-4	5284	2–4	SPs	19.70	8.22	0.86	0.71	0.23	490	838	19.56	2.396
52	1481-A-1	FG154C-5	5272	1–2, 4–6	SPs	19.99	8.46	0.90	0.76	0.23	525	883	19.23	2.362
53	1481-A-1	FG154C-6	5253	1–2, 2–4	SPs	21.31	8.28	0.95	0.77	0.23	490	903	19.10	2.574
54	1481-A-1	GF154C-7	5247	1–2, 2–4	SPr	22.08	7.63	0.99	0.91	0.23	574	1004	18.53	2.893
55	1481-A-1	FG154C-8	5249	1–2, 2–4	SPr(s)	22.38	7.77	0.99	0.85	0.23	490	988	18.38	2.880

Table XVIII-1 (Continued)

No.	Station No.	Sample No.	Water Depth (m)	Size	type	Mn (%)	Fe (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	$\pm H_2O$ (%)	Mn/Fe
56	1481-A-1	FG154C-9	5254	1–2, 2–4	SPr	23.64	5.94	1.12	0.98	0.19	336	1157	17.78	3.979
57	1481-A-1	FG154C-10	5251	1–2, 2–4	SPr	23.28	6.56	1.05	0.93	0.19	357	1103	17.76	3.548
58	1481-A-2	FG156C-1	5293	2–4	SPs	13.73	7.39	0.59	0.43	0.15	350	567	17.72	1.857
59	1481-A-2	FG156C-4	5269	1–2, 2–4	SPs	20.59	8.01	0.95	0.76	0.21	434	877	18.36	2.570
60	1484-A-1	FG155C-1	5251	1–2, 4–6	SPr	21.67	7.94	0.93	0.85	0.20	441	965	18.85	2.729
61	1484-A-1	FG155C-2	5248	1–2	SPr	23.52	5.87	1.09	0.99	0.17	350	1134	17.41	4.006
62	1484-A-1	FG155C-3	5242	1–2, 2–4	Sr	23.52	4.90	1.13	1.02	0.15	294	1281	17.25	4.800
63	1484-A-1	FG155C-4	5237	2–4	Vr	6.08	3.55	0.32	0.30	0.03	98	465	8.69	1.712

Table XVIII-2 Comparison of average values.

	This work	MORITANI *et al.* (in preparation)	MORITANI *et al.* (1979)	FUJINUKI *et al.* (1977)	CRONAN (1974)	MERO (1962)
Number of sample	67	64	118	68		54
Mn %	18.72	19.61	17.48	23.54	19.75	24.2
Fe %	9.12	12.15	11.28	7.52	14.29	14.0
Ni %	0.69	0.61	0.56	0.97	0.722	0.99
Cu %	0.54	0.44	0.44	0.95	0.366	0.53
Co %	0.25	0.36	0.27	0.19	0.381	0.35
Pb ppm	542	720	648	348		900
Zn ppm	770	670	645	1170		470
$H_2O\pm$ %	19.20	19.36	23.12	20.74		25.8*
Mn/Fe	2.05	1.61	1.55	3.13		1.73

*represented as loss on ignition.

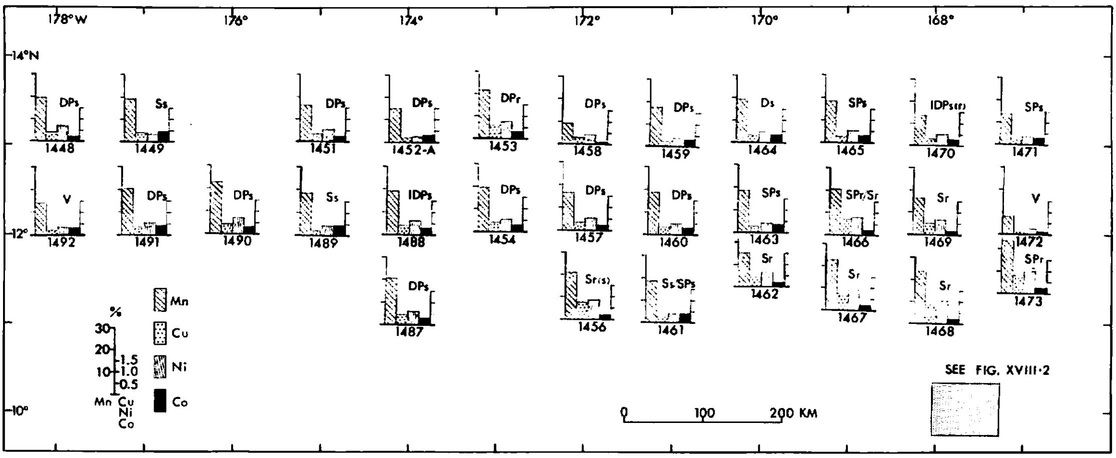

Fig. XVIII-1 Regional distribution of metal contents in the GH79-1 main survey area.

have higher average value of Mn, Ni, Cu, and Mn/Fe than the survey area. Those point to the regional variability of the averaged metal contents of the Central Pacific Basin nodules, which may be related to nodule type and/or bathymetric or geographic situation of nodule occurrence.

Geographic and bathymetric distribution of metal contents

A geographic variation of the metal contents exists within the GH79-1 area. The distribution of Mn, Ni, Cu, and Co seems to be generally irregular throughout the main survey area, except for its southeastern part where Mn, Ni, and Cu are more enriched but Co is less concentrated (Fig. XVIII-1). In the detailed survey area, a small area centered at 10°N, 167°40'W, the metals are rather uniformly concentrated, but some regular variation of the metal contents can be found along the 10°N survey line, represented by eastward increase of Mn, Ni, and Cu and decrease of Co in the same direction (Fig. XVIII-2).

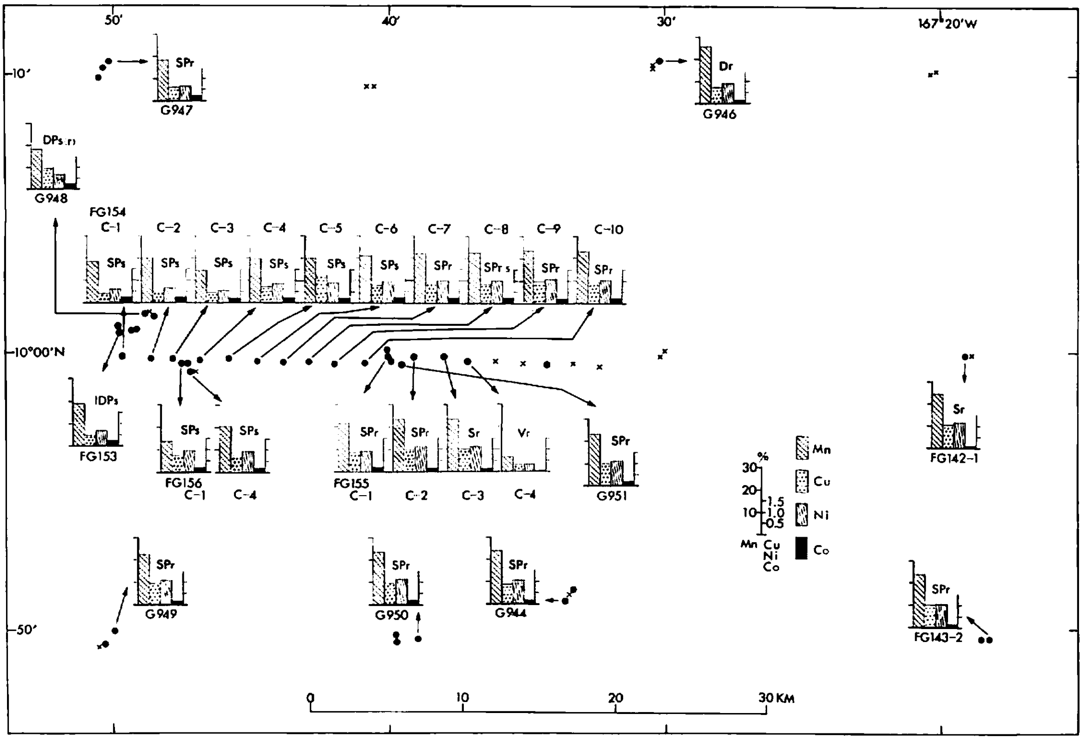

Fig. XVIII-2 Local distribution of metal contents in the GH79-1 detailed survey area.

The geographic variation may be partly related to a bathymetric situation of nodule occurrence. Figure XVIII-3 indicates that the concentration of each metal of nodules at depths of 4,900 m to 5,900 m, varies in a wide range, whereas tends to be restricted to relatively narrow range at depths above 4,800 m. We can recognize a marked upward increase of Co and Pb concentrations. No particular trend of upward increase or decrease of concentration is found for the other elements. The problem of metal concentration in relation to a depth of water will be discussed elsewhere in addition with the data from the other areas in the Central Pacific Basin.

Relationship between metal contents, nodule types, and abundance

The geographic variation of the metal contents may have been partly caused by a particular relationship between nodule types and metal contents. Table XVIII-3 shows the average metal contents of each type of nodule. In the table, the data of DPr, Dr, Vr, and Ds types are added only for reference, because the limited number of analyses may not permit adequate proof for interpretation. Despite that, definite relationship between nodule type and chemical composition is recognizable for all the types excluding Vr and V. Mn, Ni, Cu, and Zn are more enriched in Sr, SPr, SPr(s), DPr, and Dr, which have poorer contents of Fe, Co, and Pb than IDPs, IDPs(r), Ss/SPs, Ds, and DPs. This results in an apparent difference of mean values of each metal and Mn/Fe ratio (Fig. XVIII-4) between the whole r- and s-type nodules. Vr and V types are exceptionally low

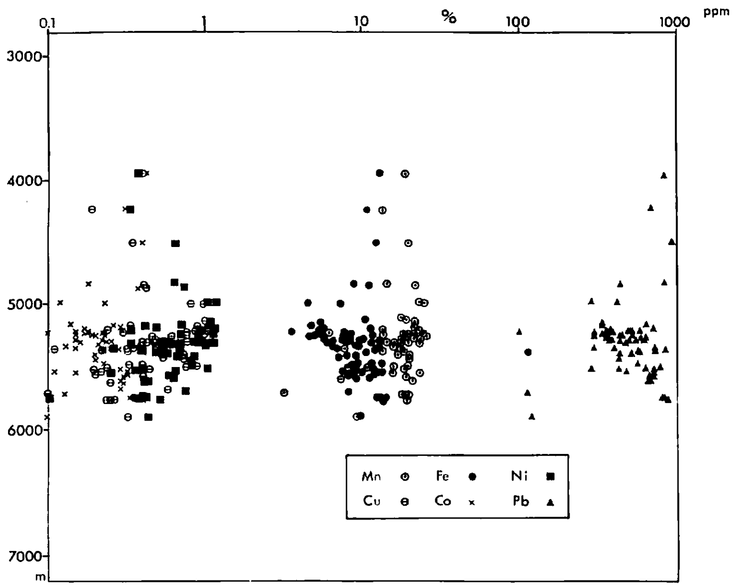

Fig. XVIII-3 Distribution of metal contents of nodules in depths of water.

Table XVIII-3 Average metal contents and Mn/Fe ratio of each type nodule.

Type	Mn %	Fe %	Ni %	Cu %	Co %	Pb ppm	Zn ppm	Mn/Fe	Numbers of sample
Sr	20.93	6.74	0.93	0.76	0.17	379	1025	3.38	6
Spr	22.55	6.38	1.01	0.89	0.18	397	1074	3.66	13
Spr(s)	20.29	8.27	0.83	0.70	0.21	476	878	2.48	3
Dpr	21.43	9.04	0.75	0.58	0.29	469	790	2.37	1
Dr	25.73	4.69	0.92	0.72	0.17	294	1228	5.49	1
Vr	6.08	3.55	0.32	0.30	0.03	98	465	1.71	1
IDPs(r)	16.93	10.39	0.57	0.39	0.26	614	636	1.62	3
Ss/Sps	18.39	10.53	0.60	0.44	0.26	623	684	1.82	18
Ds	19.22	12.78	0.52	0.36	0.34	778	621	1.50	1
IDPs	15.16	9.86	0.48	0.28	0.17	418	501	1.20	6
DPs	17.63	11.42	0.53	0.33	0.28	642	621	1.55	12
V	10.98	8.97	0.30	0.15	0.22	546	455	1.21	2
r-type*	22.19	7.02	0.89	0.73	0.20	403	999	3.46	24
s-type*	17.47	11.00	0.54	0.36	0.26	615	613	1.54	40

*except for Vr and V.

in some elements. This may be related to that the Vr and V type nodules have a manganese oxide layer thinly coating relatively large nucleus.

Ni plus Cu grade thus related to nodule type has a particular correlation with nodule abundance. Although each type does not show a definite distribution, the whole r-type and whole s-type are largely separated into two areas on Fig. XVIII-5 which shows a correlation between Ni plus Cu grade and abundance of nodules and their relation to nodule types. Generally, nodules with higher Ni plus Cu grade and rough surface occur

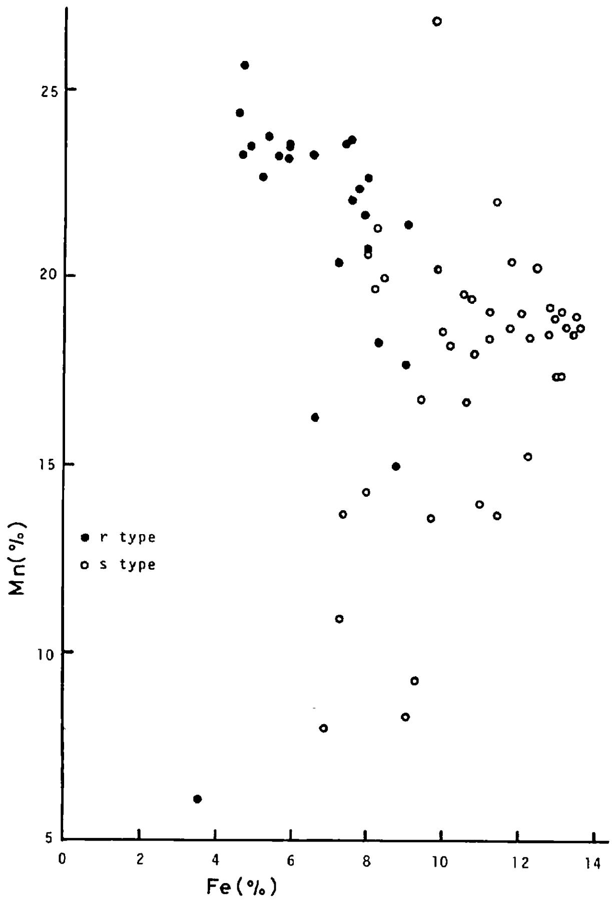

Fig. XVIII-4 Relation between Mn and Fe contents and nodule types.

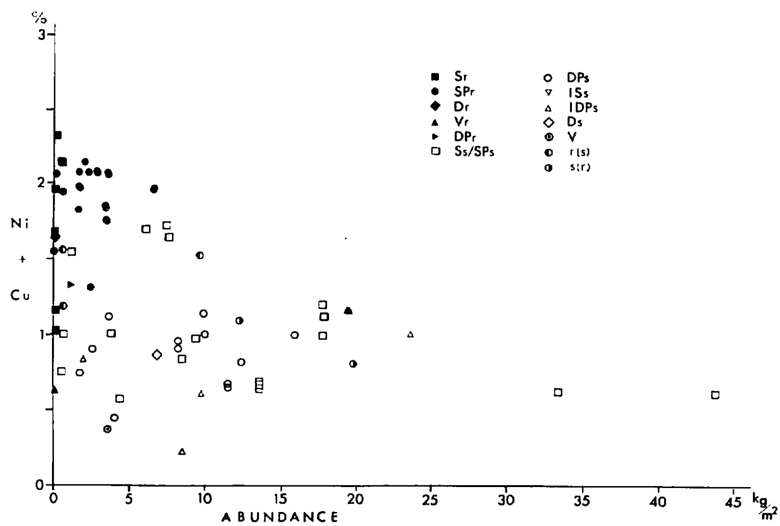

Fig. XVIII-5 Correlation between Ni plus Cu grade and abundance of manganese nodules.

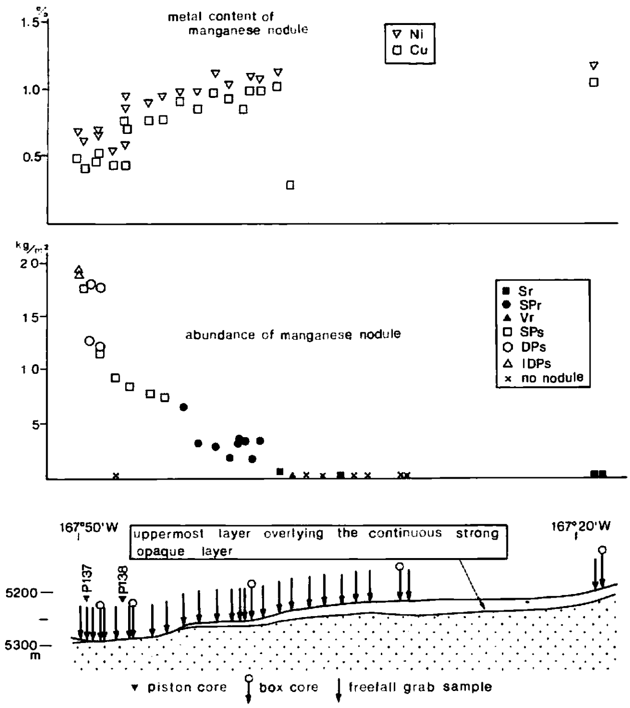

Fig. XVIII-6 Variability of manganese nodules along the survey line, 10°N, 167°50′ to 167°20′W, in the detailed survey area (after MIZUNO *et al.*, 1980).

in lower abundance, whereas those with lower Ni plus Cu grade and smooth surface occur in higher abundance as high as 44 kg/m^2, throughout the GH79–1 area. Such a relationship can be clearly observed also within the detailed survey area. Figure XVIII-6 presents an inverse relationship between Ni plus Cu grade and abundance, related to nodule types excluding Vr type, along the 10°N survey line of east-west direction in the area.

These data suggest that the origin of r- and s-types may be significant for the enrichment of metals in nodule as well as for nodule concentration.

Correlation among metal contents

It is generally known that Mn and Fe are correlated inversely. In this study, a similar tendency is obtained on the nodules with high Mn contents (more than about 18%). Those with low Mn contents (less than 18%), however, appear to have a positive correlation, as shown in Fig. XVIII-4.

Ni and Cu are of the most strongly correlating elements in manganese nodules (Table XVIII-3), thus behave almost together. There also exist clear positive correlations between both Ni, Cu, and Mn in most of high grade nodules (more than about 18% Mn). However, this correlation is somewhat ambiguous in the low grade nodules (Fig. XVIII-7). It has been known that Ni and Cu have positive correlations with Mn/Fe ratio, as represented clearly by MORITANI *et al.* (1979). The present result is illustrated in Fig. XVIII-8. Fe is positively correlated with Co, as shown in Fig. XVIII-9.

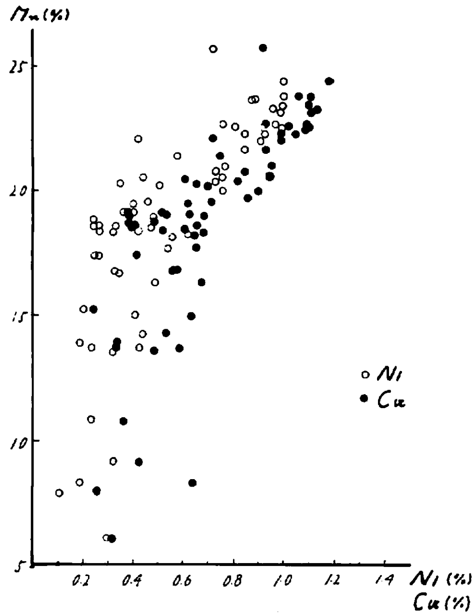

Fig. XVIII-7 Relation of Ni and Cu contents to Mn contents.

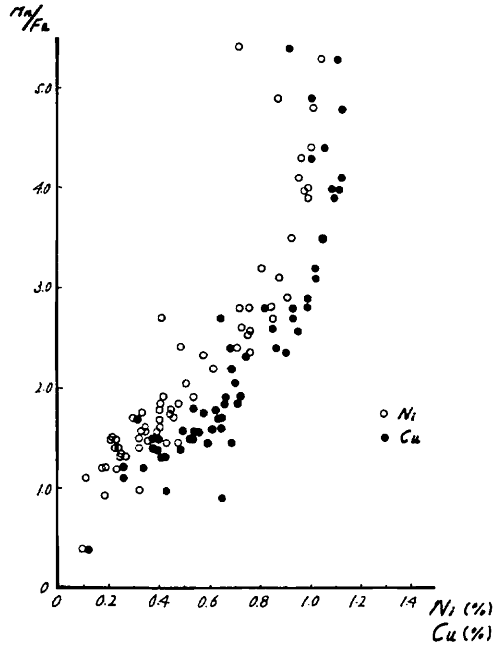

Fig. XVIII-8 Relation of Ni and Cu contents to Mn/Fe ratio.

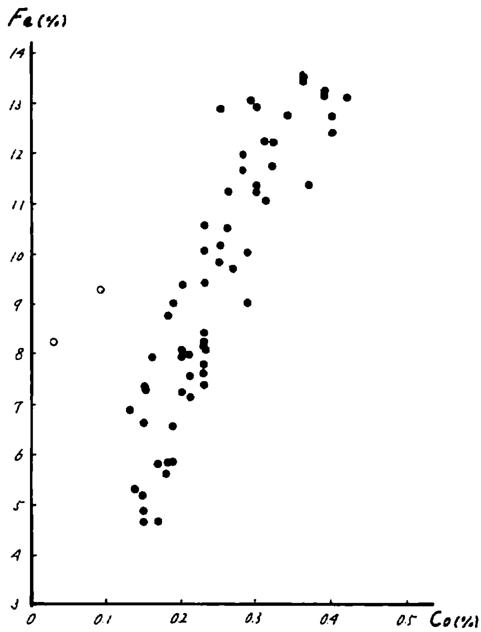

Fig. XVIII-9 Relation between Fe and Co contents.

Table XVIII-4 Geochemical distribution of some metals.

Metal	Mn-nodule (wt %) This work [A]	The earth crust (wt %) MASON (1958) [B]	Ocean-floor sediments (wt %) KATO *et al.* (1979) [C]	Sea water ($\times 10^{-7}$ g/kg) TUREKIAN (1969)	Concentration ratio: Mn-nodule [A/B]	Concentration ratio: Sediments [C/B]
Mn	18.72	0.10	0.445	4	187	4.5
Fe	9.12	5	4.2	34	1.8	0.8
Ni	0.69	0.0080	0.0137	66	86	1.7
Cu	0.54	0.0045	0.0318	9	120	7.1
Co	0.25	0.0023	0.0076	3.9	109	3.3
Pb	0.054	0.0015	0.0034	0.3	36	2.3
Zn	0.077	0.0065	0.0105	50	12	1.6
Mn/Fe	2.05	0.02	0.106	0.118		

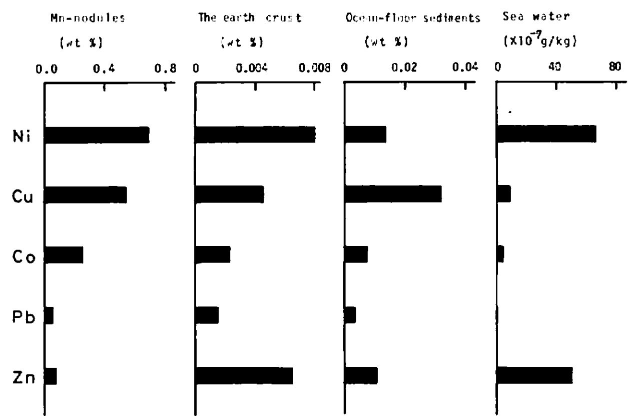

Fig. XVIII-10 Geochemical distribution of Ni, Cu, Co, Pb, and Zn (from the data on Table XVIII-4).

Geochemical distribution of some metals

Geochemical distribution of Mn, Fe, Ni, Cu, Co, Pb, and Zn for manganese nodules, the earth crust (MASON, 1958), ocean-floor sediments (KATO *et al.*, 1979) and sea water (TUREKIAN, 1969) are listed in Table XVIII-4. Concentration ratios are calculated for manganese nodule (manganese nodule/earth crust) and ocean-floor sediments (sediments/earth crust). Except for Fe, the concentration ratio of metals in the nodules and the sediments against the earth crust are 12 to 187, and 1.6 to 7.1, respectively. Fe is least concentrated in the nodules (1.8) and the sediments (0.8).

In Fig. XVIII-10, contents of Ni, Cu, Co, Pb, and Zn in the nodules and the earth crust are compared. Zn contents of the nodules are significantly lower than other metals as compared with those of the earth crust. This may arise from chemical characteristics of Zn during the nodule formation while leaving out Zn in sea water. High Cu content of the sediments may be related to a high stability of the metal in the sediments rather than in sea water.

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