XIV. METAL CONTENTS OF MANGANESE NODULES FROM THE GH78-1 AREA

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Introduction

Fifty-seven samples of manganese nodules from the GH78-1 area were analysed in bulk rock for major and some minor metal elements to provide the data for the evaluation of the chemical features of the nodules. Sample preparation was carried on following those for previous cruises (e.g. MORITANI *et al.*, 1979; FUJINUKI *et al.*, 1977). While the analyses for Mn, Fe, Co, Ni, Cu, Zn and Pb were done by atomic absorption spectrometry (TERASHIMA, 1978). Outline of the precedure is given below.

Air-dried 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 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

Table XIV-1 shows the contents of each element including total water and Mn/Fe ratio, and Table XIV-2 does average and standard deviation of each element except water, with regard to three morphological types of manganese nodules classified into smooth, intermediate and rough ones. In Table XIV-1, intermediate type of surface structure is noted by the mark "s·r" attached to the capital letter or letters indicating the shape of manganese nodules.

Relations between nodule chemistry and morphological type

Among those elements analyzed, Fe, Co and Pb are apt to have higher concentrations in the nodules of smooth surface structure type, while Mn, Ni, Cu and Zn are in rough type, as shown numerically by the ratios of averages of each element between rough and smooth types. This tendency is also shown in Fig. XIV-1(1)-(4) for Co, Zn, Pb and Cu.

Although Mn is not a typical element of which concentration shows close relation to the surface structure type of manganese nodules, Mn/Fe ratio indicates closer relation as shown in Fig. XIV-1(6) and Fig. XIV-2. Mn/Fe ratio is 1.50 in average, 0.94 at the minimum and 4.02 at the maximum (Table

Table XIV-1 Chemical composition of manganese nodules from GH78-1 area (Analysts: T. Mochizuki and S. Terashima)

No.	Station No.	Sample No.	type	Size	Mn	Fe	Cu	Ni	Co	Pb	Zn	$\pm H_2O$	Mn/Fe
					%					ppm		%	
1	1036	G(B)604	SPs	6-8	18.69	16.00	0.32	0.46	0.32	711	624	22.50	1.17
2	1037-1	G(B)605-1	SPs	4-6	19.53	14.45	0.35	0.49	0.33	725	675	21.80	1.35
3	1037-1	G(B)605-1	Ss	2-4	19.89	14.74	0.38	0.54	0.34	712	712	21.64	1.35
4	1038-A	G640	SPs	2-4	19.19	15.07	0.38	0.47	0.33	687	578	20.64	1.27
5	1038-A	G640	IDPs	4-6	19.27	14.55	0.36	0.47	0.33	720	529	21.09	1.32
6	1038-A	G640	DPs	4-6	18.99	14.62	0.41	0.54	0.32	671	594	20.61	1.30
7	1039-A	G641	IDPs	4-6	17.50	11.03	0.26	0.44	0.25	567	616	15.88	1.59
8	1045	G613	IDPs	4-6	11.69	10.95	0.23	0.42	0.09	430	515	17.05	1.07
9	1046	G614	SPs·r	2-4	20.34	9.87	0.64	0.74	0.22	484	770	19.92	2.06
10	1047	G615	SPr	4-6	19.80	9.06	0.72	0.80	0.19	394	785	17.84	2.19
11	1047	G615	SPr	2-4	19.93	9.59	0.72	0.77	0.19	470	745	18.30	2.08
12	1048	G(B)616	DPs	4-6	20.52	15.18	0.32	0.58	0.32	705	657	22.65	1.35
13	1048	G(B)616	SPs	6-8	17.29	13.48	0.46	0.51	0.27	586	673	19.83	1.28
14	1048	G(B)616	SPs	4-6	19.90	12.66	0.42	0.62	0.32	672	714	21.54	1.57
15	1048-1	G616-1	ISs	8-16	17.93	11.16	0.37	0.54	0.34	670	623	20.13	1.61
16	1048-1	G616-1	DPs	6-8	20.21	11.30	0.52	0.76	0.35	676	832	19.64	1.79
17	1049	G617	SPr	4-6	17.60	8.22	0.61	0.69	0.19	507	669	18.04	2.14
18	1049	G617	SPr	1-2	23.05	6.89	0.94	1.08	0.19	447	1098	17.21	3.35
19	1050	G618	DPs	4-6	12.28	10.48	0.33	0.57	0.19	423	522	15.86	1.17
20	1050	G618	DPs	4-6	11.68	12.36	0.29	0.49	0.20	434	615	17.01	0.94
21	1050	G618	Ss	2-4	14.10	11.74	0.36	0.55	0.24	569	616	16.33	1.20
22	1051	G619	DPs	6-8	9.71	6.40	0.34	0.58	0.14	394	480	16.74	1.52
23	1051	G619	Ss	2-4	20.13	10.27	0.54	0.79	0.34	514	798	18.73	1.96
24	1051	F G88-1	DPs	6-8	22.86	10.29	0.69	0.86	0.30	543	943	19.40	2.22
25	1053	G621	Ss	1-2	19.14	13.09	0.29	0.47	0.47	783	638	20.57	1.46
26	1054	G622	Vs	4-6	19.70	15.95	0.19	0.39	0.54	1009	516	22.74	1.24
27	1054	G622	Ss	2-4	19.53	15.20	0.21	0.43	0.51	1049	527	21.78	1.28
28	1054	F G91-2	SPs	2-4	19.29	15.00	0.19	0.45	0.54	1035	541	21.84	1.29

Table XIV-1 (Continued)

No.	Station No.	Sample No.	type	Size	Mn [	Fe	Cu %	Ni	Co]	Pb [ppm	Zn]	$\pm H_2O$ [%]	Mn/Fe
29	1056	G(B)626	SPs·r	4–6	20.05	12.74	0.49	0.70	0.31	666	651	23.13	1.57
30	1056	G(B)626	SPs·r	2–4	22.78	12.88	0.62	0.73	0.34	689	748	19.09	1.77
31	1057–2	G627–2A	Ss	6–8	20.62	10.62	0.69	0.78	0.28	593	689	18.70	1.94
32	1057–2	G627–2A	DPs	6–8	19.86	10.48	0.61	0.72	0.26	577	648	16.70	1.90
33	1057–2	G627–2B	Ss	4–6	14.38	9.98	0.42	0.55	0.20	506	483	17.04	1.44
34	1059	G629	Sr	1–2	24.06	5.99	1.06	1.17	0.15	344	1009	15.80	4.02
35	1060	G(B)623	SPs	2–4 4–6	20.54	14.09	0.31	0.53	0.43	910	583	20.96	1.45
36	1060	FG92–1	Ss	4–6	20.68	11.91	0.38	0.59	0.39	723	679	17.76	1.74
37	1061	G(B)624	Ss·r	4–6	24.77	9.34	0.75	0.96	0.30	573	963	16.32	2.65
38	1065	G632	SEr	4–6	22.08	6.64	1.05	1.09	0.14	368	969	15.75	3.33
39	1067	G634	SPs	4–6	18.98	15.19	0.34	0.47	0.30	816	527	21.22	1.25
40	1067	G634	ISPs	4–6	19.48	15.05	0.38	0.47	0.33	834	662	20.71	1.29
41	1070	G636	SPs	4–6	19.73	16.36	0.25	0.36	0.39	888	892	22.83	1.21
42	1071	G637	SPs	6–8	20.29	15.05	0.43	0.54	0.34	875	647	20.37	1.35
43	1071	G637	ISs	4–6	20.49	14.89	0.45	0.54	0.35	1046	568	19.74	1.38
44	1071	G637	Vs	4–6	20.35	15.09	0.44	0.54	0.34	877	680	20.49	1.35
45	1073	FG109–1	SPs	4–6	19.38	13.82	0.35	0.46	0.35	857	605	19.47	1.40
46	1073	FG109–1	ISs	4–6	20.27	13.63	0.39	0.52	0.35	824	639	19.59	1.49
47	1073	FG109–2	SPs	2–4	19.62	10.85	0.56	0.65	0.27	623	700	17.70	1.81
48	1073	FG109–4	IDPs	6–8	15.57	11.10	0.32	0.43	0.26	566	529	18.96	1.40
49	1073	FG109–5	SPs	4–6	19.77	14.94	0.31	0.37	0.36	832	569	20.56	1.32
50	1073	FG109–5	ISs	2–4	19.52	15.06	0.34	0.40	0.36	818	594	20.39	1.30
51	1073	FG109–6	SPs	2–4	17.22	11.27	0.41	0.55	0.28	1181	614	19.46	1.53
52	1073	FG109–7	SPs	4–6	19.29	11.83	0.43	0.55	0.28	638	675	19.34	1.63
53	1073	FG109–7	ISs	2–4	18.17	13.50	0.37	0.49	0.32	816	809	18.53	1.35
54	1073	FG109–8	SPs	4–6	19.61	13.04	0.43	0.53	0.35	799	650	20.73	1.50
55	1073	FG109–8	ISs	4–6	18.26	12.27	0.41	0.54	0.30	711	662	19.92	1.49
56	1074	FG110–1	SPs	4–6	19.57	14.36	0.33	0.46	0.39	881	559	21.46	1.36
57	1074	FG110–2	ISs	4–6	19.11	13.63	0.33	0.47	0.36	795	601	20.98	1.40

Table XIV-2 Average and standard deviation values of each element for each nodule type on surface structure

Surface structure	smooth Avr. (S.D.)	intermed Avr. (S.D.)	rough Avr. (S.D.)	all types Avr. (S.D.)	ratio of averages for rough and smooth
Mn (%)	18.51 (2.71)	21.99 (2.22)	21.09 (2.40)	19.02 (2.85)	1.14
Fe (%)	13.06 (2.12)	11.20 (1.86)	7.73 (1.44)	12.37 (2.62)	0.59
Co (%)	0.32 (0.09)	0.29 (0.05)	0.18 (0.02)	0.31 (0.09)	0.56
Ni (%)	0.53 (0.11)	0.78 (0.12)	1.03 (0.40)	0.60 (0.23)	1.94
Cu (%)	0.38 (0.11)	0.63 (0.11)	0.85 (0.19)	0.45 (0.19)	2.24
Zn (ppm)	634 (100)	783 (131)	879 (170)	670 (135)	1.39
Pb (ppm)	729 (179)	603 (94)	422 (63)	688 (192)	0.58

Table XIV-3 Average, minimum and maximum values of Cu plus Ni grade, and some significant ratios

	Cu+Ni (%)	Cu/Ni	Mn/Fe	Co/Fe	Co/Mn
Average	1.04	0.74	1.50	2.5×10^{-2}	1.6×10^{-2}
Minimum	0.58	0.42	0.94	0.8×10^{-2}	0.8×10^{-2}
Maximum	2.23	0.96	4.02	3.6×10^{-2}	2.8×10^{-2}

	Ni/Mn	Cu/Mn	Zn/Mn	Pb/Mn
Average	3.1×10^{-2}	2.3×10^{-2}	3.5×10^{-3}	3.7×10^{-3}
Minimum	1.8×10^{-2}	1.0×10^{-2}	2.7×10^{-3}	1.4×10^{-3}
Maximum	6.0×10^{-2}	4.8×10^{-2}	4.9×10^{-3}	5.8×10^{-3}

XIV-3). Almost all samples of the smooth type show rather low Mn/Fe ratio less than 2, while all those of rough type shows high value more than 2 (Fig. XIV-2).

Another chemical aspect distinguished with regard to surface structure types of the nodule is Ni plus Cu grade. Although that difference is somewhat unclear because of the bulk rock analysis, but still there is recognized a characteristic relation between the grade and occurrence of nodule, i.e. as high grade-low abundance or low grade-high abundance (Fig. XIV-3). Fig. XIV-3 suggests that the morphology (shape) of the nodule is not so important factor related to Ni plus Cu grade, excepting that the nodules having IS or IDP shapes show invariably rather low grade of Ni plus Cu less than 1.0%.

Relations among some elements

Table XIV-3 shows average, minimum and maximum values of some ratios

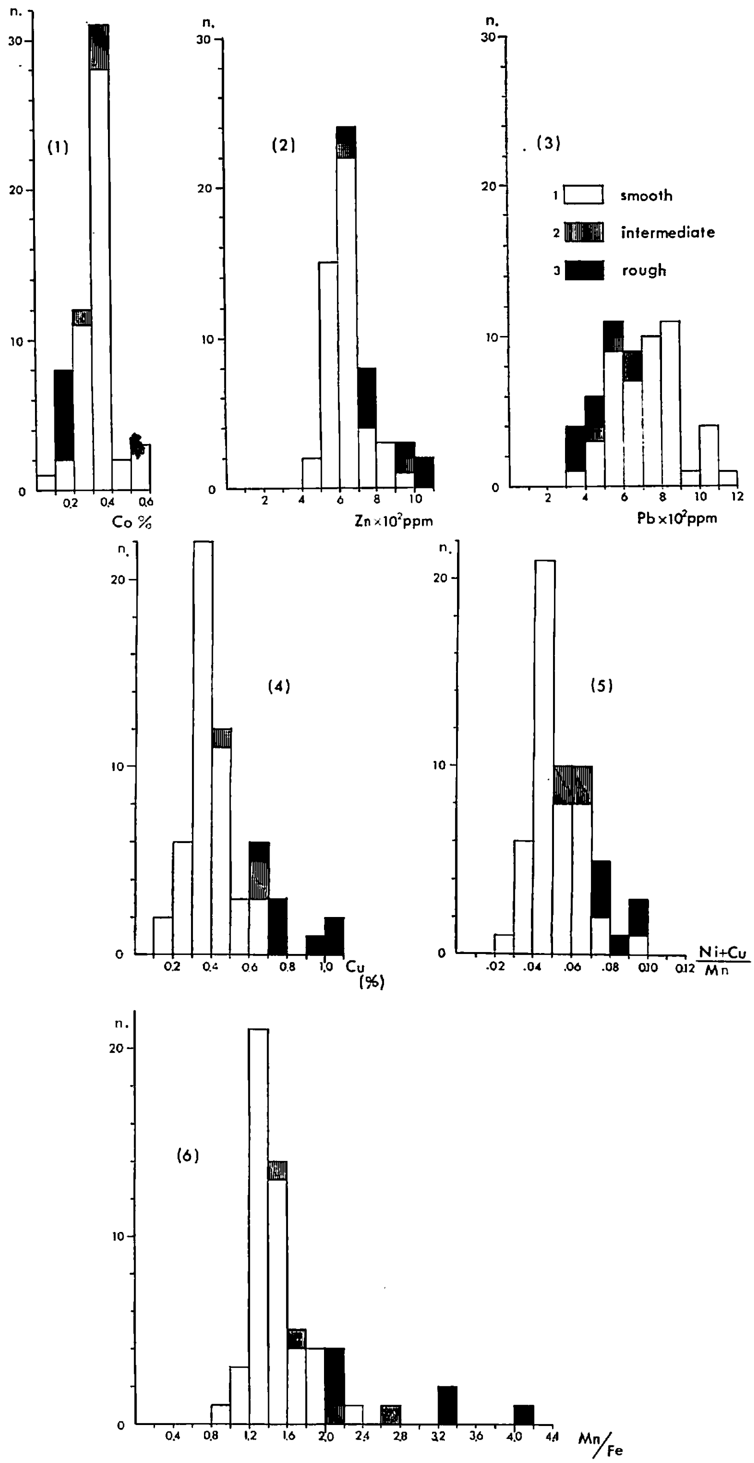

Fig. XIV-1 Histograms of some elements and their ratios, shown in the number of samples analysed, with regard to each nodule type on surface structure.

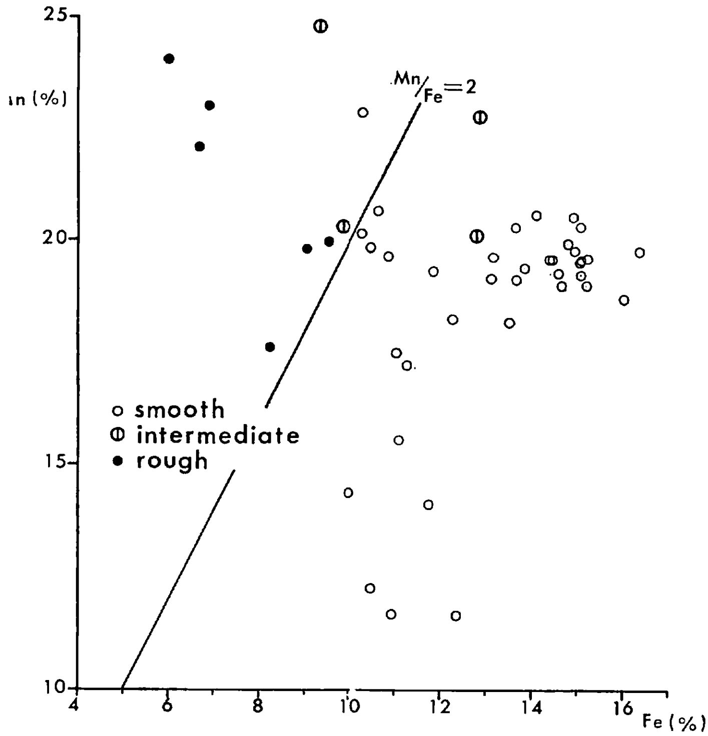

Fig. XIV-2 Relation among Mn and Fe contents, and nodule types on surface structure.

between elements, in addition to Ni plus Cu grade. While, the relation of Ni and Cu contents to Mn/Fe ratio, and relation between Fe and Co are shown in Figs. XIV-4 and XIV-5 respectively. Those figures represent intensely positive correlations between Ni or Cu content and Mn/Fe ratio, and Fe and Co, in the same manner as those in our previous works (FUJINUKI *et al.*, 1977 and MORITANI *et al.*, 1979). The positive correlation between Fe and Co had tended to lead us to an assumption of Co substitution for Fe (e.g. ARRHENIUS *et al.*, 1964). According to USUI (1979), however, Co substitution for Mn in δ-MnO_2 phase, which was demonstrated synthetically by BURNS (1976), is more reasonable to interprete that phenomenon.

Areal distribution of nodule chemistry

Fig. XIV-6 shows distribution of Mn/Fe ratio in manganese nodules in this area (represented as the average at each station) together with the topography and surface sediment facies (NAKAO and SUZUKI, 1981), including the data for three stations in the GH77-1 area. Mn/Fe ratio is selected here as the representative factor which well indicates the chemical characteristics of manganese nodules regardless of the kind of analytical data base.

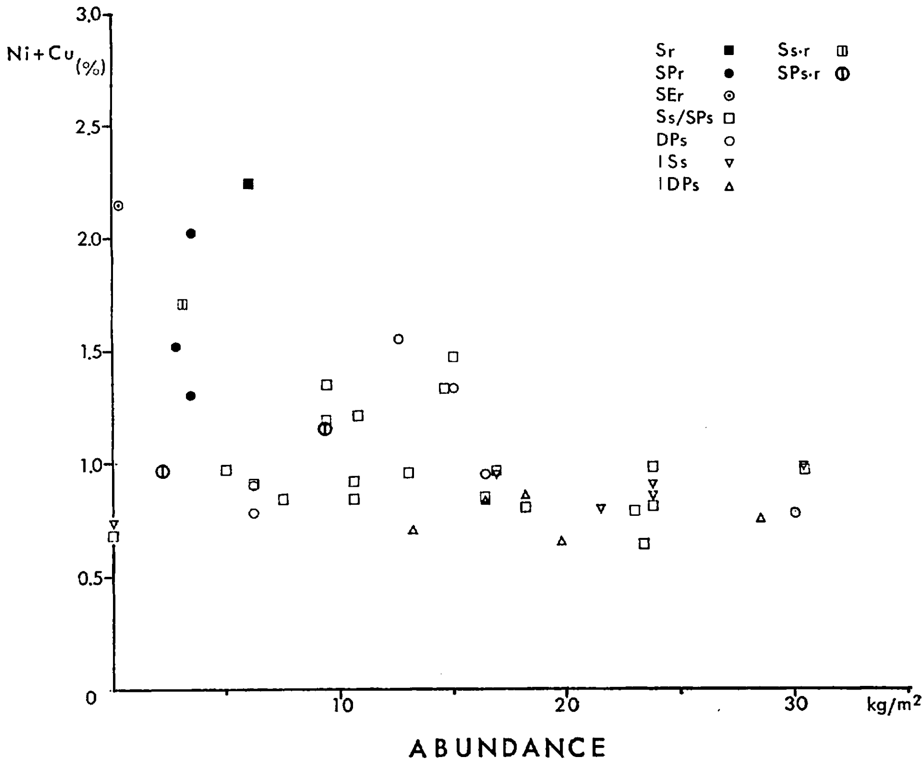

Fig. XIV-3 Relation among Ni plus Cu grade, abundance of manganese nodules and nodule types including its shape.

Though the data are not enough to discuss the relation between sedimentary facies or topography and Mn/Fe ratio of the nodules, it is indicated that relatively high Mn/Fe ratio (> 2) appears dominantly in the southern part of this area, to the south of the parallel of latitude, 9°N, and it may be possible to point out the following suggestions.

(a) Topographic highs, like a ridge, seem to be not favorable place, for the distribution of high Mn/Fe nodules.

(b) Parallel distribution of high Mn/Fe nodules to the topography is expected in deeper sites.

(c) Siliceous surface sediment including siliceous ooze seems to have some genetic relation to high Mn/Fe nodules.

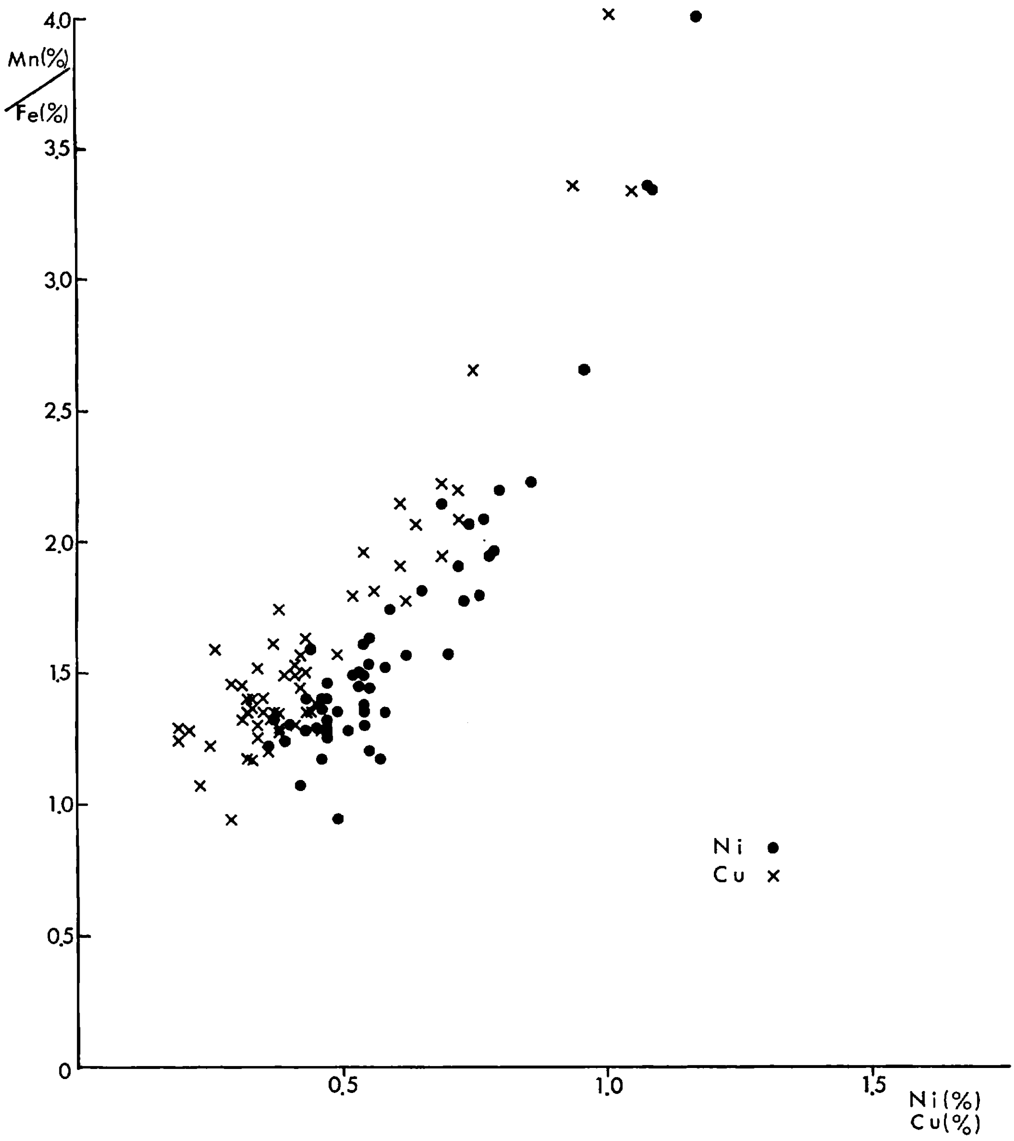

Fig. XIV-4 Relation of Ni and Cu contents to Mn/Fe ratio.

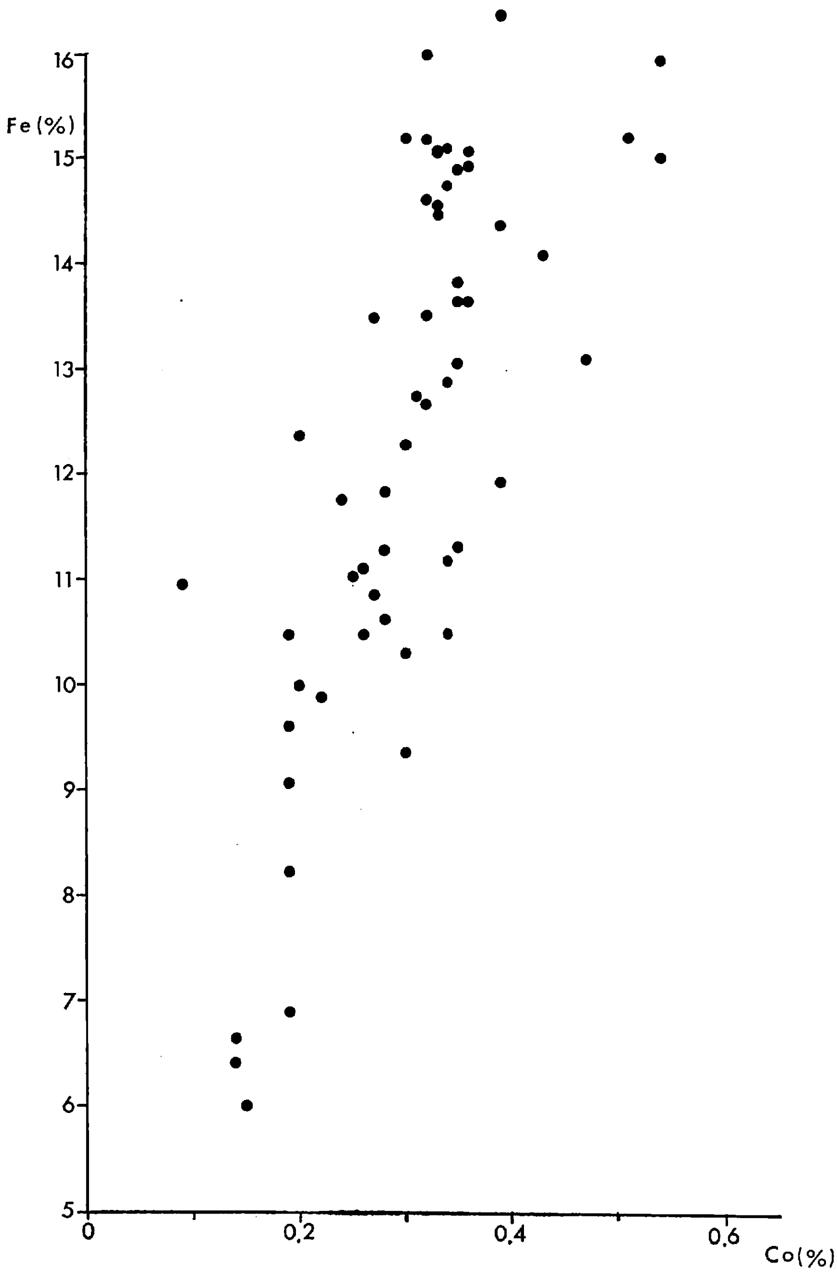

Fig. XIV-5 Relation between Fe and Co contents.

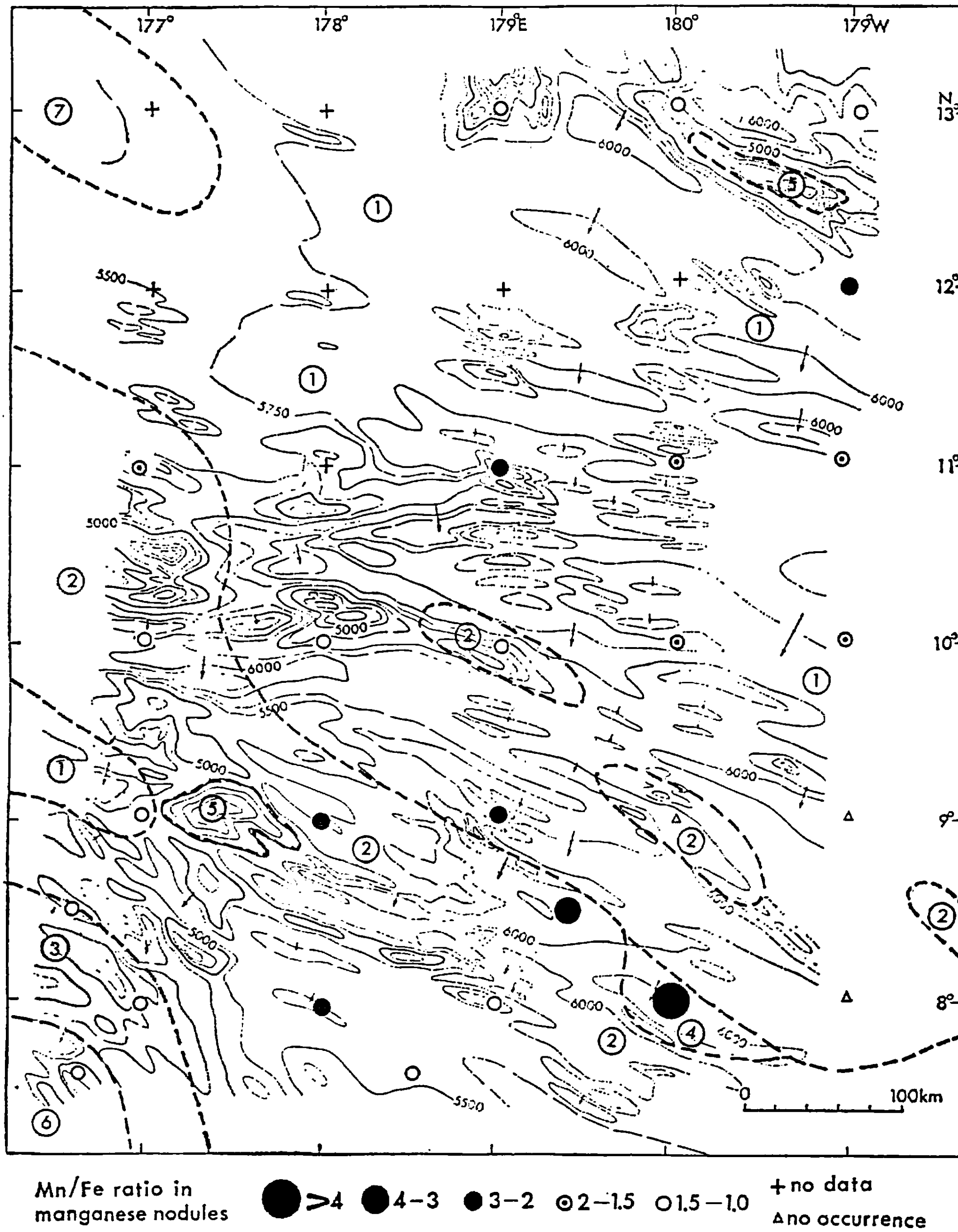

Fig. XIV-6 Areal distribution of Mn/Fe ratio of manganese nodules. Circled numbers show the facies of surface sediments as follows. 1. Deep sea clay, 2. Siliceous clay, 3. Calcareous-siliceous clay, 4. Siliceous ooze, 5. Calcareous ooze, 6. Calcareous-siliceous ooze, 7. Zeolitic mud.

References

ARRHENIUS, G., MERO, G. and KORKISCH, J. (1964) Origin of oceanic manganese minerals. *Science*, vol. 144, p. 170–171.

BURNS, R. G. (1976) The uptake of cobalt into ferromanganese nodules, soils, and manganese (IV) oxides. *Geochim. Cosmochim. Acta*, vol. 40, p. 95–102.

FUJINUKI, T., MOCHIZUKI, T. and MORITANI, T. (1977) Chemical composition of manganese nodules. *In* A. MIZUNO and T. MORITANI (*eds.*), *Geol. Surv. Japan Cruise Rept.*, no. 8, p. 162–171.

MORITANI, T., MOCHIZUKI, T., TERASHIMA, S. and MARUYAMA, S. (1979) Metal contents of manganese nodules from the GH77-1 area. *In* T. MORITANI (*ed.*), *Geol. Surv. Japan Cruise Rept.*, no. 12, p. 206–217.

NAKAO, S. and SUZUKI, T. (1981) Bottom sediments in the GH78-1 area. *In* T. MORITANI and S. NAKAO (*eds.*), *Geol. Surv. Japan Cruise Rept.*, no. 17, p. 75–102.

TERASHIMA, S. (1978) Atomic absorption analysis of Mn, Fe, Cu, Ni, Co, Pb, Zn, Si, Al, Ca, Mg, Na, K, Ti, and Sr in manganese nodules. *Bull. Geol. Surv. Japan*, vol. 29, p. 401–411.

USUI, A. (1979) Minerals, metal contents, and mechanism of formation of manganese nodules from the Central Pacific Basin (GH76-1 and GH77-1 areas). *In* J. L. BISHOFF and D. Z. PIPER (*eds.*), *Marine Geology and Oceanography of the Pacific Manganese Nodule Province*, Plenum Publ. Corp., p. 651–679.