XIV. METAL CONTENTS OF MANGANESE NODULES FROM THE GH77-1 AREA

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Introduction

118 samples of manganese nodules obtained during the GH77–1 cruise were analyzed in bulk rock for major and some minor metal elements to provide the data for the evaluation of the chemical features of the nodules. Basing on these analytical data, we discuss briefly the relationship between the metal contents and the manganese nodule types, the relationship between each metal element, and the correlation between the nodule abundance and Cu and Ni grade.

Sample preparation

For the purpose of removing adherent salt from the nodule surface, all nodules were immersed in running water for 48 hours and then in ion-free water for 24 hours. After air-dried, samples were ground in a steel percussion motar to the powder size of 150–200 mesh (105 – 74 μ). The ground samples were encased in small size paper bags without sealed, dried at 20–25°C for 24 hours in a dryer, and then kept in a desiccator as the analytical samples.

Analytical methods

The analytical methods applied are the same as the previous ones for the GH76–1 cruise samples (FUJINUKI *et al.*, 1977). Namely, Mn and Fe were measured by volumetries, Cu, Ni, Co, Pb, and Zn were determined by atomic absorption spectrometry, and total water was analysed gravimetrically.

Results

The contents of Mn, Fe, $\pm H_2O$, Ni, Cu, Co, Pb, Zn and the ratio of Mn/Fe in 118 nodule samples are given in Table XIV–1.

Discussion

General features

The maximum, minimum, and the most common values of each element are as follows. Mn ranges from 10.57% to 23.73%, being commonly 17–21%. Fe is in a range from 5.70% to 15.33%, being 10–14% in most cases. Ni has a range from 0.32% to 1.20%, being commonly 0.4–0.7%. Cu ranges from 0.19% to 1.16%, being commonly 0.3–0.6%. Co is in a range from 0.11% to 0.37%, being around 0.2% in most cases. Pb ranges from 220 ppm to 850 ppm, and Zn from 450 ppm to 1,650 ppm. $\pm H_2O$ has a range from 13.64% to 26.54%. Mn/Fe ratio shows the values ranging from 0.93 to 3.73. On these analytical values there is recognized a tendency that Mn, Cu and Ni are generally lower in GH77–1 samples as compared with those in the GH76–1 samples previously reported (FUJINUKI *et al.*, 1977).

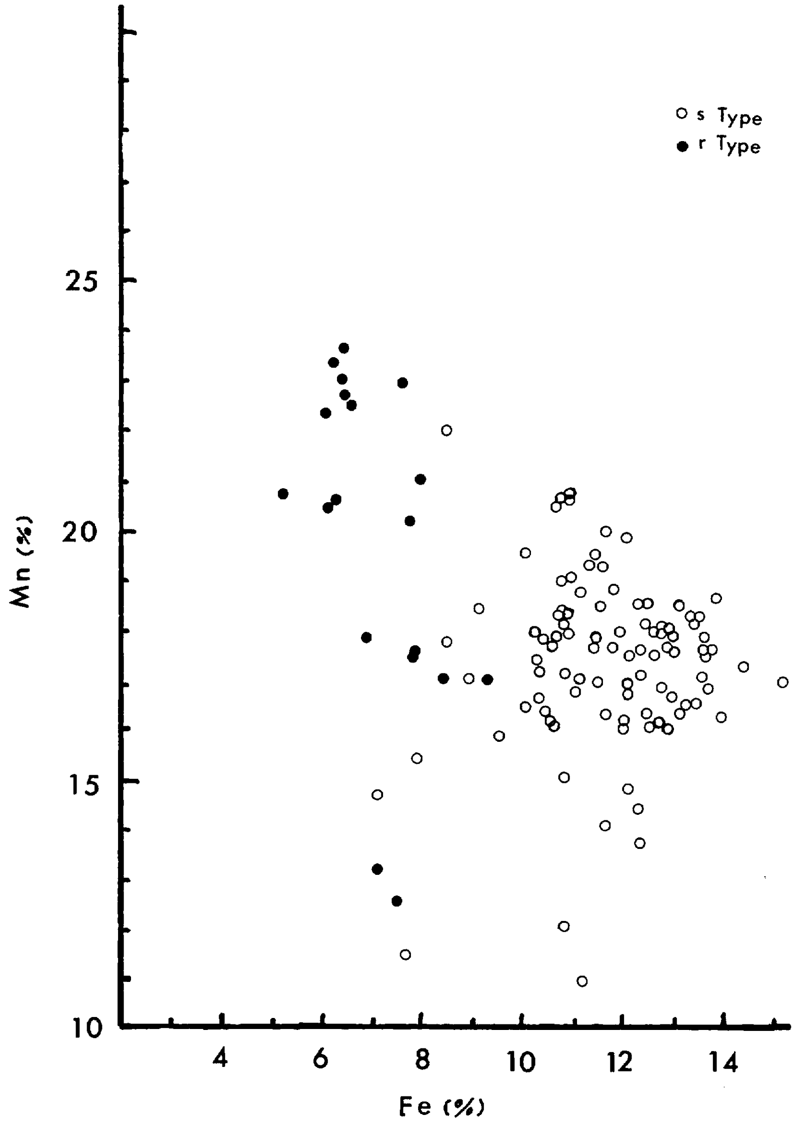

Fig. XIV-1 Relation between Mn and Fe contents and nodule types.

Generally speaking, the values are rather consistent within the same sampling station. Marked variations in the chemical contents are recognized usually over different stations of the farther distance.

Relation to nodule types

As shown in the figures both of the relationship between Mn% and Fe% (Fig. XIV-1) and of the relationship between the grade of Ni+Cu% and manganese nodule abundance (Fig. XIV-2), nodule types have some marked relations to the metal element composi-

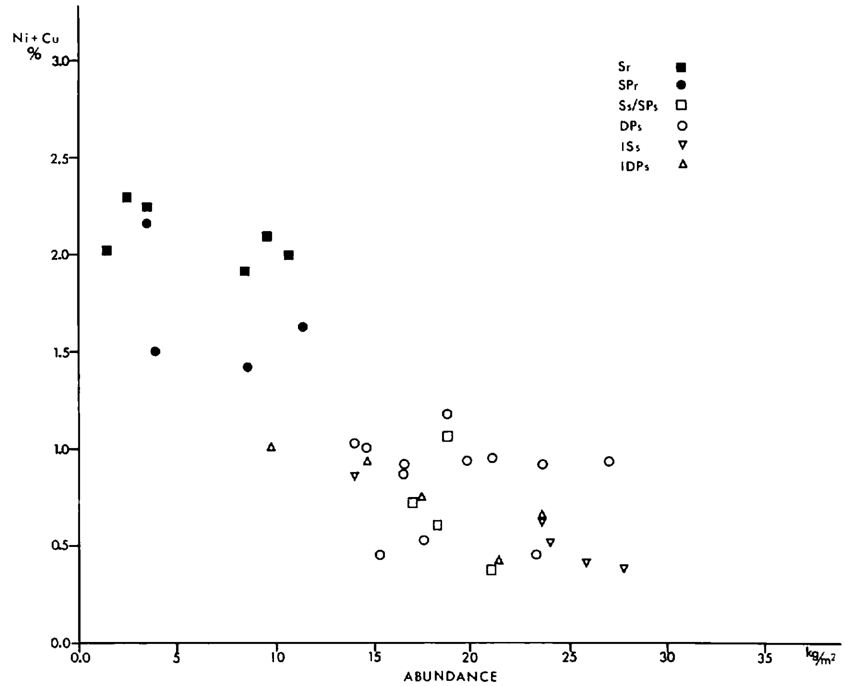

Fig. XIV–2 Correlation between Ni and Cu grade and abundance of manganese nodules.

tions, especially in terms of two major type groups of r (rough) and s (smooth) based on the surface structures of manganese nodules. Namely, Mn is more abundant in r type group, while Fe abounds contrastingly in s type group (Fig. XIV–1). Also, Ni and Cu are attracted to r type group, and decreases in s type group (Fig. XIV–2). This reflects their close relation to Mn as reported on the previous GH76–1 samples (Fujinuki *et al.*, 1977). However, in the present GH77–1 samples, the reported systematic changes of the metal contents according to an order of the individual nodule types, as Sr → SPr → Ss → Ss/SPs → DPs → ISs → IDPs, along which Mn, Ni and Cu decrease and Fe and Co increase, is not necessarily so recognized, especially within s type group.

Relationship between each metal element

Mn and Fe are, generally speaking, in inverse correlation though the tendency is represented rather as a broad pattern curve on the plotted diagram as shown in Fig. XIV–1. This broad pattern and some deviated points seem to be caused by the relative dilution of the metal contents by the larger amounts of nucleus materials due to the bulk rock analysis.

Ni and Cu are of the most strongly correlating elements, and behave almost together (Figs. XIV–4 and XIV–5).

There also exist close correlations of both Ni and Cu to Mn, but these are represented in a broad curve especially along the Mn percent below than 20% (Fig. XIV–4). Ni and

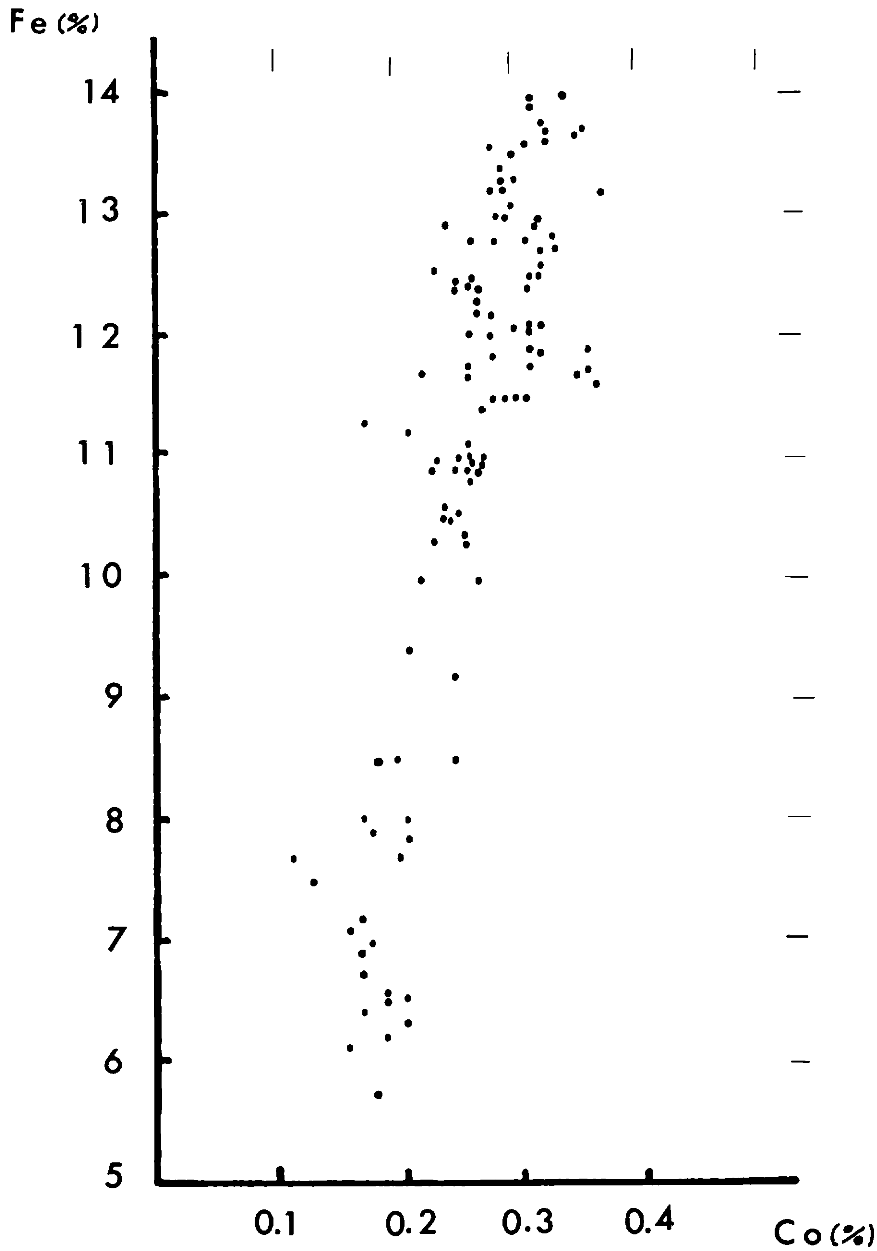

Fig. XIV-3 Relation between Fe and Co contents.

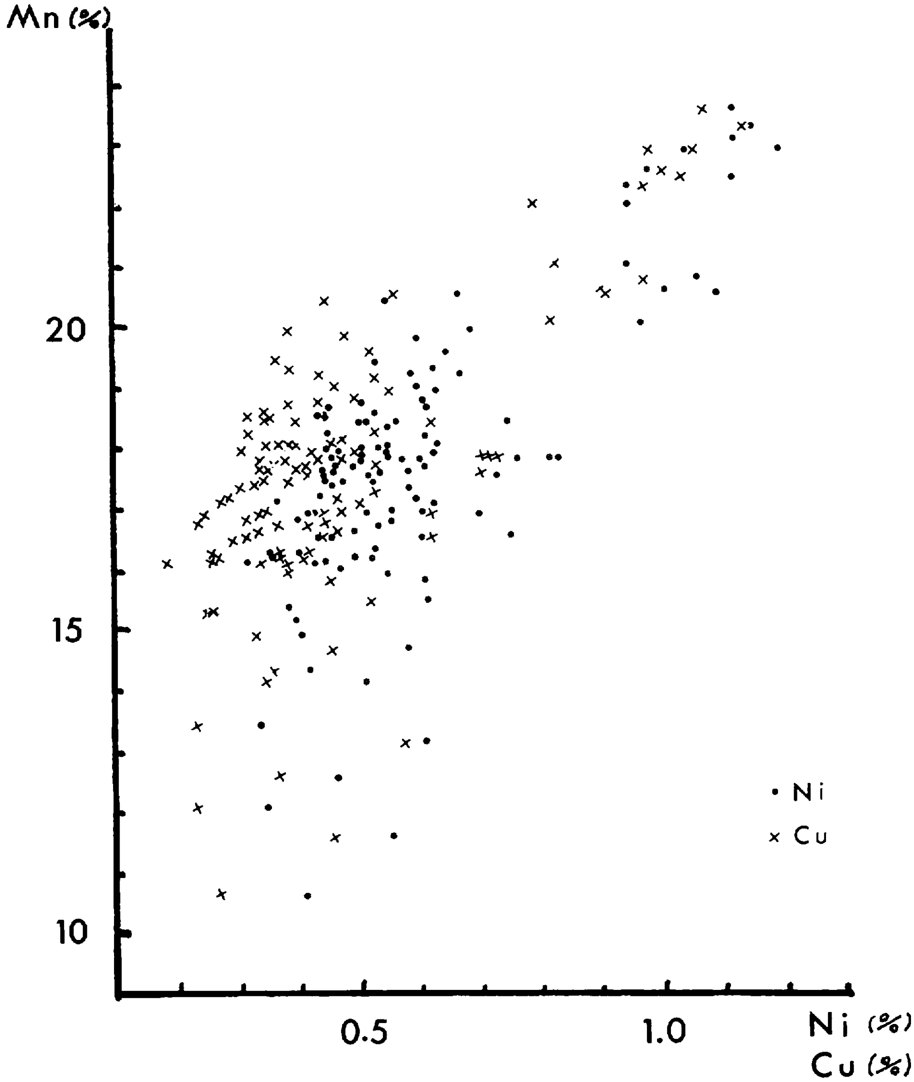

Fig. XIV–4 Relation of Ni and Cu contents to Mn contents.

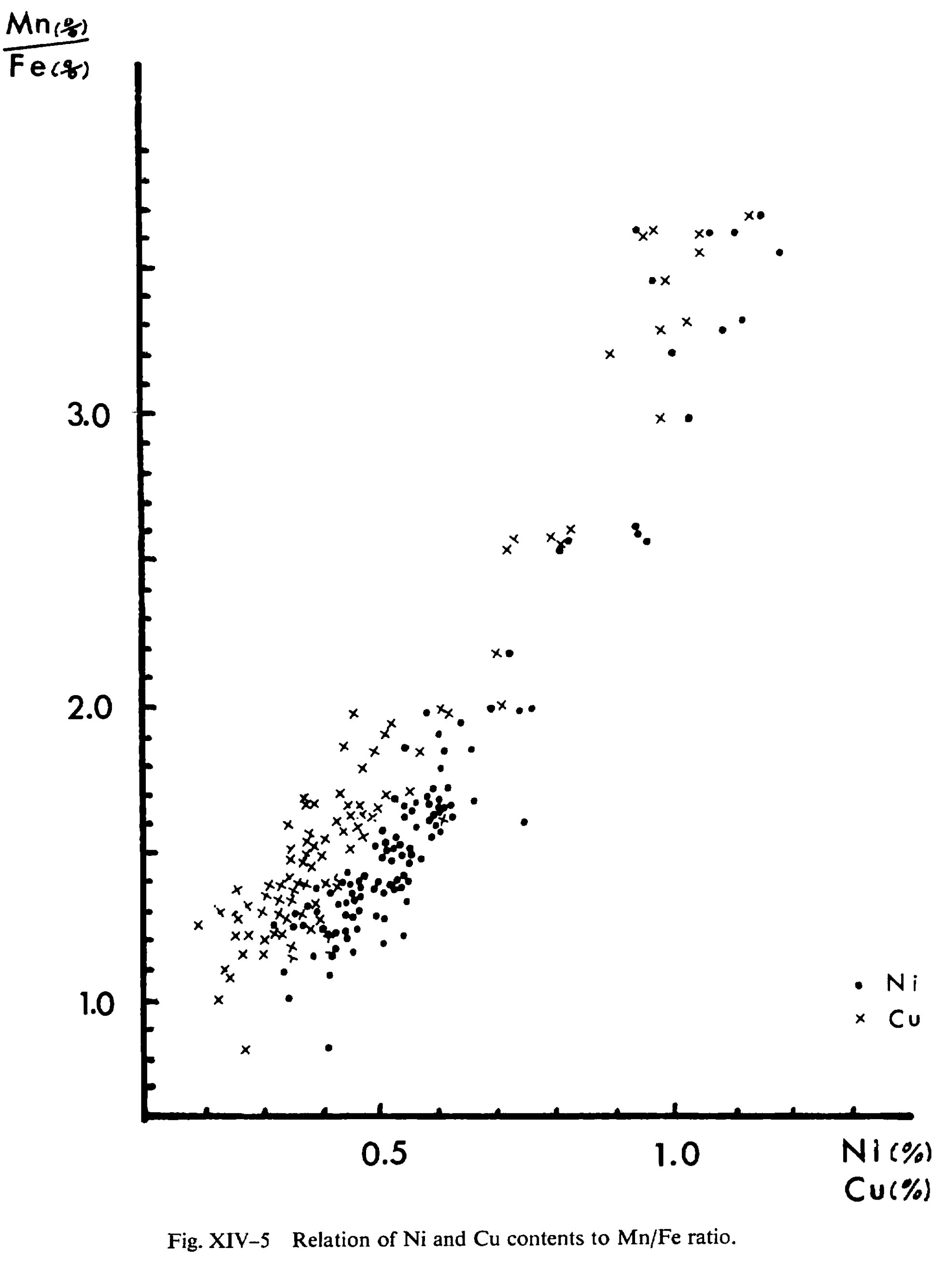

Fig. XIV–5 Relation of Ni and Cu contents to Mn/Fe ratio.

Table XIV-1 Chemical composition of manganese nodules from the GH77-1 cruise

No.	Sample no.	Size (cm)	Type	Mn (%)	Fe (%)
1	701-FG33-1	2-4	Ss/SPs	18.41	10.98
2	33-2	2-4	Ss/SPs	20.62	11.08
3	33-2	1-2	Ss/SPs	19.65	10.01
4	702-FG34-2	4-6	Ss/SPs	17.03	9.44
5	34-2	2-4	Ss/SPs	15.49	8.05
6	702-G373	6-8	IDPs	11.58	7.67
7	707-G378	4-6	SPr	17.61	7.93
8	378	2-4	SPr	17.90	6.94
9	FG39-1	6-8	SPr	12.63	7.51
10	FG39-1	2-4	SPr	13.21	7.11
11	708-G379	4-6	SPr	17.01	8.46
12	379	4-6	SPr	17.92	7.00
13	379	2-4	Sr	20.73	6.42
14	FG40-1	2-4	Sr	20.87	5.70
15	709-G380	4-6	DPs	17.98	11.57
16	380	4-6	DPs	18.80	11.79
17	710-G381	4-6	DPs	16.24	12.75
18	381	2-4	DPs	16.89	12.86
19	710-G381	2-4	IDPs	18.61	13.21
20	710-FG42-1	2-4	Ss/SPs	12.11	10.98
21	42-1	1-2	Ss/SPs	18.50	9.23
22	711-FG43-1	2-4	DPs	19.54	11.49
23	43-1	2-4	DPs	20.09	11.71
24	712-G383	4-6	DPs	16.39	10.52
25	383	2-4	DPs	17.95	10.82
26	FG44-1	4-6	DPs	17.92	10.30
27	713-G384	2-4	SPr	22.54	6.75
28	384	1-2	Sr	23.07	6.46
29	714-G385	4-6	IDPs	16.28	10.63
30	385	2-4	DPs	16.58	10.09
31	FG46-1	4-6	IDPs	16.02	10.71
32	46-1	2-4	DPs	15.98	9.63
33	718-G387	4-6	Ss/SPs	17.40	10.30
34	387	4-6	Ss/SPs	17.88	10.57
35	387	2-4	DPs	19.09	10.97
36	FG48-1	4-6	DPs	18.17	11.02
37	718-FG48-1	2-4	DPs	20.48	10.89
38	48-1	2-4	Ss/SPs	18.29	10.86
39	48-2	6-8	DPs	17.90	12.53
40	48-2	2-4	Ss/SPs	17.79	10.58
41	719-G388	6-8	ISs	16.25	12.78
42	388	4-6	IDPs	16.22	12.14
43	388	2-4	DPs	19.29	11.40
44	388	2-4	DPs	18.11	12.48
45	FG49-1	4-6	DPs	16.36	12.46
46	49-1	2-4	DPs	18.62	12.58
47	49-1	2-4	DPs	17.48	12.21
48	49-2	2-4	DPs	17.91	13.15
49	720-FG50-2	4-6	DPs	14.73	7.16
50	50-2	2-4	Ss/SPs	22.13	8.56

(Analysts: T. MOCHIZUKI and S. TERASHIMA).

±H_2O (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	Mn/Fe
23.80	0.55	0.40	0.27	660	670	1.68
23.88	0.67	0.56	0.31	640	770	1.86
21.35	0.65	0.53	0.27	640	690	1.96
21.53	0.61	0.48	0.21	560	630	1.80
20.19	0.62	0.53	0.17	380	650	1.92
15.79	0.56	0.46	0.11	220	580	1.51
22.08	0.73	0.72	0.18	430	1060	2.22
21.28	0.83	0.74	0.17	410	840	2.58
19.49	0.46	0.37	0.13	300	480	1.68
19.47	0.62	0.58	0.16	420	1440	1.86
22.72	0.70	0.62	0.18	470	910	2.01
21.82	0.82	0.73	0.18	420	1100	2.56
13.64	1.01	0.91	0.17	350	1650	3.22
20.46	1.07	0.98	0.18	320	1050	3.66
22.46	0.51	0.39	0.26	660	1210	1.55
24.50	0.51	0.44	0.31	690	1190	1.59
25.75	0.32	0.19	0.33	740	1330	1.27
25.06	0.40	0.24	0.33	800	990	1.31
25.47	0.44	0.32	0.37	850	1210	1.41
21.41	0.35	0.23	0.23	630	1000	1.10
22.26	0.75	0.63	0.25	600	820	2.00
24.05	0.53	0.37	0.31	690	630	1.70
24.20	0.59	0.39	0.36	740	700	1.71
22.93	0.53	0.42	0.24	580	580	1.56
23.30	0.56	0.46	0.26	630	610	1.66
22.56	0.60	0.44	0.23	580	620	1.74
19.36	1.13	1.04	0.17	380	730	3.34
19.17	1.20	1.06	0.19	340	1050	3.57
25.13	0.53	0.41	0.24	610	620	1.53
23.78	0.61	0.45	0.22	570	630	1.64
21.73	0.55	0.39	0.24	630	600	1.50
24.19	0.61	0.46	0.23	570	660	1.66
24.06	0.59	0.53	0.22	530	600	1.69
24.58	0.57	0.48	0.24	570	620	1.69
23.95	0.63	0.56	0.27	610	660	1.74
24.77	0.55	0.46	0.25	620	570	1.64
23.53	0.55	0.45	0.25	620	570	1.88
24.00	0.61	0.54	0.26	590	620	1.68
23.81	0.55	0.43	0.26	610	570	1.43
22.62	0.61	0.53	0.25	580	630	1.68
25.04	0.36	0.27	0.26	720	500	1.27
24.55	0.38	0.27	0.26	720	510	1.34
23.12	0.67	0.53	0.27	640	730	1.69
25.08	0.45	0.39	0.31	800	540	1.45
24.44	0.36	0.26	0.26	720	480	1.31
26.31	0.53	0.38	0.32	780	580	1.48
25.49	0.48	0.35	0.27	700	540	1.43
26.25	0.46	0.34	0.30	760	540	1.36
16.83	0.59	0.46	0.17	410	640	2.06
20.52	0.95	0.80	0.25	550	920	2.59

Table XIV-1

No.	Sample no.	Size (cm)	Type	Mn (%)	Fe (%)
51	721–G390	2–4	DPs	17.79	11.54
52	G390	2–4	DPs	18.53	11.68
53	721–FG51–1	2–4	DPs	18.78	11.89
54	721–FG51–2	2–4	DPs	19.36	11.62
55	722–G391	6–8	DPs	18.49	13.40
56	391	4–6	DPs	18.48	12.43
57	391	4–6	DPs	19.32	11.89
58	722–FG52–1	4–6	DPs	17.05	12.35
59	52–1	4–6	DPs	18.13	12.86
60	52–2	4–6	DPs	19.89	12.15
61	52–2	2–4	DPs	17.47	13.04
62	723–FG53–2	2–4	Sr	23.04	7.68
63	53–2	1–2	Sr	23.40	6.28
64	729–FG61–1	4–6	Ss/SPs	17.21	13.63
65	61–1	2–4	Ss/SPs	18.72	13.90
66	61–2	4–6	Ss/SPs	18.29	13.43
67	61–2	2–4	Ss/SPs	18.58	13.26
68	730–FG62–1	4–6	SPr	17.88	8.51
69	62–1	2–4	SPr	21.15	8.06
70	62–2	4–6	SPr	20.16	7.85
71	730–FG62–2	2–4	Sr	20.59	6.24
72	733–FG65–1	4–6	IDPs	17.73	11.52
73	65–1	2–4	DPs	19.08	11.08
74	65–2	6–8	ISs	16.18	12.61
75	65–2	4–6	ISs	17.06	11.23
76	65–2	2–4	DPs	16.60	10.29
77	734–FG66–1	4–6	SEr	22.35	6.12
78	66–1	2–4	Sr	22.71	6.53
79	66–1	2–4	Sr	23.73	6.49
80	735–FG67–1	4–6	ISs	17.97	13.73
81	67–1	2–4	DPs	17.35	13.75
82	67–2	4–6	ISs	17.00	15.33
83	67–2	2–4	DPs	17.31	14.02
84	736–FG68–1	4–6	DPs	17.71	11.85
85	68–1	2–4	DPs	17.49	12.54
86	68–2	2–4	DPs	16.78	12.09
87	68–2	2–4	Ss/SPs	16.79	13.78
88	736–G401	2–4	DPs	16.94	12.14
89	737–FG69–1	4–6	DPs	18.14	12.82
90	69–1	2–4	DPs	18.07	12.99
91	69–2	4–6	ISs	16.76	13.00
92	69–2	2–4	DPs	18.09	12.72
93	738–G402	4–6	ISs	16.31	11.69
94	402	2–4	DPs	16.88	11.07
95	FG70–1	4–6	IDPs	18.22	10.97
96	70–1	2–4	DPs	18.05	11.07
97	70–2	4–6	IDPs	16.16	12.91
98	70–2	2–4	DPs	18.84	11.90
99	739–G403	2–4	Ss/SPs	10.57	11.29
100	FG72–1	2–4	Ss/SPs	16.36	14.04

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$\pm H_2O$ (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	Mn/Fe
25.81	0.50	0.36	0.33	810	630	1.54
26.44	0.57	0.35	0.35	850	660	1.59
25.66	0.61	0.39	0.36	830	690	1.58
26.10	0.63	0.39	0.37	820	710	1.67
25.49	0.52	0.40	0.30	710	580	1.38
25.87	0.51	0.36	0.31	720	560	1.49
26.07	0.59	0.44	0.32	710	600	1.62
24.86	0.42	0.34	0.27	710	500	1.38
25.32	0.51	0.35	0.28	700	530	1.41
25.12	0.60	0.48	0.31	690	620	1.64
24.56	0.45	0.33	0.29	730	550	1.34
20.51	1.04	0.99	0.20	480	980	3.00
18.21	1.16	1.16	0.21	360	1120	3.73
26.54	0.37	0.27	0.28	720	530	1.26
26.22	0.46	0.35	0.31	760	530	1.35
25.82	0.45	0.32	0.29	760	500	1.36
24.96	0.45	0.35	0.29	740	500	1.40
22.79	0.77	0.71	0.20	550	710	2.10
21.12	0.95	0.84	0.21	470	820	2.62
21.35	0.97	0.82	0.21	450	820	2.57
20.69	1.10	0.99	0.19	420	920	3.29
24.00	0.54	0.40	0.25	690	540	1.54
22.71	0.60	0.47	0.26	640	590	1.61
23.49	0.43	0.35	0.23	630	510	1.28
23.21	0.52	0.45	0.21	580	570	1.52
23.42	0.76	0.62	0.26	460	670	1.61
20.76	0.95	0.98	0.16	440	1010	3.65
21.14	0.98	1.01	0.19	430	940	3.47
19.17	1.12	1.08	0.21	420	1000	3.65
24.82	0.47	0.31	0.36	810	530	1.31
25.48	0.46	0.31	0.35	790	520	1.26
25.61	0.42	0.25	0.35	820	580	1.11
23.95	0.44	0.29	0.34	790	560	1.23
25.16	0.58	0.41	0.28	720	580	1.49
23.66	0.53	0.39	0.32	770	580	1.39
23.03	0.54	0.37	0.30	740	580	1.39
22.26	0.55	0.42	0.32	760	630	1.22
24.87	0.46	0.32	0.32	740	530	1.40
25.43	0.54	0.37	0.31	730	570	1.41
24.62	0.51	0.40	0.32	720	560	1.39
24.21	0.50	0.34	0.28	700	550	1.29
23.86	0.55	0.43	0.32	730	580	1.42
24.42	0.50	0.38	0.26	690	530	1.40
22.56	0.56	0.47	0.26	620	560	1.52
22.38	0.63	0.48	0.26	620	630	1.66
21.76	0.63	0.50	0.28	620	600	1.63
21.93	0.47	0.39	0.24	660	520	1.25
22.98	0.61	0.51	0.31	690	570	1.58
17.59	0.42	0.27	0.17	390	430	0.93
22.95	0.39	0.27	0.31	790	480	1.17

Table XIV–1

No.	Sample no.	Size (cm)	Type	Mn (%)	Fe (%)
101	739–FG72–1	2–4	Ss/SPs	14.93	12.09
102	72–1	2–4	Ss/SPs	14.39	12.29
103	719A–FG71–1	4–6	ISs	13.81	12.42
104	71–1	2–4	ISs	16.27	13.13
105	71–2	4–6	IDPs	15.18	10.90
106	71–2	2–4	DPs	17.61	12.43
107	71–3	4–6	IDPs	17.00	11.47
108	71–3	2–4	DPs	17.19	10.96
109	71–4	4–6	DPs	18.24	13.60
110	71–4	2–4	DPs	17.51	12.48
111	71–5	4–6	DPs	14.14	11.72
112	71–5	2–4	DPs	17.12	10.29
113	71–6	4–6	DPs	16.45	13.50
114	71–6	2–4	DPs	17.64	13.60
115	71–7	4–6	ISs	16.11	12.03
116	71–7	2–4	DPs	17.62	13.70
117	71–8	4–6	ISs	16.53	13.34
118	71–8	2–4	DPs	17.66	12.96

Cu have rather closer correlations to Mn/Fe ratio as represented in the clearer curves (Fig. XIV–5). This may indicate that Mn/Fe ratio reflects more directly the composition of the metal mineral facies, especially of the todorokite as the facies rich in Mn and accompanying minor metal elements like Ni and Cu (USUI, 1979).

Correlation between Ni and Cu grade and nodule abundance

Because Ni and Cu are now thought as the main targets of the economic purposes, this relationship is the most important problem, and recently the inverse correlation was pointed out to exist in many cases of manganese nodule distribution both on regional and local scales (MENARD and FRAZER, 1978; MIZUNO and MORITANI, 1978). As shown in Fig. XIV–2, this inverse correlation is also clearly recognized in the present GH77–1 area. Besides, as already mentioned, the manganese nodule types, particularly of the fundamental groups of r type and s type, relate to this inverse correlation. Namely, r type group shows the higher Ni and Cu grade and lower abundance, while s type group is characterized by the lower Ni and Cu grade and higher abundance inversely.

References

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.

MENARD, H. W. and FRAZER, J. Z. (1978) Manganese nodules on the sea floor: Inverse correlation between grade and abundance. *Science*, vol. 199, p. 969–971.

MIZUNO, A. and MORITANI, T. (1978) Manganese nodule deposits of the Central Pacific. *Preprints 5th Int. Ocean Development Conference* (Tokyo, Sep. 25–29, 1978), B–2,

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$\pm H_2O$ (%)	Ni (%)	Cu (%)	Co (%)	Pb (ppm)	Zn (ppm)	Mn/Fe
21.70	0.41	0.33	0.31	800	480	1.23
21.72	0.42	0.36	0.27	670	500	1.17
20.38	0.34	0.23	0.25	660	450	1.11
22.78	0.41	0.28	0.30	780	510	1.24
21.62	0.40	0.27	0.27	560	460	1.39
24.21	0.47	0.36	0.25	770	550	1.42
22.32	0.56	0.38	0.30	640	580	1.48
21.83	0.60	0.48	0.23	610	590	1.57
24.19	0.56	0.40	0.31	700	600	1.34
24.73	0.53	0.44	0.32	760	560	1.40
21.46	0.52	0.36	0.22	550	530	1.21
21.21	0.63	0.51	0.26	570	610	1.66
24.60	0.45	0.32	0.30	740	510	1.22
24.57	0.45	0.36	0.33	770	540	1.30
25.13	0.44	0.28	0.28	720	530	1.34
23.86	0.45	0.35	0.33	800	560	1.29
23.27	0.44	0.30	0.30	780	540	1.24
25.54	0.48	0.36	0.32	750	540	1.36

p. 27–39.

USUI, A. (1979) Minerals, metal contents, and mechanism of formation of manganese nodules from the Central Pacific Basin. *In* J. L. BISCHOFF and D. Z. PIPER (*eds.*), *Marine geology and oceanography of the Central Pacific manganese province*, Blenum Publishing Co., (in press).