XVI. CHEMICAL COMPOSITION OF MANGANESE NODULES

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Sixty-eight manganese nodules from sixteen different stations and an additional two nodules were analyzed for major and some minor elements, and the chemical characteristics of nodules are discussed on the basis of the analytical data.

Sample preparation

For the purpose of eliminating the adherent sea water from the nodule surface, all nodules were immersed in running water for 48 hours and then in ion-free water for 24 hours. After that, the nodules were dried in air for 2 days, and clay minerals adhered to them were removed prior to crushing. Samples were crushed first in a steel percussion mortar to under 250 μm and ground further in an agate mortar to under 105 μm. The ground samples were encased in small-sized paper bags and were dried in the air for 3 days.

Analytical procedures

Mn and Fe were determined by volumetrys, Cu, Ni, Co, Pb, and Zn by atomic absorption spectrometry and total water was analyzed gravimetrically. These procedures are described in the following.

Mn and Fe

0.1 to 0.2 g of sample was decomposed with mixed acid (sulfuric, nitric, and hydrochloric acids) and evaporated until dense fumes of sulfuric acid were recognized. After cooling, the sulfates of manganese and iron were dissolved with water. To this solution was added an excess emulsion of zinc oxide boiling for a few minutes. The solution was filtered into an Erlenmeyer flask, and the precipitate in the filter paper was reserved for the determination of iron. The filtrate was titrated with a standard solution of potassium permanganate for the determination of manganese.

The reserved precipitate was dissolved with hot diluted hydrochloric acid and reduced by stannous chloride. Mercuric chloride solution and mixed acid (sulfuric and phosphoric acids) were added, and the solution titrated with a standard solution of potassium dichromate using diphenylamine sulfonate as the indicator.

Cu, Ni, Co, Pb, and Zn

The sample solution was prepared as follows: 0.1 g of sample was decomposed in mixed acid (sulfuric, nitric, and hydrochloric acids) and evaporated to dryness. The residue was dissolved with 20 ml of hydrochloric acid (3N) and filtered into a 100 ml calibrated flask. 5 ml of lanthanum chloride solution (25 g of guranteed lanthanum oxide is dissolved with 100 ml of 6N hydrochloric acid and diluted to 500 ml with water) was added to the filtrate and diluted to the mark with water.

The atomic absorbances of each element in the sample solution were measured by atomic absorption spectrometer. The concentration of each element was determined from a calibration graph, which was prepared using a series of synthetic standard solutions having a composition similar to the sample solution, at the same time.

The instrument used was a Shimadzu double-beam digital atomic absorption/flame spectrophotometer type AA650, attached with the 10 cm slot burner. The absorbance of all elements was measured using an air-acetylen flame.

The operating conditions of the atomic absorption analysis are listed in Table XVI-1.

Total water

Total water was determined by the Penfield tube method. In the analysis of the samples containing amorphous hydrate minerals such as manganese nodules, individual determinations of H_2O-(moisture) and H_2O+(bound water) are impossible. Therefore, total water ($H_2O\pm$) in air-dried sample was determined for convenience.

To discuss the economical value of the nodules from the concentration of elements, H_2O is a significant component. For example, the sample of serial no. 51 has 1.51 % Cu, 1.46 % Ni and 19.54 % $H_2O\pm$ on an air-dried base. Recalculation on a water-free base gives 1.88 % Cu and 1.81 % Ni.

Results

The contents of Mn, Fe, Cu, Ni, Co, Pb, Zn, $H_2O\pm$and Mn/Fe ratios in sixty-eight nodules and two additional nodules are given in Table XVI-2. The average composition of nodules at each station is presented in Table XVI-3, in which the variation of the determined values in each station is shown as the standard deviation.

Discussion

From the analytical data in Table XVI-2 and 3, some notes are given concerning the chemical characteristics of the nodules.

Comparison with previous data

Numerous analyses of manganese nodule have been made so far. In Table XVI-4, our data are compared with those in previous papers on Pacific Ocean nodules. Nodules from the present survey area appear to contain more Cu, Zn, and less Fe, Co, Pb as compared with other data. The Mn/Fe ratio is also far greater than others.

Relation to nodule types

The average metal contents of each type of nodule are shown in Table XVI-5, in which the data of SEr and Db types are added only for reference, because the limited number of analyses did not permit adequate data for interpretation. Except for these

Table XVI-1 Operating conditions for determinations of copper, nickel, cobalt, lead, and zinc.

Element	Wavelength (nm)	Lamp current (mA)	Slit width (nm)	Height of light beam above burner (mm)
Cu	324.8	3	0.3	4
Ni	232.0	5	0.2	4
Co	240.7	10	0.2	6
Pb	217.0	5	0.3	4
Zn	213.8	8	0.2	10

Table XVI-2 Chemical composition of manganese nodules.

Serial no.	Sample no.	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Pb (ppm)	Zn (ppm)	$H_2O\pm$ (%)	Mn/Fe	Morph. type
1	405 G169	18.28	8.05	0.79	0.66	0.13	95	1,080		2.27	Sr
2	407 G171a	17.89	10.83	0.54	0.54	0.23	500	550	25.71	1.65	ISs
3	〃 〃 b	18.54	11.16	0.49	0.58	0.26	580	600	24.79	1.66	ISs
4	〃 〃 c	18.83	10.80	0.55	0.67	0.26	480	610	23.00	1.74	ISs
5	〃 FG5–1a	18.89	11.38	0.50	0.63	0.26	580	650	24.73	1.66	ISs
6	〃 〃 b	21.41	9.79	0.75	0.68	0.26	740	810	19.66	2.19	ISs
7	〃 FG5–2a	20.88	9.83	0.68	0.84	0.25	450	750	22.40	2.12	ISs
8	〃 〃 b	20.78	10.56	0.64	0.75	0.29	515	710	21.11	1.97	ISs
9	408 G172a	15.72	10.36	0.37	0.52	0.25	480	560	23.05	1.52	IDPs
10	〃 〃 b	16.96	10.00	0.40	0.52	0.25	580	870	21.91	1.70	DPs
11	〃 〃 c	18.30	10.00	0.57	0.65	0.27	515	690	22.00	1.83	DPs
12	〃 FG6–1a	18.85	11.63	0.40	0.54	0.27	500	560	24.42	1.62	IDPs
13	〃 〃 b	19.07	11.00	0.49	0.60	0.27	580	580	21.66	1.73	DPs
14	〃 FG6–2a	18.21	10.41	0.44	0.57	0.23	450	600	22.56	1.75	IDPs
15	〃 〃 b	18.34	9.15	0.42	0.51	0.21	350	500	19.19	2.00	DPs
16	409 FG7–1, 2	25.72	5.89	1.24	1.11	0.14	255	1,140	19.75	4.37	Sr
17	411 FG9–1, 2	26.29	5.01	1.14	1.16	0.14	190	1,550	18.19	5.25	Sr
18	414 FG12–1a	20.04	9.54	0.80	0.79	0.19	450	760	21.60	2.10	DPs
19	〃 〃 b	17.14	9.45	0.70	0.78	0.16	350	690	21.26	1.81	DPs
20	〃 FG12–2a	20.04	8.81	0.94	0.82	0.17	320	780	21.60	2.27	DPs
21	〃 〃 b	22.34	7.74	1.17	1.04	0.19	385	1,000	20.89	2.89	DPs
22	417 G181	32.18	4.37	1.43	1.40	0.12	190	1,910	18.32	7.36	Sr
23	〃 FG15–1	27.57	4.66	1.34	1.28	0.16	160	1,950	18.14	5.92	Sr
25	418 G182a	30.20	4.73	1.02	0.97	0.14	160	2,600	17.23	6.83	Sr
26	〃 〃 b	28.72	4.40	1.21	1.20	0.16	130	2,160	17.91	6.53	Sr
27	〃 FG16–1a	22.24	6.92	0.80	0.86	0.14	225	1,500	18.26	3.21	Sr
28	〃 〃 b	28.62	5.22	1.13	1.14	0.16	160	2,210	17.32	5.48	Sr
29	〃 FG16–2	26.82	4.93	1.00	0.97	0.18	160	2,120	16.89	5.44	Sr
30	419 G183a	24.12	5.73	1.07	1.13	0.18	350	1,090	20.92	4.21	SPr
31	〃 〃 b	24.25	5.29	1.07	1.13	0.19	320	1,060	20.34	4.58	SPr
32	〃 FG17–1a	23.04	7.30	1.06	1.06	0.18	350	1,020	20.57	3.16	SPr
33	〃 〃 b	24.86	6.65	1.02	1.23	0.20	290	1,250	20.33	3.74	SPr
34	〃 FG17–2a	23.78	6.71	1.01	1.15	0.18	385	1,090	20.66	3.54	SPr
35	〃 〃 b	24.90	6.09	1.08	1.30	0.19	255	1,250	19.99	4.09	SPr
36	423 G187a	28.09	4.13	1.31	1.29	0.14	190	2,010	18.33	6.80	Sr

37	423 G187b	26.86	4.29	1.10	1.15	0.15	190	2,110	18.49	6.26	Sr
38	〃 FG19-1a	25.84	6.01	1.10	1.25	0.14	320	1,870	19.62	4.30	Sr
39	423 FG19-1b	28.68	4.36	1.16	1.21	0.15	190	2,340	18.04	6.58	Sr
40	〃 FG19-2a	28.09	4.46	1.29	1.35	0.12	225	1,800	18.49	6.30	Sr
41	〃 〃 b	27.40	5.09	1.07	1.09	0.15	225	2,220	18.46	5.38	Sr
42	424 FG20-2	24.40	6.51	1.06	0.91	0.17	190	1,460	17.67	3.75	Sr
43	426 G190a	28.06	5.60	1.50	1.29	0.13	255	1,400	20.35	5.01	Sr
44	〃 〃 b	26.93	6.31	1.43	1.40	0.13	255	1,360	19.55	4.27	Sr
45	〃 FG22-1a	28.02	5.41	1.58	1.34	0.12	255	1,320	19.94	5.18	Sr
46	〃 〃 b	26.98	5.82	1.53	1.38	0.13	255	1,300	19.99	4.64	Sr
47	〃 FG22-2	26.99	6.05	1.47	1.35	0.14	255	1,300	20.16	4.46	Sr
48	414A G193a	19.31	12.00	0.54	0.63	0.22	610	680	24.26	1.61	DPs
49	〃 〃 b	20.72	13.12	0.58	0.68	0.24	645	720	25.85	1.58	DPs
50	〃 A2 FG25-1	27.57	6.98	1.55	1.38	0.14	225	1,240	20.10	3.95	Sr
51	〃 〃 FG25-2	27.50	5.44	1.51	1.46	0.15	225	1,140	19.54	5.06	Sr
52	429 FG27-1a	19.11	8.31	0.75	0.68	0.20	530	600	23.78	2.30	Ss/SPs
53	〃 〃 b	20.08	8.83	0.72	0.66	0.24	385	680	21.68	2.27	Ss/SPs
54	〃 FG27-2a	19.48	8.70	0.73	0.76	0.20	420	620	22.74	2.24	Ss/SPs
55	〃 〃 b	24.15	7.30	0.93	1.02	0.19	350	860	21.39	3.31	Ss/SPs
56	407 D137	18.34	12.82	0.36	0.45	0.27	645	270	26.89	1.43	ISs
57	430 G195a	22.18	7.85	0.90	0.84	0.19	450	850	22.02	2.83	Ss/SPs
58	〃 〃 b	23.72	7.45	0.97	0.95	0.21	450	910	21.38	3.18	Ss/SPs
59	〃 〃 c	23.62	7.42	1.02	1.07	0.22	385	890	21.48	3.18	Ss/SPs
60	〃 FG28-1a	22.75	7.57	0.91	0.92	0.20	385	850	22.00	3.01	Ss/SPs
61	〃 〃 b	22.53	8.38	0.90	0.96	0.21	385	850	21.72	2.69	Ss/SPs
62	〃 FG28-2a	23.38	7.15	0.94	0.90	0.19	385	970	22.01	3.27	Ss/SPs
63	〃 〃 b	20.98	7.45	0.84	0.85	0.19	385	800	21.37	2.82	Ss/SPs
64	431 G196a	29.26	5.02	1.32	1.27	0.15	225	1,440	19.07	5.83	Sr
65	〃 〃 b	30.09	5.67	1.08	1.02	0.19	160	2,000	17.86	5.31	Sr
66	〃 FG29-1	26.85	5.88	1.18	1.20	0.14	320	1,440	19.75	4.57	Sr
67	〃 FG29-2	27.35	5.57	0.94	0.99	0.17	190	1,760	18.15	4.91	Sr
68	433 FG31-1a	25.48	6.60	1.19	1.11	0.15	290	1,080	20.67	3.86	Sr
69	〃 〃 b	25.89	7.34	1.17	1.19	0.15	290	1,180	20.11	3.53	Sr
Average of 68 nodules		23.54	7.52	0.95	0.97	0.19	348	1,170	20.74*	3.13	
(Additional analyses)											
70	407A2 FG32-2	18.51	9.02	0.80	0.75	0.18	533			2.05	SEr
71	411 G175	22.18	6.29	1.14	1.07	0.13	400			3.52	Db

*67 nodules

Table XVI-3 Avcrage composition at each station.

Station no.	Numbers of sample	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Pb (ppm)	Zn (ppm)	$H_2O\pm$ (%)	Mn/Fe
405	1	18.28	8.05	0.79	0.66	0.13	95	1,080		2.27
407	8	19.44 $\pm_{1.27}$	10.90 $\pm_{0.90}$	0.56 $\pm_{0.12}$	0.64 $\pm_{0.11}$	0.26 $\pm_{0.02}$	561 $\pm_{90}$	619 $\pm_{154}$	23.54 $\pm_{2.28}$	1.78
408	7	17.92 $\pm_{1.09}$	10.36 $\pm_{0.73}$	0.44 $\pm_{0.06}$	0.56 $\pm_{0.05}$	0.25 $\pm_{0.02}$	494 $\pm_{74}$	623 $\pm_{114}$	22.11 $\pm_{2.45}$	1.73
409	1	25.72	5.89	1.24	1.11	0.14	255	1,140	19.75	4.37
411	1	26.29	5.01	1.14	1.16	0.14	190	1,550	18.19	5.25
414	6	19.93 $\pm_{1.56}$	10.11 $\pm_{1.86}$	0.79 $\pm_{0.22}$	0.79 $\pm_{0.13}$	0.20 $\pm_{0.03}$	460 $\pm_{125}$	772 $\pm_{108}$	22.58 $\pm_{1.83}$	1.97
〃	2	27.54	6.21	1.53	1.42	0.14	225	1,690	19.82	4.43
417	2	29.88	4.52	1.38	1.34	0.14	175	1,930	18.23	6.61
418	5	27.32 $\pm_{2.76}$	5.24 $\pm_{0.88}$	1.03 $\pm_{0.14}$	1.03 $\pm_{0.12}$	0.16 $\pm_{0.02}$	167 $\pm_{31}$	2,118 $\pm_{353}$	17.52 $\pm_{0.49}$	5.21
419	6	24.16 $\pm_{0.64}$	6.30 $\pm_{0.67}$	1.05 $\pm_{0.03}$	1.17 $\pm_{0.08}$	0.19 $\pm_{0.01}$	325 $\pm_{43}$	1,127 $\pm_{90}$	20.47 $\pm_{0.29}$	3.83
423	6	27.49 $\pm_{0.94}$	4.72 $\pm_{0.65}$	1.17 $\pm_{0.09}$	1.22 $\pm_{0.09}$	0.14 $\pm_{0.01}$	223 $\pm_{46}$	2,058 $\pm_{149}$	18.57 $\pm_{0.49}$	5.82
424	1	24.40	6.51	1.06	0.91	0.17	190	1,460	17.67	3.75
426	5	27.40 $\pm_{0.49}$	5.84 $\pm_{0.32}$	1.50 $\pm_{0.05}$	1.35 $\pm_{0.04}$	0.13 $\pm_{0.01}$	255 $\pm_{0}$	1,336 $\pm_{39}$	20.00 $\pm_{0.22}$	4.69
429	4	20.70 $\pm_{2.02}$	8.28 $\pm_{0.60}$	0.78 $\pm_{0.09}$	0.78 $\pm_{0.14}$	0.21 $\pm_{0.02}$	421 $\pm_{67}$	690 $\pm_{102}$	22.40 $\pm_{0.94}$	2.50
430	7	22.74 $\pm_{0.89}$	7.61 $\pm_{0.37}$	0.93 $\pm_{0.05}$	0.93 $\pm_{0.07}$	0.20 $\pm_{0.01}$	404 $\pm_{29}$	874 $\pm_{50}$	21.71 $\pm_{0.28}$	2.99
431	4	28.39 $\pm_{1.33}$	5.34 $\pm_{0.37}$	1.13 $\pm_{0.14}$	1.12 $\pm_{0.12}$	0.16 $\pm_{0.02}$	224 $\pm_{60}$	1,660 $\pm_{236}$	18.71 $\pm_{0.75}$	5.32
433	2	25.68	6.97	1.18	1.15	0.15	290	1,130	20.39	3.68

two types, several relationships between nodule types and chemical composition are recognized.

Firstly, the contents of main elements differ in the two fundamental groups of nodules (MORITANI *et al.*, in this report). The rough surface type group is rich in Mn, while the smooth surface type group is rich in Fe, as clearly shown in Fig. XVI-1.

Secondly, as already pointed out in many previous papers, Mn is closely related with Cu, Ni, while Fe has a close relation with Co, forming the Mn-Cu-Ni group, and Fe-Co group respectively.

Thirdly, the contents of these two groups change inversely according to the order of a series of nodule types, Sr→SPr→Ss→Ss/SPs→DPs→ISs→IDPs, as shown in both Table XVI-5 and Fig. XVI-2. The Mn-Cu-Ni group decreases while Fe-Co group increases respectively. This coincides with the tendency mentioned by MEYER (1973). In our case, the Db type, presumably corresponding to his "B" type nodule with the highest economic metal contents with Mn 27.9 %, Fe 5.4 %, Cu 1.22 %, Ni 1.40 %, and Co 0.19 %, does not necessarily have the highest values of Mn, Cu, and Ni. As already mentioned, we have now only one analysis each for these two types of nodules. Therefore, we need more data conterning this problem.

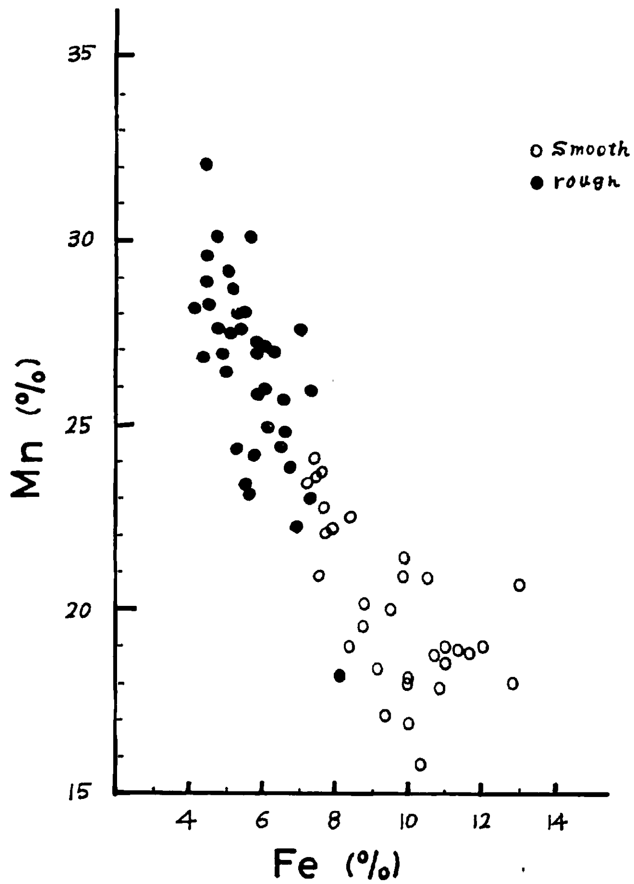

Fig. XVI-1 Relation between surface texture and Mn, Fe contents.

Table XVI-4 Comparison of average values.

	This paper	MERO (1962)	GOLDBERG (1954)	AHRENS *et al.* (1967)
Numbers of sample	68	54	11	11
Mn%	23.54	24.2	19.0	22.3
Fe%	7.52	14.0	13.8	13.4
Cu%	0.95	0.53	0.55	0.33
Ni%	0.97	0.99	0.46	0.62
Co%	0.19	0.35	0.28	0.35
Pb ppm	348	900		1,045
Zn ppm	1,170	470		627
$H_2O \pm$ %	20.74	25.8*		
Mn/Fe	3.13	1.73	1.38	1.66

*represented as loss on ignition

Table XVI-5 Average metal contents of each type nodule (weight %).

Type	Mn	Fe	Cu	Ni	Co
Sr	26.05	5.86	1.19	1.13	0.15
SPr	24.15	6.29	1.05	1.17	0.18
Db*	22.18	6.29	1.14	1.07	0.13
SEr*	18.51	9.02	0.80	0.75	0.18
Ss/SPs	21.71	7.94	0.85	0.85	0.20
DPs	19.35	10.49	0.64	0.69	0.21
ISs	18.97	11.72	0.47	0.56	0.26
IDPs(/DPs)	17.59	10.80	0.40	0.54	0.25

*Analysis data for only one sample of each type nodule.

Relation between nodule size and chemical composition

Though, the relation between nodule types and chemical composition seems to be the most important, also we examined the relation of nodule size and chemical composition.

The size of the nodule samples for which chemical analyses were made are classified into the following four size groups; 1 to 2 cm (15 samples), 2 to 4 cm (37 samples), 4 to 6 cm (13 samples), and 6 to 8 cm (3 samples).

The relation between nodule size and Mn, Fe, Cu, Ni, Co, and $H_2O\pm$ contents is illustrated in Fig. XVI-3. As shown, Mn, Cu, and, Ni contents decrease with decreasing nodule size, while Fe, Co, and $H_2O\pm$ contents increase with increasing nodule size.

Inter-element relationships

The correlation coefficients of inter-elements are presented in Table XVI-6. The relationships of inter-elements are all high. In particular, the correlation coefficient of Cu vs Ni is nearly 1. These values are divided into two group as following;

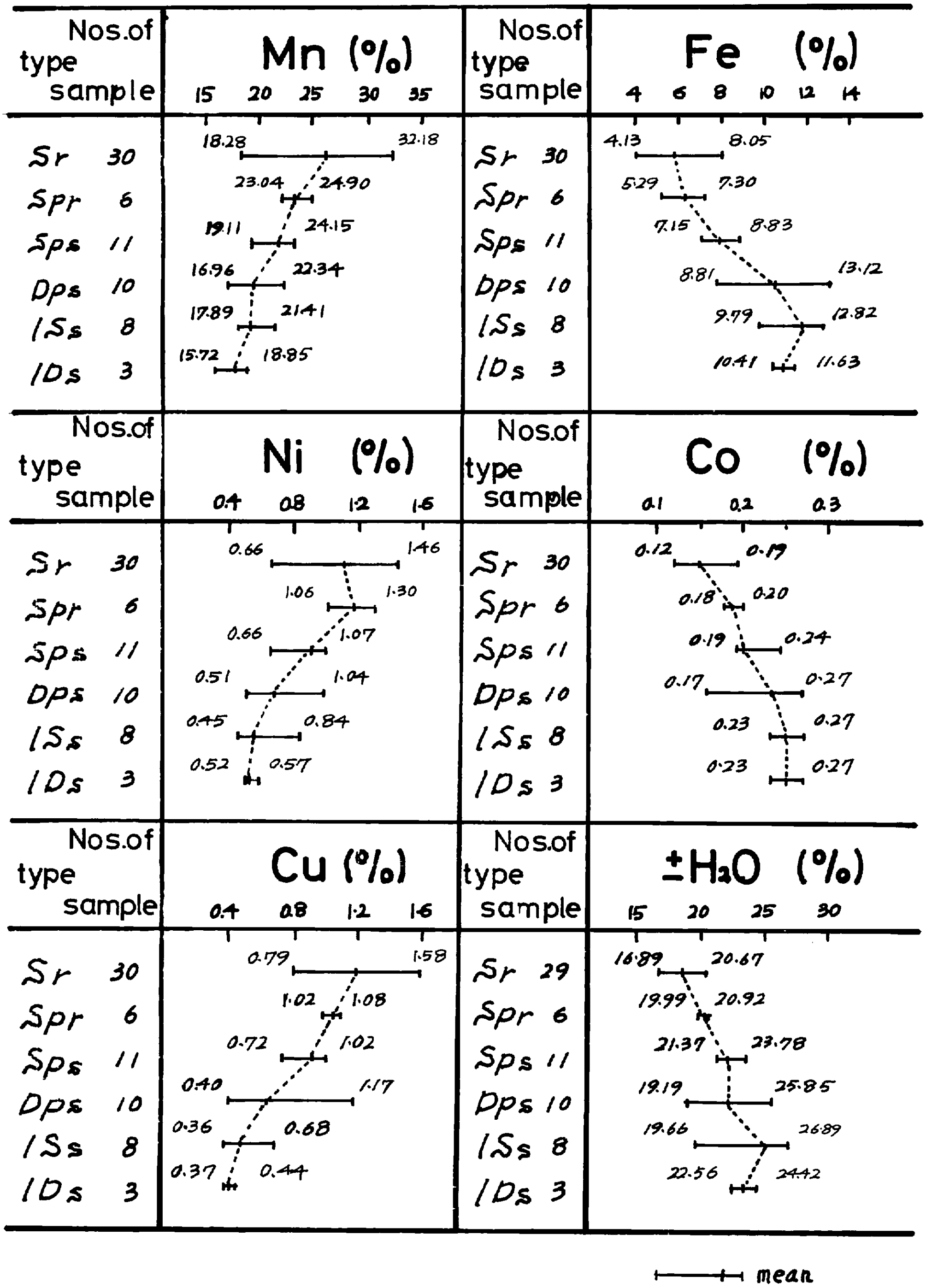

Fig. XVI-2 Relation between nodule type and chemical component.

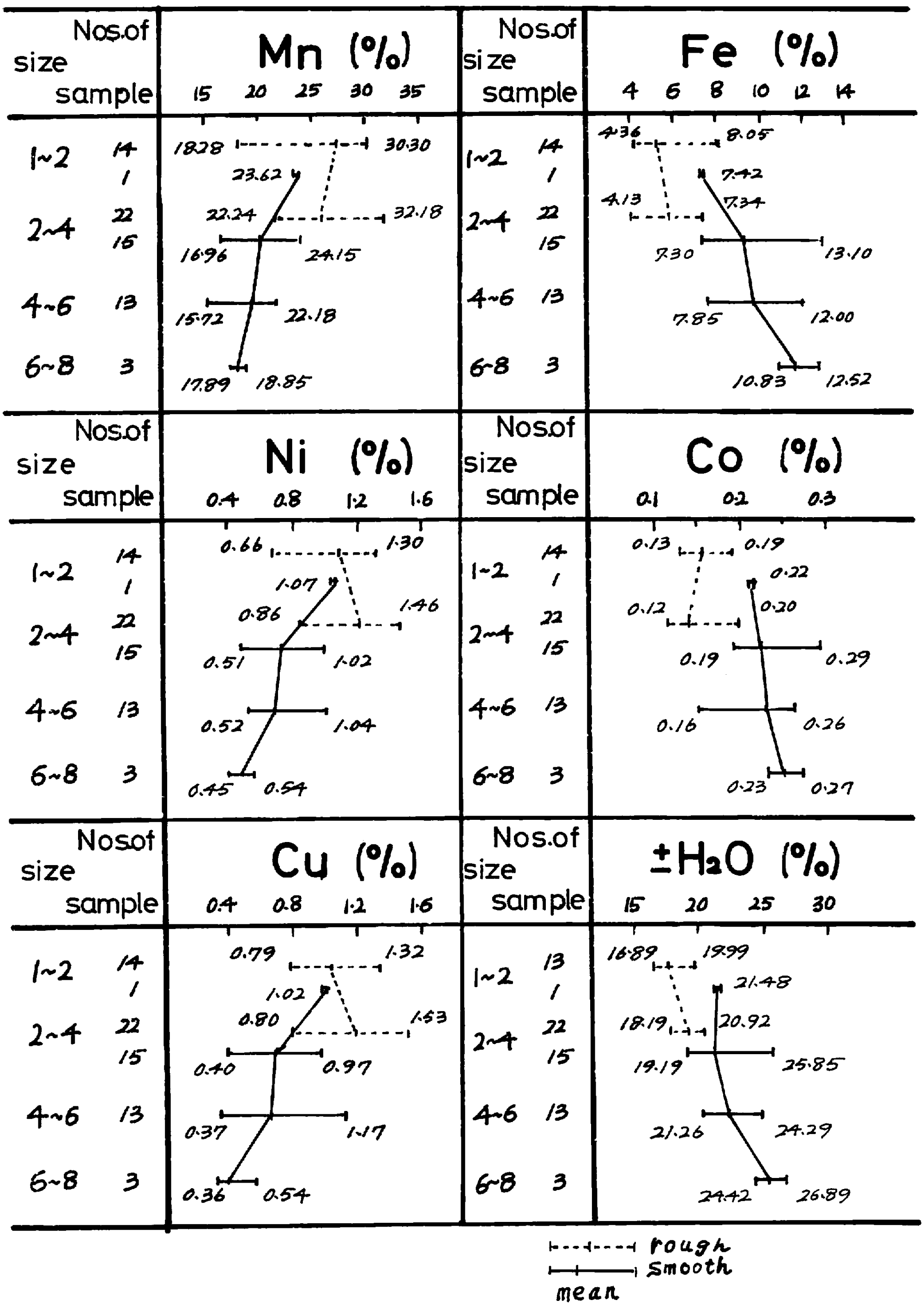

Fig. XVI-3 Relation between nodule size and chemical component.

Table XVI-6 Inter-element correlation coefficients.

Element	Zn	Pb	Co	Ni	Cu	Fe
Mn	+0.86	−0.76	−0.75	+0.89	+0.88	−0.88
Fe	−0.90	+0.87	+0.84	−0.85	−0.85	
Cu	+0.64	−0.73	−0.84	+0.96		
Ni	+0.66	−0.70	−0.79			
Co	−0.69	+0.83				
Pb	−0.80					

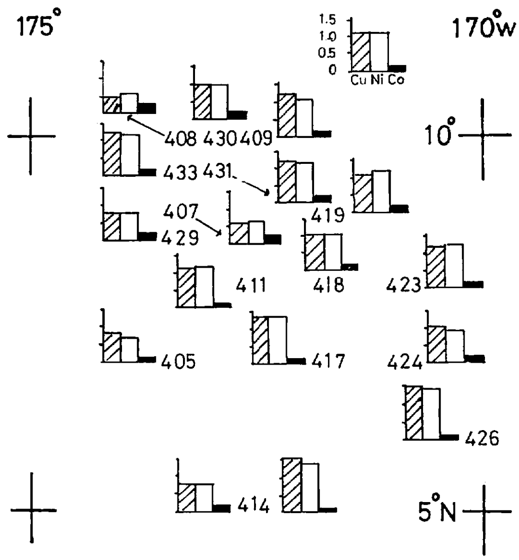

Fig. XVI-4 Areal distribution of metal concentration of nodules.

Regional distribution of Cu, Ni, and Co

In order to examine the distribution of Cu, Ni, and Co in the survey area, histograms of the average contents at each station have been prepared as shown in Fig. XVI-4. These are closely related to nodule types and partly with sediment types. In particular, the two histograms of St. 414 show a distinct change in chemical composition within the same area.

In conclusion, it is emphasized that future study should be directed towards elucidating the relationship between chemical composition and mineral composition of the manganese nodules.

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