Geological Survey of Japan Cruise Report No. 18, p. 338–354, 1982

XVI. REGIONAL VARIATION OF MANGANESE NODULE CHEMISTRY FROM WAKE TO TAHITI, GH80-1 CRUISE

Akira Usui and Tsunekazu Mochizuki

Introduction

Bulk chemical composition is one of the most variable characteristics of marine manganese nodules. MERO (1965) first pointed out the nodule compositional variations with regions in the Pacific, and later PRICE and CALVERT (1970) and others found their relationship to various marine environments. Recent detailed investigations of marine manganese deposits of many various areas have revealed that the nodule characteristics including chemical composition are also variable within small areas especially of rugged topography (MIZUNO and MORITANI, 1978; ANDREWS and FRIEDRICH, 1979; HALBACH and ÖZKARA, 1979). The results of on-site observations of manganese nodule deposits during GH80–1 cruise suggest that the regional variation is significant as well as occasional local variations.

Our previous studies in the Central Pacific Basin have revealed a remarkably close relationship between nodule morphological type and metal contents. The objective of this analysis is to characterize the regional compositional variation of nodules from various environments along the two traverses on the basis of our proposed schema on nodule type and chemistry.

Samples and analytical procedure

Among 59 stations, manganiferous materials were collected at 49 stations in the Central Pacific Basin, the Mid-Pacific Mountains, the Manihiki Plateau, and the Penrhyn Basin. Samples for analyses were taken at 40 stations. Sample numbers, localities, water depths, description of nodules, and associated geological data of sampling stations are summarized in Chapter VII (Appendix VII-1 and Appendix VII-2) (USUI, this cruise report). Nodule samples were visually selected from each retrieved sampler, i.e., a freefall grab, a box corer, a piston corer, or a dredger. In general, nodules from an individual sampler are similar to each other in external morphology and chemistry. Then one or more nodule samples were selected from each sampler. In a few cases, nodules evidently different in external feature were found in single sampler, so two or more samples were separately taken from those samplers. During sample preparation materials other than ferromanganese oxide shells such as rock nuclei were visually removed off when possible. Two subsamples were taken when a nodule has a distinct double-layered internal structure.

The samples were kept in plastic containers on board for shore-based analyses and were dried in air at room temperature in a few months after the cruise. One hundred and twelve ground samples were prepared for atomic absorption spectroscopic analyses of Mn, Fe, Cu, Ni, Co, Pb, and Zn. The analytical procedure follows the method described by MOCHIZUKI *et al.* (1981), and the analyses were carried out on the air-dried powdered samples. Total water contents ($H_2O\pm$) were measured by gravimetric method also on the air-dried powdered samples. Acid insoluble fractions were not determined, though these fractions occasionally amount several tens of per cent of nodules.

Results

Concentrations of metal elements and water contents are shown in Chapter XV (Appendix XV-1) (MITA *et al.*, this cruise report) with the analytical data for the associated sediments.

Discussion

Metal contents and morphological type of nodules

Simple arithmetrical averages of chemical composition for all nodules are compared to previous compositional data for Pacific manganese nodules in Table XVI-1. The nodules of the GH80–1 cruise are slightly more enriched in Mn, Cu, and Ni than the average of the Pacific manganese nodules (PRICE and CALVERT, 1970). The table also shows the average and standard deviation of metal contents and ratios between elements of various type nodules from the traverses.

These chemical data with the nodule type classification seems to provide more important information than for all type nodules, and a simple averaging is often meaningless.

Figures XVI-1 and -2 show frequency distribution patterns of metal contents of various types of nodules. Fe and Mn are major elements of manganese nodules of any types. The sum of Mn and Fe of most samples generally falls within a range from 25 to 40%. The concentration of Mn in r-type nodules is slightly higher than in s-type nodules from the Central Pacific Basin and the Penrhyn Basin. Fe of type r is much less than in type s. The variation range of Fe concentration is much greater than those of Mn concentration.

Ni, Cu, and Zn of type r are significantly higher than those of type s. The concentration ranges of these three elements for types s and r are markedly separated and consequently the frequency distribution for all type nodules often shows a bimodal distribution. Co and Pb, especially the former, are also separated in concentrations in types s and r. However, the separation is obscure in comparison with Ni, Cu, Zn, and Fe.

Regional variation of chemical characteristics

The traverses, Lines A and B of the GH80–1 cruise, cross the GH76–1, GH77–1, GH78–1, and GH79–1 cruise areas between 5° and 13°N in the northern Central Pacific Basin. We defined two characteristic nodules types in these areas, that is, smooth type (s) and rough type (r) (MORITANI *et al.*, 1977). These two types are significantly different in chemical composition (FUJINUKI *et al.*, 1977) as well as in mode of distribution, occurrence on the sediment surface, and external morphology. This nodule type classification was proved to be also applicable to the Penrhyn Basin nodules in the Sourth Pacific during this cruise. Noticeable is that variation of manganese nodule facies including nodule type, occurrence, and abundance, are generally consistent with the geological provinces (USUI, this cruise report). The regional variations of nodule chemical characteristics are also remarkable, corresponding with manganese nodule facies (Fig.

Table XVI-1 Metal contents and ratios of manganese nodules from the Wake to Tahiti Transect and *: for Cu+Ni.

	This study							
	Type r (C.P.B.)		Type s (C.P.B.)		Type s (Penrhyn Basin)		Type s (Manihiki Plateau)	
number of analyses	35		29		27		6	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Mn	24.3	4.6	18.5	3.3	17.8	3.1	11.5	6.2
Cu	1.18	0.37	0.34	0.11	0.33	0.17	0.26	0.09
Ni	1.23	0.34	0.51	0.10	0.52	0.23	0.36	0.11
Zn	0.115	0.033	0.056	0.007	0.061	0.011	0.048	0.014
Cu+Ni+Zn	2.52	0.70	0.91	0.20	0.91	0.41	0.66	0.21
Fe	6.4	1.4	13.0	2.3	14.4	3.2	9.7	5.4
Pb	0.042	0.015	0.097	0.028	0.107	0.035	0.058	0.044
Co	0.16	0.05	0.34	0.10	0.37	0.11	0.22	0.18
Mn/Fe	4.12	1.62	1.43	0.28	1.31	0.43	1.21	0.28
Fe/Mn	0.28	0.13	0.73	0.17	0.85	0.30	0.86	0.17
Cu/Mn	0.048	0.010	0.019	0.005	0.019	0.008	0.027	0.014
Ni/Mn	0.051	0.010	0.028	0.007	0.029	0.010	0.037	0.014
Zn/Mn	0.0047	0.0008	0.0031	0.0004	0.0034	0.0005	0.0047	0.0013
(Cu+Ni+Zn)/Mn	0.104	0.018	0.050	0.0012	0.051	0.019	0.069	0.029
Co/Mn	0.0069	0.0023	0.0182	0.0034	0.0211	0.0060	0.0170	0.0049
Co/Fe	0.026	0.008	0.026	0.005	0.026	0.006	0.020	0.005
Pb/Fe	0.0065	0.0017	0.0073	0.0016	0.0073	0.0014	0.0055	0.0012
Cu/Ni	0.96	0.13	0.69	0.13	0.63	0.09	0.72	0.14

XVI-3). The variation well agrees to the nodule types throughout all stations in these traverses, except for a local great variation at St. 1635.

The r-type nodules are distributed in the siliceous ooze/clay area of the Central Pacific Basin. They are enriched in Ni, Cu, Zn, and Mn and poor in Fe, Co, and Pb. The average composition of type r is quite similar to that of high grade nodules from the so-called Manganese Belt in the northeastern equatorial Pacific. The Cu + Ni + Zn grade and Cu/Ni ratio are even higher.

The s-type nodules are dominant in the pelagic/zeolitic clay area in the northern Central Pacific Basin, the Mid-Pacific Mountains area, and the Penrhyn Basin. They are two- or threefold lower in Cu, Ni, and Zn than type r, and rich in Fe, Co, and Pb. The chemical characteristics of the s-type nodules from the Central Pacific Basin and the Penrhyn Basin are surprisingly similar, even though the external morphology such as color and surface feature is quite different and the areas of distribution are distant. The only difference is recognized in ratio Fe/Mn which is slightly higher in the Penrhyn Basin nodules than in the Central Pacific Basin nodules. A possible explanation is a simple addition of iron to similar assemblage of nodule components.

The s-type nodules are also distributed near the Manihiki Plateau though very sporadically. Both Fe and Mn are lower than in other provinces, which is probably attributable to a large fraction of non-ferromanganese materials such as detrital rock fragments and nuclei. However, the ratio (Cu + Ni + Zn)/Mn is considerably high for s-type nodules.

comparison with previous chemical data. All elements in wt%. C.P.B.: Central Pacific Basin,

All nodules (GH80-1)		Northeast Pacific Manganese Belt HEIN (1977)	Southwest Pacific South Penrhyn Basin LANDMESSER *et al.* (1976)	Pacific PRICE and CALVERT (1970)
112		1261	7	202
Mean	S.D.	Mean	Mean	Mean
19.4	5.5	26.7	15.8	18.0
0.61	0.45	1.05	0.14	0.53
0.73	0.41	1.25	0.29	0.72
0.076	0.033	0.13	0.047	—
1.43	0.88	2.43	0.48	1.25*
10.8	4.2	6.4	14.9	12.1
0.075	0.038	0.050	0.11	0.09
0.26	0.13	0.24	0.39	0.36
2.25	1.58	4.18	1.06	1.48
0.62	0.31	0.24	0.95	0.67
0.030	0.015	0.039	0.009	0.029
0.037	0.014	0.047	0.018	0.040
0.0039	0.0010	0.0049	0.0030	—
0.071	0.029	0.091	0.031	0.069*
0.0145	0.0070	0.0090	0.0247	0.020
0.024	0.007	0.038	0.026	0.030
0.0068	0.0017	0.0078	0.0073	0.0074
0.77	0.18	0.84	0.50	0.74

The regional variations of Mn/Fe and Cu+Ni grade with nodule type and abundance throughout the traverses are graphically summarized in Fig. XVI-4.

Ratios of metal concentration

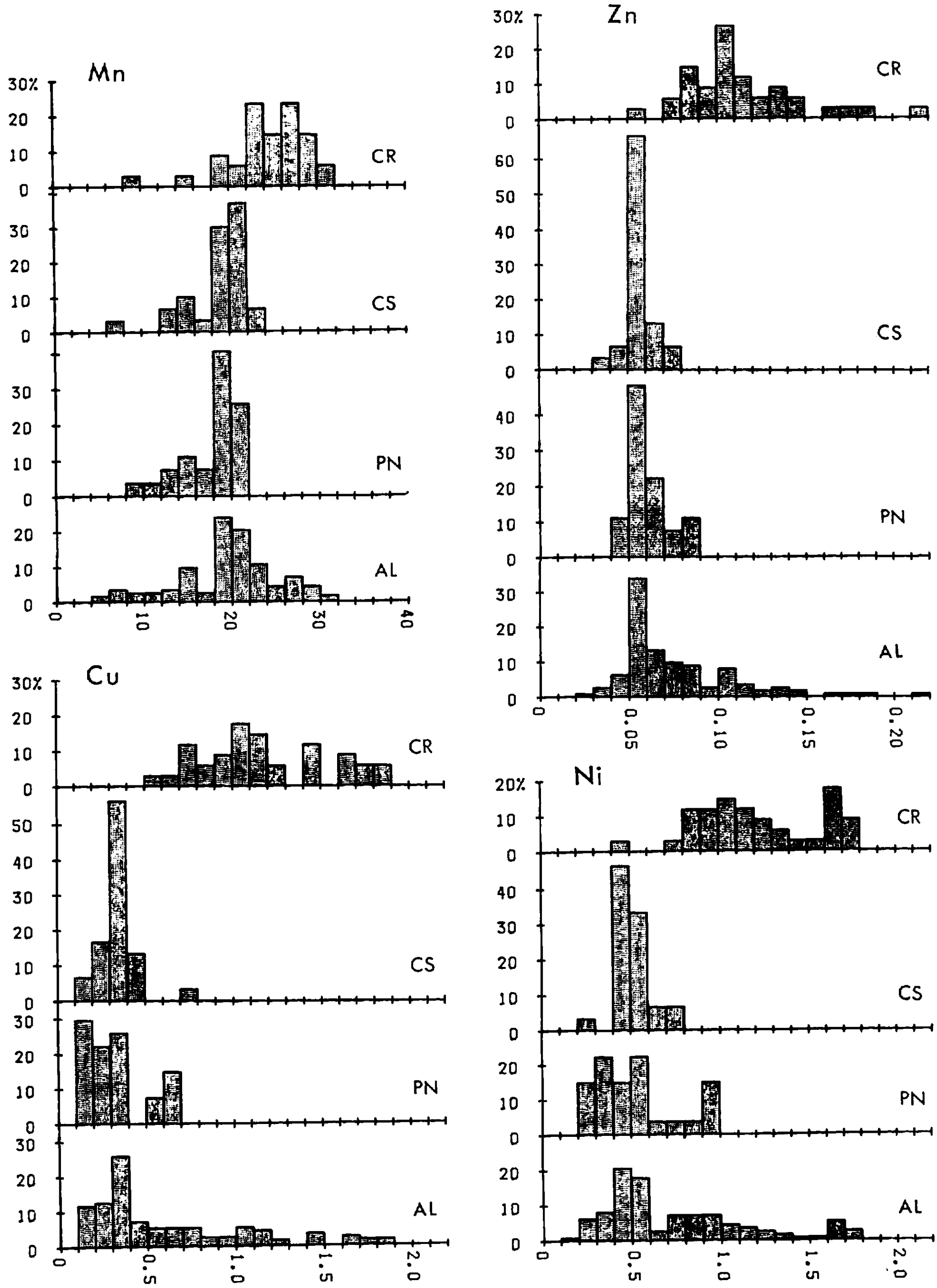
Ratios of metal concentrations are more significant parameters for nodule geochemistry than the bulk compositions because the bulk compositions are subject to the amount of acid insoluble fraction, water content, and even the method of sample preparation. Among ratios of metal concentrations, Fe/Mn or Mn/Fe is the most sensitive parameter to characterize manganese nodule facies because it is approximately directly related to the mineral composition. As reported by USUI *et al.* (1979), manganese nodules are generally composed of three constituents;

1) iron-free and roughly stoichiometrical manganate, containing lattice-held Cu, Ni, and Zn (10 Å manganite phase),

2) submicroscopic mixture of poorly crystalline 2 line form δ-MnO_2 and hydrous ferric oxide which contain roughly similar amounts of iron and manganese, though the ratio Fe/Mn varies considerably (δ-MnO_2 phase), and

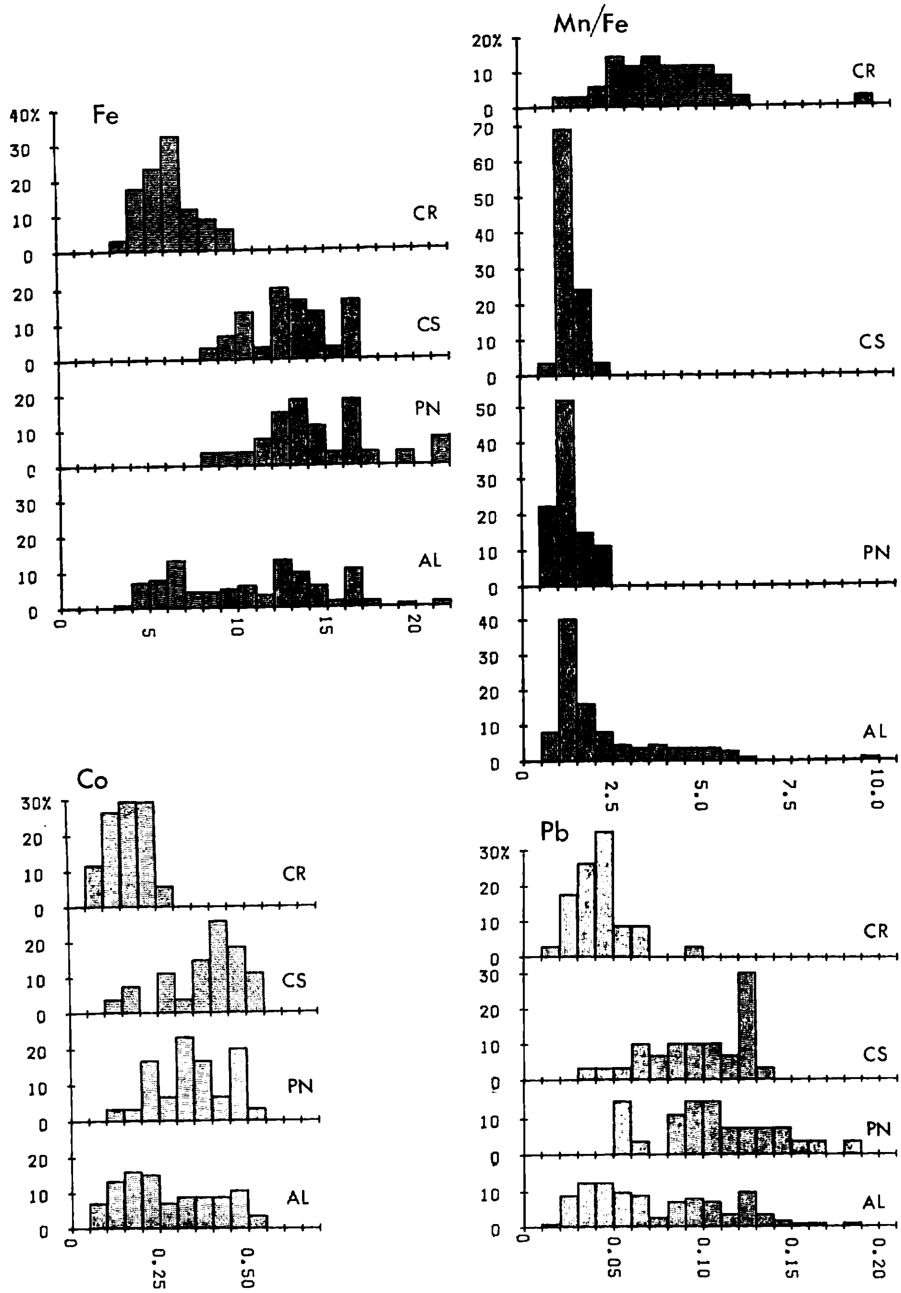
3) megascopic to submicroscopic silica and aluminosilicate matters and other foreign materials such as nuclei.

Therefore, the ratio of Mn/Fe may be regarded as a function of relative amount of 10 Å manganite phase and δ-MnO_2 phase. High Mn/Fe ratio means high content of

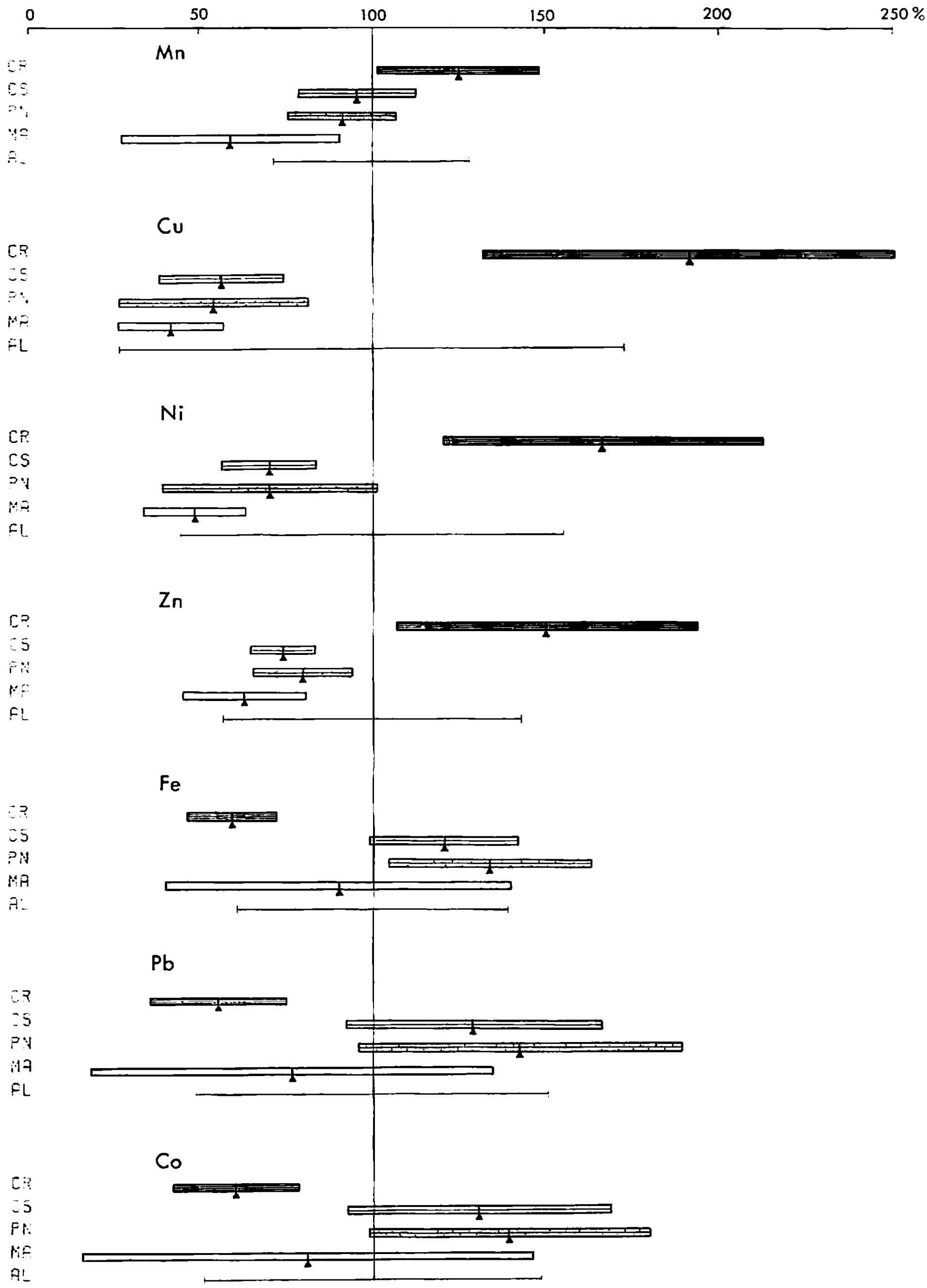


(1)

Fig. XVI-1 Frequency distribution of metal contents and Mn/Fe of manganese nodules. Concentration in wt. %. CR: type r from the Central Pacific Basin (35 data), CS: type s from the Central Pacific Basin (29 data), PN: type s from the Penrhyn Basin (27 data), AL: all types of GH80–1 nodules (112 data).

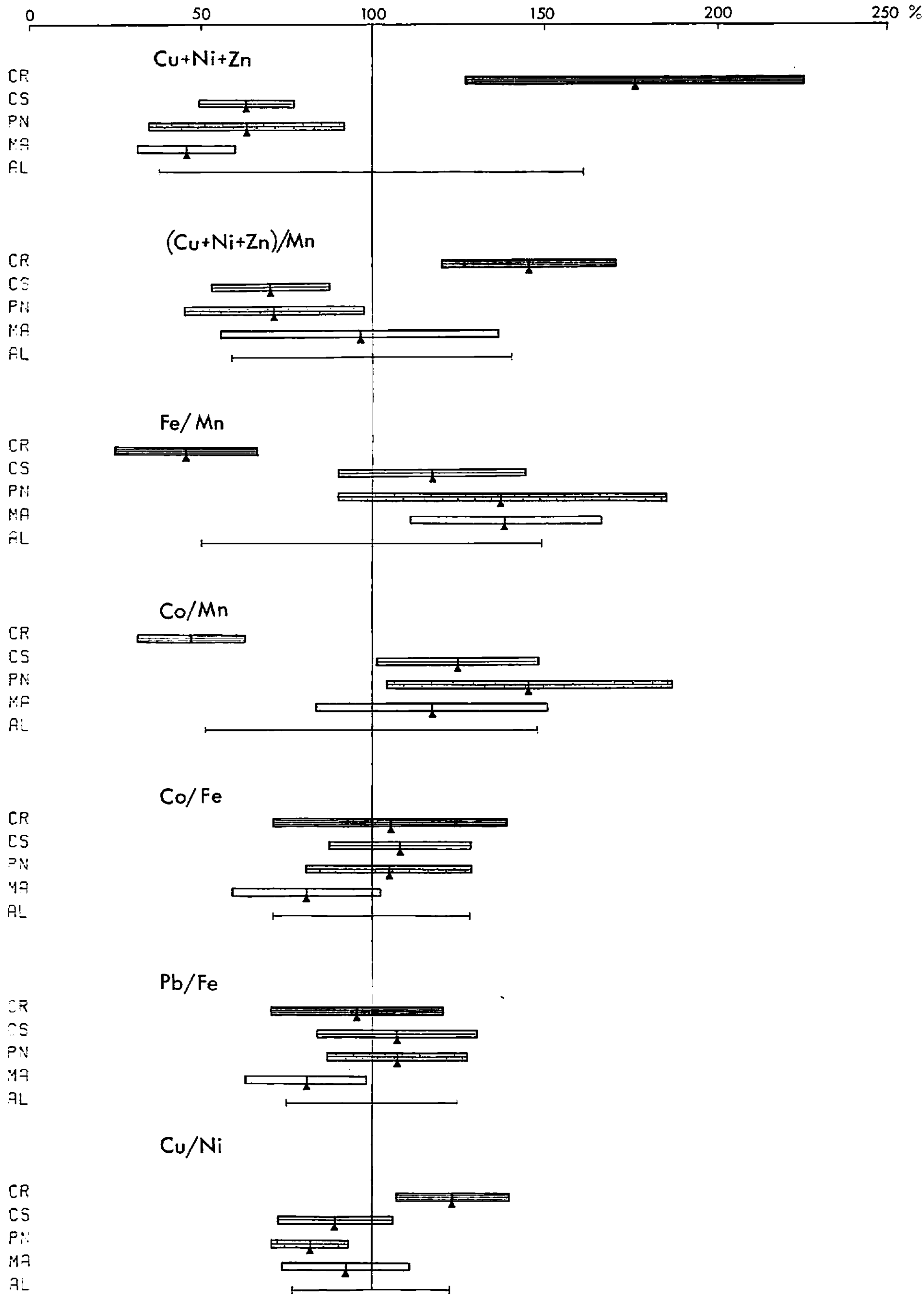


(2)



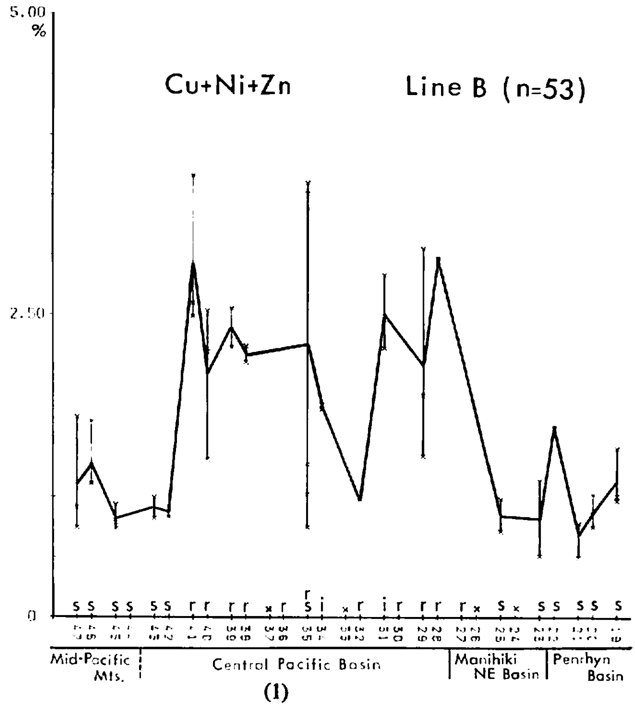
(1)

Fig. XVI-2 Diagram of normalized averages and standard deviations of metal concentrations and concentration ratios of manganese nodules. All values are normalized to the average of each component for all types. The half length of each bar indicates one standard and the triangle indicates the average.

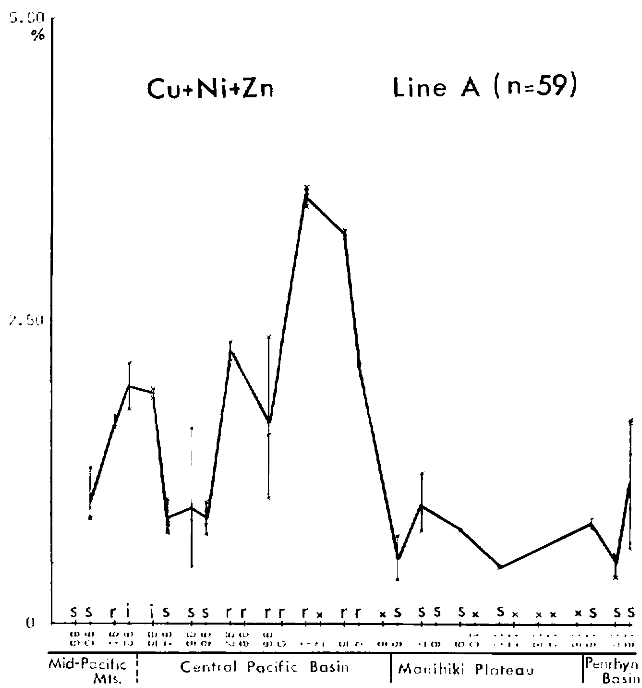


0
50
100
150
200
250 %
Cu+Ni+Zn
(Cu+Ni+Zn)/Mn
Fe/ Mn
Co/Mn
Co/ Fe
Pb/Fe
Cu/Ni
CR
CS
PN
MA
AL

(2)

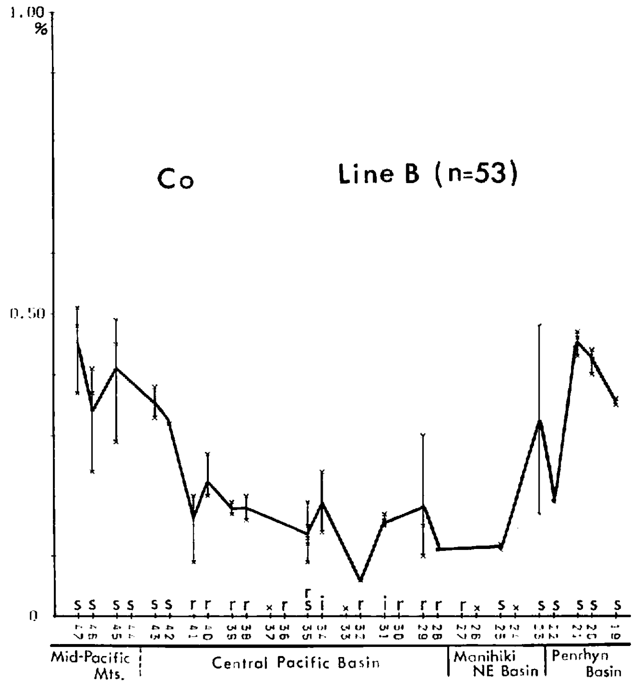


(1)

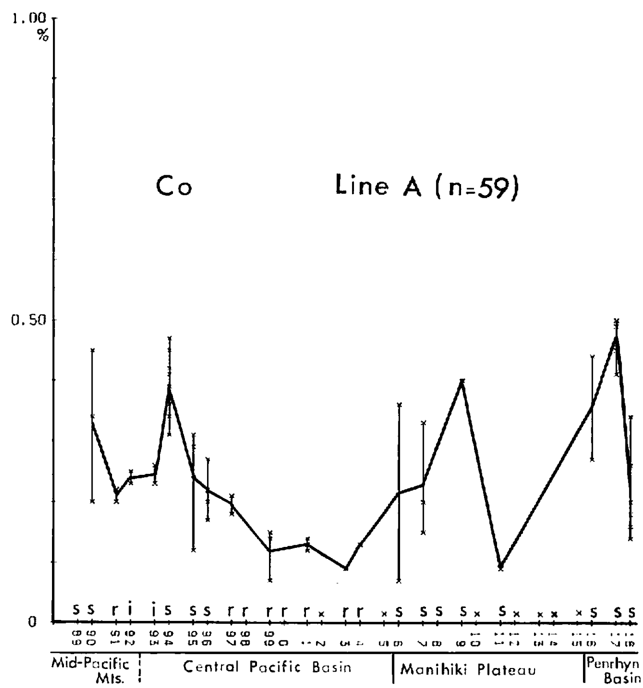


(2)

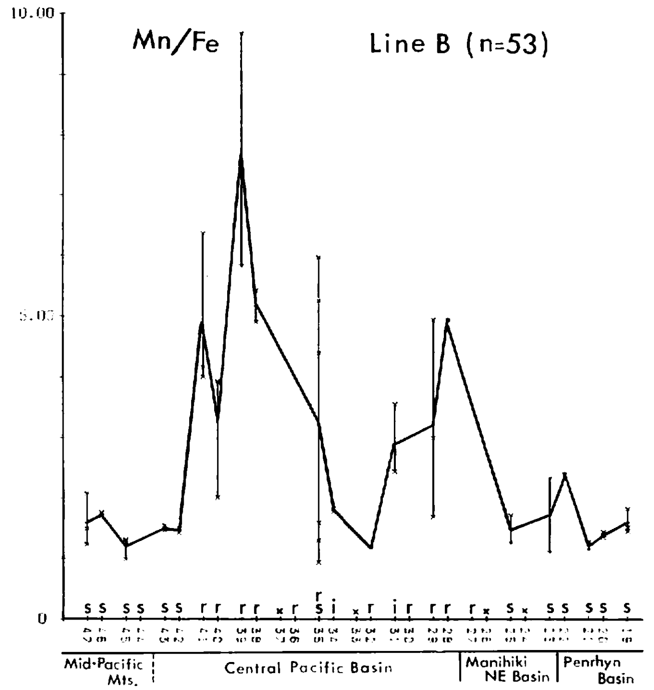
Fig. XVI-3 Regional and local variations of metal contents and ratios of manganese nodules. Crosses indicate individual analyses, and vertical lines ranges of local variation. Combined lines demonstrate regional variation of station averages. The horizontal axis is in proportion to actual distance. Station (number of last two digits shown under the axis) are located 60 or 100 nautical miles apart. Symbols on the axis denote nodule types (s: smooth, r: rough, i: intermediate type, × : no nodule).


1.00
%
0.50
0
Co
Line B (n=53)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki NE Basin
Penrhyn Basin

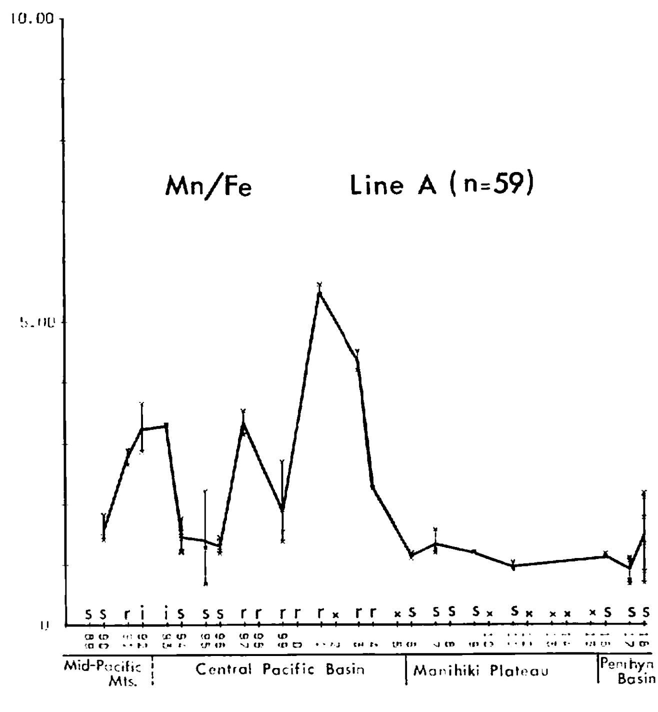
(3)


1.00
%
0.50
0
Co
Line A (n=59)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki Plateau
Penrhyn Basin

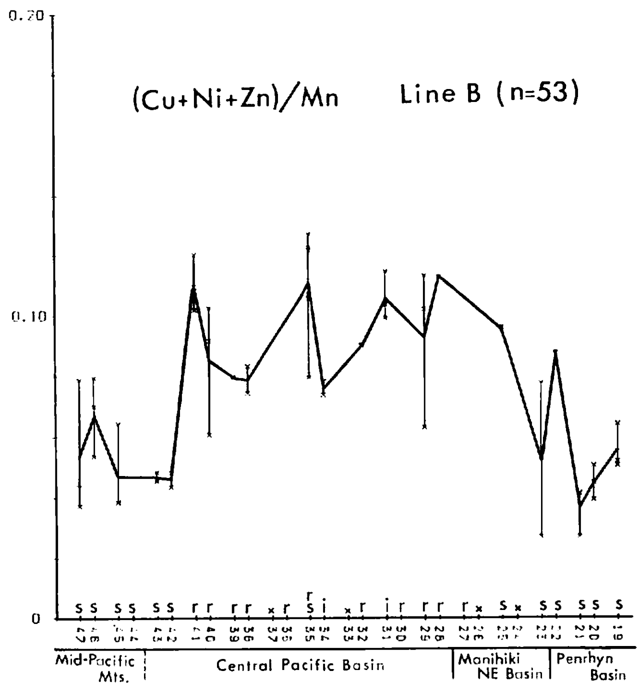
(4)


10.00
5.00
0
Mn/Fe
Line B (n=53)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki NE Basin
Penrhyn Basin

(5)

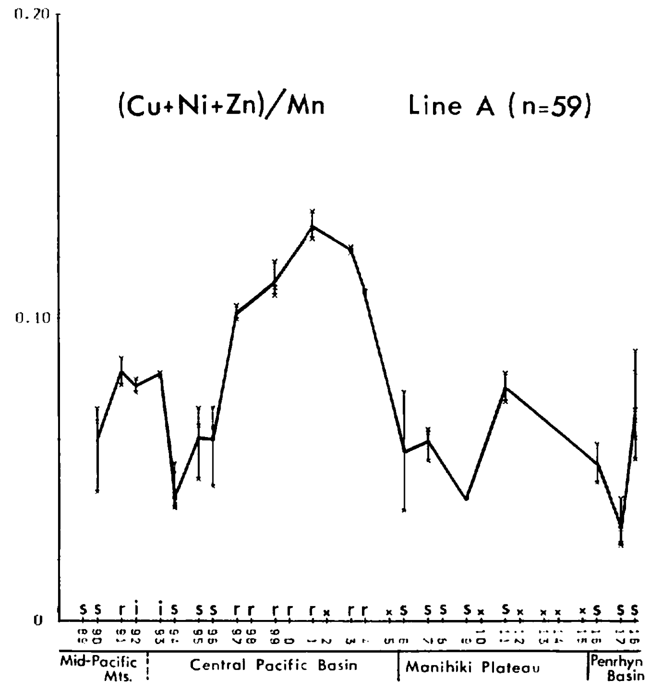

10.00
5.00
0
Mn/Fe
Line A (n=59)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki Plateau
Penrhyn Basin

(6)



0.20
0.10
0
(Cu+Ni+Zn)/Mn
Line B (n=53)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki NE Basin
Penrhyn Basin

(7)



0.20
0.10
0
(Cu+Ni+Zn)/Mn
Line A (n=59)
Mid-Pacific Mts.
Central Pacific Basin
Manihiki Plateau
Penrhyn Basin

(8)

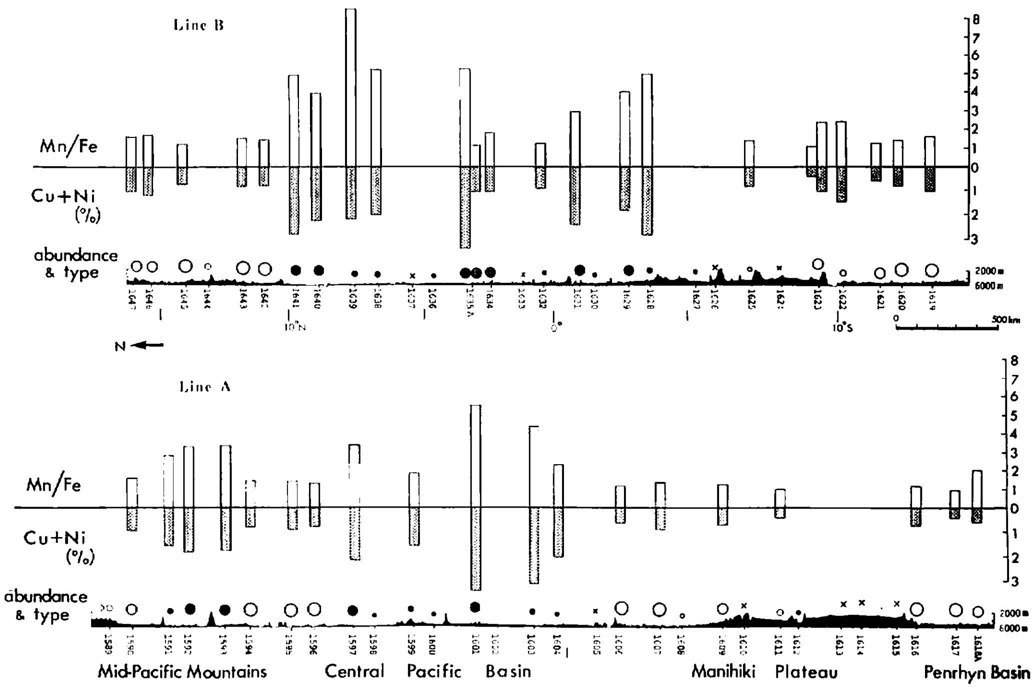


Fig. XVI-4 Regional variations of Mn/Fe ratio and metal grade Ni+Cu and relationship to nodule type and abundance. The values are averaged in each station. Nodule type: solid circle; type r, open circle; type s, hatched circle; intermediate type. Nodule abundance: more than 10 (kg/m^2), 10–1, 1–0.1, less than 0.1 in size order of circles, cross; no nodule.

10 Å manganite phase whereas the low ratio high content of δ-MnO_2 phase. Figure XVI-4 shows a regional variation of Mn/Fe consistent with the nodule types.

The ratios of Ni/Mn, Cu/Mn, Zn/Mn, and (Ni+Cu+Zn)/Mn are also a function of mineral composition. The ideal ratio divalent metals to Mn in pure 10 Å manganite is evaluated 0.167 by means of synthesis experiments (Usui, 1979). Therefore, the (Ni+Cu+Zn/Mn) ratios of manganese nodules are expected not to exceed around 0.16, and the higher the relative content of 10 Å manganite is the closer this ratio comes to this value. Maximum value 0.135 of (Ni+Cu+Zn)/Mn was encountered in nodules from St. 1635, which is a reasonable one to the above evaluation. Exceptional cases were encountered at Sts. 1638 and 1639 where this ratio of nodules is relatively low despite very high Mn/Fe ratio of them.

Plotting on ternary diagrams of metal content ratio well represents nodule chemical characteristics (Fig. XVI-5). This plotting is independent of masses of nuclei and detrital materials and water contents. Zn is included as a top component in this diagram instead of Co on the mineralogical basis, while Bonatti *et al.* (1972) first proposed Mn/Fe/(Cu+Ni+Co). The figure well demonstrates differences of chemical characteristics with nodule type. It shows a remarkable difference between types s and r, and a close similarity of the s-type nodules from the Central Pacific Basin and from the Penrhyn Basin. These differences are consistent with mineralogical variation.

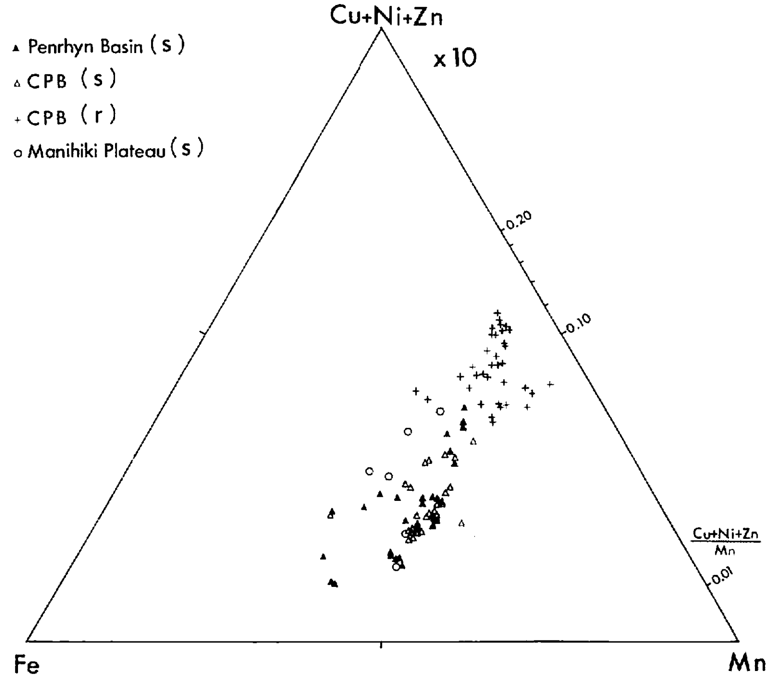


Fig. XVI-5 Ternary diagram of ratio Mn/Fe/(Cu+Ni+Zn), showing distinct differences of chemical characteristics with nodule type. Symbols in parentheses denote nodule types. CPB: the Central Pacific Basin.

Inter-element relationships

As previously reported by many geochemists, concentrations of metals of marine manganese nodules are often correlated to each other. The most marked is the positive correlation between Cu, Ni, and Mn. Other positive correlations are those of Pb and Co with Fe and the negative correlation between Fe and Mn.

The general trends of inter-element correlations for all types of GH80–1 nodules are similar to those reported. Table XVI-2 shows the results of calculations for each nodule types from the traverses. The most clear correlations, i.e., positive correlations between Mn, Cu, Ni, and Zn and between Fe, Co, and Pb and a negative one between these two groups, are encountered in the correlation matrix for all nodule types. These unusual trend of inter-element correlations are generally explainable based on the mineralogical characterization of the two mineral constituents by Usui *et al.* (1979). The correlations are presumably resulted from the characteristic difference of mineral composition of two nodule types s and r.

However, the inter-element correlation for each type becomes obscure as compared to that for all types. For instance, unusual positive correlation of Pb and Co with Mn are encountered in s-type nodules of the Central Pacific Basin. This is presumably because the effect of dilution by non-ferromanganese materials. As the mass of nuclei and included detrial matters are considerably large and variable in the s-type nodules, concentrations of minor elements is expected to be dependent of major element concentrations.

Table XVI-2 Correlation matrix for the nodule data. n: number of data sets, values significant at 99.99% confidence level, ++ and ——; significant at 99% confidence level, + and —; significant at 95% confidence level, *: no correlation at 95% confidence level.

		Mn	Cu	Ni	Zn	Fe	Pb	Co
All types		Mn	Cu	Ni	Zn	Fe	Pb	Co
	Mn	1						
n=112	Cu	+0.73	1					
	Ni	+0.74	+0.96	1				
	Zn	+0.80	+0.85	+0.80	1			
	Fe	——	−0.72	−0.68	−0.61	1		
	Pb	*	−0.60	−0.55	−0.49	+0.88	1	
	Co	*	−0.58	−0.53	−0.39	+0.85	+0.91	1
Type s		Mn	Cu	Ni	Zn	Fe	Pb	Co
(C.P.B.)	Mn	1						
n=29	Cu	++	1					
	Ni	+	+0.72	1				
	Zn	+0.69	++	+0.77	1			
	Fe	++	*	—	*	1		
	Pb	+0.72	*	*	++	+0.74	1	
	Co	+0.80	*	*	+	+0.80	+0.91	1
Type s		Mn	Cu	Ni	Zn	Fe	Pb	Co
(Penrhyn Basin)	Mn	1						
n=27	Cu	++	1					
	Ni	++	+0.97	1				
	Zn	+0.70	+0.90	+0.94	1			
	Fe	*	−0.82	−0.85	−0.66	1		
	Pb	*	——	——	*	+0.83	1	
	Co	*	——	——	*	+0.68	+0.76	1
Type r		Mn	Cu	Ni	Zn	Fe	Pb	Co
(C.P.B.)	Mn	1						
n=35	Cu	+0.74	1					
	Ni	+0.65	+0.91	1				
	Zn	+0.81	++	+	1			
	Fe	−0.60	−0.60	—	−0.72	1		
	Pb	*	—	*	——	++	1	
	Co	*	——	—	*	*	++	1
Type s		Mn	Cu	Ni	Zn	Fe	Pb	Co
(Manihiki Plateau)	Mn	1						
n=6	Cu	*	1					
	Ni	*	+	1				
	Zn	*	*	+	1			
	Fe	++	*	*	*	1		
	Pb	+	*	*	*	++	1	
	Co	++	*	*	*	++	++	1

Another important factor related to inter-element correlations is geochemical behavior of metal elements. Co is not clearly correlated to Mn except for the positive correlation for type s from the Central Pacific Basin, and it is not significantly correlated with Fe for type r. It suggests a complicated behavior of Co in the marine environments, e.g., the indefinite valence state related to the preference of incorporation to mineral phases as stated by BURNS (1976).

The correlations between metal concentrations of nodule bulk samples are, therefore, not always meaningful to consider geochemical characteristics of manganese nodules, because the bulk concentrations are controlled by several factors such as the ratio of ferromanganese minerals, contents of nuclei, water contents, and/or preferential incorporation of metal elements into mineral phases.

Summary and conclusion

The regional variation of metal contents and ratios with geological provinces are quite evident on the traverses and is generally dependent of the morphological type of nodules. Type r in the Central Pacific Basin is enriched in Mn, Cu, Ni, and Zn, while type s is enriched in Fe, Co, and Pb. This is quite consistent with the mineral composition of the nodules. The chemical characteristics of s-type nodules from the Central Pacific Basin (including the Mid-Pacific Mountains area) and the Penrhyn Basin are surprisingly similar to each other in spite of their different external features, though the Penrhyn Basin nodules are slightly higher in Fe.

Ratios between metal contents proved to be more significant parameters than bulk concentrations. Mn/Fe, Ni/Mn, Cu/Mn, Zn/Mn, Co/Mn are evidently different with nodule type, which is generally controlled by mineral composition. The ratio Cu/Ni is highest in type r. Pb/Fe and Co/Fe are not significantly different with nodule type.

Strong positive correlations between Mn, Cu, Ni, and Zn and between Fe, Co, and Pb and a negative one between these two groups are recognized for all type nodules. These correlation are generally consistent with previous data. However, such correlations become obscure for individual nodule type and even unusual positive correlations of Mn with Co and Fe are recognized. Therefore, inter-element correlations in nodule bulk composition are dependent of relative amounts of manganese minerals, dilution by non-manganese manganese and other factors.

References

ANDREWS, J. E. and FRIEDRICH, H. W. (1979) Distribution patterns of manganese nodule deposits in the Northeast Equatorial Pacific. *Marine Mining*, vol. 2, p. 1–44.

BONATTI, E. K., KRAEMER, T., and RYDELL, H. (1972) Classification and genesis of submarine iron-manganese deposits. *In* HORN D. R. *(ed.)*, *Ferromanganese Deposits on the Ocean Floor*. National Science Foundation, Washington, D. C., p. 149–166.

BURNS, R. G. (1976) The uptake of cobalt into ferromanganese nodules, soils, and synthetic 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* MIZUNO, A. and MORITANI, T. *(eds.)*, *Geol. Surv. Japan*

Cruise Rept., no. 8, p. 162–171.

HALBACH, P. and ÖZKARA, M. (1979) Morphological and geochemical classification of deep-sea ferromanganese nodules and its genetical interpretation. *In* LALOU, C. (*ed.*), *La Genèse des Nodules de Manganèse*. Colloques Internationaux du C. N. R. S. no. 289, p. 77–89.

HEIN, P. (1977) Geochimie des nodules de pacifique nord-est etude statistique. *Scientific and Technical Rept.*, no. 35, 74p., CNEXO.

LANDMESSER, C. W., KROENKE, L. K., GLASBY, G. P., SAWTELL, G. H., KINGAN, S., UTANGA, E., UTANGA, A., and COWAN, G. (1976) Manganese nodules from the South Penrhyn Basin, Southwest Pacific. *South Pacific Marine Geological Notes,* vol. 1, no. 3, p. 17–40.

MERO, J. L. (1965) *The Mineral Resources of the Sea*. Elsevier, Amsterdam, 312p.

MIZUNO, A. and MORITANI, T. (1978) Manganese nodule deposits of the Central Pacific Ocean. *Preprints, the 5th International Ocean Development Conference,* B2-27 to 39.

MOCHIZUKI, T., TERASHIMA, S., MIZUNO, A., and NAKAO, S. (1981) Metal contents of manganese nodules from the GH79–1 area. *In* MIZUNO, A. (*ed.*), *Geol. Surv. Japan Cruise Rept.,* no. 15, p. 245–256.

MORITANI, T., MARUYAMA, S., NOHARA, M., MATSUMOTO, K., OGITSU, T., and MORIWAKI, H. (1977) Description, classification, and distribution of manganese nodules. *In* MIZUNO, A. and MORITANI, T. (*eds.*), *Geol. Surv. Japan Cruise Rept.,* no. 8, p. 136–158.

PRICE, N. B. and CALVERT, S. E. (1970) Compositional variation in Pacific ferromanganese nodules and its relationship to sediment accumulation rates. *Mar. Geol.*, vol. 9, p. 145–171.

USUI, A. (1979) Nickel and copper accumulation as essential elements in 10 Å manganite of deep-sea manganese nodules. *Nature,* 279, p. 411–413.

————, TAKENOUCHI, S., and SHOJI, T. (1979) Mineralogy of deep sea manganese nodules and synthesis of manganese oxides: Implications to genesis and geochemistry. *Mining Geol.,* vol. 28, p. 405–420.