

Geochemistry of Ferromanganese Nodules from Different Areas in North Equatorial Pacific

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Among the analysed manganese nodules from VA-05/1, VA-08/1 and VA-13/2 areas, interelemental relationships, regardless of topography and morphology indicate a close affinity among Mn, Ni, Cu, Cd and Zn distribution. Unlike the earlier reports, Co behaves sympathetically with both Mn and Fe. P follows Al rather than Ca. Ca stands independently. Hg does not show any association with the analysed elements whereas Cd is harmonic with Mn, As with Fe and Zn. VA-13/2 area samples show large variation in the metal values. Wider difference in Mn/Fe ratio of nodules from VA-13/2 area, compared to the nodules from other areas in the region is attributed to the observed topographic variability and the differences in the morphology of the nodules. The distinct contrasting relationship of Mn and its associates with Ca, Al and P suggest the clear divergence in the mode of incorporation as authigenic and lithogenic components. Higher concentrations of Hg, As and Cd and their relationships with other elements suggest the probability of their supply from many sources. The overall geochemical behaviour of these nodules suggests the domination of hydrogenous origin over the early diagenetic process.

Geochemical studies on manganese nodules have indicated variations in nodules obtained from different regions in the Pacific Ocean¹⁻⁹. The present study has been made to understand the process of accretion, geochemical constraints responsible for the differences in growth pattern of nodules as well as the incorporation, source of heavy metals and base level distribution of pollutants which may have direct impact during mining.

Materials and Methods

Nodule samples were collected during different cruises of *RV Valdivia*. The area covered during cruise VA-13/2 (lat. 9°23' to 9°53'N; long. 145°58' to 146°18'W) is characterised by abyssal hill topography in the depth range of 4750-5400 m and consists of 3 small sea-peaks named north, east and west peaks, each with a relief of 400-500 m. The area lies in the siliceous ooze province where much of the activity of 'economic grade' manganese nodule has taken place. VA-08/1 cruise area (lat. 9° to 12°36'N; long. 145°30' to 150°W) is the western extension of VA-13/2 area and represents varying topography with characteristic abyssal hill and valley but the relief is less pronounced than in VA-13/2 area. There are NS, ENE and NW trending ranges with peaks around 500 m. The topography appears to be determined by faulting. The

topography of cruise VA-05/1 area (lat. 8° to 11°12'N; long. 146° to 152°45'W) which lies north of VA-08/1 area is not so variable but isolated sea mounts are present with different heights of about 1000 m. Therefore, closeby samples have been collected along the lines parallel and perpendicular to the slope of the abyssal hills or sea mounts in all the 3 areas. The nodules were digested¹⁰ in 25% HCl-25% HNO₃-40% HF mixture (5:3:8) in a teflon bomb and the elemental determination made on a Perkin Elmer atomic absorption spectrophotometer 303 with HGA 70.

Results and Discussion

Element distribution is given in Table 1. Elemental interrelationship and variation in metal content with the area of collection in these nodules are provided in Tables 2 and 3 respectively. Compared to nodules from VA-13/2 and VA-08/1 areas, those from VA-05/1 area shows commonly nuclei of a-type with very low Mn/Fe ratio and high non-authigenic constituents. As expected, the nuclei consisting of broken fragments of earlier nodule (a₂-type) show higher levels of both Mn and Fe, thus showing higher Mn/Fe ratio (av. 4.5) over the other 2 nuclei i.e. a-type (av. 2.5) and a₁-type (av. 2.05), which have a direct relationship with Mn-enrichment in the nodules. The core materials are rich in lithogenous components which are reflected by the

Table 1—Elemental Distribution in the Nodules from North Equatorial Pacific

Station No.	Sample	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Zn (%)	Al (%)	Ca (%)	P (%)	Cd (ppm)	Hg (ppb)	As (ppm)
VA-13/2 area													
147*	a2	26.30	04.82	1.08	1.30	0.17	0.081	2.35	0.73	0.94	15.2	180	71
	b	27.20	05.25	0.91	1.46	0.16	0.125	2.40	0.74	0.28	22.0	80	50
148*	a	12.80	03.64	0.47	1.12	0.10	0.065	3.60	0.91	1.72	9.0	200	42
	b	20.50	13.19	0.46	1.10	0.34	0.070	1.63	0.81	0.66	14.2	200	131
150*	a2	32.00	03.40	0.18	0.30	0.18	0.032	5.00	0.29	0.76	8.6	580	49
	b	19.70	11.38	0.46	1.06	0.32	0.060	2.08	0.68	0.36	16.4	120	95
151*	a1	13.30	09.76	0.14	1.72	0.12	0.029	3.00	0.86	3.64	8.4	200	101
	b	20.50	11.25	0.36	0.46	0.28	0.049	1.35	1.55	0.82	14.2	310	102
	a2	24.30	06.68	0.98	1.46	0.21	0.089	3.60	1.01	1.04	18.0	100	146
	b	24.50	09.63	0.58	1.12	0.25	0.075	1.43	0.77	0.26	2.0	240	105
152*	a2	28.80	03.32	1.36	1.98	0.21	0.181	1.48	0.78	1.00	18.0	450	84
	b	26.20	04.75	1.08	1.88	0.18	0.131	2.30	0.70	0.32	16.8	100	61
153*	a	14.80	05.20	0.64	0.92	0.12	0.097	3.64	0.54	0.48	10.0	320	106
	b	27.20	05.19	0.92	1.35	0.18	0.167	1.38	0.68	0.56	28.0	620	78
85*	a1	20.30	10.40	0.44	1.06	0.30	0.057	1.32	0.99	0.44	12.2	300	74
	b	37.42	16.27	1.25	1.59	0.43	0.104	2.78	1.37	0.59	8.2	260	177
87*	a2	21.66	09.16	0.42	0.88	0.32	0.049	1.32	0.83	0.52	16.2	840	122
	b	23.30	09.13	0.62	1.06	0.29	0.075	1.45	0.68	0.62	16.4	500	94
89*	a2	16.50	06.72	0.46	1.08	0.29	0.065	1.58	0.83	1.32	9.6	260	56
	b	24.40	07.63	0.75	1.25	0.28	0.098	1.43	0.68	0.82	19.6	5400	43
91*	a1	16.40	05.04	0.60	1.08	0.20	0.057	3.28	0.59	1.24	16.4	1480	82
	b	17.80	06.75	0.65	0.99	0.19	0.080	3.12	0.50	0.92	16.4	1480	54
93*	a	07.68	08.62	0.39	0.40	0.13	0.017	4.65	0.48	0.37	4.4	280	52
	b	25.80	03.84	0.98	1.50	0.24	0.137	1.56	0.77	0.36	15.6	560	67
	a2	26.06	04.00	0.24	0.30	0.04	0.036	0.60	0.64	1.05	8.2	120	-
	b	15.10	02.19	0.78	1.00	0.09	0.017	1.00	0.92	0.37	12.4	90	-
	c	21.60	02.04	1.48	1.60	0.15	0.164	1.84	1.42	0.27	10.4	100	-
	d	19.68	02.80	1.11	1.22	0.15	0.024	1.84	1.66	0.10	2.1	150	-
120*	a2	16.56	08.90	0.34	0.73	0.25	0.065	1.30	1.62	1.42	2.1	120	-
	b	16.60	08.65	0.41	0.84	0.16	0.078	0.88	1.56	0.44	1.0	230	-
121*	a2	15.40	09.73	0.40	0.84	0.18	0.070	2.06	1.60	0.70	4.8	230	-
	b	19.46	09.89	0.50	0.74	0.24	0.097	1.38	1.54	0.25	4.2	110	-
122*	a1	19.20	07.36	0.51	1.07	0.21	0.086	1.32	1.38	0.33	8.2	350	-
	b	14.90	10.10	0.30	0.47	0.17	0.047	1.26	1.44	0.34	4.0	250	-
123*	a1	10.30	09.57	0.22	0.24	0.09	0.040	3.18	2.22	0.71	5.2	80	-
	b	13.40	08.79	0.33	0.46	0.19	0.058	1.46	2.08	0.05	8.2	110	-
	c	16.90	07.00	0.61	1.12	0.16	0.092	1.46	1.52	0.12	7.5	210	-
125*	a	06.30	06.40	0.19	0.24	0.08	0.032	2.46	0.98	0.59	2.0	390	-
	b	15.90	08.36	0.43	0.53	0.21	0.061	1.46	1.60	0.42	2.0	250	-
	c	21.60	02.60	1.07	1.19	0.12	0.208	1.16	0.92	0.38	8.0	180	-
	d	17.60	04.60	0.84	1.26	0.20	0.125	1.60	1.50	0.45	6.2	170	-
60*	a	17.30	05.34	0.84	0.99	0.14	0.090	2.38	1.56	0.76	4.9	280	-
	b	20.80	03.14	1.27	1.39	0.16	0.130	1.90	1.32	0.63	24.1	130	-
	c	16.80	05.10	0.87	1.16	0.20	0.110	1.46	1.66	0.61	4.8	140	-
61*	a1	15.50	06.20	0.71	0.93	0.15	0.088	3.70	1.56	3.50	4.1	820	-
	b	21.76	02.70	1.15	1.49	0.20	0.135	1.80	1.36	0.40	6.7	100	-
	c	19.20	04.65	0.89	1.33	0.19	0.116	1.52	1.60	0.26	11.3	150	-
62*	a2	19.56	07.00	0.79	0.91	0.10	0.099	1.72	1.32	0.38	4.8	760	-
	b	16.60	02.60	1.34	1.46	0.15	0.200	1.94	1.56	0.22	28.2	720	-
	c	17.65	03.72	0.98	1.26	0.16	0.130	1.74	1.64	0.46	3.8	180	-
63*	a1	12.00	07.40	0.47	0.57	0.10	0.060	4.00	2.60	0.52	4.7	160	-
	b	19.84	04.60	1.09	0.10	0.10	0.130	2.12	1.46	0.32	6.3	150	-
	c	19.80	05.20	0.92	1.46	0.22	0.125	1.66	2.26	0.24	5.8	420	-
65*	a	08.30	02.80	0.32	1.19	0.07	0.056	4.00	0.74	0.52	4.6	340	-
	b	19.26	05.50	0.82	0.61	0.20	0.113	1.74	1.78	0.29	4.0	190	-

(Contd.)

Table 1 -- Elemental Distribution in the Nodules from North Equatorial Pacific -- *Contd*

Station No.	Sample	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Zn (%)	Al (%)	Ca (%)	P (%)	Cd (ppm)	Hg (ppt)	As (ppm)
VA-05/1 area													
18*	a	16.00	06.20	0.40	1.02	0.22	0.053	1.60	0.42	0.80	3.6	260	65
	b	19.50	12.12	0.47	0.86	0.32	0.060	1.88	0.66	0.52	12.8	150	87
47*	a	13.70	03.16	0.72	0.80	0.10	0.053	1.68	0.45	5.73	13.4	160	156
	b	24.30	05.38	1.11	1.50	0.17	0.095	3.00	0.68	0.32	26.8	100	65
90*	a	04.80	06.40	0.12	0.28	0.10	0.017	4.48	2.24	0.18	9.2	350	41
	b	21.80	08.52	0.40	1.50	0.17	0.067	1.28	0.91	0.44	13.4	1680	144
109 ⁺ (4a)	a	02.60	10.80	0.12	0.20	0.05	0.011	1.56	0.59	1.24	8.6	400	78
	b	23.50	08.30	0.75	1.70	0.30	0.096	0.50	0.48	2.20	13.2	2350	140
(2b)	a	03.53	03.90	0.15	0.10	0.08	0.010	5.50	0.96	3.20	6.2	760	130
	b	21.90	12.94	0.53	0.97	0.25	0.084	2.10	0.79	0.50	8.4	160	50
(53/2/B)	a	03.45	05.40	0.10	0.15	0.10	0.025	4.80	0.60	2.60	6.2	500	108
	b	23.50	09.13	0.65	1.44	0.33	0.086	1.73	0.62	0.34	24.0	160	92
(KAF 53)	a	04.15	04.45	0.12	0.13	0.12	0.015	5.75	0.58	1.65	8.2	80	68
VA-05/3	b	21.40	10.94	0.38	0.90	0.24	0.046	1.68	0.86	0.50	13.4	220	86
353 @	a	05.40	10.40	1.86	1.68	0.16	0.141	1.08	0.83	0.76	22.0	380	53
	b	26.00	05.00	1.28	1.96	0.17	0.115	2.43	0.72	0.36	22.4	240	45
VA-08/1 area													
17*	a1	19.00	07.16	0.38	0.80	0.18	0.067	1.88	0.74	0.72	12.8	400	79
	b	21.30	11.56	0.60	1.02	0.26	0.065	2.23	0.75	0.28	12.0	200	16
18*	a2	18.40	08.28	0.44	1.14	0.17	0.067	2.08	0.91	1.16	12.0	140	26
	b	19.40	10.08	0.36	0.78	0.32	0.051	1.12	0.78	1.08	11.2	580	142
58 ⁺	a	16.20	05.56	0.56	0.32	0.17	0.057	2.68	0.91	1.48	12.4	200	98
	b	22.90	07.31	0.86	1.33	0.22	0.083	1.63	0.68	0.34	15.0	340	51
59 ⁺	a2	20.40	07.84	0.40	0.88	0.26	0.061	1.32	0.83	1.12	8.8	280	126
	b	25.60	06.80	0.48	1.42	0.28	0.107	1.60	0.77	0.92	14.6	440	87
63*	a2	28.70	03.00	0.94	1.32	0.21	0.077	2.00	0.66	0.08	11.0	100	58
	b	22.50	08.25	0.78	1.22	0.24	0.068	2.23	0.74	0.44	1.8	120	80
81 ⁺	a2	21.80	9.00	0.46	1.18	0.36	0.063	1.60	1.09	0.76	14.0	260	157
	b	17.90	13.31	0.37	0.69	0.30	0.048	2.00	0.79	0.82	10.0	420	107

a - nuclei (core) of Zeolitic material, a1 - nuclei of hard silicious material, a2 - nuclei of old nodule fragments, b - inner layer next to core, c - middle layer and d - outer layer of the nodule.

Sample collection: *Free fall grab; ⁺Dredge; and @ Box corer.

higher level of P content. Among the nuclei, the distribution of P is more in a-type of core than the other 2 types. There is an inverse relationship between Al and Ca in them (Table 2). This fact suggests the presence of relatively larger number of silicates bearing nuclei in the nodules. Higher values of Hg, Cd and As in the core material, as compared to sediments of these areas¹¹ indicate that the core material is subjected to free diagenetic growth on a par with the nodule layers.

The secondary elements' distribution in the nodules does not show any significant change to the reported values of the earlier workers¹¹⁻¹⁴. However their interrelationship among the analysed elements points out characteristic drift. It is felt that a brief discussion on some of them, here, will be of much use for understanding the role of the principle elements. It can be seen from Table 2 that Zn displays a good positive correlation with Mn, Ni, Cu and Cd, negative correlation with Fe, Al and P, and no such relationship

with As, Co and Hg. Cronan and Tooms¹⁵ could not substantiate the relationship of Mn and Zn in a suite of abyssal nodules from the Indian Ocean. Ahrens *et al.*¹⁶ have shown a characteristic affinity of Zn with Cd in the Pacific nodules as in the present case, and attributed the cause to the dominant hydrogenous precipitation because of the existence of such affinity in the bottom water also. Goldschmidt¹⁷ also from the findings of the close binding between Zn and Cd in marine phosphorites, ascribed the derivation of Zn to the marine organisms, which ultimately reach to the seawater. The close geochemical affinity of Zn to Ni, Cu, Mn and Cd, and the increased concentration of Zn in the a₂-type nuclei and outer layers of the nodules lead to the possibility of its inclusion during the growth of the nodules from hydrogenetic as well as diagenetic processes.

The negative correlation of Ca to As and Cd (Table 2), these being of biogenic or hydrothermal

Table 2—Correlation Coefficients of Inter-Element Relationships of Ferromanganese Nodules Investigated

Element	Mn	Fe	Cu	Ni	Co	Zn	Al	Ca	P	As	Hg
Fe	-0.36										
Cu	0.43	-0.33									
Ni	0.56	-0.13	0.68								
Co	0.56	0.56	0.60	0.33							
Zn	0.45	-0.31	0.79	0.01	0.12						
Al	-0.40	-0.20	-0.29	-0.35	-0.38	-0.35					
Ca	-0.20	-0.02	0.08	-0.16	-0.15	-0.15	-0.06				
P	-0.30	-0.09	-0.23	-0.14	-0.22	-0.26	0.28	-0.26			
As	0.19	0.38	-0.17	0.11	0.48	-0.27	0.09	-0.56	0.39		
Hg	0.10	0.05	-0.01	0.10	0.15	0.02	-0.09	-0.18	0.11	0.14	
Cd	0.37	-0.06	0.43	0.50	0.23	0.37	-0.13	-0.38	-0.05	0.32	0.20

99% level of significance for As (52)-0.32 but for others (83)-0.26

Table 3—Coefficient of Variation for Major Metal Content of Nodules in Comparable Areas of NE-Equatorial Pacific Region

Area	Mn	Fe	Cu	Ni	Co	Zn
VA-13/2	2.8	7.4	4.5	4.2	4.3	12.0
VA-05/1	1.3	2.4	3.4	2.3	1.9	2.0
VA-08/1	1.6	3.4	2.5	2.2	2.1	2.2
Wahine ²⁶	1.2	1.9	2.0	2.2	2.0	1.6
VA-13/1 ²	1.3	2.1	5.0	2.9	2.0	2.9
4-C ²⁵	1.3	1.2	5.0	2.9	2.3	2.9
Domes Sites ²⁷	1.9	2.0	3.0	1.5	1.7	2.7

precipitates and also to Al, an element of lithogenic supply indicates independent behaviour. Such distributional relationship of Ca leads to compare the analysed nodules with the first group of nodules of high Ca, Ni, Cu and Co in which Ca accumulation is suggestive of the mode of incorporation by adsorption into Mn-Fe phases. In this respect the observations are similar to those of Greenslate *et al.*¹⁸.

The disharmonic relationship of P with Ca as in the case of P rich sediments of East Pacific Rise¹⁹ postulates that P is mainly derived from the bottom water which is expected to have saturated P rather than Ca. This relationship in the opinion of Corliss²⁰ is due to P passing from basalt to seawater. Hart²¹ showed the concentration of P during the submarine weathering of tholeiitic basalts in which the outer layers were enriched in Fe and P due to quenching and extraction of them from seawater. However, no correlation between P and Fe is noticed in the studied nodules similar to other reports^{22,23}. P and As are found to be enriched in SW Pacific nodules as authigenic components from seawater¹³. The harmonic correlation among P, As and Al and lack of such correlation of P with Mn and Fe may be ascribed to the supply of them mainly from the hydrogenetic source, probably through lithogenic components also.

Compared to sediments, the nodules and their nuclei exhibit many fold enrichment in Hg. Krauskopf²⁴ accounted the concentration of Hg in nodules largely to the very fine grain size and high surface areas of ferromanganese oxide phase where adsorption plays a major role. The present observation of enrichment factor of Hg in nodules, well over the average abundance²² is found to be within the limits of Glasby¹⁴ who proposed a factor of 3 to 10 times in relation to the average crustal abundance. Amongst the 3 areas, VA-05/1 area shows higher levels of Hg which may be referred to the added role of high volcanic activity known from the region. The higher concentration of Hg level in the nodules and lack of correlation (Table 2) with all the other analysed elements may be assigned in line with Hariss *et al.*²⁵ to the derivation from a multi-source including extra terrestrial one.

Cd shows a positive relation with Ca and also with As and Al which are maintaining antipathic relationship with Ca. Such behaviour of Cd supplements the multi-source of derivation such as dissolution of siliceous-biogenous debris in which Cd is present in appreciable levels along with the mineralising solution and coprecipitation and sorption of metals present in seawater which may be enhanced by local volcanic supplies.

The principal elements in the nodules exhibit a marked variability in composition (Table 1). The difference in the metal content in nodules from VA-13/2 area when compared to that observed in area 4-C of Carlsberg Ridge of the Indian Ocean²⁶, Wahine area²⁷ and Domes sites²⁸ (Table 3) supports the view of Craig⁷ who attributed such a difference to changes in morphology and micro-bathymetry of the sea floor. It may be mentioned that area VA-13/2 has been selected to elucidate the characters of sharp topographic differences and their influence on nodule occurrence,

morphology, mineralogy and geochemistry. It is of interest to note that Mn/Fe ratio *vs* Ni (Fig. 1b) and Mn/Fe ratio *vs* Cu (Fig. 1c) show an increase with depth ranging 5000-5250 m in tracks consisting of sts 148, 150-152; 85, 87-89; and 91-93 (Table 1). In spite of the mixed morphology in VA-13/2 area, compared to areas under VA-08/1 and VA-05/1, greater variation in chemical composition both of nuclei and nodules is noticed. It brings out that nodule composition is related to nodule morphology which results in a secondary relationship between the nodule composition and water depth or even size class⁸.

A positive relationship exists between Cu + Ni and Mn/Fe ratio (Fig. 1a). The data in Table 1 show that the older nodule fragments display higher Mn/Fe ratio and proportionally higher contents of transition elements like Ni, Cu and Zn. Such a distribution may be due to close relationship of Mn with those of the transition elements and longer exposure to diagenetic growth of these elements in the sediment column. In general, Mn/Fe ratio varies from 0.89 to 10.59 in VA-13/2 area, 1.34 to 9.57 in VA-05/1 and 0.24 to 4.34 in VA-08/1 areas. When average Mn/Fe ratios are compared, VA-13/2 area (5.72) is found to be more manganiferous than the other 2 areas (2.14 and 3.08). In this respect present observations are correlatable to those of Halbach *et al.*²⁹. In the present study areas, Mn/Fe ratio around 5 shows the highest enrichment of Ni + Cu while on either side of this ratio marks a decrease of Ni + Cu concentration. In order to

elaborate these affinities, Mn/Fe *vs* Ni + Cu, Mn/Fe *vs* Ni, and Mn/Fe *vs* Cu are plotted (Figs. 1a-c). They clearly show the progressive enrichment of Ni and Cu around Mn/Fe ratio of 5 after which the linearity is somewhat unsympathetic, taking a regressive trend. Co shows a trend different (Fig. 1d) to that of Ni and Cu pattern. In view of the positive correlation between Mn and Co, earlier workers³⁰⁻³² have ascribed the presence of Co in the nodules in the 10 Å manganate phase even though some of the Co present in MnO₂ phase as Co³⁺, substituting for Mn in the 2 lines form of MnO₂. Benjamin and Felmy³³ have also proved a very strong binding of Co with manganese oxide phase. On the other hand, others^{1,3,16,34} have found Co in the abyssal nodules commonly associated with Fe as Co³⁺ in the hydrated oxide phase while Glasby³⁵ and Cronan and Tooms³⁶ could not recognise a clear relationship between Co and Fe. In the present study, a close affinity and good correlation of Co with both Mn and Fe are noticed, similar to the observations of Skornyakova³⁷ in nodules from polygon 5988, 5996 and 6298.

Negative correlation of Al and P with Mn, Cu, Ni, Co and Zn (Table 2) indicates different mode of precipitation or origin in such a way that the elements of Mn and its associates are likely to be present as authigenic constituents while Al and P are considered to be either from the volcanic source like ash, tuff, etc. Because of the harmonic association amongst P, As and Al, the supply of P to the nodule material is

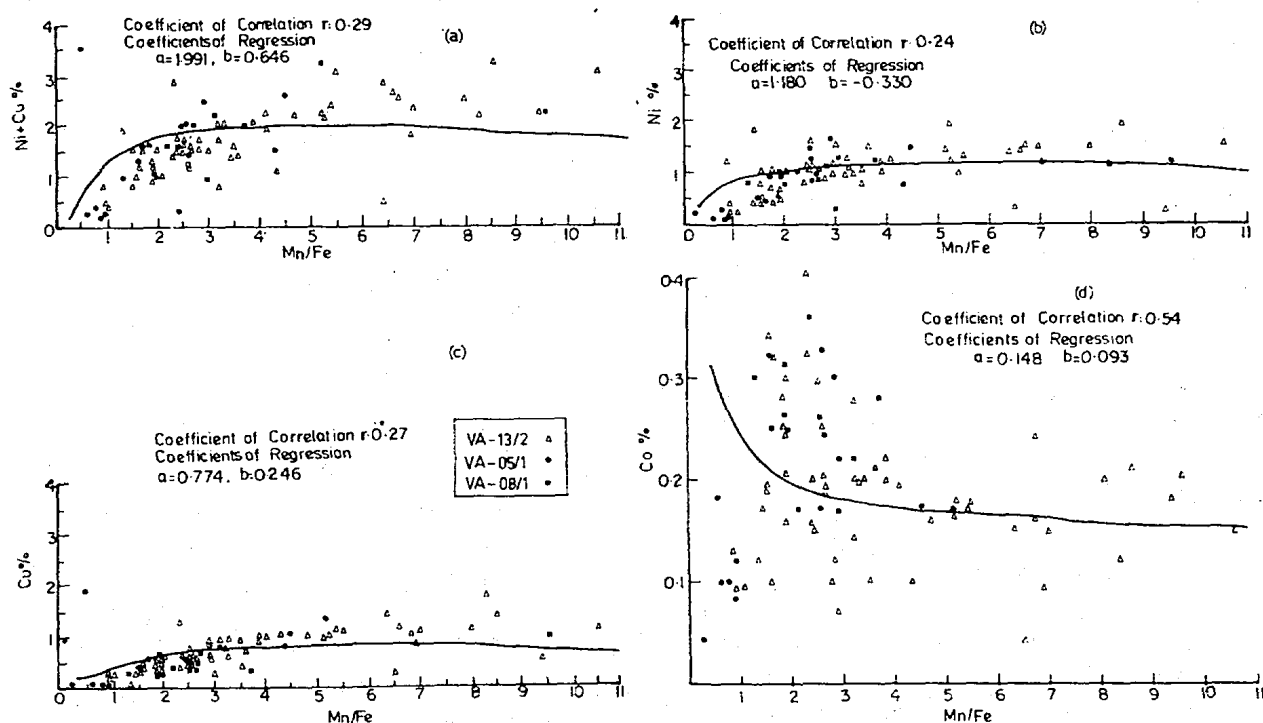


Fig. 1—Hyperbolic regression curves for Mn/Fe ratio *vs* Ni + Cu (a), *vs* Ni (b), *vs* Cu (c) and *vs* Co (d)

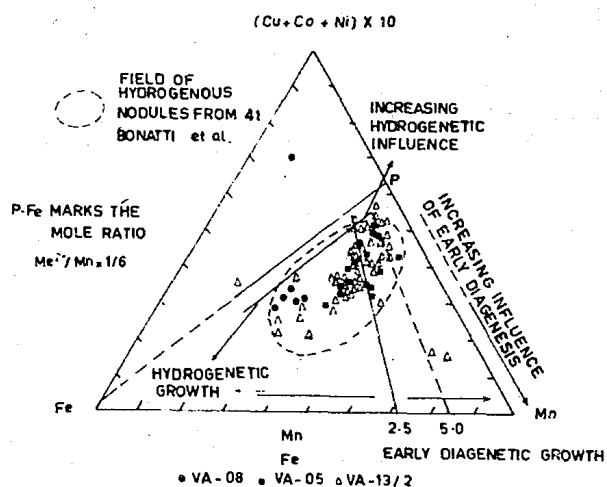


Fig 2—Three component diagram showing relationship between geochemistry and genetic types of nodules and hydrogenetic encrustations

ascribed to the source both from clay-hydrolysate materials and volcanic fragments. This is supported by the higher values of P on 'a' and 'a₁' types of nuclei material. Sharp enrichment of Hg, As, Cd and Zn has been observed in the bottom waters which supply these to the nodules mainly in the regions around volcanic emanations^{38,39}. Wedepohl⁴⁰ suggested the derivation of these elements in the sedimentary rocks and in seawater to the product of magmatic degassing of the lower parts of crust and the upper regions of mantle. Enrichment of As in pelagic sediments as compared to the igneous rocks has been noted as also the difficulty in establishing correlation of Hg with other elements in aqueous environments. It may in part be due to peculiar geochemical behaviour of Hg to its low mobility and the readiness of hydrolysate sediments in absorbing Hg. Very similar to the distribution in the bottom waters of submarine volcanic areas, the harmonic relationship prevailing among the pairs of Zn/Cd, Fe/As, Fe/Co and Co/As in the studied nodules help to conclude their derivation from volcanogenic source.

As which is commonly noticed in the authigenic components of the nodules¹³, indicate the probability of their incorporation in the analysed nodules through the authigenic components and that too, in the ferruginous phase, because of not only the direct relation of As with Fe and Co, but also due to their nearness in atomic radii. The positive correlation of As with P which is surmised to be the derivative from metalliferous sediments and the strong negative correlation of As with Ca supplements the suggestion of its incorporation in the nodules from the sedimentary components which ultimately depends on submarine volcanic emanations.

When Fig. 2 is compared with figures of Halbach *et al.*⁴², VA-08/1 and VA-05/1 area nodules show influence of hydrogenetic growth while those from VA-13/2 area indicates inclination towards the diagenetic growth. This is supported by lower Mn/Fe ratio, Ni, Cu and Zn in nodules from VA-08/1 area than in those from VA-13/2 area. The higher concentration of Co in nodules in the Mn/Fe range between 1 and 3 may be assigned to the influence of hydrogenetic growth. In such a situation Co is positively correlated with Mn in hydrogenetic types and with Fe in nodules of early diagenetic type. However, the progressive relationship of Co with both Mn and Fe in the present investigation, may be attributed to the presence of both types. Lack of complete correlation of Hg with other elements and good correlation of Cd to Zn, As to Fe and As to P suggests the dominant supply by hydrogenous source to the accretion of nodule growth.

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