

DISTRIBUTION OF IRON, MANGANESE, COBALT AND NICKEL IN SEDIMENT CORES OF THE NORTHEASTERN ARABIAN SEA

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Abstract

A study of the distribution of iron, manganese, cobalt and nickel in sediment cores from the shelf, slope and basin regions of Bombay-Kathiawar coast of India shows that cobalt and nickel are derived from the overlying sea water as adsorbants of manganese and iron hydroxides, clay minerals, and organic matter present in the sediment. Since the cores represent differing environments, the inter-relationship and the factors governing adsorption and fixing them in the sediment vary considerably.

Mn/Fe ratio decreases uniformly with depth in the shelf sediments excepting in one core, whereas on the slope and the basin, it indicates a gain which is due to the enclosed slum and turbidite deposits. The manganese : iron ratios for (a) the shelf cores are 1 : 72; 3 : 205; and 6 : 265; (b) for the slope it is 1 : 116; and (c) the basin 6 : 170. The values are highest in one core. This suggests an enrichment of manganese in the shelf region and in the basin, but great mobility in the slope and parts of the shelf resulting in depletion.

Iron-cobalt and manganese-nickel are the covariants, and hence correlatable. Significantly, the organic matter in the slope sediment is inversely proportional to the amount of manganese present in the sediment. One core shows some unusually high values (56 ppm cobalt and 75 ppm nickel) as against the average values of 13 and 55, respectively, for near-shore sediments (total sediment) of North Atlantic and North Pacific.

INTRODUCTION

The five sediment cores which were collected aboard R/V OCEANOGRAPHER, U.S. Coast and Geodetic Survey ship during 1967 were studied earlier, and a description of the stratigraphy and lithology of the cores, and of the distribution of phosphate, carbonate and organic matter content in them presented separately (Setty, 1972; Setty and Rao, 1972). The present paper deals mainly with the distribution of iron, manganese, cobalt and nickel with a discussion on the geochemical environment as revealed through their high and low value fluctuations at different depths of the cores.

A total of 45 samples, taken approximately at 10-30 cm depth intervals from the 15 segments of the five sediment cores, were analysed. Of the five sediment cores, three (Nos. 3, 4 and 5 taken at stations 66, 73 and 146 at 19°32.8'N, 71°21.5'E; 20°10.0'N, 70°26.9'E and 20°04.5'N, 69°26.0'E at a depth of 64, 73 and 63 m respectively) are from the shelf; one core (No. 1 taken at station 29, at 17°57.9'N, 70°46.0'E at a depth of 649 m) is from the slope; and another (No. 2 taken at station 43, at 18°35.2'N, 69°17.2'E at a depth of 2960 m) is from the basin area of the Arabian Sea (Fig. 1).

METHOD OF STUDY

Iron was estimated using 2-2' dipyrilidil, and manganese by the colorimetric method both as described by Sandell (1959). Nickel was determined by the wine red colour formed when dimethyl glyoxime is added to a basic solution containing a nickel

salt, and cobalt by the nitroso-R-salt method both as described by Chester and Hughes (1968). All the measurements were made using the Unicam Spectrophotometer Sp 500. The results are given in Table I.

The lithology of the cores has been described earlier (Setty, 1972). Table I shows the distribution of iron (per cent), and manganese, cobalt and nickel (in ppm) in the whole sample and also on carbonate-free basis for purposes of comparison.

RESULTS]

Iron

Though iron is present in sea water in an oxidised state and in various physical forms, it is, among other related elements, supplied through streams, rivers and the

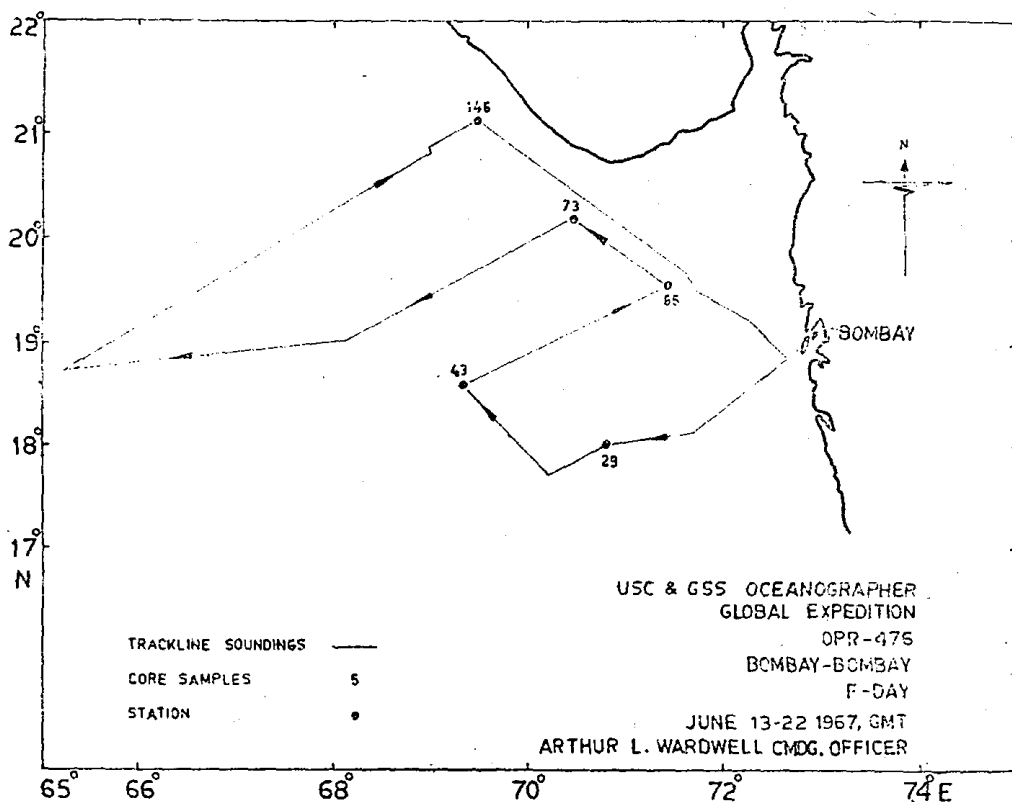


Figure 1. Location map of cores (1-5) collected by R/V *Oceanographer* in the Arabian Sea.

like to the ocean, in particulate and dissolved forms. Cores from the shelf (Nos. 3, 4 and 5) show high iron (up to 7.5 per cent) and low organic matter content in the sediment; among the three, core No. 3 shows very high iron and the values are fairly uniform throughout the core. Calcium carbonate is very low in core No. 3 but is very high in core Nos. 4 and 5. With the increase in calcium carbonate and decrease in organic matter content, iron is observed to decrease.

In the three cores from the shelf, the iron content is very high in the top layers and varies from 7.32 to 2.74 to 5 per cent which represents the environmental conditions present in the overlying waters and indicates the rate of supply of lithogenous material from the nearby source area. Comparatively, it is noticed that the organi

SL. NO.	Depth in Cms	Organic Matter PerCent Dry Weight	CaCO ₃ Per-Cent Dry Weight	Fe (%)		Mn (ppm)		Co (ppm)		Ni (ppm)	
				Whole Sample	CaCO ₃ Free	Whole Sample	CaCO ₃ Free	Whole Sample	CaCO ₃ Free	Whole Sample	CaCO ₃ Free
CORE NO.1--SLOPE											
1	2	8.00	51.7	1.15	2.39	N.D	N.D	65	134	81	168
2	25	6.70	63.0	1.24	3.35	-	-	67	181	70	189
3	50	4.00	69.0	0.81	2.60	-	-	38	123	75	235
4	60	3.80	67.0	0.83	2.50	-	-	36	110	50	151
5	85	3.60	68.0	1.07	3.35	51	180	42	121	64	135
6	110	2.65	64.0	1.33	3.65	206	570	19	53	37	103
7	120	2.70	66.5	1.33	3.95	206	615	23	59	37	112
8	145	2.90	64.0	1.33	3.70	154	427	21	60	62	172
9	175	2.70	64.0	1.38	3.80	257	711	15	43	50	138
CORE NO.2--BASIN											
10	2	123	46.0	2.19	4.10	1030	1907	9	10	62	115
11	25	200	65.5	1.40	4.05	515	1493	28	65	43	126
12	40	158	64.0	1.41	3.80	515	1431	12	33	63	178
13	50	137	60.0	1.45	3.80	568	1418	9	24	50	125
14	70	0.86	5.25	1.68	3.95	515	1058	6	17	40	84
15	90	2.09	4.55	2.18	4.00	721	1335	17	31	37	70
16	100	0.77	48.5	1.90	4.10	824	1600	13	36	62	120
17	120	1.20	4.85	1.84	3.43	515	972	7	13	56	105
18	140	1.60	63.0	1.24	3.35	463	1254	5	26	50	135
19	150	2.59	57.0	1.50	3.48	515	1198	16	39	53	124
20	170	2.00	65.0	2.14	6.50	618	1994	8	27	30	125
21	190	2.90	65.0	1.30	3.71	310	888	18	51	41	118
CORE NO.3--SHELF											
22	2	2.52	9.0	7.32	8.04	1442	1584	58	64	112	123
23	15	1.80	10.5	7.32	8.17	1236	1381	43	48	103	116
24	30	1.58	11.5	7.32	8.27	1185	1339	46	53	75	85
25	40	2.20	11.0	7.50	8.42	1133	1273	68	77	67	75
26	55	2.30	11.0	7.32	8.22	1185	1332	81	91	50	56
27	70	1.90	12.0	7.33	8.38	1236	1405	50	57	43	50
28	80	2.16	10.5	6.75	7.54	1236	1381	49	55	68	76
29	100	2.65	12.0	6.98	8.01	1391	1598	50	58	75	86
30	115	2.10	11.5	6.98	7.87	1133	1281	60	68	81	92
CORE NO.4--SHELF											
31	2	1.10	34.0	2.74	4.15	515	781	16	25	31	47
32	25	0.90	30.0	1.91	2.72	10	443	14	20	15	21
33	50	0.70	40.0	1.50	2.50	205	344	4	8	6	10
CORE NO.5--SHELF											
34	2	1.80	21.5	5.00	6.40	927	1189	33	43	43	55
35	30	1.56	37.0	4.00	6.25	721	1145	18	28	31	49
36	60	1.10	50.0	2.21	4.42	412	824	12	24	27	55
37	70	1.56	56.5	1.91	4.39	567	1304	12	27	12	28
38	95	1.20	55.5	1.73	3.93	464	1055	33	75	9	19
39	115	1.73	58.0	2.06	4.90	721	1717	14	34	25	59
40	125	1.53	56.0	2.14	5.00	824	1873	50	35	28	85
41	150	1.56	58.0	2.00	4.76	515	1226	14	34	32	77
42	175	1.51	57.0	2.30	5.34	721	1677	29	67	18	43
43	185	1.63	56.5	3.26	7.40	463	1052	7	16	25	57
44	210	1.65	55.5	2.75	6.30	721	1639	9	21	25	56
45	235	1.73	58.0	2.55	5.79	618	1405	10	23	27	62

TABLE I. Distribution of iron, manganese, cobalt and nickel in five (1-5) sediment cores at different depths.

matter and the calcium carbonate content decrease. Core No. 3 represents reducing conditions with very low value (9%) of calcium carbonate and high value (2.52%) of organic matter, while in contrast, oxidising conditions are observed with high values of calcium carbonate (34 to 40%) in No. 4, and (21.5 to 58%) in No. 5 and low values of organic matter (0.70 to 1.10% in No. 4 and 1.10 to 1.80% in No. 5). With the increase in calcium carbonate and organic matter in the slope and basin regions (Nos. 1 and 2) iron decreases considerably, under low redox potential. It appears that the iron compounds reach the limit of solubility even earlier than the manganese compounds do, and hence tend to precipitate early (Bonatti *et al*, 1971). Thus it may be considered that iron is fixed early in the sediment nearer to the source area and gets reduced due to limited transport to the offshore, slope and basin region where production of organic matter and deposition of calcium carbonate are generally high. Further, the wide range of concentrations observed in the cores may partly be the result of random distribution of floccular iron colloids. Cores from the shelf (Nos. 3, 4 and 5) derive much of their material from the altered volcanics of the Deccan Traps; hence the iron content in the sediments becomes significant. El Wakeel and Riley (1961) have shown that ferrous iron increases in such conditions.

The vertical distribution of iron is remarkably uniform (on carbonate and water-free basis) with minor fluctuations in the sediments of the slope (core No. 1) and basin (core No. 2). At 50 and 60 cm depth (core No. 1) the iron content suddenly shows a decline (0.81 to 0.83 per cent) from its uniform rate of precipitation, whereas organic matter increases (3.80 to 4.00%). This is considered to be due to the fact that iron is highly mobilised and consequently removed for want of sulphur to fix iron (Fe^{++}) as sulphide. The overlying layers showing higher values for iron (1.15 to 1.24 per cent) and organic matter (6.70 to 8.00%) are considered to be the slump deposits (Setty, 1972).

The vertical uniform distribution of iron in core No. 2 may be due to the presence of stable colloids of hydrated ferric oxide which occurs at all depths (Hood, 1966) and also partly biologically derived, particularly from shell fragments, foraminiferans, other organisms, or calcareous debris stained dark red, and such remains after the calcareous parts are partly dissolved (Carroll, 1958; Chester, 1965), or hydrothermal activity connected with submarine volcanism (Bonatti *et al*, 1971), or a combination of most of these factors. Certain higher values noticed at various levels of the cores in the shelf sediments are either due to primary conditions prevailing during precipitation or due to mobility of iron in stagnant or nearly stagnant conditions (as in core No. 3); reduction and acidification are conducive (as in core No. 5); calcium carbonate is replaced by iron (as in core No. 2) (Goldschmidt, 1962); micronodules or micrometeorites of cosmic origin (?) (Goldberg, 1954; Chester and Hughes 1969).

Manganese

The top layers of all cores except No. 1 and 4 are rich in manganese (very rich in Nos. 2 and 3, moderately rich in No. 5). Manganese (on carbonate-free basis) is directly related to the amount of calcium carbonate present in the sediment. Core No. 3 (Table I) reveals very characteristic features: it is high in organic matter, iron, manganese, cobalt and nickel, but low in calcium carbonate when compared with other cores (Nos. 4 and 5) from the shelf region. Though manganese is highly enriched in the top layers, it shows a gradual decrease with depth. Carbonate being

very low, it may be considered that both elements have precipitated together since the solubility rates of iron and manganese carbonates are not different and the Eh-pH relationship, low temperature and pressure (i.e. geochemical environment) and the presence of manganese in the lattice structure of clay minerals being favourable. Emery and Rittenberg (1952) observed that when redox potential is positive in the near surface sediment it is negative with depth.

The high manganese values noticed in core No. 2 are comparable to any ocean basins; however, the fluctuations noticed at depth with that of calcium carbonate are considered to be related to paleoclimatic events or variations (Bonatti, 1971). Large variations may also be due to random inclusions of micro-manganese nodules (?) in the samples (Chester, 1965). High manganese in the cores of the shelf indicates large incidence of manganese from the nearby land areas through lithogenous supply and its retention in the finer fraction of the sediment in an oxidising environment. Interestingly, however, manganese is not detected or found deposited in the upper 85 cms of sediment in the slope region but present progressively in larger amounts in the lower 100 cms thick sediment. This may be due to high organic matter content and highly anaerobic conditions and post-depositional migration with depth (Li *et al.*, 1969).

Cobalt

Deposition of cobalt at present is highest (181 to 134 ppm carbonate-free basis) on the slope (core No. 1); moderately high (64 ppm carbonate-free basis) in the 'closed' basin (core No. 3); low (43 ppm carbonate-free basis) on the shelf; and very poor (18 ppm carbonate-free basis) in the basin region (core No. 2). Core No. 5 gives two opposing values (43 ppm and 75 ppm) representing two differing lithologies within it.

Invariably, it is found in the cores that cobalt values are high in the upper few layers of the sediment and with depth, but it is negative in some with a few fluctuations which are due to turbidite flows, oxidising conditions or influx of fresh material (Setty, 1972). The cobalt content is markedly high in all parts of the cores collected at the sediment-water interface and at a little depth below, particularly so in the shelf region than in the slope and basin. The higher steady values noticed in core No. 3 are considered to be due to dark muds, which according to Goldschmidt (1962) contain sulphides and arsenides, and also bituminous shales having cobalt in the lattice structure of clay minerals like illite (Chester, 1965). Goldberg and Griffin (1970) and Stewart *et al.* (1965) have reported the occurrence of montmorillonite (50-70%), illite (0-20%), chlorite (0-10%) and kaolinite (0-10%) in the sediments of this region. Chester and Hughes (1969) believe that 68-98% of the total cobalt is hydrogenous in origin, more than 95% of which is associated with micronodules. Whether micronodules are present (?) in the sediments of the cores from the shelf (Nos. 3 and 5) and the basin (No. 2) is not very clear. However, the possible occurrence of micronodules on the shelf here is only a conjecture in view of the high values noticed rather than established as a fact by the authors. The enrichment of cobalt in certain sections of the cores may also be due to high organic content in the sediment besides scavenging (from sea water), migration and precipitation of hydrous iron oxide and/or manganese dioxide. Scavenging of cobalt from the sea water through organic matter is considerable (Krauskopf, 1956).

Nickel

Nickel concentration (Table I) is highest in the slope (239 to 189 ppm) to high in the basin (176 to 126 ppm). The values contrast with those of the shelf where it is 123 to 116 ppm in core No. 3 and poor to very poor in Nos. 4 and 5 (47 and 21 ppm). All these values are referred to on carbonate-free basis.

Though very high concentrations are noticed in the present upper few layers, it is found that the values decrease with depth in the cores, with minor variations which are relative to changes in lithology.

Nickel seems to concentrate in the lower sections of the cores unlike cobalt. According to Chester and Hughes (1969) it is hydrogenous in origin, and after its initial concentration at the top water-sediment interface, it tends to migrate downward. The other source of nickel is primarily cosmogenous, though the lithogenous fraction varies between 21-43 per cent of the total nickel. According to Krauskopf (1956) nickel is adsorbed by organic matter, clays and apatite and hence is concentrated in organic-rich sediments; however, it is scavenged from sea water by iron/manganese oxides under conditions of low redox potential. Further, like cobalt, it is increasingly found in sediments of dark muds, sulphides and bituminous shales (Goldschmidt 1962). It appears that nickel concentrates with certain hydrolysate silicates like bentonite or minerals of chlorite group.

DISCUSSION

Landergren (1943) proposed the term 'the ferrides' for a coherent group of transitional elements such as iron, manganese, cobalt, and nickel, together with vanadium and titanium found to occur always together in nature. Though the term is not very much in vogue presently, the distribution pattern of the four elements indicates the existence of such a close relationship.

Fig. 2 shows the vertical distribution pattern of iron, manganese, cobalt and nickel with depth in each core. Iron is present vertically almost uniformly in all the cores except in core No. 5 wherein it is high at the top layer but decreases sharply up to 60 cm depth and maintains a fairly uniform concentration throughout the depth of the core, since this core represents two different lithologies separated by a definite stratigraphic break (Setty, 1972). The high concentration of iron noticed in core No. 3 is lithogenous and mostly derived from the weathered 'rock flour' of the adjoining Deccan Traps. The concentration, however, remains constant throughout the depth of the core. Like iron, manganese is also high at the surface layers but decreases with depth, maintaining a particular concentration. Core No. 3 is rich in manganese as iron. Similarly, cobalt and nickel are also found to be rich in the top layers; these two trace elements are concentrated with depth also. Lynn and Bonatti (1965) have shown that in the Pacific also the top layers of the sediments are in an oxidising condition and they are underlain by layers of reduced condition (see also Goldschmidt, 1962); hence it may be considered that the concentration decreases with depth, whereas the top layers remain rich. The wide range of concentrations observed may also be due to the random distribution of floccular iron colloids.

Manganese and iron show higher concentrations in the shelf cores. Landergren (1954) has opined that these elements precipitate in a ratio (Mn/Fe) regulated by the pH, pE (redox potential), presence of carbon dioxide, and other factors prevailing in the milieu; and there is no correlation between manganese and the grain size of the

sediment. Mn/Fe ratio decreases with depth in the shelf uniformly excepting in No. 3, whereas on the slope and basin, a gain is noticed which is directly related to the slump and turbidite deposits enclosed within them. The Mn:Fe ratios are (a) for the shelf area 1:72; 3:205; and 6:265; (b) for the slope, it is 1:116; and (c) for the basin 6:170. The values are highest in core No. 3. This proves that there is an enrichment of manganese in the shelf and the basin, whereas a great mobility has taken place in the region of the slope (hence no deposition in the upper layers) and parts of the shelf (No. 4) resulting in depletion. Marching (1972) feels that the thickness of the oxidation zone thins out along the middle part of the slope in the Arabian Sea which enriches manganese to its maximum, and therefore, attributes this factor to the migration of manganese in its dissociated form within the sediment under reducing conditions. This argument and the concentrations of manganese and (iron) in the core No. 1 corroborate well with the results.

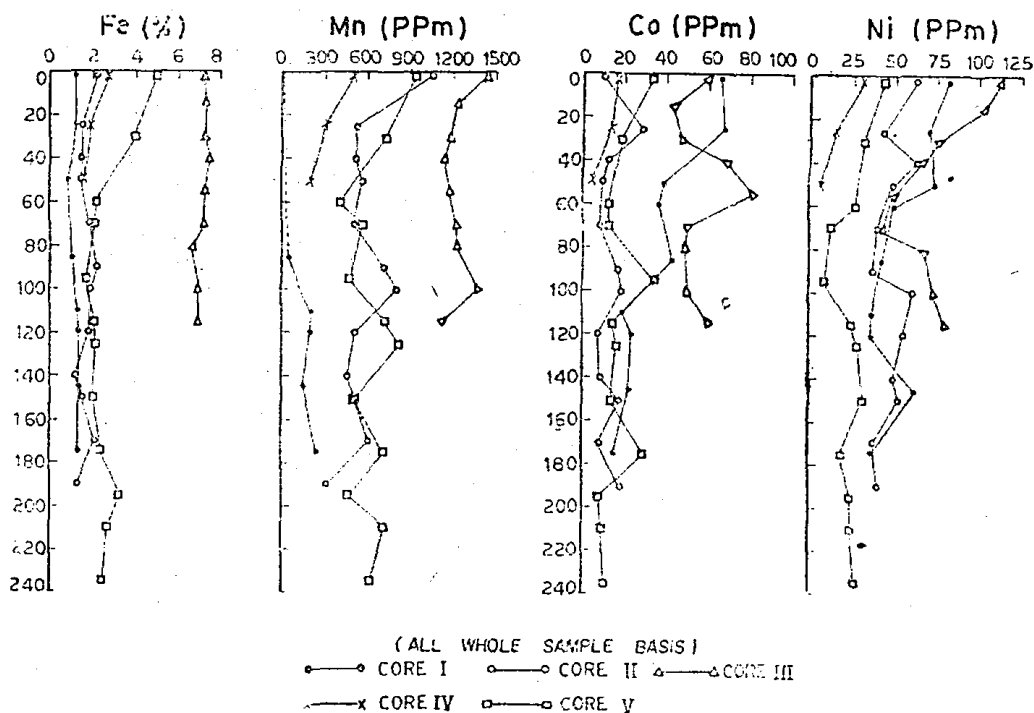


Figure 2. Vertical distribution of iron (per cent), manganese, cobalt and nickel (in ppm) in five (1-5) sediment cores (all whole sample basis)

Some of the iron found in excess of that found in the argillaceous sediments is considered to be biologically derived and particularly from the foraminifera or other organic remains like shell fragments, calcareous debris stained dark red and the like (Chester 1965), with clay minerals and directly precipitated from sea water (Goldberg, 1954) as seen in the cores under study (core Nos. 3 and 5). Thus, the environmental conditions of deposition/precipitation vary from one region to another and due to various causes prevailing within the same region. However, the source of manganese seems to be primarily lithogenous (derived from weathering of continental material, and leaching of the rock 'flour') but very negligibly so from the biogenous source. It is significant to note that the organic matter of the slope is inversely proportional to the amount of manganese present in the sediment.

Cobalt and nickel are normally strongly concentrated in marine sediments relative to igneous rocks and nearshore sediments. The high concentrations of cobalt is attributed to (a) colloidal fraction in sea water (Goldberg and Arrhenius, 1958), (b) detrital clays and dissolved material derived from rivers (Carr and Turekian 1961; Riley and Chester 1971) and volcanic exhalation (Wedepohl, 1960). Similarly, nickel concentration is referred to a source from (a) co-precipitation by hydrous iron oxide from sea water (Laevatsu and Mellis, 1955), (b) cosmic origin (Pettersen, 1959), (c) scavenged by manganese dioxide directly from sea water (Goldberg, 1954) and (d) adsorbed by organic matter, clay minerals and apatite (Krauskopf, 1956). Thus, it is high in organic rich sediments (core No. 3 and also in Nos. 1 and 2). Nickel may be removed from the sea water under low pE and organic reactions which act as controlling factors (Chester, 1965). The low values noticed in cores Nos. 4 and 5 and several sections in cores 2 and 3 are indicative to this effect. Chester and Hughes (1969) have stated that nickel, unlike cobalt, concentrates in the lower sections of the core and shows a decrease towards the top. However, it is found here that though nickel and cobalt show higher values in the lower sections of all the cores, it also shows higher values at the top of all the cores. An analysis of Table I and the pattern of high and low values indicates that cobalt and nickel are enriched in organic-rich sediments in the deep sea area rather than on the shelf. It is of interest to note that core No. 3 shows some unusually high values (56 ppm for cobalt and 75 ppm for nickel) as against the averages 13 and 55, respectively, for nearshore sediments (total sediment) for North Atlantic and North Pacific (Riley and Chester, 1971).

Bender and Schultz (1969) who studied the distribution of manganese, nickel, cobalt and copper stated that the concentration of these elements increased from near continental to deep sea region in the Indian Ocean, in the same manner as that reported in the Atlantic and the Pacific Oceans. Thus a correlation is established and proves that these elements are precipitated under similar conditions of environment in all the oceans of the world.

CONCLUSIONS

(1) Manganese/iron ratio decreases in the shelf sediments (excepting in one core) while it shows a gain in the slope and basin cores. (2) Cobalt and nickel are chiefly hydrogenous in origin and fixed in the sediment as adsorbants of manganese and iron hydroxides, clay minerals and organic matter present. (3) Manganese is enriched in the sediments of the shelf and basin region while it is depleted in the slope and parts of the shelf. It is also inversely proportional to the organic matter present in the sediment. (4) Iron is mostly lithogenous in origin and it is highly concentrated in the shelf area. With the increase in calcium carbonate and organic matter in the sediments it decreases considerably under low redox potential. (5) Cobalt and nickel are in high concentration in the top layers but nickel seems to concentrate more in the lower sections of the cores. (6) Manganese/iron ratios for the shelf are 0.017 in No. 3; 0.017 in No. 4; and 0.024 in No. 5; for the slope 0.009 and for the basin 0.035. (7) One core (No. 3 on the shelf) is rich in iron and manganese, and also shows unusually high values of cobalt and nickel for nearshore sediments. (8) Manganese, cobalt and nickel concentrations in the sediments indicate conditions of environment in the Northern Indian Ocean as similar to those in the Atlantic and the Pacific Oceans.

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