

Geochemistry of the Continental Margin Sediments of the Central West Coast of India

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Abstract. The modern sediments accumulating on the western continental margin of India between 17° and 13° latitude are composed predominantly of terrigenous material in the inner shelf with moderate organic carbon content (<3%), carbonate sediments in the outer shelf with low organic carbon content (<1%) and organic carbon rich (upto 12%) carbonate sediments in the slope region. The bulk and partition geochemistry of the surface sediments reflect the complex intermixture of several sedimentary components (lithogenic, authigenic and biogenic) and enable the identification of geochemical processes that are responsible for the incorporation of elements into the sediments. The elemental concentrations are found to be related to the distribution of three major components i.e. terrigenous debris (Si, Al, Ti, Fe, Mn, Cu), authigenic Calcium Carbonate (Sr, P) and organic carbon (P, Ni, Zn).

Keywords. Geochemistry, Marine Geology, West Coast of India, Continental margin sediments.

INTRODUCTION

In the past, a few papers have appeared reporting the bulk as well as partition geochemistry of sediments of the western continental shelf of India (Gogate *et al.* 1970; Marchig, 1972; Murthy *et al.* 1973; Rao *et al.* 1974). However, all these studies were of a restricted nature based on few samples and they were chiefly concerned with establishing the overall distribution pattern of the elements. These total elemental concentrations are a poor means of assessing the carriers and pathways by which metals have entered and remained in the sediments. They are also of little value in determining the potential availability of toxic heavy metals to the biota (Loring, 1978; Jenne and Luoma, 1975). Hence, bulk and partition geochemistry of the continental margin sediments of the central west coast of India have been undertaken in order to understand the geochemical processes and also to establish the chemical signature due to upwelling.

METHODS

Sediment samples at 226 locations were obtained from different parts of the region with a La Fond-Dietz snapper/Van Veen Grab. The grab samples were placed in plastic bags and refrigerated on board the ship until returned to the laboratory.

Representative portions of the samples were dried at 50°C in an oven, powdered and stored in airtight vials. For the analyses of major and trace elements two different portions of the samples are used. In the first portion after fusion with NaOH, silicon and aluminium are determined colorimetrically following the method of Shapiro and Brannock (1962). All other elements are determined on

second portion after dissolution with HF-HClO₄. Along with the samples, the USGS International Reference Rock Standards AGV & BCR are also prepared. The elements Fe, Mn, Ni, Cu, Zn and Sr are determined using a Hilger and Watts Model M 1550 atomic absorption spectrophotometer. Titanium and Phosphorus are determined on all samples by colorimeter (Riley, 1958; Strickland and Parsons, 1971).

Following bulk analyses for elemental concentrations, selective chemical attacks were made on the samples using an adaption of leach procedure evolved by Chester and Hughes (1967), Cronan (1976).

Leach Procedure

Reagent for Leach	Elements associated in different phases
1) 10% Acetic acid	Carbonate mineral constituents, loosely sorbed ions and interstitial water evaporates.
2) Acetic acid + Hydroxylamine hydrochloride	Fe-Mn oxide phases reducible by Hydroxylamine hydrochloride including the above.
3) 50% Hot Hcl	Everything including iron oxide minerals, except the more resistant silicates and aluminosilicates insoluble in Hcl.

Because the chemical attacks were made on different subsamples of each sample and not sequentially on individual samples the portion of each element is obtained by subtracting one from the other.

The precision of the atomic absorption and colorimetric analyses of both bulk samples and leached fractions is better than $\pm 5\%$ in the case of major elements and $\pm 10\%$ in the case of trace elements on the basis of replicate analyses. The accuracy has been checked by analyses of USGS rock standards.

SEDIMENTARY FRAMEWORK

Texturally, the sediments of the central western continental margin of India exhibit a clear cut zonation (Stackelberg, 1972; Nair *et al.* 1978). The inner-shelf region (40–50 m water depth) is covered by modern silty clays or clayey silts. These are followed seaward by sands, silty sands or clayey sands in the outershelf region (50–150 m). In the continental slope region, fine-grained sediments (Clayey silts, sandy clays) are encountered which are olive-grey to green in colour, and extend upto a depth of 1500 m beyond which brown muds occur. The green muds present in the slope region are the result of oxygen deficient conditions within a large body of water at depth range of 150–1500 m leading to reducing conditions particularly north of 12°N Lat. in the Arabian Sea (Sen Gupta and Naqvi, 1984). Thus, the slope sediments are predominantly in contact with oxygen-poor waters. Seasonal fluctuations in the thickness of isothermal layer may also expose the sediments of the outershelf to the oxygen-deficient water during periods of upwelling.

The outershelf sediments are relict in nature and were originally deposited during the Holocene period (Nair, 1975). Chemically the innershelf sediments are characterised by very low CaCO_3 content (<5%). The coarse-grained sediments in the outer shelf region are having high CaCO_3 content (upto 85%). In the slope region the carbonate content of the sediment is relatively low (40%–70%) when compared to the carbonate content of the outershelf sediments. The sediments of the slope region are characterised by very high (upto 12%) content of organic carbon, those of the outershelf region by low content (<1%) and the intermediate values (2–3%) are associated with the innershelf sediments (Paropkari *et al.* 1987).

RESULTS AND DISCUSSION

The total elemental concentrations (Si, Al, Ti, Fe, P, Mn, Zn, Cu, Ni, Sr) measured in the sediments are shown in Figs. 1–10. Also the bulk elemental concentration ranges as well as in different leaches and their percentage contributions to the total content are given in Table 1 (in respect of Al, Fe, Ti, Mn, P, Cu, Ni, Zn, Sr).

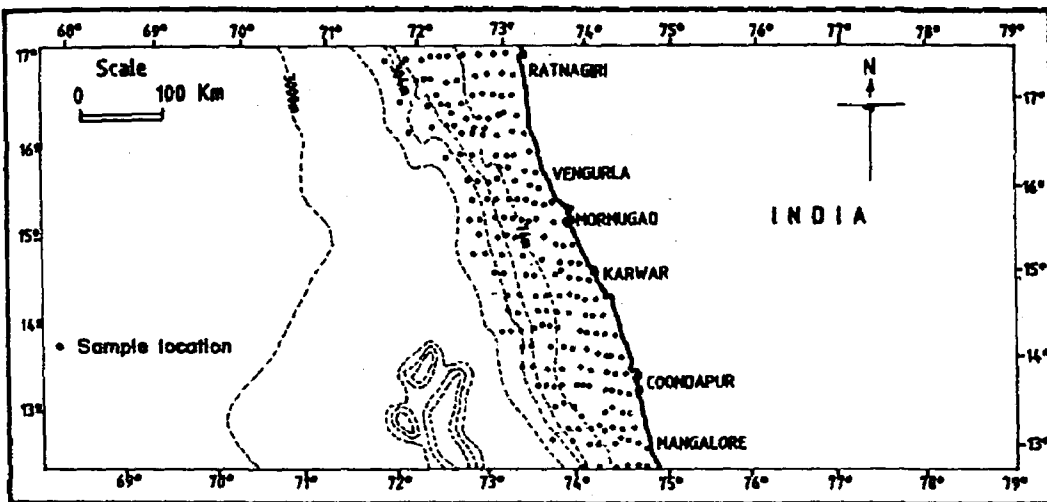


Fig. 1. Location map.

Major elements

An examination of the Figs. 1–6 shows that the major element concentrations reflect the mixture of terrigenous, biogenic and authigenic phases and mirrors the distribution pattern of surface sediment facies. Thus, the concentration of Si (Fig. 1) is highest in a rather narrow nearshore zone corresponding with the area covered by nearshore terrigenous fine-grained sediments. The concentrations decrease rapidly away from the coast and are low in the central and outer parts of the shelf and slope except central shelf off Mangalore coast, wherein the coarse-grained relict quartz sands are present. Higher Al (Fig. 2) content in the innershelf sediments depicts the distribution of fine-grained aluminosilicates, mainly the clay minerals.

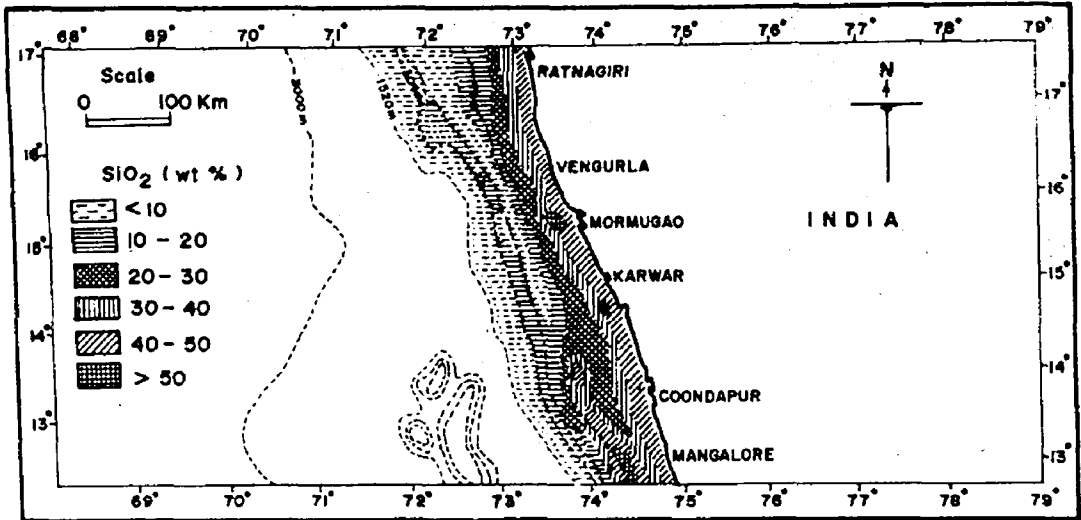


Fig. 2. Map showing the distribution of silica.

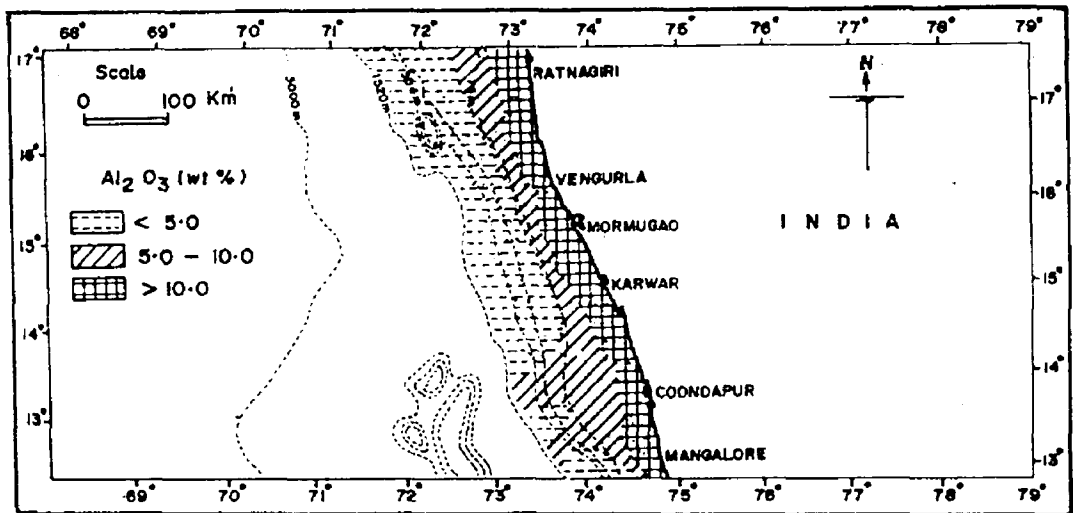


Fig. 3. Map showing the distribution of aluminium.

Further partition studies have indicated that about 80% of the total aluminium is present in the HCl soluble fraction and 20% is present in the HCl insoluble detrital phase, whereas very minute amounts are present in the other phases (Table 1) thus confirming its association with clay minerals.

The distribution of Ti and Fe (Figs. 3 & 4) is similar to that of Al; high values are found in the innershelf zone and low values are found in the outershelf and slope. Ti has a positive correlation with Al ($r=0.96$). However Ti/Al ratios (0.04–0.11) are variable in the shelf sediments which resulted in the scattering of points around the regression line suggesting the controlling nature of detrital minerals on the distribution of Ti. From the chemical partition data (Table 1) it is found that

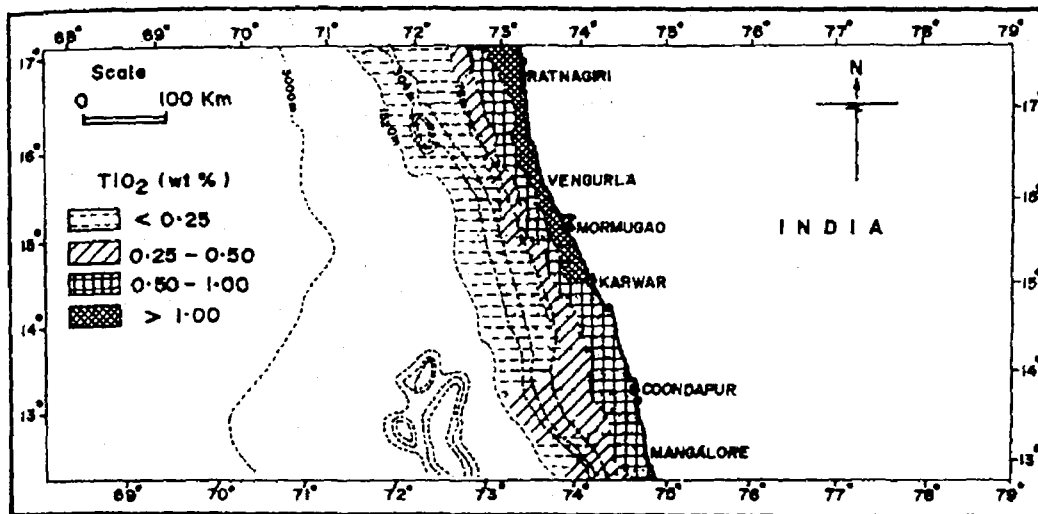


Fig. 4. Map showing the distribution of titanium.

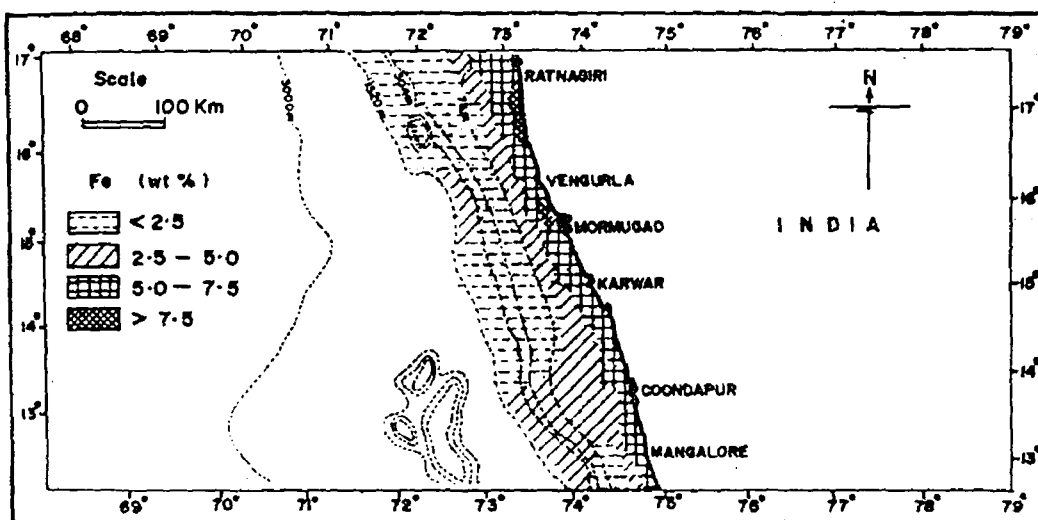


Fig. 5. Map showing the distribution of iron.

more than 60% of Ti is associated with detrital minerals i.e. HCl insoluble fraction. The remainder about 20–40% of Ti is present in HCl soluble fraction i.e. clay minerals. Presence of Ti in the lattice of all clay minerals by substitution for Fe^{3+} and Al^{3+} has been reported by Wright (unpublished thesis). Contributions made by acetic acid and acid reducible fraction are not shown in the table since these concentrations are negligibly low (< 50 ppm) when compared to the bulk concentrations. The relationship between Fe and Al shows that the Fe/Al ratio (0.60–1.12) is somewhat variable. The presence of glauconite in the outershell, pyrite in the slope, ilmenite and colloidal hydroxides of iron in the innershell sediments increases the ratio markedly. Moreover, the partition data suggest that Fe exists in

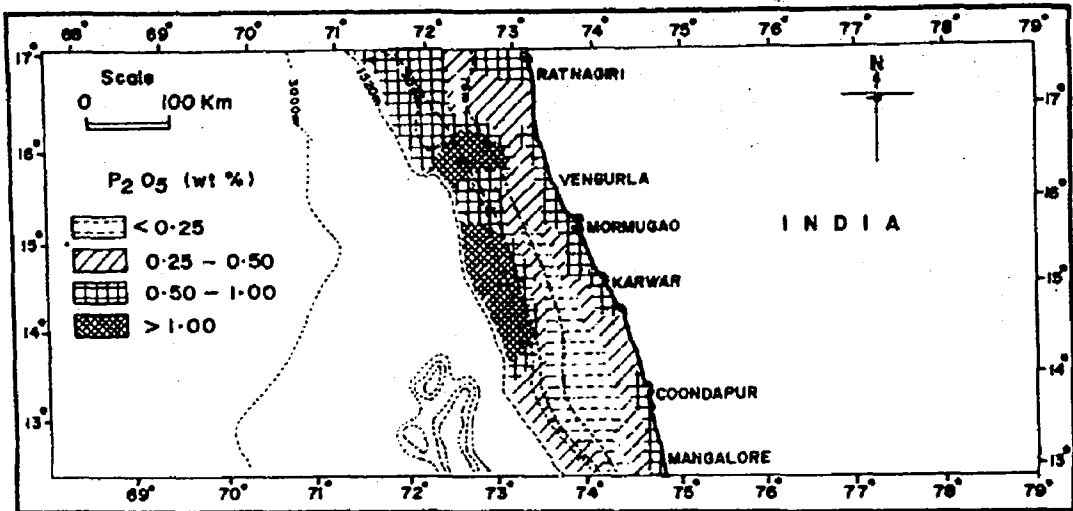


Fig. 6. Map showing the distribution of phosphorus.

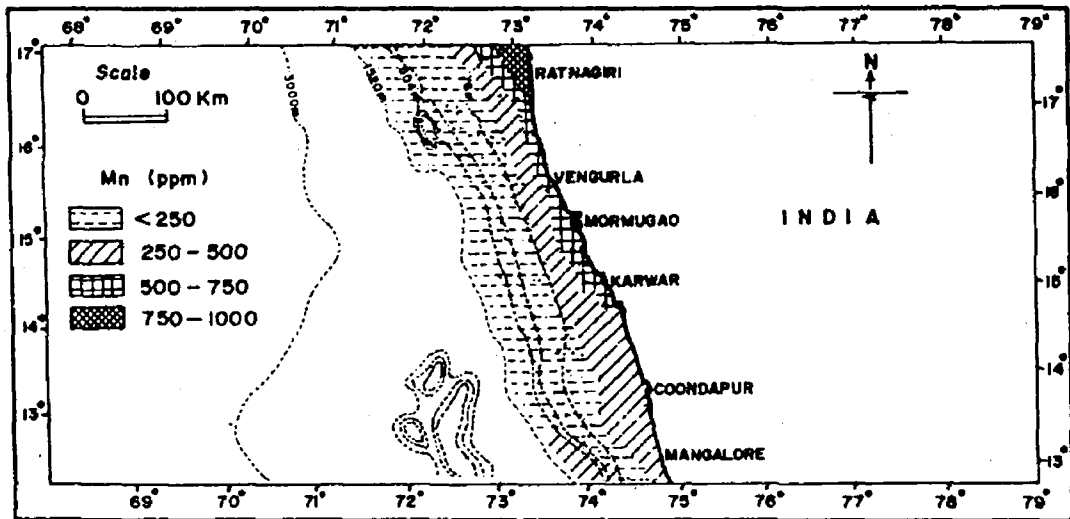


Fig. 7. Map showing the distribution of manganese.

phases other than those that contain Al. Otherwise it is well-correlated with Al ($r=0.94$) in the sediments of this region. From the partition data (Table 1), it can be seen that Fe in the noncarbonate sediment is much more concentrated ($\sim 65\%$) i.e. in the fraction soluble in HCl than in any of the other fractions. It is present in considerable quantities in the detrital phase and it only occurs in minor amounts in the acid-reducible fraction containing the ferromanganese oxides. Considerable quantities of Fe in the HCl insoluble fraction of the sediments point to high concentration of detrital iron-bearing minerals.

The distribution of phosphorus (Fig. 5) indicates that maximal values are found in the outershelf and slope region as pockets and moderate to high concen-

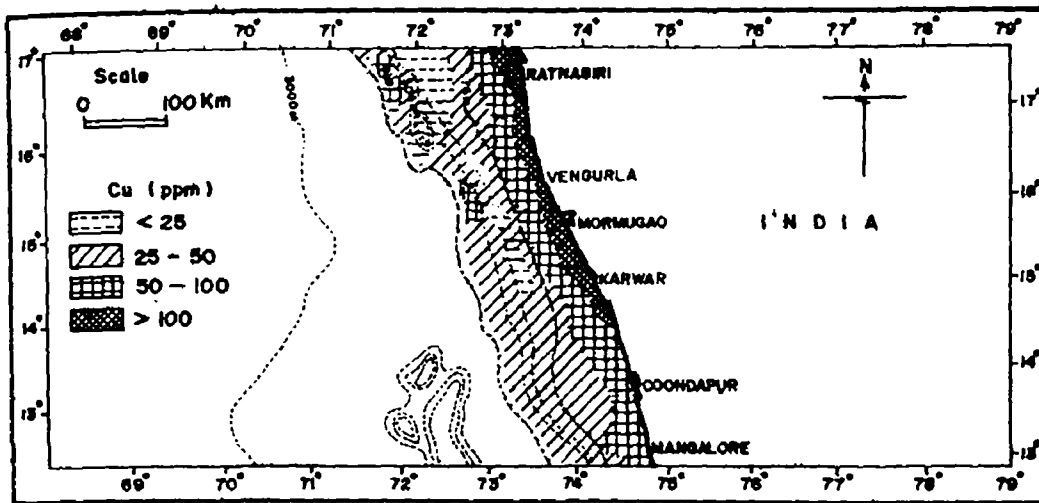


Fig. 8. Map showing the distribution of copper.

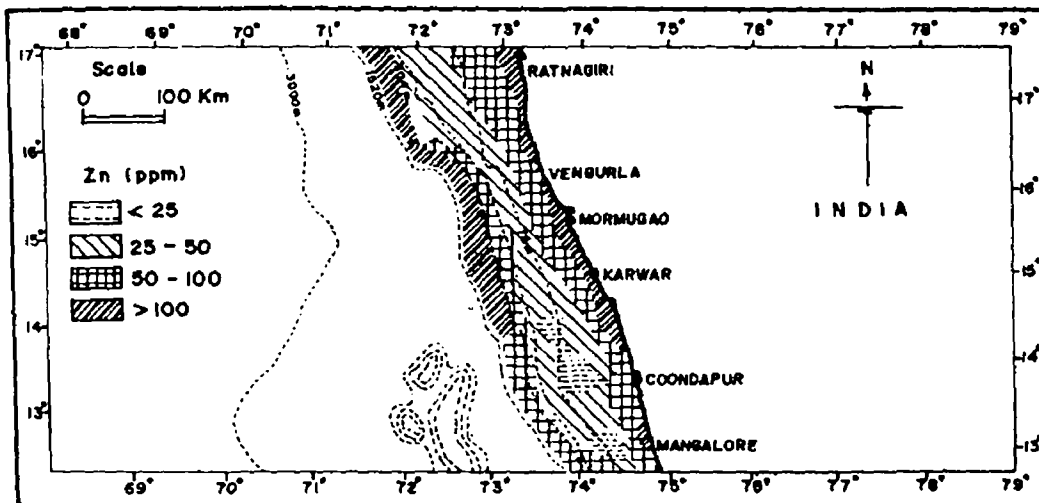


Fig. 9. Map showing the distribution of zinc.

trations are found in the innershelf fine-grained sediments and low levels are seen in the entire shelf slope region of the southernmost part of the study area. It is found that the bulk samples analysed here contain small quantities of newly formed, fine-grained and dispersed phosphorite as evidenced by apatite peaks on bulk sample x-ray data as well as fish debris (Rao *et al.* 1987).

An examination of partition data shows (Table 1) that the contributions to the total P content by acetic acid soluble fraction varies from 22–40% in the innershelf zone and 30–80% in the highly calcareous sediments of the outershelf/slope. High percentage contributions by this fraction in the outershelf/slope sediments indicate the authigenic nature of the phosphate. Further this is confirmed by the presence of apatite peak. In contrast HCl soluble fraction is more in the innershelf (< 60–78%).

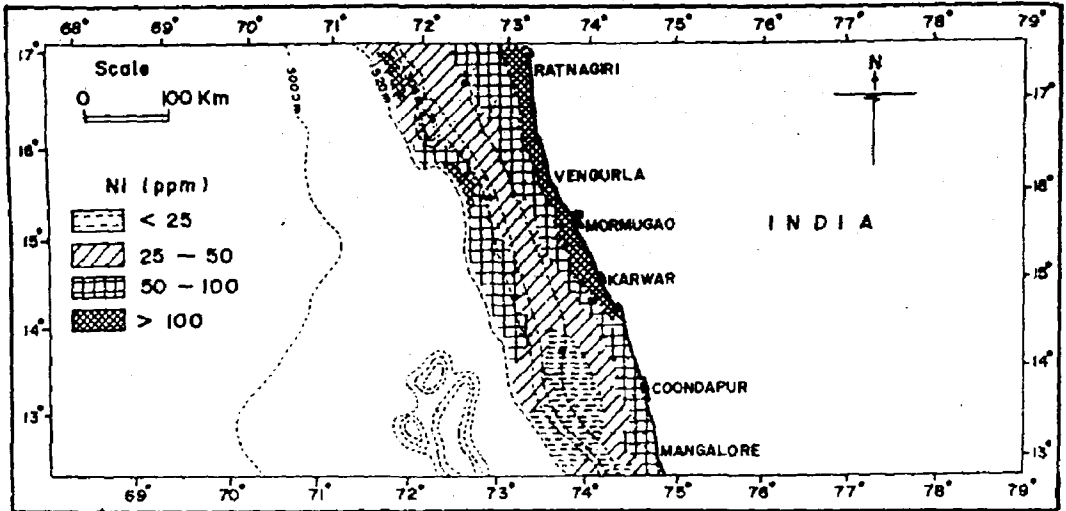


Fig. 10. Map showing the distribution of nickel.

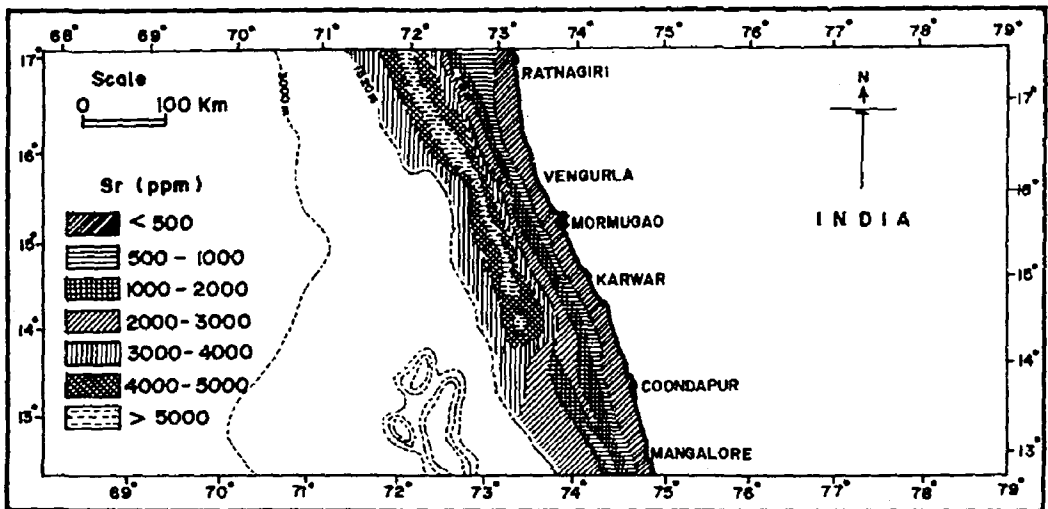


Fig. 11. Map showing the distribution of strontium.

This form of P is perhaps held in the crystal lattice of clay minerals. As high phosphate contents are found in unconsolidated sediments of the outershelf and slope regions, it is likely that the phosphatization is recent. C-14 dating of the phosphatized oolites gave age of 9000–11000 years B.P. (Nair, 1975). Moreover, the high concentrations of phosphorus in the interstitial waters, the impingement of oxygen minimum layer in the slope region, higher organic carbon content in the slope sediments which forms a source for phosphorus, low sedimentation rates and upwelling all favour phosphatization. Similar environmental conditions have been documented off Namibia and Peru–Chile coasts where modern phosphorite is being formed (Burnett, 1981; Baturin, 1970).

The distribution of Mn (Fig. 6) on the bulk concentrations is broadly similar to that of Al, Fe and Ti, higher concentrations are found in the innershelf zone and very low values are found in the outershelf and slope region. In general, the very low levels (<100 ppm) of Mn in the slope region is due to the presence of reducing conditions in that region. Further, chemical partitioning data indicates the absence of acid reducible fraction in the slope region of the northern area suggesting the absence of oxides of Fe and Mn due to reducing conditions. Partition data of Mn also suggest that it differs from the other major elements in respect of its association with non-lithogenous phase in significant amounts. In the innershelf zone nearly 30%–40% of Mn occurs in the non-lithogenous phase (i.e. in acetic acid leach + acid reducible fraction) as hydroxides, the remainder is predominantly held in the crystal lattice of clay minerals as seen from the HCl soluble fraction. Another important observation made regarding the distribution of Mn is that it decreases with the decrease in montmorillonite percentage from north to south (Nair *et al.* 1982) which suggests that this element is mainly associated with the clay mineral, montmorillonite.

Minor Elements

The distribution of Cu, Ni, Zn are very similar in the surface sediments and can be conveniently considered as a single group. Uniformly high concentrations of these elements occur in the inner shelf zone (Figs. 7–9). Very low values are found in the calcareous sediments of the outer shelf and moderate to high concentrations have come across in the slope region. Eventhough the levels are low in the slope region, when compared to the uniformly high concentrations of the innershelf but some of the samples collected beyond 200 m depth in the slope region have two-to three-fold increase in their concentrations suggesting that there is some enrichment of these metals. These sediments are composed almost entirely of biogenous material either dispersed organic matter or skeletal material and a few dispersed grains of apatite and pyrite. This can be seen by comparing the Al contents (Fig. 2) as a reflection of the relative amounts of aluminosilicate debris in the various sediments. Thus, in the slope region these metals occur in substantial amounts in phases other than those that contain Al. Further this is confirmed by the small amounts aluminosilicates, absence of correlation with Al and from high metal/Al ratios (Cu = 0.90–2.35; Zn = 0.58–3.70; Ni = 0.57–3.87).

From the partition data, it is quite evident that all the four chemical fractions of the sediments of the innershelf contain high concentrations of these metals. But the HCl soluble fraction contributions is very substantial. Further, the data (Table 1) suggests that these metals to a large extent are introduced into the sediments in association with the lithogenous phase of the sediments i.e. metals held in clay minerals and in detrital heavy minerals. The elements of HCl soluble fraction mainly occur within the lattice positions of clay minerals. Although metal concentrations in HCl soluble fractions are high throughout the shelf, their greater concentrations in the fine-grained inner shelf sediments suggest that good amount of HCl soluble metals are associated with clay minerals. Elsewhere, similar associations have been reported (Goldberg and Arrhenius, 1958; Hirst, 1962).

Partition data also indicate high concentrations of non-lithogenous metals in

the fine-size material of the innershelf sediments. The high correlation ($r = > 0.6$) with Al, Fe(NL), Mn(NL) and organic carbon demonstrates that fine-grained material closely controls the abundance and distribution of the non-lithogenous contributions. In the inorganic fraction, the high correlation of metals with Fe(NL) and Mn(NL) suggests that some of the contributions are derived from Fe-Mn oxide grain coatings, a site that has often been observed elsewhere (Jenne, 1968; Loring, 1978) or with Fe, Mn hydroxides. Correlation of these elements with Al (Cu, $r = 0.62$; Ni, $r = 0.87$; for Zn, $r = 0.87$) suggests that a part of soluble elements are adsorbed on clay minerals. Chester (1965) stated that a fraction of the Cu in oceanic sediments may have been adsorbed from the overlying waters by clay minerals. Further, the above suggestion is supported by the partition data, that acetic acid soluble fraction contains significant concentration of these elements.

The strong correlation between these metals and organic carbon ($r = > 0.78$) in the innershelf sediments implies either a primary association with this fraction or a secondary grain size relationship as organic matter also increases significantly with decreasing grain size.

The high positive correlation of metals with Fe, Li, Mg ($r = 0.70$) suggests that the elements may be structurally combined with the ferromagnesian silicate minerals (amphiboles, pyroxenes, garnets etc.) that make up the bulk of heavy mineral fraction (Siddiquie and Mallik, 1972; Kidwai *et al.* 1981). In addition, the partition data reveal that detrital fraction contains considerable amounts of these elements (3–32 ppm).

Strontium content varies from 96 to 6065 ppm. Unlike other elements Sr levels are low in the fine-grained sediments of the innershelf, whereas elevated levels are encountered in the outershelf/slope sediments (Fig. 10). The partition data (Table 1) indicate that about 90–150 ppm of Sr corresponds to its association with the lithogenous fraction of the sediments, major part of which is present in the HCL soluble fraction (clay mineral lattices) and a minor amount is in association with detritals (most probably with feldspars). In the innershelf, very little (< 10 ppm) Sr is present in the acetic acid soluble fraction. In contrast 99% of the total Sr occurs in the acetic acid soluble fraction of the outershelf/slope sediments. This is in accordance with the observation that high content of Sr is associated with the carbonate in the sediments (Goldbergs & Arrhenius, 1958; El Wakeel and Riley, 1961; Turekain, 1964; Calvert, 1976). The carbonate is almost entirely aragonitic and the elevated levels of Sr observed in the highly calcareous sediment are consistent with the presence of about 8000 ppm, typical of aragonitic carbonate sediments (Kinsman, 1969). It is known that diadochic replacement of Ca by Sr is permissible in aragonite.

The inter elemental relationships between major and minor elements in the surface sediments have been examined thus far in terms of the areal distributions of individual elements and pair-wise correlations. From this approach several elemental associations have been recognised in the surface sediments.

Factor Analysis

The complex interrelationships between these variables can be conveniently expressed by means of factor analysis (Harman, 1960). Such an analysis was carried

out on the major and minor element data using the R. mode method developed by Fernandes and Mahadevan (1982). The factor analysis program uses an iterative technique to derive factor loadings. A varimax rotation scheme was applied to provide an orthogonally rotated factor pattern. The varimax factor matrix is shown in Table 2.

The analysis produced three factors. The third factor, however is not very significant. They are all readily identified with the main features of the geochemical variability already discussed and provide a convenient summary of the inter-element relationships.

Factor-1 explaining about 86% of variance is characterised by high statistical loadings on all the elements except CaCO_3 , P(NL) and Sr(NL). It is interpreted as a combined fine-grained alumino-silicates and organics factor and thus includes the effects of element incorporation into crystalline lattice structures, scavenging by metal coatings, precipitation of Fe-Mn oxides, complexation with organics and sorption onto fine-grained particles. The loadings on elements Si, K, Mg, Ni(NL), Fe(T), Mn(T), Cu(L), Zn(L), Sr(L) and Al suggest inclusion in crystalline lattice structures, while the loadings on Fe(NL), Mn(NL) indicate the presence of oxide coatings and precipitates. Many authors (Hirst, 1962a; Chester and Messiah-Hanna, 1970; Gibbs, 1977; Loring, 1978; 1979) have shown that Cu, Zn, Ni have been found to occur within crystal lattice structures. Inclusion of Cu(NL), Zn(NL) and Ni(NL) in this factor indicates that significant amounts of these elements appear to have been associated with oxide phases/oxide coatings of Fe-Mn (Jenne, 1968; Spencer *et al.* 1968; Reinson, 1975). Chemical partition data of many of these elements confirm the above conclusions. From enrichment of organic matter in the fine-grained sediments of the innershelf, it is expected that organic matter is associated with this factor. Inclusions of most of the elements in this factor probably reflect multiple geochemical association.

Factor II explains about 10% of total variance. It is characterised by high loadings on CaCO_3 , Sr(NL) and relatively high subordinate loadings on P(NL). This is identified as carbonate factor which controls the geochemistry of Sr. In sediments the association of Sr with CaCO_3 is well-known and its highest concentrations have been recorded in calcareous oozes (Goldberg and Arrhenius, 1958; El Wakeel and Riley, 1961; Calvert, 1976). Significant loadings of P(NL) in this factor could be accounted for by the contribution by authigenic apatite to the carbonate factor.

The regional distribution trend and the chemical partition data clearly establish that there is a substantial supply of the elements from land to the innershelf region. The elements are brought to the marine regime mainly held in the lattice structure of clay minerals.

The globigerina ooze on the slope region is exceptionally rich in organic matter (~12%). It is entirely of planktonic origin, a direct reflection of upwelling and small terrigenous inputs into this region from the adjacent land masses leading to minimal dilution of marine sediment components by terrigenous materials. The organic matter evidently accumulates at a high rate, suffering relatively little degradation during its brief transit time through the short water column. Further, the presence of oxygen minimum layer present in the slope region enhances the preservation of organic matter. The combination of high phosphorus content and

TABLE 2
Correlation matrix, for all the shelf/slope sediments (n = 220)^a

	Si	Al	Ti	Mg	Na	K	C _{org}	CoCO ₃	Fe(T)	Fe(NL)	Mn(T)	Mn(NL)	P(T)	P(NL)	Ni(L)	Ni(NL)	Co(L)	Co(NL)	Cu(L)	Cu(NL)	Zn(L)	Zn(NL)	Sr(L)	Sr(NL)	Li
Si	1.00																								
Al	0.88	1.00																							
Ti	0.88	0.96	1.00																						
Mg	0.78	0.90	0.94	1.00																					
Na	0.86	0.94	0.96	0.93	1.00																				
K	0.86	0.91	0.92	0.87	0.95	1.00																			
C _{org}	0.25	0.53	0.48	0.50	0.44	0.45	1.00																		
CoCO ₃	-0.80	-0.87	-0.86	-0.78	-0.81	-0.80	0.58	1.00																	
Fe(T)	0.86	0.97	0.98	0.92	0.94	0.92	0.52	-0.85	1.00																
Fe(NL)	0.88	0.85	0.88	0.83	0.87	0.87	0.27	-0.77	0.88	1.00															
Mn(T)	0.87	0.93	0.93	0.87	0.92	0.89	0.38	-0.78	0.93	0.87	1.00														
Mn(NL)	0.83	0.89	0.89	0.84	0.90	0.86	0.30	-0.70	0.88	0.85	0.98	1.00													
P(T)	-	0.21	-	0.20	-	0.18	0.79	-0.28	0.20	0.80	0.51	0.17	1.00												
P(NL)	-0.35	-	-0.19	-	-0.19	-	0.52	-	-	-0.30	-0.27	-0.29	0.86	1.00											
Ni(L)	0.56	0.80	0.75	0.73	0.72	0.69	0.87	-0.80	0.77	0.55	0.67	0.60	0.61	0.25	1.00										
Ni(NL)	0.58	0.82	0.75	0.74	0.72	0.69	0.82	-0.78	0.76	0.57	0.70	0.63	0.55	0.20	0.97	1.00									
Co(L)	0.76	0.92	0.91	0.85	0.87	0.83	0.63	-0.90	0.90	0.74	0.85	0.77	0.33	-0.49	0.86	0.85	1.00								
Co(NL)	0.59	0.82	0.80	0.77	0.79	0.76	0.60	-0.70	0.81	0.59	0.77	0.71	0.35	-	0.79	0.80	0.87	1.00							
Cu(L)	0.78	0.96	0.94	0.88	0.91	0.87	0.62	-0.88	0.95	0.79	0.89	0.84	-0.31	-0.52	0.86	0.86	0.94	0.86	1.00						
Cu(NL)	0.85	0.96	0.95	0.89	0.93	0.90	0.50	-0.84	0.96	0.85	0.93	0.89	0.19	-0.16	0.77	0.78	0.90	0.82	0.96	1.00					
Zn(L)	0.52	0.75	0.71	0.70	0.67	0.66	0.87	-0.76	0.72	0.52	0.63	0.55	0.66	0.33	0.93	0.90	0.81	0.75	0.87	0.72	1.00				
Zn(NL)	0.61	0.83	0.78	0.77	0.75	0.73	0.79	-0.79	0.79	0.61	0.73	0.67	0.50	0.17	0.92	0.92	0.85	0.78	0.86	0.81	0.95	1.00			
Sr(L)	0.78	0.87	0.84	0.77	0.83	0.77	0.50	-0.73	0.83	0.72	0.83	0.80	0.24	-	0.75	0.78	0.85	0.84	0.86	0.86	0.69	0.76	1.00		
Sr(NL)	-0.74	-0.84	-0.82	-0.76	-0.75	-0.76	-0.61	0.98	-0.82	-0.73	-0.75	-0.66	-0.30	0.67	-0.79	-0.79	-0.88	-0.69	-0.86	-0.86	-0.76	-0.78	-0.76	1.00	
Li	0.81	0.96	0.94	0.90	0.93	0.89	0.56	-0.83	0.95	0.82	0.91	0.87	0.24	-	0.81	0.82	0.91	0.82	0.95	0.95	0.76	0.84	0.86	-0.81	1.00

^aFor r > ±0.15, P < 0.05

T = Total, L = Lithogenous; NL = Non-lithogenous

TABLE 2a
Correlation matrix, clastic sediments (n = 119)^a

	Si	Al	Ti	Mg	Na	K	C _{org}	CaCO ₃	Fe(T)	Fe(NL)	Mn(T)	Mn(NL)	P(T)	P(NL)	Ni(L)	Ni(NL)	Co(L)	Co(NL)	Cu(L)	Cu(NL)	Zn(L)	Zn(NL)	Sr(L)	Sr(NL)	LI
Si	1.00																								
Al	-	1.00																							
Ti	-	0.93	1.00																						
Mg	-	0.94	0.91	1.00																					
Na	-	0.95	0.91	0.92	1.00																				
K	0.25	0.92	0.91	0.88	0.93	1.00																			
C _{org}	-	0.81	0.81	0.79	0.79	0.84	1.00																		
CaCO ₃	-0.61	-0.72	-0.75	-0.64	-0.70	-0.80	-0.64	1.00																	
Fe(T)	-	0.94	0.94	0.92	0.93	0.90	0.80	-0.73	1.00																
Fe(NL)	-	0.56	0.53	0.53	0.52	0.56	0.42	-0.56	0.59	1.00															
Mn(T)	-	0.88	0.86	0.86	0.85	0.84	0.69	-0.61	0.85	0.49	1.00														
Mn(NL)	-	0.75	0.71	0.74	0.73	0.67	0.55	-0.34	0.70	0.41	0.91	1.00													
P(T)	-	0.73	0.68	0.68	0.73	0.76	0.88	-0.56	0.71	0.38	0.61	0.52	1.00												
P(NL)	-	0.54	0.46	0.50	0.53	0.51	0.69	-0.28	0.49	0.25	0.45	0.46	0.89	1.00											
Ni(L)	-	0.91	0.90	0.89	0.91	0.94	0.91	-0.71	0.90	0.47	0.82	0.68	0.82	0.58	1.00										
Ni(NL)	-	0.91	0.87	0.87	0.91	0.92	0.88	-0.64	0.87	0.43	0.83	0.71	0.81	0.59	0.98	1.00									
Co(L)	-	0.87	0.93	0.87	0.88	0.90	0.78	-0.80	0.89	0.46	0.81	0.60	0.66	0.39	0.88	0.84	1.00								
Co(NL)	-	0.89	0.89	0.90	0.91	0.86	0.75	-0.59	0.88	0.40	0.83	0.70	0.68	0.46	0.88	0.88	0.90	1.00							
Cu(L)	-	0.93	0.94	0.91	0.94	0.92	0.80	-0.72	0.95	0.53	0.87	0.74	0.71	0.50	0.92	0.90	0.90	0.92	1.00						
Cu(NL)	-	0.92	0.91	0.90	0.91	0.88	0.76	-0.66	0.94	0.56	0.88	0.78	0.69	0.47	0.88	0.87	0.85	0.89	0.97	1.00					
Zn(L)	-	0.89	0.86	0.85	0.85	0.87	0.88	-0.70	0.84	0.50	0.81	0.66	0.80	0.61	0.90	0.89	0.82	0.81	0.85	0.84	1.00				
Zn(NL)	-	0.90	0.86	0.86	0.86	0.85	0.85	-0.64	0.83	0.46	0.85	0.72	0.76	0.55	0.89	0.89	0.81	0.84	0.86	0.86	0.97	1.00			
Sr(L)	-	0.90	0.85	0.85	0.91	0.83	0.72	-0.65	0.88	0.42	0.73	0.62	0.68	0.47	0.85	0.84	0.82	0.88	0.89	0.88	0.82	0.82	1.00		
Sr(NL)	-0.54	-0.75	-0.77	-0.68	-0.73	-0.80	-0.66	0.96	-0.75	-0.58	-0.63	-0.38	-0.56	-0.31	-0.72	-0.67	-0.80	-0.61	-0.75	-0.69	-0.72	-0.67	-0.69	1.00	
LI	-	0.94	0.91	0.93	0.95	0.89	0.80	-0.63	0.92	0.47	0.86	0.78	0.74	0.55	0.92	0.91	0.86	0.92	0.94	0.92	0.85	0.87	0.90	0.60	1.00

^aFor $r > \pm 0.20$, $P < 0.05$

T = Total; L = Lithogenous; NL = Non-lithogenous

TABLE 2b
Correlation matrix, outer shelf sediments (n = 62)^a

	Si	Al	Ti	Mg	Na	K	C _{org}	CaCO ₃	Fe(T)	Fe(NL)	Mn(T)	Mn(NL)	P(T)	P(NL)	Ni(L)	Ni(NL)	Co(L)	Co(NL)	Cu(L)	Cu(NL)	Zn(L)	Zn(NL)	Sr(L)	Sr(NL)	Li
Si	1.00																								
Al	0.91	1.00																							
Ti	0.93	0.95	1.00																						
Mg	0.74	0.76	0.76	1.00																					
Na	0.91	0.85	0.85	0.74	1.00																				
K	0.81	0.76	0.78	0.73	0.93	1.00																			
C _{org}	-0.32	-	-	-	-	-	1.00																		
CaCO ₃	-0.93	-0.91	-0.91	-0.71	-0.87	-0.80	-	1.00																	
Fe(T)	0.86	0.93	0.95	0.74	0.80	0.75	-	-0.88	1.00																
Fe(NL)	0.71	0.79	0.78	0.68	0.78	0.82	-0.34	-0.77	0.79	1.00															
Mn(T)	0.79	0.86	0.83	0.70	0.80	0.71	-	-0.78	0.82	0.66	1.00														
Mn(NL)	0.79	0.83	0.81	0.72	0.83	0.76	-	-0.77	0.80	0.71	0.98	1.00													
P(T)	-	-	-	-	-	-	0.73	-	-	-	-	-	1.00												
P(NL)	-	0.68	-	-	-	-	0.62	-	-	-	-	-	0.90	1.00											
Ni(L)	-	-	-	-	-	-	0.85	-	0.35	-	-	-	0.60	0.53	1.00										
Ni(NL)	-	-	-	-	-	-	0.73	-	-	-	-	-	0.58	0.55	0.87	1.00									
Co(L)	0.70	0.75	0.75	0.57	0.67	0.54	-	-0.70	0.68	0.45	0.71	0.67	-	-	-	-	1.00								
Co(NL)	0.59	0.69	0.63	0.63	0.55	0.37	-	-0.62	0.52	0.25	0.63	0.56	-	-	0.29	0.37	0.82	1.00							
Cu(L)	0.77	0.89	0.86	0.67	0.71	0.61	-	-0.82	0.85	0.55	0.79	0.75	-	-	0.28	-	0.73	0.68	1.00						
Cu(NL)	0.81	0.88	0.85	0.69	0.76	0.68	-	-0.81	0.86	0.62	0.80	0.78	-	-	-	-	0.73	0.65	0.88	1.00					
Zn(L)	-	-	-	-	-	-	0.79	-0.57	0.45	-	-	-	0.66	0.59	0.83	0.78	-	0.32	0.29	-	1.00				
Zn(NL)	-	-	-	-	-	-	0.63	-	-	-	-	-	0.46	0.44	0.78	0.82	0.25	0.34	0.34	0.27	0.77	1.00			
Sr(L)	0.42	0.52	0.46	0.36	0.42	0.28	-	-0.48	0.37	-	0.49	0.44	-	-	0.33	0.35	0.63	0.84	0.59	0.45	0.31	0.31	1.00		
Sr(NL)	-0.92	-0.90	-0.92	-0.72	-0.88	-0.81	-	0.97	-0.88	-0.79	-0.81	-0.80	-	-	-	-	-0.69	-0.59	-0.83	-0.81	-	-	-0.50	1.00	
Li	0.77	0.85	0.80	0.66	0.76	0.71	-	-0.80	0.79	0.62	0.76	0.75	-	-	-	-	0.75	0.66	0.80	0.77	-	0.32	0.54	-0.81	1.00

^a For $r > \pm 0.25$, $P < 0.05$

T = Total; L = Lithogenous; NL = Non-lithogenous

TABLE 2c
Correlation matrix, slope sediments (n=39)^a

	Si	Al	Ti	Mg	Na	K	C _{org}	CaCO ₃	Fe(T)	Fe(NL)	Mn(T)	Mn(NL)	P(T)	P(NL)	Ni(L)	Ni(NL)	Co(L)	Co(NL)	Cu(L)	Cu(NL)	Zn(L)	Zn(NL)	Sr(L)	Sr(NL)	LI
Si	1.00																								
Al	0.91	1.00																							
Ti	0.81	0.81	1.00																						
Mg	0.66	0.63	0.92	1.00																					
Na	0.79	0.74	0.93	0.88	1.00																				
K	0.86	0.84	0.81	0.63	0.84	1.00																			
C _{org}	-	-	-	-	-	-	1.00																		
CaCO ₃	-0.92	-0.91	-0.84	-0.68	-0.83	-0.89	-	1.00																	
Fe(T)	0.90	0.94	0.91	0.75	0.65	0.89	-	-0.93	1.00																
Fe(NL)	0.58	0.69	0.74	0.67	0.71	0.68	-0.52	-0.77	0.75	1.00															
Mn(T)	0.73	0.78	0.81	0.66	0.79	0.87	-	-0.83	0.85	0.83	1.00														
Mn(NL)	0.58	0.69	0.74	0.62	0.74	0.77	-0.38	-0.77	0.73	0.68	0.94	1.00													
P(T)	-	-	-	-	-	-	0.87	-	-	-0.51	-0.33	-0.37	1.00												
P(NL)	-	-	-	-	-	-	0.85	-	-	-0.56	-0.41	-0.47	0.98	1.00											
Ni(L)	-	-	-	-	-	-	0.93	-	-0.99	-0.50	-0.30	-0.42	0.89	0.88	1.00										
Ni(NL)	-	-	-	-	-	-	0.86	-	-	-0.56	-0.36	-0.31	0.80	0.79	0.89	1.00									
Co(L)	0.52	0.61	0.53	0.46	0.46	0.53	0.38	-0.51	0.55	-	0.39	-	0.40	0.36	0.43	-	1.00								
Co(NL)	0.32	0.40	0.30	-	0.31	0.53	0.49	-0.41	0.36	-	0.36	-	0.44	0.34	0.36	0.33	0.69	1.00							
Cu(L)	0.80	0.87	0.71	0.53	-0.70	0.82	0.52	-0.83	0.86	0.53	0.69	0.56	-	-	-	-	0.56	0.45	1.00						
Cu(NL)	0.80	0.86	0.76	0.59	0.77	0.86	-	-0.86	0.88	0.67	0.75	0.68	-	-	-	-	0.56	0.47	0.87	1.00					
Zn(L)	-	-	-	-	-	-	0.89	-	0.56	-0.33	-0.40	-	0.77	0.72	0.89	0.79	0.46	0.37	-	-	1.00				
Zn(NL)	0.34	0.31	-	-	-	-	0.63	-	-	-	-	-	0.45	0.43	0.63	0.55	0.40	-	0.30	-	0.82	1.00			
Sr(L)	-	0.95	-	-	-	-	0.33	-	-	-	-	-	0.39	-	-	-	0.38	0.78	-	-	0.31	-	1.00		
Sr(NL)	-0.88	-0.81	-0.82	-0.66	-0.84	-0.86	-	0.96	-0.87	-0.78	-0.86	-0.84	-	-	-	-	-0.45	-0.42	-0.76	-0.81	-	-	-0.30	1.00	
LI	0.81	0.88	0.78	0.66	0.77	0.78	-	-0.82	0.80	0.58	0.71	0.57	-	-	-	-	0.55	-	0.79	0.79	-	-	-	-0.75	1.00

^aFor r > ± 0.30, P < 0.05

T = Total; L = Lithogenous; NL = Non-lithogenous

organic matter serve to distinguish relatively shallow water upwelling sediments from the deep ocean sediments forming beneath upwelling zones.

In addition to the markedly high organic matter and phosphorus content the slope sediments are also enriched in minor metals compared with the adjacent facies and is the site of precipitation of phosphorite. The metal enrichments are unusual by virtue of the over whelmingly biogenous nature of the sediments and contain less than 10% by weight lithogenous aluminosilicate material. The metal concentrations of these biogenous sediments when compared to terrigenous sediment concentrations, are found to be two to-three-fold high. A marked increase of metals occur in places of highest organic productivity, where the number of concentrating organisms is high, for example, in the areas of upwelling. The change will be particularly great if high productivity is combined with a low mixing rate of the bottom water (Schultz and Turekian, 1965). Thus, in the area of study, strong seasonal upwelling (Banse, 1968; Sharma, 1966) results in higher productivity, which enhances the accumulation of these metals. Moreover, increased concentrations of organic matter in these sediments will significantly increase the exchange capacities and, thus, enhance sorption of various elements (Schnitzer, 1965). Kee and Bloomfield (1961) have suggested that adsorption onto degraded organic material may account for the enrichment of several metals in sediments. The sulfide fraction could also play an important role in the minor metal geochemistry of the sediments. The mechanisms of formation of iron sulfides are quite well known (Berner, 1964) but the precipitation of other metal sulfides in such sediments has not been examined in detail. The co-precipitation of minor metals by iron sulfides has been advocated by some authors (Korolev, 1958; Doff, 1969; Bertine, 1972; Krauskopf, 1956). Calvert (1976) has suggested that such a mechanism could explain the remarkably high levels of metals in many modern sediments. From the above it can be concluded that the host for these excess metals in these sediments are of course organic matter, sulphides or both.

CONCLUSIONS

1. The regional distribution trends, correlation matrix and partition data clearly establishes that there is a substantial supply of elements from land to the innershelf region.
2. Most of the elements have lithogenous source, clay is an important constituent wherein the metals are held in crystal lattice positions.
3. Covariance of elements partition data with Al, Fe(NL), Mn(NL), C_{org} and correlation matrix suggest that clays, oxyhydroxides of Fe, Mn and organic carbon and/or sulphides act as carriers for most of the elements while $CaCO_3$ acts as diluent except for Sr. Carbonate sediments are the major sink for Sr.
4. In the slope sediments the excess metal contents are fixed through organic carbon and/or sulphides.
5. The high concentrations of organic carbon, phosphorus and metals like Ni, Zn in the slope sediments and small quantities of oxidate elements (Mn) serve to identify an upwelling environment.

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