

Geochemistry of calcareous sediments from the SW Carlsberg Ridge: Evidence for deeper carbonate compensation depth

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Concentration of Mn, Fe, Ni, Co, Zn, Ca, Mg, K, Al, Si, Ti, P and CaCO_3 show wide range for the calcareous sediments from Sw Carlsberg Ridge (CR). Compared with the average pelagic clays, the CR sediments are enriched by Mg, Ni, Co, and Zn trace metals and are depleted in the other. Variation with respect to depth is significant for CaCO_3 (8.5-79.8%) and benthic ratios (1.5-32.5) whereas P_2O_5 (0.28-0.38%) and organic carbon (0.18-0.46%) is low and constant. Correlation matrix on moisture, organic carbon (C) and CaCO_3 (MOC) free basis suggest three main processes responsible for the incorporation of various elements. It appears that biogenic process is most dominant among the others for the supply of Ca, Si, Mg, P, Cu, Ni and Zn elements due to high surface biological (calcareous) productivity. Mn and Fe are hydrogenous and Al, K and Ti are either terrigenous or *in situ* due to alteration of basalts. Occurrence of deeper lysocline (4700 m) and deeper carbonate compensation depth (CCD) (> 5100 m) in the region is evident from the CaCO_3 -depth relationship which is different than that reported earlier. Inverse relationship between benthic ratio and CaCO_3 also supports high surface biological productivity, whereas increase in the benthic ratio point towards increase in the degree of dissolution with depth.

Chemical and mineralogical composition of Arabian Sea sediments were studied¹⁻⁷ and regional distribution of CaCO_3 , opal, quartz and other minerals were reported. Spreading activity on the Carlsberg Ridge (CR) was reported⁸⁻¹⁰ and the mineralogical and compositional variations in the ferromanganese nodules from CR were also studied which showed the occurrence of poor grade nodules having less economic value¹¹⁻¹⁷.

Variations in sediments from 20 locations in the south western (SW) flank of the CR were examined and their distinct sources of metal supply is discussed. Association of various elements was deduced from their behaviour by comparing carbonate and non-carbonate fractions on the bulk as well as on CaCO_3 free basis.

Materials and Methods

Surface sediment samples were collected with a modified Peterson grab during 86th and 87th cruises of R.V. *Gaveshani* during Jan.-March 1981. Two sediment samples were collected on the NE flank in the Arabian Sea whereas the rest were located on the SW flank of the CR (Fig. 1). The topography was rugged as indicated by the 3.5 kHz sounding profiles and the water depth varied from 4000 to 5400 m.

The bulk chemical composition of the sediment was determined by titrimetry and atomic absorption spectrometry after acid digestion¹⁸. Samples were washed to remove the salt before digestion with HCl, HF and HNO_3 . The solutions (in duplicate) were analysed for Mn, Fe, Cu, Ni, Co, Zn, K and Mg elements using double beam atomic absorption spectrophotometer (Perkin Elmer PE-5000), whereas Si, Al, Ti and P were analysed¹⁹ on Bousch & Lamb spectrophotometer (Spectronic 1000). All the samples were reanalysed on Philips X-ray fluorescence analyser (XRF, model 1480) by pressed pellet technique to verify the reliability of AAS analysis. The analytical values obtained by both the methods were quite close and the agreement between analytical technique in most cases suggests a precision of $\pm 5\%$. Total CaCO_3 was determined by Karbonate Bombe²⁰ whereas organic C was determined by titration of chromic acid against ferrous ammonium sulphate²¹. Portion of each subsample was washed and wet sieved for the benthic and planktonic foraminiferal studies. About 500 foraminiferal specimen (if present) were counted under binocular microscope to determine the benthic ratio²² (i.e. ratio of benthic to planktonic Foraminifera). The sediment fraction less than 0.063 mm were mainly the calcareous clay.

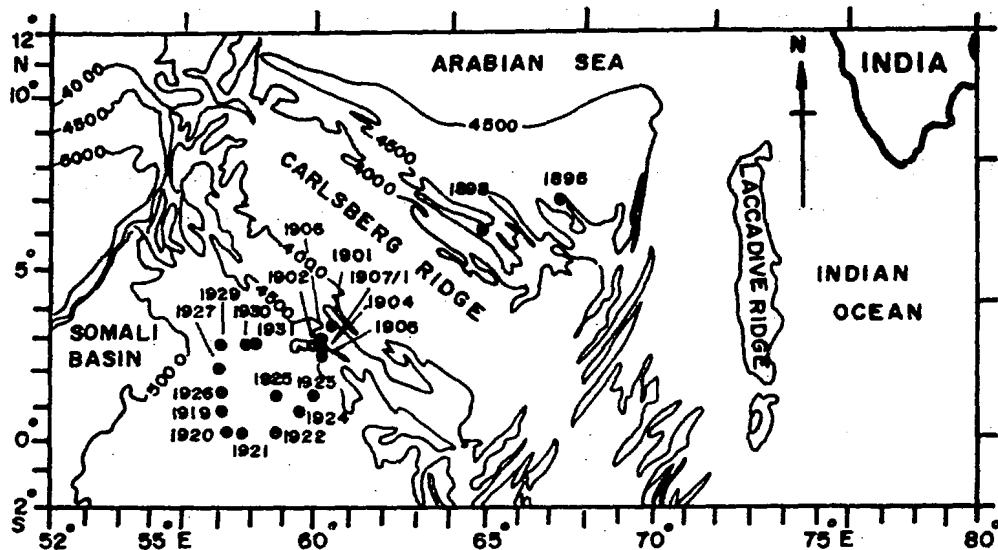


Fig. 1—Sample locations

Results

The sediments mainly consist of white to dark brown calcareous oozes. Among them the foraminiferal oozes were obtained from the topographic highs whereas siliceous oozes were found in the valleys. Ocean Drilling (ODP) studies on the sediments in the vicinity of the study area showed abundance of Pleistocene nanno fossils²³.

Bulk chemical analysis of CR sediments (Table 1) display wide range in composition and also in respective ratios (Table 2). Lowest values for all elements except for CaCO_3 was observed for station 1904 (Table 1). Compared to the average pelagic clays, the bulk chemistry of CR sediments are enriched in Mg, Ni, Co and Zn, and are depleted in other elements along with large variation in SiO_2 (9.89-51.1%), CaCO_3 (8.5-79.75%) content with respect to depth (Table 1).

Sediments were highly calcareous and therefore they were recalculated on CaCO_3 free basis. As the organic C is low and nearly constant and the moisture content is independent factor, they were combined with CaCO_3 for recalculating the values on moisture, organic C and CaCO_3 (MOC) free basis (Table 3), for minimizing the masking or dilution effect of biogenous CaCO_3 . The variations in TiO_2 (0.46-2.84%, Table 1) and benthic ratio (1.48-32.42, Table 2) are significant whereas values for P_2O_5 (0.28-0.38%, Table 1) and organic C (0.18-0.46%, Table 2) are nearly constant.

Relationship between CaCO_3 and water depth is shown in Fig. 2 where a sharp decline in CaCO_3 occurs at around 4700 m. Limited number of plots (3) below 5000 m depth in Fig. 2 are mainly due to the limited

sampling below 5000 m depth but in this regard, present observation is similar to those of Naqvi and Naik²⁴. Benthic ratio and CaCO_3 show inverse correlation. Correlation coefficient matrix for the sediments (MOC free basis, Table 4) shows excellent correlation between P and Mg (0.95); Cu and Zn (0.85); and Ni and Zn (0.82). The data also show good correlation between Ni and Cu (0.60); P and Ni (0.59); and Ti and K (0.57); whereas Mn and Fe are weakly correlated (0.46).

Al shows positive relationship with K, Ti and Si respectively on bulk chemical composition (Fig. 3). Similarly, Fe and P have strong positive relationship (Fig. 3C). In fact, exactly opposite correlation is seen for the above elements on MOC free basis in Table 4. This could be due to the role of biogenous CaCO_3 .

Discussion

Earlier, Naqvi and Naik²⁴; and Kolla *et al.*²⁵ reported variations in CaCO_3 with depth from this area. Although Naqvi and Naik observed a sharp decrease in CaCO_3 content occurring between 4400 and 4800 m, they preferred to use the lower values of lysocline (~ 4000 m) and CCD (4800 m) given by Kolla *et al.*²⁵ for their interpretation considering that the values of Kolla *et al.*²⁵ were based upon large number of regional sampling and therefore should be more accurate which in fact includes only 3 from the study area as against 20 in the present study. It is felt that, the CCD should lie below this lysocline depth because, in the CCD zone, the rate of carbonate supply equals to that of dissolution and the carbonate content in the sample below carbonate compensation depth is reduced to $< 10\%$. Higher CaCO_3 content in

Table 1—Chemical composition of the sediments from the Carlsberg Ridge

St. no.	SiO ₂ (%)	Al ₂ O ₃ (%)	FeO (%)	Fe ₂ O ₃ (%)	TiO ₂ (%)	CaCO ₃ (%)	MgO (%)	K ₂ O (%)	P ₂ O ₅ (%)	MnO (%)	NiO (%)	CuO (%)	CoO (%)	ZnO (%)	Total (%)
1896	51.10	15.21	5.12	5.79	2.84	08.50	6.10	2.78	0.37	0.65	0.041	0.022	0.041	0.017	98.581
1898	31.31	10.07	3.27	3.69	2.43	42.05	4.45	1.82	0.36	0.41	0.029	0.015	0.010	0.012	99.926
1901	34.30	11.71	3.81	4.30	1.56	36.72	5.14	1.84	0.38	0.55	0.029	0.015	0.031	0.011	100.396
1902	18.65	06.58	2.04	2.30	1.41	62.50	3.39	0.99	0.32	0.30	0.023	0.012	ND	0.006	98.521
1904	09.89	03.08	0.95	1.07	0.72	79.75	2.75	0.49	0.31	0.11	0.018	0.008	0.010	0.005	99.161
1905	34.30	11.44	3.58	4.05	1.65	34.90	4.11	1.68	0.37	0.80	0.047	0.028	0.020	0.014	96.989
1906	30.16	10.00	3.08	3.48	1.77	45.00	3.99	1.48	0.36	0.57	0.034	0.025	0.010	0.011	99.970
1907/1	24.40	08.15	3.22	3.64	1.32	52.87	3.95	1.23	0.36	0.57	0.029	0.019	0.010	0.011	99.779
1919	21.63	05.27	2.77	3.12	0.93	60.80	3.10	0.79	0.34	0.33	0.018	0.013	ND	0.005	99.116
1920	23.02	05.41	1.59	1.79	0.72	59.75	2.99	0.77	0.32	0.13	0.080	0.025	0.007	0.034	96.636
1921	17.50	03.70	1.36	1.53	0.81	69.37	3.08	0.83	0.33	0.13	0.053	0.062	0.007	0.050	98.840
1922	16.57	04.11	1.09	1.23	0.46	70.25	2.84	0.65	0.31	0.11	0.053	0.012	0.007	0.050	97.742
1923	29.24	10.00	3.04	3.43	1.41	43.76	4.04	1.40	0.35	0.50	0.034	0.025	0.020	0.011	101.760
1924	44.90	12.88	4.08	4.61	1.98	20.52	4.53	1.88	0.38	0.52	0.041	0.028	0.031	0.014	96.394
1925	17.27	05.89	1.72	1.95	0.96	65.62	3.17	0.80	0.31	0.24	0.029	0.013	ND	0.005	97.977
1926	18.41	06.30	1.90	2.15	1.11	62.50	3.22	0.91	0.32	0.28	0.053	0.038	0.013	0.047	97.251
1927	27.83	09.93	1.79	2.02	1.56	47.88	4.06	1.41	0.37	0.17	0.039	0.032	0.018	0.029	96.956
1929	30.85	10.28	2.90	3.28	1.86	41.62	3.82	1.35	0.28	0.63	0.032	0.022	0.020	0.012	96.956
1930	25.78	08.01	2.36	2.66	1.56	51.25	3.79	1.22	0.32	0.87	0.018	0.022	0.020	0.014	97.894
1931	39.36	12.81	4.17	4.71	2.27	25.75	4.91	2.03	0.33	0.35	0.018	0.041	0.031	0.017	96.797
Av	27.32	07.95	2.69	3.04	1.47	49.07	3.87	1.32	0.34	0.41	0.036	0.024	0.015	0.020	98.382
Av p c	53.48	15.87		9.29			2.10	3.48		0.87	0.029	0.032	0.009	0.001	

Av p c = Average pelagic clays³²; ND = Not determine

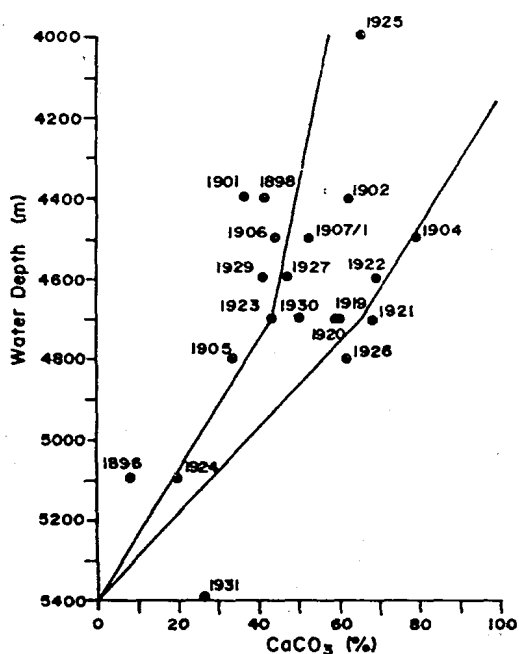
Table 2—Organic carbon and other elemental ratios for the Carlsberg Ridge sediments

St. no.	Depth (m)	Moisture (%)	CaCO ₃ (%)	Org. C (%)	Benthic ratio*	Mn/Fe	Si/Al	Al/(Al + Fe + Mn)
1896	5100	6.32	08.50	0.46	15.38	0.12	2.99	0.64
1898	4400	3.24	42.05	0.27	11.63	0.12	2.74	0.65
1901	4400	3.40	36.72	0.36	03.13	0.15	2.59	0.64
1902	4400	2.70	62.50	0.32	11.70	0.15	2.44	0.66
1904	4500	1.74	79.75	0.32	01.48	0.11	2.83	0.66
1905	4800	6.56	34.90	0.32	29.94	0.22	2.65	0.64
1906	4500	3.34	45.00	0.27	18.58	0.18	2.66	0.65
1907	4500	3.40	52.87	0.46	19.67	0.20	2.64	0.59
1919	4700	3.62	60.80	0.41	14.52	0.12	3.62	0.53
1920	4700	4.64	59.75	0.36	16.09	0.08	3.76	0.68
1921	4700	2.50	69.37	0.23	07.51	0.09	4.20	0.62
1922	4600	3.00	70.25	0.23	02.78	0.10	3.55	0.70
1923	4700	5.38	43.76	0.27	22.27	0.16	2.55	0.65
1924	5100	7.68	20.52	0.32	15.40	0.13	3.08	0.65
1925	4000	2.74	65.62	0.23	14.42	0.14	2.59	0.69
1926	4800	3.96	62.50	0.18	14.85	0.15	2.58	0.66
1927	4600	4.38	47.88	0.32	32.42	0.09	2.47	0.77
1929	4600	5.06	41.62	0.32	26.97	0.21	3.25	0.61
1930	4700	4.84	51.25	0.23	08.40	0.36	2.84	0.63
1931	5400	7.56	25.75	0.32	ND	0.08	2.71	0.66
Range	4400-5400	1.70-7.68	08.50-79.75	0.18-0.46	1.48-32.42	0.08-0.36	2.47-4.19	0.53-0.77
Av.	4660	4.30	49.07	0.31	15.11	0.15	2.94	0.65

* = Ratio of benthic to planktonic Foraminifera²²

Table 3—Recalculated (MOC free basis) analysis for the Calrsberg Ridge sediments

St. no.	Mn (%)	Fe (%)	Cu (%)	Ni (%)	Co (%)	Zn (%)	Mg (%)	K (%)	Al (%)	Si (%)	Ti (%)	P (%)
1896	1.14	09.13	0.04	0.07	0.07	0.03	08.29	5.20	17.99	53.84	3.83	0.36
1898	1.11	08.99	0.04	0.08	0.03	0.03	09.34	5.27	18.56	50.94	5.05	0.56
1901	1.44	09.60	0.04	0.07	0.08	0.03	09.84	4.86	19.69	50.90	2.95	0.54
1902	1.31	08.95	0.06	0.10	0.00	0.03	11.37	4.60	19.81	48.33	4.66	0.78
1904	0.86	07.72	0.07	0.14	0.08	0.04	17.01	4.23	16.72	47.38	4.41	1.33
1905	2.03	09.24	0.07	0.12	0.05	0.04	08.09	4.56	19.75	52.32	3.20	0.52
1906	1.61	08.97	0.07	0.10	0.03	0.03	08.87	4.52	19.46	51.84	3.90	0.59
1907/1	1.90	11.02	0.06	0.10	0.03	0.04	10.32	4.42	18.66	49.35	3.42	0.69
1919	1.36	11.76	0.05	0.08	0.00	0.02	10.08	3.55	15.01	54.33	2.96	0.81
1920	0.56	06.93	0.11	0.35	0.03	0.15	09.98	3.56	15.80	59.39	2.38	0.77
1921	0.69	07.34	0.33	0.29	0.04	0.43	12.70	4.71	13.31	55.85	3.28	1.02
1922	0.62	06.31	0.07	0.31	0.04	0.29	12.57	3.96	16.00	56.82	1.98	1.03
1923	1.47	09.09	0.08	0.10	0.06	0.03	09.24	4.42	20.03	51.73	3.18	0.57
1924	1.09	08.68	0.06	0.09	0.06	0.03	07.36	4.20	18.35	56.45	3.17	0.46
1925	1.15	08.45	0.06	0.14	0.00	0.03	11.88	4.44	19.36	50.08	3.54	0.87
1926	1.27	08.71	0.17	0.24	0.06	0.22	11.24	4.39	19.28	49.79	3.82	0.81
1927	0.52	05.74	0.10	0.13	0.06	0.09	09.97	4.77	21.37	52.82	3.79	0.65
1929	1.85	08.70	0.06	0.07	0.06	0.04	08.74	4.26	16.84	54.70	4.21	0.46
1930	2.89	08.01	0.07	0.06	0.07	0.05	09.85	4.35	18.23	51.81	4.00	0.60
1931	0.77	09.43	0.09	0.04	0.07	0.04	08.48	4.83	19.39	52.58	3.89	0.40
Av	1.28	08.64	0.09	0.13	0.05	0.08	10.26	4.46	18.18	52.56	3.58	0.69

Fig. 2—Variation of CaCO₃ with depth

majority of the samples clearly place the CCD in the area below 4700 m depth. It is evident from the abrupt change in the CaCO₃-depth relation in Fig. 2 that the carbonate lysocline lie around 4700 m which is different and deeper than reported (4000 m) earlier^{24,25}.

Figure 2 further shows much deeper CCD, i.e. > 5100 m. Such deeper CCD has been encountered

earlier in the western Somali Basin^{24,25} and reported as the carbonate critical depth (CCrD) where CaCO₃ content reduced to <10%. Comparatively, the western Somali Basin is about 800 km west from the present sampling area. Due to the insignificant variations in Ca, Naqvi and Naik²⁴ opined that the critical carbonate ion concentration in the area ($90 \pm 5 \mu M.kg^{-1}$) corresponding to the critical degree of saturation should be the dominant factor of carbonate dissolution and that the area consists of supersaturated waters responsible for the lysocline depth (~4000 m) representing that of Kolla *et al.*²⁵. However, a different explanation can be given for the observed deeper lysocline and the CCD. The CCD (> 5100 m) in the area is mainly due to the high surface carbonate productivity which is evident from high CaCO₃ content, high benthic ratio and also from the presence of coccoliths in the samples. With the high surface biological productivity, there can be increased input of biogenic carbonates depressing the CCD²⁶.

Like CaCO₃, the planktonic Foraminifera are more susceptible to dissolution than benthic Foraminifera^{27,28} and in general the highest CaCO₃ content correlates with the lowest benthic ratio. The benthic ratio²², which has wider range (1.48-32.42) similar to that of the CaCO₃ content (20.52-79.75%; excluding samples from 1896 and 1898 which were from the NE flank of the CR in the Arabian Sea), increases with decrease in CaCO₃ content with depth. Increase in benthic ratio is therefore due to the

increase in the dissolution with depth. The linear trend also supports the view of increase in supply of planktonic Foraminifera due to high surface productivity.

The larger variation in the CaCO_3 is due to the varying degree of carbonate dissolution at different depths. Also, high surficial biological (i.e. carbonate) productivity is possible because the area is

within the equatorial region²⁹. According to Qasim,^{30,31} it is a productive area; and Naqvi and Naik²⁴ had reason to approximate precipitation of 1 to $2 \times 10^{-3} \text{ g CaCO}_3 \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$. Also the increase in Ca:Cl ratios²⁴ with depth due to the phenomenon of biological uptake of CaCO_3 by organisms in the upper layers, supports high biological productivity in the area. The data further imply that the CCRD should

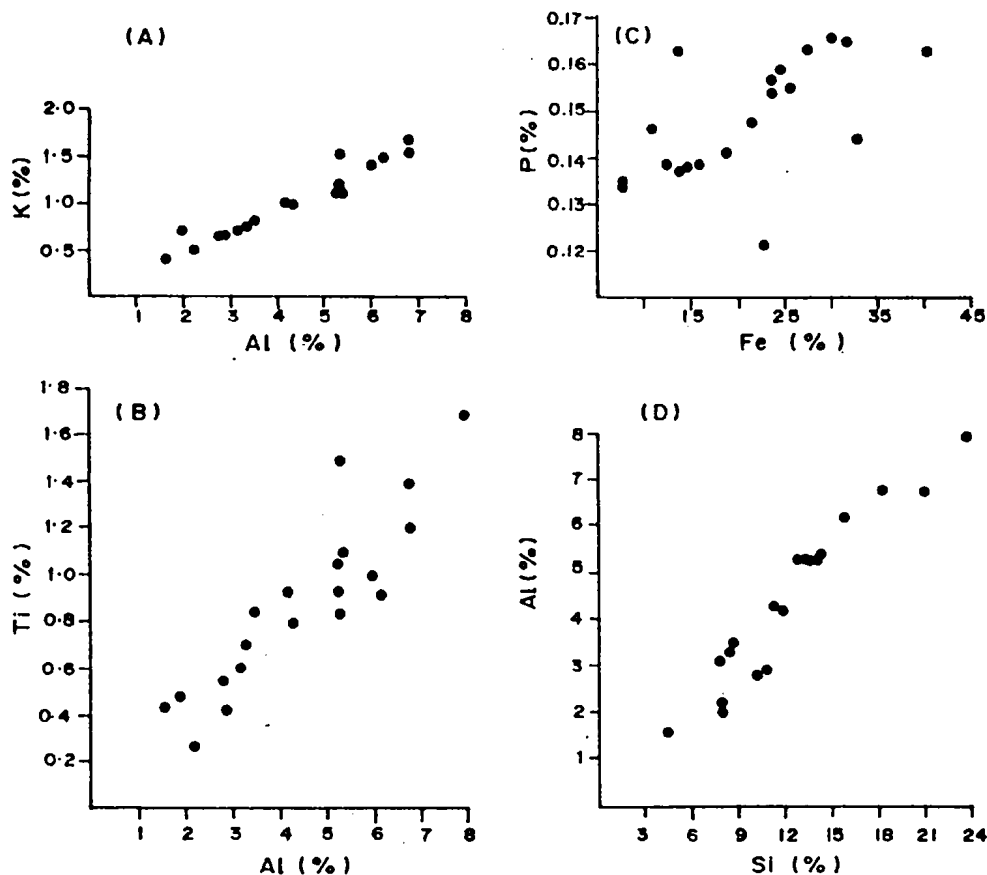


Fig. 3—Relationship between (A) K and Al, (B) Ti and Al, (C) P and Fe, and (D) Al and Si

Table 4—Correlation-coefficient matrix (MOC free basis) for the Carlsberg Ridge sediment

	Fe	Cu	Ni	Co	Zn	Mg	K	Al	Si	Ti	P
Mn	0.46	-0.31	-0.52	0.08	-0.42	-0.32	0.02	0.23	-0.32	0.22	-0.40
Fe		-0.35	-0.59	-0.24	-0.52	-0.33	0.02	0.07	-0.33	0.13	-0.40
Cu			0.60	0.02	0.85	0.30	0.01	-0.46	0.24	-0.14	0.37
Ni				-0.18	0.82	0.43	-0.43	-0.51	0.48	-0.55	0.59
Co					-0.02	-0.06	0.30	0.17	-0.01	0.05	-0.24
Zn						0.39	-0.13	-0.58	0.42	-0.39	0.49
Mg							-0.21	-0.37	-0.35	0.05	0.95
K								0.47	-0.41	0.57	-0.41
Al									-0.54	0.33	-0.48
Si										-0.64	-0.16
Ti											-0.13

N = 20; R = 0.423 for r = 95%

occur below 5100 m depth. Less intensive fragmentation of the carbonate shells observed under microscope also point towards deeper CCD.

Si values range from 47.38 to 59.39% (Table 3), and Si and Al show good positive relationship (Fig. 3D). The excess silica³² is low (0.35-12.03%) and indicate moderate amount of contribution of biogenic silica on local scale. The Si/Al ratio is high at 6 stations (viz. 3.62 at st. 1919; 3.76 at st. 1920; 4.20 at st. 1921; 3.55 at st. 1922; 3.08 at st. 1924; and 3.25 at st. 1929; Table 2). High Si/Al ratio (2.47-4.19) therefore suggest that part of the silica is biogenous³³ (i.e. Si/Al > 3) indicating higher siliceous productivity in the area. Absence of excess silica at other stations is probably due to the different degree (patches) of siliceous biological productivity in the region.

Kolla *et al.*⁴, demarcated the present study area as *in situ* province indicating supply of elements in the region by authigenic or by *in situ* weathering process. The bulk Al shows strong relationships with K, Ti and Si respectively (Fig. 3) whereas K and Al (0.47), and K and Ti (0.57) have strong correlation (Table 4). Therefore, these lithic elements should have a common source either land derived (terrigenous) or *in situ* (alteration of basalts). The negative correlation for Si with Al, K and Ti (Table 4) indicates different source for Si. As mentioned above, the high Si concentration in the sediment seems to be influenced by high surface biological (siliceous) productivity.

The Mg values (7.36-17.01%; Table 3) are high and MgO/Al₂O₃ ratios (0.35-0.89) are much higher than those of average pelagic clays (0.25). The negative correlation of Mg with Al (-0.37) does not suggest terrigenous or *in situ* source. Hence, the source for P and Mg is biogenous.

Fe has negative correlation with all other elements except Mn (0.46). Therefore, Mn and Fe phases should be separate and both must be coming from different sources than others. Mn can be authigenic similar to Cu and Ni, but in the present case it shows negative correlation with its commonly associated elements i.e. Cu and Ni. Possibility of lower Mn due to the poor oxidizing conditions in the area¹⁷ may be the reason for lower Mn/Fe ratios (0.08-0.36; Table 2) compared with average pelagic clays (0.1). The organic C content determined (0.46% maximum) does not suggest high oxic conditions in the area. Low riverine discharge in the region and dissolution of Mn in anoxic conditions can account for lower Mn content as observed by Calvert and Price³⁴.

Cation adsorption as a function of pH has been demonstrated by Balistrieri and Murray³⁵, where they found that the affinity of the binding characteristic and concentration of certain elements

in the interfacial sediments has definite sequence which increases with pH of the seawater. It was also shown that the amount of metal content increases with increase in the pH. In the present case, the average pH measured at 10 stations was 7.91 which is quite close to the value reported (7.82) by Balistrieri and Murray³⁵. Hence, the affinity sequence of Pb > Fe ≥ Sn ≈ Co > Mn > Cu > Ba > Sc > Zn > Ni > Cd > Cs etc. is also valid here, which supports that the selective enrichment of Fe, Mn and Co is hydrogenous due to their stronger binding capacity. This can account for the observed hydrogenous character of the interfacial sediment and also for the absence of correlation between metals derived by hydrolysis (Fe, Mn and Co) and those by the adsorption.

It appears that Cu, Ni and Zn have been incorporated biogenically due to overlying productivity. Cu shows very strong positive correlation with Zn (0.85) and Ni (0.60), and therefore they have a common source. Further, strong correlation of Ni with P (0.59), Si (0.48) and Mg (0.43); and that of Zn with P (0.49) and Si (0.42) suggests that they have been influenced by the biogenic factor. Although, correlation of Cu with P, Si and Mg is not significant, its strong association with Ni and Zn is clearly indicated.

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