

GEOCHEMISTRY OF SEDIMENTS OF THE EASTERN CONTINENTAL SHELF OF INDIA

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ABSTRACT

The bulk and partition geochemistry of Al, Fe, Ti, Mn, Zn and Cu have been investigated in the sediments of the eastern continental shelf of India. The results show that (1) the bulk geochemistry varies from one shelf unit to the other, (2) all the elements studied have both lithogenous and non-lithogenous components in the sediments, and (3) the percentage contributions made by the lithogenous component to the concentrations in the bulk samples are highest in respect of Al and Ti, followed next in order by Fe, lowest in respect of Mn, while the values for other elements lie in between the percentage contributions for Al and Ti on the one hand and Mn on the other hand. The variations in the bulk geochemistry of the sediments have been explained in terms of the variations in the percentage contributions made by the lithogenous and non-lithogenous components to the concentrations of the elements in the bulk samples, textural variations and dilution by the calcium carbonate phase of the sediments. In the non-lithogenous fraction, Fe hydroxide and Mn hydroxide appear to be the dominating constituents contributing to the concentrations of these elements in this fraction and also other elements, through their ability to absorb trace metals from the waters. The inter-relationships obtained among the various elements support this conclusion.

Similarity in the metal/Al ratios computed for the elements in the continental shelf region with those computed for the fluvial sediments from the adjacent river systems, suggest that colloids of Fe and Mn hydroxides could have been formed in the river systems, transported through the estuaries along with their trace metal content without any modification and deposited in the shelf region.

Key-words: Geochemistry, Sediments, Eastern shelf, India.

INTRODUCTION

A few papers appeared on some of the chemical aspects of the sediments of the eastern continental shelf and slope of India dealing with distribution of calcium carbonate, organic matter, phosphate and trace elements. (Subbarao, 1958; Naidu, Rao and Rao, 1967; Rao and Murty, 1968; Murty and Reddi, 1968; Seetharamaswamy, 1968; Venkatarathnam and Tilak, 1968; Rao and Rao, 1969, 1973; Sarin, Borole and Krishnaswami, 1979; Kalesha, Rao and Somayajulu, 1980). However, it may be mentioned here, that the investigations conducted on the elemental distributions were somewhat partial in that (i) they were confined to a few small sectors of the shelf in most of the cases and (ii) in the majority of the cases, the investigations were confined to clay fraction of the sediments only. Consequently, we do not have

any information on the elemental concentrations associated with the bulk samples and their fractionation among the different components of the sediments which can provide an insight into the different processes operating in the different regions of the shelf for the incorporation of the elements into the sediments. Hence, detailed geochemical investigations have been undertaken on the sediments of the eastern continental shelf and slope of India and the results pertaining to the bulk and partition geochemistry of Al, Fe, Ti, Mn, Zn and Cu are presented in this paper.

Description of the Area

The continental shelf along the east coast of India (Figs. 1A and 1B) is about 40 km wide on an average except in the vicinity of large deltas where it is either too wide (as off Ganges and Brahmaputra, 160 km) or too narrow (as off Godavari, Krishna, Penner and Coleroon, 20 km). The shelf edge is around 90 to 180 m except off the deltas where it shoals to 40 m (Shepard, 1967). The eastern continental shelf can be divided into four regional shelf units: (1) The east-west Ganges-Brahmaputra shelf and the shelf region from 'Swatch of No Ground' to Chilka Lake, (2) Chilka Lake to Kakinada, (3) Kakinada to Penner confluence, and (4) Penner confluence to Calimere Point. Environmentally, units (1) and (3) can be grouped together since they exist near river mouths. The shelf regions off Chilka Lake-Kakinada coast and Penner confluence-Calimere Point are not influenced by discharge from major

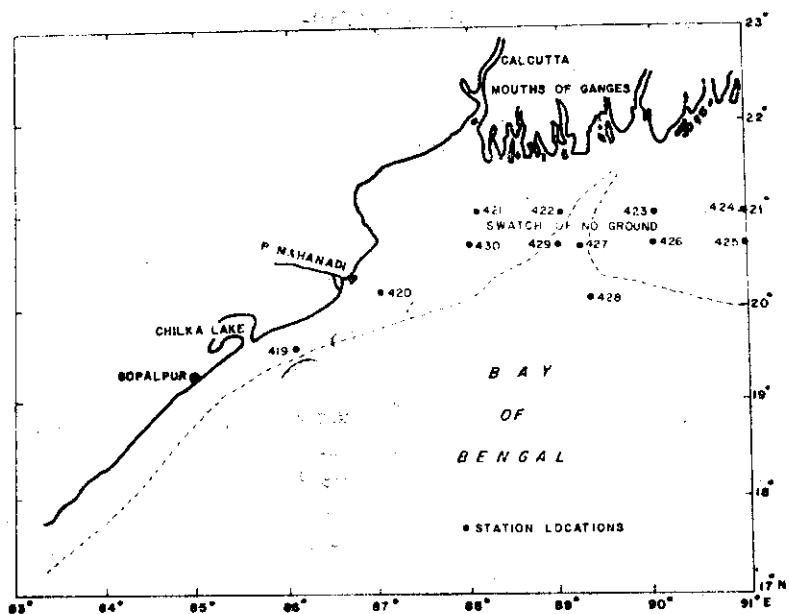


Fig. 1A. Map showing station locations in the Ganges-Brahmaputra shelf unit.

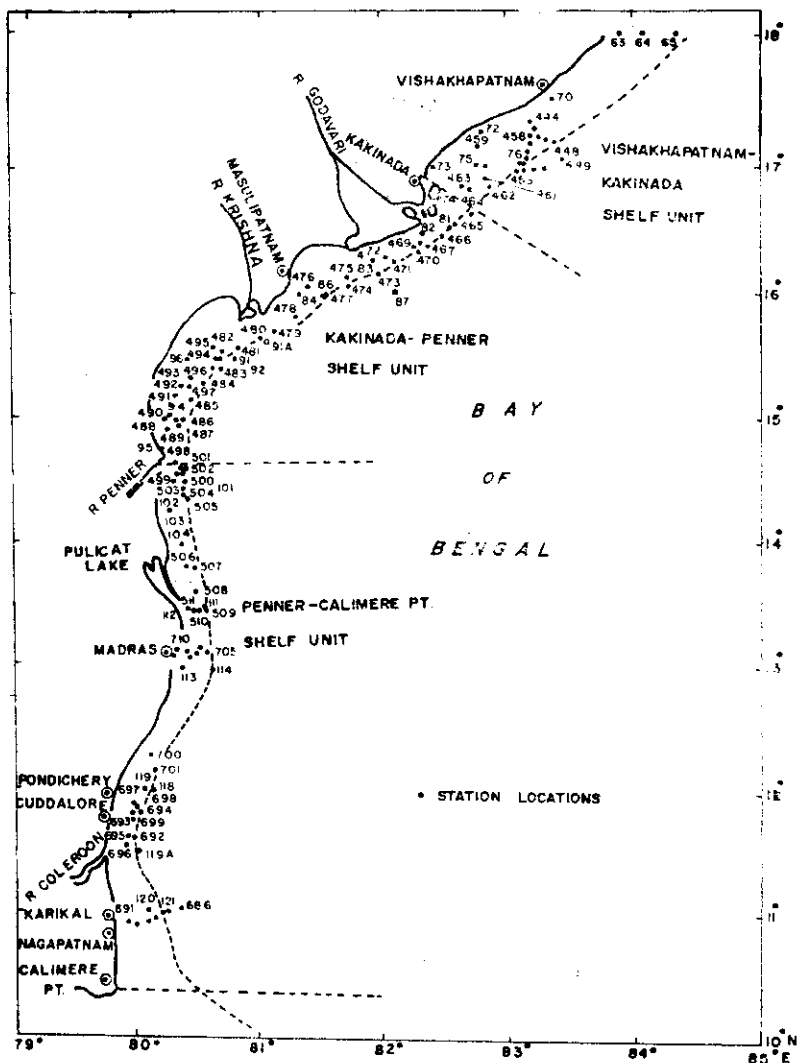


Fig. 1B. Map showing station locations in the shelf region between Vishakhapatnam and Calimere Pt.

Only a number of small rivers are present in these two regions which may be active in the monsoon period only and their sediment load supply to the shelf may not be considerable.

The differences in the environmental settings of the four regional shelf units mentioned in the preceding paragraph are well reflected in the nature of bottom sediments encountered in these regions. The Ganges-Brahmaputra shelf and the shelf region between 'Swatch of No Ground' and Chilka Lake where 3 major rivers — Ganges, Brahmaputra and Mahanadi supply considerable amounts of sedimentary material to the shelf region, are carpeted by sediments

which are mostly clayey in nature (except near the coast where fine sand bottom is reported) and are light ash-grey in colour when they are dry. They do not contain more than 5% of calcium carbonate. The shelf region between Chilka Lake and Kakinada, on the other hand, consists of a variety of sediments ranging from coarse sands in the nearshore to clays in the continental slope on the one hand and from highly calcareous to purely clastic on the other. Detailed studies carried out off Vishakhapatnam revealed the presence of a clearcut zonation of the sediments from the coast to the upper continental slope: (1) sands from the coast to 27 m water depth with calcium carbonate content upto 5%; (2) clays from 27 to 54 m with 5 to 15% CaCO_3 ; (3) sand-silt-clay from 54 to 81 m with 15 to 50% CaCO_3 ; (4) shelly and oolitic sands from 81 to 180 m with 50 to 80% CaCO_3 ; and (5) clays beyond 180 m with 10 to 15% CaCO_3 . From Kakinada to Penner confluence, the shelf is too narrow and mostly covered by brown and green muds with CaCO_3 content varying between 5 and 15%. Again the shelf begins to widen south of Penner confluence and fine muds yield place to coarse sediments (Subba Rao, 1958). Detailed investigations conducted between Madras and Calimere Point have revealed the shelf to be entirely covered by sands and as off Vishakhapatnam coast, the CaCO_3 content shows a progressive increase away from the coast and the outer shelf sediments are characterised by the presence of oolites and benthic foraminifera of shallow water origin (Rao and Murty, 1968). The highly calcareous sediments between 90 and 180 m off Chilka Lake-Kakinada coast and those lying between 54 and 180 m off Madras-Calimere Point coast have been described as relict sediments deposited during lower stands of sea level on the outer shelf (Subbarao, 1958, 1964, Rao and Murty, 1968). The relict band of sediments which have their maximum spread off Vishakhapatnam are replaced by mixed clastics and finally by a veneer of Godavari muds towards Kakinada. The point of location of sample 461 is roughly the northern most limit to which recent deltaic sediments of Godavari River are dispersed (Naidu, 1968). Similarly, in the region north of Vishakhapatnam, the zone of lime deposition pinches out under the silty clays of Mahanadi River.

MATERIALS AND METHODS

The locations of the stations from where samples of bottom sediments were obtained are shown in Figs. 1A and 1B. The samples were collected using La Fond-Dietz snapper and Phleger corer. In the present study the results were obtained by analysing only surficial samples (0-4") (collected by the snapper) and top 4" portions of the core samples.

The analyses done in this paper were performed using atomic absorption and colorimetric techniques. The bulk samples were digested with hydrofluoric acid and aqua regia in sealed teflon bombs following the method of Buckley and Cranston (1971). Mn, Zn and Cu were estimated using Perkin Elmer Atomic Absorption Spectrophotometer Model 5000. Fe and Ti were also estimated from the same solution colorimetrically following the method

of Riley (1958). For the estimations of Al, 'A' solution (Shapiro and Brannock, 1969) was prepared for each sample and the colorimetric method of Rand, Greenberg and Taras (1975) was followed.

Following the bulk analyses for the elemental concentrations, selective chemical attacks were made on the samples using adaption of the leach procedure evolved by Chester and Hughes (1967). Two accurately weighed representative subsamples about 1 g each were obtained from each sample. The first subsample was leached with an excess of mixed acid-reducing reagent consisting of acetic acid and hydroxylamine hydrochloride, stirred for 4 hrs and filtered. The second subsample was leached with 50% hot HCl and kept hot for 4 hrs prior to filtration. The dissolved materials were always filtered through previously weighed filter papers (Whatman No. 42) and the residues were weighed. The leach solutions were analysed by atomic absorption spectrometry for Mn, Zn and Cu and by colorimetry for Al, Fe and Ti. This procedure was followed to analyse (i) the total elemental concentrations present in the sediments as loosely sorbed ions and interstitial water evaporates, and those associated with ferro-manganese oxide phases reducible by hydroxylamine hydrochloride and (ii) everything including iron oxide minerals, except the most resistant silicates and aluminosilicates insoluble in hydrochloric acid. Because the chemical attacks were made on different subsamples of each sample and not sequentially on individual samples, the portion of each element soluble in hydrochloric acid but not in mixed acid-reducing mixture and the portions associated with insoluble residues were obtained by subtraction.

The precision of the atomic absorption and colorimetric analyses of both bulk samples and leached fractions is better than 10% on the basis of duplicate analyses. The accuracy was checked by analysis of U.S. Geological Survey standard rocks.

Results

The concentrations of the various elements associated with the bulk samples are given under Column 'A' of Table I along with station number and water depth. The partition values of the elements in the leaches of acid-reducing mixture, hot 50% HCl and acid insolubles expressed in terms of % of the concentrations in the total samples, i.e. Column 'A' are given in Columns 'B', 'C' and 'D' respectively. The inter-relationships obtained among the elements studied are shown in the form of correlation matrix in Table II. The scatter plots between aluminium and other elements are shown in Figs. 2 to 6. The metal/Al ratios computed for the elements are given in Table IV. The analysis of the data presented here is briefly given below separately for the bulk and partition geochemistry of the sediments.

Bulk geochemistry: An analysis of the data allows us to make the following generalisations in regard to the bulk geochemistry of the sediments:

Table I: Partition Analyses

Station No.	Water Depth in meters	Aluminium (%)				Iron (%)				Titanium (%)			
		A	B	C	D	A	B	C	D	A	B	C	D
Ganges-Brahmaputra Shelf													
421	18	5.22	0.75	36.50	62.75	2.46	7.75	67.57	24.68	0.36	1.01	28.26	70.73
422	81	7.09	1.38	44.37	54.25	3.93	6.47	78.27	15.26	0.42	1.71	23.05	75.24
423	81	8.02	0.98	49.56	49.46	4.43	6.47	78.90	14.63	0.49	1.41	38.73	59.86
424	54	6.62	0.99	52.88	46.13	4.76	6.10	81.79	12.11	9.45	1.61	48.72	49.67
425	77	4.29	1.96	39.61	58.43	2.79	8.55	77.58	13.87	0.29	1.83	19.46	78.71
427	360	7.84	1.58	58.44	39.98	4.76	5.02	82.31	11.17	0.48	2.09	30.24	67.67
428	720	8.21	1.79	53.53	44.68	4.76	5.02	83.81	11.17	0.48	1.66	31.96	66.38
429	162	8.40	2.10	53.92	43.98	5.24	7.05	77.69	15.26	0.46	0.95	32.56	66.49
430	90	8.21	1.93	61.39	36.78	5.41	6.25	77.84	15.91	0.50	1.09	31.22	67.69
Vishakhapatnam-Kakinada Shelf													
63	45	6.34	2.46	74.24	23.30	4.59	8.64	83.34	8.00	0.43	2.33	35.19	62.48
64	63	5.04	0.96	97.04	2.00	4.42	7.63	69.37	23.00	0.57	1.25	31.49	67.26
65	—	8.02	2.84	86.11	11.05	5.64	5.08	92.14	2.78	0.47	4.16	32.69	63.15
70	61	4.66	2.51	53.12	44.37	—	—	—	—	0.33	2.18	38.39	59.43
444	34	7.09	2.06	45.98	51.96	4.92	6.87	83.52	9.61	0.56	1.11	39.16	59.73
445	54	—	—	—	—	3.93	5.66	79.08	15.26	0.54	1.11	36.00	62.89
446	75	6.16	2.28	68.84	28.88	4.92	4.61	90.30	5.09	0.42	1.65	37.73	60.62
447	104	1.87	2.61	40.85	56.54	1.97	10.50	72.36	17.14	0.11	16.67	39.18	44.15
448	130	2.05	2.15	68.96	28.89	1.80	3.97	74.09	21.94	0.13	17.12	32.56	50.32
450	216	5.04	1.87	81.83	16.30	3.77	4.74	87.61	7.65	0.33	6.64	28.78	64.58
72	35	6.90	2.46	53.93	43.61	4.75	7.50	86.00	6.50	0.56	1.11	38.71	60.18
459	34	6.90	2.14	56.28	41.58	4.92	8.32	82.07	9.61	0.61	0.60	31.33	68.07
458	47	7.28	1.83	67.26	30.91	5.25	6.21	85.59	8.20	0.49	2.50	35.85	61.65
457	72	5.04	2.00	75.26	22.74	4.43	4.76	71.23	24.01	0.48	0.68	29.07	70.25
76	276	7.46	3.30	81.44	15.26	5.60	4.67	89.69	5.64	0.58	4.04	31.63	64.33
454	162	6.72	1.79	97.20	1.01	0.43	4.61	87.28	8.11	0.43	3.31	32.77	63.92
453	198	7.28	—	—	—	5.74	4.71	83.09	12.20	0.50	1.79	33.02	65.19
452	207	7.84	1.88	70.56	27.56	5.74	4.85	82.95	12.20	0.47	5.83	31.03	63.14
75	103	3.54	3.21	79.14	17.65	3.44	9.80	76.28	13.92	0.29	4.38	39.06	56.56
460	74	7.09	2.57	75.20	22.23	4.92	—	—	—	0.50	1.23	36.56	62.21
461	126	7.65	3.48	81.31	15.20	6.40	7.56	86.30	6.14	0.60	3.47	33.99	62.54
462	180	7.46	3.32	85.78	10.90	6.56	5.86	86.77	7.35	0.62	3.76	34.38	61.86
73	22	3.08	3.59	64.90	31.51	3.28	10.91	68.18	20.91	0.56	1.48	37.10	61.42
463	72	7.46	3.14	81.61	15.25	6.58	6.79	77.95	15.26	0.63	1.25	32.56	66.19
464	124	8.21	3.05	60.17	36.78	6.39	5.66	82.41	11.93	0.62	3.19	30.08	66.73
Kakinada-Penner Shelf													
74	42	3.17	—	—	—	7.21	6.17	92.43	1.40	0.78	2.30	33.99	63.71
81	710	7.46	2.95	96.65	0.40	7.38	—	—	—	0.76	1.41	36.02	62.57
82	52	7.46	2.62	79.96	17.42	6.89	4.80	14.79	80.41	0.85	1.14	26.00	72.86
468	36	6.34	3.78	96.22	—	7.05	7.04	78.09	14.87	1.00	0.79	37.13	62.08
466	198	—	—	—	—	—	—	—	—	—	—	—	—
469	36	6.90	2.86	72.44	24.82	6.56	4.11	87.41	8.48	0.94	0.04	39.45	60.51
472	36	7.28	2.92	90.12	6.96	7.71	6.34	74.43	19.23	0.95	1.10	36.37	62.49
83	35	3.08	3.13	94.94	1.93	7.05	—	—	—	0.82	1.32	36.61	62.07
473	146	7.28	3.14	83.78	13.08	7.38	4.48	90.93	4.59	0.81	1.76	36.94	61.42
87	960	7.46	2.83	79.75	17.42	7.22	3.86	84.47	11.67	0.89	1.00	30.27	68.73

SEDIMENT GEOCHEMISTRY OF EASTERN SHELF

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Manganese (ppm)				Zinc (ppm)				Copper (ppm)			
A	B	C	D	A	B	C	D	A	B	C	D
525	65.14	27.23	7.61	87	40.22	49.22	10.56	41	53.65	14.63	31.70
455	31.64	59.12	9.23	126	23.01	62.69	14.28	67	56.74	32.83	16.41
633	—	—	11.84	111	—	—	—	44	40.90	38.63	20.45
782	47.57	41.56	10.86	142	48.59	35.91	15.49	63	28.57	34.92	36.50
558	56.27	30.10	13.62	62	56.45	33.87	9.68	42	42.85	26.19	30.95
588	—	—	—	126	30.95	63.49	5.55	52	65.38	7.69	26.92
590	42.00	22.54	35.42	125	26.40	68.00	5.60	55	32.72	41.81	25.45
615	40.65	27.31	32.00	117	59.82	30.76	13.60	48	31.25	43.75	25.00
628	44.74	29.29	26.27	130	53.84	23.84	22.32	62	29.03	43.54	27.41
531	50.49	26.55	16.95	96	40.62	44.79	14.58	63	28.57	25.39	46.03
488	41.80	40.36	17.82	86	33.72	43.02	23.25	35	22.85	42.85	34.28
430	34.42	24.88	40.69	149	24.83	53.73	15.43	63	20.63	47.61	31.74
325	62.76	25.53	11.69	62	40.32	51.61	8.06	59	22.03	18.64	59.32
522	75.67	23.75	0.57	94	53.19	31.91	14.89	60	30.00	28.33	41.66
418	76.31	10.28	13.39	71	53.52	29.57	16.90	46	47.82	13.04	39.13
402	63.18	23.63	13.18	103	34.95	45.63	19.41	42	61.90	30.95	7.14
197	53.29	—	—	81	40.74	11.11	48.14	242	61.15	20.66	17.88
100	54.00	33.00	13.00	122	45.90	16.41	47.79	30	56.66	13.33	30.00
321	59.19	13.08	20.00	117	19.65	65.81	14.52	80	17.50	25.00	57.50
581	70.74	17.21	12.05	—	—	—	—	67	19.40	31.34	49.25
572	54.89	26.39	18.70	102	30.39	66.30	3.31	51	29.41	62.74	7.84
442	80.09	13.57	13.33	129	27.13	42.63	30.23	68	19.11	70.58	10.29
464	41.37	29.95	28.66	75	44.00	44.00	12.00	35	48.57	25.71	25.71
418	43.77	31.81	24.40	123	—	—	—	102	—	—	—
412	52.66	41.01	6.31	100	25.00	72.00	3.00	59	23.72	45.76	30.50
349	68.18	31.80	—	125	28.80	57.60	13.60	75	17.33	56.00	26.60
359	33.14	63.78	3.06	125	23.20	61.6	15.20	83	21.68	42.16	36.14
302	56.66	32.78	10.59	83	33.73	62.65	3.61	41	21.95	60.97	17.07
556	52.69	38.84	8.45	134	21.64	47.01	31.34	53	30.18	27.74	5.66
613	58.56	28.87	12.56	163	17.79	60.12	22.08	84	47.61	14.28	38.09
513	62.96	25.73	11.30	136	20.58	70.58	8.82	92	19.56	66.30	14.13
404	54.95	37.37	7.67	92	20.65	38.04	41.30	59	22.03	35.59	42.37
681	62.40	30.10	7.48	145	36.55	42.75	20.68	94	14.89	47.87	37.23
630	65.87	24.12	10.00	—	—	—	—	94	14.89	74.46	10.63
1096	59.30	38.86	—	145	20.68	61.37	17.93	129	15.50	58.13	26.35
572	58.04	31.29	10.66	146	19.86	65.06	15.06	120	19.16	61.66	19.16
1162	78.48	9.81	11.70	114	15.78	—	—	154	9.09	85.71	5.19
953	63.48	24.65	11.85	169	37.28	43.19	20.71	129	—	—	—
—	—	—	—	156	41.02	28.84	30.12	147	23.12	39.45	37.41
846	77.06	18.32	4.69	132	20.45	58.33	21.21	126	46.51	22.48	31.00
976	71.00	24.30	4.61	114	24.56	—	—	177	55.36	6.21	38.41
790	83.16	15.90	0.88	163	18.40	65.64	15.95	146	27.32	78.76	14.10
892	74.66	17.15	8.18	131	48.09	—	—	146	27.39	58.21	14.28
690	53.47	41.15	5.65	186	17.20	63.44	19.35	163	11.04	50.30	38.65

Station No.	Water Depth in meters	Aluminium (%)				Iron (%)				Titanium (%)			
		A	B	C	D	A	B	C	D	A	B	C	D
475	30	6.72	—	—	—	7.38	—	—	—	1.01	1.30	17.75	80.94
476	480	6.90	3.70	50.30	6.00	7.22	5.01	86.40	8.59	0.93	0.77	33.69	65.54
86	504	7.65	1.96	88.11	9.93	7.05	4.23	90.36	5.41	0.78	1.48	27.29	71.23
477	147	7.65	2.72	67.24	30.04	7.71	4.13	75.68	20.19	1.00	0.72	37.20	62.08
84	35	6.72	—	—	—	7.05	—	—	—	0.96	0.75	39.46	59.79
478	144	7.28	3.00	88.38	8.62	7.05	3.84	87.60	8.56	0.81	0.99	34.60	64.51
479	324	6.72	2.81	67.21	29.98	7.45	3.37	73.28	23.35	1.18	0.53	37.07	62.40
480	144	5.60	—	—	—	6.49	—	—	—	0.81	1.11	34.38	64.51
91A	350	7.28	—	—	—	7.38	—	—	—	1.27	—	—	—
481	153	6.90	—	—	—	6.72	3.85	87.64	8.51	0.74	0.98	32.80	66.22
482	36	6.53	—	—	—	6.56	8.00	90.30	1.70	0.88	0.82	38.25	60.93
91	480	7.09	3.58	92.50	3.92	6.89	3.76	58.78	7.46	0.72	1.34	35.68	62.98
96	201	7.09	—	—	—	6.95	—	—	—	0.77	1.55	35.61	62.84
92	50	6.72	—	—	—	7.05	4.06	88.43	7.51	0.76	0.93	36.49	62.58
496	108	7.09	3.40	88.10	8.50	6.40	5.16	91.02	3.82	0.79	1.13	34.20	64.67
483	171	7.09	—	—	—	6.89	6.47	87.15	6.38	0.79	0.99	39.05	59.96
493	34	7.46	3.62	83.30	13.08	6.40	5.16	92.18	2.66	0.81	1.11	35.93	62.96
484	144	7.28	5.48	88.13	6.39	6.56	—	—	—	0.74	1.21	35.94	62.85
492	—	2.98	1.85	19.88	78.27	—	—	—	—	—	—	—	—
497	47	6.53	—	—	—	6.72	4.32	68.43	27.25	0.83	0.77	34.28	64.95
491	—	—	—	—	—	2.95	8.47	61.83	29.70	0.39	0.94	33.59	65.47
485	171	10.26	1.83	64.55	33.62	6.89	3.47	89.07	7.46	0.76	0.94	34.05	65.01
490	36	5.04	—	—	—	4.26	9.04	74.39	16.57	0.61	1.17	35.44	63.39
494	40	—	—	—	—	—	—	—	—	—	—	—	—
488	77	6.72	—	—	—	6.23	5.66	84.54	10.80	0.69	1.14	33.77	65.09
487	126	7.09	2.35	93.72	3.93	6.79	3.52	84.90	11.58	0.76	1.17	35.44	63.39
489	47	6.53	—	—	—	6.23	—	—	—	0.73	1.38	36.09	62.53
95	33	6.34	—	—	—	5.67	—	—	—	0.69	—	—	—
498	41	4.48	2.03	37.81	60.16	2.95	7.14	49.10	43.76	0.68	—	—	—
Penner-Calimere Pt. Shelf													
501	126	5.41	—	—	—	6.23	3.51	82.12	14.37	0.68	1.16	34.46	64.38
502	306	6.53	—	—	—	6.56	12.29	84.88	2.83	0.71	2.38	32.72	64.90
499	54	6.90	—	—	—	5.76	—	—	—	0.52	1.95	30.30	67.85
102	36	3.54	1.20	12.53	86.27	0.93	42.52	44.77	12.71	0.06	8.30	14.05	77.65
101	250	2.24	—	—	—	6.65	—	—	—	0.69	1.03	29.40	69.57
503	162	6.90	4.14	87.48	8.38	5.74	11.21	86.92	1.87	0.68	0.95	31.92	67.12
504	549	3.73	—	—	—	6.13	10.56	86.11	3.33	0.64	2.29	32.93	64.78
505	270	5.22	—	—	—	5.41	10.14	81.62	8.24	0.61	1.92	34.49	63.59
105	—	—	—	—	—	—	—	—	—	—	—	—	—
104	63	3.36	2.81	64.80	32.39	3.12	8.20	82.19	9.61	0.40	2.12	36.46	61.42
506	42	3.91	3.23	46.44	50.33	2.72	11.07	67.88	21.05	0.35	0.83	27.37	71.80
507	144	2.05	—	—	—	1.97	7.07	75.79	17.14	0.19	11.02	33.72	55.26
112	46	3.17	2.77	53.48	43.75	2.30	11.24	67.52	21.24	0.34	1.42	36.37	62.21
511	63	0.37	—	—	—	2.69	6.36	73.56	20.08	0.43	2.16	35.28	62.56
510	113	1.31	—	—	—	1.97	7.07	75.79	17.14	0.14	12.82	39.09	48.09
509	189	6.53	4.08	90.39	5.63	5.31	6.35	89.89	3.76	0.56	3.54	32.27	64.19
111	440	6.72	—	—	—	6.00	2.98	93.33	3.69	0.60	1.68	34.74	63.58
709	27	3.92	1.91	10.51	87.58	0.98	15.94	75.45	9.61	0.07	2.60	33.09	64.31

Manganese (ppm)				Zinc (ppm)				Copper (ppm)			
A	B	C	D	A	B	C	D	A	B	C	D
1022	—	—	—	119	—	—	—	132	—	—	—
976	70.90	16.90	12.19	112	28.57	—	—	116	28.44	39.93	33.62
734	66.34	22.34	11.30	173	17.91	57.22	24.85	116	36.20	58.62	5.17
892	77.57	14.23	8.18	112	28.57	—	—	128	33.53	32.81	33.59
822	68.49	26.64	4.86	—	—	—	—	149	14.09	51.06	34.89
727	77.71	21.32	0.13	173	53.75	14.45	31.79	150	25.33	59.33	15.33
939	66.53	18.53	15.02	92	33.69	—	—	162	32.71	48.14	19.13
1162	67.98	8.60	23.41	128	21.09	69.53	9.37	146	43.83	35.61	20.54
1000	49.60	—	—	—	—	—	—	—	—	—	—
1208	74.33	2.48	23.18	124	51.61	—	—	153	41.17	50.32	8.49
813	69.12	28.04	2.83	105	22.85	70.47	6.66	129	27.13	62.79	10.07
674	63.94	22.70	13.35	124	20.96	73.38	7.25	145	7.80	47.58	44.82
674	66.02	30.41	13.35	124	25.80	—	—	152	9.20	71.05	19.73
767	66.62	25.42	7.95	126	21.42	72.22	6.34	117	19.65	45.29	35.04
744	74.19	18.01	7.79	139	48.92	41.00	10.07	116	33.62	39.65	23.27
790	57.21	42.78	—	195	15.38	48.20	36.41	160	—	—	—
697	58.96	35.86	5.16	155	23.87	43.87	32.25	121	26.44	38.01	35.53
743	80.08	9.95	9.95	131	30.53	49.61	19.84	118	40.67	28.81	30.50
—	—	—	—	—	—	—	—	—	—	—	—
790	64.81	21.26	13.92	126	52.38	25.39	22.22	120	15.00	47.50	37.50
451	82.48	13.08	4.43	68	39.70	—	—	40	32.50	32.50	35.00
679	65.97	25.03	8.98	160	38.12	37.50	21.25	125	20.80	43.20	36.00
442	68.55	24.88	6.58	98	26.53	28.57	44.89	62	33.87	51.61	14.51
—	—	—	—	114	30.70	—	—	104	30.76	46.15	23.07
577	61.24	27.16	11.59	—	—	—	—	—	—	—	—
593	47.72	50.25	2.82	115	18.26	70.43	11.30	126	28.57	53.96	17.46
672	45.53	51.34	31.12	115	16.96	80.86	2.60	98	—	—	—
567	67.37	—	—	105	—	—	—	78	—	—	—
521	15.16	58.34	26.48	120	52.50	37.50	10.00	33	45.45	42.42	12.12
—	—	—	—	—	—	—	—	—	—	—	—
583	51.97	47.68	0.39	190	10.52	23.68	65.78	129	9.30	50.38	40.31
534	61.98	37.26	0.56	164	18.90	42.68	38.41	98	47.95	39.79	12.24
553	64.55	16.99	18.44	120	—	—	—	60	25.00	46.66	28.35
303	81.18	9.57	9.24	105	—	—	—	57	19.29	15.78	64.91
577	43.67	48.87	7.45	164	13.41	56.09	30.48	113	11.50	83.18	5.30
509	64.63	19.84	15.52	165	18.18	43.63	38.18	106	70.75	1.88	27.35
674	71.06	20.47	8.45	164	27.43	32.31	40.24	107	—	—	—
464	56.46	32.11	11.42	194	18.04	43.39	38.65	98	23.46	40.81	35.71
—	—	—	—	—	—	—	—	—	—	—	—
373	59.24	9.11	31.63	82	—	—	—	36	27.71	44.44	27.77
278	58.63	38.48	2.87	196	—	—	—	35	25.71	60.00	14.28
164	58.53	26.82	14.63	190	—	—	—	39	41.02	38.46	20.51
303	62.37	26.40	11.22	80	36.14	36.25	26.25	34	38.23	44.11	17.64
349	43.83	35.81	20.34	69	46.37	40.57	13.04	35	42.85	5.71	51.42
145	60.00	13.10	26.89	94	32.97	22.34	44.68	40	35.00	10.00	55.00
454	43.61	38.32	18.06	151	20.52	48.34	31.12	76	14.47	76.31	9.21
443	39.27	39.50	21.20	—	—	—	—	—	—	—	—
793	—	—	—	—	—	—	—	11	—	—	—

Station No.	Water Depth in meters	Aluminium (%)				Iron (%)				Titanium (%)			
		A	B	C	D	A	B	C	D	A	B	C	D
708	45	4.10	1.82	25.84	72.34	1.31	9.39	75.35	15.26	0.14	—	—	—
707	68	3.17	1.64	29.04	69.32	1.31	9.39	75.35	15.26	0.21	1.35	40.40	58.25
114	210	4.29	5.54	93.72	1.74	8.03	3.62	90.46	5.92	0.39	5.51	42.44	52.05
113	40	6.90	2.31	68.17	29.52	4.26	6.80	80.11	13.09	0.50	2.51	27.32	70.17
700	43	3.54	—	—	58.83	1.97	—	—	14.83	0.15	3.47	49.41	47.12
701	90	3.54	—	—	63.40	2.36	—	—	15.26	0.19	3.14	44.83	52.03
119	35	2.05	2.85	28.76	68.39	1.97	8.08	77.03	14.89	0.13	5.68	41.04	53.28
118	160	6.90	2.21	52.36	15.43	5.08	4.69	88.17	12.14	0.49	2.93	28.27	68.80
697	335	6.53	2.49	22.35	75.16	4.59	4.54	34.72	60.74	0.42	1.14	25.71	73.15
698	518	6.72	2.76	88.99	8.25	4.92	6.30	87.10	6.60	0.15	7.66	87.17	5.17
693	475	7.09	3.94	73.83	22.23	5.41	3.31	80.23	16.46	0.43	3.99	35.01	61.00
692	173	2.61	3.26	89.87	6.87	3.28	11.73	—	50.28	0.36	3.83	20.63	75.54
119A	—	7.28	1.93	71.62	26.45	4.59	6.07	84.32	9.61	0.43	8.72	33.15	58.13
120	39	3.17	2.87	32.92	64.21	2.53	12.59	60.78	26.63	0.31	2.92	45.89	51.19
691	14	2.05	2.69	13.11	84.20	1.31	15.72	0.58	83.70	0.36	—	—	—
690	29	3.36	2.61	55.24	42.15	2.46	13.17	56.13	30.70	0.49	0.95	43.80	55.25
689	54	1.31	5.97	81.95	13.08	1.64	9.86	63.30	16.84	0.31	1.19	60.64	38.17
688	90	1.68	2.71	35.92	61.37	3.44	3.23	48.42	48.35	1.84	0.25	52.25	47.50
687	324	3.17	1.65	80.16	18.19	2.30	5.19	73.57	21.24	0.23	3.13	43.28	53.59
121	218	2.24	4.36	60.83	34.81	2.89	7.26	84.18	7.56	0.11	—	—	—
686	1058	6.53	2.44	96.90	0.66	5.90	3.91	88.99	7.10	0.47	2.49	32.27	65.24
125	40	5.04	2.00	81.70	16.30	3.34	5.35	85.48	9.17	0.33	0.35	33.27	56.38

(1) The bulk geochemistry of the sediments exhibits considerable variations from unit to unit and also within the units sometimes. In the east-west Ganges-Brahmaputra shelf unit, lower concentrations of all the elements are associated with the sandy sediments and the higher concentrations with clayey sediments and do not exhibit any specific distribution pattern either along or across the shelf region. In the Vishakhapatnam-Kakinada shelf region, the elemental concentrations follow closely the zonation of the sediments. High concentrations of all the elements are associated with the nearshore and slope clays, medium concentrations with the sand-silt-clay zone and the low concentrations with the relict band of sediments and the nearshore sands. As between the nearshore clays and clays in the continental slope region, the latter appear to be slightly enriched in their zinc and copper contents and depleted in their manganese content relative to the nearshore clays. Towards the southern end of this unit (south of station No. 461) the influence of Godavari River can be clearly seen from the presence of the terrigenous clayey sediments all over the shelf region and the high concentrations of the elements associated with them.

In the Kakinada-Penner shelf region which is under the influence of the major rivers — Godavari, Krishna and Penner is carpeted by brown and green muds, uniformly high concentrations of all the elements are encountered both in the shelf and slope regions. The concentrations of aluminium recorded in

Manganese (ppm)				Zinc (ppm)				Copper (ppm)			
A	B	C	D	A	B	C	D	A	B	C	D
149	47.65	45.63	6.71	122	—	—	—	29	44.82	—	—
163	37.42	57.05	5.52	70	—	—	—	42	47.61	16.66	35.71
311	42.44	32.15	25.40	83	34.93	55.42	9.63	47	38.29	31.91	29.78
449	69.69	26.57	3.32	191	20.41	46.07	33.50	72	18.05	48.11	—
240	62.91	24.16	1.56	112	39.28	—	—	20	50.00	50.00	33.33
255	66.66	31.76	1.56	82	37.50	37.50	23.40	22	—	—	—
186	89.24	7.52	3.22	103	24.27	52.42	23.30	28	39.28	32.14	28.57
433	48.03	35.56	16.39	128	—	—	—	62	35.48	32.25	32.25
325	44.00	5.23	50.76	134	19.40	75.37	5.22	68	14.70	14.70	70.58
383	46.21	44.90	8.87	139	20.14	61.15	18.70	63	71.42	16.17	11.11
348	44.25	37.06	18.68	114	—	—	—	68	23.52	44.11	32.35
176	74.43	7.95	17.61	121	27.27	36.36	30	—	—	—	—
278	52.52	—	—	—	—	—	—	—	—	—	—
278	43.52	54.31	2.15	62	38.70	46.77	14.51	29	62.06	30.76	10.34
325	32.92	23.07	44.00	74	27.02	—	—	42	28.57	19.04	4.76
349	36.38	31.23	32.37	83	42.16	57.83	13.69	38	55.26	5.26	39.47
242	65.28	28.92	5.78	83	42.16	13.25	44.57	15	73.33	13.33	13.33
720	9.44	57.36	33.19	128	28.12	35.93	35.93	15	—	—	—
163	51.53	47.85	0.61	57	64.90	—	—	46	54.34	15.21	38.43
70	—	—	—	172	37.20	—	—	150	24.66	40.66	34.66
314	35.66	38.21	26.11	135	34.61	37.03	34.07	96	18.75	32.29	48.95
139	—	—	—	110	29.09	65.45	5.45	51	35.29	29.41	35.29

A = Bulk sample. B = Acid reducing mixture. C = Hot 50% HCl. D = Acid insolubles.
Values in columns B, C, D are in % of the total samples A.

these sediments are on par, the concentrations of iron, manganese, titanium and copper are far higher, and concentrations of zinc do not conspicuously show any increase over those recorded in the clays of the two northern units. Among the elements studied, only in the case of manganese, a conspicuous depletion is noticed in the clays of the slope region relative to the nearshore clays.

In the Penner-Calimere Point shelf unit, in the region between Penner River and Pulicat Lake the sediment distribution is somewhat patchy, in that, both sands and muds occur all over the shelf region while muds only are present in the slope region. Consequently, low as well as high concentrations of the elements are present all over the shelf region, the former associated with the sands and the latter with clayey sediments. In the region south of Pulicat Lake where the shelf is mostly carpeted by sands and the slope with clayey sediments, uniformly low concentrations of the elements are encountered in the shelf region, while comparatively high concentrations are encountered in the slope region. Even among the sands, the concentrations associated with the nearshore sands are little higher than those associated with the sands in the outershelf.

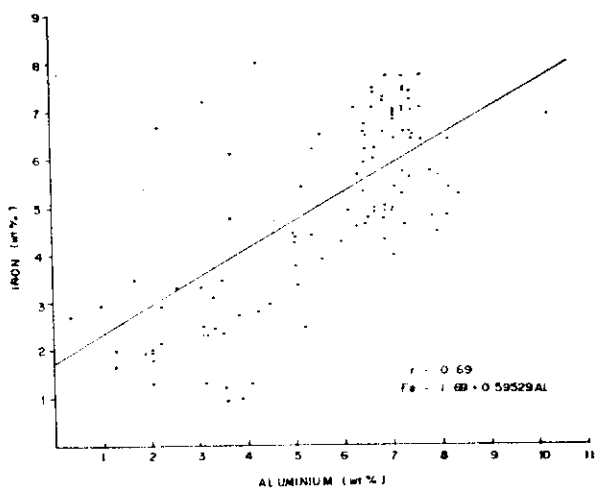


Fig. 1.

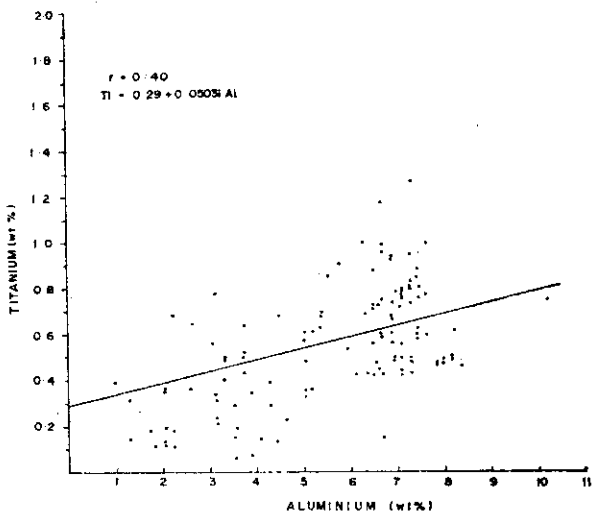


Fig. 2.

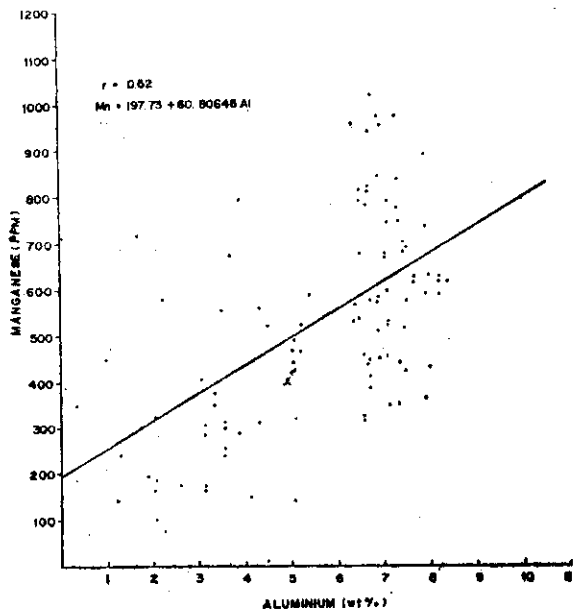


Fig. 3.

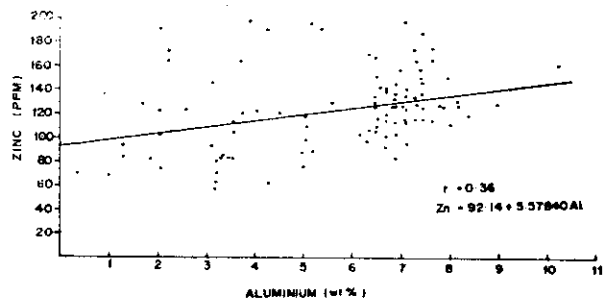


Fig. 4.

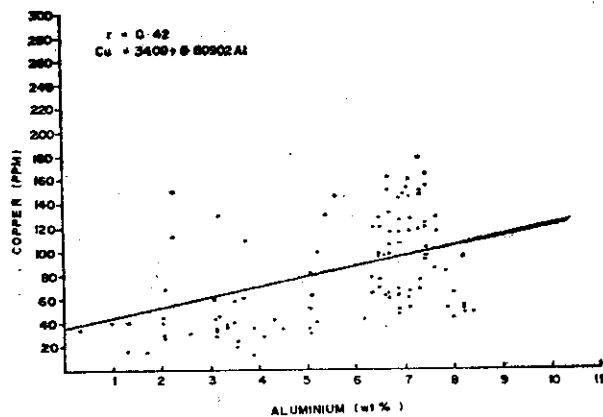


Fig. 5.

Figs. 2-6. Scatter diagrams showing relationship between Al & Fe; Al & Ti; Al & Mn and Al & Cu.

(2) The inter-relationships obtaining among the elements (Table II) show that there is covariance among all the elements.

(3) The scatter diagrams of the elements plotted against aluminium content show a positive correlation between the elements concerned and aluminium, which indicate that part of them are transported from land. Further, they also show that there are significant intercepts between Fe-Al, Ti-Al, Mn-Al, Zn-Al and Cu-Al suggesting that part of these elements have a non-lithogenous component.

Partition Geochemistry: As in the case of bulk geochemistry, the partition geochemistry of the elements exhibits considerable variations from one shelf region to the other and also between the different chemical fractions. The partition patterns of the elements are described below element-wise.

Aluminium: More than 95% of Al is held together in the HCl soluble and HCl insoluble fractions of the sediments (Cols. C and D of Table I). In the study area, in the sandy sediments, higher percentages of the element are held in the HCl insoluble fraction of the sediments than in the HCl soluble fractions while the reverse is true in the case of clayey sediments. The difference in the percentages of the element held in these two fractions does not exceed 20% in the case of Ganges-Brahmaputra shelf unit. In the Visakhapatnam-Kakinada shelf unit, the percentages of the element held in the HCl soluble fraction are higher and exhibit an increasing trend away from the coast as the percentages held in the HCl insoluble fraction show a reverse trend. The difference in the percentages of the element held in the two fractions varies very widely: 96 to 9%. In the Kakinada-Penner shelf unit, by and large most of the Al is held in the HCl soluble fractions of the sediments with only minor percentage of the element being present in the HCl insoluble fraction. In the Penner-Calimere Point shelf unit, where a major portion of the shelf is carpeted by sands and slope region by silts and clays, higher percentages of the element are associated with the HCl insoluble fractions of the sediments in the shelf than in the HCl soluble fractions and in the reverse way in the slope region. Along the sections off Madras and Karikal, it could be clearly seen that the percentages of the element associated with the HCl soluble fractions show an increasing trend away from the coast and reversing the trend observed in the shelf region in the slope region.

Table II. Correlation Matrix (n = 105)*

	Al	Fe	Ti	Mn	Cu	Zn
Al	1.00					
Fe	0.69	1.00				
Ti	0.40	0.70	1.00			
Mn	0.52	0.74	0.79	1.00		
Cu	0.42	0.70	0.51	0.62	1.00	
Zn	0.36	0.51	0.28	0.24	0.43	1.00

* For $r > \pm 0.19$, $P < 0.05$

Insignificant amounts of Al are associated with the acetic acid-hydroxylamine hydrochloride leaches of the sediments (1 to 5% of Al of the bulk samples).

Iron: More than 90% of iron is held in the HCl soluble and insoluble fractions of the sediments and invariably higher percentages of the element are held in the HCl soluble fraction than in the insoluble fraction. The differences in the percentages held in the HCl soluble and insoluble fractions vary from one unit to the other. In the Ganges-Brahmaputra shelf, they vary from 72–43% while in the other three units, i.e. Visakhapatnam-Kakinada shelf, Kakinada-Penner shelf and Penner-Calimere Point shelf, they vary from 90–47%; 91–6% and 90–0%, respectively. Further, the percentages of iron held in the HCl soluble fractions exhibit a decreasing trend away from the coast in the shelf region and again show a slight increase in the slope region. This is particularly true of Visakhapatnam-Kakinada shelf and to some extent in the Kakinada-Penner shelf and Penner-Calimere Point shelf. In the sandy sediments of the Penner-Calimere Point shelf, the percentages of the HCl soluble iron in the shelf region are comparatively low as compared to the percentages in the same fractions of other units and also in the same fraction of the clayey sediments in this unit.

The percentage of iron held in the acetic acid-hydroxylamine hydrochloride leaches of the sediments varies from 2.98 to 16.82%, and relatively higher percentages of the element are associated with the leaches of nearshore regions than that of the outershelf and slope sediments. While the percentages of the element (associated with this leach) encountered all over the study region are more or less of the same order, a few anomalous values are registered in the shelf region between Penner-Calimere Point (10–15%).

Titanium: Between 84 to 99% of the element is housed in the HCl soluble and insoluble fractions of the sediments. Invariably higher percentages of the element are associated with the insoluble fractions of sediments and the partitioned values are more or less similar in the different shelf units.

By and large, the percentages associated with the leaches of the acetic acid-hydroxylamine hydrochloride mixture are meagre (less than 5% of the bulk concentration in majority of the cases).

Manganese: In general, relatively high percentages of manganese are held in the leaches of the acetic acid-hydroxylamine hydrochloride mixture than in the HCl soluble and insoluble fractions of the sediments. The ranges of percentages of manganese held in this leach in the different shelf units are 31–65%; 33–80%; 45–83% and 9–89% for Ganges-Brahmaputra, Visakhapatnam-Kakinada, Kakinada-Penner and Penner-Calimere Point shelf units respectively. Although the ranges of percentages exhibit some amount of similarity among the three units other than Ganges-Brahmaputra shelf, a closer examination of the data reveals some subtle differences among the different shelf units. In the Kakinada-Penner shelf unit, uniformly more than

60% of manganese is held in this leach while only at a few locations manganese in the ranges of 50—60% and less than 50% is encountered. In the Visakhapatnam-Kakinada shelf unit, the leaches of the acid reducing mixture are characterised by the presence of manganese in the higher two ranges, i.e. greater than 60% and 50—60% predominantly. Manganese in the range of less than 50% is encountered only at a few locations. In the Penner-Calimere Point shelf, the leaches are characterised by the presence of high as well as low percentages of manganese (greater than 60% and less than 50%) and both the ranges are evenly distributed in the area. Leaches having manganese in the range of 50—60% are encountered only at a few places. In the Ganges-Brahmaputra shelf, the manganese content of the leaches in general is less than 50% of manganese held in the bulk samples. Further, the percentages of the element associated with the leaches of the nearshore clays are relatively high compared to those associated with the leaches of the clays in the slope region. However, in the case of sandy sediments of the Penner-Calimere Point shelf, the percentages of the element held in the leaches are comparatively low as compared to those in the leaches of the clayey sediments and sometimes they are either equal to or lower than those held in the HCl soluble/insoluble fractions.

As regards the partition between HCl soluble and insoluble fractions, with a few exceptions here and there, manganese held in the insoluble fractions is always less than 25% of the manganese content of the bulk samples. In the HCl soluble leaches, the manganese content shows differences from one shelf unit to the other. In the Ganges-Brahmaputra shelf, in general the leaches contain manganese between 25 and 50%. In the Visakhapatnam-Kakinada shelf unit, it occurs in two ranges 25—50% and less than 25% and both the ranges are evenly distributed in the area. In the Kakinada-Penner shelf unit, the manganese content is predominantly below 25% of the content of the bulk samples. At a few places, although manganese content in the range of 25—50% is encountered, in the Penner-Calimere Point shelf unit, the leaches are characterised by a higher content of manganese (25—50%) although at a few locations lower percentages of the element (less than 25%) are registered.

Zinc and Copper: The ranges of percentage contributions made by different chemical fractions of the sediments in the different shelf units to the bulk concentrations of Zn and Cu are given in Table III. Apart from this, the table also gives the number of samples which fall in each range to evaluate which particular range predominates in a given shelf unit. An analysis of the table shows the following partition pattern for these two elements.

Zinc: As can be seen from the table, the percentage contribution made by the HCl insoluble fraction to the bulk zinc concentrations is less than 25% in the case of northern three units. In marked contrast, in the Penner-Calimere point shelf unit the percentage contribution made by this fraction are slightly higher (25—50%) and followed next in decreasing order

Table III. The ranges of percentage contributions of sediment chemical fractions to the bulk of Zn & Cu.

Shelf units	Ranges (%)	B		C		D	
		Zn	Cu	Zn	Cu	Zn	Cu
Ganges-Brahmaputra	General	23.01-59.82	28.57-65.38	23.84-68.00	7.69-43.75	5.60-22.32	16.41-36.50
	< 25	(3)	(—)	(1)	(2)	(8)	(2)
	25-50	(2)	(6)	(4)	(6)	(—)	(7)
	50-60	(3)	(2)	(—)	(—)	(—)	(—)
> 60	(—)	(1)	(3)	(—)	(—)	(—)	
Vishakhapatnam-Kakinada	General	17.79-53.52	14.89-61.90	11.11-76.58	13.04-14.46	3.00-48.14	5.66-59.32
	< 25	(7)	(14)	(2)	(4)	(16)	(7)
	25-50	(14)	(7)	(10)	(13)	(5)	(14)
	50-60	(2)	(1)	(3)	(1)	(—)	(2)
> 60	(—)	(2)	(6)	(5)	(—)	(—)	
Kakinada-Penner	General	15.38-53.75	7.80-55.36	14.45-80.86	6.21-85.71	2.60-44.89	5.17-38.65
	< 25	(16)	(10)	(1)	(2)	(18)	(15)
	25-50	(13)	(19)	(10)	(15)	(5)	(15)
	50-60	(4)	(1)	(3)	(8)	(—)	(—)
> 60	(—)	(—)	(8)	(5)	(—)	(—)	
Penner-Calimere Point	General	10.52-64.90	9.30-73.33	22.34-75.37	1.88-83.18	5.22-65.78	4.76-70.58
	< 25	(10)	(10)	(3)	(11)	(8)	(11)
	25-50	(14)	(16)	(13)	(15)	(13)	(15)
	50-60	(—)	(2)	(2)	(1)	(—)	(2)
> 60	(1)	(4)	(3)	(3)	(1)	(2)	

B = Acetic acid-hydroxylamine hydrochloride leach, C = HCl soluble fraction, D = HCl insoluble fraction.

The numbers in parenthesis indicate the number of samples falling in a particular range.

by less than 25% range. In the HCl soluble fractions the percentage contributions in the range of 25—50% dominate over other ranges. As regards the contributions made by the acetic acid-hydroxylamine hydrochloride leaches the percentage contributions are evenly distributed between less than 25% and 25—50% ranges in the southern two units (Kakinada-Penner and Penner-Calimere Point shelf unit) while in the Visakhapatnam-Kakinada shelf unit 25—50% range dominate over other ranges. In the Ganges-Brahmaputra shelf unit the percentage contribution show wide variations in that the values are present in all the three ranges i.e. less than 25%, 25—50% and 50—60%.

It could be seen from the above that the major contribution for Zinc concentrations in bulk samples mainly comes from HCl soluble and acetic acid-hydroxylamine hydrochloride leaches.

Copper: The percentage contributions made by the HCl insoluble fractions to the concentrations in the bulk samples are broadly within the range of 25—50% in the case of Ganges-Brahmaputra and Visakhapatnam-Kakinada shelf units followed next in the decreasing order by less than 25% range. In the southern two units the percentage contributions made by this fraction are evenly distributed between less than 25% and 25—50%. In the HCl soluble fractions the percentage contributions are predominantly in the range of 25—50% in the northern two units while in the southern two units although more than 50 per cent of the samples are contributing in the range of 25—50%, an equal number of samples contribute in the varying ranges (less than 25%, 50—60% and greater than 60%). In so far as acetic acid-hydroxylamine hydrochloride leaches are concerned in the southern two units and northern most unit the contributions are predominantly in the range of 25—50% while in the Visakhapatnam-Kakinada shelf unit the percentage contribution in the range of less than 25% predominate over the other ranges.

DISCUSSION

The results presented in the preceding section have clearly brought out the following facts: (1) All the elements studied have a lithogenous and non-lithogenous component in them; (2) the percentage contributions made by the lithogenous component to the concentrations in the bulk samples are the highest in respect of Al and Ti followed by Fe next in the order. Among the other elements, the percentage contributions made by the lithogenous component to the concentrations in the bulk samples are the lowest in respect of Mn while the percentage contributions in respect of the other elements (Zn and Cu) lie in between the values for Al, Ti and Fe on the one hand and Mn on the other hand, and (3) within the lithogenous component which comprises of the detrital minerals and the clay minerals, the percentage contributions made by the detrital minerals are invariably higher than those contributions made by the clay minerals in respect of Ti while in the case of

All the percentage contributions made by the clay fraction are more than the percentage contributions made by the detrital minerals to the concentrations in the bulk samples in the case of clayey sediments and less in the case of sandy sediments. In respect of all other elements (Fe, Mn, Zn, and Cu) the percentage contributions made by the clay fractions (HCl soluble fraction) to the concentrations in the bulk samples are invariably far higher than those contributed by the resistant minerals contained in the HCl insoluble residues.

The distribution pattern of the elements associated with the lithogenous component of the sediments is to a great extent controlled by the type and relative amounts of the various detrital minerals present in them including the clay minerals and their provenance. A survey of the available literature (Mallik, 1968; Venkataratnam, 1968; Mallik, 1976) shows the presence of the following detrital minerals in the shelf region :- the heavy mineral assemblage in the Ganges-Brahmaputra shelf region is characterised by the presence of hornblende, tremolite/actinolite, opaques (magnetite, ilmenite, hematite, hydroxides of iron and pyrites), zircon, pyroxenes, garnet, sillimanite, chlorite, muscovite, biotite, epidote, monazite, kyanite, staurolite, etc. which are mainly derived from the crystalline and Pre-Cambrian complex of the Himalayas and the Cenozoic sediments occurring in the drainage basin of Ganges and Brahmaputra rivers and their tributaries. In the shelf region between Visakhapatnam and Pulicat Lake, the heavy mineral assemblage consists of garnet, sillimanite, zircon, monazite, epidote, hornblende, pyroxenes, rutile, tourmaline, opaques (mainly magnetite) and glauconite. This assemblage indicates that the sediments are mainly derived from metamorphic and igneous rocks occurring in the catchment areas of Godavari, Krishna and Penner rivers. Thus the sediments occurring in the region north of Godavari Delta are mainly derived from the high rank metamorphic rocks and as such the contribution of gneissic rocks increases near the Godavari Delta. The minerals present in the Krishna Delta are derived mainly from gneisses, charnockites and khondalites occurring in the catchment area of the Krishna river south of Krishna Delta; in the region between Krishna and Penner, khondalites and charnockites appear to have contributed a major part of the sediments while in the region between Penner river and Pulicat Lake, the mineralogy points to the derivation of sediments from hornblende bearing rocks namely hornblende schists, hornblende granites and gneisses.

As regards the distribution of clay minerals, the dominant clay mineral present in the Ganges-Brahmaputra shelf unit is illite followed by chlorite and montmorillonite with presence of minor amounts of kaolinite (Siddiquie, 1967; Goldberg and Griffin, 1970; Venkatarathnam and Biscaye, 1973; Ramamurty and Srivastava, 1979). Almost similar assemblage consisting of illite and montmorillonite, mixed layer montmorillonite and illite, and also chlorite and kaolinite was reported by Subba Rao (1963) in the sediments off Visakhapatnam. However, in the region further south i.e. between Kakinada and Calimere Point, the clay mineral assemblage shows a marked change in its composition

in that dominant clay mineral is Na^+ montmorillonite followed by minor amounts of kaolinite and illite (Seetharamaswamy, 1968; Venkatarathnam, 1968).

From the mineral contents of the sediments of the different shelf units it could be seen that the differences in the percentage contributions made by the lithogenous fraction to the concentrations in the bulk samples from region to region and also within the same region are to be attributed to the differences in the mineral assemblages obtaining in the different regions and to the differences in the relative abundances of the minerals from station to station within the same shelf unit.

As regards the percentage contributions made by the non-lithogenous fractions to the concentrations in the bulk sample, in so far as Al and Ti are concerned, they are very insignificant. It is due to the fact that these two elements are geochemically very inactive, particularly aluminium (less than 1% exchangeable; Goldberg and Arrhenius, 1958). In respect of the other elements i.e. Fe, Mn, Zn and Cu, the percentage contributions made by this fraction are very significant and require an explanation as to the manner in which they are incorporated into the sediments and where the non-lithogenous fraction could have been formed, whether in the marine environment or fluvial environment.

The amounts of the elements associated with the non-lithogenous fraction of the sediments represent those incorporated into the sediments in association with carbonate phase, Fe and Mn hydroxides of authigenic origin and adsorption on the clay minerals. However, since all these processes cannot be expected to operate with same intensity all over the shelf region, an effort is made to evaluate the role of each of these processes.

Carbonate phase: Distribution pattern of calcium carbonate in the sediments shows that the sediments of the Ganges-Brahmaputra shelf region and Kakinada-Penner shelf region are predominantly clastic sediments with very low carbonate content, whereas off Chilka Lake-Kakinada coast and off Madras-Calimere Point coast relict band of sediments with high calcium carbonate content occur in the outer shelf regions. The bulk geochemistry of sediments shows that the relict band of sediments are characterised by relatively very low elemental contents as compared to the nearshore and slope sediments. While small amounts of elemental associations with the carbonate phase of these sediments cannot be precluded, the large differences occurring between the elemental contents of these sediments and those with the nearshore and slope sediments suggests that the carbonate phase of these sediments has only a dilution effect and is not a significant factor to be reckoned with for the incorporation of the elements studied.

Adsorption on clays: The composition of the clay mineral assemblages, particularly the presence of montmorillonite and illite in larger percentages is favourable for adsorption of elements from water and their incorporation into

the sediments. However, 3 factors viz. (i) these clay minerals are detrital in origin and are introduced into the marine environment through rivers/estuarine systems, (ii) they may be stripped of the trace elements adsorbed by them in the fluvial environment to a greater or lesser extent on contact with sea water (Kharkar, Turekian and Bertine, 1968); and (iii) high sedimentation rates obtaining in the shelf region (Sarin, Borole and Krishnaswami, 1979; Kalesha, Rao and Somayajulu, 1980) render them ineffective as good adsorbers. Studies on the concentrations of iron in the acetic acid leaches of these sediments have indicated that the iron content associated with these leaches (which represent the amounts of the elements associated with the sediments with carbonate phase and in adsorbed form) do not exceed 5% of the concentrations of iron present in the bulk samples. This supports our surmise that the carbonate phase as well as adsorption on clays are not significant factors for incorporation of elements into these sediments.

Iron and Manganese hydroxides: By the elimination of the above mentioned two factors, we are left with ferric and manganese hydroxides as the dominant constituent of the non-lithogenous fraction contributing to the elemental concentrations in the bulk samples. Colloids of these hydroxides can be formed geochemically either in the marine environment or fluvial environment. In order to know where these are formed, metal/Al ratios have been computed (Table IV) for the elements studied in the shelf region. The ratios obtained indicate that they vary from region to region. However, when they are compared with the metal/Al ratios computed for the different elements

Table IV. Metal — Aluminium Ratios

Station No.	Fe/Al	Ti/Al	Mn/Al	Cu/Al	Zn/Al
Ganges-Brahmaputra Shelf					
421	0.47	0.07	10.05	0.78	—
422	0.55	0.06	6.47	0.94	1.66
423	0.55	0.06	7.89	0.55	1.77
424	0.72	0.07	11.81	0.95	1.38
425	0.65	0.07	13.00	0.98	1.44
427	0.58	0.06	7.50	0.66	1.60
428	0.58	0.06	7.18	0.67	1.52
429	0.63	0.05	7.32	0.57	2.10
430	0.66	0.06	7.65	0.75	1.58
Vishakhapatnam-Kakinada Shelf					
63	0.72	0.07	8.37	0.99	1.51
64	0.87	0.11	9.68	0.69	1.70
65	0.70	0.06	5.36	0.78	1.85
70	—	0.07	—	1.26	—
444	0.69	0.08	7.36	0.85	1.32
446	0.80	0.07	6.52	0.68	1.67
447	1.05	0.06	10.53	12.94	4.33
448	0.88	0.06	4.88	1.46	5.95
450	0.75	0.06	6.34	1.59	2.32

Station No.	Fe/Al	Ti/Al	Mn/Al	Cu/Al	Zn/Al
72	0.69	0.08	6.42	0.97	—
459	0.71	0.09	8.29	0.74	1.47
458	0.72	0.07	5.79	0.93	1.77
457	0.88	0.09	9.20	0.69	1.48
76	0.75	0.08	5.60	1.37	1.64
454	0.73	0.06	6.13	0.88	1.48
453	0.79	0.07	4.79	1.03	1.71
452	0.73	0.06	4.57	1.06	1.59
75	0.97	0.08	8.53	1.16	2.34
460	0.69	0.07	7.84	0.75	1.88
461	0.83	0.08	8.01	1.02	2.13
462	0.88	0.08	7.44	1.23	1.82
73	1.06	0.18	13.11	1.90	2.98
463	0.88	0.08	9.12	1.26	1.94
464	0.78	0.07	7.67	1.14	—
Kakinada-Penner Shelf					
74	2.27	0.25	34.57	4.07	4.57
81	0.99	0.10	7.66	1.61	1.95
82	0.92	0.11	15.57	2.06	1.52
468	1.11	0.16	15.03	2.03	2.66
466	1.10	0.11	13.61	2.10	2.22
469	0.95	0.14	12.26	1.83	1.91
472	1.05	0.13	13.40	2.43	1.56
83	0.97	0.11	10.85	2.00	2.23
475	1.09	0.15	15.20	2.00	1.77
87	0.96	0.12	9.24	2.18	2.49
476	1.05	0.13	14.14	1.68	1.62
86	0.92	0.10	9.59	1.52	2.26
477	1.00	0.13	11.66	1.67	1.48
84	1.05	0.14	12.23	2.22	—
478	0.97	0.11	9.98	2.06	2.37
479	1.10	0.17	13.97	2.41	1.37
480	1.16	0.14	20.75	2.61	2.28
481	0.97	0.10	17.50	2.22	1.83
482	1.00	0.13	12.45	1.97	1.60
91	0.97	0.10	9.50	2.04	1.75
96	0.98	0.11	9.50	2.26	1.75
92	1.05	0.11	11.41	1.74	1.88
496	0.90	0.11	10.49	1.64	1.96
483	0.97	0.11	11.14	2.26	2.60
493	0.86	0.10	9.34	1.62	2.08
484	0.90	0.10	10.20	1.62	1.80
497	1.03	0.13	12.09	1.84	1.93
491	2.98	0.39	45.55	—	6.86
485	0.67	0.07	6.61	1.22	1.56
490	0.84	0.12	8.76	1.23	1.94
488	0.93	0.10	8.58	1.55	1.69
487	0.96	0.11	8.36	1.78	1.62
489	0.95	0.11	10.29	1.03	1.76
95	0.89	—	8.94	1.23	1.65
498	0.66	0.15	11.62	0.74	2.68

Station No.	Fe/Al	Ti/Al	Mn/Al	Cu/Al	Zn/Al
Penner-Calimere Point Shelf					
501	1.15	0.12	10.77	2.38	3.51
502	1.00	0.11	8.17	1.50	2.51
499	1.27	0.14	14.82	1.60	3.22
102	0.26	0.02	8.55	1.61	2.96
101	2.97	0.30	25.75	5.04	7.32
503	0.83	0.10	7.37	1.54	2.39
504	1.64	0.17	18.07	2.87	4.31
505	1.04	0.12	8.88	1.88	3.72
103	0.71	0.09	—	—	—
104	0.93	0.12	11.10	1.07	2.44
506	0.69	0.17	7.11	0.92	5.01
507	0.96	0.09	8.00	1.90	9.27
112	0.72	0.10	9.56	1.07	2.52
511	7.27	1.16	94.37	9.45	18.60
510	1.50	0.10	11.06	3.05	7.17
509	0.81	0.08	6.95	1.16	2.31
111	0.89	0.09	6.59	1.43	2.05
709	0.25	0.02	20.27	0.28	—
708	0.32	0.03	3.63	0.70	2.97
707	0.41	0.07	5.14	1.32	2.25
113	0.62	0.07	6.50	0.68	1.20
114	1.87	0.09	7.20	1.68	4.45
700	0.56	0.04	6.77	0.56	3.16
701	0.67	0.05	7.20	0.62	2.32
119	0.96	0.06	9.07	1.36	5.02
118	0.74	0.07	6.27	0.89	1.85
697	0.70	0.56	4.97	1.04	2.05
698	0.73	0.02	5.69	0.94	2.07
693	0.76	0.06	4.90	0.96	1.60
692	1.26	0.14	29.10	1.15	4.58
120	0.79	0.09	8.76	0.91	1.95
691	0.64	0.17	15.85	2.05	3.61
690	0.73	0.06	10.32	1.13	2.47
689	1.25	0.24	18.47	1.14	6.33
688	2.04	1.09	42.85	0.89	7.62
687	0.72	0.07	5.14	1.45	1.79
121	1.29	0.05	3.12	47.55	7.67
686	0.90	0.07	4.80	1.47	2.06
125	0.66	0.06	2.75	1.01	2.18

from the fluvial environment from the limited data available (Martin and Meybeck, 1979; Sarin, Borole and Krishnaswami, 1979), the metal/Al ratios of the different regions are found to be similar to the ratios obtaining in the adjacent river systems. This clearly shows that the colloids of Fe and Mn hydroxides which are capable of adsorbing the trace elements from the solutions in the environment are formed in the fluvial environment, transported through the estuarine systems without any modification along with their adsorbed elements and are deposited in the marine environment. Subbarao

(1962) established that manganese is supplied to the shelf region from the land in association with finer fractions of the sediments (silts and clays).

The bulk geochemistry of the sediments shows considerable variations from region to region and also within the same region. These could be ascribed to (1) textural differences, (2) the relative contributions made by the lithogenous and non-lithogenous fractions of the sediments to the elemental concentrations in the bulk samples, (3) dilution by the calcium carbonate content and (4) association of some of these elements with important constituents of sediments like organic matter. While this is so, the relatively low concentrations of Mn encountered in the slope regions compared to those in the nearshore regions could be attributed to the reduction of manganese from higher valency state to the lower valency state due to the reducing environment obtaining in the slope region. At the same time, the higher concentrations of other elements like Zn, and Cu in these sediments could be attributed to the high organic matter content present in the slope sediments (Subbarao, 1960). All the findings reported here are supported to a large extent by the inter-relationships obtaining among the elements Al, Fe, Ti, Mn, Zn and Cu.

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REFERENCES

- Buckley, D.E. and R.E. Cranston, 1971. Atomic Absorption Analysis of 18 elements from a single decomposition of aluminosilicates. *Chemical Geology*, **7**: 273-284.
- Chester, R. and M.J. Hughes, 1967. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and absorbed trace elements from pelagic sediments. *Chemical Geology*, **2**: 249-262.
- Goldberg, E.D. and G.O.S. Arrhenius, 1958. Chemistry of Pacific pelagic sediments. *Geochimica et Cosmochimica Acta*, **13**: 153-201.
- Goldberg, E.D. and J.J. Griffin, 1970. The sediments of the northern Indian Ocean. *Deep — Sea Research*, **17**: 513-537.
- Kalesha, M., K.S. Rao and B.L.K. Somayajulu, 1980. Deposition rates in Godavari Delta. *Marine Geology*, **34**: M57-M66.
- Kharkar, D.P., K.K. Turekian and K.K. Bertine, 1968. Stream supply of dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium and Cesium to the oceans. *Geochimica et Cosmochimica Acta*, **32**: 285-298.
- Mallik, T.K., 1968. Heavy minerals of shelf sediments between Visakhapatnam and Penner Delta, Eastern coast of India. *Bulletin of the National Institute of Sciences of India*, **38**: 502-512.

- Mallik, T.K., 1976. Shelf sediments of the Ganges Delta with special emphasis on the mineralogy of the western part, Bay of Bengal, Indian Ocean. *Marine Geology*, **22**: 1-32.
- Martin, J.M. and M. Meybeck, 1979. Elemental mass-balance of material carried by major world rivers. *Marine Chemistry*, **7**: 173-206.
- Murty, P.S.N. and C.V.G. Reddy, 1968. Distribution of phosphorus in the marine sediments off the east coast of India. *Bulletin of the National Institute of Sciences of India*, **38**: 405-410.
- Naidu, A.S., G.K. Rao and C.B. Rao, 1967. Geochemistry of manganese in Recent clay-size marine sediments of the Godavari Delta. *Geochemical Society of India Bulletin*, **2**: 20-26.
- Naidu, A.S., 1968. Radiocarbon date of an oolitic sand collected from the shelf off the east coast of India. *Bulletin of the National Institute of Sciences of India*, **38**: 467-471.
- Rand, M.C., A.E. Greenberg and M.J. Taras, 1975. Standard method for examination of water and waste water. *American Public Health Association, Washington D.C.* pp. 1193.
- Rao, Ch. M. and P.S.N. Murty, 1968. Studies on the shelf sediments off the Madras coast. *Bulletin of the National Institute of Sciences of Indian*, **38**: 442-448.
- Rao, M.P., 1957. Some important observation in the marine geology of Bay of Bengal (along the east coast of India). *C. R. Pan. Indian Ocean Science Association. Rend. 3 e Tananarive, Section C*: 143-148.
- Rao, N.V.N.D. and M.P. Rao, 1969. Some geochemical aspects of the continental shelf sediments off Visakhapatnam coast. *Geochemical Society of India Bulletin*, **4**: 1-8.
- Rao, N.V.N.D. and M.P. Rao, 1973. Trace elements distribution in the continental shelf sediments off the east coast of India. *Marine Geology*, **45**: M43-M48.
- Rama Murty, M. and P.C. Srivastava, 1979. Clay minerals in the shelf sediments off the northwestern part of the Bay of Bengal. *Marine Geology*, **33**: M21-M32.
- Riley, J.P., 1958. The rapid analysis of silicate rocks and minerals. *Analytica Chimica Acta*, **19**: 413-428.
- Sarin, M.M., D.V. Borole and S. Krishna Swamy, 1979. Geochemistry and geochronology of sediments from the Bay of Bengal and the equatorial Indian Ocean. *Proceedings of the Indian Academy of Sciences*, **88A**: 131-154.
- Seetharamaswamy, A., 1968. Some aspects of the sediments of the Krishna Delta and Nizampatnam Bay, East coast of India. *Bulletin of the National Institute of Sciences of Indian*, **38**: 428-435.
- Shapiro, L. and W.W. Brannock, 1969. Rapid analysis of silicate, carbonate and phosphate rocks. *Bulletin of the U. S. Geological Survey*, **1144-A**, *United States Department of Interior*, 1-A 56.
- Shepard, F.P., 1967. *Submarine Geology*, Harper International: pp. 557.
- Siddiquie, H.N., 1967. Recent sediments of the Bay of Bengal. *Marine Geology*, **5**: 249-291.
- Subbarao, M., 1958. Distribution of calcium carbonate in the shelf sediments off East coast of India. *Journal of Sedimentary Petrology* **28**: 274-285.

- Subbarao, M. 1960. Organic matter in marine sediments off east coast of India. *Bulletin of the American Association of Petroleum Geologists*, **44**: 1705-1713.
- Subbarao, M., 1962. Manganese in the shelf sediments off East coast of India. *Proceedings of the Indian Academy of Sciences*, **56**: 274-284.
- Subbarao, M., 1963. Clay mineral composition of shelf sediments off the East coast of India. *Proceedings of Indian Academy of Sciences*, **58**: 6-15.
- Subbarao, M., 1964. Some aspects of continental shelf sediments off the east coast of India. *Marine Geology*, **1**: 59-87.
- Venkatarathnam, K., 1968. Studies on the sediments of the continental shelf off the regions — Visakhapatnam-Pudimadaka and Pulicat Lake-Pennar river confluence along the east coast of India. *Bulletin of the National Institute of Sciences of Indian*, **38**: 472-482.
- Venkatarathnam, K. and P.E. Biscaye, 1973. Clay mineralogy and sedimentation in the eastern Indian Ocean. *Deep-Sea Research*, **20**: 727-738.
- ✓ Venkatarathnam, K. and V.V.S.S. Tilak, 1968. Trace elements in the sediments of the continental shelf off certain parts of east coast of India. *Bulletin of the National Institute of Sciences of India*, **38**: 463-466.