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Distribution of Fe, Mn, Ni, Co, Cu & Zn in Non-lithogenous Fractions of Sediments of Gulf of Kutch

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Contributions made by non-lithogenous fractions of sediments constitute a significant portion of the concentrations of the elements associated with the total sediment samples. The minor differences found in their distribution patterns can be attributed to compositional differences in the individual samples. From an evaluation of the processes of incorporation of elements into sediments in association with non-lithogenous fractions, it is tentatively concluded that the elements particularly trace elements are incorporated more through adsorption on clays than through other processes. However, the absence of covariance among different elements appears to be due to the differential behaviour of elements in regard to adsorption and desorption as a result of the churning of bottom sediments constantly by tidal bores.

Distribution patterns of Al, Fe, Ti, Mn, Ni, Co, Cu, Zn and calcium carbonate in the surficial sediments of the Gulf of Kutch, on the total sample basis, have been reported[1]. In continuation, distribution patterns of Fe, Mn, Ni, Cu, Co and Zn in the leaches of the acid-reducing mixture consisting of acetic acid and hydroxylaminehydrochloride have been studied and the results presented here. According to Chester and Hughes[2], the amounts of the elements associated with these leaches (non-lithogenous fraction, NLF) would represent those incorporated into the sediments in association with (i) carbonate phase and (ii) ferric and manganese hydroxides and through (iii) adsorption on mineral surfaces including clay minerals, i.e. they would represent the contributions made by these 3 processes to the concentrations of the elements associated with total sediment samples (TSS). An attempt has also been made to evaluate the role of the 3 processes in the incorporation of elements into the sediments.

Suitable aliquots of the representative samples collected from 15 stations during the 2nd cruise of *RV Gaveshani* (February/March 1976) were leached with the acid-reducing mixture and the test solutions prepared as described by Chester and Hughes[2]. The elemental concentrations were measured on Hilger and Watts Atom Speck H 1550. Data obtained are presented in Table 1 and the data on texture of sediments, water depth, calcium carbonate content were same as reported earlier[1]. To understand the inter-relationships among the different elements, correlation coefficients have been calculated (Table 2).

Data presented in Tables 1 and 2 permit the following observations:

(1) Texture of sediments has no appreciable influence on the distribution of the elements associated with the NLF in view of the fact that similar ranges of amounts of the elements are associated with all the 3 types of sediments—(a) silty clays and clayey silts (b) sand-silt-clay and (c) silty sands and clayey sands.

(2) Contributions made by the NLF of sediments constitute a significant portion of the concentrations of the elements associated with the TSS. This is particularly true in the case of all the elements except iron.

(3) Cu and Co exhibit a marginal correlation with Mn and Cu with Ni while others exhibit no relationship either with Fe or Mn or among themselves.

Contributions made by the LF of sediments to the concentrations in the TSS clearly indicate that considerable amounts of the elements are fixed in the sediments in a solid state in association with the lithogenous material. The present studies also indicate that to some extent the elements are incorporated into the sediments either through all the 3 or 1 of the processes that contribute to the amounts associated with the NLF. However, since all the 3 processes cannot be expected to be operating with the same intensity all over the region, an evaluation of the role of these processes is attempted in the following paragraphs from the available data.

Carbonate phase—Calcium carbonate content varies between 10 and 50%. The fine-grained sediments are characterised by very low carbonate content while coarser sediments have a relatively high content. Coarse fraction studies by Hashimi *et al.*[3] have revealed the presence of foraminifera and molluscs, and a close relation between the percentage of carbonate material in the coarse fraction and the carbonate content of the sediments has been reported[1].

Investigations[4,5] on the sediments of the adjacent shelf region have indicated that even in sediments having 75 to 90% calcium carbonate, the carbonate phase is not a significant contributing factor to the

Table 1—Contributions Made by Non-lithogenous Fractions (A) and Lithogenous Fractions (B) to the Concentration of Elements in the Total Sediment Sample

St No.	Fe %		Mn ppm		Ni ppm		Co ppm		Cu ppm		Zn ppm	
	A	B	A	B	A	B	A	B	A	B	A	B
K 35	0.16	1.43	580	322	16	39	28	6	13	11	40	13
K 36	0.05	3.87	330	688	11	60	0	40	13	15	26	73
K 37	0.06	4.64	555	400	11	61	15	10	15	24	47	67
K 38	0.23	4.08	405	584	11	55	0	40	5	28	37	67
K 39	0.23	4.42	465	437	18	64	0	39	18	17	33	80
K 40	0.15	3.77	420	453	8	63	2	19	13	25	29	76
K 49	—	—	331	571	13	55	13	32	5	37	24	54
K 50	0.08	4.61	400	444	15	69	2	50	16	30	34	63
K 51	0.19	3.35	390	366	11	50	4	42	7	22	34	39
K 53	0.05	2.01	316	266	2	43	10	27	5	13	33	15
K 54	0.04	2.84	334	277	6	38	15	21	5	19	40	17
K 55	0.06	4.69	452	450	15	63	8	29	18	35	42	55
K 56	0.02	3.50	350	348	24	31	2	52	13	25	40	31
K 57	—	—	365	537	13	71	11	31	5	34	62	33
K 58	—	—	375	498	18	45	2	37	18	15	45	40

Table 2—Correlation Coefficients between Various Elements

Correlation between	r value	Correlation between	r value
Fe and Mn	+0.36	Mn and Cu	+0.49
Fe and Zn	−0.22	Cu and Co	−0.22
Fe and Ni	+0.07	Cu and Ni	+0.56
Fe and Co	−0.16	Co and Zn	+0.007
Fe and Cu	+0.09	Co and Ni	−0.16
Mn and Zn	+0.23	Co and Zn	+0.27
Mn and Ni	+0.23	Ni and Zn	+0.20
Mn and Co	+0.45		

trace element content of the sediments and that the contributions made by it are only of the order of < 10 ppm in the case of the trace elements and > 50 ppm in the case of Mn. Thus it is highly unlikely that sediments with a low carbonate content can derive their trace element content in any significant measure from the carbonate phase.

Iron and manganese hydroxides—Partition patterns of Fe and Mn and other elements have been reported[4,5]. Higher concentrations of Fe and Mn associated with NLF of the fine-grained terrigenous sediments of the innershelf region (0-60 m water depth) have been attributed to the flocculation of the colloids of Fe and Mn transported to the sea through river systems. Further it is explained the higher concentrations of the other elements such as Ni, Cu, Co, etc. associated with this fraction as being due to the adsorption of these elements by the colloids of Fe and Mn. The chemical[1] and mineralogical[3] studies carried out on the sediments of the Gulf region have indicated that the sediments transported from the north are deflected into the Gulf and are not transported further south in any significant measure. In this situation it is but reasonable to suppose that the relationship existing between Fe and Mn hydroxides and other elements should be same as the one reported from the adjacent shelf region. However, in reality it is not so. In the Gulf sediments, except for marginal correlation that exists between Mn and Cu and Co and Ni with Cu, there is practically no relationship between Mn and Fe and other elements. This implies that fixation of the trace elements in association with the Mn and ferric hydroxide colloids is not a potent factor in the Gulf region. The possibility whether the limited number of samples studied could be a limiting factor for the absence of any correlation has been examined and ruled out in view of the fact that on the same set of samples the authors reported significant relationships among the various elements on the bulk sample basis.

Adsorption on clays—Clay minerals make a small but important contribution to the composition of the oceanic sediments by their ability to adsorb elements from sea water. Studies carried out on the clay minerals in the Gulf of Kutch region and the region north of it have shown that the general concentration is illite (40-50%), montmorillonite (30-50%), chlorite (20-30%) and kaolinite (0-10%)[6,7]. This clay mineral assemblage particularly the presence of illite and montmorillonite in significant amounts is favourable for the adsorption of the elements especially trace elements and their incorporation into the sediments. From the elimination process as well as the presence of favourable clay mineral assemblage, it is tentatively suggested that the trace elements associated with the NLF of the sediments are to a considerable extent incorporated into the sediments through adsorption on clays. However, if no interrelationship could be

noticed among the different elements, it is possibly due to the differential behaviour of the elements in regard to the desorption and adsorption taking place in an environment where there is constant churning up of bottom sediments by the prevailing tidal bores.

Dissolved oxygen measurements in the bottom waters revealed highly oxygenated waters (4 to 5 ml/litre)[8]. Thus the environment in general being an oxidising one in the Gulf, the minor differences found in the elemental concentrations of the sediments may be due to the compositional differences of the individual samples than to environmental changes.

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Distribution of Al, Mn, Ni, Co & Cu in the Non-lithogenous Fractions of Sediments of the Northern Half of the Western Continental Shelf of India

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Higher amounts of elements are associated with the non-lithogenous fractions of the finegrained terrigenous sediments of the innershelf region with low carbonate content than with the corresponding fractions of the coarsegrained sediments of the outershelf region with high calcium carbonate content and all the elements covary with each other in the environment. From an evaluation of the role of different processes associated with the incorporation of elements, particularly trace elements into the non-lithogenous fractions, it is inferred that in the innershelf region they are incorporated in association with the hydroxides of iron and manganese while in the outershelf region they are associated with the carbonate phase.

In continuation of reports[1,2] on elemental distributions in the surficial sediments of northern half of western continental shelf of India, distribution of Al, Mn, Ni, Co and Cu have been studied in the non-lithogenous fraction (NLF) of these sediments and the results reported here.

Fig. 1 gives location of stations from where surficial sediment samples were collected. Suitable aliquots of the oven dried samples were leached with acid reducing mixture and the test solutions prepared[3]. Al[4], Mn[5], Ni, Co and Cu[6] were estimated colorimetrically.

The results obtained are presented in Table 1 along with other essential data such as depth of sampling, texture of sediments[7] and the contributions made by the lithogenous fractions (LF) of sediments to the concentrations in the total sediment sample. This parameter has been included only to give an idea of the relative contributions made by NLF and LF to the concentrations in the total sediment samples. Concentrations of elements associated with NLF have been computed from the values given in column A and their distribution patterns for Al, Mn, Ni and Co are shown in Figs 2-5. For copper, the values are recorded in Table 1 itself under column C. Inter-elemental relationships have been worked out and the r values obtained are given in Table 2.

From the data presented and the distribution pattern of calcium carbonate reported earlier[2], the following inferences can be drawn in regard to the distribution pattern of the sediments and the distribution patterns of the elements in NLF of sediments:

(1) Texturally, the innershelf (0-60 to 70m) is floored by finegrained sediments of terrigenous origin (clays, silty clays, clayey silts, sandy clays and sandy silts) with low calcium carbonate content while the outershelf

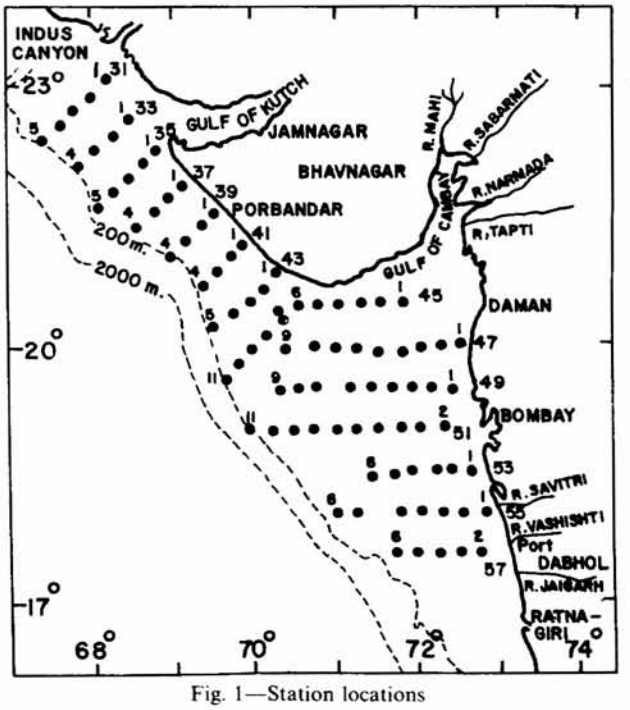

Fig. 1—Station locations