

Partition Patterns of Copper in the Sediments of the Western Continental Shelf of India

CH. M. RAO, P. S. N. MURTY & C. V. G. REDDY
National Institute of Oceanography, Panaji

Received 15 October 1973; revised received 16 January 1974

Copper has both a lithogenous and non-lithogenous component in the sediments of the western continental shelf of India. The overall distribution pattern of the element (on the total sample basis) and its partition patterns between the two components are described. The processes leading to the incorporation of the element in the bottom sediments are discussed.

PARTITION patterns of iron, manganese, nickel and cobalt in the shelf sediments off the west coast of India (between Bombay and Quilon) have been described¹. In continuation, the partition patterns of copper have been studied and the results reported in this communication. It may be mentioned that except for the studies carried out by Gogate *et al.*² in a limited way on the sediment samples collected from the shelf and slope regions off Bombay and Ratnagiri, there is no information on the distribution pattern of copper in the sediments of the western continental shelf of India.

Materials and Methods

Fig. 1 gives the locations of the stations from where the bottom sediment samples were collected. In the area under study, the bottom sediments exhibit texturally and chemically certain well-defined distribution patterns. The inner shelf (up to 20 fm) is covered by silty clays or clayey silts with very low carbonate content and this is followed seaward by a zone of silty or clayey sands on the rest of the shelf and slope regions characterized by a high carbonate content³. This is particularly so between Quilon and Karwar while off Bombay the shelf is covered for a greater part by fine grained sediments. Representative sediment samples were washed chloride free and estimations of copper were carried out (i) in the bulk sample, to determine the concentrations in the total sediment samples (TSS) and the overall distribution patterns; and (ii) in the acidic sediment leaches obtained by the method of Chester and Hughes⁴, to get an idea of the contributions made by the lithogenous and non-lithogenous fractions (LF and NLF) to TSS. The method followed for the estimation of copper was that of Chester and Hughes⁵ and the analyses were carried out using Unicam spectrophotometer SP 500.

Results and Discussion

Concentrations of copper associated with the TSS and the contributions made by the LF and NLF of the sediments to the concentrations in the TSS are depicted in Fig. 2. Further, as the quantity of acid soluble fraction varies from sample to sample, for purposes of comparison, the concentrations in the NLF of the sediments have also been

computed and are given in Table 1 along with the depth of sampling. In order to understand the relationship copper bears to other important constituents of the sediments such as calcium carbonate, organic matter, iron and manganese, scatter diagrams have been drawn (Fig. 3). Values of calcium carbonate, are taken from Nair *et al.*³, organic matter from Murty *et al.*⁶ and manganese and iron from Murty *et al.*¹ for this purpose.

Analysis of the data permits the following generalizations to be made in regard to the distribution pattern of copper in the sediments under study:

(i) Fine-grained sediments in the innershelf region (less than 20 fm depth) with low carbonate content are characterized by higher concentrations of copper

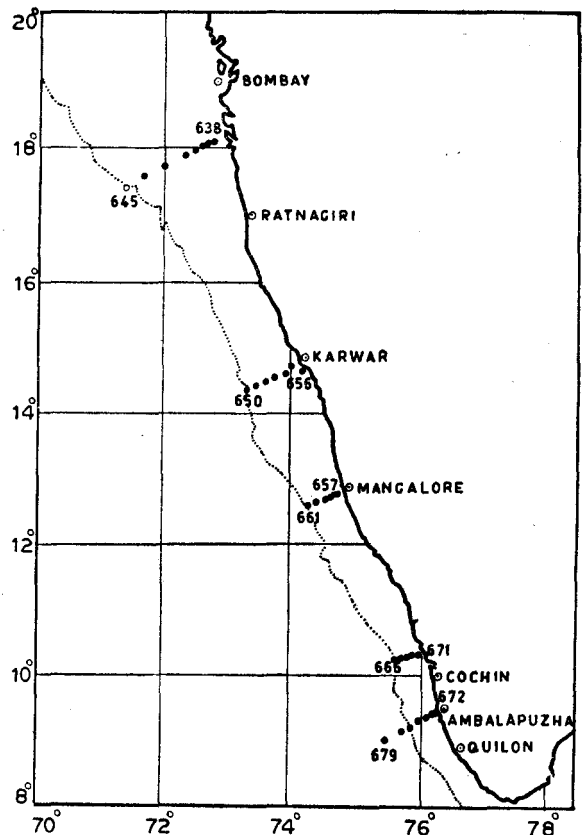


Fig. 1 — Map showing station locations

than the silty or clayey sands of the outershelf and slope regions with higher carbonate content.

(ii) Contributions made by LF of the fine grained sediments (in the innershelf region) to the concentrations in TSS are relatively higher than the contributions made by the corresponding fractions of the outershelf sediments. This is particularly true along all the sections except off Mangalore and Cochin where the values do not show similar relation.

(iii) NLF of the sediments of the innershelf region are characterized by higher concentrations of copper than those of the outershelf and slope sediments.

(iv) Sediments off Karwar and Mangalore have relatively higher concentrations of copper than the sediments in the other three sections (on the total sample basis). The same trend is maintained on the carbonate-free basis also.

(v) NLF of the sediments off Mangalore and Cochin are characterized by higher concentrations of copper than the NLF in the other three sections.

(vi) Copper co-varies with both iron and manganese in both TSS and NLF of the sediments. The correlation between iron and copper is significant at levels 0.01 and 0.001 in TSS and NLF respectively while the correlation between manganese and copper is significant at 0.001 level in both the fractions. With calcium carbonate, it has a strong negative correlation significant at 0.01 level. It does not show any significant relationship with the organic matter content of the sediments.

The trends mentioned under observations (i) and (ii) in the preceding para clearly establish the fact that there is a substantial supply of the element from land to the innershelf region through copper held in the lattice structure of the detrital minerals. With a few exceptions here and there, the percentage contributions made by the LF to the concentrations in TSS (values not given in the paper) also indicate that the contribution by the LF is substantial all over the shelf region. Hence, the differences observed in the concentrations of copper (on the total sample basis) along the different sections may be attributed to the differences in the source rocks present along the different parts of the west coast

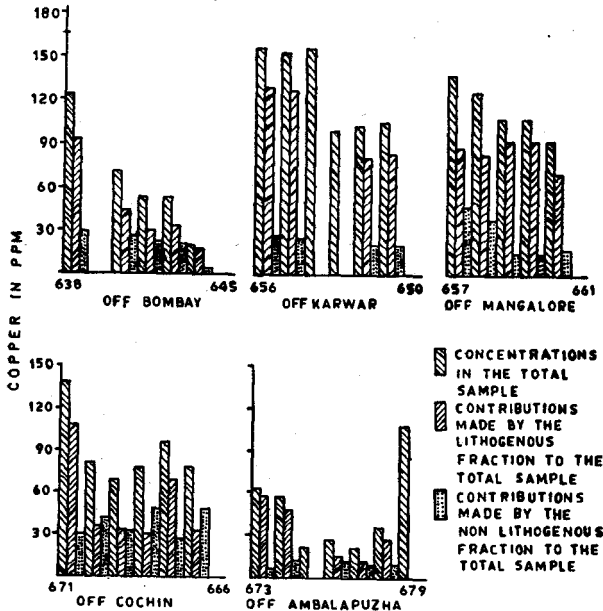


Fig. 2 — Concentrations of copper in the total sediment samples and the contributions made by the lithogenous and non-lithogenous components of the sediments to them

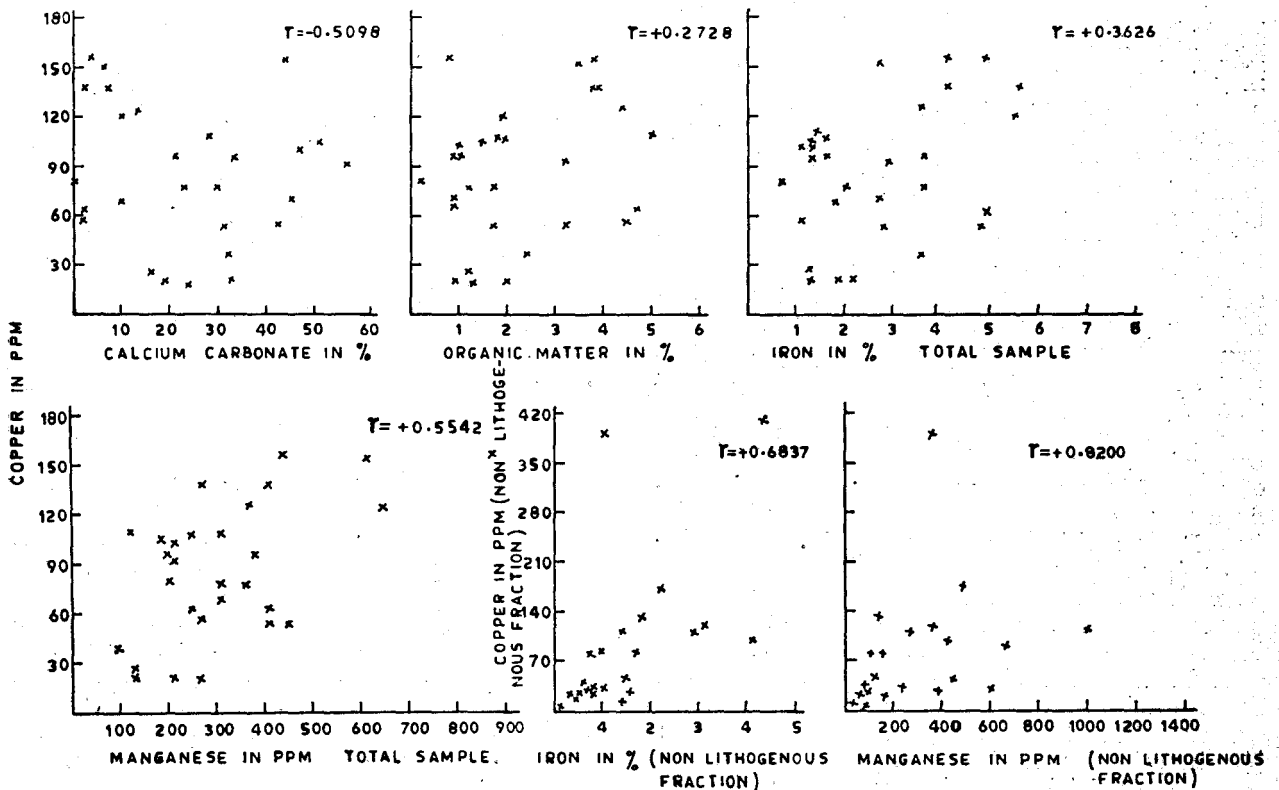


Fig. 3 — Scatter diagram showing the relationship between copper and other elements of the sediments

of India and to the corresponding differences in the mineralogical composition of the sediments in the different regions. While this is so, the uniformly high values of copper present in the sediments along the section off Karwar appear to be due to an additional factor — the presence of discrete copper minerals along this coast⁷.

It is evident from the foregoing that the element has been fixed to a large extent in the sediments in a solid state through the detrital minerals supplied from the land. Apart from this mode of fixation of the element in the sediments, relatively higher concentrations of non-lithogenous copper in the innershelf region indicates that the element is being removed more effectively from the overlying waters in the innershelf region and fixed in the sediments through other processes also. Among the various processes suggested by Krauskopf⁸ for the removal of trace metals from the overlying waters and their incorporation in the sediments, the fixation of copper in the sediments through precipitation as an insoluble compound or through precipitation by sulphide ion can be ruled out for the reasons stated earlier by the authors¹ in respect of nickel and cobalt. The significant negative correlation between the carbonate content and the concentrations of copper in the sediments suggests that the contributions from the carbonate phase of the sediments to the concentrations in the NLF of the sediments is negligible. The absence of any significant correlation between the organic matter content of the sediments and the concentrations of copper indicates that copper is not bound with the organic matter to any considerable extent. Murty *et al.*¹ reported higher concentrations of iron and manganese in the NLF of the sediments of the inner-shelf region and attributed them to the flocculation of the colloids of iron and manganese brought by the rivers. It is quite likely that adsorption by hydrated ferric oxide and manganese hydroxide may be responsible for higher concentrations of copper associated with the NLF of the fine grained sediments. The significant correlation between copper and iron and manganese (both on the total sample basis as well as in the NLF) supports this inference.

With a view to determining the concentrations of copper associated with the clay fractions of the sediments and the pattern of distribution they exhibit, clay fractions separated from some of the samples along the different sections were analysed for their copper content. The values (Table 1) show that higher concentrations of copper are confined to the areas characterized by the presence of predominantly montmorillonite and illite (area A of the Table) while lower concentrations are confined to the areas having predominantly kaolinite (area B of the Table) group of minerals⁹. The differences observed in the ranges of values and the means between the three northern sections and the two southern sections also lends support to this conclusion. This suggests that part of the copper in the NLF has been fixed through adsorption by the clay minerals. The concentrations associated with the NLF of the sediments thus appear to be due to two processes: (i) adsorption by the hydrated oxides of iron and manganese and (ii) adsorption by the clay minerals. But the differences found in the concentrations of

TABLE 1 — CONCENTRATIONS OF COPPER IN THE CLAY AND NON-LITHOGENOUS FRACTIONS OF THE SEDIMENTS

Station No.	Depth fm	Copper conc. ppm	
		Clay fraction	Non-lithogenous fraction
AREA A*			
Off Bombay			
638	13	90	86
640	19	28	35
641	19	38	43
642	26	60	30
643	38	—	4
Off Karwar			
656	10	98	99
655	12	94	110
654	25	91	—
652	42	59	24
651	66	46	24
Off Mangalore			
657	10	86	415
658	17	—	120
659	23	38	25
660	43	18	25
661	105	91	26
AREA B†			
Off Cochin			
671	13	30	173
670	14	—	394
669	17	29	114
668	23	34	81
667	32	—	83
666	46	9	132
Off Ambalapuzha			
673	9	45	30
672	10	49	—
674	20	19	—
675	27	30	48
676	29	—	31
677	85	—	11

Range and mean of copper conc.: *Clay fraction—18 to 98, 64; non-lithogenous fraction—4 to 415, 76. †Clay fraction—9 to 49, 31; non-lithogenous fraction—11 to 314, 110.

copper in this fraction along the different sections and the divergence between the trends observed in the clay fractions and the NLF in regard to the mean values in area 'B' may be attributed to the differences in the intensities of different processes operating in different regions and the concentrations of the element available in the waters in different regions. Gogate *et al.*² reported that the trace elements in the sediments studied by them are associated with the clay mineral illite, through adsorption. Sankaranarayanan and Reddy¹⁰, reported very high concentrations of copper in the inshore waters along the Goa coast which they

attributed to the influence of the land run off from the ore-bearing terrain.

Acknowledgement

Authors wish to express their gratitude to Shri H. N. Siddiquie, Head, Geological Oceanography Division, for his helpful suggestions in the preparation of the paper.

References

1. MURTY, P. S. N., RAO, CH. M. & REDDY, C. V. G., *Indian J. mar. Sci.*, **2** (1973), 6.
2. GOGATE, S. S., SASTRY, V. N., KRISHNAMURTHY, T. M. & VISWANATHAN, R., *Curr. Sci.*, **39** (1970), 171.
3. NAIR, R. R. & ABRAHAM PYLEE, *Bull. natn. Inst. Sci. India*, **38** (1968), 411.
4. CHESTER, R. & HUGHES, M. J., *Chem. Geol.*, **2** (1967), 245.
5. CHESTER, R. & HUGHES, M. J., *Trans. Instn. Min. Metall. (Appl. Earth Sci.)*, **77** (1969), 37.
6. MURTY, P. S. N., REDDY, C. V. G. & VARADACHARI, V. V. R., *Proc. natn. Inst. Sci. India*, **35** (1969), 377.
7. *Geological & mineral map of Mysore & Goa* (Geological Survey of India), 1969.
8. KRAUSKOPF, K. B., *Geochim. Cosmochim. Acta*, **9** (1956), 1.
9. MURTY, P. S. N., RAO, CH. M. & REDDY, C. V. G., *Curr. Sci.*, **39** (1970), 30.
10. SANKARANARAYANAN, V. N. & REDDY, C. V. G., *Curr. Sci.*, **42** (1973), 223.