

Partition Studies in the Sediments of Deep Sea Drilling Project Site 220 in the Southeastern Arabian Sea

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Partition patterns of Al, Fe, Mn, Ni, Co and Cu have been studied in sediments. These studies have revealed that all the elements have both acid insoluble and non-lithogenous components in these sediments and exhibit differences in their distribution pattern in the sedimentary column. While the concentrations of different elements associated with the acid insoluble fractions are fixed in sediments in a solid state and the differences found can be attributed to differences in the nature of the material the site received during different periods, the concentrations associated with the non-lithogenous component of sediments appear to have been fixed in a number of ways. While Al, Fe and Mn seem to be associated with the clays and carbonate phase, Ni, Co and Cu in sediments appear to have been fixed through adsorption on clays and organic matter and by ferric and manganese hydroxides. Considering the depositional history of the site, rates of sedimentation during different geological periods and the nature of the material deposited, it is tentatively suggested that the differences found in the concentrations of different elements in the nonlithogenous fraction are related to a large extent to differences in rates of sedimentation and to the character of the material in the different lithological units.

DISTRIBUTION patterns of Fe, Mn and Ti in sediments of site 220 have been described¹. In continuation, partition patterns of Al, Fe, Mn, Ni, Co and Cu are studied in these sediments and the results reported in this communication. The need for the present studies stems from the fact that the information available so far on the distribution patterns of various elements^{1,2} do not throw any light on the partition of elements among different components of sediments and the processes leading to their incorporation in the sediments.

Details of location of site and lithology are reported earlier¹. Lithologic summary of site 220 is given in Table 1 (ref. 2).

Methods

The methods adopted for the digestion of bulk samples and preparation of acid sediment leaches are the same as described¹. Concentrations of Al³, Fe and Mn⁴, and Ni, Co and Cu⁵ were estimated in different fractions of sediments.

Results

Elemental analyses of both the total sediment samples and the acid sediment leaches together with the total carbonate content and organic carbon content of the sediments are given in Tables 2 and 3. Distribution patterns of Fe and Mn in the total sediment samples are not discussed in the paper and are used only for calculating component contributions.

Overall distribution patterns of elements — On bulk sample basis, sediments of unit I are characterized by higher concentrations of aluminium, nickel and copper than the sediments of units II to IV. Cobalt

does not exhibit any conspicuous trend in regard to its distribution pattern.

Contribution made by acid-insoluble fraction to total contents of bulk sediment samples — Contributions made by AIF (acid-insoluble fraction) to the contents of Fe, Ni, and Al in the TSS (bulk sediment sample) of unit I are higher than those of units II to IV. In terms of percentage contributions made by AIF to the concentrations in TSS, they range from 86 to 98, 11 to 93 and 95 to 99% for Fe, Ni and Al respectively. In the case of Mn, contributions made by AIF to concentrations in TSS broadly follow the overall distribution pattern of the element and the percentage contributions range from 34 to 98%. In respect of Co, except for a few random high values, contributions are uniformly low throughout the sedimentary column and percentage contributions range from 7 to 78%. For Cu, contributions

TABLE 1 — LITHOLOGIC SUMMARY, SITE 220

Lithologic units	Thick- ness (m)	Sub- bottom depth (m)	Cores
I Orange to brown nanno-detrital clay and detrital clay nanno ooze; few foram sand beds	c. 69	0-69	1-5
II White nanno ooze and chalk	c. 151	69-220	6-11
III Light orange rad spicule rich nanno ooze/chalk with thin ash beds	c. 70	220-290	12-16
IV Light orange micarb-rich nanno chalk with thin chert beds	39	290-329	16-18
V Basalt flows with thin inter-bedded sediment layers	21	329-350	18-21

TABLE 2 — CONCENTRATIONS OF Al, Fe AND Mn IN DIFFERENT FRACTIONS OF SEDIMENTS ALONG WITH SAMPLE DESIGNATION, DEPTH BELOW SEA-BED

(A = concentrations in total sediment, B = contributions made by acid insoluble fraction to concentration in total sediment, C = contributions made by non-litho-
genous fraction to concentrations in total sediment, D = concentrations in non-lithogenous fraction, E = percentage contributions to concentrations in total sediment
by acid insoluble fraction of sediments)

Sl No.	Sample designation hole/barrel/ section/horizon, cm	Depth m	Al ₂ O ₃ , %					Fe, %					Mn, ppm				
			A	B	C	D	E	A*	B	C	D	E	A*	B	C	D	E
UNIT I																	
1	220.1.1.120-122	1-20-1-22	8-66	—	—	—	—	1-82	1-64	0-18	0-29	90-1	258	165	93	152	63-8
2	220.1.2.120-122	2-70-2-72	17-31	17-16	0-15	3-6	99-1	2-95	2-88	0-07	0-17	97-6	679	639	40	97	94-1
3	220.1.3.120-122	4-20-4-22	10-55	10-47	0-08	0-16	99-1	1-92	1-85	0-07	0-12	96-3	736	682	54	95	92-8
4	220.2.3.102-105	13-02-13-05	8-16	8-09	0-07	0-12	99-1	1-77	1-70	0-07	0-12	95-9	584	424	160	265	72-6
5	220.4.1.120-122	28-20-28-22	12-02	11-91	0-11	0-22	99-1	2-63	2-58	0-05	0-10	98-1	876	733	143	184	83-7
6	220.5.2.120-122	38-70-38-72	8-16	8-14	0-02	0-03	99-7	1-42	1-39	0-03	0-04	97-9	122	42	80	121	34-4
UNIT II																	
7	220.6.1.120-122	94-20-94-22	1-51	1-47	0-04	0-04	97-3	0-22	0-20	0-02	0-02	90-9	118	65	53	56	55-0
8	220.7.1.120-122	103-20-103-22	2-72	2-68	0-04	0-04	98-5	0-35	0-34	0-01	0-01	97-1	185	79	106	119	42-7
9	220.8.3.120-122	115-20-115-22	1-79	1-75	0-04	0-04	97-8	0-29	0-28	0-01	0-01	96-5	320	267	53	56	83-4
10	220.9.2.120-122	152-70-152-72	1-76	1-72	0-04	0-04	97-7	0-49	0-48	0-01	0-01	97-9	196	143	53	59	72-9
11	220.10.2.120-122	162-70-162-72	1-96	1-92	0-04	0-04	97-9	0-35	0-34	0-01	0-01	97-1	511	431	80	92	84-30
12	220.11.1.105-107	199-00-199-02	12-02	11-76	0-26	0-33	97-8	1-30	1-19	0-11	0-14	91-5	623	530	93	118	85-10
13	220.11.1.120-122	199-20-199-22	1-08	1-06	0-02	0-02	98-1	0-26	0-22	0-02	0-02	91-6	140	47	93	102	33-60
UNIT III																	
14	220.12.2.120-122	234-70-234-72	1-79	1-77	0-02	0-03	98-9	0-35	0-30	0-05	0-06	85-7	460	326	134	179	70-80
15	220.13.1.87-89	241-87-241-89	2-02	1-98	0-04	0-06	98-0	0-36	0-34	0-02	0-03	94-4	651	611	40	57	93-50
16	220.13.4.5-7	245-55-245-57	1-96	1-92	0-04	0-06	97-9	0-28	0-27	0-01	0-01	96-5	550	—	—	—	—
17	220.14.1.63-65	250-63-250-65	1-66	1-62	0-04	0-06	97-6	0-33	0-32	0-01	0-01	96-9	365	325	40	55	89-0
18	220.14.3.45-47	253-45-253-47	1-44	1-37	0-07	0-09	95-1	0-24	0-21	0-03	0-04	87-5	1145	1105	40	55	96-50
19	220.14.3.120-122	254-20-254-22	1-70	1-63	0-07	0-10	95-9	0-27	0-24	0-03	0-04	89-3	1977	1683	294	438	85-1
20	220.15.2.131-133	261-81-261-83	2-31	2-27	0-04	0-06	98-3	0-37	0-33	0-04	0-06	89-1	668	615	53	75	91-1
21	220.15.5.48-50	265-48-265-50	2-44	2-40	0-04	0-06	98-4	0-39	0-36	0-03	0-04	92-3	511	471	40	58	92-2
22	220.15.6.47-49	266-97-266-99	1-74	1-70	0-04	0-06	97-7	0-34	0-33	0-01	0-01	97	1353	1273	80	113	94-1
UNIT IV																	
23	220.17.1.45-47	297-45-297-47	2-53	2-49	0-04	0-06	98-4	0-50	0-47	0-03	0-04	94	2941	2901	40	56	98-6
24	220.18.2.118-120	328-68-328-70	4-04	4-00	0-04	0-06	99	1-37	1-31	0-06	0-09	95-6	2251	2198	53	78	97-6

*Veerayya *et al.* 1.

TABLE 3—CONCENTRATIONS OF Ni, Co, Cu, ORGANIC CARBON AND CALCIUM CARBONATE IN DIFFERENT FRACTIONS OF SEDIMENTS

(Sample designation, depth and details of fractions same as in Table 2)

Sl No.	Ni, ppm					Co, Ppm					Cu, ppm					Organic carbon %	CaCO ₃ %
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E		
1	43	35	8	13	81.4	15	4	11	10	26.4	133	109	24	39	81.9	0.51	58.7
2	45	35	10	24	77.8	15	2	13	31	13.3	149	120	29	70	80.5	0.53	37
3	32	21	11	20	65.6	21	8	13	23	38.1	167	115	42	75	68.9	0.48	53
4	68	56	12	20	82.3	20	6	14	23	30	144	81	63	105	56.2	0.50	52.8
5	42	39	3	6	92.8	23	14	9	18	60.9	182	155	27	49	85.2	0.36	44.2
6	67	—	—	—	—	41	27	14	21	65.8	154	—	—	—	—	0.23	63.6
7	17	10	7	7	58.8	7	3	4	4	42.85	127	105	32	34	82.7	0.06	92.6
8	10	5	5	6	50	7	1	6	7	14.3	97	87	10	11	89.7	0.22	80.2
9	8	3	5	5	37.5	8	2	6	6	25	97	93	4	4	95.9	0.16	92.8
10	14	11	13	3	78.6	18	4	14	15	22.2	107	100	7	8	93.4	0.23	89.4
11	12	5	7	8	41.7	10	3	7	8	30	112	104	8	9	92.8	0.22	86.6
12	19	13	6	7	68.4	36	28	8	10	77.8	123	116	7	9	94.3	0.15	76.8
13	14	11	3	3	78.5	18	11	7	7	61.1	112	105	7	8	93.7	0.18	89.8
14	9	1	8	11	11.1	8	2	6	8	25	105	102	3	4	97.1	0.25	70.4
15	13	—	—	—	—	7	2	5	7	28.6	107	104	3	4	97.2	0.22	67.4
16	13	9	4	6	69.2	26	18	8	11	69.2	127	119	8	11	93.7	0.25	70.7
17	8	6	2	3	75	20	12	8	11	60	109	106	3	4	97.2	0.22	69.3
18	13	10	3	4	76.9	20	5	15	20	25	101	96	5	7	95.5	0.15	70
19	24	14	10	14	58.3	42	12	30	45	28.6	192	102	90	134	53.1	0.2	62.2
20	13	6	7	10	46.1	13	1	12	17	7.7	105	102	3	4	97.1	0.22	69.3
21	12	9	3	4	75	16	4	12	18	25	114	111	3	4	97.4	0.18	65.4
22	12	8	4	6	66.7	15	—	—	—	—	129	124	5	7	96.1	0.22	66.9
23	15	12	3	4	80	20	8	12	17	40	72	68	4	6	94.4	0.19	68.2
24	29	21	8	12	72.4	18	4	16	21	22.2	147	118	29	43	80.2	0.22	68

made by AIF to concentrations in TSS are uniformly high throughout the sedimentary column and the percentage contributions range from 56 to 97%.

Contributions made by non-lithogenous fraction to total contents of bulk sediment sample and the contents associated with the non-lithogenous fractions of sediments

—Contributions made by NLF (non-lithogenous fraction) of sediments to the concentrations in TSS as well as the concentrations associated with NLF of sediments are higher for Fe, Ni, Cu and Al in sediments of unit I than in other units. Except for 2 high values in unit III, higher values are encountered for Mn in sediments of units I and II than of units III and IV. In the case of Co, sediments of units I and IV and the lower half of unit III are characterized by higher values by way of contributions as well as the concentrations associated with NLF of the sediments than in sediments of the rest of the sedimentary column.

Discussion

All clay minerals contain Al in their crystal lattices and much of Al in deep sea sediments is located in these positions. Goldberg and Arrhenius⁶ have found that Al content of Pacific pelagic sediments show a small variation with the igneous rock average and they have suggested that the main occurrence of Al is in aluminosilicate minerals and that <1% is exchangeable. It has been used as an index of inorganic or argillaceous fraction of the sediments. Partition patterns of Al indicate that most of the Al in the sediments is associated with the acid-insoluble fractions of the sediments and that the contribution from the non-lithogenous sources is negligible. Consideration of these data in conjunction with the depositional history of the site⁷ clearly indicates the mixed nature of the

sediments of unit I and the non-lithogenous nature of the sediments of units II to IV. Thus, the differences found in different units can be attributed to the difference in the character of sediments and their mineralogy including clay minerals and their relative abundances⁸. Very low percentage of Al associated with the NLF of sediments throughout the sedimentary column could perhaps be due to its association with the biogenic phase of the sediments.

Partition patterns of Fe and Mn support the earlier findings¹ that a major portion of these elements are associated with the acid-insoluble fractions of the sediments and are fixed in the sediments in a solid state. While it is so in regard to the concentrations associated with the AIF of the sediments, the concentrations of these 2 elements associated with the NLF of sediments suggest that they could have been derived from other sources. Considering the fact that oxidizing conditions prevailed throughout the period of sedimentation at the site and clay minerals like montmorillonite appear only in units I, II and IV, it is considered possible that part of Fe and Mn associated with the NLF of the sediments may be tied up with the clay minerals by adsorption and in part with the biogenic phase of the sediments. Higher concentrations of these elements associated with the NLF of sediments of unit I in the case of Fe and of units I and II in the case of Mn than with sediments of other units coupled with their differences in sedimentation rates support this surmise. However, the possibility of some portion of Mn being associated with the authigenic Mn minerals can not be precluded, although there is no information on this aspect.

Partition patterns of Ni, Co and Cu indicate that they have both an acid-insoluble and a non-lithogenous component in these sediments. In the absence of

any discrete minerals of Ni, Co and Cu in the sedimentary column, concentrations of these elements associated with the acid-insoluble fractions of sediments (by way of contributions from AIF to concentrations in the TSS) can be regarded as those in the crystal lattices of various detrital minerals and other acid-insoluble materials that were introduced into the sedimentary column in a particulate state. Thus, differences found in the concentrations of these elements in sediments of different units are related to differences in the nature of the acid-insoluble material present in different units and their relative abundances. While this is so in regard to the concentrations associated with the acid insoluble fraction of sediments, the concentrations of these elements associated with the NLF of sediments may have been fixed in a number of ways. Krauskopff⁹ made an extensive study of factors controlling the concentrations of several trace elements in sea water. He investigated in detail 4 processes, viz. (i) precipitation as insoluble compounds with anions normally present in sea water, (ii) precipitation by sulphide ion in local regions of low oxidation potentials, (iii) adsorption by materials such as ferrous sulphide, hydrated ferric oxide, hydrated manganese dioxide and clay and (iv) removal by metabolic action of organisms. According to Nicholls and Loring¹⁰ and Hirst¹¹ organic carbon can act as an adsorbant for fixing elements like Ni, Co, Cu, etc. in sediments. In the present case, removal of elements through processes (i) and (ii) could be eliminated for obvious reasons. In order to understand the manner of fixation of these elements in other ways, interrelationships obtained between each of these elements and the other constituents of sediments such as calcium carbonate, organic carbon, Fe, Mn, etc. have been attempted and the r values obtained are given in Table 4.

Consideration of the data shows that (i) the 3 elements covary with each other on the total sample basis, (ii) they all show an inverse relationship with the calcium carbonate content, (iii) on the total sample basis, Cu and Ni bear a significant relationship to Fe content of sediments while Co does not exhibit the same trend, (iv) all the 3 elements exhibit a significant correlation with Fe content of the NLF of sediments, (v) conspicuously all the 3 elements do not exhibit any significant relationship with Mn content on the total sample basis while they exhibit a significant relationship with the same element in the NLF of sediments and (vi) Ni and Cu show a significant correlation with the organic carbon content of sediments while Co does not. The manner of fixation of all the 3 elements appear to be same to a large extent in that they are all to a significant measure associated with Fe and Mn of non-lithogenous origin. Apart from this association, another factor contributing to the concentrations associated with the NLF of sediments is by adsorption of these elements on the clays. Thus while more than one process is responsible for the concentrations of the elements associated with the NLF of sediments, the higher concentrations encountered in sediments of unit I than in the other units (with the exception of cobalt) may be attributed to differences in the rates of sedimentation and consequently the rates

TABLE 4 — CORRELATION COEFFICIENT VALUES BETWEEN VARIOUS ELEMENTS IN BULK SAMPLES AND NON-LITHOGENOUS FRACTIONS OF SEDIMENTS

Correlation between	r in bulk samples	Level of significance %	r in the non-lithogenous fraction	Level of significance %
Ni and Co	+0.43	0.05	—	—
Ni and Cu	+0.63	0.001	—	—
Cu and Co	+0.56	0.01	—	—
Cu and CaCO ₃	-0.59	0.01	—	—
Cu and Organic C	+0.46	0.02	—	—
Cu and Mn	+0.08	NS	+0.63	0.001
Cu and Fe	+0.6	0.001	+0.58	0.01
Ni and CaCO ₃	-0.42	0.05	—	—
Ni and Organic C	+0.68	0.001	—	—
Ni and Mn	-0.05	NS	+0.42	0.05
Ni and Fe	+0.77	0.001	+0.62	0.001
Co and CaCO ₃	-0.29	NS	—	—
Co and Organic C	-0.09	NS	—	—
Co and Mn	+0.25	NS	+0.64	0.001
Co and Fe	+0.22	NS	+0.35	0.1

NS = not significant.

of adsorption. Significant correlation obtained between organic carbon and Ni and Cu (in the bulk samples) indicates that part of the concentrations of these elements are associated with the organic matter of sediments perhaps through adsorption.

Though, further partitioning to determine the extent to which the elements are associated with (i) carbonate phase; (ii) clays by adsorption; (iii) moderately reducible phase; and (iv) organic phase is possible, it could not be done due to the paucity of the samples.

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