

Partition Patterns of Al, Fe, Mn, Ni, Co & Cu in the Sediments of the Deep Sea Drilling Project Site 219

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All the elements studied have both lithogenous and nonlithogenous component in the sediments of the DSDP Site 219. Overall distribution patterns of elements and their partition patterns between the two components are described and the processes leading to the incorporation of elements in the sediments are discussed. Relatively higher concentrations of elements associated with lithologic Unit V of the site seem to suggest that the rhyolitic tuffs and the sediments of this unit in association with the montmorillonite and zeolitic clays such as phillipsite and clinoptilolite constitute an important geochemical environment for the accumulation of trace elements.

IN marine environment, major and trace element contents of sediments may be broadly divided into 2 fractions — nondetrital fraction which is removed directly from sea water and detrital fraction which is introduced into the sediment in the solid state. Elemental content of any sediment will have its origin in one or more usually both of these components, and in any discussion on the distribution of elements in oceanic sediments, a distinction between these 2 fractions must be made for proper understanding of the factors governing the distribution of elements in the oceanic sediments. Distribution patterns of some of the elements (Mg, Ti, Mn, Cr, Cu, Ni, Fe, V and Ba) in the sediments of site 219 have been reported earlier by Whitmarsh *et al.*¹ on a semiquantitative basis. Subsequently, Siddiquie *et al.*² have described the overall distribution patterns of Fe, Mn and Ti in these sediments. However, it is not known to what proportions each of the elements studied is of detrital and nondetrital origin. Hence, a detailed study of the partition patterns of various elements has been made with a view to understanding the contributions made by different components of sediments to the concentrations of various elements in the total samples and the processes of their incorporation into the sediments. In the present paper, partition patterns of Al, Fe, Mn, Ni, Co and Cu are described and the possible processes of their incorporation into the sediments indicated.

Site 219 is situated on the Laccadive-Chagos Ridge in the 9° Channel (9°01.75'N, 72°52.67'E). Drilling was done in a water depth of 1764 m and the hole penetrated 411 m below the sea bed. A complete penetration of a stratigraphic sequence ranging from Upper Palaeocene to Recent was achieved.

The shipboard party¹ divided the strata encountered at the site into 5 major units. Subsequently, Siddiquie *et al.*² made substantial changes in the description of Units IV and V.

Methods

Sixty-three samples collected from different levels from Units I to V were utilized in the present study.

Analyses were carried out (i) on the total sediment samples by digesting them with hydrofluoric acid and perchloric acid following the method of Chester and Hughes³ with a view to understanding the concentrations of various elements associated with bulk samples and their 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 lithogenous (LF) and nonlithogenous (NLF) fractions of the sediments to the concentrations in the total sediment sample (TSS). For the estimation of Al the method of Riley⁵ was used. Estimations of Fe and Mn were carried out using 2-2'-dipyridyl and potassium periodate respectively as described in Sandell⁶. Estimations of Ni, Co and Cu were made following the methods given by Chester and Hughes³.

Results

Concentrations of various elements associated with total sediment samples, contributions made by the LF and NLF of the sediments to the concentrations in the total sediment samples are given in Table 1 along with the sample designation and depth below the sea bed. Since the percentage of acid soluble fraction (NLF) varies from sample to sample, for purposes of comparison, concentrations of the elements in the NLF of the sediments have also been computed and given in Table 1. The following partition patterns can be distinguished for various elements studied.

Overall distribution patterns of the elements — On the total sample basis, with the exception of a few low values interspersed in between, sediments of the subunits Vb and Vc are characterized by their highest alumina content while sediments of the subunit Va and the lithological Units II to IV by their lowest alumina content. Sediments of the Unit I have their alumina content in a range intermediate between the ranges encountered in subunits Vb and Vc and the Units II to IV. Highest concentrations of Fe are encountered in subunits Vb and Vc and lowest concentrations in Units II to IV while sediments of the lithologic Unit I and

TABLE 1 — CONCENTRATIONS OF Al, Fe, Mn, Ni, Co AND Cu IN DIFFERENT COMPONENTS OF SEDIMENTS ALONG WITH DEPTH OF SAMPLING BELOW THE SEA BED

| Sample designation | Depth m | Al ₂ O ₃ % | | | | | Fe % | | | | | Mn ppm | | | | | |
|--------------------|---------------|----------------------------------|-------|-------|-------|-------|----------|-------|-------|-------|-------|--------|-----|-----|-------|-------|---|
| | | A | B | C | D | E | A | B | C | D | E | A | B | C | D | E | |
| 219-1-1-44-46 | 0.44-0.46 | 6.73 | 6.64 | 0.09 | 0.11 | 98.66 | UNIT I | 1.22 | 0.08 | 0.1 | 93.44 | 331 | — | — | — | — | |
| 219-1-1-144-146 | 1.44-1.46 | 9.37 | 9.26 | 0.11 | 0.19 | 98.82 | 2.16 | 2.08 | 0.14 | 96.29 | 253 | — | — | — | — | — | |
| 219-1-2-140-142 | 2.9-2.92 | 9.13 | 9 | 0.13 | 0.19 | 98.58 | 1.83 | 1.74 | 0.09 | 95.08 | 326 | — | — | — | — | — | |
| 219-1-3-140-142 | 4.4-4.42 | 9.62 | 9.55 | 0.07 | 0.12 | 98.27 | 2.41 | 2.32 | 0.15 | 96.26 | 253 | — | — | — | — | — | |
| 219-1-4-144-146 | 5.94-5.96 | 8.66 | 8.57 | 0.09 | 0.16 | 98.96 | 2.59 | 2.49 | 0.1 | 96.14 | 253 | 186 | 67 | 116 | 73.52 | — | |
| 219-1-CC | 6 | 9.13 | 8.91 | 0.22 | 0.32 | 97.59 | 1.09 | 0.94 | 0.15 | 86.24 | 253 | — | — | — | — | — | |
| 219-2-1-72-74 | 6.72-6.74 | 8.9 | 8.79 | 0.11 | 0.14 | 98.76 | 1.06 | 0.98 | 0.1 | 92.45 | 331 | — | — | — | — | — | |
| 219-2-1-100-102 | 7.7-02 | 7.69 | 7.65 | 0.04 | 0.07 | 99.48 | 2.41 | 2.32 | 0.09 | 96.26 | 230 | — | — | — | — | — | |
| 219-2-2-85-87 | 8.35-8.37 | 9.37 | 9.28 | 0.09 | 0.15 | 99.04 | 2.07 | 1.96 | 0.11 | 94.68 | 270 | — | — | — | — | — | |
| 219-2-3-60-62 | 9.6-9.62 | 9.37 | 9.26 | 0.11 | 0.21 | 98.83 | 2.29 | 2.2 | 0.09 | 96.07 | 292 | — | — | — | — | — | |
| 219-2-4-100-102 | 11.5-11.52 | 8.16 | 8.09 | 0.07 | 0.1 | 99.14 | 1.86 | 1.77 | 0.09 | 95.16 | 213 | 146 | 67 | 101 | 68.54 | — | |
| 219-2-5-10-12 | 12.1-12.12 | 9.13 | 9.04 | 0.09 | 0.16 | 99.01 | 2.28 | 2.20 | 0.08 | 96.49 | 196 | 23 | 173 | 300 | 11.73 | — | |
| 219-2-5-113-115 | 13.13-13.15 | 4.8 | — | — | — | — | 1.36 | 1.29 | 0.07 | 94.85 | 241 | — | — | — | — | — | |
| 219-2-CC | 15 | 9.13 | — | — | — | — | 2.08 | 1.99 | 0.09 | 95.67 | 270 | 203 | 67 | 105 | 75.18 | — | |
| 219-3-1-100-102 | 16-16.02 | 9.13 | — | — | — | — | 2.44 | 2.36 | 0.08 | 96.72 | 309 | — | — | — | — | — | |
| 219-3-2-118-120 | 17.68-17.7 | 7.22 | — | — | — | — | 1.49 | 1.39 | 0.1 | 93.29 | 202 | — | — | — | — | — | |
| 219-3-3-120-122 | 19.2-19.22 | 8.66 | 8.59 | 0.07 | 0.1 | 99.19 | 1.73 | 1.61 | 0.12 | 93.06 | 241 | 188 | 53 | 76 | 78 | — | |
| 219-3-4-120-122 | 20.7-20.72 | 9.13 | 9.02 | 0.11 | 0.19 | 98.79 | 2.53 | 2.31 | 0.22 | 91.3 | 146 | — | — | — | — | — | |
| 219-4-1-120-122 | 25.2-25.22 | 8.41 | 8.3 | 0.11 | 0.16 | 98.69 | 1.81 | 1.73 | 0.08 | 95.58 | 286 | — | — | — | — | — | |
| 219-4-2-120-122 | 26.7-26.72 | 7.69 | 7.67 | 0.02 | 0.03 | 99.74 | 1.81 | 1.73 | 0.08 | 95.58 | 213 | — | — | — | — | — | |
| 219-4-3-120-122 | 28.2-28.22 | 8.41 | 8.28 | 0.13 | 0.19 | 98.45 | 1.87 | 1.78 | 0.09 | 95.19 | 219 | — | — | — | — | — | |
| 219-4-4-120-122 | 29.7-29.72 | 8.41 | 8.34 | 0.07 | 0.1 | 99.17 | 1.94 | 1.72 | 0.22 | 88.66 | 241 | 148 | 93 | 139 | 61.41 | — | |
| 219-5-1-120-122 | 34.2-34.22 | 9.13 | 9.02 | 0.11 | 0.17 | 98.79 | 1.85 | 1.73 | 0.12 | 93.51 | 298 | 258 | 40 | 61 | 86.58 | — | |
| 219-6-1-120-122 | 43.2-43.22 | 7.69 | 7.56 | 0.13 | 0.19 | 98.31 | 2 | 1.86 | 0.14 | 93 | 230 | 110 | 120 | 174 | 47.83 | — | |
| 219-7-2-120-122 | 53.7-53.72 | 8.66 | 8.45 | 0.21 | 0.31 | 97.57 | 1.73 | 1.59 | 0.14 | 91.9 | 191 | 98 | 93 | 138 | 51.31 | — | |
| 219-8-2-120-122 | 62.7-62.72 | 7.22 | 7.13 | 0.09 | 0.12 | 98.75 | 1.34 | 1.29 | 0.05 | 96.27 | 175 | 168 | 107 | 147 | 61.09 | — | |
| 219-9-1-120-122 | 70.2-70.22 | 6.26 | 6.19 | 0.07 | 0.09 | 98.88 | 1.3 | 1.22 | 0.08 | 93.85 | 285 | — | — | — | — | — | |
| 219-10-1-120-122 | 79.2-79.22 | 6.73 | 6.6 | 0.13 | 0.18 | 98.07 | 1.53 | 1.37 | 0.16 | 89.54 | 287 | 127 | 160 | 215 | 44.25 | — | |
| 219-11-1-120-122 | 83.2-83.22 | — | — | — | — | — | 1.12 | 1.10 | 0.02 | 98.21 | 196 | 76 | 120 | 157 | 38.77 | — | |
| 219-12-2-120-122 | 93.7-93.72 | 4.52 | 4.46 | 0.06 | 0.08 | 98.67 | 1.23 | 1.16 | 0.07 | 94.31 | 196 | 116 | 80 | 110 | 59.18 | — | |
| 219-13-1-120-122 | 120.2-120.22 | 1.85 | 1.85 | — | — | 100 | UNIT II | 0.09 | 0 | 100 | 129 | 9 | 120 | 130 | 6.98 | — | |
| 219-14-1-90-92 | 128.9-128.92 | 0.93 | 0.91 | 0.02 | 0.02 | 97.85 | 0.43 | 0.429 | 0.001 | 99.77 | 129 | 9 | 120 | 129 | 6.98 | — | |
| 219-14-3-105-107 | 132.05-132.07 | 0.91 | 0.89 | 0.02 | 0.02 | 97.8 | 0.12 | 0.115 | 0.005 | 95.83 | 124 | 17 | 107 | 113 | 13.71 | — | |
| 219-14-4-120-122 | 133.7-133.72 | 1.39 | 1.39 | — | — | 100 | 0.13 | 0.128 | 0.002 | 98.46 | 191 | — | — | — | — | — | |
| 219-14-5-129-130 | 135.29-135.3 | 1.53 | 1.49 | 0.04 | 0.04 | 97.38 | 0.37 | 0.369 | 0.001 | 99.73 | 123 | — | — | — | — | — | |
| 219-14-6-15-17 | 135.65-135.67 | 1.09 | 1.08 | 0.01 | 0.01 | 99.08 | 0.24 | 0.239 | 0.001 | 99.58 | 22 | — | — | — | — | — | |
| 219-15-1-5-7 | 156.05-156.07 | 1.08 | 1.04 | 0.04 | 0.04 | 96.29 | UNIT III | 0.2 | 0.183 | 0.017 | 91.5 | 208 | 88 | 120 | 131 | 42.31 | — |
| 219-15-5-100-102 | 163-163.02 | 1.06 | 1.05 | 0.01 | 0.01 | 99.06 | 0.2 | 0.188 | 0.012 | 94 | 152 | — | — | — | — | — | |
| 219-15-5-115-117 | 163.15-163.17 | 1.49 | 1.48 | 0.01 | 0.01 | 99.33 | 0.17 | 0.156 | 0.014 | 91.76 | 181 | — | — | — | — | — | |
| 219-16-6-70-72 | 173.2-173.22 | 1.66 | 1.64 | 0.02 | 0.02 | 98.79 | 0.24 | 0.228 | 0.012 | 95 | 185 | 132 | 53 | 62 | 71.35 | — | |
| 219-18-4-40-42 | 187.9-187.92 | 1.66 | 1.648 | 0.012 | 0.015 | 99.3 | 0.12 | 0.116 | 0.004 | 96.66 | 157 | 77 | 80 | 97 | 49.04 | — | |
| 219-19-6-100-102 | 200.5-200.52 | 2.36 | 2.34 | 0.02 | 0.03 | 99.15 | 0.35 | 0.349 | 0.001 | 99.71 | 230 | 96 | 134 | 173 | 41.74 | — | |
| 219-20-2-120-122 | 203.7-203.72 | 1.78 | 1.76 | 0.02 | 0.03 | 98.87 | 0.29 | 0.288 | 0.002 | 99.31 | 219 | 72 | 147 | 209 | 32.87 | — | |
| 219-21-2-120-122 | 212.7-212.72 | 2.06 | 2.04 | 0.02 | 0.03 | 99.03 | 0.52 | 0.518 | 0.002 | 99.61 | 207 | — | — | — | — | — | |

TABLE 1 — CONCENTRATIONS OF Al, Fe, Mn, Ni, Co AND Cu IN DIFFERENT COMPONENTS OF SEDIMENTS ALONG WITH DEPTH OF SAMPLING BELOW THE SEA BED — *Cont'd*

| Sample designation | Depth m | Al ₂ O ₃ % | | | | | Fe % | | | | | Mn ppm | | | | |
|--------------------|---------------|----------------------------------|-------|------|-------|-------|---------|-------|-------|-------|-------|--------|------|------|-------|-------|
| | | A | B | C | D | E | UNIT IV | | | | | A | B | C | D | E |
| 219-25-1-108-110 | 247-08-247-1 | 1-17 | 1-09 | 0-08 | 0-09 | 93-16 | 0-55 | 0-32 | 0-23 | 0-27 | 53-18 | 3463 | 3383 | 80 | 96 | 97-69 |
| 219-25-1-138-140 | 247-38-247-4 | 3-55 | 3-17 | 0-38 | 0-44 | 88-29 | 0-59 | — | — | — | 864 | 797 | 67 | 78 | 92-94 | |
| 219-26-1-135-137 | 256-35-256-37 | 2-36 | 2-3 | 0-06 | 0-08 | 97-45 | 0-67 | 0-668 | 0-002 | 99-7 | 8476 | 3136 | 5340 | 7275 | 36-99 | |
| 219-27-1-95-96 | 264-95-264-96 | 15-38 | 15-31 | 0-07 | 0-09 | 99-54 | 0-63 | 0-622 | 0-008 | 98-73 | 219 | 126 | 93 | 150 | 57-53 | |
| 219-27-1-148-150 | 265-48-265-5 | 4-61 | 4-59 | 0-02 | 0-02 | 99-56 | 0-3 | 0-283 | 0-017 | 94-33 | 230 | 137 | 93 | 104 | 59-56 | |
| 219-27-3-90-92 | 267-9-267-92 | 1-06 | — | — | — | — | 0-24 | 0-224 | 0-016 | 93-33 | 258 | 163 | 93 | 127 | 63-18 | |
| | | | | | | | UNIT V | | | | | | | | | |
| 219A-3-2-27-28 | 300-77-300-78 | 1-62 | 1-53 | 0-09 | 0-1 | 94-44 | 0-59 | 0-5 | 0-09 | 84-74 | 654 | 346 | 308 | 340 | 52-90 | |
| 219A-4-3-60-62 | 311-6-311-62 | 1-87 | 1-83 | 0-04 | 0-05 | 97-86 | 0-74 | 0-51 | 0-23 | 68-91 | 1043 | 464 | 579 | 652 | 44-87 | |
| 219A-5-2-117-120 | 319-67-319-7 | 3-08 | 3-01 | 0-07 | 0-09 | 97-72 | 2-19 | 1-39 | 0-8 | 63-47 | 860 | 552 | 308 | 417 | 64-19 | |
| 219A-6-2-34-35 | 327-84-327-85 | 4-24 | 4-17 | 0-07 | 0-09 | 96-69 | 2-32 | 1-81 | 0-51 | 78-02 | 896 | 555 | 341 | 450 | 61-92 | |
| 219A-7-3-48-49 | 338-48-338-49 | 16-14 | 16-01 | 0-13 | 0-32 | 98-28 | 8-06 | 7-05 | 1-01 | 87-47 | 1274 | 274 | 1000 | 2445 | 21-51 | |
| 219A-8-2-35-40 | 345-85-345-9 | 6-73 | 6-6 | 0-13 | 0-25 | 98-07 | 3-77 | 2-73 | 1-04 | 72-41 | 442 | 192 | 250 | 483 | 43-44 | |
| 219A-8-5-22-23 | 350-22-350-23 | 9-13 | 8-92 | 0-21 | 1-18 | 97-69 | 3-67 | 2-63 | 1-04 | 71-66 | 581 | 286 | 295 | 1661 | 49-22 | |
| 219A-10-2-127-128 | 364-77-364-78 | 16-52 | 16-14 | 0-38 | 4-03 | 95-39 | 3-67 | 2-63 | 1-04 | 71-66 | 852 | 489 | 363 | 3853 | 57-39 | |
| 219A-10-3-130-131 | 366-3-366-31 | 16-32 | 15-55 | 0-77 | 4-1 | 90-56 | 5-16 | 4-13 | 1-03 | 80-06 | 1096 | 505 | 591 | 3152 | 46-08 | |
| 219A-12-3-115-116 | 384-15-384-16 | 35-57 | 34-55 | 1-02 | 6-61 | 97-13 | 5-69 | 5-51 | 0-18 | 96-84 | 1164 | 891 | 273 | 1770 | 76-54 | |
| 219A-13-2-60-63 | 389-1-389-13 | 6-16 | 5-12 | 1-04 | 13-42 | 83-12 | 3-08 | 2-69 | 0-39 | 87-34 | 637 | 251 | 386 | 4980 | 39-4 | |
| 219A-14-3-32-33 | 405-32-405-33 | 16-14 | 15-93 | 0-21 | 0-41 | 98-69 | 3-8 | 3-62 | 0-18 | 95-26 | 1823 | 1266 | 557 | 1076 | 69-44 | |
| 219A-14-3-138-140 | 406-38-406-4 | 18-32 | 18-83 | 0-49 | 5-53 | 98-38 | 3-62 | 2-63 | 0-99 | 72-65 | 615 | 388 | 227 | 2562 | 63-09 | |
| | | | | | | | UNIT I | | | | | | | | | |
| 219-1-1-44-46 | 0-44-0-46 | 36 | 27 | 9 | 11 | 75 | 19 | 7 | 12 | 36-8 | 56 | 40 | 16 | 20 | 71-43 | |
| 219-1-1-144-146 | 1-44-1-46 | 58 | 49 | 9 | 15 | 84-48 | 20 | 5 | 15 | 25 | 67 | 39 | 28 | 49 | 58-21 | |
| 219-1-2-140-142 | 2-90-2-92 | 52 | 43 | 9 | 14 | 82-69 | 26 | 11 | 15 | 32-41 | 61 | 37 | 24 | 36 | 60-65 | |
| 219-1-3-140-142 | 4-40-4-42 | 57 | 49 | 8 | 13 | 85-96 | 21 | 7 | 14 | 33-33 | 25 | 6 | 19 | 32 | 24 | |
| 219-1-4-144-146 | 5-94-5-96 | 55 | 50 | 5 | 9 | 90-9 | 30 | 18 | 12 | 60 | 72 | 59 | 13 | 23 | 81-94 | |
| 219-1-CC | 6 | 45 | 35 | 10 | 15 | 77-77 | 7 | — | — | — | 22 | 3 | 19 | 28 | 13-64 | |
| 219-2-1-72-74 | 6-72-6-74 | 29 | 23 | 6 | 8 | 79-31 | 18 | 3 | 15 | 16-6 | 7 | 2 | 5 | 7 | 28-57 | |
| 219-2-1-100-102 | 7-7-02 | 56 | 48 | 8 | 15 | 85-71 | 31 | 20 | 11 | 64-52 | 27 | 23 | 4 | 7 | 85-18 | |
| 219-2-2-85-87 | 8-35-8-37 | 44 | 37 | 7 | 12 | 84-09 | 12 | 7 | — | — | 21 | 6 | 15 | 25 | 28-57 | |
| 219-2-3-60-62 | 9-60-9-62 | 60 | 53 | 7 | 14 | 88-33 | 15 | 7 | 8 | 46-66 | 29 | 25 | 4 | 7 | 86-21 | |
| 219-2-4-100-102 | 11-50-11-52 | 45 | 39 | 6 | 9 | 86-66 | 19 | 4 | 15 | 21-05 | 25 | 21 | 4 | 6 | 84 | |
| 219-2-5-10-12 | 12-10-12-12 | 51 | 41 | 10 | 17 | 80-39 | 27 | 15 | 12 | 55-55 | 16 | 10 | 6 | 911 | 62-5 | |
| 219-2-5-113-115 | 13-13-13-15 | 37 | 30 | 7 | 9 | 81-08 | 21 | 11 | 10 | 52-38 | 6 | 4 | 2 | 4 | 66-6 | |
| 219-2-CC | 15 | 51 | 49 | 2 | 3 | 96-08 | 11 | 1 | 10 | 9-09 | 17 | 8 | 9 | 15 | 47-06 | |
| 219-3-1-100-102 | 16-16-02 | 51 | 44 | 7 | 13 | 86-23 | 6 | — | — | — | — | — | — | — | — | |
| 219-3-2-118-120 | 17-68-17-70 | 45 | 37 | 8 | 12 | 82-22 | 7 | — | — | — | 22 | — | — | — | — | |
| 219-3-3-120-122 | 19-20-19-22 | 36 | 30 | 6 | 9 | 83-33 | 13 | 3 | 10 | 23-07 | 11 | 10 | 1 | 4 | 90-9 | |
| 219-3-4-120-122 | 20-70-20-72 | 45 | 36 | 9 | 16 | 80 | 7 | — | — | — | 17 | 13 | 4 | 8 | 36-43 | |
| 219-4-1-120-122 | 25-20-25-22 | 52 | 44 | 8 | 12 | 84-61 | 17 | 3 | 14 | 17-65 | 19 | 3 | 23 | 23 | 15-79 | |
| 219-4-2-120-122 | 26-70-26-72 | 49 | 44 | 5 | 7 | 89-79 | 28 | 15 | 13 | 53-57 | 32 | 23 | 9 | 23 | 71-87 | |
| 219-4-3-120-122 | 28-20-28-22 | 45 | 38 | 7 | 10 | 84-44 | 13 | 3 | 10 | 23-07 | 17 | 16 | 8 | 13 | 52-94 | |
| 219-4-4-120-122 | 29-70-29-72 | 58 | 50 | 8 | 12 | 86-21 | 13 | 3 | 10 | 23-07 | 27 | 16 | 11 | 12 | 59-26 | |

the upper part of Unit V have their concentrations in between. With the exception of highest concentrations of Mn (3463, 864 and 8476 ppm) recorded in samples 25-1-108-110, 25-1-138-140 and 26-1-135-137 in Unit IV, sediments of the Unit V are characterized by uniformly high concentrations of Mn (442-1823 ppm) and sediments of Unit II by uniformly low concentrations. Among the other units, sediments of Unit I have higher concentrations of Mn than sediments of Unit III. Sediments of Unit I and the upper half of Unit IV are characterized by highest concentrations of Ni and sediments of Units II, III, lower half of Unit IV and the subunit Va by the lowest concentrations and sediments of subunits Vb and Vc having their concentrations in between. Highest concentrations of Co are associated with sediments of the Unit V and upper half of the Unit IV and lowest concentrations with sediments of the Units II, III and lower half of Unit IV while concentrations intermediate in range are associated with sediments of Unit I interspersed with low values at a few levels. Maximum concentrations of Cu are encountered in sediments of subunits Vb and Vc and minimum concentrations in the top 45 m of Unit III. Among the other units, highest concentrations are met with in sediments of subunit Va, Unit IV and lower 10 m of Unit III followed by sediments of Unit II and Unit I having their concentrations in the decreasing order.

Contributions made by LF to concentrations in the total sediment sample — Contributions made by LF to concentrations of alumina in TSS broadly follow the overall distribution pattern of alumina in the sedimentary column. But in terms of percentage contributions made by LF to the concentrations in TSS, they are uniformly high throughout the sedimentary column. Contributions made by the LF to concentrations of Fe in TSS are the highest in sediments of the subunits Vb and Vc and the lowest in the sediments of the subunit Va and Units II, III and IV with contributions in the Unit I coming in between. However, in terms of percentage contributions, they are higher in sediments of the Units I to IV than in sediments of Unit V. In the case of Mn, with the exception of few values encountered at levels 27-1-95-96, 27-1-148-150 and 27-3-90-92 in Unit IV, contributions associated with sediments of the Units IV and V are the highest in the sedimentary column and the lowest in the Units II and III while those associated with the sediments in Unit I have an intermediate range. In terms of percentage contributions, while they are the lowest in Unit II, they vary widely in the other units, ranges being 11.7 to 78% in Unit I, 32.8 to 71.4% in Unit III, 36.9 to 97.6% in Unit IV and 21.5 to 76.5% in Unit V. As regards Ni, sediments of Unit I are characterized by higher contributions than sediments in Units II to V. However, in terms of percentage contributions, Ni is higher in sediments of Units I to III than in sediments of Units IV and V. Contributions made by LF to the concentrations of Co in TSS are higher in sediments of subunits Vb and Vc than in sediments of the rest of the sedimentary column. Percentage contributions also exhibit broadly a similar

pattern. Contributions made by LF to concentrations of Cu in TSS broadly follow the overall distribution pattern of Cu in TSS.

Contributions made by NLF to concentrations in TSS and the concentrations associated with NLF of sediments — Contributions made by NLF to concentrations of alumina and Fe in TSS as well as concentrations associated with NLF are the highest in sediments of the subunits Vb and Vc and the lowest in sediments of the subunit Va and Units II to IV while the concentrations intermediate in range are associated with sediments of Unit I. With the exception of the high value at level 26-1-135-137, sediments of Unit V are characterized by higher values of Mn by way of contributions made by NLF to concentrations in TSS as well as concentrations in NLF than in sediments in the rest of the sedimentary column. Contributions made by NLF to concentrations of Ni in TSS are higher in sediments of Unit V and I than those in sediments of Units II to IV. While this is so in regard to the contributions, concentrations associated with NLF of sediments are the highest in sediments of the subunits Vb and Vc and the lowest in sediments of the Units II to IV and Va. Concentrations intermediate in range are associated with sediments of Unit I. Higher concentrations of Co are associated with sediments of I, IV and V by way of contributions made by NLF to the concentrations in TSS than those associated with sediments of Units II and III. In regard to the concentrations of Co in NLF of sediments, the highest concentrations are associated with sediments of Units Vb and Vc and the lowest with the sediments of Units II and III with the concentrations in the sediments of Units I and IV and subunit Va lying in between. Concentrations of copper associated with NLF of sediments of subunit Vc are the highest while those associated with sediments of subunits Va, Vb and lower half of Unit IV, Units III, II and I (except for top 10 m) are the lowest. Concentrations intermediate in range are associated with sediments of the upper half of Unit IV and the top 10 m of Unit I. Contributions made by NLF to concentrations in TSS broadly follow the same pattern.

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 Arhenius⁷ 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 less than 1% is exchangeable. It has been used as an index of the inorganic or argillaceous fraction of sediments because it is located mainly in the aluminium silicates. Fe in marine sediments may be (i) associated with lithogenous ferromagnesian minerals of the sediments^{7,8}, (ii) incorporated directly from sea water⁹ (iii) derived through biological processes^{8,10} and (iv) associated with clay minerals either as essential constituent or as minor constituent within the crystal lattice or as iron oxide on the surface of the mineral platelets¹¹. The origin of

Mn supplied to the deep sea has been discussed^{7,9,12-14} Mn associated with solids is introduced into the oceans as a result of continental weathering or terrestrial or submarine volcanicity. In addition, there are 3 major pathways by which Mn in solution can reach the oceanic sediment surfaces — continental weathering, volcanic activity and migration from subsurface sediments. Large quantities of Mn are introduced into the sea water by hydrothermal solutions associated with submarine volcanism¹⁴. Some of the Mn thus received is undoubtedly precipitated from sea water. Graham¹⁵ has suggested that stable organic complexes of Mn are formed in marine organisms by metabolic processes and that these complexes could act as a source for Mn in nodules/sediments. Goldberg and Arhenius⁷ have indicated that biological processes which involve extraction of Mn from water and its incorporation into foraminiferal tests may make a contribution to the process of bringing Mn to sediment. Li *et al.*¹⁶ and Price and Clavert¹⁷ have provided evidence for the post depositional migration of Mn from reducing zones and its fixation in the oxidizing zones. Ni, Co and Cu are strongly concentrated in deep sea sediments relative to both igneous rocks and nearshore sediments^{7,8,18,19}. Goldberg⁹ has found a linear relationship between Mn and Ni and Fe and Co in the Mn nodules on the basis of which he suggested that Ni and Co have been scavenged directly from sea water by hydrous manganese oxide and hydrous iron oxide respectively. Regarding Cu he has suggested that it apparently follows Mn which suggests that it has been scavenged by hydrous manganese oxide. But according to Krauskopff²⁰ Co can be effectively adsorbed by hydrous ferric oxide. Goldberg and Arhenius⁷ have shown that apart from their occurrence in the ferromanganese minerals, these elements occur in the colloidal fractions of the pelagic sediments and also in the clay mineral lattices. In the case of Cu, a biogenous origin has also been indicated by Revelle *et al.*²¹ for some portion of Cu in the pelagic clays. Both Nichols and Loring²² and Hirst²³ have suggested that there is a correlation between Ni and Co content of the sediments and organic carbon and they consider that the latter acts as an adsorbant. According to Bruty *et al.*²⁴ the palaeo Atlantic zeolitic clays contain higher amounts of Mn, Ni, Co and Cu than either the other palaeo clays in the cores studied by them or the Atlantic deep sea clays.

X-ray analyses of the untreated bulk, 2-20 μm and less than 2 μm size samples^{2,25} drawn from the various stratigraphic units have revealed that calcite is the major mineral in most of the samples except in Unit V where montmorillonite is dominant. Dolomite is the only other carbonate mineral which occurs in traces in Unit I only. K-feldspars are reported from Units I and II. Plagioclase is reported in samples from all the units but particularly higher percentages are noted in Unit V. Among the clay minerals illite/mica and minor amounts of kaolinite and chlorite occur only in Units I and II. Montmorillonite occurs throughout the stratigraphic column in trace or as a major component. It is occurring as the major or main component and over

90% of the less than 2 μm fractions of many samples in Unit V. It is generally associated with plagioclase and traces of clinoptilolite and phillipsite. The other nonclay minerals in Unit V are pyrite and anatase.

Heavy mineral studies² in these sediments have revealed that the assemblage is characterized by hornblende, garnet, anatase, glauconite, collophane, kyanite, epidote, zircon, mica, barite, etc. One conspicuous feature noticed in this mineral assemblage is that it represents 2 different components: a terrigenous component containing hornblende, garnet, zircon, monazite, kyanite, sillimanite, epidote, etc., and an authigenic component containing glauconite, anatase, collophane, etc. The authigenic assemblage marks dominantly the volcanic sediments and rocks of Unit V and lower part of Unit IV whereas the terrigenous assemblage is associated with the overlying biogenous sediments.

Partition patterns of alumina coupled with the calcium carbonate content of the sediments indicate the inorganic nature of the sediments of subunits Vb and Vc, the biogenic nature of the sediments of subunit Va and Units IV, III and II and the mixed nature of the sediments of Unit I. They further indicate that most of the alumina in the sediments is fixed in the sediments in the solid state and that the contribution from the non-lithogenous sources is negligible except in the sediments of the subunits Vb and Vc. Thus while the differences in the alumina content of the sediments in the different units can be attributed to the differences in the mineralogy of the sediments including their clay minerals and their relative abundances, the higher alumina content associated with the non-lithogenous fraction of the sediments of the subunits Vb and Vc may be attributed to the association of the authigenic clay minerals like phillipsite and clinoptilolite with them. Siddiquie *et al.*² described the overall distribution patterns of iron and manganese in these sediments and discussed at length the manner of their fixation in the sediments. According to them, the iron content of the sediments may be largely attributed to the iron and titanium bearing minerals occurring in the different units, the volcanic glass and volcanic ash occurring in Unit I and to the montmorillonite clay occurring in subunits Vb and Vc. They further indicated that most of the iron in the sediments is tied up with the detrital material. While the partition patterns of iron do substantiate their observations, they also indicate that a considerable amount of iron in Unit V is derived from non-lithogenous sources and fixed in the sediments. This could be attributed to the authigenic minerals like anatase, pyrite, glauconite and clay minerals like phillipsite and clinoptilolite associated with these sediments. In regard to Mn, Siddiquie *et al.*² have indicated that in Unit V it is largely associated with the montmorillonite and pyroclastics while in the upper 4 units, a major part of it may be biogenic though part of it may be associated with the detrital material. Partition patterns of Mn also indicate that a considerable amount of Mn is derived from non-lithogenous sources and considering the nature of the sediments and their mineralogy it is quite likely that it is

associated with the biogenic material in Units I to IV and with volcanic material in Unit V. Partition patterns of Ni, Co and Cu indicate that they have both a lithogenous and nonlithogenous component in these sediments. In the absence of any discrete minerals of Ni, Co and Cu in the sedimentary column, concentrations of these 3 elements associated with LF of sediments (by way of contributions from LF to the concentrations in TSS) can be regarded as those associated with the crystal lattice of the various detrital minerals that were introduced into the sedimentary column in a physical state. Thus the differences found in the concentrations of these elements in sediments of the different units are related to the differences in the nature of the detrital minerals and other acid insoluble biogenic materials such as diatoms present in different units and their relative abundances. While this is so in regard to the concentrations associated with LF of sediments, concentrations of these 3 elements associated with NLF of sediments may have been fixed in a number of ways in sediments. In order to understand the manner of their fixation in sediments, inter relationships obtaining between each of these elements and the other constituents of sediments such as calcium carbonate, organic carbon, Fe, Mn etc., have been attempted and correlation coefficient (r) values obtained are given in Table 2.

A consideration of the data shows that the 3 elements covary with each other in NLF of sediments and further they bear a significant relationship with Fe and Mn contents of this fraction. This is suggestive of the fact that the 3 elements have been fixed in the sediments in association with Fe and Mn contents of non-lithogenous origin. Thus differences found in the concentrations of these elements in the different units seem to be related to differences in the contents of Fe and Mn of non-lithogenous origin. On the total sample basis also, all the 3 elements bear a significant relationship with Fe while with Mn only cobalt bears a significant relationship. This only confirms the fact that all the 3 elements are to a great extent fixed in the sediments through the detrital minerals and that the sources for Fe and Mn are different as indicated by Siddiquie *et al.*². The relationship with organic carbon indicates that part of the Co and Cu are fixed in sediments through adsorption by the organic carbon. Thus it can be seen that apart from the fixation of these elements in sediments in association with detrital minerals and or acid insolubles in a physical state, they are also fixed in sediments in association with Mn and Fe of nonlithogenous origin and through adsorption by organic carbon.

Based on the mineralogy and geochemistry of sediments, Siddiquie *et al.*² divided sediments at site 219 into 2 types — dominantly volcanic rocks and sediments of Palaeocene (subunits Vb and Vc) and biogenous sediments of Units IV, III, II and I. Higher concentrations of the various elements associated with the total samples as well as NLF of the sediments of Unit V suggest that sediments and tuffs of Unit V in association with the montmorillonite clay and other authigenic clays like

TABLE 2 — CORRELATION COEFFICIENT (r) VALUES BETWEEN VARIOUS ELEMENTS IN DIFFERENT COMPONENTS OF THE SEDIMENTS

| Correlation between | r value in bulk samples | r value in the NLF of the sediments |
|--------------------------|---------------------------|---------------------------------------|
| Calcium carbonate and Ni | -0.26 | — |
| Calcium carbonate and Cu | -0.62 | — |
| Calcium carbonate and Co | -0.34 | — |
| Organic carbon and Ni | 0.09 | — |
| Organic carbon and Cu | 0.41 | — |
| Organic carbon and Co | 0.51 | — |
| Fe and Ni | 0.33 | 0.69 |
| Fe and Cu | 0.64 | 0.85 |
| Fe and Co | 0.59 | 0.80 |
| Mn and Ni | -0.06 | 0.75 |
| Mn and Cu | 0.26 | 0.53 |
| Mn and Co | 0.59 | 0.74 |
| Cu and Co | — | 0.86 |
| Cu and Ni | — | 0.46 |
| Ni and Co | — | 0.86 |

clinoptilolite and phillipsite constitute an important geochemical environment for the trace element accumulation.

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