

## Distribution of Iron, Manganese & Titanium in Sediments of Deep Sea Drilling Project Site 220 in the South-Eastern Arabian Sea

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Sediments of lithologic Unit I are characterized by relatively higher concentrations of iron and titanium than the sediments of Units II, III and IV. Sediments of Unit IV and lower half of Unit III are characterized by higher concentrations of manganese than the sediments from the rest of the sedimentary column. All the 3 elements are largely fixed in sediments in a solid state. However, they seem to have entered the site through different paths in that iron and titanium appear to be more associated with the clay minerals of **detrital** origin while manganese is to a large extent associated with the volcanic material which the site received intermittently. **Distribution** patterns observed are in conformity with the depositional history of the site.

**D**EEP Sea Drilling Project has drilled 3 holes in the south-eastern Arabian Sea during March 1972. Site 220 (long.  $70^{\circ}59'02''E$ , lat.  $6^{\circ}30'97''N$ ) the sediments of which form the subject matter of this paper, is situated on a broad irregular platform which lies west of the nearby Laccadive-Chagos Ridge and east of the deeper Arabian Sea Abyssal plain. Drilling was done in a water depth of 4036 m and the hole penetrated 350 m below the sea bed. A complete penetration of Pleistocene through lower Eocene strata plus the underlying oceanic basalt was recorded at this site.

Limited data on the distribution patterns of the trace elements (Mg, Ti, Mn, Cr, Cu, Ni, Fe, V and Ba) have been reported earlier by Whitmarsh *et al.*<sup>1</sup>. The authors have taken up a detailed study of these sediments aimed at understanding (i) overall distribution pattern of various elements in relation to the depositional history of the sites, (ii) contributions made by the different components of sediments to the absolute concentrations of various elements in the total sediment samples, and (iii) processes of incorporation of elements into sediments. As a part of these studies, the overall distribution patterns of iron, manganese and titanium in the sediments of site 220 have been worked out and the same are described in this paper in relation to the depositional history of the site.

### Lithology

The shipboard party<sup>1</sup> divided the strata encountered at the site into 5 major units on the basis of the visual examination, compositional variations noted on the smear slides, carbonate analyses, etc. The lithologic units are summarized in Table 1 and the site summary is given in Fig. 1.

### Methods

In all 24 samples collected from different levels covering the Units I to IV were utilized in the present study. All the samples were digested with hydro-

fluoric acid and perchloric acid following the method of Chester and Hughes<sup>2</sup>. Iron, manganese and titanium were estimated spectrophotometrically. For the estimation of iron and manganese, 2,2'-dipyridyl and potassium periodate were used respectively as described in Sandell<sup>3</sup>. Titanium was estimated using the hydrogen peroxide reagent as described by Riley<sup>4</sup>. For purposes of understanding the relationship obtaining between (i) calcium carbonate and iron, manganese and titanium, (ii) acid insolubles and iron, manganese and titanium, calcium carbonate and percentage of acid insolubles were also estimated in the sediments. Calcium carbonate and percentage of acid insolubles were estimated following the methods of Muller<sup>5</sup> and Chester and Hughes<sup>6</sup> respectively. Further, percentage contributions made by the lithogenous fraction to the concentrations of iron and manganese in the total sediment samples have also been estimated after leaching sediments with the acid reducing mixture suggested by Chester and Hughes<sup>6</sup>.

### Results

Values of iron, manganese, titanium, calcium carbonate, percentage of acid insolubles and percentage contributions made by the lithogenous fraction to concentrations of iron and manganese in the total sediment samples are given in Table 2 along with the sample designation and depth below the sea bed. Depthwise distribution of iron, manganese and titanium is also depicted in Fig. 2. Relationships obtaining between (i) percentage of acid insolubles and iron, manganese and titanium, (ii) calcium carbonate and iron, manganese and titanium, and (iii) iron and titanium, iron and manganese, and manganese and titanium, are shown in scatter plots (Fig. 3).

A careful examination of the data has revealed the following distribution patterns for elements under study:

Sediments of Unit I are characterized by relatively higher concentrations of iron and titanium

TABLE 1 - SUMMARY OF LITHOLOGIC UNITS

Lithologic unit	Description	Age	Sub-bottom depths m	Cores	Range of	
					CaCO <sub>3</sub> %	Acid insolubles %
I Orange to brown detrital clay and detrital clay nanno ooze. Few sand beds	Sediments are massive and soft and consist of nanno detrital clay with intervals of detrital clay nanno ooze. Sediments are occasionally glass, foram or spicule bearing. Thin foram sand layers with sharp upper and lower bedding contacts could be distinguished at a few levels	Middle Miocene through Late Pleistocene	0-69	1-5	11-67	39-81.9
II White nanno ooze and chalk	Sediments in this unit differ from those in Unit I in their white colour and gradual appearance of well bedded chalk intervals alternating with nanno oozes. Nanno chalk bands are of varying thickness and they and the nanno ooze contain about 95% of the nanno fossils. The unit is locally sponge spicule, foram or rad bearing and sometimes volcanic glass rich	Late Eocene through Early Miocene	69-220	6-11	76.8-92.8	6-21
III Light orange rad spicule rich nanno ooze/chalk with thin ash beds	Radiolaria and sponge spicules are significant constituents of this unit. Minor amounts of forams, micarb and volcanic glass are present in this unit. A number of thin ash beds and a few black scattered ashy spots also occur in this unit	Middle through Early Eocene	220-290	12-16	62.2-70.7	25-32.9
IV Light orange micarb-rich nanno chalk with thin chert beds	This unit consists of massive light orange micarb-rich nanno chalk with chert bands. Many intervals in this unit are foram, spicule-rad or volcanic glass bearing. At its base, the unit is in contact with basalt. For about 115 cm above the contact, the sediments have a pale yellowish green colour and exhibits lamination. There is no visible effect of the underlying basalt on the sediment	Early Eocene	290-329	16-18	68-68.2	28.5-32.4
V Basalt flows with thin inter-bedded sediment layers	This unit is represented by basaltic flows and by 2 thin inter-bedded sediment layers. At least 6 flows could be distinguished based on the chilled margins which are tan in colour. Chilled zones consist of an outer layer of unaltered brown glass grading downwards into variolitic basalt consisting of spherules of plagioclase and pyroxene. Several zones of glass on top surface of flows and sparse vesiculation in the basalts indicate extrusion of lava on the ocean floor. Rock is extremely fresh and no secondary alteration could be detected. Calcareous sediments occur in a 4 and 0.5 cm bed in cores 19 and 20 respectively. Lowest sediment bed is 15 m above the base of the deepest penetrated basalt which suggests that additional deeper sediment layers are not present	Undated	329-350	18-21	Not determined	

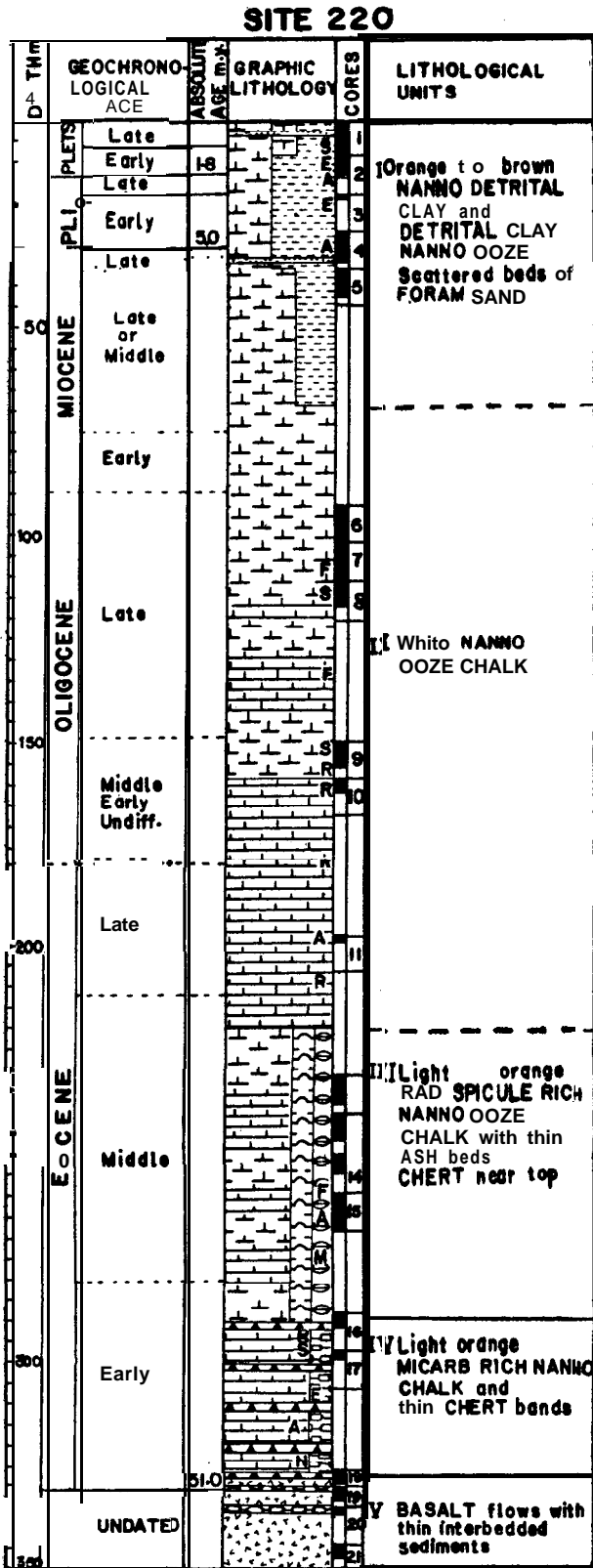


Fig. 1 — Lithological summary of site 220

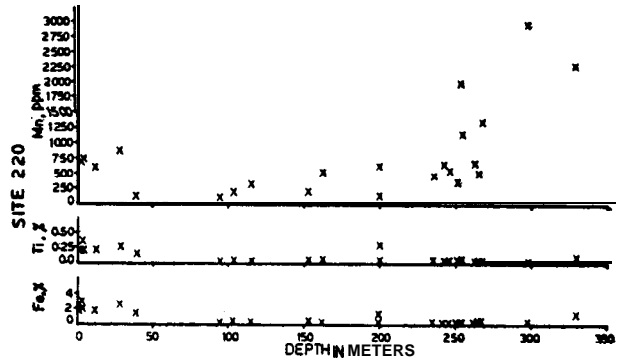


Fig. 2 — Vertical distribution of iron, titanium and manganese in sediments

than sediments of Units II to IV. Manganese in sediments shows a somewhat different distribution pattern. Except for the concentrations at the levels 15-2-131-133 and 15-S-48-50, highest concentrations of manganese (1145-2941 ppm) are encountered in the sediments of Unit IV and the lower half of Unit III while the lowest values (less than 400 ppm) are encountered at the top and bottom portion of Unit I, upper half of Unit II and its bottom portion and at the level 14-1-63-65 in Unit III. The sediments at other levels in the sedimentary column are associated with concentrations ranging from 460 to 876 ppm.

Iron and titanium contents of sediments broadly follow the distribution pattern of the percentage of acid insolubles in the sediments. Manganese content of sediments does not show any such trend with the percentage of acid insolubles (Fig. 3).

Iron and titanium contents of sediments exhibit a significant inverse relationship with the calcium carbonate content of sediments while the manganese content does not show any such relationship (Fig. 3).

Iron and titanium covary in these sediments. Manganese does not show any relationship with iron and titanium.

#### Discussion

Distribution pattern of the percentage of acid insolubles shows that the highest percentages are associated with the sediments of Unit I and the lowest percentages are associated with the sediments of Unit II while the values in between are associated with the sediments of Units III and IV. X-ray diffraction analyses carried out by Matti *et al.*<sup>7</sup> on the samples taken from Units I to IV have revealed that the clay mineral assemblage in Unit IV is dominated by montmorillonite while in the Units I and II it is characterized by a multi-mineral assemblage suggesting derivation from different sources. Bulk samples analyses show that in Units II to IV calcite occurs as the only constituent mineral while in Unit I along with calcite, quartz and mica occur in considerable amounts and dolomite, K-felspar, plagioclase, kaolinite, chlorite and montmorillonite in trace amounts. On the whole, the analysis has not revealed the presence of any discrete minerals of iron, manganese and titanium in the sedimentary column. Considering the fact that favourable conditions did

TABLE --CONCENTRATIONS OF IRON, MANGANESE AND TITANIUM IN SEDIMENTS ALONG WITH DEPTH OF SAMPLING AND PERCENTAGES OF CALCIUM CARBONATE, ACID INSOLUBLES (AI) AND CONTRIBUTIONS MADE BY LITHOGENOUS FRACTION. (LF) TO THE CONCENTRATIONS OF IRON AND MANGANESE IN THE TOTAL SEDIMENT SAMPLES (TSS)

Unit	Sample No.	Depth m	Fe %	Mn ppm	Ti %	CaCO <sub>3</sub> %	AI %	Per cent contri. by LF to concentrations of iron and manganese in TSS	
								Iron	Manganese
I	220-1-1-120-122	1-2-1-22	1.82	258	0.21	58.7	39	90.1	63.9
	220-1-2-120-122	2-7-2-72	2.95	679	0.35	37	58.7	97.6	94.1
	220-1-3-120-122	4-2-4-72	1.92	73s	0.21	53	44	96.3	92.8
	220-2-3-102-105	13-02-13-05	1.77	584	0.2	52.8	40	95.9	86.3
	220-4-1-120-122	28-2-28-22	2.63	876	0.27	44.2	50.8	98.1	89.4
	220-5-2-120-122	38-7-38-72	1.42	122	0.14	63.6	33.8	97.9	93.5
II	220-6-1-120-122	94-2-94-22	0.22	118	0.033	92.6	6	90.9	55
	220-7-1-120-122	103-2-103-22	0.35	185	0.042	80.2	10.8	97.1	71.3
	220-8-3-120-122	115-2-115-22	0.29	320	0.038	92.8	6	96.5	83.4
	220-9-2-120-122	152-7-152-72	0.49	196	0.059	89.4	10	97.1	72.9
	220-10-2-120-122	162.7-162.72	0.35	511	0.05	86.6	12.8	97.1	84.3
	220-11-1-105-107	199-199-02	1.3	623	0.31	76.8	21	91.5	85.1
	220-11-1-120-122	199-2-199-22	0.24	140	0.031	89.8	9	91.6	33.6
III	220-12-2-120-122	234-7-234-72	0.35	460	0.05	70.4	25.0	85.7	85.4
	220-13-1-87-89	241-87-241-89	0.36	651	0.06	67.4	30	94.4	93.8
	220-13-4-5-7	245-55-245-57	0.28	550	0.056	70.7	28	96.5	—
	220-14-1-63-65	250-63-250-65	0.33	365	0.059	69.3	27.5	96.9	89
	220-14-3-45-47	253-45-253-47	0.24	1145	0.059	70	27	87.5	96.5
	220-14-3-120-122	254-2-254-22	0.27	1977	0.058	62.2	32.9	89.3	92.6
	220-15-2-131-133	261-81-261-83	0.37	668	0.04	69.3	29	89.1	92.1
	220-15-5-48-50	265-48-265-5	0.39	511	0.054	65.4	31.5	91.4	91.9
	220-1 5-6-47-49	266.97-266.99	0.34	1353	0.035	66.9	29.5	97	94.1
IV	220-17-1-45-47	297-45-297-47	0.5	2941	0.025	68.2	28.5	94	98.6
	220-18-2-118-120	328-68-328-7	1.37	2251	0.09	68	32.4	95.6	97.6

not exist for the formation of authigenic clay minerals, clay mineral assemblages encountered in the sedimentary column are regarded mostly as of detrital origin\*. Clay mineral assemblage in Unit IV suggests a volcanic source while assemblage in the Units I to III suggests derivation from different sources such as southerly transport of Indus River sediments transported through the water column, the Arabian Sea eolian source to the west and a Deccan Trap source to the east and the Carlsberg Ridge to the west. It may be mentioned here that although montmorillonite could have been derived from sources such as Carlsberg Ridge, the Deccan Traps on the Indian Peninsula could also be regarded as a source for the montmorillonite to some extent. This was shown by Goldberg and Griffin for the present day sediments.

Iron and titanium contents of sediments bear a significant inverse relationship to the calcium carbonate content of sediments. This clearly suggests that the carbonate phase (mainly biogenic) is not a significant contributor of these elements. In the absence of any reducing zones in the sedimentary column, fixation of elements with sulphide ion is also ruled out. This is also borne out by the absence of sulphide minerals in X-ray analyses. The relationship between the percentage of acid insolubles and the iron and titanium contents of the sediments and the linear relationship between iron and titanium suggest that acid insolubles in sediments are the major source for iron and titanium in sediments and that there is a close relationship between iron and tita-

nium in sediments. Hence, it is quite likely that iron and titanium contents of sediments are to a large extent derived through clay minerals and to a small extent through volcanic glass and ash. The fact that major part of these elements are associated with acid insolubles is supported by the percentage contributions made by the lithogenous fraction to concentrations in the total sediment samples estimated and given in Table 2 for iron. In view of the close relationship obtaining between iron and titanium, it holds good for titanium too.

Manganese in the sediments exhibits a distribution pattern altogether different from that of iron and titanium. Highest concentrations of manganese are encountered in the basal sediments (Unit IV and upper half of Unit III) and not in the sediments of Unit I as in the case of iron and titanium. In the rest of the sedimentary column, values ranging from 460 to 876 ppm are encountered at different levels interspersed with values less than 400 ppm. In short it can be said that its distribution in the Units I, II and upper half of Unit III is a bit random one. Manganese content of sediments does not bear any relationship to the calcium carbonate content of sediments indicating that it is not bound with the carbonate phase of sediments (mainly biogenic). Highest concentrations of manganese associated with basal sediments of the sedimentary column and the absence of reducing zones in the sedimentary column shows that migration of manganese from one level to another has not given rise to the pattern of distribution observed (in Units II, 1 and upper half of III).

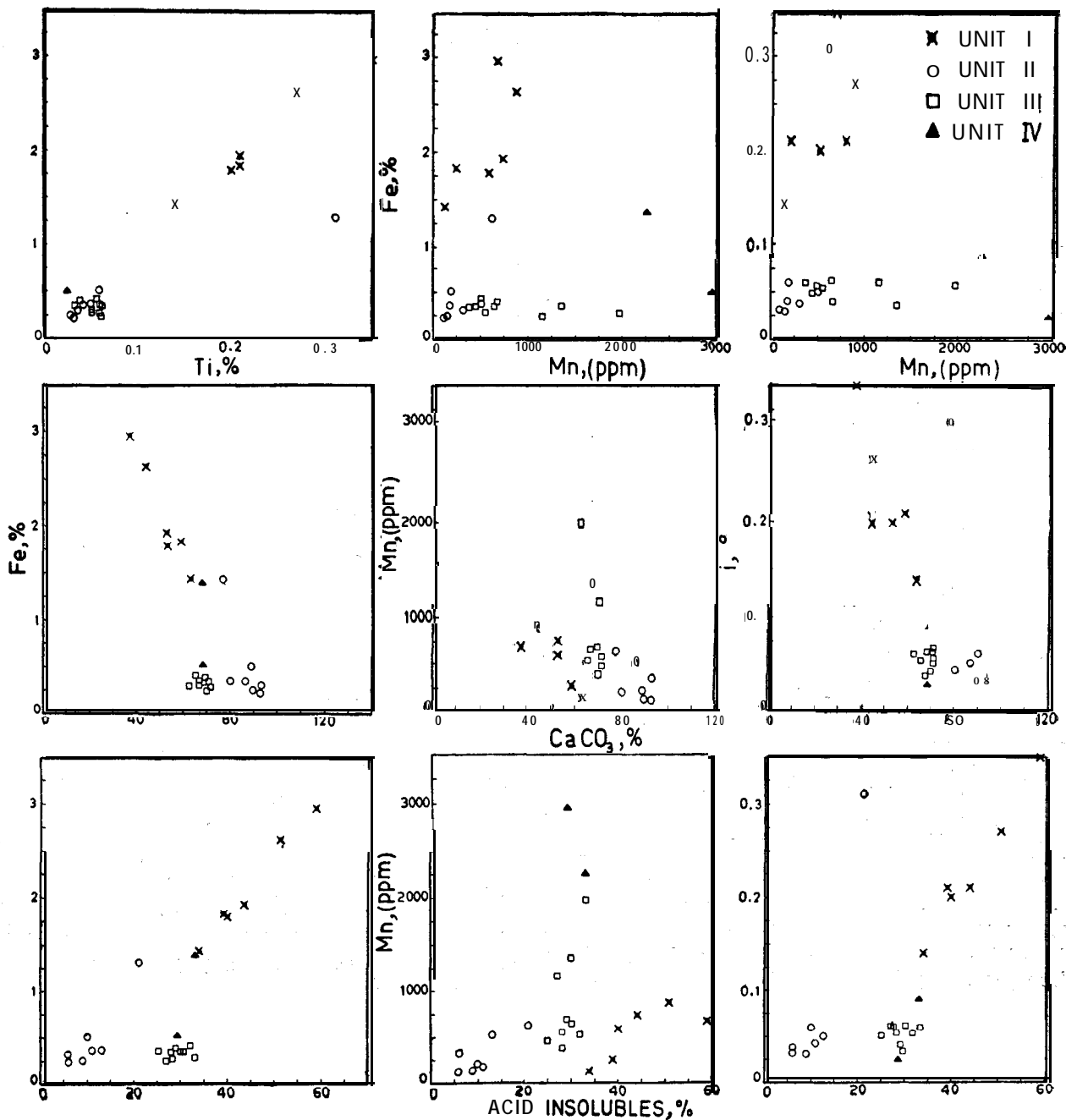


Fig. 3 — Scatter plots showing relationships between (i) per cent of acid insolubles and iron, manganese and titanium, (ii) CaCO<sub>3</sub> and iron, manganese and titanium, (iii) iron and titanium, manganese and iron and manganese and titanium

Manganese content of sediments does not show any significant correlation with the percentage of acid insolubles in sediments. This shows that apparently it is not tied up with acid insolubles of sediments. However, peculiarly enough, percentage contributions made by lithogenous fractions to the concentrations in the total sediment samples (Table 2) indicate that major portion of manganese is introduced into the environment in a solid state only and not through chemical precipitation or adsorption, etc. One inference that can be drawn here is that, no doubt, manganese has been introduced into the sediment column in a solid state

and yet if there is no relationship between the manganese content and the percentage of acid insolubles in sediments it could be due to either the material contributing to the manganese content in sediments may be forming only a small fraction of the acid insoluble material present in the sediments or the material contributing to manganese content may be having a random distribution in the sediment column and thus giving rise to a random distribution for manganese. A close examination of the occurrence of manganese in higher 2 ranges shows that they are invariably associated with the presence of volcanic glass or volcanic ash material while

sediments with manganese content below 400 ppm, are free from volcanic material. It, therefore, appears that the distribution of manganese is more related to the volcanic material that the site received during different periods of the depositional history of the site and to a small extent to the other constituents of the acid insolubles.

A consideration of the depositional history of the site<sup>1,8</sup> shows that the formation of igneous oceanic crust ceased in Early Eocene times at site 220. The sparse vesiculation and the formation of glass at the top surfaces of the basaltic flows indicate a deep water and extrusive origin for the basalts. The presence of 2 thin sediment layers between the basalt flows indicate that short periods of sedimentation were interspersed with the last phase of extrusion of basalts. Soon after the cessation of the formation of the igneous crust, biogenic sedimentation started taking place at the site and the deposition of nanno fossil oozes was accompanied by large amounts of radiolaria and sponge spicules. The presence of a well preserved foraminiferal assemblage near the bottom of the stratigraphic column in the Eocene oozes of Unit IV attests to the relatively shallow water aspect of the deep water fossils as they accumulated at the crest of a spreading ridge. The surface productivity and the shallow depositional depth resulted in an initial high rate of sediment accumulation during Early Eocene and Late Eocene. By Late Eocene, the surface productivity had ceased and the site started migrating into increasing water depths. The abundance of siliceous tests dropped of considerably from earlier Eocene occurrences and the pure nanno fossils, few foraminifera and slightly larger amounts of radiolaria and sponge spicules were the only source of sediment constituents which accumulated during the period between Late Eocene and Late Oligocene. The fact that the site passed into deeper waters is shown by the most corroded aspect of the foraminiferal assemblage and by the reduction in depositional rates to between 6 and 12 m/m.y. A major change in the depositional regime occurred

in Middle Miocene times when the continuous sediment accumulation consisting of nearly equal proportions of nanno fossils and the detrital brown clays started taking place and is continuing to the present day at the site. Occurrence of glass at places in different parts and thin ash beds indicate an intermittently active volcanic provenance.

Distribution patterns of iron, manganese and titanium obtained in the sediments are in close conformity with the depositional history of the site too in that the sediments representing periods of biogenic sedimentation are characterized by low concentrations of iron and titanium while the sediments consisting of a mixture of brown clays and nanno oozes are characterized by higher concentrations of these elements and the manganese content of the sediments to a large extent controlled by the volcanic material that the site received intermittently.

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