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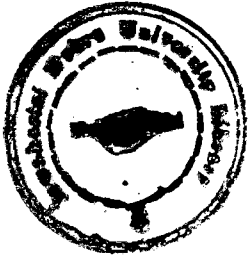
TRACE ELEMENT GEOCHEMISTRY OF A SEDIMENT CORE FROM ARABIAN SEA

**A DISSERTATION SUBMITTED TO THE JAWAHARLAL NEHRU UNIVERSITY
IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF PHILOSOPHY**

BY

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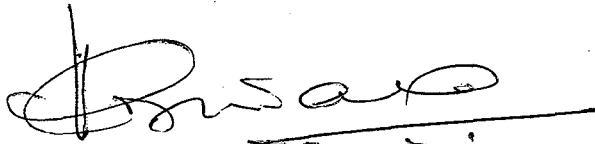
**SCHOOL OF ENVIRONMENTAL SCIENCES
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI - 110067
1987**



DEDICATED TO PARENTS AND GRANDPARENTS

CERTIFICATE

Certified that the work embodied in this dissertation entitled "TRACE ELEMENT GEOCHEMISTRY OF A SEDIMENT CORE FROM ARABIAN SEA", has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted in part or in full for any other degree or diploma in this or in any other University.



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DKS

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ABBREVIATIONS USED

| | |
|-----|-------------------------------------|
| AAS | Atomic Absorption Spectrophotometer |
| M/S | Mud/Sand |
| OM | Organic Matter |
| PC | Principal Component |
| ppm | parts per million |

CHAPTER I

INTRODUCTION

Elements present in crustal rocks are also present in deep-sea sediments. Obviously, the concentration of the elements may differ from those of continental and near-shore sediments to deep-sea sediments. In some of the cases, deep-sea sediments have characteristic trace element assemblages which are indicative of a particular set of conditions of marine environment.

In oceanic conditions, besides detrital fraction, nondetrital fraction is also very important which refers to the selective removal of trace elements from sea water and further incorporation into the sediments.

Thus, the overall concentration and distribution of trace elements are governed by various factors-physical, chemical and biological. Physical variables are: nature and source of sediment supply, water current direction, wind current direction, depth etc. Eh, pH, ΣCO_3 and ΣS etc. are important chemical factors. Nature of biological organisms and organic matter do also play very important

role. These factors, besides others, are responsible for lateral as well as vertical variations in trace element concentrations.

There have been relatively few investigations on the geochemistry of the deep-sea sediments from the Arabian Sea and thus we have little knowledge about the nature of the chemical constituents of these sediments, their sources and their conditions of deposition. Especially, it is true for continental slope regions.

It is important to know the sediment contributions and distribution patterns from all sources all along the continental boundary. Of particular interest is the knowledge about the characteristics, deposition rates and the chemistry of the continental shelf and continental slope sediments. Studies on these sediments not only help to understand the variations in climate, weathering patterns in the adjacent landmasses but also throw light on the possible changes in the chemistry and mineralogy of the materials that are likely to reach the deep-sea.

A continuous section of the sediments provides a good opportunity to examine the changes in the hydrography

and hydrochemistry of a basin which is reflected in the geochemistry of the accumulated sediments. It provides a record of varying oxic and anoxic marine conditions. Given the large variability in space and time of the hydrodynamic processes and the great diversity of possible sources of material able to supply deep-sea sediments, these parameters seem likely to provide important information for sedimentological reconstructions.

It is also worth analysing the correlation coefficients among the different trace elements and also their relation with organic matter, carbonate content, texture etc.

The R-mode factor analysis provides a better insight to the multicomponent complex system and the relationship among different variables and its effect on others.

CHAPTER II
PREVIOUS WORK

2.1 ARABIAN SEA

The Arabian Sea has an area of 7.5 million square kilometers (exclusive of the Gulfs of Aden and Oman; Schott, 1935; cited in Goldberg and Griffin, 1970) where the southern boundary extends from the Indian coast near Goa, along the west side of the Laccadive Islands to the equator and thence to a point on the East African coast near Mombasa at about 5°S.

2.2 EVOLUTION OF WESTERN CONTINENTAL MARGIN OF INDIA

It is generally accepted that the Arabian Sea evolved by sea-floor spreading following the break up of the Gondwanaland. The evolutionary history of the Arabian Sea is derived in large part from the study of magnetic anomalies. The western basin is underlain by oceanic crust and was generated by the process of sea-floor spreading beginning about 63 m.y. ago (Valdiya, 1984). It has been suggested by Naini (1980) that the crust under this basin was generated by a thermally induced process during which the continental crust was subject to extensional forces that

thinned and ruptured it. This was followed by dyke injection and extensive volcanism extending over a very wide region, rather than along a narrow central rift such as at the mid-oceanic ridges.

The northeastern Arabian Sea is suggested to have a two phase evolutionary history (Naini, 1980). The western margin of India, and the adjoining eastern basin, evolved by a process of rifting during the Late Cretaceous. During the phase of rifting, the Cambay graben, the eastern basin and the Chagos - Laccadive ridge - Laxmi Ridge complex came into existence. Beginning in the Early Paleocene, active sea-floor spreading began along centres of spreading, oriented east-west, during which the western basin began to evolve. During the phase of active sea-floor spreading, the western margin of the eastern basin i.e. the western boundary of the Laxmi and Chagos-Laccadive ridge complex experienced shearing, thus, making it a shear boundary. During this same period, some of the crust within the eastern basin generated by initial phase of rifting, may have been sheared. This, therefore, would have obscured the original nature of the crust, underlying the eastern basin, and western margin of India, and given rise to the present, complicated nature of setting along the western margin of India.

2.3 GEOMORPHIC FEATURES

The Chagos-Laccadive Ridge is a linear north-south ridge that extends for over 2200 km. between the Chagos archipelago at about 10° S and the Laccadive Islands at about 12° N. It is a slightly arcuate aseismic ridge with the convex side facing to the east. The Kavaratti and Kalpeni atolls have developed on the Chagos-Laccadive ridge during several sea-level changes (Mallik, 1979).

A NW-SE isolated submarine structure was detected during R/V Conrad cruise in 1974 and was subsequently named as the Laxmi Ridge (Naini, 1980), which may extend further to the NW beneath the sediments of the Indus Cone.

Murray Ridge has an isolated and elongated topographic features such as guyots, seamounts and trenches. The Murray Ridge is believed to be a continuation of the geanticlinal structure of West Pakistan into the Gulf of Oman (Rao, 1976). Barker (1966; cited in Rao, 1976) had concluded that the Murray Ridge is unlikely to be of continental origin and is probably a volcanic complex.

The Indus Cone was formed by deposition of the sediments brought into the Arabian Sea by the Himalayan

river, the Indus, discharging 48×10^{10} gm/yr of sediments into the Arabian Sea (Holeman, 1968) which helps to build the submarine cone. The Fig. 1 (after Naini, 1980) depicts the main topographical features of Indian Ocean and adjoining area.

2.4 NATURE OF SEDIMENTS

In the Arabian Sea, the main potential sources of elements to marine sediments include terrigenous detritus, organic remains, the products of modern submarine volcanic activity from the Carlsberg Ridge, the alteration of ancient volcanic rocks and authigenic minerals. The Arabian Sea receives its fluvial input primarily from the Indus river which drains the Himalayas, Pakistan and northwest India. A number of smaller rivers, chiefly the Narmada and Tapti drain the middle portion of India where the soils are derived from the weathering of the Deccan traps. The Persian Gulf and the Red Sea are not considered as important sources of sediment to this basin (Goldberg and Griffin, 1970).

Wind borne transport of terrigenous material to the northwestern Indian Ocean may also be effective although

Kolla et al. (1976) have suggested that it is dominant only in the western part. However, using mineralogical tracers, Goldberg and Griffin (1970) have suggested an aeolin contribution to sediments in the north western Indian Ocean from both the Rajasthan desert and the Deccan traps in India while Aston et al. (1976) favoured the Rajasthan desert as the principal source. Also input from the deserts of Somalia and Arabia has been suggested by Goldberg and Griffin (1970) and Kolla et al. (1976) as possible aeolin sources.

Sinking organic remains will also supply a proportion of the elements to the Arabian Sea sediments. Similarly, volcanic activities might contribute through the incorporation of volcanoclastic material and the alteration products of submarine basalts. Possibility of minor amounts of authigenic minerals in deep-sea sediments can not be ruled out.

Mineralogically, illite and montmorillonite concentration in the less than 2μ size class of the sediments is reported. The illite seems to be from the arid region of north and montmorillonite is due to the weathering of the augite basalts of the Deccan traps (Goldberg and

Griffin, 1970). Presence of dolomite has been reported by Stewart et al. (1965) and Goldberg and Griffin (1970).

Kolla et al. (1976) have mapped the western Indian Ocean in terms of clay mineralogy. The present core samples belong to the Group II mineral provinces in the western Indian Ocean which indicates that minerals are derived from continents volcanic activities in southern ocean and with significant effects of several modes of long-distance sediment transport.

2.5 GEOCHEMISTRY

The systematic study of deep sea sediments began with the voyage of the HMS challenger (1872 - 1876) which established the general morphology of the oceans and the types of sediments they contained. But it was the Discovery Expedition to the Antarctic Sea (Neaverson, 1934), the Meteor Expedition to the Atlantic and Indian Oceans (Correns, 1937; Schott, 1955) and the Snellius Expedition to the Dutch East Indies (Neeb and Knenen, 1943) that have greatly added to our knowledge of the chemistry of marine sediments (all references cited in El Wakeel and Riley, 1961). After the Second World War, the development of

piston corer has added a new dimension to the study of marine sediments.

However, many of the initial studies on the geochemistry of deep-sea sediments (e.g. Young, 1954; Goldberg and Arrhenius, 1958; El Wakeel and Riley, 1961 and Landergren, 1964) were limited to the major elements. This early work revealed that there are very large variations between the concentrations of the major elements of deep-sea sediments of different lithologies which are largely a result of variations in the proportions of the principal minerals in them.

The chemical compositions of deep-sea sediments are governed by a number of complex inter-relating controls. Riley and Chester (1961) have cited most important factors as: (i) the relative proportion of the minerals constituting the sediments, (ii) the paths by which the elements are introduced into the marine environment, (iii) the mechanisms by which the elements are incorporated into the sediments and (iv) the overall pattern of sedimentation in a particular oceanic area.

There are two types of trace elements: (i) those held in 'lattice positions' within lithogenous minerals and

(ii) those held in surface and inter-sheet position i.e. trace elements which have been removed from solutions. Chester and Hughes (1967) outlined a chemical technique to separate these two types of trace elements. Chester and Messiha-Hanna (1970) have used this technique to study the partition of elements like Fe, Mn, Ni, Co, Cr, V, Ga, Sr and Ba between lithogenous and non-lithogenous fractions of a number of deep-sea and near shore North Atlantic sediments. The same technique has been used in sediment cores of the western equatorial Indian Ocean (Murty et al., 1978; Paropkari et al., 1980) in DSDP sites (Murty et al., 1977; Rao et al., 1978) in shelf sediments off west coast of India (Murty et al., 1973, 1978), in Saguenay fjord (Loring, 1976) and in North Atlantic Ocean (Horowitz and Cronan, 1976).

Co-precipitation, adsorption and ion-exchange reactions exert fundamental controls on the geochemistry of certain deep-sea sediments. Krauskopf (1956) made a classic study of the process which controls the concentrations of some thirteen trace elements in sea water. From the experiments dealing with adsorption, Krauskopf (1956) concluded that this process was a possible control on the concentration of Zn, Cu, Pb, Bi, Cd, Hg, Ag, and Mo, but not on those of V, Co, Ni, W and Cr. An element can be removed

from sea water and introduced into the sediments in several ways: (i) through precipitation of insoluble compounds with ions 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 and hydrated manganese dioxide and clay and (iv) removal by metabolic action of organisms (Krauskopf, 1956).

CHAPTER III

MATERIALS AND METHODS

Core samples were collected in January 1986 by R/V Gaveshani during the cruise 163. Three box corer (gravity) samples were collected. The details are as follows:

| Core No. | Depth of Water Column | Nature | Technique | Latitude | Longitude |
|----------|-----------------------|-------------|-----------|-----------|-----------|
| 1) 3800 | 1725 m | Core Sample | Box Cores | 12°4.2'E | 72°15.3'N |
| 2) 3810 | 2593 m | do | do | 09°59.7'E | 71°44.9'N |
| 3) 3811 | 1450 m | do | do | 12°10.2'E | 73°54.2'N |

For the present study, Core No. 3800 was selected (Fig. 2). It was a core of fine grained sediment material of 120 cm length. The top 10 cm could not be made available. The rest of the core was sub-sampled at intervals of 5 cm for further investigations.

3.1 LABORATORY INVESTIGATIONS

The different methods and works carried out in laboratory are listed as follows :

- a. Megascope study
- b. Sample preparation
- c. Total organic content analysis
- d. The mechanical sediment textural analysis
- e. Carbonate content analysis
- f. Bomb Digestion.

3.1.a. Megascope study

There is a strong feeling of clay-silt dominance in the sediment fraction. The colour of the core varies with depth. From 10 cm to 60 cm depth, the colour is yellowish grey sometimes with greenish layering, especially distinct after a cut with a knife. The column in between 60 and 80 cm has olive grey colour. However, the change in colour is gradational with a greenish tint. Beyond 80 cm depth, the colour is olive green. In general fossil shells are numerous especially those of foraminifers and ostracods. In lower part of the core fish teeth are also noticed.

3.1.b. Sample preparation

Each sub-sample is thoroughly washed with distilled water in order to remove sodium chloride present in the pore spaces of the sediments. The process is

repeated twice and the sample was then transferred to crucible and dried in an electric oven at about 50°C. After drying, the sample was crushed for a homogeneous mixing to minimise the errors in further studies and investigations.

3.1.c. Total organic content analysis

Organic matter is a highly potent factor in the evolution of the biosphere. The study of the factors governing distribution, transformation and cycling of organic matter and its accumulation in sediments is of considerable practical and theoretical value, particularly for the evolution of lithology and for understanding the formation patterns of deposits of numerous useful minerals. There could be two sources of organic matter in the ocean—autochthonous organic matter derived from photosynthesizing plants and allochthonous organic matter due to river and subterranean runoff.

For the purpose of organic content analysis, oven dried and crushed samples of known weight were treated with hydrogen peroxide (10% v/v) repeatedly to oxidize the organic matter present. Difference in weight of dried sample before and after hydrogen peroxide treatment was taken as total organic matter.

3.1.d The mechanical sediment textural analysis

The mechanical analysis normally begins with the sieve procedures, the separation of the sand fractions ($>63 \mu$) from the fine - grained sediment particles. These are then separated into silt and clay fractions by allowing the heavier particles to settle using water as suspension medium. However, this method can cause an error due to contamination of the sediment out of metal corrosion of the sieve walls and base. For this reason, it is preferred to place all samples irrespective of grain size in a suspension-medium and separate the $<2 \mu$ fraction by repeated suspension and settlement cycles. This is followed by separation of the increasingly coarser silt fractions.

The Institut für Sedimentforschung of Heidelberg University and others introduced the method of separating the fine grained sediment at the silt/clay interface. Since the fraction $<2 \mu$ contain not only clay minerals but also hydrous oxides, sulfides, organic substances and other material, it is generally termed as 'pelitic fractions'.

The separation is carried out in Atterberg sedimentation cylinders with dry and organic content free

samples in order to minimize the possibilities of flocculation of clay minerals.

3.1.d.i Atterberg sedimentation cylinders

It is 35 cm long having 5 cm diameter and is provided with a siphon at 3 to 4 cm above the base. Cylinders were graduated in cm with the zero mark coinciding with the siphoning layer of the liquid. The siphon tube was connected to a rubber (latex) tube which was provided with a pinch cork. Cylinder at the mouth (top) was provided with a glass cork.

A homogenized suspension in water was prepared from washed samples. Homogenisation was carried out with the aid of mechanical stirring. The strength of the suspension was maintained about 15 gm/l. The suspension was transferred to Atterberg sedimentation cylinders and again was shaken before keeping for size separation. The different fractions are evaporated at 60°C in a porcelain dish.

The fraction $< 2 \mu$ is removed only once or twice in the grain size analysis in order to minimise the possibility of contamination.

3.1.d.ii. Principle of size separation by Atterberg sedimentation cylinder

Stock's law governs the size separation of sediments which states the law of settling velocity:

$$V = 2/g (d_1 - d_2 /n) gr^2$$

Where V = Velocity or rate of settling, cm/sec
 d_1 = density of particles, gm/cm³ = 2.65
(taken as constant for quartz)
 d_2 = density of the fluid medium, gm/cm³
 g = acceleration due to gravity, cm/sec² = 980
 n = viscosity of fluid in centipoises.
 r = radius of sphere, cm.

Fall time for a given diameter of particle is

$$t = h/v$$

Where h = fall height of suspended column in cm.
 v = settling velocity for a given diameter in cm/sec.

3.1.e. Carbonate content analysis

Deep-sea sediments are expected to be carbonate rich. In general, calcium is largely present as calcium carbonate. For the estimation of carbonate content, each

sample was treated by 10% dilute HCl. The acid was added slowly until effervescence stopped. Then the sample was heated to 80 - 90°C and more dil. HCl was added until no effervescence stage reached. Then some water was added. The liquid was decanted and repeated washing was done with the help of filter paper and funnel. The sample was dried in an electric oven at about 50°C. Difference in weight of dried sample before and after acid treatment was taken as total carbonate content.

3.1.f. Bomb digestion

50 mg of sample was taken in a teflon and 0.5 ml HNO_3 + 1.5 ml HCl and 5 ml HF was added. The teflon was kept in a sealed bomb which was heated in an electric oven for about two hours at 110°C. In the case of a seal bomb, some pressure develops inside which facilitates the decomposition of relatively resistant minerals. After cooling, some water was added and again heated for one hour. It was allowed for cooling to room temperature and was diluted with distilled water to 100 ml. Further trace element concentration studies were carried out by ASS - Instrumentation-751-USA model in University Scientific Instrumentation Centre, Roorkee.

3.2 FACTOR ANALYSIS

In most of cases of our study, our each observation unit or specimen was characterized by several variables. It is not difficult to understand the structure of any specimen having one variable or two variables. A specimen with one variable, can be represented by variation along one axis, while two variables can be represented by a point on a two axes coordinate system. But a specimen having more than two sets of variables needs multicoordinate axes system and it is difficult to visualize the structure and to appreciate the problem.

Multivariate methods are extremely powerful because they allow to consider more variables at a time. However, they are complicated both in their theoretical structure and in their operational methodology. Never the less, these methods seem to be of utmost importance for obtaining good results in geological investigations since most of the problems in geology involve complex and interacting forces, which are impossible to isolate and study individually.

The technique commonly used for the analysis of multivariate data include the cluster analysis, multiple

regression analysis, discriminant function analysis, factor analysis etc.

In the present study, R-mode Factor Analysis has been used. This technique has been successfully used by Mather (1972) in sedimentology, by Hitchon et al. (1971) in subsurface brine geochemistry by Reinson (1975) in mud geochemistry, by Calvert and Batchelor (1978) in deep sea sediment geochemistry.



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3.2.a R-mode Factor Analysis

The technique is concerned with the determination of principal components of a variance - covariance matrix. The principal components are the eigen vectors of a variance - covariance matrix. By the spectral character of the eigen structure of a matrix, the variance of the variables is spread across all factors. The first factor will be a weighted average of all the variables present. The principal components provide significant insight into the structure of the matrix, and they often may be interpreted in much the same way as follows.

If a number of variables are measured on a set of variables, then a linear transformation of these variables will yield new variables. This new set of variables will be independent of each other and may account for as much of total variation as of principal components.

As these factors are usually not readily interpretable, it is accustomed practice to rotate the reference axes by some appropriate method. By rotating the axes, we try to place the factors so that each contains only a few highly loaded variables, and to diminish the loadings on non-significantly contributing variables. The visual result of the rotation will then be that some of the loadings will be augmented while others will become greatly lower.

The R-mode analysis has been carried out by the computer programme given by Davis (1973) at Roorkee University Regional Computer Centre.

RESULTS AND DISCUSSION

4.1 TEXTURAL ANALYSIS

The textural analysis carried over the core sample is presented in Table I. The textural classification has been based on Shephard's (1953) sand-silt-clay ternary plot. Fig. 3 reveals that sediments underlie 5 percentile clay line in general except the sample of depth 35 cm. All the samples have sediment distribution from silty sand to sandy silt.

Out of 15 the samples which have Mud/Sand ratio >1 (Fig. 5), 11 samples lie in the field of sandy silt, whereas other four samples lie in silty sand field. The overall concentration in a small area gives the indication that the sediment supply rate and amount was almost same throughout the time length of the core.

The maximum clay percentage is 6.66 (Figs. 4 and 6) while the minimum clay percentage is 1.1 with an average mean of 2.69% and standard deviation 1.39. The maximum silt

percentage is 56.48 and the minimum silt fraction is 41.15% with an average mean of 50.40% and standard deviation of 4.53. The sand percentage has maximum and minimum values of 56.59 and 41.79 respectively, with an average mean of 47.34% and having a standard deviation of 4.96. The low standard deviation indicates that the sediments are mature and well sorted.

Clay fraction exhibits a strong correlation with organic matter which is obvious. The negative correlation of clay fraction with carbonate content indicates that most of the carbonate has been contributed either by skeletons of the shells or are the result of precipitation.

Sample No.6 shows highest ratio of Mud/Sand (1.71) while sample No. 14 shows lowest ratio of Mud/Sand (0.77).

4.2 ORGANIC MATTER

In the recent years, much stress has been given to the study of OM in recent sediments for the elucidation of the processes and mechanisms responsible for sedimentation and the origin of petroleum and natural gas. Sediments with high OM content are also of interest as a source of natural

fertilisers. Geochemical studies concerned with the principles governing the distribution and accumulation of OM in sediments are of high practical importance. The total organic content, however, can fluctuate widely in response to variations in environmental parameters, such as primary productivity, redox potential, rates of deposition, mineralogy, etc.

In general, OM in most parts is adsorbed on pelitic particles and incorporated within them. So, a general conclusion can be drawn that high OM content are found in the fine dispersed fraction of the sediments. In the present core, it is also more or less true. Highest OM content is 4.91% corresponding to 105 cm depth level (Fig. 7), which has fairly high fraction of $< 2 \mu$ (4.0%) but the Mud/Sand ratio is less than one (0.82). The second highest peak corresponds to 40 cm depth level which is low in clay content but Mud/Sand ratio is appreciably high.

It seems that high OM content is not only attributed to $< 2 \mu$ fraction but also the (2 - 63 μ) fraction, i.e. pelitic or mud fraction. These size fractions have condensed arrangement of layers and basal

sheets in tetrahedral lattice which favours ionic substitution in various positions resulting in strong bonding of the organic ions with the mineral part of the sediment and causes the better preservation of organic compounds than of individual free molecules.

High OM content also indicate negative Eh values due to the fact that in the absence of free oxygen, biochemical oxidation reactions are shifted towards the formation of intermediate products resulting from partial degradation of OM.

The present OM content values can be compared with sediments of continental slopes of western Africa (3.88%), of the Pacific (3.48%) (Romankevich, 1984). The lowest OM content determined is 1.19% corresponding to 15 cm depth level, which is low in clay (1.21%) and Mud/Sand ratio is also less than one (0.84). There is no general trend in variation of OM with depth, having a high noise level, but most of the samples have values close to the mean of all (2.66%). The two lower peaks corresponding to 15 cm and 115 cm can be due to relative oxidising environment which facilitates the decomposition of OM.

4.3 CARBONATE CONTENT

Carbonate content in the core ranges from 61% in the top region to 50% in the bottom region. The maximum carbonate content recorded is 73% and the lowest content is 30%. The two minima recorded at 25 cm and 55 cm have values 41% and 30% respectively. In general it has a decreasing tendency with depth (Fig. 8).

Arrhenius (1952; cited in Guptha and Hashimi, 1985) has suggested that the variation in carbonate in down core is directly responsible to the change in climate. Subsequent workers have been treating the variation in carbonate content as a function of fluctuation in Quaternary climate. The abundance of carbonate content is attributed to the high productivity in the interglacial period.

Based on the sharp changes in the percentage of carbonate content at 25 cm and 55 cm, it has been suggested that these levels represent the upper and lower limits of the V Glacial period. The time range reported is between 15,000 yr. and 30,000 yr. which matches with our core if we assume roughly a rate of sedimentation about $2 \text{ cm } 1000 \text{ yr}^{-1}$, as reported by many workers on the continental slope of India (Heye, 1970; cited in Guptha and Hashimi, 1985).

Broecker (1971) has suggested an age of 8000 to 3000 yr as peak of interglacial period and age from 19,000 to 14,000 as peak of glacial period. Based on the published data of Emiliani (1958) average calcium carbonate of a glacial section would be about 35% while for interglacial sediments, the average calcium carbonate content could be about 60%. In the light of these facts, the 25 cm depth may, as we have already mentioned, may indicate the upper limit of V Glacial period. Similarly, at 55 cm, the sharp change in the gradient of the curve may indicate a change in temperature.

Whether precipitation or dissolution of solid carbonate compounds takes place depends on the concentration of CO_3^{2-} and on the factors that affect its addition to, or removal from the system primarily carbon dioxide flux and these are frequently reflected by changes in pH (Cloud, 1965). Krauskopf (1956) has shown that an increase of one pH unit diminishes the solubility of simple divalent carbonates by a factor 10. So, a change in pH together with temperature is responsible for variation in carbonate content.

4.4 ELEMENTAL GEOCHEMISTRY

Copper

Copper is carried by the mud particles in the rivers to the ocean. The concentration of copper in weathering solutions and the distance of transport are controlled both by adsorption and by the solubility of sulphides, phosphates, hydroxides, carbonates etc. A further fixation of copper by precipitation or absorption in sea water and concentration of copper continues during the very slow sedimentation of particles of the deep sea.

In the core, the copper content is very high in the top layers, upto 110 ppm, which represents the oxidising environmental conditions. A higher concentration of copper in marine oxidate sediments is well established (Goldschmidt 1958). The overall depletion of copper with depth in a profile is remarkable (Fig. 9).

Copper shows a strong correlation with Li, Zn, Sr and carbonate content. A negative correlation with clay fraction may be due to a reduced adsorption potential of the partially less crystalline or amorphous substances (Forstner

and Wittman, 1981). Riley (1937-38) has indicated that highest concentration values were found in water of low salinity indicating that copper is very speedily removed from sea water, most probably by organic matter, since it is very strongly absorbed by organic matter. The seasonal cycle includes binding of copper to organic matter and release of copper from bottom mud. However, copper is not as mobile as manganese, which is more clearly seen in post-depositional cases and enriching the oxidized zone. A plot of Cu concentration to organic matter also seems to be depth dependent (Fig. 20).

Manganese

Manganese is concentrated considerably in deep-sea pelagic sediments compared with continental igneous rocks (El. Wakeel and Riley, 1961). In general, the core is rich in manganese, and shows a gradual decrease with depth except few low and high peaks at 25 cm and 55 cm respectively. Again, beyond 100 cm we get higher value of manganese content (Fig. 10). Manganese shows strong correlation with Cr and Fe and a fair correlation with Sr, carbonate content and organic matter. However, it is pertinent to notice that manganese shows highest degree of correlation with organic

matter as compared to other elements like Cu, Co, Fe, Li, Cr etc.

In the hydrolysate sediments, the amount of Mn depends very much on the conditions of sedimentation and geochemical environment. The post-depositional mobilization and migration of manganese has been suggested by Lynn and Bonatti (1965) and Li et al. (1969). There are two processes involved: one leading to selective solution of manganese from the hydrolysate material, the other causing a selective fixation. If the conditions in the sedimentary environment are reducing, divalent manganese ions are released in carbonated waters in the form of soluble manganese bicarbonate, $Mn(HCO_3)_2$. The manganese, thus released in the interstitial waters will remain in solution until upward migration or precipitation occurs. Under reducing conditions the sediment-interstitial water complexes are rich in organic matter and this can affect the subsequent fate of the sediments. The other process occurs under oxidising conditions and consists of the immobilization of manganese as the insoluble dioxide. So, we feel that at 55 cm and probably at 110 cm level we have oxidising layers. Fate of manganese can even be predicted from the colour of sediments (Goldschmidt, 1958). Below 60 cm depth, the

colour varies from olive grey to olive green, which suggests leaching of manganese, whereas yellowish grey colour is indicative of fixation and reprecipitation of manganese.

The process of selective reduction is important in post-depositional reactions and will affect Mn and Fe, but manganese will be preferentially dissolved because Mn(OH)_2 is a much stronger base than Fe(OH)_2 due to larger size of manganese ion. However, this process is unlikely to be responsible for the direct release of Co, Zn, Ni and Cu (Riley and Chester, 1971).

A plot of Mn concentration to organic matter is also depth dependent which tends to stabilise with depth (Fig. 21).

The quantitative importance of post-depositional migration is difficult to estimate. Because, the degree of mobilization before migration will be a function of redox potential, pH, organic matter content and carbonate content.

Iron

Ferric oxides formed by weathering are invariably very fine grained and as a result are carried by rivers either as stabilized colloids or as adsorbed coatings on

detrital particles. Carroll (1958) in his classic paper has demonstrated the importance of clay minerals as agents for the transport of adsorbed iron oxide.

The vertical distribution of iron is uniform with minor fluctuations below 50 cm depth. However, above 50 cm there is high fluctuation. From 15 cm to 25 cm depth the iron content suddenly shows a decline (0.31%) whereas the organic content increases (1.19% to 2.42%) (Fig. 11). It is due to the fact that iron is highly mobilized and consequently removed for want of sulphur to fix iron (Fe^{++}) as sulphide. From 35 cm to 45 cm depth the iron content again suddenly shows a decline (0.34%) whereas the organic content first shows an increase (3.05% to 4.01%) and then a decrease (4.01% to 2.58%). In the previous case, due to prevailing reducing conditions, iron is incorporated into the solution. A careful examination of the correlation coefficients permits the following generalizations :

1. Iron covaries with Zn, Mn and Li; it has a stronger correlation with zinc than that with manganese. It has very poor correlation with Mud/Sand and organic matter.

2. It shows better correlation with Mud/Sand than that with clay fraction indicating thereby that the fractions $< 63 \mu$ are better for transportation of iron than only $< 2 \mu$ size fraction.

The geochemistry of both manganese and iron is intimately related. Landergren (1954; cited in Rao and Setty, 1976) has stressed that the ratio of Mn/Fe are regulated by the pH, redox potential and presence of CO_2 . Mn/Fe ratio is highest at the top (Fig. 12) and it has a little tendency to decrease with depth; the average being 1:145. Invariably there is fluctuation but a sudden increase at 50 cm interval and a gradual increase from 90 to 110 cm in Mn/Fe ratio is remarkable. The interval at 50 cm is an oxidation zone and manganese is unlikely to diffuse through the oxic layer, rapidly causing a precipitation (Riley and Chester, 1971). Beyond 90 cm, a gradual increase in Mn/Fe may be due to increase in oxidising condition or increase in acidic condition which promote the iron to be present in solution. It is seemingly not due to increase in oxidising condition, since organic matter is increasing and hence the latter assumption seems to be correct. However, Baas-Becking et al. (1960) have shown that the pH of marine sediments is relatively invariable with almost all values

falling between 6.8 and 8.2. The pH of sea water is even more restricted, falling between 7.6 and 8.3. So, for our purpose, sea water conditions in ΣS and ΣCO_2 is actually more relevant. Fe content is almost constant, hence not being used by sulphur to form pyrite. However, there is a little increase in calcium carbonate content. So, we think that some of the calcium of the $CaCO_3$ has been replaced by iron to form siderite.

Nickel

Nickel is strongly concentrated in pelagic sediments relative to both igneous rocks and near-shore sediments (El Wakeel and Riley, 1961). Nickel concentration is more or less constant with depth (Fig. 13) except at three depth levels, viz. 15 cm, 50 cm and 100 cm; the peak at 50 cm being the sharpest. It is pertinent to notice that these sediments are poor in organic matter. The enhancement of peaks can be seen in the Ni/OM Vs. depth plot (Fig. 19).

The ratio between the maximum and minimum nickel contents is high (12:1). These variations and the relative high content of nickel has been explained as a cosmic source for excess nickel (Pettersson, 1959); but this idea has been

rejected by Goldberg (1954). Goldberg (1954) has suggested that nickel content has been scavenged directly from sea water by hydrous manganese dioxide and has not originated from meteoritic matter. However, Krauskopf (1956) has shown other major adsorbents in the oceanic environment, such as clay minerals, apatite and organic matter to be effective in removing nickel from sea water. Based on his observation of relatively high concentration of nickel in organic-rich sediments, Krauskopf (1956) has stressed the importance of organic reactions as a controlling factor in the removal of nickel from sea water. But in the present study, we find a low negative correlation between organic matter and nickel concentration. Murty et al. (1970) have also found no relationship between nickel and organic carbon. However, nickel shows a strong correlation with manganese, chromium, strontium and carbonate content. So, hydrous manganese dioxide and other colloidal fractions of the sediments seem to be more active than organic matter, as also suggested by Goldberg (1954) and Goldberg and Arrhenius (1958). But it is true only under conditions of low redox potential, where high percentage of organic matter is assumed. According to Chester (1965) nickel may be probably removed permanently from sea-water under conditions of low redox potential when organic rich sulphide-bearing sediments are formed. Also it

has been stressed that approximately half to one-third of nickel are bound in the ferromanganese minerals, probably replacing manganese or iron in the disordered layers of the manganese and ferric magnetites (Buser and Grutter, 1956; cited in El Wakeel and Riley, 1961).

Zinc

Zinc has low solubility in natural waters, so its major transport and accumulation in the sedimentary environment is to be expected in detrital matter (Murty et al., 1985). Zinc has higher concentration in the continental slope region than the continental shelf (Murty et al., 1985).

The concentration of zinc varies very widely; 284 ppm to 8160 ppm with three distinct peaks at 20, 35 and 60 cm depth (Fig. 14). Zinc shows strong correlation with Li, Fe and Cu and some correlation with Sr, carbonate content and Mud/Sand ratio. The negative correlation which zinc exhibits with fraction $< 2 \mu$ clearly indicates that clay is not a contributing factor for zinc concentration in these sediments, rather pelitic part is more responsible. The

significant correlation of zinc with Li, Fe and Cu could be due to the presence of zinc in the crystal lattice of clay minerals, of which these are also an essential constituent. Secondly, the relationship with Fe could be due to the presence of zinc in the form of sulphides in association with Fe under the reducing conditions. There is not much relationship of zinc with the organic matter; so the process of adsorption by materials like ferrous sulphide, hydrated ferric oxide and hydrated manganese dioxide and clay could be the process for removal of zinc from sea water and introduction into the sediment (Krauskopf, 1956).

Below 65 cm depth, zinc concentration is low and almost constant. This vertical uniform distribution of zinc may be due to the presence of stable colloids of hydrated oxides which may occur at these levels. Certain high peaks of zinc may be due to its concentration in considerable amounts as sulphides in stagnant sea water together with iron (Goldschmidt, 1958). Some high values may be partly biologically derived, indicated by rather high amounts of zinc taken up by various marine organisms, amounts exceeding those of any other heavy metals (Goldschmidt, 1958).

Cobalt

Cobalt is strongly concentrated in marine sediments relative to igneous rocks (El Wakeel and Riley, 1961; Goldberg and Arrhenius, 1958) and in pelagic clays compared to near shore clays (Wedepohl, 1960; Madusudhana Rao and Setty, 1976). Concentration of cobalt shows high fluctuations (Fig. 15) which may be due to turbidite flows, oxidising conditions or influx of fresh material (Setty, 1972). It shows a correlation with Mud/Sand ratio, carbonate content, iron, manganese and organic matter. It has been suggested by many authors that cobalt may be adsorbed by organic matter. A plot of Co/OM indicates an increase in wide fluctuations (Fig. 22). The higher values may be due to reduced sediments (Goldschmidt, 1958). Chester and Hughes (1969; cited in Rao and Setty, 1976) have postulated that about 68-98% of the total cobalt is hydrogenous in origin and more than 95% of this is associated with micronodules. Whether micronodules are present (?) in the sediment of the core is not clear at all. The enrichment of cobalt in certain sections of the core may be due to migration and precipitation of hydrous iron oxide and/or manganese dioxide. Scavenging of cobalt from the sea water through organic matter is possible (Krauskopf, 1956).

Cobalt shows a negative correlation with clay fraction, but shows a positive correlation with Mud/Sand ratio; indicating thereby that particles less than 63 μ have more dominant role than only $< 2 \mu$ fraction.

Strontium

Strontium is concentrated in pelagic clays relative to near shore clays (Young, 1954). It is well known that carbonates contain a high proportion of the strontium in marine sediments.

The vertical distribution of strontium is not uniform as indicated by many fluctuations (Fig. 16). The minimum Sr content recorded is 8 ppm and the maximum is 228 ppm. Sr strongly co-varies with Cr, Cu and carbonate content. A low level of correlation can be seen with Mn, Ni and Zn. A negative correlation exists with clay fraction and organic matter.

According to Turekian and Kulp (1956), calcium carbonate ooze is the main contributor of this element to the equatorial Atlantic sediments. El. Wakeel and Riley

(1961) have found that the calcareous deep-sea sediments contain the highest content of strontium. He has also reported that Sr may also be associated with clay minerals. It is worthy of notice that neither the lowest value of Sr nor the highest value of Sr is found in the lowest or highest percentage of carbonate present in the sediment. However, Riley and Chester (1971) have indicated that Sr can be held in the 'lattice positions' of the lithogenous components, hydrogenous components of montmorillonite and the zeolites and the skeletal biogenous component. So, for an explanation of higher content of Sr, all the above three factors have to be considered. Chester and Messiha-Hanna (1970) have shown that 80% of the total content of this element is held in calcareous shell material. Besides this, feldspar and clay minerals are also responsible for high Sr content, especially where carbonate content is low. Strong correlation of Sr with Cr and Cu suggest that a impressive amount of Sr is also held in 'lattice positions' of the lithogenous component. Its association with Mn could be due to the fact that Sr is concentrated in manganese dioxide sediments (Goldschmidt, 1958). At the depth of 75 cm, anomalous low Sr concentration may be due to the fact that it may contain a relatively high proportion of detrital carbonate deficient in Sr due to recrystallization (Kinsman,

1969; Sayles and Manheim, 1975). This sample also bears the highest $>63 \mu$ fraction (57%) and lowest Mud/Sand ratio (0.77).

Chromium

Chromium has a similar abundance in near-shore muds and deep-sea clays, and they are largely lithogenous in origin (Wedepohl, 1960; Young, 1954); but Chester (1965) has suggested that this element is slightly concentrated in near-shore environment. The average content of near-shore sediments is 100 ppm. (El Wakeel and Riley, 1961) which is much lower than the values of magmatic rocks i.e. 200 ppm. (Goldschmidt, 1958).

In our study, the case is just opposite. The minimum Cr content is 132 ppm and the maximum content is 3630 ppm. (Fig. 17) which could be compared with the Cr content of chondrites having value 3460 ppm (Mason, 1971). Chromium shows a strong correlation with Ni, Mn and Sr. On the other hand, it exhibits a negative low correlation with carbonate content, organic matter and clay fraction.

Goldberg and Arrhenius (1958) have suggested that an excess of chromium over 100 ppm in sediments is a useful

indication of the presence of altered or unaltered basaltic pyroclasts. The negative correlation with clay fraction can be explained on the basis of observation made by Goldberg and Arrhenius (1958) that chromium in Pacific pelagic clays is strongly concentrated in the size fraction which contains ferromagnesian minerals (chiefly augite) and to a lesser extent in the clay fractions. Also, Chester and Messihanna (1970) have shown that about 70% of the Cr in North Atlantic deep-sea sediments is in 'lattice-held' positions which is reflected in our case as a negative correlation with organic matter. This overall picture suggests that most of the sediments have been derived from the adjoining Deccan traps, carried by Narmada, Tapti and also by Indus which are by far the principal sources of terrigenous material to the northwestern Indian Ocean. However, a possibility of modern submarine volcanic activity from the Carlsberg Ridge and the alteration of ancient volcanic rocks can not be ruled out.

It is probable that the bulk of the chromium occurs in the common marine hydrolysate sediments. The solute chromium compounds are present in sea water, probably as chromate (Goldschmidt, 1958). Precipitation may follow reduction of chromate to the trivalent cation which is

highly immobile. The concentration peaks in depth profile, however, seem to be more related with high supply of ferromagnesian minerals like micas, clay minerals particularly illite, chromite and chromium spinel (Ghode et al. 1976; Najafi, 1981; Krishnan, 1982). The very low values of chromium may be due to oxidising conditions which result in its partial loss from the sediments.

Lithium

Deep-sea carbonate sediments have lower lithium content (5 ppm) than deep-sea clays (57 ppm) (Turekian and Wedepohl, 1961). The Li content is a function of detrital mineralogy, newly formed minerals and organic materials.

The vertical distribution of lithium is almost uniform with a low standard deviation (8.24) and a decreasing trend (Fig. 18). The maximum lithium content is 36 ppm and the minimum is 2 ppm, average Li content being 12 ppm. It shows a strong positive correlation with Zn, Cu and Fe and rather a poor correlation with Sr, organic matter and Mud/Sand ratio.

Lithium is bound to marine hydrolysate sediments (Goldschmidt, 1958). It most probably occurs in one or several of the layer-lattice minerals which are characteristic constituents of clays and marine muds e.g. montmorillonite, illite and other hydromicas, degraded chlorites and other magnesian hydrosilicates.

Lithium is released as Li in the solution and gets incorporated in clay minerals (Heier and Billings, 1970) during weathering and transportation before entering the depositional basin. In all cases, silt and clay fraction contains larger Li.

4.5 R-MODE FACTOR ANALYSIS

R-mode factor analysis is used here to determine the distribution and association of elements in the sediments. Factor analysis provides an indirect means to group sediment parameters. The parameters within each group are associated in the sense that they are controlled by the same factor. Each factor can then be interpreted on a geochemical and mineralogical basis.

The analysis confirms most of the element-associations deduced from the correlation matrix and

provides a summary of the interelemental relationships. Five factors account for 84% of the total variance in the original data. Rotation of more than 5 factors, although accounting for more of the total variance, made interpretations meaningless on a geochemical basis. The loadings of five factors have been represented diagrammatically in Fig. 25.

Factor_1

This factor is statistically dominant, accounting for over 31% of the total variance among the variables with highest eigen value (3.7059). It is characterized by a strong positive association of Cu, Li, Sr and Zn. This factor has been interpreted as a detrital mineral factor which reflects the dominant control that the mineralogy of the detrital component has on the concentration and association of Cu, Li, Sr and Zn in the sediments. Cu, Li and Zn are all believed to be in the crystal lattice of clay minerals of which these are also considered as essential constituents (Murty et al., 1985). Association of Sr probably is due to the concentration of this element in the structural positions of the plagioclase feldspars and clay minerals, preferably in feldspars (Calvert, 1976).

Factor 2

The second factor represent the second highest eigen value (2.3644) which contributes about 20% of the total variance in the sediments. This factor has strong loadings of Ni, Cr, Mn and Sr. This factor has been interpreted as reflecting the formation of sulphide and hydroxide minerals under reducing conditions and Sr representing a carbonate factor.

The association of Ni, Cr, Mn is not surprising due to their association in ferromanganese minerals. This also confirms our earlier idea that hydrous manganese dioxide together with other colloidal fractions are able to precipitate Ni and Cr from the oceanic waters as hydroxides in reducing conditions. Under such conditions, chromate is reduced to the trivalent form and Ni can be removed from the oceanic waters under low redox potential in sulphide rich sediments. The reappearance of Sr in the second factor is a carbonate factor which takes into account the calcareous skeletal sands which are widespread at low latitudes (Pettijohn, 1984).

Factor 3

This factor contributes about 14% of the total variance in the sediments. This factor is characterized by the strong loadings on organic matter and clay fraction of the sediment. It has been interpreted as fine grained OM rich factor. The OM is, in general adsorbed on the clay fractions and incorporated within them.

This factor also indicates that the dispersal of elements is controlled by the overall dispersal of fine grained fractions and organic matter in the system. This may represent the removal of elements from solution through adsorption onto suspended matter, their inclusion in oxide coatings or their additional preference for fine grained fraction and organic matter in general. From the loadings on the elements, it seems that the input of the elements adsorbed onto the clay fraction and organic matter is more in Mn than Fe. The negative loadings on Cr, Ni, Sr and Cu suggest that fine grained fractions and organic matter do not have influence, rather coarse fraction is more responsible which is reflected by a negative loading on Mud/Sand ratio.

Factor 4

This factor is characterized by the strong association of Co and Mud/Sand ratio. This factor has been interpreted as cobalt enrichment in pelitic fraction of the sediments. We have observed that samples with Mud/Sand ratio < 1 is enriched in cobalt, while samples having Mud/Sand ratio > 1 is poor in cobalt concentration. So, there is a grain size control in case of cobalt enrichment. Mn, Li and Sr also show poor positive loadings. Elemental concentration in the pelitic fraction is in the order of Co Mn. The negative correlation of Cu and Zn indicates that they have a tendency to concentrate in the sand fraction of the sediments.

Factor 5

This factor contributes rather low percentage of variance (7%). It has strong loadings on Fe, Zn, Li and Mud/Sand ratio. It has been interpreted as a detrital factor. It can be noted that iron appears for the first time in this factor. The association of Fe-Zn in silicates is known (Loring, 1976). It is suggested that the Fe is derived largely from detrital minerals, such as ferric

vermiculite and iron hydroxide and is mobilized upon reduction into the sulphide phase. Appreciable zinc transport is expected to occur in colloidal iron oxides and iron oxide coatings on other minerals. In general, chlorite and magnetite are better zinc carriers. Li may be present in lattice positions of the clay minerals. Obviously these things will be facilitated by the presence of pelitic fractions.

The bivariate plot (Fig. 26) between PC I and PC II loadings shows the relationship among different variables. The field of association of Ni, Cr, Mn, Sr and Mud/Sand and Co can be delineated. Although PC I and PC II both contribute towards Sr, the loading of PC I is more than PC II. In the bivariate plot between PC I and PC III (Fig. 27), the closeness of Mn, Fe and Co to that of (clay - OM) field gives the order for affinity to adsorb the elements on the clay fraction and organic matter. Also, a distinct field of association of Zn, Sr, Li, Cu defines the 1st factor. In the bivariate plot of PC I and PC IV (Fig. 28), association of OM with Mn and of Cr, Ni, Fe is distinct. In PC I-PC V plot (Fig. 29), association of Zn and Li and Cr, Ni and Co are distinct. The plot of PC I and PC V gives a general idea of the association of Fe, Zn, Li and Mud/Sand (Fig. 30).

The graph between the varimax scores of factor 1 and factor 2 gives interesting results (Fig. 31). Sample 9 is highly loaded with factor 2 and factor 1. It is characterized by the highest elemental concentration of Ni, Mn, Cr and Sr; and it has the lowest percentage of $>63 \mu$ fraction. Sample 6 is highly loaded with factor 1 and small loadings from factor 2. It is characterized by the highest concentration of Fe, Zn and Li and it has the highest percentage of $<2 \mu$ fraction; and $(2-63 \mu)$ fraction. So, this sample bears the highest Mud/Sand ratio.

CHAPTER V

SUMMARY AND CONCLUSION

Core no. 3800 was taken from a depth of 1725 m from the central portion of the lower continental slope region of Arabian Sea. The vertical distribution of the various elements besides clay, silt and sand, organic matter and carbonate content have been analysed, after dividing the continuous core in 22 samples.

Textural Study

In the sand-silt-clay ternary plot, all samples lie under 5 percentile clay line covering the field from silty sand to sandy silt. Only seven samples out of total twenty two samples have Mud/Sand ratio less than one. It seems certain that the materials delivered to the Arabian Sea present a certain consistency in their texture as also indicated by their clustering in a small area in the ternary plot. Thus, it is presumed that the sediment supply rate and the amount was almost same throughout the time length of

the core. This conclusion is further supported by the fact that clay, silt and sand percentage distribution bears a very low standard deviation.

Organic Matter

High organic matter content are associated with fine dispersed fraction of the sediments. However, not only clay but also silt should be considered together. These pelitic or mud fractions have condensed arrangement of layers and basal sheet resulting in strong bonding of organic ions with the mineral part of the sediment which also causes better preservation. Though there is no general trend in variation of OM with depth, but most of the samples have value close to the mean of all (2.66%).

Carbonate Content

Variation in carbonate content has been treated as a function of fluctuation in Quaternary climate (Arrhenius, 1952; Brocker, 1971; Guptha and Hashimi, 1985). High carbonate content is attributed to interglacial period. Based on the sharp changes in the percentage of carbonate content at 25 cm and 55 cm level, it has been concluded that most probably the time interval between the sediment column

of 25 cm and 55 cm represent the upper and lower limits of V Glacial period. These levels also coincide with the absolute ages in years, if we assume roughly a rate of sedimentation about $2 \text{ cm } 1000 \text{ yr}^{-1}$ as reported by various authors.

Bulk Geochemistry

A good deal of information is available on the distribution of elements such as Fe, Mn, Ni, Cu, Co and Sr in the sediments of the western continental shelf and slope of India, and of the Indus shelf (Rao et al., 1976; Rao and Setty, 1976; Murty et al., 1978, 1983). Average concentration of elements computed from these cited literature in surface sediments from (a) the western continental shelf of India, (b) the Indus shelf and (c) the north western continental slope of India are given in Table VII. Comparison of these values with that of the data obtained in this present work (Table II) shows a number of features of interest, as discussed below:

With respect to the western continental shelf sediments, there is a considerable enrichment of Ni, Zn, Co and Mn. But there are no enrichments of Fe and Cu in the

present core relative to those from the western Indian continental shelf.

With respect to the Indus shelf sediments; Ni, Zn, Mn and Fe are enriched in the core 3800. Practically there is little enrichment of Cu in the deep-sea core relative to the Indus shelf sediments.

Except Ni, Fe and Zn; there are no enrichments of Mn and Cu in the core relative to their values in sediments from the western continental slope of India.

It is evident from these comparisons that the elements Fe and Cu are not enriched in the core relative to the western continental margin sediments. Thus, it may be concluded that lithogenous sources probably also supply much of the Fe and Cu to the present deep-sea sediment. This conclusion is further supported by our factor analysis results, where Fe and Cu appear in factor 5 and factor 1 respectively which has been interpreted as detrital mineral factor which reflects the dominant control that the mineralogy of the detrital component has on the concentration of elements.

At the other hand; Ni, Zn and Mn are enriched to a greater or lesser extent relative to the western continental shelf sediments as well as to the Indus shelf sediments. This suggests a source of Ni, Zn and Mn in these sediments additional to lithogenous sources. The same idea has emerged from factor 2 which controls the formation of sulphide and hydroxide minerals under reducing conditions (valid only for Ni and Mn). Appreciable Zn transport is expected to occur in colloidal form as coatings on other minerals.

The geochemistry of Mn and Fe is intimately related. They are very sensitive to conditions of sedimentation and geochemical environment. The post-depositional mobilization and migration of Mn is more pronounced than Fe. But oxidising conditions act as a barrier to the migration of Mn causing formation of insoluble dioxide and reprecipitation of manganese. On these basis, it seems possible that the sediment layer at 55 cm and perhaps also at 100 cm represent relatively higher oxidising conditions. It is further confirmed by high Mn/Fe ratio corresponding to these levels. Presence of oxidate sediments indicate increase in dissolved free oxygen in bottom waters. Dissolved free oxygen in ocean waters may be

circulated by the migration of water masses. It seems that currents of cold, and therefore comparatively heavy, surface water of Antarctic origin, which brings oxygenated waters to these depths.

Like Cu and Fe, which are held in 'lattice positions' within lithogenous minerals, Sr and Li can also be grouped together. Besides calcareous shells, feldspar and clay minerals provide access in their lattice positions to strontium while lithium is supported by illite, montmorillonite and other hydromicas.

From an 'area source' (higher content value) to a final depositional zone (low-content values) generally a decreasing gradient exists. Here, by far the most important source is Deccan trap province from where sediments are carried by Narmada and Tapti rivers with some contribution from Indus river. Chromites are characteristic component of olivine-basalts and pyroxenites; chromium spinels have also been reported (Ghodke et al., 1976; Najafi, 1981; Krishnan, 1982). This could be the possible source and reason behind high value of chromium. Besides this alteration of basaltic pyroclasts, submarine volcanic emissions will provide chromium to sea water, which in turn can be effectively

removed by hydrous manganese dioxide and colloidal fractions. This view can also be supported by second factor.

R-Mode Factor Analysis

In order to visualize the present data set and appreciate the problem, R-mode Factor Analysis has been carried out taking into consideration twelve variables at a time. It has given most efficient linear combination of variables. The term 'most efficient' meaning the one which accounts for the greatest amount of total variance. We have taken into consideration five factors which account for almost 84% of the total variance. These factors explain the association of different elements as well as their concentration in the sediments together with their relation to OM, pelitic fraction and carbonate content.

The first factor is detrital mineral factor which affects Cu, Li, Sr and Zn, i.e., these elements have mainly lithogenous component held in the 'lattice-positions' of the minerals showing similar distribution to the continental shelf sediments as well as deep-sea sediments. The second factor is sulphide and hydroxide factor together with carbonate factor which affects Ni, Cr, Mn and Sr. This

factor explains the enrichment of Ni, Cr and Mn in deep-sea sediments since hydrous manganese dioxide and colloidal fractions are able to precipitate Ni and Cr from oceanic water in a reducing condition. Reappearance of Sr in the second factor denote Sr other than lattice-held portion like surface and inter-sheet portions. The third factor is a fine grained organic matter rich factor and this association is well known. Further it also governs the dispersal and adsorption of elements on the clay particles and organic matter. As inferred from the higher positive loadings on the elements, adsorption of Mn will be more than Fe which may be due to greater ionic radii of Mn than Fe. The fourth factor expresses the strong association of Co and Mud/Sand indicating cobalt enrichment in pelitic fraction. It has been noticed that samples having Mud/Sand ratio < 1 are richer in cobalt. It is due to the fact that cobalt is probably derived by precipitation of the sulphides of the solute elements in sea water in reduced sediment where organic matter content is also high. The fifth factor is also a detrital factor which affects Fe, Zn, Li and Mud/Sand. In contrary to the first detrital factor which has a negative Mud/Sand loading, this factor has positive high loading on Mud/Sand ratio. Fe, which is lithogenous showing no enrichment in deep-sea sediments relative to those from

the western Indian continental shelf sediments, and part of Zn and Li are transported as pelitic fraction to deep-sea.

So, on the basis of this limited work on the continuous sediment core, we feel that the geochemical conditions were not similar throughout the time during the deposition of sediments. The sediment layer at 55 cm and perhaps also at 110 cm represent relatively high oxidising conditions. Enrichment of certain elements like Ni, Cr and Mn indicates that there are other sources of supply of these elements, other than detrital minerals. Pelitic particles and organic matter play very important role in transportation and absorption of elements especially in case of Mn, Fe and Co. During 15,000 and 30,000 yr which corresponds to the sediments at 25 cm and 55 cm, there was change in temperature, and hence we presume that this time interval represent the fifth Glacial period.

TABLE I
TEXTURAL, CARBONATE CONTENT AND ORGANIC MATTER ANALYSIS
OF CORE NO. 3800

| Sample No. | Depth interval in cm | Clay% (<2 μ) % | Silt (2-63 μ) % | Sand (>63 μ) % | Mud/ Sand | Carbonate % | Organic matter % |
|------------|----------------------|---------------------|----------------------|---------------------|-----------|-------------|------------------|
| 1 | 10-15 | 1.10 | 48.23 | 50.67 | 0.97 | 60.68 | 3.47 |
| 2 | 15-20 | 1.21 | 44.33 | 54.46 | 0.84 | 72.56 | 1.19 |
| 3 | 20-25 | 0.51 | 51.71 | 47.78 | 1.09 | 60.82 | 2.68 |
| 4 | 25-30 | 2.41 | 55.65 | 41.94 | 1.38 | 41.19 | 2.42 |
| 5 | 30-35 | 2.70 | 51.76 | 45.54 | 1.19 | 58.67 | 2.08 |
| 6 | 35-40 | 6.66 | 56.48 | 36.86 | 1.71 | 58.18 | 3.05 |
| 7 | 40-45 | 1.50 | 53.47 | 45.04 | 1.22 | 46.69 | 4.01 |
| 8 | 45-50 | 1.50 | 49.99 | 48.55 | 1.06 | 52.59 | 2.58 |
| 9 | 50-55 | 1.47 | 56.73 | 41.79 | 1.39 | 57.84 | 1.94 |
| 10 | 55-60 | 3.36 | 50.97 | 45.67 | 1.19 | 30.35 | 2.41 |
| 11 | 60-65 | 1.67 | 54.32 | 44.00 | 1.27 | 46.66 | 2.90 |
| 12 | 65-70 | 4.15 | 46.57 | 49.28 | 1.03 | 45.11 | 2.00 |
| 13 | 70-75 | 3.05 | 45.67 | 51.27 | 0.95 | 50.91 | 2.18 |
| 14 | 75-80 | 3.70 | 49.27 | 56.59 | 0.77 | 45.14 | 3.17 |
| 15 | 80-85 | 3.96 | 43.78 | 52.26 | 0.91 | 44.89 | 1.70 |
| 16 | 85-90 | 3.92 | 42.75 | 53.33 | 0.88 | 49.48 | 3.00 |
| 17 | 90-95 | 2.78 | 52.09 | 45.13 | 1.22 | 50.06 | 2.38 |
| 18 | 95-100 | 2.86 | 51.19 | 45.95 | 1.18 | 52.24 | 1.82 |
| 19 | 100-105 | 3.64 | 55.96 | 40.40 | 1.48 | 50.79 | 3.98 |
| 20 | 105-110 | 4.00 | 41.15 | 54.85 | 0.82 | 56.34 | 4.91 |
| 21 | 110-115 | 1.82 | 53.32 | 44.86 | 1.23 | 44.39 | 3.04 |
| 22 | 115-120 | 1.23 | 53.44 | 45.33 | 1.21 | 49.46 | 1.55 |

TABLE II
ELEMENTAL CONCENTRATION OF SEDIMENTS IN PPM

| Sample No. | Cu | Ni | Co | Mn | Fe | Zn | Cr | Li | Sr |
|------------|-----|------|------|-----|-------|------|------|----|-----|
| 1 | 110 | 1650 | 450 | 648 | 23580 | 742 | 506 | 14 | 84 |
| 2 | 76 | 3516 | 406 | 736 | 44900 | 3880 | 2098 | 8 | 156 |
| 3 | 90 | 754 | 502 | 458 | 33420 | 5700 | 696 | 24 | 210 |
| 4 | 66 | 778 | 832 | 362 | 30760 | 1342 | 156 | 12 | 68 |
| 5 | 56 | 1404 | 822 | 560 | 40720 | 1096 | 340 | 14 | 136 |
| 6 | 84 | 716 | 692 | 720 | 65120 | 8160 | 582 | 36 | 88 |
| 7 | 74 | 1282 | 460 | 722 | 57040 | 5880 | 726 | 26 | 128 |
| 8 | 76 | 1224 | 624 | 506 | 43220 | 440 | 476 | 18 | 164 |
| 9 | 66 | 5756 | 798 | 966 | 46238 | 1918 | 3630 | 10 | 228 |
| 10 | 50 | 896 | 674 | 534 | 39920 | 510 | 132 | 18 | 58 |
| 11 | 58 | 1344 | 1340 | 698 | 46800 | 3660 | 926 | 12 | 120 |
| 12 | 44 | 466 | 384 | 480 | 33520 | 438 | 916 | 8 | 86 |
| 13 | 44 | 1200 | 350 | 476 | 48200 | 376 | 430 | 4 | 46 |
| 14 | 44 | 1954 | 666 | 590 | 42180 | 464 | 296 | 14 | 8 |
| 15 | 26 | 1090 | 458 | 442 | 38840 | 600 | 1022 | 6 | 62 |
| 16 | 44 | 608 | 570 | 560 | 40140 | 326 | 176 | 8 | 112 |
| 17 | 30 | 928 | 1042 | 436 | 39500 | 284 | 944 | 6 | 68 |
| 18 | 52 | 2394 | 494 | 458 | 39540 | 590 | 926 | 2 | 32 |
| 19 | 40 | 3240 | 702 | 704 | 45600 | 422 | 1676 | 16 | 96 |
| 20 | 38 | 674 | 588 | 672 | 39900 | 384 | 248 | 4 | 64 |
| 21 | 28 | 1328 | 584 | 750 | 40080 | 374 | 538 | 4 | 90 |
| 22 | 22 | 636 | 476 | 426 | 27400 | 2112 | 764 | 4 | 46 |

TABLE III

CORRELATION COEFFICIENTS OF VARIABLES IN SAMPLES

| | Cu | Ni | Co | Mn | Fe | Zn | Cr | Li | Sr | OM | Clay | Mud/ sand | Carbo- nate |
|----------------|-------|-------|-------|------|------|-------|-------|-------|-------|-------|-------|--------------|----------------|
| Cu | 1.00 | | | | | | | | | | | | |
| Ni | 0.16 | 1.00 | | | | | | | | | | | |
| Co | -0.07 | 0.07 | 1.00 | | | | | | | | | | |
| Mn | 0.25 | 0.66 | 0.15 | 1.00 | | | | | | | | | |
| Fe | 0.09 | 0.19 | 0.16 | 0.50 | 1.00 | | | | | | | | |
| Zn | -0.54 | -0.02 | 0.04 | 0.29 | 0.54 | 1.00 | | | | | | | |
| Cr | 0.08 | 0.88 | 0.07 | 0.60 | 0.18 | 0.13 | 1.00 | | | | | | |
| Li | 0.63 | -0.10 | 0.09 | 0.22 | 0.51 | 0.74 | -0.11 | 1.00 | | | | | |
| Sr | 0.51 | 0.43 | 0.12 | 0.46 | 0.16 | 0.40 | 0.55 | 0.33 | 1.00 | | | | |
| OM | 0.12 | -0.18 | 0.11 | 0.33 | 0.21 | 0.06 | -0.31 | 0.31 | -0.09 | 1.00 | | | |
| Clay | -0.21 | -0.20 | -0.04 | 0.11 | 0.04 | -0.14 | -0.20 | -0.17 | -0.21 | 0.57 | 1.00 | | |
| Mud/ sand | -0.01 | 0.10 | 0.34 | 0.31 | 0.31 | 0.30 | 0.16 | 0.30 | 0.14 | 0.07 | -0.25 | 1.00 | |
| Carbo- nate | 0.42 | 0.37 | -0.22 | 0.33 | 0.03 | 0.36 | -0.37 | 0.03 | 0.48 | -0.18 | -0.32 | -0.06 | 1.00 |

TABLE IV

EIGEN VALUES AND PERCENTAGE OF THEIR CONTRIBUTION

| Factors | Eigen value | Percentage of trace | Cumulative percent of trace |
|---------|-------------|---------------------|-----------------------------|
| 1 | 3.7059 | 30.88 | 30.88 |
| 2 | 2.3644 | 19.70 | 50.58 |
| 3 | 1.7374 | 14.48 | 65.06 |
| 4 | 1.3711 | 11.42 | 76.49 |
| 5 | 0.8781 | 7.32 | 83.80 |
| 6 | 0.6175 | 5.15 | 88.95 |
| 7 | 0.4848 | 4.04 | 92.99 |

TABLE V
ROTATED FACTOR MATRIX

| Variables | Factors | | | | |
|--------------|---------|---------|---------|---------|---------|
| | 1 | 2 | 3 | 4 | 5 |
| Cu | 0.9244 | 0.1002 | -0.0033 | -0.0898 | 0.0258 |
| Ni | 0.0127 | 0.9407 | -0.1125 | 0.0184 | 0.0047 |
| Co | 0.0137 | 0.0624 | 0.0766 | 0.9075 | -0.0319 |
| Mn | 0.1711 | 0.7569 | 0.3513 | 0.1425 | 0.3611 |
| Fe | 0.0522 | 0.2117 | 0.1584 | 0.0586 | 0.8682 |
| Zn | 0.6073 | 0.0046 | -0.0792 | -0.0019 | 0.6588 |
| Cr | 0.0108 | 0.9300 | -0.2265 | 0.0219 | 0.0596 |
| Li | 0.7223 | -0.1680 | 0.0601 | 0.1248 | 0.5671 |
| Sr | 0.6407 | 0.5565 | -0.1109 | 0.1228 | -0.0189 |
| O.M. | 0.1582 | -0.1335 | 0.8801 | 0.1538 | 0.1464 |
| Clay | -0.2200 | -0.0502 | 0.8566 | -0.1567 | -0.0541 |
| Mud/ Sand | -0.0207 | 0.0860 | -0.1750 | 0.6298 | 0.5165 |

TABLE VI
VARIMAX SCORES

| Sample No. | Factors | | | | |
|---------------|---------|-------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | 5 |
| 1 | 2.52 | -1.78 | 0.49 | -2.36 | -2.33 |
| 2 | 6.50 | 13.98 | -4.80 | -0.27 | 3.26 |
| 3 | 11.01 | 1.12 | -1.73 | 0.34 | 5.24 |
| 4 | -3.37 | -8.15 | -1.13 | -0.48 | -4.09 |
| 5 | 0.49 | -0.45 | -1.16 | 0.87 | -0.17 |
| 6 | 18.59 | 5.94 | 3.37 | 7.08 | 19.98 |
| 7 | 13.34 | 5.31 | 3.22 | 3.26 | 12.91 |
| 8 | 3.46 | -0.29 | -0.74 | -0.14 | 0.85 |
| 9 | 12.20 | 30.92 | -5.18 | 6.74 | 10.74 |
| 10 | -2.68 | -6.11 | 0.39 | -0.69 | -2.02 |
| 11 | 5.15 | 5.18 | 0.65 | 5.64 | 6.23 |
| 12 | -6.54 | -6.11 | -1.64 | -3.85 | -7.12 |
| 13 | -7.25 | -6.41 | -0.51 | -3.92 | -5.94 |
| 14 | -5.24 | -5.62 | 2.19 | -2.16 | -3.91 |
| 15 | -9.01 | -5.84 | -2.11 | -3.99 | -8.10 |
| 16 | -4.63 | -5.98 | 1.29 | -2.51 | -4.72 |
| 17 | -7.28 | -4.66 | -0.95 | 0.49 | -5.04 |
| 18 | -7.09 | -2.23 | -2.59 | -2.64 | -6.24 |
| 19 | 2.27 | 8.24 | 1.57 | 3.53 | 4.72 |
| 20 | -8.90 | -9.17 | 12.21 | -3.46 | -5.32 |
| 21 | -3.55 | 0.89 | 0.43 | 2.15 | 0.23 |
| 22 | -10.01 | -8.40 | -3.29 | -3.64 | -9.15 |

TABLE VII
RANGES AND AVERAGE CONCENTRATION OF VARIOUS ELEMENTS
IN THE SEDIMENTS FROM DIFFERENT REGIONS
(EXCEPT IRON, OTHER VALUES ARE MENTIONED IN PPM)

| | Western continental shelf sediments | | Indus shelf sediments | Western continental slope sediments | | Sample core No.3800 | |
|-----|-------------------------------------|------|-----------------------|-------------------------------------|----------|---------------------|--|
| | A | B | B | B | A | B | |
| Fe% | 0.38-7.73 | 4.26 | 3.69 | 3.19 | 2.3-6.5 | 4.07 | |
| Mn | 27-1466 | 491 | 5.43 | 3435 | 362-966 | 586 | |
| Ni | 19-365 | 491 | 107 | 168 | 466-5756 | 1538 | |
| Cu | 6-218 | 90 | 43 | 91 | 22-110 | 55 | |
| Zn | 2-158 | 6 | 201 | 206 | 284-8160 | 1804 | |
| Co | 3-57 | 22 | - | - | 350-1340 | 632 | |

A - Range of values in the bulk sample

B - Average value in the bulk sample

Data taken from Murty et al. (1983).

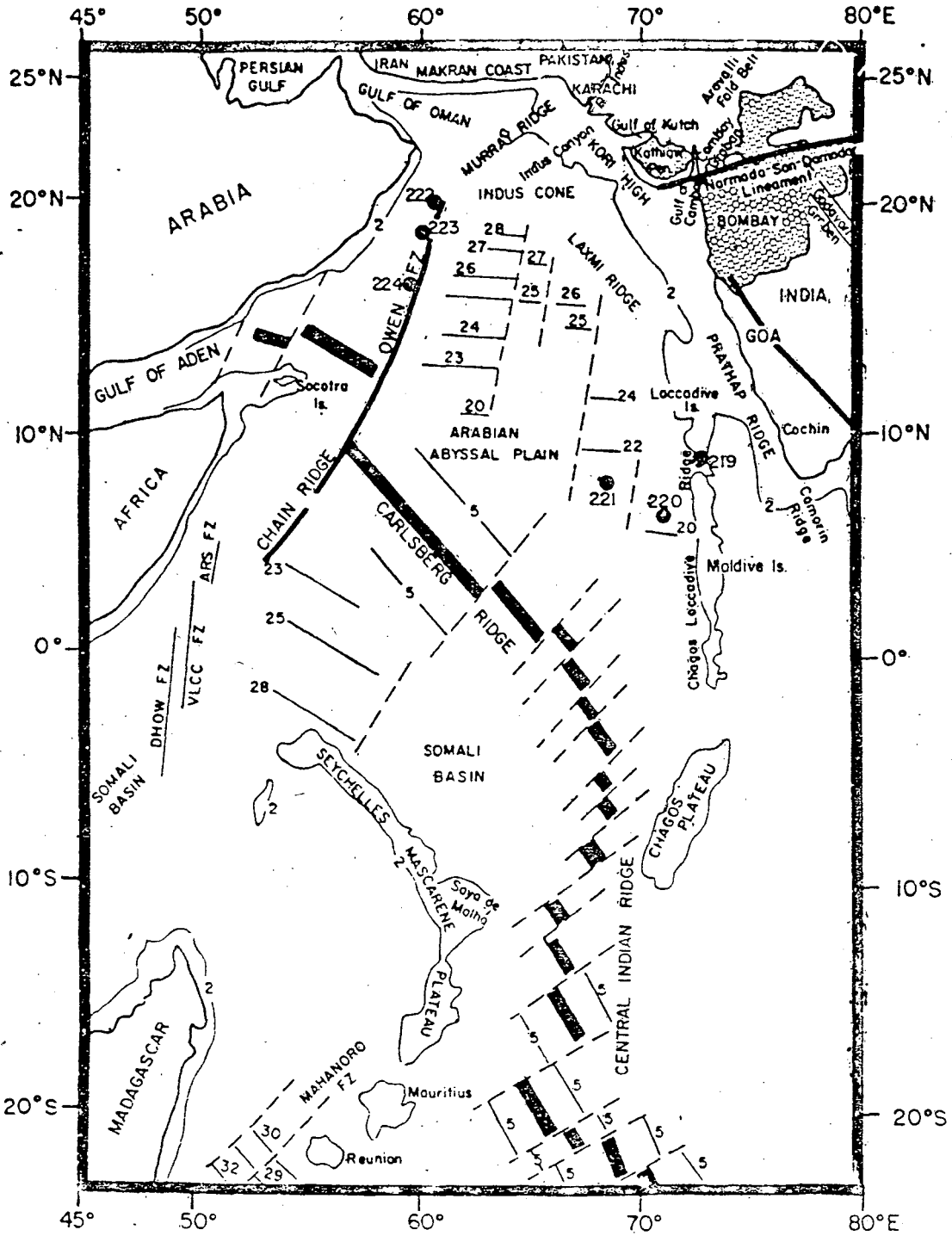


Figure 1 (After Naini, 1980)

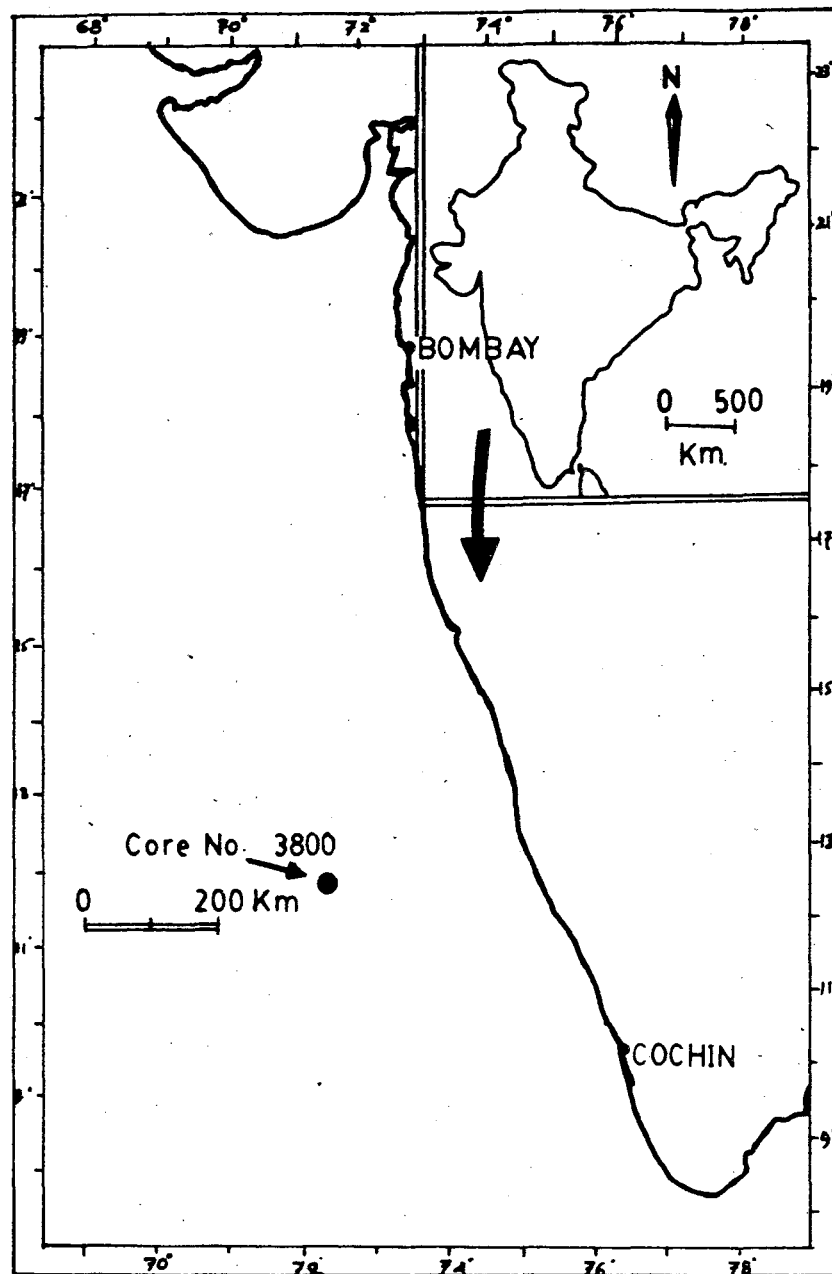
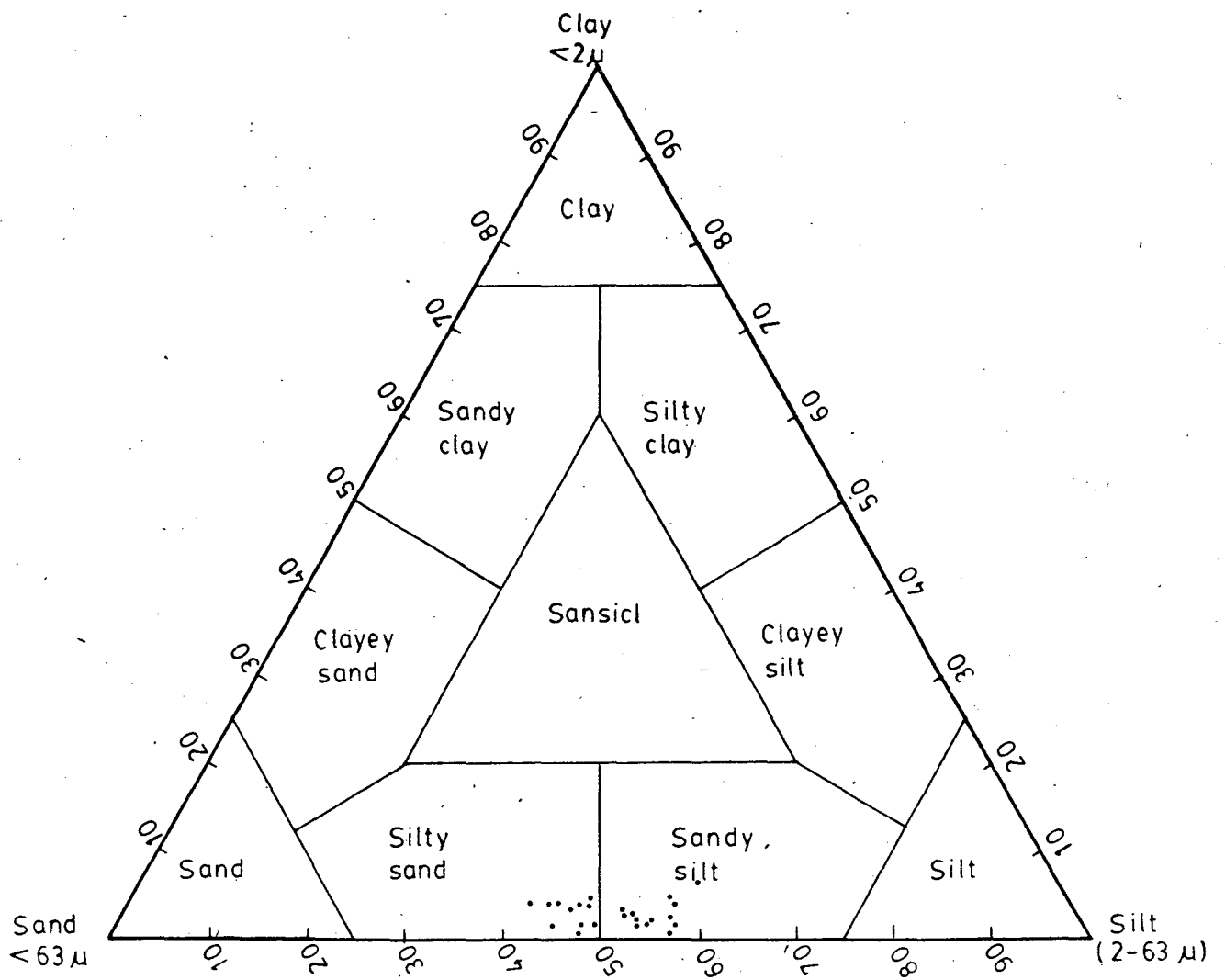
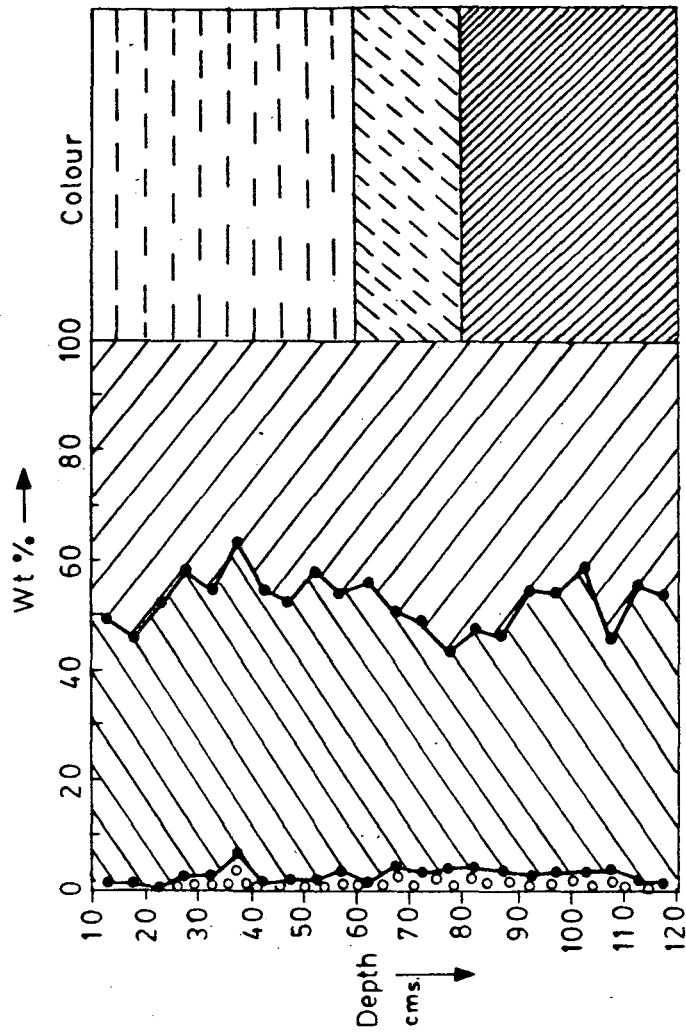


Fig. 2



After Shephard (1953)

Fig. 3



I N D E X

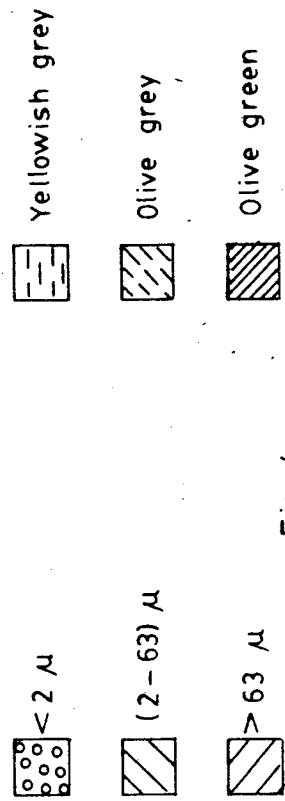


Fig. 4

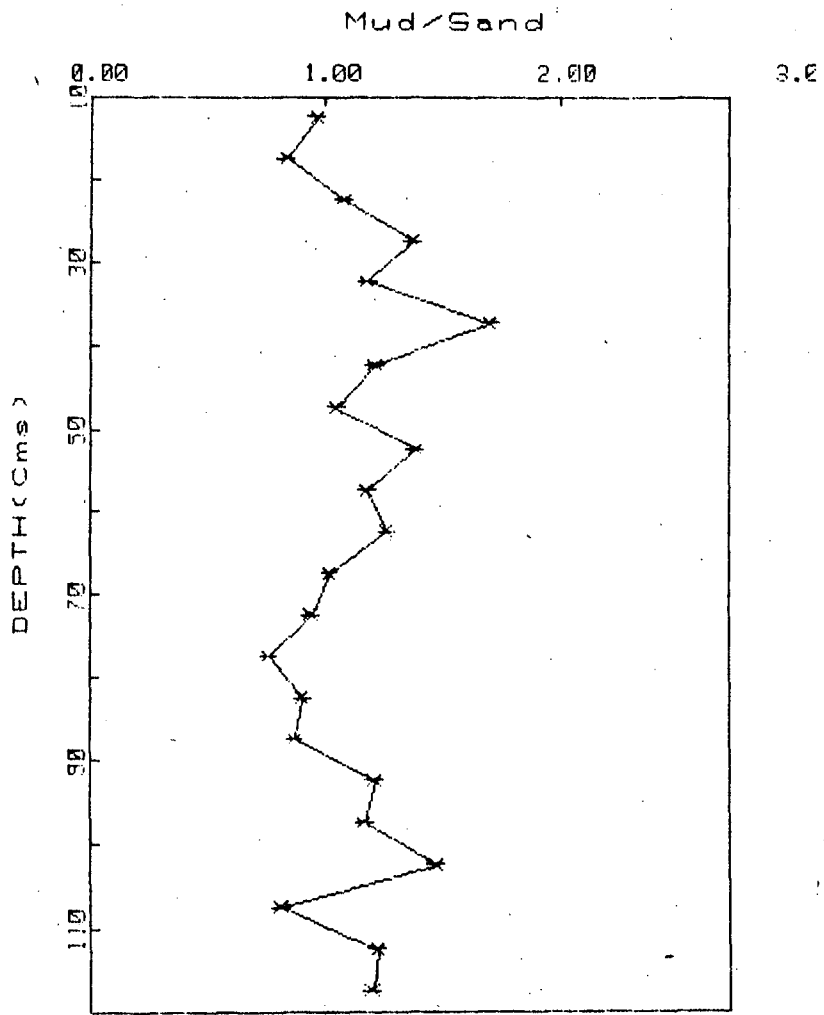


Fig. 5

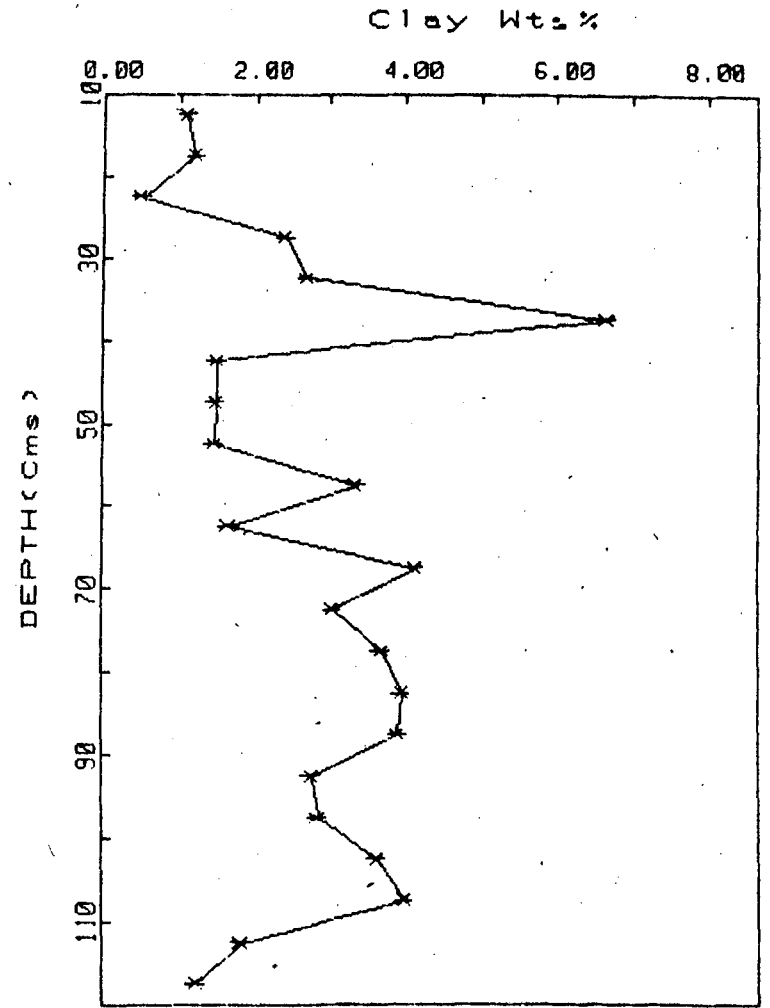


Fig. 6

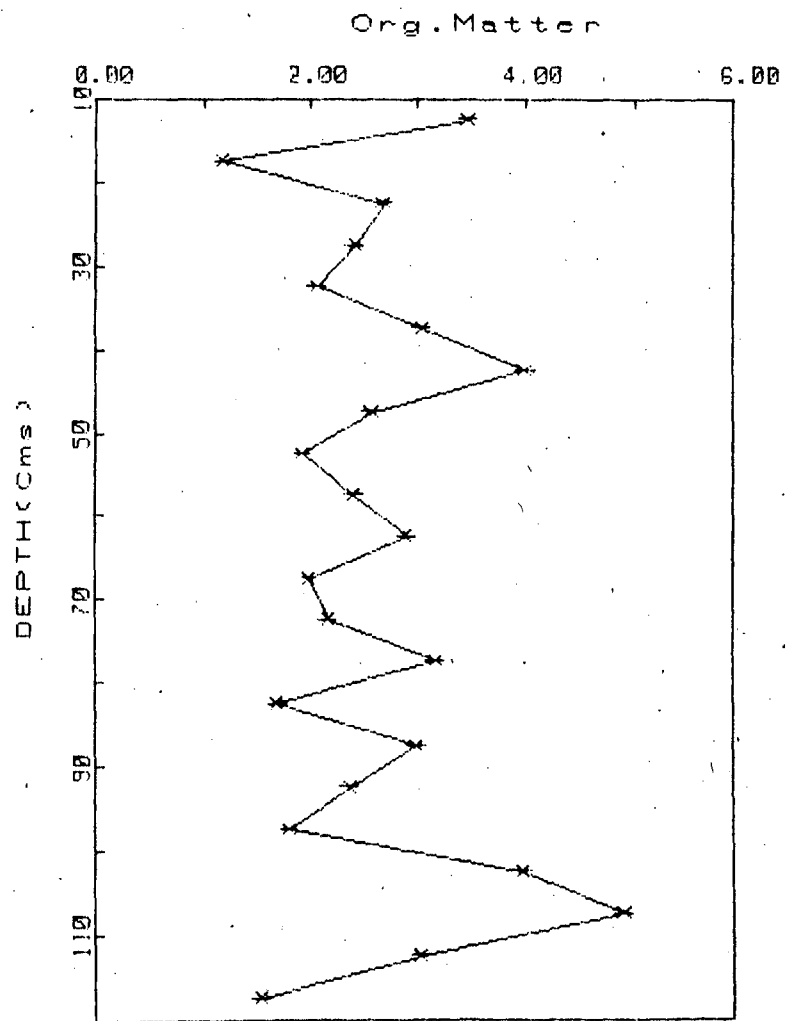


Fig.7

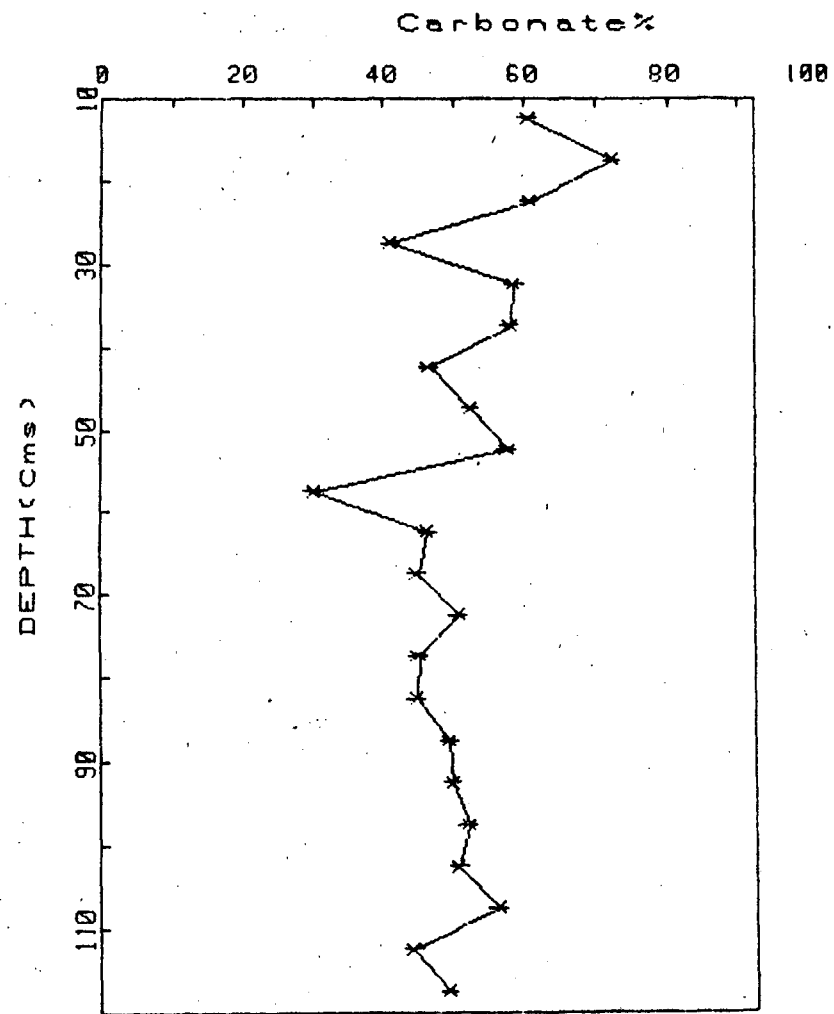


Fig.8

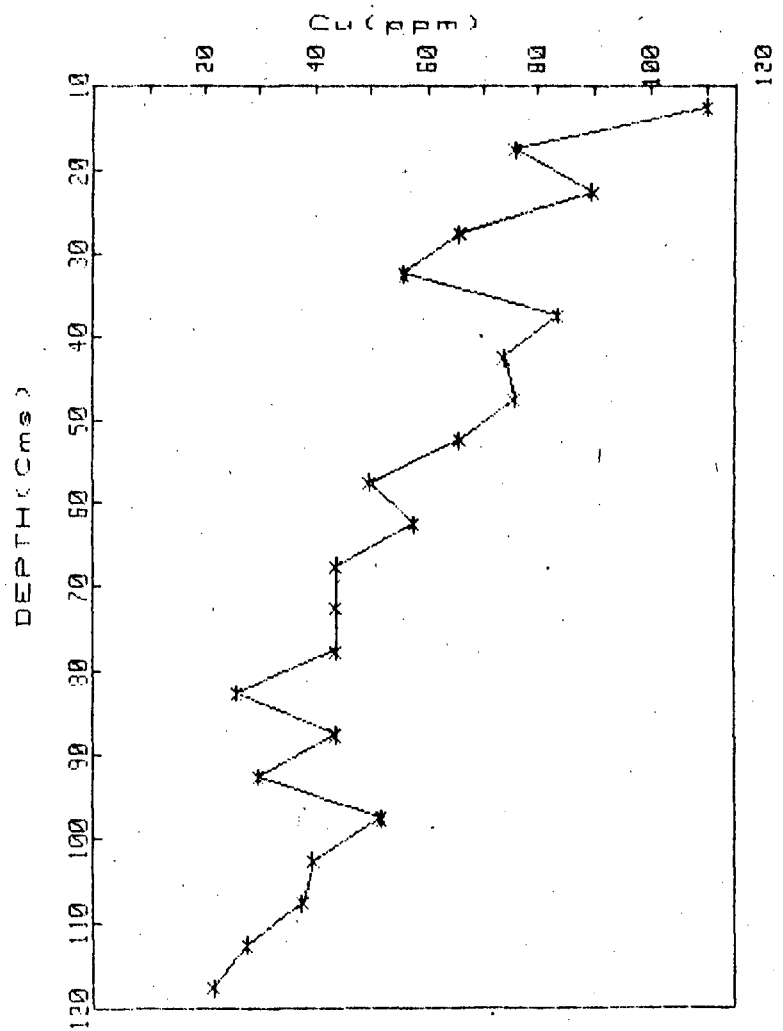


Fig. 9

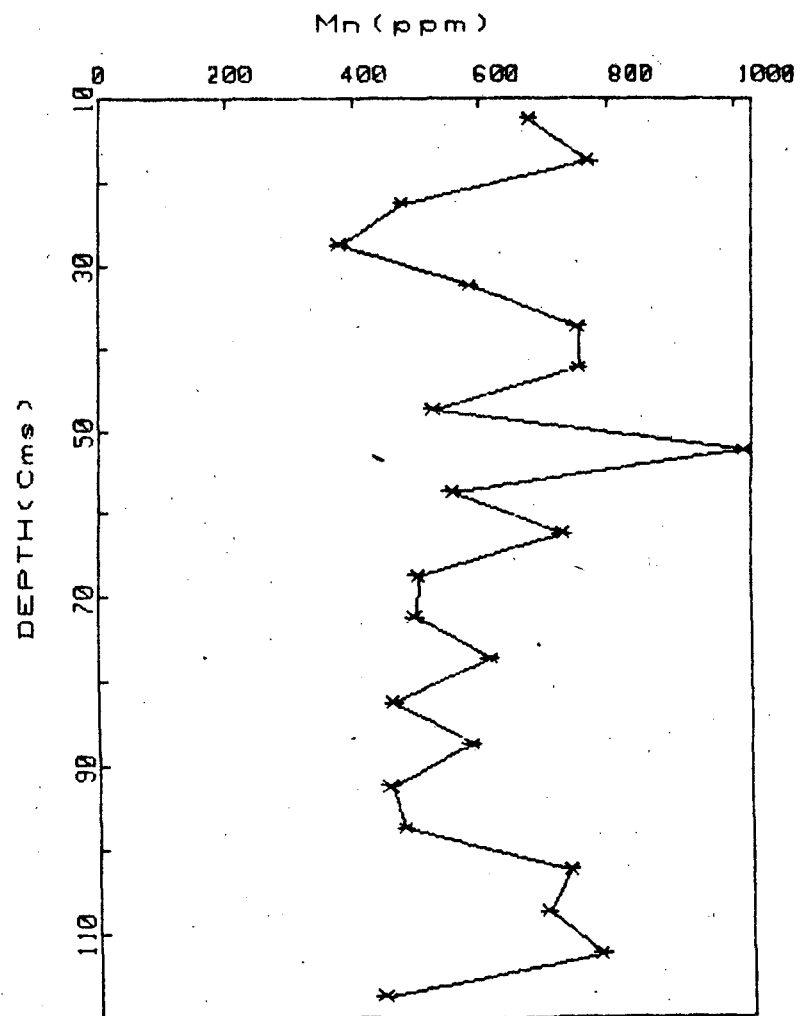


Fig. 10

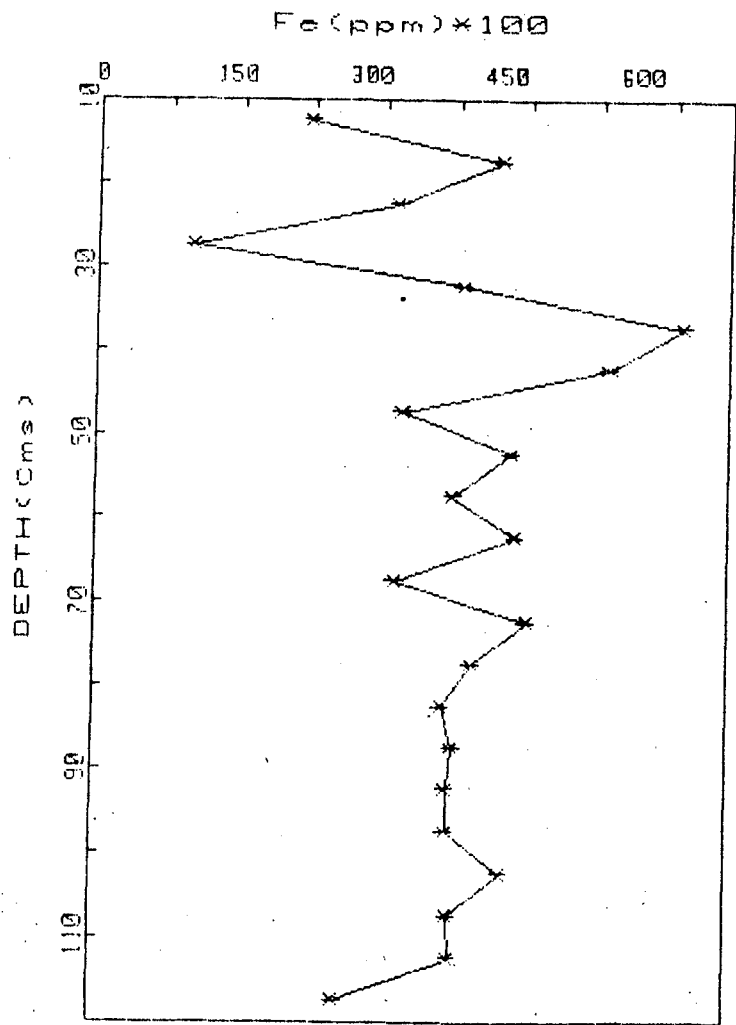


Fig.11

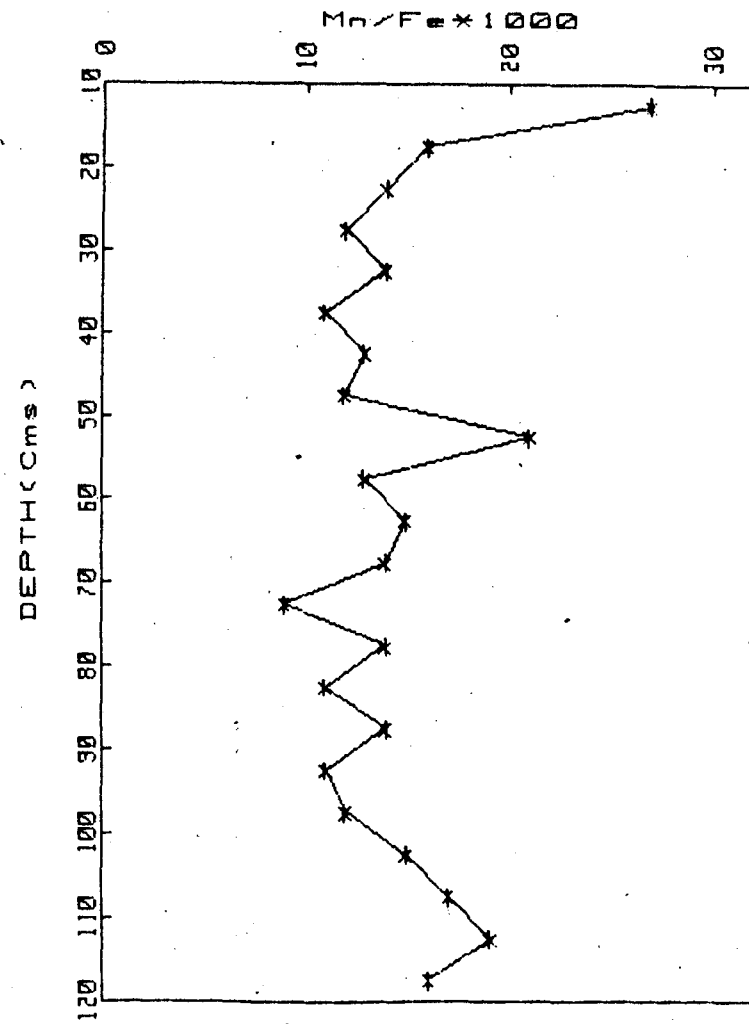


Fig. 12

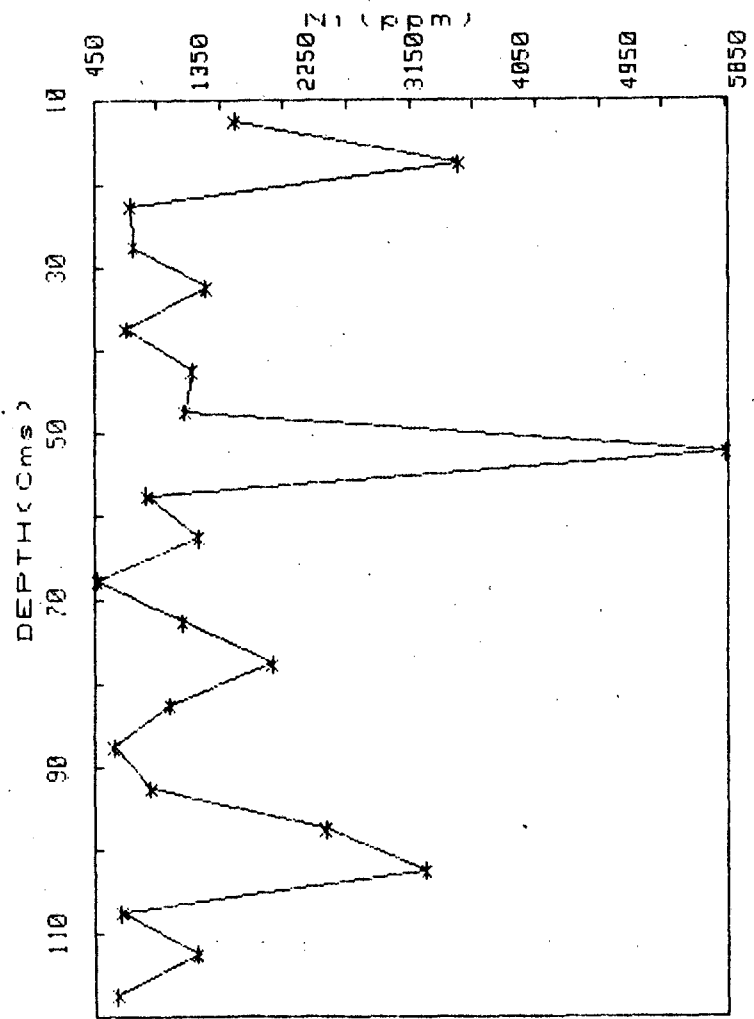


Fig. 13

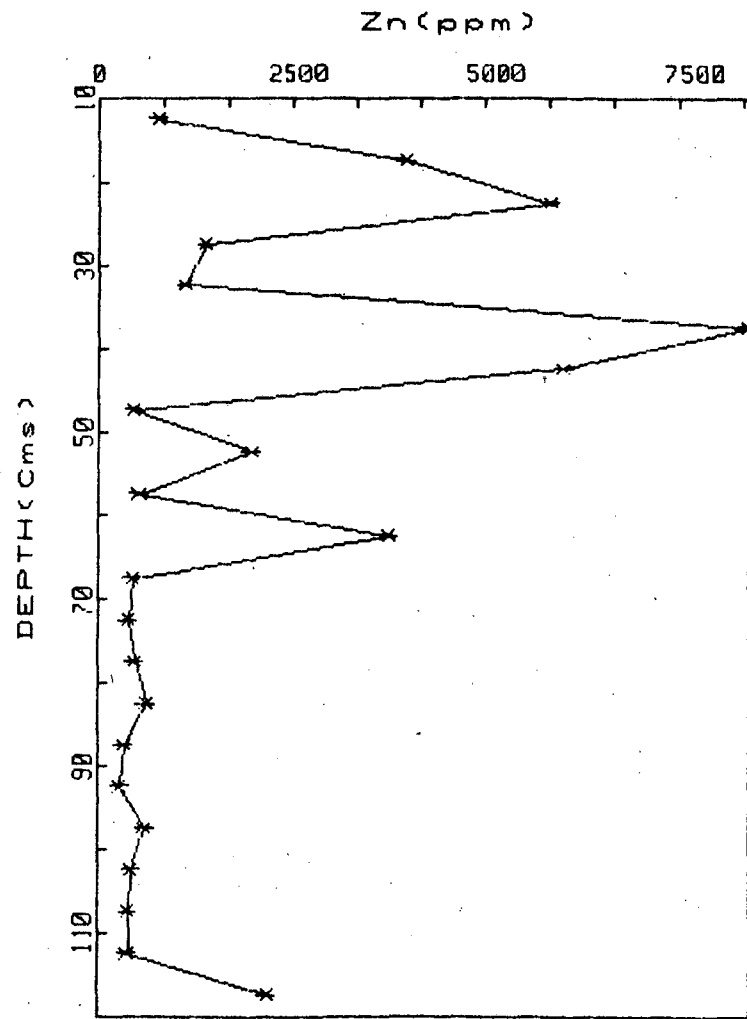


Fig. 14

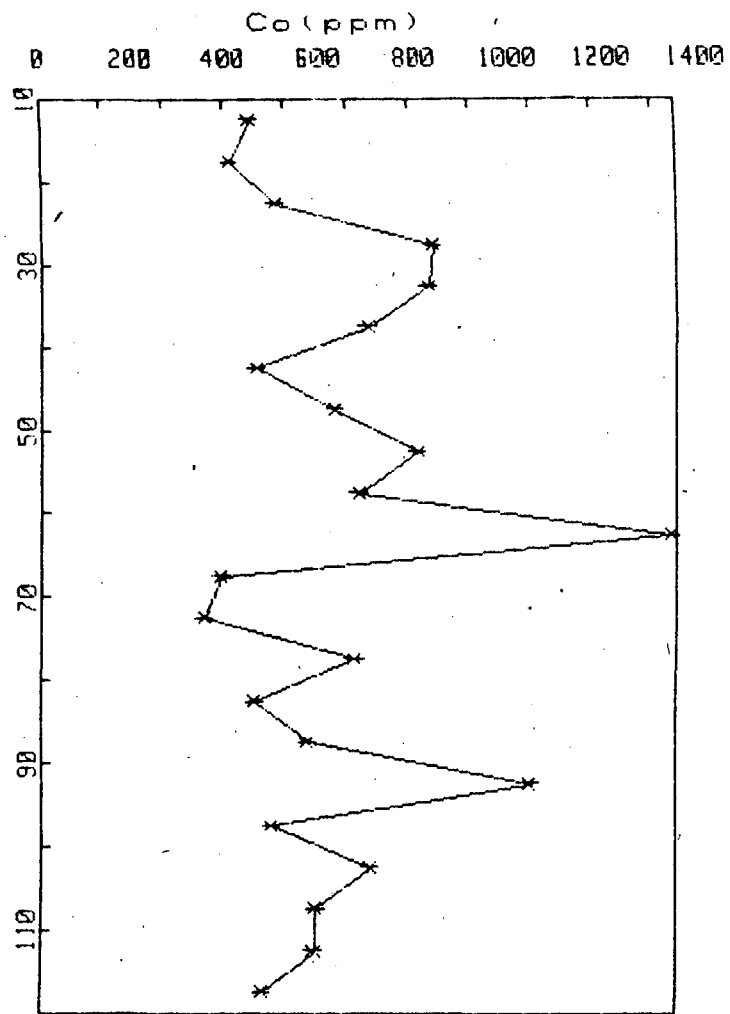


Fig. 15

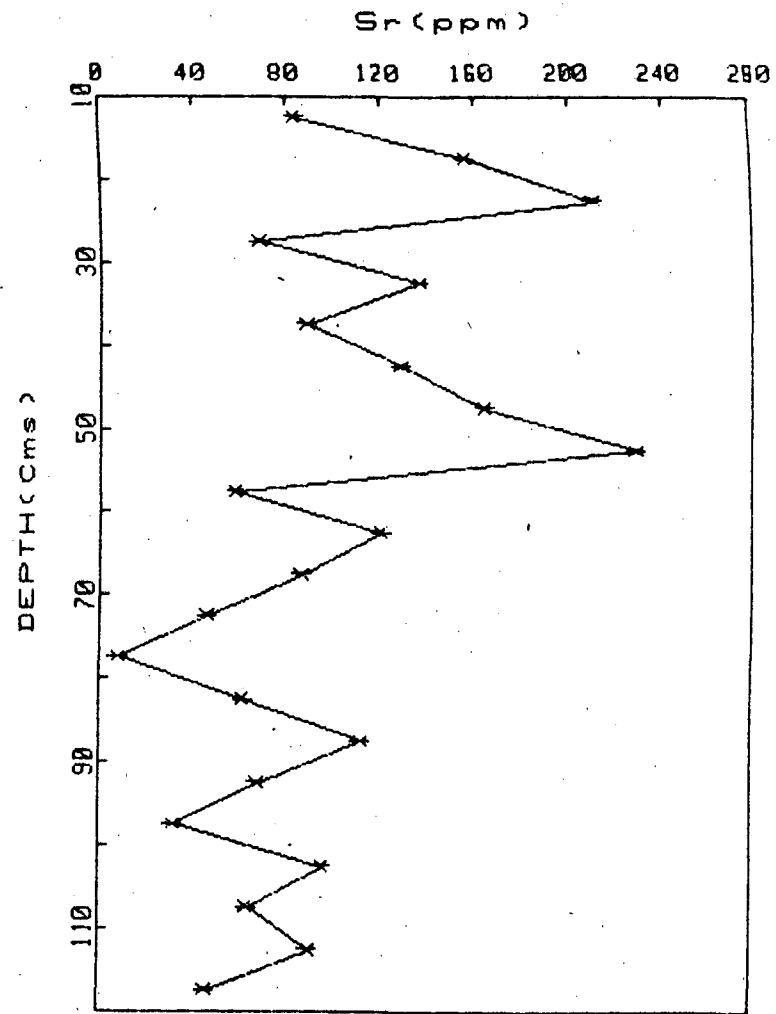


Fig. 16

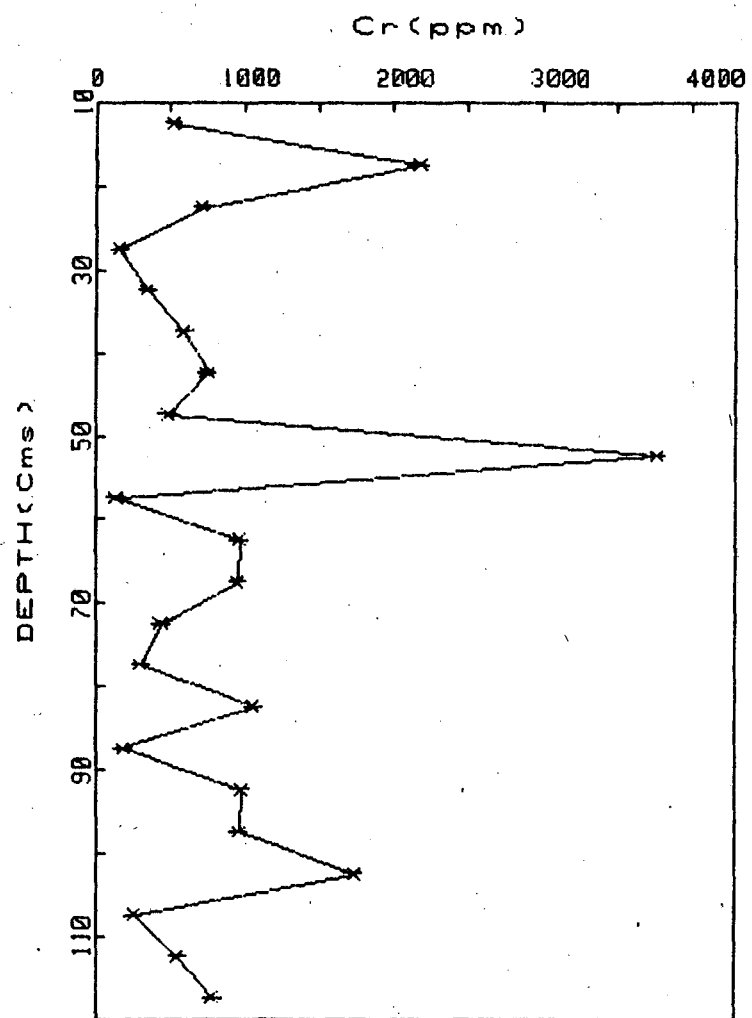


Fig. 17

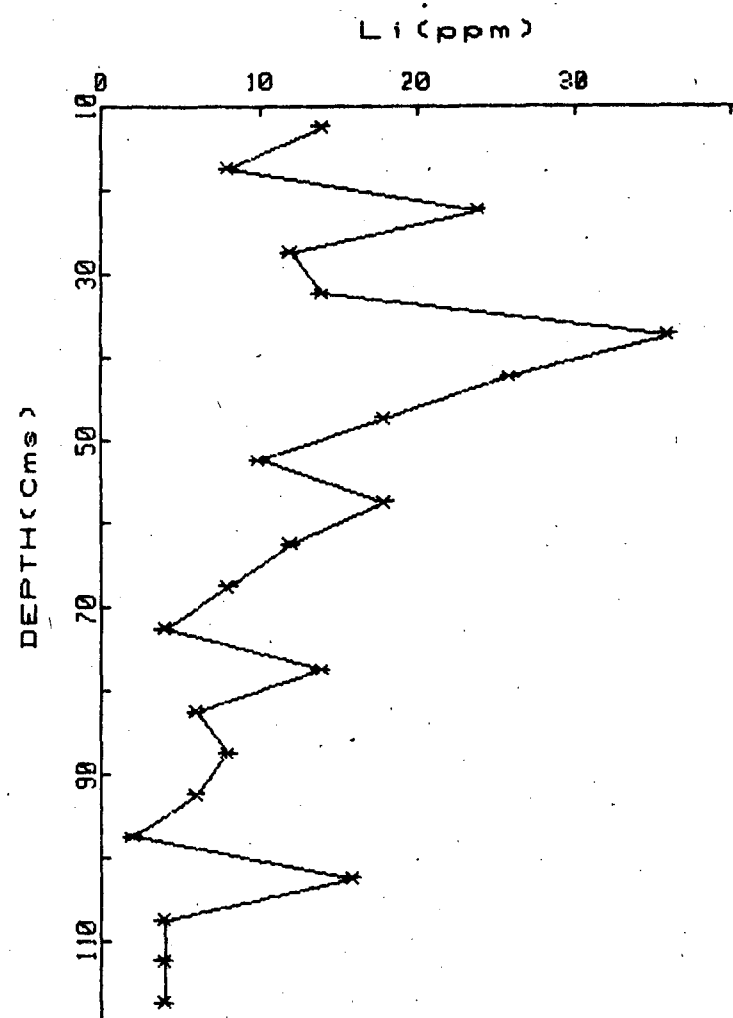


Fig. 18

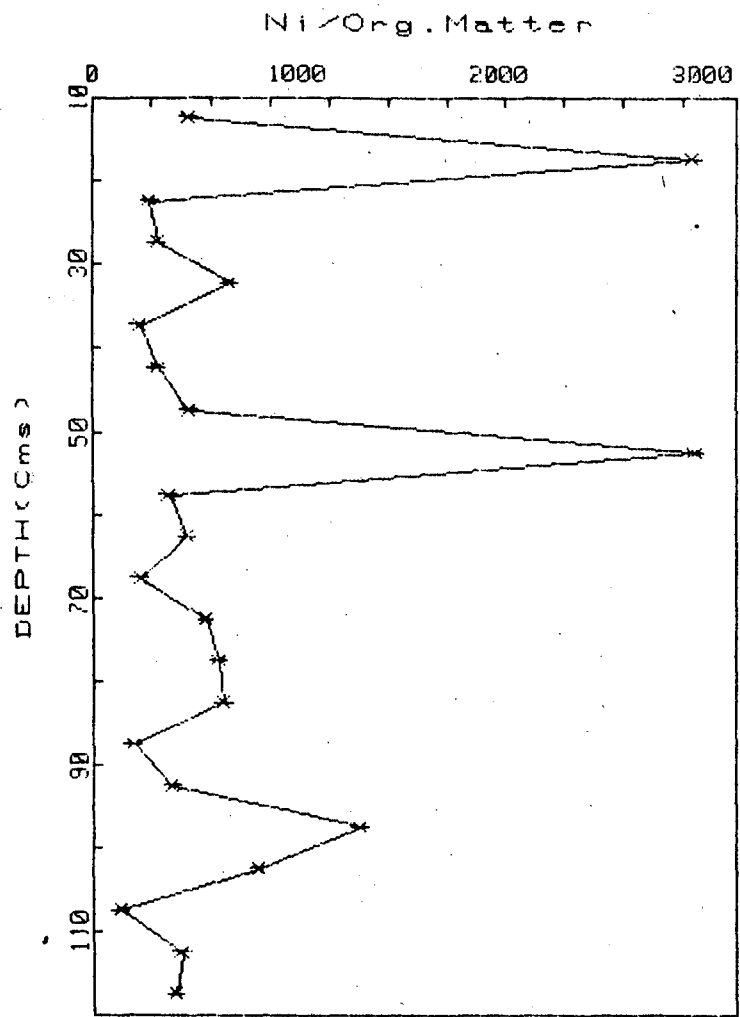


Fig. 19

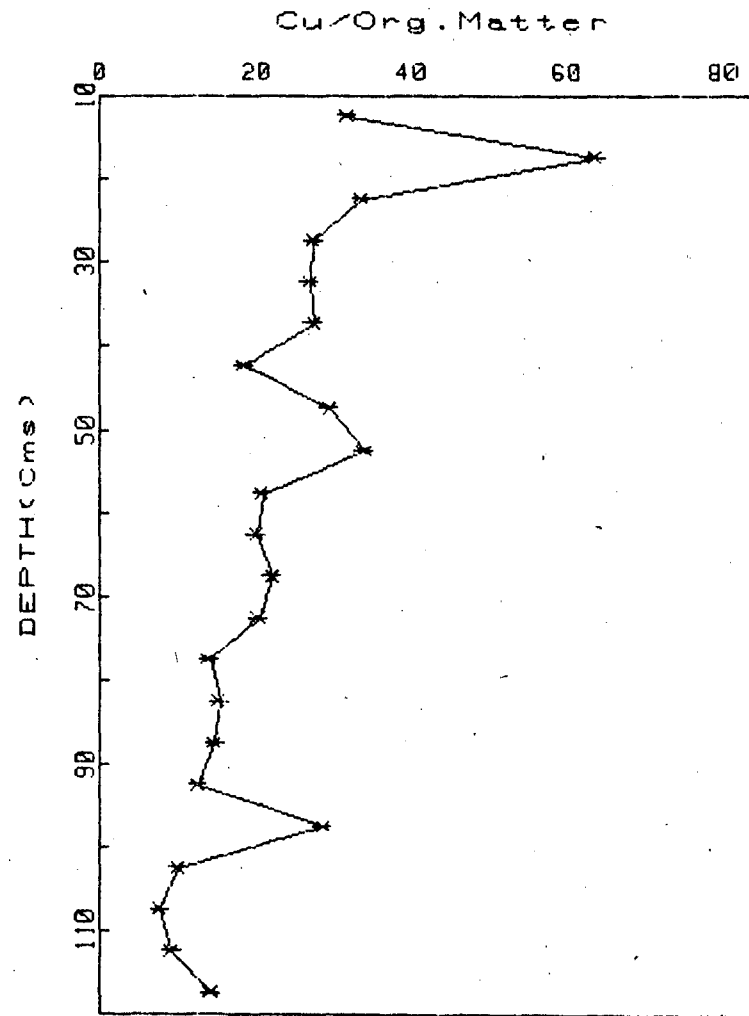


Fig. 20

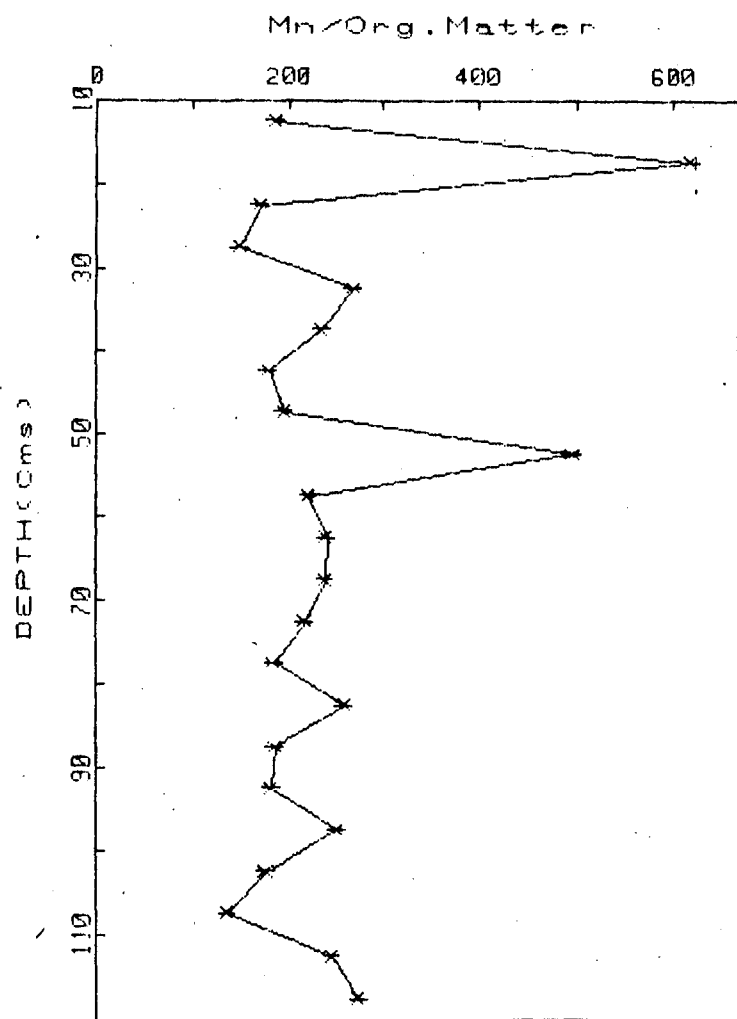


Fig. 21

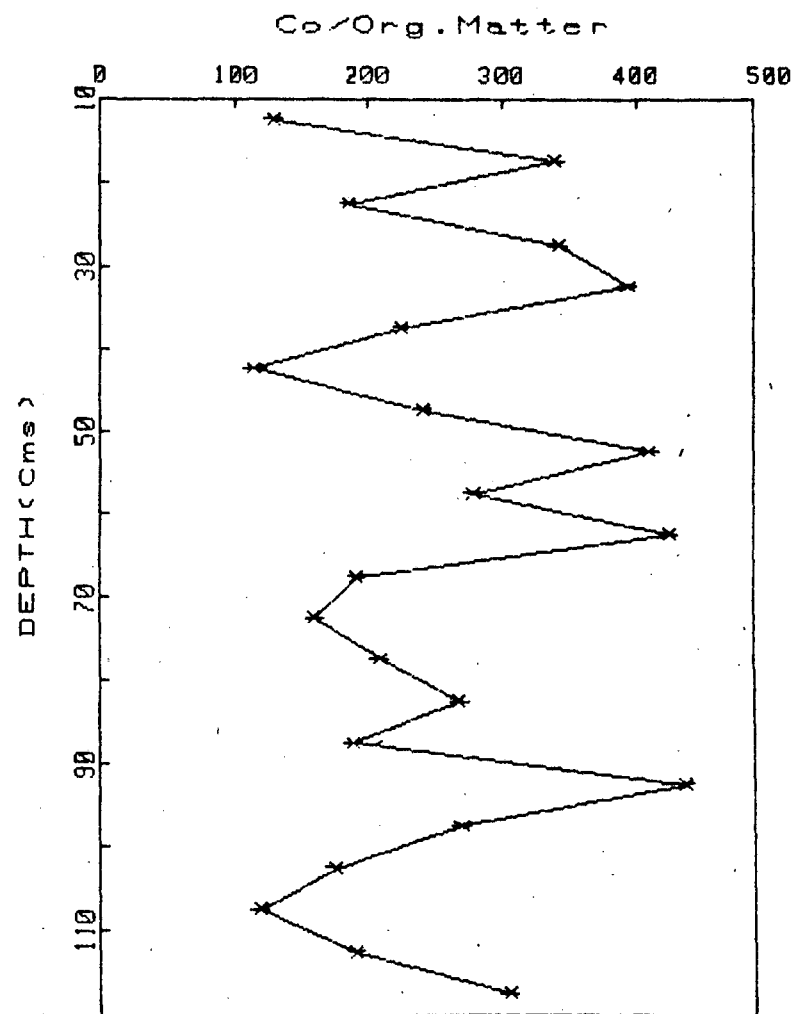


Fig. 22

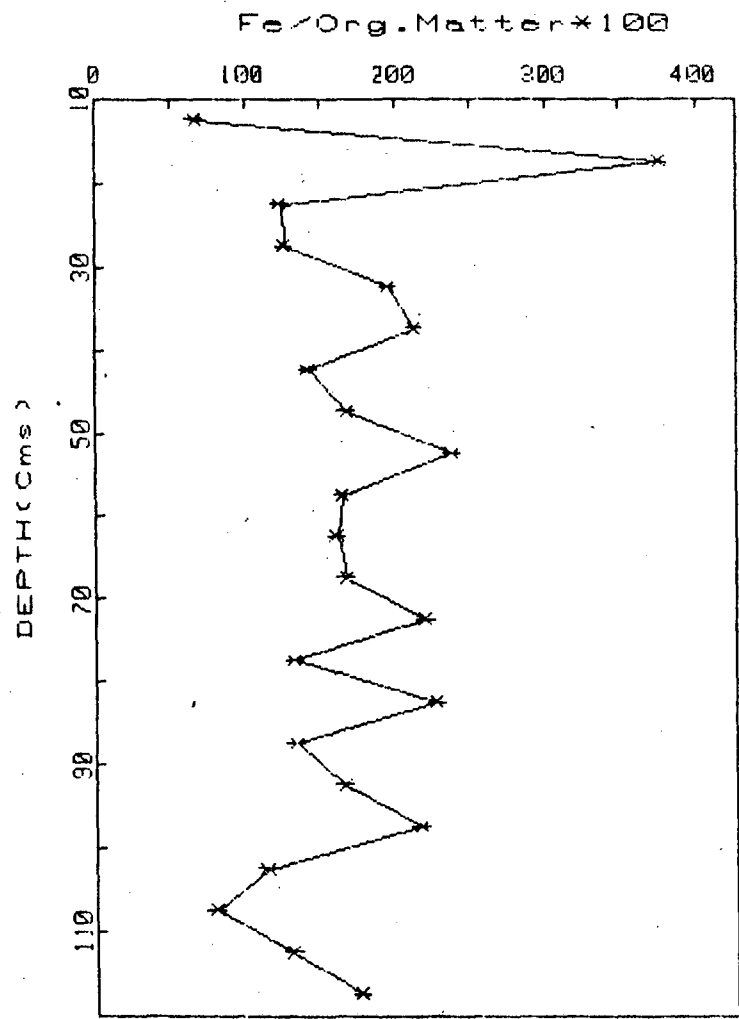


Fig. 23

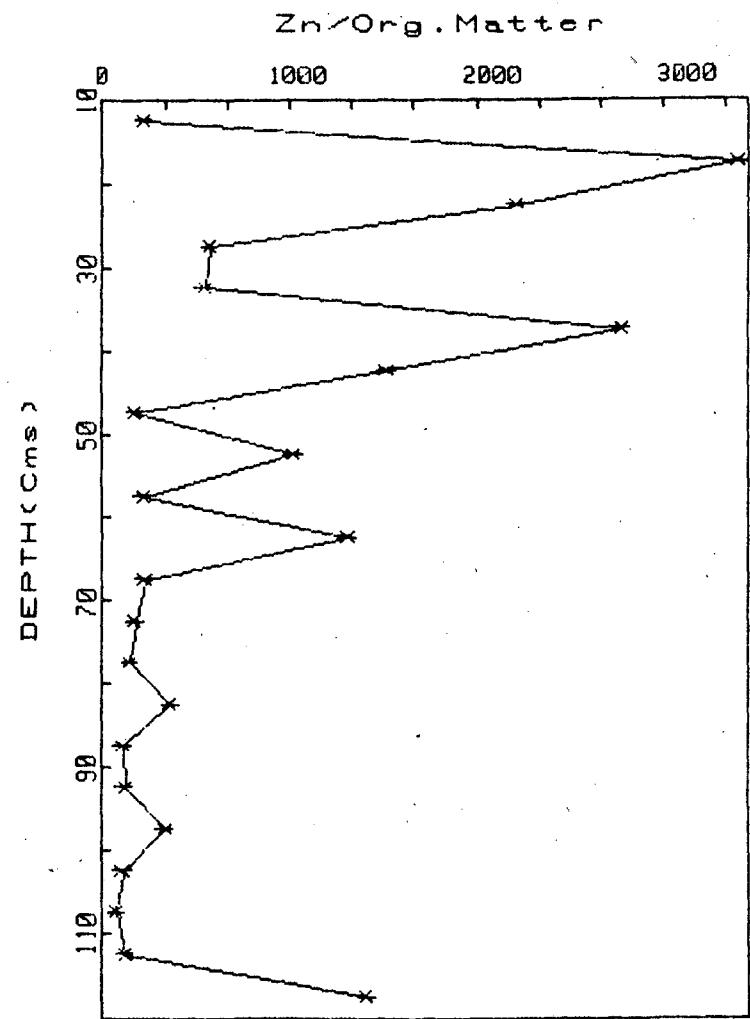
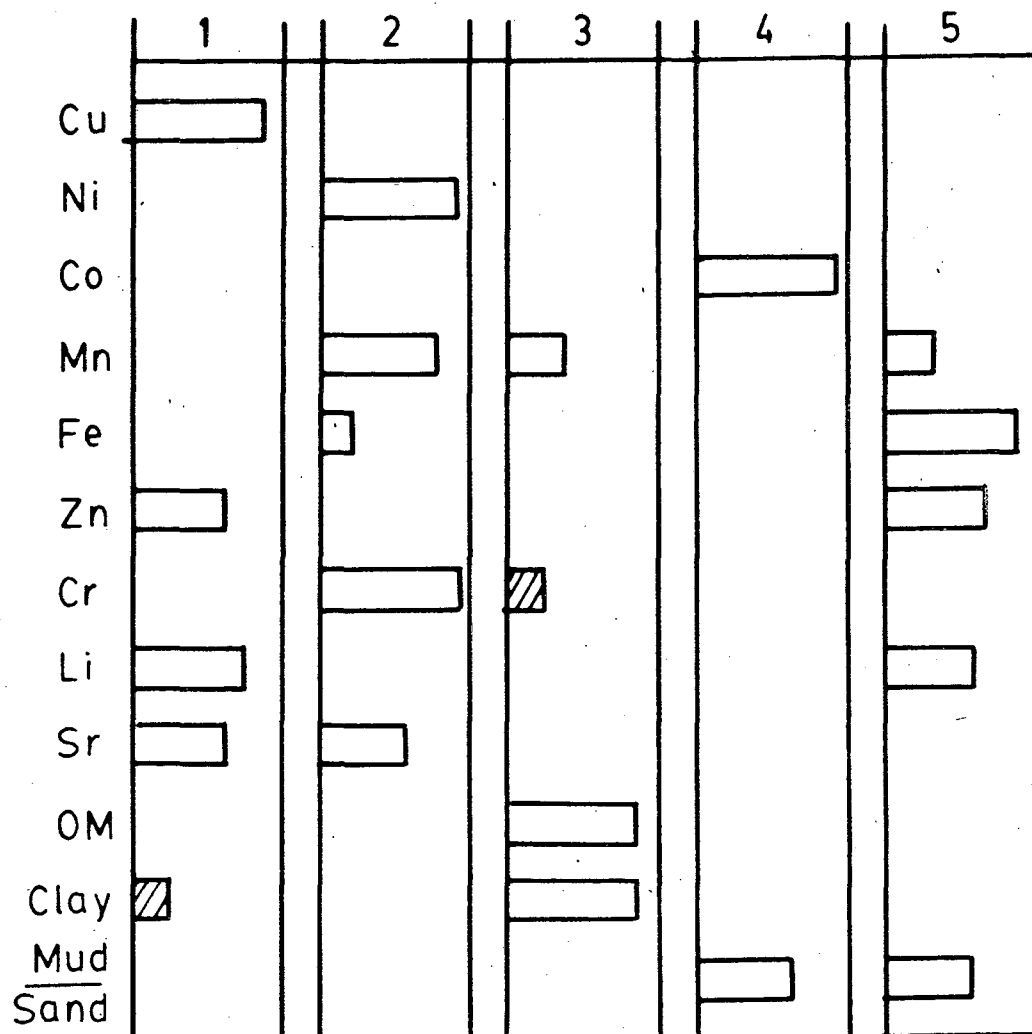


Fig. 24



Positive loadings

Negative loadings

0.0 .5 1.0

Magnitude of loadings

Fig. 25

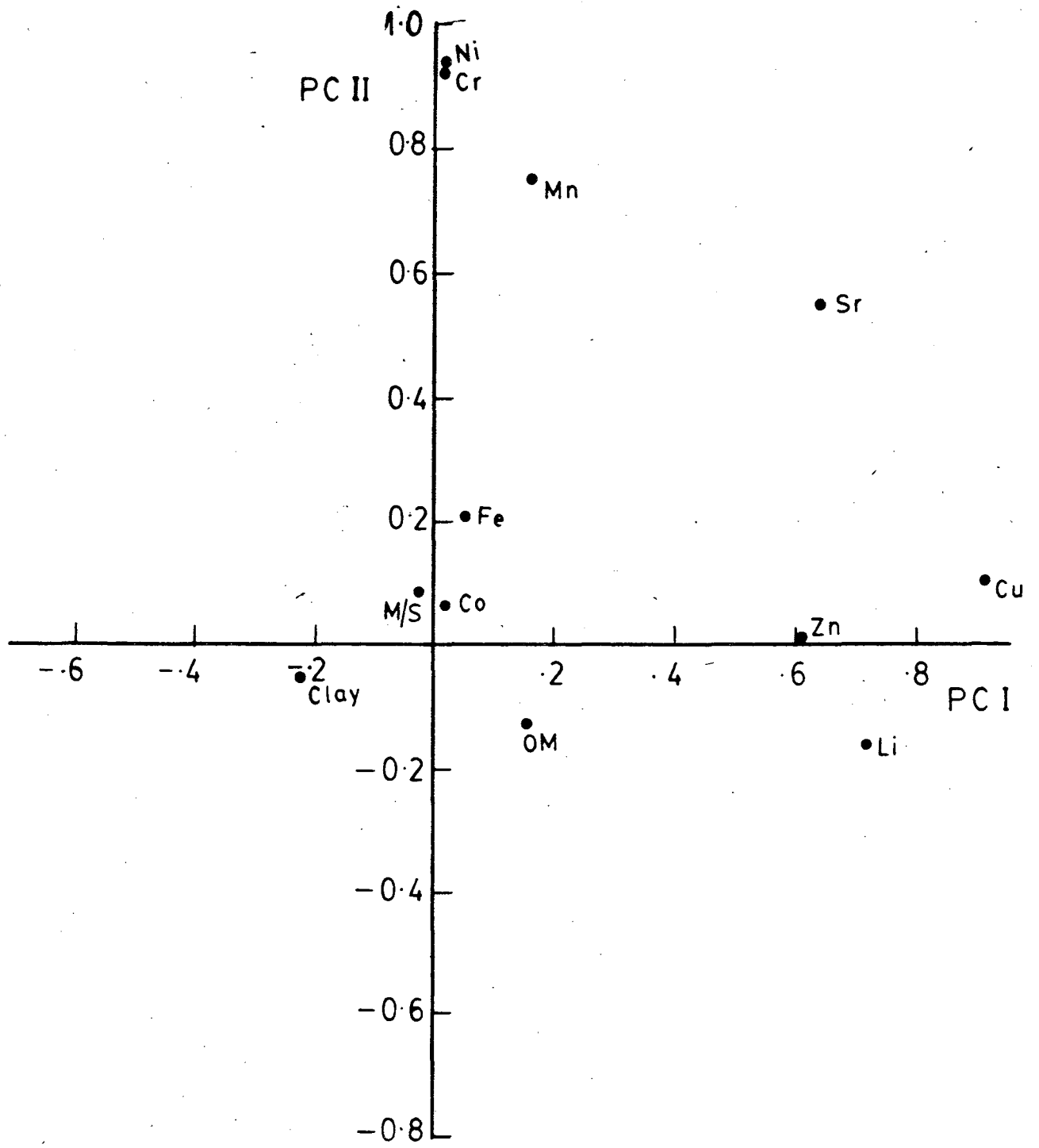


Fig. 26

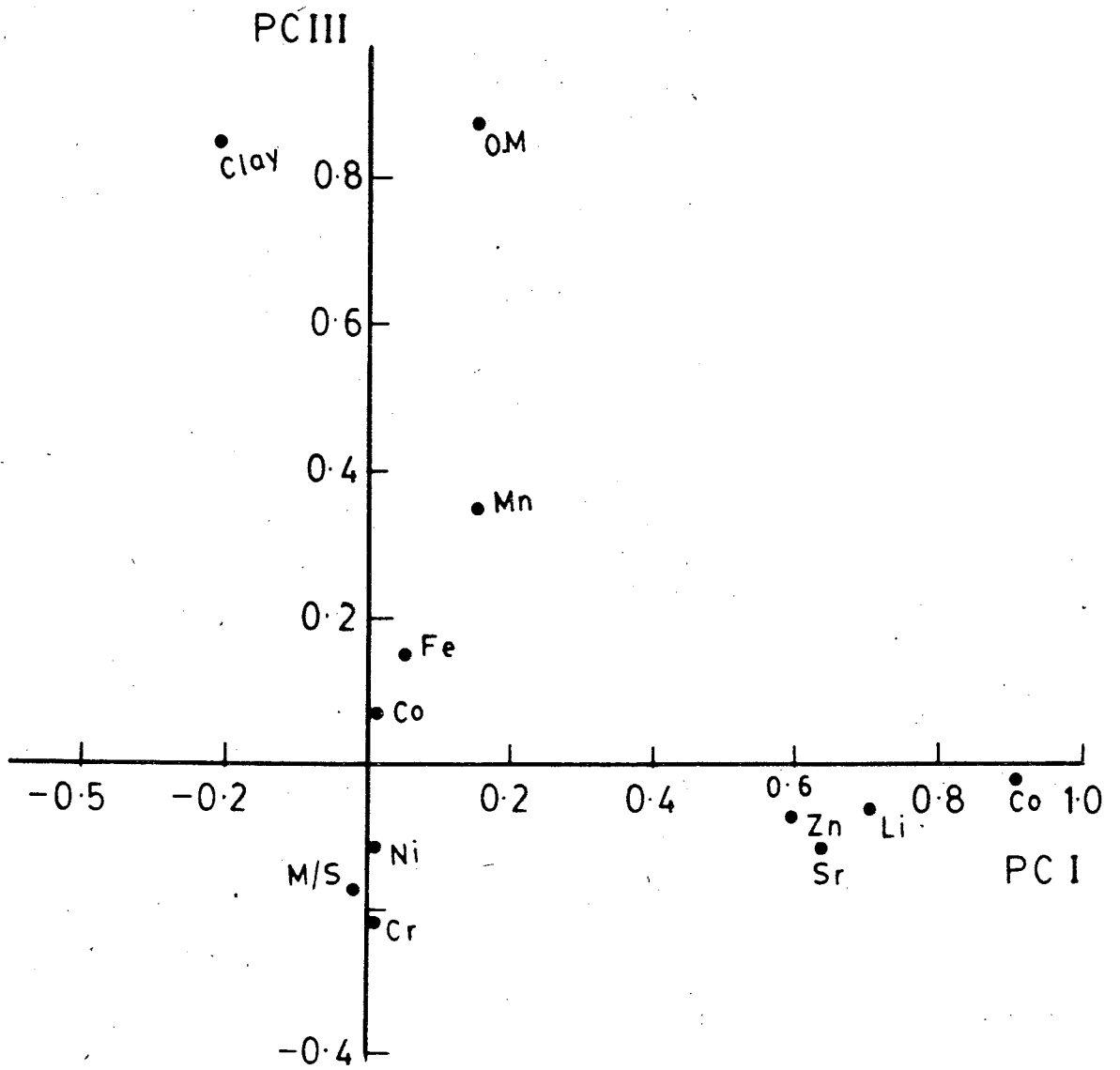


Fig.27

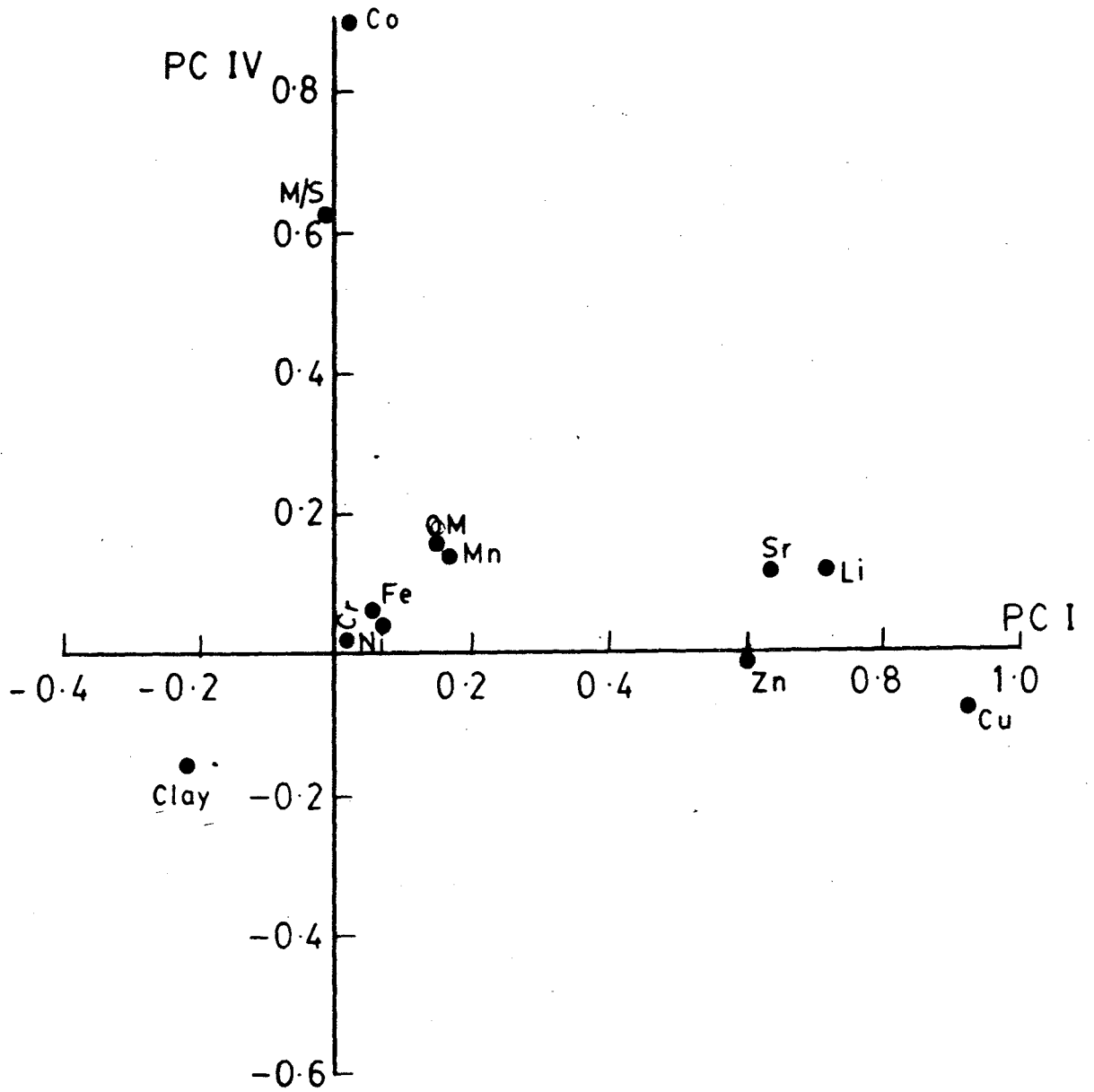


Fig. 28

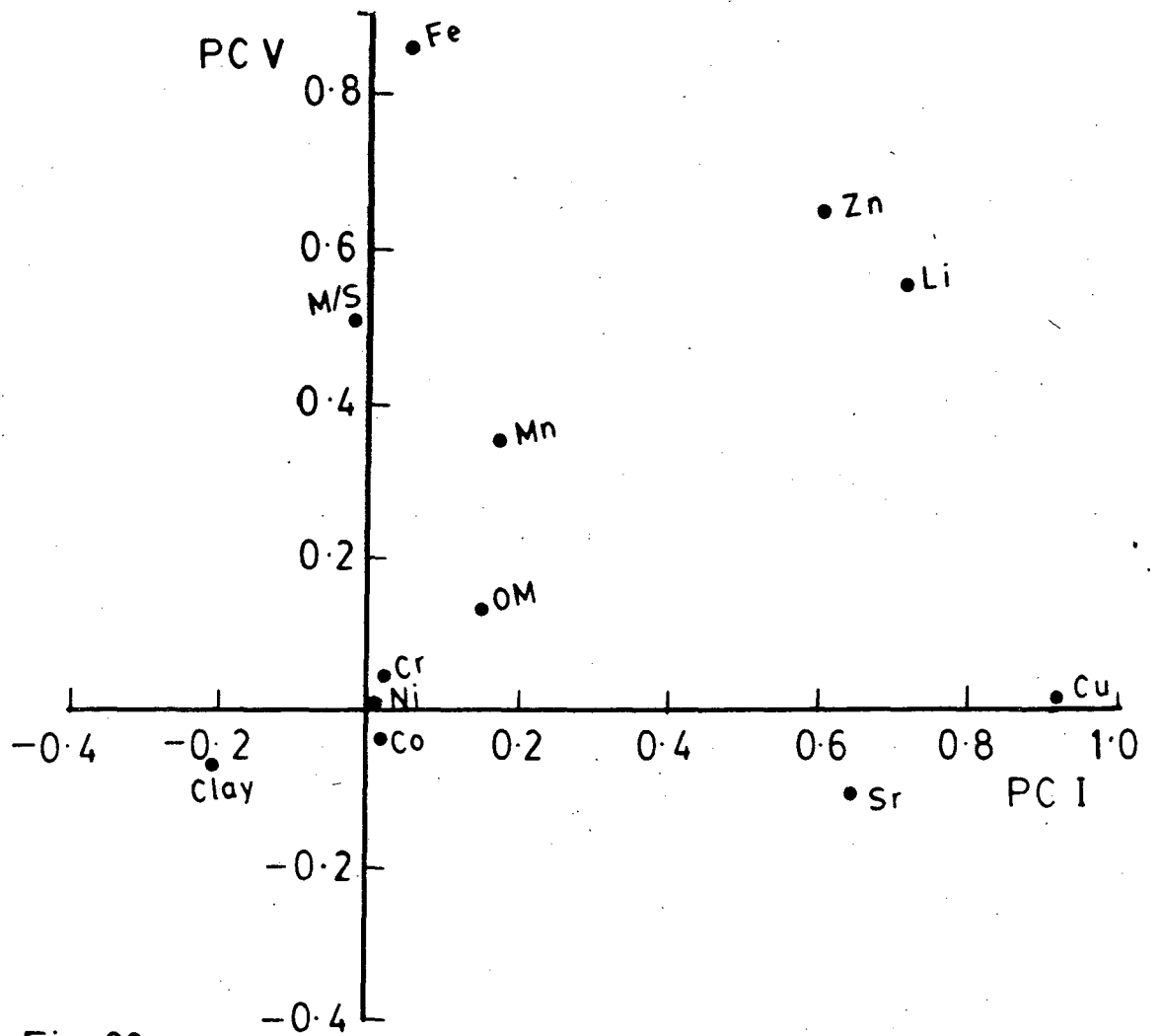


Fig. 29

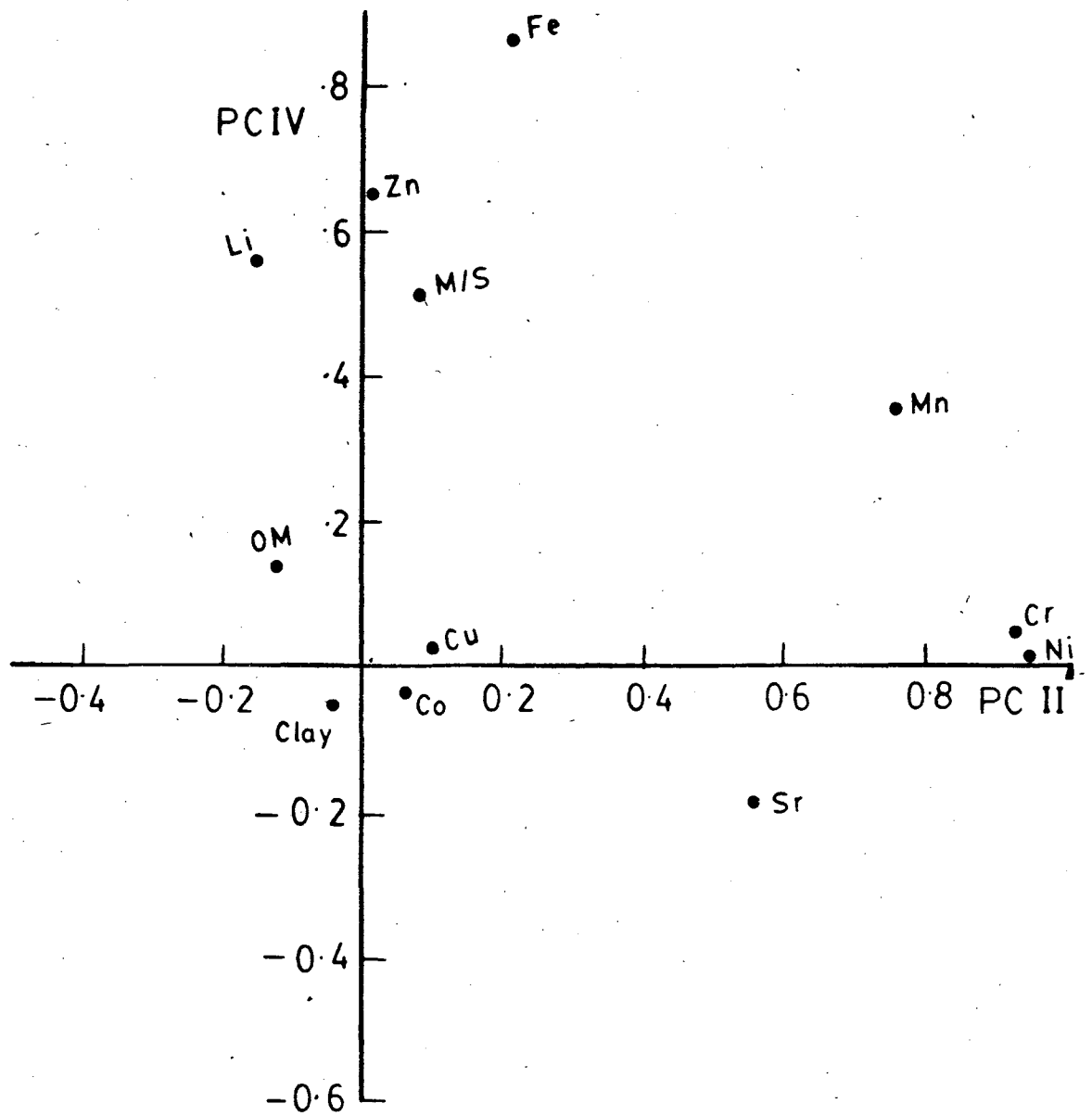


Fig. 30

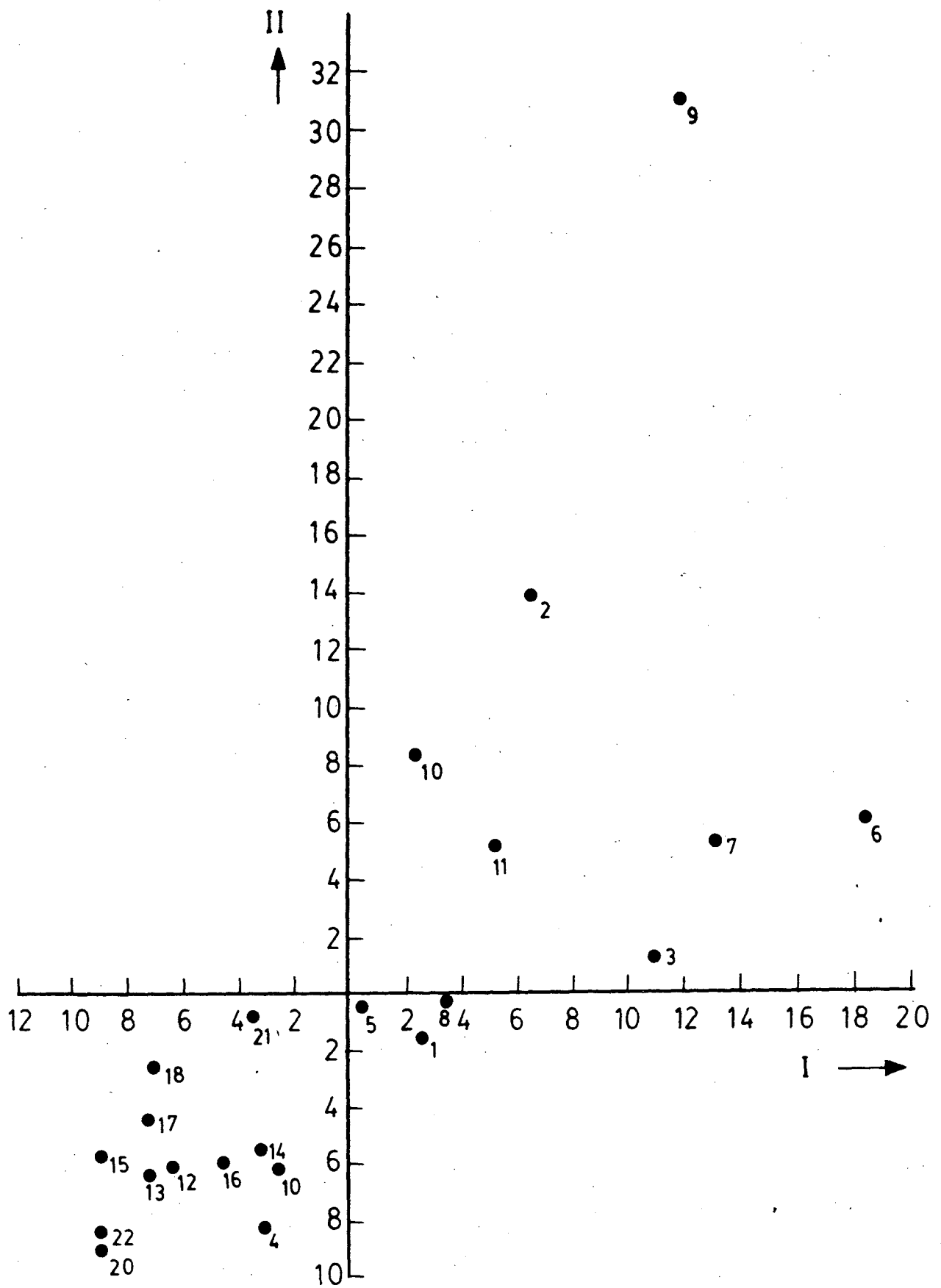


Fig. 31

PLATE I BACK VIEW OF R/V GAVESHANI

PLATE II GRAVITY BOX CORER READY FOR LOWERING DOWN

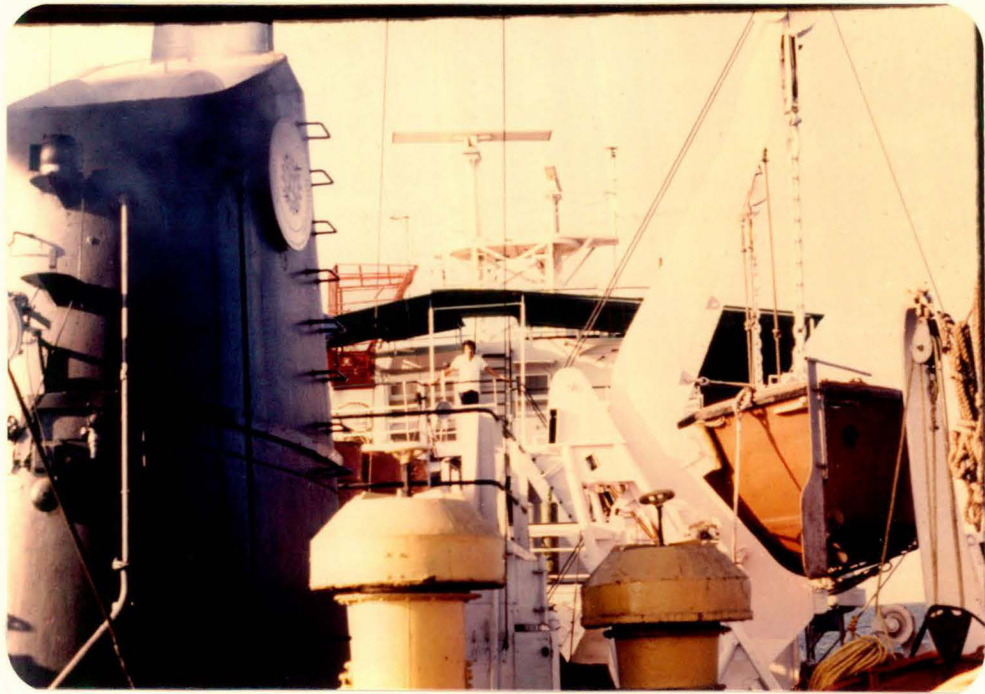


PLATE III BOX CORE AFTER TAKING THE SAMPLES

PLATE IV SUB-SAMPLING OF THE CORE AT THE INTERVAL OF 5 cm



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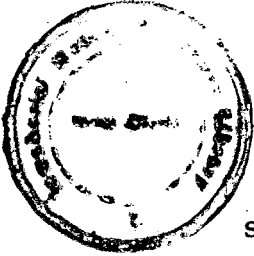
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PRINCIPLE OF ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS)



AAS makes use of the fact that neutral or ground state atoms of an element can absorb electromagnetic radiation over a series of very narrow, sharply defined wavelengths. The sample, in solution, is aspirated as a fine mist into a flame where it is converted to an atomic vapor. Most of the atoms remain in the ground state and are therefore capable of absorbing radiation of a suitable wavelength. This discrete radiation is usually supplied by a hollow cathode lamp, which is a sharp line source consisting of a cathode containing the element to be determined along with a tungsten anode.

When a sufficient voltage is impressed across the electrodes, the filler gas is ionized and the ions are accelerated towards the cathode. As these ions bombard the cathode, they cause the cathode material to 'sputter', and form an atomic vapor in which atoms exist in an excited electronic state. In returning to the ground state, the lines characteristic of the element are emitted and pass through the flame where they may be absorbed by the atomic vapor. Since, generally, only the test element can absorb this radiation, the method becomes very specific in addition to being sensitive.