Pakistan Journal of Hydrocarbon Research
Vol.11, (January 1999). p.51-58, 3 Figs.

Accumulation of Organic Carbon in Northwestern Arabian Sea Sediments

Athar Ali Khan[1]

ABSTRACT

In this study accumulation of organic carbon in marine sediments of northwestern Arabian sea has been discussed. This paper presents the geochemical analysis of Organic carbon content and accumulation, δ^{13} stable carbon isotope and Ba/Al. The primary objective was to investigate the high resolution information about the variations in paleoproductivity and source of organic matter in sediments below an upwelling area. Undisturbed sediments (Piston core NIOP-486) of late Pleistocene time were collected during Netherlands Indian Ocean Program (NIOP-1992-93). The core NIOP-486 was raised from a depth of 2077 meters near the Owen Ridge. This core records deposition history of last 200,000 years and includes 4 warm and 3 cold periods. The distribution of organic carbon content in studied core shows a pronounced cyclicity during glacial and interglacial stages. Organic carbon accumulation trends show that high sedimentation rates in glacial stages results in rapid burial and hence increase organic carbon accumulation. Paleoproductivity indicator Ba/Al has been used to compare with the organic carbon content and is correlated with the warm and cold periods variations in monsoons upwelling intensity. Generally, low paleoproductivity is found in glacial stages. The organic carbon content and accumulation, in sediments however seems to differ from the paleoproductivity trends shown by Ba/Al in glacial sediments of stage 6. δ^{13} C.org isotope results of the core NIOP-486 confirm that organic matter in sediments is predominantly marine (-20 to -23°/°°).

INTRODUCTION

The distribution of organic carbon in modern marine sediments is very complex. In general, shelf/upper slope sediments are enriched in organic carbon, whereas sediments from the open ocean show lower organic carbon content. Organic carbon is higher in marine sediments accumulating beneath biologically productive water. Generally it reaches concentrations > 1%. These organic rich sediments can form source rocks and have a great geological significance. The difference in both amount and composition of the organic matter occurs because different mechanisms control the accumulation of organic matter in the marine realm. These mechanisms are environment-dependent and are controlled by climatic and oceanographic factors: (i) high plankton productivity in the surface waters (ii) high terrigenous fluvial input, especially under hot and humid climatic conditions, and (iii) high sedimentation rates which increase burial efficiency and prevents oxidation of organic matter (iv)sluggish circulation which causes in extreme cases a layering and stagnation of deeper water masses. To understand the spatial distribution of organic carbon in modern sediments is of special interest for several reasons:

(i) The investigation of the quality and quantity of organic matter in marine sediments may yield depositional models, which may help to explain the formation of fossil organic carbon rich sediments and sedimentary rocks (i.e.; black shales). Since black shales are major petroleum source rocks, understanding their formation has not only a scientific value, but may also be of interest for petroleum source rock prospecting.

(ii) The study of marine organic matter and its changes through time may give information about changes in surface water productivity and /or changes in oxygen content of deep water. Since surface-water productivity influences the exchange of CO_2 between ocean and atmosphere, changes in bioproductivity may affect the concentration of atmospheric CO_2 which is an important factor controlling the global climate.

(iii) The study of terrigenous organic matter in marine sediments and its changes through time may give information about the climate evolution of the surrounding continents.

There are two hypothesis about the origin of organic rich sediments: (1) preservation of organic matter due to anoxic condition by stagnation of deep water masses or anoxic conditions due to a mid-water Oxygen Minimum Zone (OMZ) impinging on the continental slope, (2) high plankton productivity caused by upwelling. These hypothesis can be tested by analysis of planktonic foraminifers and by geochemical nutrient/productivity tracers (Ba, Cd, opal and by the hydrogen index of organic matter). Studies from the Black Sea (Calvert et al, 1991), Peruvian and sw African margin (Pederson and Calvert, 1990) and from the Northern Arabian Sea (Calvert and Pederson, 1992) suggest that productivity enhance the high organic matter in marine sediments. On the other hand the influence of the OMZ has been shown an important factor for the preservation of organic matter (von Stackelberg, 1972, Paropkari et al, 1993). The preservation of organic material in the sediments is also affected by hydrographic regime, particle size, oxygen content, and sedimentation rate (Emerson and

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[1] National Institute of Oceanography, Karachi.

Hedges, 1988). The Arabian sea is characterised by strong seasonal variability of monsoons upwelling and high primary productivity (Kabanova, 1968; Krey and Babenerd, 1976).The occurrence of organic rich sediments in the Arabian sea (von Stackelberg, 1972; Slater and Kroopnick, 1984, Paropkari et al. 1992, 1993) has stimulated a controversial discussions of organic matter accumulation processes (Pederson et al; 1993 Calvert et al. 1995).

In the northwestern Arabian sea sediments, it has been shown that changes in the intensity of monsoon winds have affected the distribution and quantity of organic matter (Khan, 1989). The amount of organic matter produced over time should be related to the development of regional upwelling, which depends directly on the intensity of monsoon winds in the northwestern Arabian sea. During warm (interglacial) periods, southwest monsoon winds were stronger, resulting in enhanced upwelling whereas upwelling tended to be weaker during cold (glacial) events (Prell and Curry, 1981; Prell and Kutzbach, 1987; Khan, 1989). As a result of stronger SW monsoon upwelling, paleoproductivity and organic carbon accumulation increase in interglacial stages whereas low productivity and lower organic carbon occurs in glacial stages (Khan,1995). In order to investigate the variations in organic carbon accumulation during glacial and interglacial times for better understanding the sedimentation of organic material in the northwestern Arabian sea a sediment core (NIOP-486) collected during Netherlands Indian Ocean Program (NIOP-92-93) has been studied.

GEOLOGICAL SETTING

The sediment core site is located on the Owen Ridge in the northwestern Arabian sea (Figure1). The Owen Ridge is an asymmetric, northeast-trending ridge near the Owen Fracture Zone, and extends to about 20° N, 61' E, where it merges with the Murray Ridge. The western flank of the ridge dips more gently (about 4°) and merges in to the Owen Basin at about 3500 m. The ridge dips steeply (about 15°) to the east, where it abuts the Indus Fan at about 4000 m (Figure 1). The crest of the ridge varies from 1900 m to 2100 m below sea level and has thick, smooth and subhorizontal pelagic sediments. The origin of the Owen Ridge and the age of the underlying basement rocks are associated with both the early separation of Madagascar and India and to the middle Tertiary reorganisation of seafloor spreading in the Indian Ocean. Since the Owen Fracture Zone has been the major transform between spreading centers to the north and south of the Arabian margin, the plate geometry places the Owen Ridge and Owen Basin on the passive Arabian margin and assigns them a Jurassic age. However, the Deep Sea Drilling Programme (DSDP) in the area has questioned the age and nature of the basement underlying the Owen Ridge and basin. The uplift of the Owen Ridge has been attributed to the compression along the Owen Fracture Zone caused by changes in preading direction associated with the continued collision of India and Asia and the opening of the Gulf of Aden (Whitmarsh, 1979). Following its uplift above the reach of turbidite deposition, the ridge crest has

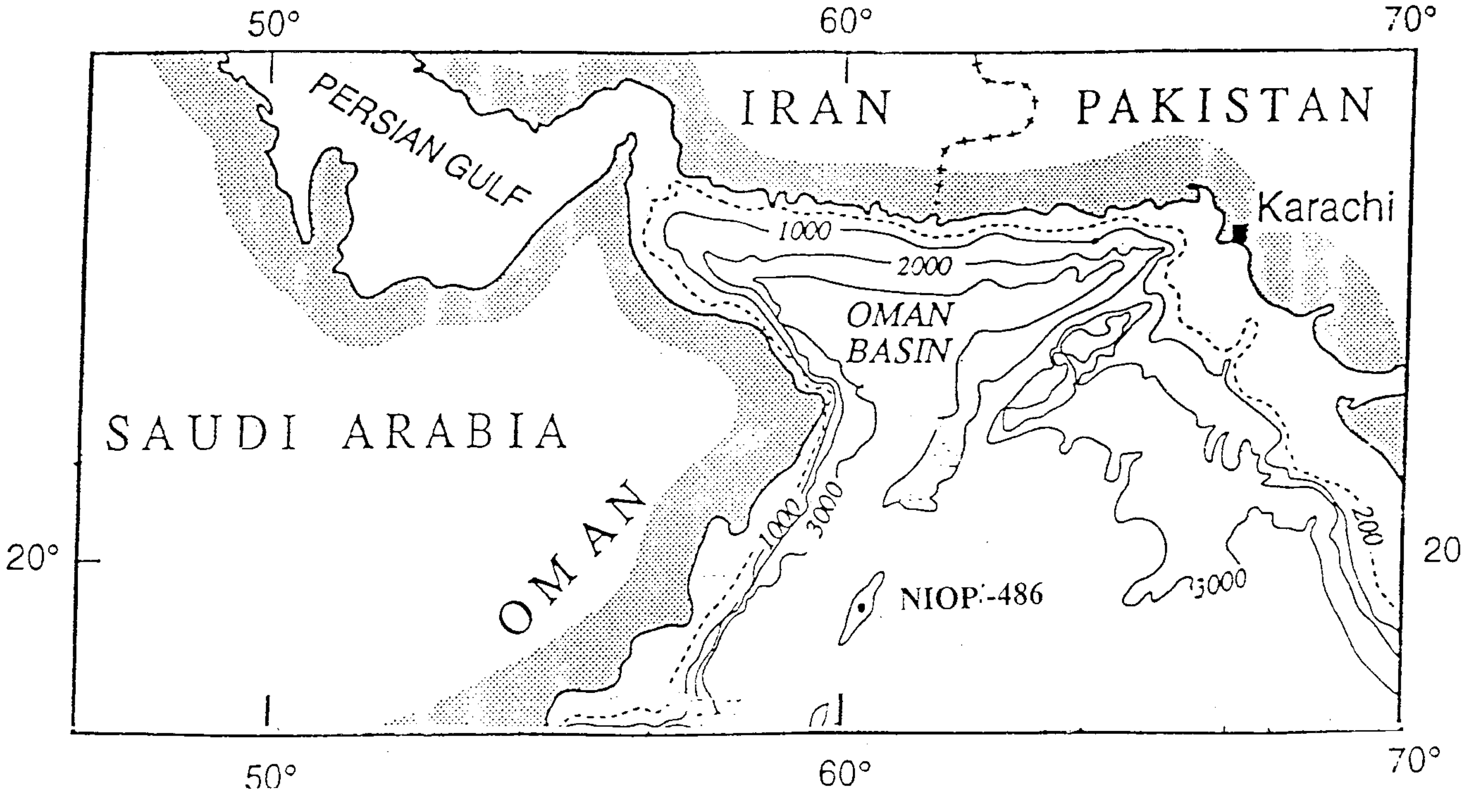

Figure 1- Location map of core NIOP-486 collected during Netherlands Indian Ocean Programme (1992-93).

accumulated predominantly pelagic, carbonate rich sediments during the late Neogene (Whitmarsh et al. 1974; Prell, 1984).

OCEANOGRAPHIC SETTING

The Arabian sea is characterized by variable seasonal winds due to monsoons climate. This brings large changes in oceanography. Southwesterly winds associated with the summer monsoon cause upwelling of nutrient rich water along the coast of Arabia. These nutrient rich water sustain high levels of oceanic productivity. In summer months the surface productivity, up to 400 gC/m^2/yr making northwestern Arabian sea one of the worlds most productive areas (Kabanova, 1968; Codispoti, 1991). During the winter monsoon productivity is generally low. The Arabian sea OMZ is one of the most pronounced low oxygen environments in the open ocean. In the OMZ oxygen concentrations reaches values < 0.05ml/l (Van Bennekom and Heihle, 1994). High primary productivity and limited ventilation of the thermocline (Swallow, 1984; You and Tomczak, 1993) leads to an intense OMZ. It has been shown that the OMZ has varied considerably in the past (Hermelin, 1991; Ten Kate et al. 1991; Altabet et al. 1995).

MATERIAL AND METHODS

The piston core described in this study was recovered during the Netherlands Indian Ocean Program (1992-1993). A long piston core (10 m) NIOP-486 raised from the northwestern part of the Arabian sea (19°.09'.1" N, 60°.37'.0" E water depth 2077m). The location of the sediment core is shown in Figure 1. The core site NIOP-486 is located near the crest of the Owen Ridge. It is positioned above the regional carbonate lysocline to avoid major dissolution changes in the calcareous deposits. The sediments on the Owen Ridge lie beneath the high productive region of the northwestern Arabian sea, affected by monsoon-driven upwelling. The sediments should record long term variations in the strength of the monsoon and local upwelling. The sediments consists of hemipelagic foram bearing mud. The color of the sediments ranges from light olive gray, gray and dark greenish gray (7,5y 5/2, 5/3,6/2 and 10Gy, 7/1 6/2).

Analytical Methods

The sediments were sampled at 10 cm interval. The sediments were weighed before and after drying at 80 °C for 24 hours. The dried sediment sample was homogenised in an agate mortar. A 250 mg aliquot of dried sample was dissolved in a mixture of HNO3, HF and HClO4 in a Teflon beaker. The beaker was sealed with a screw cap and was placed overnight in an oven at 95 °C. The solution was evaporated on a sandbath until just dry, the residue was taken up in 50 ml 1 M HCl (AR), and the solution was analysed by ICP-AES (ARL 34000). International standards were applied to check the accuracy and precision of the methods. For this paper Al, Ba and Ca results have been used, measured with relative precision of +/- 3%. For the analysis of organic carbon and isotopic composition of organic carbon δ^{13} C 1 gram of dry sediment was weighed in a centrifuge tube. Carbonate was dissolved in 1 M HCl by mechanical shaking during 12 hours after which the samples were rinsed in deionized water in order to remove $CaCl_2$ and subsequently dried. Volumetrically the organic carbon content was determined, followed dry oxidation with CuO at 900 °C in a closed circulation system at 0.2 atm oxygen. The released CO_2 gas was cryogenically separated from the other gases. The δ^{13} C was measured with a VG SIRA mass spectrometer with a precision better than 0.1%. The isotope data reported are relative to the PDB standard.

CHRONOSTRATIGRAPHY

A time scale developed for the investigated core is based on correlation with the carbonate stratigraphy of core Ocean Drilling Programme (ODP) 722 (16° 30'.3"N; 59° 47'.8" E; 2027 m water depth). Such an approach has limitations but has been used satisfactorily in other areas where oxygen isotope or carbon dating is unavailable (vander Gasst et al. 1984; Lyle et al. 1988). The core ODP 722 has also been dated by tuning the oxygen isotope signal recorded in the planktonic foraminifera with SPECMAP δ^{18} O (Imbrie et al. 1984) (see Figure 2). The age model shows depositional history of about 200 k.years of Pleistocene period. The chronostratigraphy of core NIOP-486 (Figure 2) shows the isotopic stages 1 through 7 of Emiliani (1955). The odd number shows the warm interglacial period and even number denotes the cold glacial times. The age boundaries of different isotopic stages have been placed developed by Martinsoen et al. (1987).

RESULTS

Sedimentation Rate

Sedimentation rates effects organic carbon preservation in marine sediments (Heath et al. 1977; Muller and Suess 1979; Sarnthein et al. 1988). Deposition rates in units of thickness per unit time have been established. This was done assuming constant and continuous sedimentation between dated levels. Sedimentation rates are computed in cm/1000 years using both dated points and linear interpolation between these points. There is a limitation on the accuracy of the sedimentation rates reported here because of the dating of cores. Average sedimentation rates in cm/1000 years for glacial and interglacial stages are plotted against age in figure 3. Sedimentation rates for studied core shown in figure 3 display marked temporal variations. Average sedimentation rates in core NIOP-486 is low i.e. 3-5cm/1000 years. Trends of temporal variations is such that Holocene and interglacial stages tend to show low sedimentation rates, whereas even isotopic (cold) Stages 2, 4, 6 display increased sedimentation rates. Highest sedimentation rates, i.e. 5-9cm/kyrs are seen in glacial Stage 2. Similarly interglacial Stage 3 in the core also shows higher sedimentation rates. Stage 4 is intermediate and Stage 6 displays sedimentation rates lower than Stage 2, i.e. 4 -7cm/kyrs. Sedimentation rates are low in interglacial Stages 5 and 7. In the lower part of stage 5 sedimentation rate is very low i.e. 1-2cm/kyrs. In the upper part it is almost of same magnitude as seen in Stage 4.

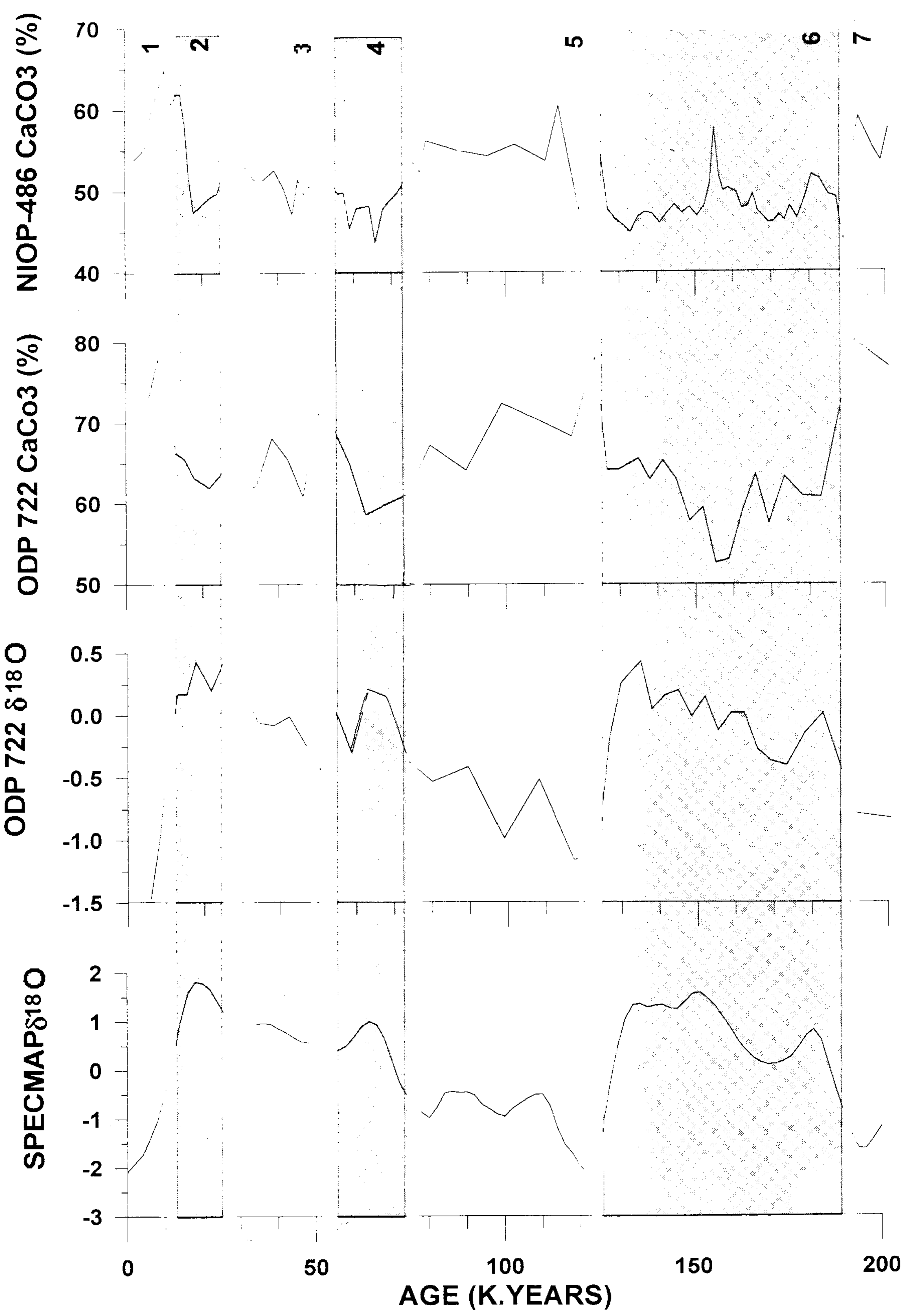

Figure 2- SPECMAP, ODP 722 and NIOP-486 Chronostratigraphic framework.

Paleoproductivity

The Ba/Al ratio in the studied sediments has been used as an indicator of paleoproductivity. Goldberg and Arrhenius (1958) correlated the barium concentration of the Pacific ocean with surface biological productivity. A correlation of Ba with $CaCO_3$ and organic matter has been indicated on the East Pacific rise (Church, 1979). He proposed that the Ba content in pelagic sediments is largely controlled by a biochemical cycle in the ocean. Dehairs et al. (1980), Bishop (1988) and Dymond et al. (1992) showed that (BaSO4) was precipitated in decaying suspended marine particulate matter in oceanic waters. Ba in corals and foraminifera (Lea and Boyle, 1989) has been used as an indicator of upwelling. Schmitz (1987), Shimmield and Mowbray (1991) suggested that Ba may be used as paleoproductivity indicator.

The Ba/Al ratio in the analysed core NIOP-486 is shown in figure 3. The Ba/Al profile exhibits vertically significant variations. Despite the fact that there are certain limitations in using Ba/Al as a productivity tracer, the similarity of cyclicity with SPECMAP (δ^{18} O profile, Figure 2) suggests the climatic control on paleoproductivity. It has been observed that paleoproductivity (Ba/Al ratio) in Holocene (Stage-1) and interglacial stages tends to increase whereas glacial stages show a decline in paleoproductivity. The highest Ba/Al ratio i.e. 3 occurs in Holocene stage 1. Interglacial stages 5 and 7 also indicate higher values of Ba/Al ratio. In interglacial stage 5 there are 3 prominent peaks. The high Ba/Al ratio i.e. 2.5 is in lower part of stage 5. The Ba/Al ratio steadily increases upward. At stage boundary 5 and 6 it increases from 0.5 to 2.5. The middle and upper peaks show Ba/Al values of about 2 and 1.5 respectively. Ba/Al ratio in isotopic stage 7 is relatively higher than stage 5. In glacial stages 2,4 and 6 Ba/Al ratio generally tends to decrease in the lower parts. Higher values are seen in the upper part of glacial stages 2 and 6.

Total Organic Carbon (T.O.C)

The total organic carbon content in sediments ranges between 0.5% to 4.0%. Down the core sediments show cyclicity during glacial and interglacial isotopic stages (Figure 3). The lowest organic carbon content of < 0.5 % is seen in glacial stage 2. Glacial stages 4 and 6 suggest an increasing trend. The organic carbon content in sediments of these stages is relatively high between 1% and 4 %. In stage 4 T.O.C varies between 1% and 3%. In the upper part T.O.C value is high i.e. 3.5%. The highest organic carbon content >4.0% occurs in upper part of stage 6. In Holocene stage 1 and interglacial stages 3,5 and 7 organic carbon content in sediments shows some increase but less conspicuous than glacial stage 6. T.O.C values ranges between 2% to 3%.

Organic Carbon Accumulation

Trends in organic carbon accumulation variations are similar to sedimentation rate changes down the core NIOP-486. The general trend for different climatic stages is that glacial stages (i.e. 2,4 and 6) tend to have higher fluxes than interglacial stages. During the Holocene (Stage 1) low C.org fluxes are seen. In warm interglacial stages (i.e. 3 and 5), an increase in trend is discernible in the lower parts of these stages, while the upper parts show decrease in C.org fluxes. The highest organic carbon accumulation is found in glacial stage 6, up to 70 mg/cm^2/kyrs. For much of the glacial stage 6, values varies between 30-60 mg/cm^2/kyrs. At the boundary of stage 3/4 organic carbon accumulation appears to increase up to 60 mg/cm^2/kyrs and remains 40-60 mg/cm^2/kyrs in the lower part of stage 3. In interglacial stage 5 organic carbon accumulation is very low i.e.; 10-25 mg/cm^2/kyrs.

Carbon Isotopes δ^{13} C

δ^{13} C values fall between -20°/°° and -23°/°° relative to PDB. These values are consistent with the reported marine derived organic carbon in Arabian sea (Fontugne and Duplessy, 1981). The variation in δ^{13} C values, although small however appear to show some cyclicity (Figure 3). For instance, an increase in δ^{13} C from -22°/°° to -21°/°° occurs between the Holocene and the last glacial maximum (18,000 years BP). Surface sediment and some other Holocene horizons show a δ^{13} C of -21.0°/°° which is very similar to that of modern plankton. This implies that organic carbon is of marine origin. δ^{13} C organic carbon values are relatively more negative in glacial stage 2 and interglacial stage 5 and 7 i.e. -22 °/°°. The lowest δ^{13} C value -22.0°/°° occurs in sediments of stages 5 and 7. Interglacial stage 3 and glacial stages 4 show more or less similar δ^{13} C values i.e.-20°/°°. For stages 3 and 4, the δ^{13} C is between -20 °/°° and -21.0 °/°°. In stage 5 δ^{13} C values are relatively low (-22.5°/°°) especially in its lower and upper parts.

DISCUSSION

Organic carbon content in core NIOP-486 ranges between 0.8 to 4.0 %. This range is similar to most other oceanic sediments associated with high biological productivity in overlying waters (Listizin 1972; Degens and Ross, 1974; Fontugne and Duplessy, 1986). Accumulation of organic carbon in marine sediments requires special environmental conditions such as increased surface-water productivity, increased preservation under anoxic conditions and enhanced preservation due to rapid burial. Organic carbon variation in the studied core can be explained by one of the above factors which control accumulation of organic matter in marine sediments.

In core NIOP-486 at depth, during different climatic stages considerable variations in organic carbon and paleoproductivity signal (Ba/Al) ratio have been noted (Figure 3). The variation of organic carbon and paleoproductivity (Ba/Al) is likely to be associated with SW monsoon upwelling. During warm interglacial periods strong SW monsoon induce upwelling along the Arabian coast (Prell, 1984). Nutrient rich water will be brought to the surface enhancing the primary productivity and contributing organic input to the underlying sediments. Nair et al. (1989) have shown that organic flux from sediment trap is higher during SW monsoon. In this study of northwestern Arabian sea sediments a coherent pattern is seen in both organic carbon and paleoproductivity (Ba/Al) profiles. This supports that during warm periods of increased productivity organic carbon content in sediments is high. However, certain

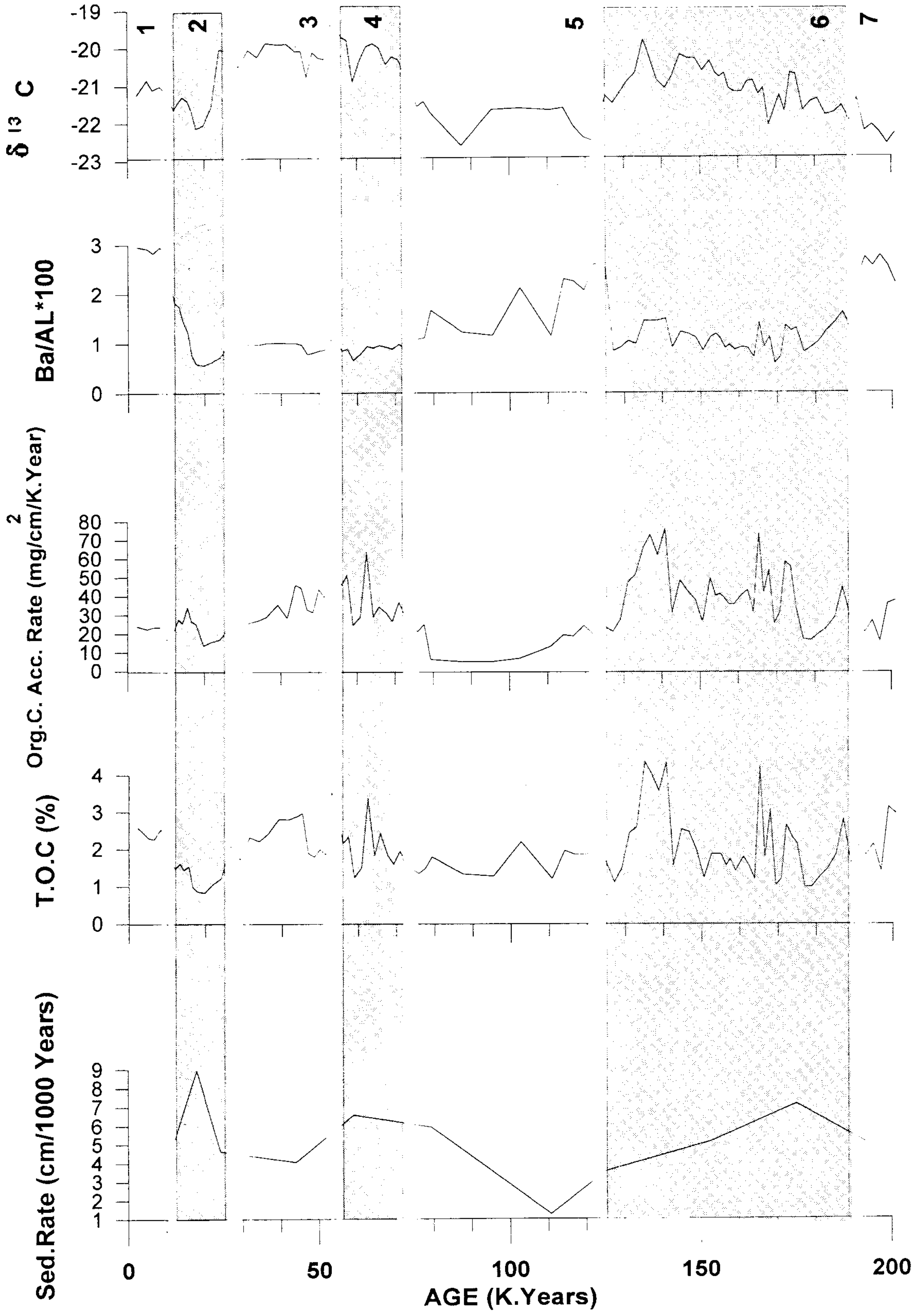

Figure 3- Sedimentation rate, TOC, Org. carbon accumulation rate, Ba/Al δ^{13}C variations in core NIOP-486.

inconsistencies are observed for example in stage 6, the paleoproductivity i.e. Ba/Al trend differs from that of organic carbon. This lack of correspondence is difficult to resolve. A significant enrichment in organic carbon has been noted in sediments of glacial stage 6 deposited between 125 and 180 K.yrs ago. This maximum zone corresponds to highest sedimentation rates (Figure 3). Ba/Al profile shown in figure 3 suggests that organic carbon concentration in glacial stage 6 appears to record variations in deposition/ preservation rather than production.

δ^{13} C isotopic data of core has confirmed that organic matter in the NW Arabian Sea is predominantly marine in origin. Even in glacial stage 2, i.e. 18,000 years BP, when aeolian input was at a maximum δ^{13} C values, i.e. -22.0°/°°, suggest that terrestrial organic input in the NW Arabian Sea sediments was insignificant. Studies (Fontugne and Duplessy, 1986) show that organic matter in the NW Arabian sea is predominantly marine in origin. Thus it is believed that organic matter preserved in the sediments of Arabian sea is derived from the marine source as a result of biological productivity above in the surface water. The paleoproductivity profile Ba/Al shown in figure 3 reflects the past variations in biological productivity due to monsoons changes during glacial and interglacial stages. Ba/Al profile in Holocene and in interglacial stage 5 clearly suggest that paleoproductivity was higher during 100-127,000 years. Diagenetic loss of organic carbon may have occurred in Holocene surface sediments. C.org flux variations in the core broadly indicates relative changes in biological productivity between glacial and interglacial stages. Recently, sediment trap data has shown that C.org flux is high during the SW monsoon (Nair et al., 1989). Thus it can be envisaged that the C.org flux during interglacial stages 3,5 and 7 is associated with enhanced upwelling resulting from stronger SW monsoon winds (Prell, 1984). However, the decreased flux in stages 3, 5 may be related to other factors affecting the environment of deposition. High values in glacial stages 4 and 6 are a result of bulk accumulation rates preserving carbon from oxidation. Enhanced accumulation of organic matter in stage 6 may have resulted by high burial rates.

From the above discussion it can be inferred that increasing trends of organic carbon and paleoproductivity during interglacial stages are associated with enhanced bioproductivity resulting from stronger SW monsoon upwelling. δ^{13} C data from this core NIOP-486 shows predominant marine organic carbon. The relatively higher organic carbon content in glacial stage 6 probably suggest rapid burial.

ACKNOWLEDGMENTS

This work was supported by the Netherlands Geosciences Foundations (GOA). The fellowship awarded by the GOA to carry out post cruise analytical work on sediment cores collected during Netherlands Indian ocean program 92-93 is highly acknowledged. Special thanks are due to Dr.J.Stell, Director, GOA for his continuos encouragement and help in post cruise analysis. The author wishes to express his sincere thanks to the Prof.Dr. C.H.Weijden, Dr.Reichart, Dr.Martin Prince, Henrich visser and others at Department of marine geochemistry, Utrecht University, the Netherlands for their help and extending facilities during laboratory work.

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