OXYGEN AND CARBON ISOTOPES IN INDIAN OCEAN SEDIMENTS AND THEIR PALAEOCLIMATIC IMPLICATIONS

by

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CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any University or Institution.

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SYNOPSIS

The most important feature in the climatic system of the northern Indian ocean and adjoining regions is the 'monsoon'. Due to its profound impact on the economy of the Indian subcontinent,it has received enormous attention from climatologists and planners alike.For predicting the future behaviour of monsoon, it has therefore been crucial to understand its variation in the past.For recovering the short term variations in the past monsoon,natural recorders like tree rings, coastal sediments etc. act as proxy meteorological 'observatories'. However, in order to know long term climatic changes related to the monsoon,spanning time scales from a few thousand years to a few million years, deep sea sediments are the ideal repositories.This is because, apart from the Indian sub-continent,the monsoon also has a pronounced effect on the northern Indian ocean.

The strong SW monsoon during the summer months brings heavy rainfall over the Indian subcontinent and produces a huge river discharge in the Bay of Bengal and the Arabian sea. Pronounced coastal upwelling takes place off Arabia and along the west coast of India due to this monsoon.During winter the SW monsoon disappears and the NE monsoon is activated, producing winter precipitation in NE India and along the east coast of peninsular India.The signatures of these monsoons are attested in the ocean by a variety of physico-chemical changes namely changes in temperature, salinity, nutrient supply and so on and can be traced by stable isotopes of oxygen and carbon in marine calcitic shells of foraminifera from the sediments of this ocean.The oxygen isotopic composition ($\delta^{18}O$) of the foraminiferal shells depend on (i) the temperature of the ocean water in which these organisms grow;and (ii) the $\delta^{18}O$ composition of the sea water,which in turn is related to its salinity.

Similarly, the carbon isotopic composition ($\delta^{13}C$) of foraminiferal shells depends on the $\delta^{13}C$ composition of total dissolved CO_2 in the ocean.From the stable isotope studies on sediment cores from the other oceans viz. the Atlantic and the Pacific,it has been possible to know about the glacial (cold) and interglacial (warm) climatic changes for at least the last 2 million years.Variation in the oceanic carbon cycle and its nature has also been studied. It is then a pertinent question to ask what was the response of local monsoonal system to such global climatic changes. Monsoon induced upwelling largely controls the biological productivity in the northern Indian ocean.Any change in monsoon intensity therefore is capable of perturbing the oceanic productivity. The timing and the causative mechanisms of these changes form an important part of such inquiries.To know the timing of these climatic events for last 40, 000 years (40 kyr),radiocarbon (^{14}C, $t_{1/2}$~5.73 kyr) dating is necessary and has been widely used. In addition, the chronology based on ^{230}Th ($t_{1/2}$~75.2 kyr) can also be used to date sediments as old as 300 kyr.Many of these climatic changes are transient in nature and hence high resolution (~1000 years) studies are necessary to get a detailed picture.

This thesis is an attempt to study palaeoclimatic and palaeo-oceanographic conditions in the northern Indian ocean based on precise measurements of $\delta^{18}O$ and $\delta^{13}C$ of foraminiferal shells in the sediments from this region.Aim of this work was to:-

1. Fabricate an experimental system of CO_2 extraction for precise measurement of $\delta^{18}O$ and $\delta^{13}C$ (expressed in terms of per mil, $^{o}/oo$) in minute (~ 0.5 mg) quantities of foraminiferal carbonate.

2. Study of long term changes of monsoon-intensity with a high resolution of 1000 years, and its effect on upwelling and oceanic productivity.

3. Obtain ^{14}C and ^{230}Th measurements for dating these climatic events as well as calculation of the accumulation rates of sediments.

Important findings of the present study based on sediment cores from the Arabian sea and the Indian ocean are:

1. During last glacial maximum (~ 18 kyr B.P.),the entire Arabian sea was more saline than today.However,the northern Arabian sea was characterised by higher salinity than southern part caused by an excessive evaporation due to dry trade winds of the stronger NE

monsoon circulation. This, coupled with a low river discharge (due to a weak SW-monsoon) increased the salinity gradient in the Arabian sea.

2. The NE monsoon oceanic circulation was stronger than today ~ 20-16 kyr back.

3. Oceanic productivity increased around 14 kyr B.P. due to an increased upwelling, which perhaps has an important role in controlling $\delta^{13}C$ of ΣCO_2 in ocean water.

4. Local reducing condition within the sediment column or low oxygenated bottom water condition during the LGM prevailed in the eastern Arabian sea leading to the removal of uranium from the sea water.

This thesis is divided into four chapters.

In Chapter I, a brief introduction is given about the application of stable isotope systematics in marine sediments. Deep sea sediments have yielded important information about the past changes in the global build up of continental ice, sea surface temperature (SST),ocean circulation, sea level changes as well as changes in the concentration of atmospheric CO_2. $\delta^{18}O$ and $\delta^{13}C$ changes in formainifera of the ocean sediments yield information about both global and local changes in climate.By subtracting the global effects one can determine the local climatic changes.

This chapter also gives a brief review of the earlier work done in the Indian ocean sediments,particularly the

Arabian sea. Stable isotope studies in this part have shown that beside the normal global signature of glacial-interglacial cycles, marked changes in local hydrography had taken place in the past. These studies revealed that:-

1. The SW monsoon was weaker than today at around 18 kyr B.P. coinciding with the last glacial maximum (LGM).

2. As a consequence the upwelling in the western Arabian sea was much less intense during LGM.

3. The sea surface temperature (SST) was warmer by about $1^{o}C$ during LGM in some locations of the Arabian sea.

4. A CO_2 rich, O_2 poor water characterised the deep sea (> 2000 m) during LGM.

These studies though did not yield a detailed picture of the climatic changes, served as a basis for conducting the present investigation. Along with the weak SW monsoon during LGM, the possibility of a stronger NE monsoon was indicated by earlier studies but no oxygen isotope evidence was available for it. Excepting $\delta^{18}O$, other climatic parameters namely $\delta^{13}C$, calcium carbonate were not measured by earlier workers. Additionally, the absolute chronologies for these events were not available. The present work aims at providing these information together so as to make a better picture of climatic changes in the northern Indian ocean. For this purpose, five deep sea cores have been raised namely SK-20-185, SK-20-186, CD-17-15, CD-17-30 and CD-17-32.

The cores CD-17-30, CD-17-15 and CD-17-32 are representatives of the northern Arabian sea where salinity is high and coastal upwelling plays a dominant role today. Core SK-20-185 is located in the eastern Arabian sea, close to the region where some salinity reduction takes place during winter time due to the NE monsoon current but is not affected by coastal processes. The core SK-20-186 comes from the equatorial Indian ocean and represents an open ocean condition.

Chapter II deals with the experimental techniques employed viz., preparation of foraminiferal samples, extraction of CO_2 by acid reaction and its mass-spectrometric measurements for $\delta^{18}O$ and $\delta^{13}C$, radiochemical purification for U-Th isotopes and their assay, ^{14}C measurements and estimation of $CaCO_3$ and coarse fraction (> 150 μm). $\delta^{18}O$-$\delta^{13}C$ measurements in deep sea cores require a rapid analysis of large number of samples. Towards this an on-line CO_2 extraction system has been fabricated which could analyse minute quantities (~ 0.5 mg) of foraminiferal shells. The reproducibility of the measurements in this system is better than $\pm$ 0.1 ‰. This is about a factor of two better than the conventional extraction system earlier employed at PRL, where we achieved a reproducibility of $\pm$ 0.2 ‰. An interlaboratory comparison of standard carbonates between PRL and the stable isotope laboratory (Godwin Lab.) at the University of Cambridge shows that the absolute $\delta^{18}O$-$\delta^{13}C$ values agree within $\pm$ 0.1 $^{o}/oo$. For the present work, about 600 samples have been analysed routinely accompanied by standard calcium carbonate measurements.

Before mass-spectrometric analysis foraminiferal shells are generally cleaned by ultrasonication, H_2O_2 treatment as well as roasting at 400°C under vacuum. These are done to avoid contamination from extraneous carbonates as well as organic matter. However it has been shown in the present study that neither H_2O_2 treatment nor roasting at high temperatures, is required to get reproducible δ-values as long as pure and near 100% orthophosphoric acid is used. However, ultrasonication was routinely employed to remove extraneous particles though the present experiment did not show any difference between ultrasonicated and non-ultrasonicated samples.

In Chapter III, results of various studies are presented and discussed.

Chapter III is divided into three sections. In Section III.1 geochronological studies of the sediment cores are presented. The dating of various levels of sediments from the cores based on different dating methods viz. ^{14}C, U-Th series isotopes and $\delta^{18}O$ stratigraphy, is discussed in this section. Twelve ^{14}C dates were obtained for SK-20-185. These data give a constant sedimentation rate of 2.2 $\pm$ 0.1 cm/10^3 yrs, for the last 30,000 years. A dozen measurements on U-Th series radionuclides have been made on this core. There is a significant uranium enrichment (authigenically precipitated) at certain levels, by and large coinciding with the glacial periods. After correcting for both detrital and authigenic uranium, the ^{230}Th (excess) (on bulk sediments) based sedimentation rate is ~ 2.5 ± 0.5 cm/10^3 yrs.

In the core SK-20-186, ten ^{14}C measurements have been made. In this core a change in sedimentation rate is noted. The Holocene rate is 2.4 ± 0.1 cm/10^3 yrs in comparison to 0.6 ± 0.1 cm/10^3 yrs prevalent during the glacial period. ^{230}Th measurement at ten levels gives a rate of 0.6 ± 0.1 cm/10^3 yrs (both on bulk and $CaCO_3$ free basis). The ^{230}Th rate does not show any break in rate. In both the cores SK-20-185 and SK-20-186, ^{230}Th (excess) based rates agree with ^{14}C based rates within a factor of two.

However, since these cores are mostly calcareous oozes, ^{14}C dates and sedimentation rates are taken to be closer to the real age and sedimentation rates. Considering the SPECMAP stage boundaries as true ages, the sedimentation rates have been calculated based on $\delta^{18}O$ stratigraphy. For SK-20-185 this gives a rate of 2.0 cm/10^3 yrs which is close to ^{14}C based rate. For SK-20-186, however, this yields a rate ~ 1.1 cm/kyr and agrees only with gross ^{14}C based rate (~ 1.3 ± 0.1 cm/kyr) which does not consider the breaks. Four ^{14}C dates have been generated for core CD-17-30, which gives a sedimentation rate ~ 7.7 cm/kyr. This core comes from the strong upwelling zone in the western Arabian sea and hence has a higher sedimentation rate due to a high productivity.

The oxygen isotope data obtained on the five cores from the Arabian sea and the equatorial Indian ocean, are presented in Section III.2.An intercomparison among them is attempted and palaeoclimatic interpreation is derived therefrom. It has been shown in the present work that,though analysis of a few individuals from large size fractions of foraminifera, shows a significant intrasample variability, analysis of a large number of individuals per aliquot, picked up from a very narrow size range (e.g. 250-400μm) exhibits much less variability. A mean intrasample variability of $\pm$ 0.15 $^{o}/oo$ has been found in these ocean cores. For the long term $\delta^{18}O$ stratigraphy,G. sacculifer alone has been analysed in all the cores.The core top $\delta^{18}O$ values of this species indicate that they grow most likely in isotopic equilibrium with the ambient sea water.

A correlation has been attempted between climatic stages obtained in these cores and those obtained from the global data of SPECMAP. This correlation, along with ^{14}C dates, shows that core SK-20-185 has a well preserved oxygen isotope stratigraphy.Its length spans from the present upto stage 5e corresponding to an age of 120 kyr,including all the oxygen isotope substages. $\delta^{18}O$ stratigraphy of core SK-20-186 goes upto stage 11 i.e. upto 430 kyr. Core CD-17-30 goes upto stage 3 i.e. a record for 30 kyr.In SK-20-185 and SK-20-186, glacial-interglacial amplitudes beyond last glacial maximum (LGM) are reduced. By $\delta^{18}O$ analyses of solution resistant and solution susceptible species it has been shown that dissolution is unimportant in core SK-20-185 (also,it is located at a depth shallower than Calcium Carbonate Compensation Depth, CCD). Core SK-20-186, though comes from a depth closer to CCD, has a high $CaCO_3$ content throughout its length indicating the near absence of dissolution. It has also been shown that bioturbation is not significant in SK-20-185. Hence the $\delta^{18}O$ amplitude reduction is attributed to the coarse sampling where few kyr signals are averaged out. In SK-20-186, however, bioturbation may have some role in this regard, owing to its lesser sedimentation rate in the deeper section of the core.

Holocene-LGM amplitude (analysed at close intervals in all the cores) shows a difference between southern core SK-20-185 and northern cores CD-17-30 and CD-17-15. The amplitudes in these cores are 2.12, 2.28 and 2.33 $^{o}/oo$ respectively. Such large amplitudes in the Arabian sea indicate that the salinity during the LGM was higher than today. Core top foraminifera in these cores show an enrichment (~ 0.4 $^{o}/oo$) from south to north in Arabian sea, explained by increasing salinity and decreasing temperature in the same direction. During the LGM this gradient increased (~ 0.6 $^{o}/oo$) with the excess enrichment in northern cores, thereby making the difference in the LGM-Holocene amplitudes in these cores and is consistent with the earlier observation by Duplessy (1982). This is explained by excessive evaporation over the northern Arabian sea during the LGM mainly due to the stronger dry trade winds caused by a reinforced NE-monsoon. This, coupled with a low river discharge in the Arabian sea due to a weaker SW-monsoon, increased the salinity gradient.

Against these values in the Arabian sea, Holocene-LGM amplitude in the equatorial core SK-20-186 is much less i.e. 1.5 $^{o}/oo$. This is explained by either increased precipitation over this oceanic region during LGM or a reduced ice volume effect (~ 1.1 $^{o}/oo$) coupled with ~ 2^{o}C decrease in SST.

Apart from the long term $\delta^{18}O$ stratigraphies in various cores, high resolution $\delta^{18}O$ analysis in multiple species of planktonic foraminifera were performed from the core SK-20-185 in order to find out short term transient climatic events, especially during the LGM. While determining the sedimentation rate by U-Th series isotopes in this core, high authigenic precipitation of uranium was observed at the glacial levels. This is probably due to the fixation of uranium from pore water under a locally reducing condition or removal of uranium from sea water under a low oxygenated bottom water condition during the glacial period. This in turn indicates that benthic mixing was probably less and the original $\delta^{18}O$ signals are not seriously affected. Along with the bulk sample, different fractions of sediments from same layers were also dated by ^{14}C. All the fractions show almost the same age indicating no contamination in the ^{14}C concentrations. Hence short term climatic signals could be reliably recovered from this core if high resolution analyses are done. The purpose of such analyses along with the salient results obtained, are described below.

Earlier work in this region showed that the SW monsoon and related coastal upwelling was weaker during the LGM. However, there was no $\delta^{18}O$ evidence for the increased activity of the NE monsoon, a suggestion which came mainly from pollen and mineralogical studies. To find this, the core SK-20-185 was analysed from the Holocene to the LGM level with a high resolution (1-2 cm). Core SK-20-185 was chosen for the following reasons: At present the NE monsoon, a relatively weaker monsoon, brings low salinity water from the western Bay of Bengal to the west coast of India and along 5^{o}N. If during the glacial time, the NE monsoon was stronger, this salinity reduction would have been more pronounced, perhaps reaching further north upto the present location of core SK-20-185. Three surface dwelling and two deeper dwelling planktonic foraminifera were analysed. Surface dwelling species show a strong negative excursion of $\delta^{18}O$ of upto ~ 1 $^{o}/oo$ during LGM between 20-16 kyr (^{14}C dates). This is explained by a combination of $2^{o}C$ relative warming of SST in the Arabian sea (due to the weaker upwelling and mixed layer thickening since upwelling brings up cooler, nutrient rich bottom water) and reduction in salinity by 2 $^{o}/oo$. Since the temperature coefficient of calcitic $\delta^{18}O$ is ~ 0.2 $^{o}/oo/^{o}C$, warming would decrease $\delta^{18}O$ by 0.40 $^{o}/oo$. Additionally 2 $^{o}/oo$ salinity decrease will reduce $\delta^{18}O$ by 0.60 $^{o}/oo$ (for 1 $^{o}/oo$ salinity change, $\delta^{18}O$ change in the Arabian sea is about 0.32 $^{o}/oo$), thus making the total reduction in $\delta^{18}O$ close to ~ 1 $^{o}/oo$.

The salinity reduction has been attributed to a stronger NE monsoon current which transported low salinity water from the western Bay of Bengal to the eastern Arabian sea. Deeper species however do not show this change since the salinity change is essentially a surface phenomenon.

Another core SK-20-186 has also been analysed with a similar high resolution from the LGM to the Holocene.But the negative excursion during the LGM (as found in SK-20-185) is absent in this core.This is because the NE monsoon current did not reach this equatorial region during the LGM;it does not reach this region even today.

During LGM, increased amount of low salinity water was brought by the reinforced NE monsoon current in the southern Arabian sea. This water was driven further northward by a stronger thermohaline circulation caused by the enhanced salinity gradient between the northern and the southern parts.

The data on $\delta^{13}C$, $CaCO_3$, coarse fraction, etc. are presented in section III.3 and their palaeoclimatic significance discussed. A high resolution $\delta^{13}C$ analysis of multiple species of planktonic foraminifera shows that the $\delta^{13}C\ \Sigma CO_2$ in the Arabian sea was depleted by upto ~ 0.5 $^{o}/oo$ relative to the present around 9 kyr back.Also an enrichment of upto ~ 0.6 $^{o}/oo$ relative to 9 kyr is observed during the LGM. This is explained by strong upwelling (and perhaps strong SW-monsoon) around 9 kyr B.P. which brought the $\delta^{13}C$ depleted water from the deeper levels to the surface. Consequently the enrichment during the LGM represents a weaker upwelling (and a weaker SW monsoon). This is further corroborated by the fact that the glacial period was characterised by a lower $CaCO_3$ productivity relative to the Holocene (due to a weaker upwelling and less nutrient supply).

Both the $CaCO_3$ and the coarse fraction (> 150 μm, mainly foraminifera) in the core SK-20-185 decrease by a factor of two from the Holocene to the glacial value, indicating that most of the $CaCO_3$ is biogenic. In core SK-20-186 too, $CaCO_3$ decreases from Holocene 90% to glacial 80% ($CaCO_3$ estimation has an error of $\pm$ 1%). Such changes in the productivity has also been found from the northern and the western Arabian sea. This low glacial productivity increased around 14 kyr B.P., and was almost coincidental with the onset of deglaciation.

A power spectrum analysis of the $\delta^{18}O$ and the $CaCO_3$ variation indicates that both of them are in phase and their variations are controlled probably by the orbital change in the obliquity (41 kyr) and the precessional (23 kyr) cycles of the earth. Chapter IV highlights the important conclusions derived from the present work and the recommendations for future work in this region.

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CHAPTER I

INTRODUCTION