Nitrogen being a polyvalent element; its speciation, transformation and fluxes in aquatic environments are controlled by ambient oxygen (O₂) concentrations. As seawater is generally oxygenated, nitrogen in the ocean occurs largely in the most oxidized (5+) state, viz. nitrate ions (NO₃⁻) except only in a few regions where a part of the water column gets nearly stripped of O₂. In these suboxic regions, microbes convert NO₃⁻ to molecular nitrogen (N₂), a process known as denitrification, which is the most important pathway for fixed nitrogen loss and a key player in the nitrogen budget. The most intense mid-water column oxygen deficient zones (ODZs) are found to occur in the Pacific and Indian Oceans. In the Pacific Ocean zones, ODZ occurs below the productive tropical eastern boundary upwelling zones whereas in the Indian Ocean it is located in the northern region, especially in the northeastern Arabian Sea. This anomaly results from its unusual Indian Ocean geography, i.e. mainly the presence of Asian landmass that restricts its northern expanse to the tropics and, to a smaller extent, a porous eastern boundary (openings between the Indonesian islands), which allows the exchange of water with the Pacific Ocean. The resultant circulation is not conducive for strong upwelling off the coasts of Myanmar and Australia, in comparison to that found off the west coasts of America. Instead, the most intense upwelling and consequently very high rates of primary production (PP) occur along the northwestern boundary of the Indian Ocean (the Somali and Arabian coasts). Despite the lateral supply of high salinity intermediate waters
from the Persian Gulf and the Red Sea, subsurface water renewal in the Indian Ocean occurs largely because of advection from the south. The waters derived from the Southern Hemisphere gradually lose O₂ but accumulate metabolic products (CO₂, nutrients) during their northward movement. Thus, a lower supply of O₂ together with its enhanced demand produces intense O₂ deficiency (Winkler O₂ < 0.1 mL L⁻¹; ~4 μM) over a wider depth range (~100/150 to 1,000 m) in the north, particularly in the North Eastern Arabian Sea.

Due to the semi-enclosed nature of the North Indian Ocean, the OMZ (oxygen minimum zone) impinges upon a very large area of the continental margin. Bottom waters with O₂ < 0.5 mL L⁻¹ (22 μM) and < 0.2 mL L⁻¹ (9 μM), are estimated to cover about 1.15 x 10⁶ and 0.76 x 10⁶ km² of the marginal seafloor in the region. However, the zone of perennial mid-water column denitrification is confined to the open ocean. Suboxic conditions develop over the inner and mid-shelf off the west coast of India only seasonally (during late summer and autumn). As compared to the open ocean system, the coastal suboxic system covers two orders-of-magnitude less volume, but experiences more extreme conditions (i.e. greater nitrate consumption leading to complete anoxia). Coastal hypoxia also appears to have intensified in the past few decades presumably due to enhanced nutrient loading from land.

Although a number of studies have been carried out both, in the open ocean and coastal regions of the Arabian Sea with respect to nitrogen cycling, very little information is available on the behaviour of redox sensitive trace metals (such as Fe, Mn, Mo, V and Co). Like nitrogen, these elements also undergo speciation changes depending upon the O₂ levels, and either get
deposited in or mobilized from sediments. However, several concerns are known in regard to the interpretation of metal trends with respect to past environmental variability. The most important of these is the diagenetic effect because of which metal concentrations in the sediments may not necessarily reflect redox conditions in overlying waters at the time of sediment deposition. Due to these constraints, a multi-proxy approach has to be adopted to reconstruct, from the sedimentary records, past variability of processes in the water column.

Over the past ten years, a number of sedimentary records of $\delta^{15}$N have been published from different sites in the Arabian Sea representing a range of oceanographic settings and sedimentation rates. These records show higher enrichment of $\delta^{15}$N (>8‰) in surface sediments not only throughout the Holocene but also during all interglacial periods over the past 1 Ma. In contrast lighter isotopic enrichment (~5-6‰), comparable to that found in non-reducing environments today, characterizes sediments accumulated during the glacial stages indicating the weakened denitrification or its absence during such periods. However, only a few of the cores studied so far, have been sampled from the core of the denitrification zone, and none of the previous work dealt with the seasonal coastal system.

In view of the limited proxies used previously to reconstruct past changes in Arabian Sea denitrification, and poor geographical coverage, the present study has been aimed to adopt a multi-proxy approach covering shallow as well as deep Arabian Sea. The results will help us to decipher the variations in the water column by providing insights into the response of
subsurface reducing environment to global and regional changes in climate and oceanographic processes (productivity and circulation). The present study is the first to use stable nitrogen isotopes and redox sensitive metals proxies, to construct paleo-redox conditions, in well-dated sediments of both the open ocean and coastal suboxic regions. The present study is dealt within six chapters.

**Chapter 1** provides the introduction to the topic of research and study area - the Arabian Sea. It gives the background information covering the relevant works previously carried out in the region and other regions of the world oceans with pronounced OMZs. The need for undertaking the present work following a multi-proxy approach is emphasized, and the scope and objectives of the study are defined.

**Chapter 2** contains descriptions of the material and methods used in the study, i.e. the details about the field work, techniques used for collection, handling and processing of samples. It also describes various analytical instruments used for chemical and isotopic analyses. Briefly, an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was used for trace metal measurements. The stable oxygen and carbon analyse/is were carried out using an Isotopic Ratio Mass Spectrometer (IRMS). Isotopic ratios of $^{15}\text{N}/^{14}\text{N}$ in sedimentary organic matter were measured using an elemental analyzer coupled with IRMS (EA-MS).

**Chapter 3** gives a general account of the hydrography and circulation in the Arabian Sea, both in the offshore and coastal regions. Details about the open ocean system have long been available, and being the subject of several previous works, these are briefly dealt with here. Instead, greater
emphasis is laid on the coastal system. Seasonal changes that affect the biogeochemical cycling over the western continental margin of India are highlighted. These details of biogeochemical cycling over the Indian shelf and its changes, including evidence for recent intensification of the coastal oxygen-deficient environment, are provided.

**Chapter 4** presents the results for the three short and shallow cores – CR-2, SaSu-1 and SaSu-3B, collected from the inner- and mid-shelf regions (water depths 45, 35 and 50 m, respectively) off Goa. Dating techniques employed for these cores indicate the temporal resolutions in all the three cores to be comparably high. Decreasing trends in $\delta^{15}$N and $\delta^{13}$C in both cores suggest increase in terrestrial inputs in the last few decades, consistent with the trace metal data (especially Al in SaSu-1). $\delta^{15}$N does not appear to be a good proxy of denitrification in these cores. Enhancement of biological productivity in the region over the past few decades, suggested by the historical water column data, is supported by records of a number of proxies (especially N, P, CaCO$_3$ and Ba contents). In conformity with the increased productivity, the redox sensitive metals are indicative of intensified denitrification.

**Chapter 5** presents the results for two deep-sea gravity cores, AAS – 42/15 (length 440 cm; taken from Raman Seamount; water depth 2525) and AAS – 42/12A (length 530 cm; taken from Wadia Seamount; water depth 2250 m). Both cores came from beneath the most intense water-column denitrification, but the sediments at the coring sites are currently not exposed to the OMZ (bottom water dissolved oxygen concentration close to the coring.
sites is presently 2-2.5 mL/L). Oxygen isotope records were generated for planktonic foraminifer, *Globigerinoide ruber* in both the cores. The $\delta^{18}O$ record was similar in structure to the well-established oxygen isotope curves of the deep sea cores in that the first 6 Oxygen Isotope Stages (OIS) could be clearly identified for AAS-42/15, while in core AAS-42/12A the first 8 complete OIS with a part of OIS 9 could be identified. The upper portion of this core was subjected to AMS $^{14}C$ dating. Based on combined $^{14}C$ and $^{18}O$ data, this core has a very good chronology, covering a period of ~165 Ky and ~320 Ky respectively.

Since the OMZ does not reach the seafloor at the coring sites, the records generated enable evaluation of changes in the intermediate as well as bottom waters through comparison of different proxies of conditions in the two domains. For example, while the sedimentary $\delta^{15}N$ record can be taken to represent denitrification, those of benthic $\delta^{13}C$ and trace metals are expected to reflect conditions prevailing in near-bottom waters. The most important and unexpected result obtained in the present study is that the environmental changes in the intermediate and bottom waters, very often occurred in opposite directions, probably caused by reorganization of the subsurface circulation, over the past climatic cycles. A relaxation/cessation of denitrification during the glacial periods and intensification during interglacial times, as suggested by earlier works, is confirmed by results of this study as well. Moreover, such periods also appear to be characterized by low and high values of Ba/Al, respectively, indicating that productivity changes contributed to changes in denitrification. Records of other redox-sensitive metals
exhibiting changes, are in agreement with the $\delta^{13}$C record rather than with the $\delta^{15}$N record, which is consistent with the assumption that oxygenation in the mesopelagic and benthic environments is not occurring in the same way.

Chapter 6 summarizes the major findings of the present study and makes recommendations for future research.
ACKNOWLEDGEMENTS

First and foremost, I am greatly indebted to Dr. S.W.A. Naqvi, Deputy Director and former Head, Chemical Oceanography Division, National Institute of Oceanography (NIO), Goa for his regular inspirations and patience for providing every necessary facility to complete this work. I have no words to thank him for introducing and acquainting me into the field of scientific research, not only in chemical oceanography but also in the broad domain of paleoceanography. I sincerely thank him for his scholarly insights and keen interest in my research work. Without his constant support and selfless efforts (especially during the writing of thesis), it would not have been possible for me to complete this work. I am obliged to you Sir!

I would like to express my deep sense of gratitude to my research guide Dr. Dileep Kumar, Deputy Director, National Institute of Oceanography, Goa, for his sustained interest in this work, regular encouragement, valuable suggestions and patience during the entire course of the study, without which it would not have been possible for me to reach my goal. I am highly grateful to him for also providing me a favourable working environment to accomplish all my tasks.

My sincere thanks are due to Dr. E. Desa, former Director, NIO, Goa, for providing the necessary research infrastructure with communication facilities.

I appreciate Shri Rasik Ravindra, Director, NCAOR, Goa, and Mrs Ravindra for the constant support made available at all times without any hesitation, and for providing a homely atmosphere which was most necessary.

I thank Professor G. N. Nayak, Dean, Faculty of Life Sciences and Environment, Goa University, for his valuable advice and vital administrative support.

I also thank my co-guide, Dr. S. Upadhay, for his non-ending support at all times. Due thanks are to Dr. V. M. Matta, for being the vice chancellor nominee and for advising me suitably whenever required.

My special thanks to Dr. P. V. Narvekar, Scientist, National Institute of Oceanography, Goa, for faithfully introducing me to a sophisticated instrument like the ICP-AES and giving tremendous training on it. I am very much indebted to
sir for finalizing all the figures other than the data plots. I admire sir's patience in cautiously doing the figures step by step without any hesitation.

**Drs. Rajesh Agnihotri and Siby Kurian** are also thanked exceptionally for allowing me to use their unpublished data in this work.

My hearty thanks to **Dr. Mangesh Gauns, Ms Celsa, Krishnan and Anthony** (dear brother), who made up to the completion of this thesis on time with their dedicated selfless work.

Timely help from **Hema, Anil, Gayatri, Ankush, Keshav, Reshma, Rajdeep, Damodar, Dalvi, Photu, Sunita, Anand and Maya** is highly appreciated. My special thanks to **Hema** for providing me all the required the figures without any hesitation.

Sincere thanks to my teacher, **Dr. Ganpat Naik** for the constant moral support and timely help provided, mostly on proof reading even though time bound with lot of responsibilities.

I would like to acknowledge the **Council of Scientific and Industrial Research (CSIR), New Delhi**, for providing financial assistance in the form of Senior Research Fellowship. Also the network project **CMM 0009**, for allocating the funds for AMS dating of the cores and the **CLP- indo French** project for funding the ICP-AES are duly acknowledged.

I gratefully acknowledge the assistance of all the officers and crew of the research vessels - ORV Sagar Kanya, CRV Sagar Sukti and M/V A. A. Siderenko, for their help at sea particularly while collecting sediment cores.

**Ms. Supriya Karapurkar**, for the isotopic analysis on IRMS at NIO, **Ann Nichol** for AMS dates at WoodShole, **Katherine** for sedimentary isotopic carbon and nitrogen analysis at Germany and **Ravi Bhushan** for organic carbon and nitrogen analysis at PRL (Ahmedabad) are equally thanked. **Mr. Kamlesh** is thanked for providing good background about the activities of benthic foraminifers and important references. Thanks are also due to my computer friends **Mr. Vaman Dabholkar** and **Nixon Barretto** for providing instant online support with the software bugs without getting irritated for the silly approaches at times!

A special note of thanks is due to my friend **Ms. Ujwala Posnaik** for her
constant encouragement and positive attitude, which made me sustain cheerful moments at times of total darkness. I greatly appreciate the goodwill and support of my colleagues Dr. Rahul, Sushant, Prashant, Ashish, Archana, Anand, Kalindi, Lalit, Anayat and many more at NCAOR, Goa.

My very special thanks to Dr. Thamban Meloth for extending his support and providing me every freedom to work in the laboratory.

A special note of thanks is due to my uncle, Mr. Thomas D'Souza who has been the active motivator for all my scholastic career achievements.

I would like to apologize to all those not mentioned by name. I am sure without their timely help my work would not have been a success. I thank them one and all.

Once again I would like to take the opportunity to thank my dear brother for extending his full support and helping me especially in arranging all the references, and being focal in getting the thesis to a completion with lot of patience during the last few days before submission.

Last but not least I would like to thank my family members for their unending love, support, guidance and extreme patience at all times.