Spatial and temporal variations of Os, Nd, Sr isotopes and redox sensitive elements in waters and sediments of the Arabian Sea and their implications

A THESIS

Submitted for the Award of Ph.D. degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

Faculty of Science

by

Vineet Goswami



Under the Supervision of

Dr. Sunil Kumar Singh

ASSOCIATE PROFESSOR PHYSICAL RESEARCH LABORATORY, AHMEDABAD

DEPARTMENT OF GEOLOGY MOHANLAL SUKHADIA UNIVERSITY, UDAIPUR

2012

DECLARATION

I, Vineet Goswami, S/o Mr. Madan Goswami, resident of K-212, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled "Spatial and temporal variations of Os, Nd, Sr isotopes and redox sensitive elements in waters and sediments of the Arabian Sea and their implications" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required.

I solely own the responsibility for the originality of the entire content.

Date:

(Vineet Goswami)

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Spatial and temporal variations of Os, Nd, Sr isotopes and redox sensitive elements in waters and sediments of the Arabian Sea and their implications" embodies a record of the results of investigations carried out by Vineet Goswami under my guidance.

He has completed the following requirements as per Ph.D. regulations of the University

(a) Course work as per the university rules

(b) Residential requirements of the university

(c) Presented his work in the departmental committee

(d) Published/accepted minimum of two research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

Date:

Name and designation of supervisor Sunil Kumar Singh, Associate Professor

Countersigned by Head of the Department Dedicated to Mommy, Papa, Ashu & Dimpy This thesis work was not possible without the help and support of many people. I would like to thank all of them for their help and cooperation.

First and foremost, I would like to express my sincere gratitude to my thesis supervisor, Dr. Sunil K. Singh. His supportive and humble nature is one of the many nice things I appreciate in him. He was always there to share with me, his knowledge and skill in the field of isotope geochemistry and mass spectrometry. Whenever I was in the slightest of the doubts, a discussion with him was enough to get to the right working direction. I appreciate his meticulous stance in teaching me even the slightest of the details of isotope geochemistry; working with mass spectrometers, especially TIMS; chemical processing of samples; analysis and interpretation of data. I acknowledge him for his consistent support and guidance and for providing me ample opportunities and freedom of undertaking my research work.

I also express my most sincere gratitude to Prof. S. Krishnaswami for his encouragement and advice that helped in shaping my research skills. His valuable comments and suggestions were very helpful in my development as a researcher. I really appreciate his comprehensive knowledge, efficient approach in tackling scientific problems and a drive for perfection in every aspect of life. His understanding of the subject, encouraging attitude and personal guidance has been the source of inspiration to me. It was an honour working with such a great geochemist. I sincerely thank Prof. M. M. Sarin for his support and suggestion during my thesis work. His systematic approach towards scientific problems and meticulous ways in handling the scientific instruments have been very encouraging to me.

I am extremely thankful to Prof. J. N. Goswami, the Director, Prof. Anjan S. Joshipura, Dean and Prof. A. K. Singhvi, former Dean, Physical Research

Laboratory, for providing me support and facilities for the thesis work. I thank academic committee members for timed evaluation of my research work. I would like to thank Profs. R. Ramesh, S. V. S. Murty, R. E. Amritkar and Drs. J. S. Ray, R. Rangarajan, A. D. K. Singh, D. Banerjee for their informative lectures during the course work.

I would like to thank all members of the Chemistry Lab for their help, encouragement and support during my thesis work. First of all, I would like to thank Bhavsar bhai for helping me throughout the thesis work. I really appreciate his meticulous methods and skill to make things work with even the minimum of the available resources. It was really nice to work with him in the lab as well as on oceanographic expeditions. I thank Dr. Santosh K. Rai for his help and guidance on chemical processing of samples during early years of my PhD thesis. I thank Dr. Ravi Bhushan for his encouragement and support during the thesis. It was a pleasure to work with him. I acknowledge Dr. R Rengarajan, Sudheer and Neeraj bhai for their suggestions during the thesis work. I sincerely thank my lab-mates Satinder, Damu, Srinivas, Sneha, Saweeta, Upasana, Venky, Prashant, Jayati, Dipjyoti, Balaji and Aslam for their help and support. I would also like to thank my ex lab-mates Gyana, Rahaman, Kirpa Ram and Ashwini for making things comfortable in the lab. I duly acknowledge the help provided by Vaishali and Shantaben.

I am thankful to Dr. V. K. Rai for helping me with the measurements on the MC-ICP-MS. I would also like to acknowledge his efforts in teaching me the operation and working of the MC-ICP-MS. I am grateful to Durgaprasad and Narendra for helping with the measurements on the PLANEX ICP-MS. I am thankful to Gyana for sharing with me the basics of Inverse modelling technique. I sincerely thank Ketan for helping me with the computer programming.

I accord my thanks to all other members of the Geosciences Division for providing a pleasant working atmosphere in the division during the entire course of my research. I am grateful to all the staff-members of Library, Computer Centre, Workshop, Administration, Dispensary and Maintenance section of PRL for their assistance and cooperation. Special thanks are due to Mr. Pranav Adhyaru, Mr. Manan Shah and Mr. Lakan Singh for their early diagnosis and repair of the experimental facilities, especially TIMS. I thank Bankim for the fabrication of the Carius tubes.

I would like to thank Department of Space (DOS) for the scholarship and support for the research. Thanks are due to MoES and INSA for providing the partial funding during the research work. Sincere thanks to Dr. K. Balakrishna and Dr. C. H. Sujatha for the sediment samples of the Nethravathi and Periyar Rivers and Dr. Anirban Das, for sediment samples from Western Ghat streams. I am grateful to the captain, crew and scientific party of FORV *Sagar Sampada* cruise No. 256, 259 and the GEOTRACES oceanographic expedition onboard RV *Hakuho Maru* (cruise No. KH-09-5; Eridanus expedition). I thank Prof. T. Gamo, Dr. Hajime Obata and Dr. Noriko Nakayama for their help on the Eridanus expedition.

I take an opportunity to express gratitude to all my friends at PRL. I would like to thank my batch mates of JRF06; Anand, Ashok, Amzad, Arvind, Bhaswar, Pankaj, Naveen, Rabiul, Rohit, Sandeep, Soumya, Sreekanth, Suratna and Vimal for making my stay joyful. Special thanks are due to Negi, Avdhesh, Yashpal, Gourav (both Sharma and Tomar), Gulab, Monojit, Zulfi, Raju, Parshv and Fazlul for a very nice company during my stay at Thaltej hostel. Much needed company of my seniors and juniors made my stay pleasant at PRL. I would like to specially thank the tea time group (commonly called chat group) for much of the needed entertainment during the breaks at PRL. Special tribute to Ketan and Vimal for coming up with the newest of ideas for the entertainment and to Arvind, Amzad and Pankaj for providing the support during those brain teasing sessions.

Last but not the least; I thank my parents for always being with me and for supporting me through all these years. Without their support and sacrifice, I would not have reached this point.

ABSTRACT

The prime focus of this thesis is application of spatio-temporal distributions and associated variations in the concentration and isotopic composition of selected trace elements to understand contemporary and paleo processes operating in the Arabian Sea and on the nearby continents. The study encompasses the ocean circulation, aeolian dust deposition, role of denitrification on distribution of redox sensitive elements, seawater ¹⁸⁷Os/¹⁸⁸Os evolution, erosion-climate coupling and pattern of dispersal of sediments in the Arabian Sea. The study of Nd concentration and ε_{Nd} of waters of the Arabian Sea along with inverse model calculations suggest return of deeper water masses towards south in the eastern Arabian Sea along the western flange of Chagos-Laccadive ridge. Nd content in surface waters of the Arabian Sea show an enrichment due to aeolian dust flux, estimated to be 8 \pm 2 g m⁻² y⁻¹. Further, the distributions of dissolved redox sensitive elements Re, U and Mo display conservative nature with no influence of suboxic/denitrifying layers of the Arabian Sea. Salinity seems to control their distribution in the Arabian Sea. The salinity-concentration link further supports that the distribution of these elements is governed by physical processes such as advection, mixing and evaporation. The temporal evolution of ¹⁸⁷Os/¹⁸⁸Os in the Arabian seawater show significant variation on glacial-interglacial timescale. The ¹⁸⁷Os/¹⁸⁸Os record of Arabian seawater shows deviation from the global ocean trend during the Last Glacial Maxima (LGM). This was due to anoxic/suboxic conditions deeper waters of the Arabian Sea because of reduced transport of North Atlantic Deep Water (NADW) into the Arabian Sea, resulting in its partial isolation from rest of the oceans during LGM. Results on Sr and Nd isotopic composition of sediments from north-eastern Arabian sea suggest the stablility in provenances of the sediments since last 40 ka whereas sediments from the southeastern Arabian Sea exhibit two major variation in proportions of sediment sources coinciding with two major climate change events; the LGM and the Holocene Intensified Monsoon Phase (IMP) resulting from the transport of sediments of the Bay of Bengal to the Arabian Sea during LGM and vice versa during IMP suggesting significant role of climate and ocean currents in erosion, dispersal and deposition of sediments in the Arabian Sea.

CONTENTS

| List o | of Tables | iv | | | | |
|-----------|---|--|--|--|--|--|
| List o | List of Figuresvi | | | | | |
| Chapter 1 | Introd 1.1 1.2 1.3 | action1-11Introduction2Objectives of the thesis9Structure of the thesis9 | | | | |
| Chapter 2 | Materi 2.1 | als and Methods12-56Materials132.1.1Sediment Samples13 | | | | |
| | 2.2 | 2.1.2 Seawater Samples | | | | |
| | | 2.2.2 Re, U and Mo concentration measurement of seawater samples | | | | |
| | | 2.2.2.2 U and Mo concentration measurement of seawater samples | | | | |
| | | composition measurements in silicate fraction of sediments | | | | |
| | | and hydrogenous leach of the sediments from the Arabian Sea44 2.2.5 Re concentration measurement in bulk sediments from the Arabian Sea55 | | | | |
| Chapter 3 | Nd isot waters using i 3.1 3.2 3.3 | sediments from the Arabian Sea | | | | |

| | | 3.3.1.3 Contribution of different water | | | |
|-----------|-------|--|--|--|--|
| | | masses in the Arabian Sea71 | | | |
| | | 3.3.1.4 Excess Nd and its ε _{Nd} 77 | | | |
| | 3.4 | Conclusions81 | | | |
| | | | | | |
| Chapter 4 | Disso | olved redox sensitive elements, Re, U and Mo | | | |
| | in in | tense denitrification zone of the Arabian Sea83-108 | | | |
| | 4.1 | Introduction84 | | | |
| | 4.2. | The Arabian Sea and its suboxic water column | | | |
| | 4.3 | Results | | | |
| | | 4.3.1 General observations 89 | | | |
| | | 4.3.2 Re, U and Mo distributions 92 | | | |
| | 4.4 | Discussion100 | | | |
| | | 4.4.1 Re, U and Mo in the water column of the | | | |
| | | Arabian Sea100 | | | |
| | | 4.4.2 Re, U and Mo in the Arabian Sea | | | |
| | | Sediments106 | | | |
| | 4.5 | Conclusions107 | | | |
| ~ - | | | | | |
| Chapter 5 | Varia | ations in ¹⁰⁷ Os/ ¹⁰⁸ Os of the Arabian seawater | | | |
| | durii | ng past 30 ka109-125 | | | |
| | 5.1 | Introduction | | | |
| | 5.2 | Results and discussion | | | |
| | | 5.2.1 Os concentration and its isotope | | | |
| | | composition of bulk sediments | | | |
| | | 5.2.2 Re concentration of bulk sediments114 | | | |
| | | 5.2.3 Os concentration and isotopic | | | |
| | | composition of hydrogenous fraction of | | | |
| | | $core SS-3101G \dots 116$ | | | |
| | | 5.2.3.1 Os concentration variations in the | | | |
| | | leachable fraction | | | |
| | | 01 SS-3101G118 | | | |
| | | 5.2.3.2 Temporal variation in $1870 - 1880 - 56$ | | | |
| | | US/ US of seawater | | | |
| | 53 | Conclusions 120 | | | |
| | 5.5 | | | | |
| Chanter 6 | Tem | poral variations in 87 Sr/ 86 Sr and symin | | | |
| Chapter 0 | sedin | nents of the south-eastern Arabian Sea: | | | |
| | Impa | oct of monsoon and surface water circulation | | | |
| | 6.1 | Introduction | | | |
| | 6.2 | Results | | | |
| | 0.2 | 6.2.1 River sediments129 | | | |
| | | 6.2.2 Arabian Sea sediments132 | | | |
| | 6.3 | Discussion | | | |
| | | 6.3.1 Core SS-3104G 139 | | | |
| | | 6.3.2 Core SS-3101G | | | |
| | | 6.3.2.1 Provenance of sediments during | | | |
| | | | | | |

Last Glacial Maximum (LGM).....141

| | | 6.3.2.2 Provenance of sediments during | |
|--------------------|-----|--|---------|
| | | Holocene Intensified Monsoon | |
| | | Phase (IMP) | 143 |
| | 6.4 | Conclusions | 145 |
| Chapter 7 | Sum | mary and future perspectives | 147-153 |
| | 7.1 | Nd and ε_{Nd} of water from Arabian Sea: | |
| | | quantification of water masses and estimation | |
| | | of dust flux using inverse model approach | 148 |
| | 7.2 | Distribution of Re, U and Mo in the Arabian Sea | 149 |
| | 7.3 | Temporal evolution of ¹⁸⁷ Os/ ¹⁸⁸ Os of seawater | |
| | | from the Arabian Sea | 150 |
| | 7.4 | Temporal variation in 87 Sr/ 86 Sr and ε_{Nd} of the | |
| | | sediments of eastern Arabian Sea | 151 |
| | 7.5 | Future Perspectives | 151 |
| | | - | |
| References. | | | 154-171 |

| List of publications | • | |
|----------------------|---|--|

LIST OF TABLES

| Table | Contents | Page |
|--------------|--|----------|
| 2.1 | Details of the sediments cores | 14 |
| 2.2 | Calibrated ¹⁴ C ages of the sediments of cores | 16 |
| 2.3 | Location of sediment samples from west flowing rivers | 18 |
| 2.4 | Details of sampling for seawater in Arabian Sea | 20 |
| 2.5 | Various analytical techniques used in this thesis | 22 |
| 2.6 | Abundances of Nd isotopes in the sample and spike | 27 |
| 2.7 | Calibration of Nd Spike using Nd standard of known strength | 27 |
| 2.8 | Nd isotopic composition of GEOTRACES samples | 30 |
| 2.9 | Nd concentration measured in GEOTRACES samples | 32 |
| 2.10 | Nd isotopic composition of GEOTRACES standard | 33 |
| 2.11 | Replicate analysis for Nd concentration measurements | 33 |
| 2.12 | Replicate analysis for the Nd isotopic composition | 34 |
| 2.13 | Abundances of Re isotopes in the sample (natural) and spike | 35 |
| 2.14 | Calibration of Re spikes | 35 |
| 2.15 | Abundances of U isotopes in the sample (natural) and spike | 36 |
| 2.16 | Abundances of Mo isotopes in the sample (natural) and spike | 36 |
| 2.17 | Calibration of U and Mo spikes | 5/ |
| 2.10 2.10 | Replicate analysis of L and Ma concentrations | 30 40 |
| 2.19 | Measurement of Re. II and Mo in SAFe water sample | 40 /1 |
| 2.20 | The astronomic of Re, O and Wo in SAFe water sample | 41 |
| 2.21 | Replicate analysis of Sr, 67 Sr/ 60 Sr, Nd and ε_{Nd} in sediments | 43 |
| 2.22 | Abundances of Os isotopes in the sample (natural) and spike | 45 |
| 2.23 | Calibration of Os Spike | 45 |
| 2.24 | Replicate analysis of Os and ¹⁰ Os/ ¹⁰⁰ Os in samples | 52 |
| 2.25 | Measurement of Os and ¹⁸⁷ Os/ ¹⁸⁸ Os in USGS SCo-1 standard | 53 |
| 2.26 | Total procedural blank for Os analysis (bulk sediment analysis) | 54 |
| 2.27 | Total procedural blank for Os analysis (Hydrogenous leaching) | 54 |
| 2.28 | Blank of reagents used for hydrogenous Os leaching procedure | 54 |
| 2.29 | Replicate analysis of Re concentration in sediment samples | 55 |
| 2.30 | Measurement of Re concentration in USGS SCo-1 standard | 56 |
| 2.31 | Total procedural blank for Re measurements in bulk sediments | 56 |
| 3.1 | Salinity, pot. Temp., Nd and ϵ_{Nd} in profiles from Arabian Sea | 62 |
| 3.2 | A priori and a posterior values of the water mass end-members | 69 |
| 3.3 | Excess Nd and its ε_{Nd} in the Arabian Sea waters | 77 |

| 4.1 | Re, U and Mo concentration in profiles from the Arabian Sea | 94 |
|-----|---|-----|
| 4.2 | Statistics of Re, U, Mo concentration with different DO levels | 101 |
| 4.3 | Re, U and Mo in Arabian Sea and other basins (at 35 salinity) | 106 |
| 4.4 | Enrichment of Re, U, Mo in Arabian Sea sediments over UCC | 106 |
| 5.1 | Os content and ¹⁸⁷ Os/ ¹⁸⁸ Os of bulk sediments from Arabian Sea | 113 |
| 5.2 | Re concentration in bulk sediments from the Arabian Sea | 115 |
| 5.3 | Os content of the leachable fraction and ¹⁸⁷ Os/ ¹⁸⁸ Os of seawater | 117 |
| 6.1 | Sr, Nd isotopic composition of river sediments | 130 |
| 6.2 | Sr, Nd content and isotopic composition of SS-3104G silicates | 132 |
| 6.3 | Sr, Nd content and isotopic composition of SS-3101G silicates | 134 |
| 6.4 | $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} of potential end members | 138 |
| | | |

LIST OF FIGURES

| Figure | Contents | Page |
|--------|--|--------|
| 2.1 | Scheme of sampling and initial processing of samples | 14 |
| 2.2 | Location of seawater and sediment cores used in this thesis | 15 |
| 2.3 | ¹⁴ C chronology of SS-3101G and SS-3104G | 16 |
| 2.4 | Location of river sediments used in this thesis | 19 |
| 2.5 | Research vessel, collection and processing of samples | 21 |
| 2.6 | Analytical techniques for measurement of various proxies | 23 |
| 2.7 | Setup for extraction of REEs using C18 cartridges | 24 |
| 2.8 | Extraction of REEs using C18 cartridges | 25 |
| 2.9 | Separation of Nd from REEs by the LN-C50-B resin | 26 |
| 2.1 | Measurement of ¹⁴³ Nd/ ¹⁴⁴ Nd of JNdi-1 on TIMS | 28 |
| 2.11 | Measurement of ¹⁴³ Nd/ ¹⁴⁴ Nd of JMC-321 on MC-ICP-MS | 29 |
| 2.12 | Nd isotopic composition of GEOTRACES samples | 31 |
| 2.13 | Measurement of "unknown" GEOTRACES standard | 32 |
| 2.14 | Measurement of ⁸⁷ Sr/ ⁸⁶ Sr of NBS-987 on TIMS | 43 |
| 2.15 | Measurement of ⁸⁷ Sr/ ⁸⁶ Sr of NBS-987 on MC-ICP-MS | 44 |
| 2.16 | Sediment samples in Carius tube before sealing | 46 |
| 2.17 | Bromine refluxing in the digestion vessel for Os extraction | 49 |
| 2.18 | Measurement of ¹⁸⁷ Os/ ¹⁸⁸ Os of standard on TIMS | 52 |
| 3.1 | Location of stations for Nd isotopic composition | 59 |
| 3.2 | Nd and ε_{Nd} in vertical profiles from the Arabian Sea | 64 |
| 3.3 | Contour plots for distribution of various water masses | 73-75 |
| 3.4 | Nd_{excess} and its corresponding ϵ_{Nd} | 80 |
| 4.1 | Representative θ -S plots for two stations from Arabian Sea | 90 |
| 4.2 | Contour plots for temp, salinity, DO, nitrite, Re, U and Mo | 91-93 |
| 4.3 | Salinity, DO, nitrite, Re, U and Mo in Arabian Sea | 97-100 |
| 4.4 | Frequency distribution of Re, U and Mo concentrations | 102 |
| 4.5 | Re, U and Mo concentration versus salinity | 105 |
| 5.1 | Os and ¹⁸⁷ Os/ ¹⁸⁸ Os in Arabian Sea sediments with time | 114 |
| 5.2 | Re content in Arabian Sea sediments with time | 116 |
| 5.3 | Temporal variation of ¹⁸⁷ Os/ ¹⁸⁸ Os of Arabian seawater | 118 |
| 5.4 | Temporal variation in Re, Os content and organic carbon | 119 |
| 5.5 | ¹⁸⁷ Os/ ¹⁸⁸ Os of Arabian seawater with other oceanic basins | 122 |
| 6.1 | Location of two sediment cores analyzed | 129 |

| 6.2 | Sr-Nd isotope plot of contemporary river sediments | 131 |
|-----|---|-----|
| 6.3 | Temporal variation in 87 Sr/ 86 Sr and ε_{Nd} of SS-3104G | 135 |
| 6.4 | Temporal variation in 87 Sr/ 86 Sr and ε_{Nd} of SS-3101G | 136 |
| 6.5 | Sr-Nd isotopic plot of sediments from cores used in study | 137 |
| 6.6 | Surface currents in the Arabian Sea during monsoon | 142 |

CHAPTER 1

Introduction

1.1 INTRODUCTION

Trace elements and isotopes (TEIs) play important role in ocean as nutrients, as proxies of several processes in the present, in the past and as contaminants. The cycling of trace elements in the ocean has direct implication to marine biogeochemistry, ocean circulation, climate dynamics, etc. Further, the study of trace elements and their isotopes in the marine sediments provide information pertaining to the past processes operating in the ocean as well as on the land. The aim of this thesis is to use trace elements and isotopes to study some of the contemporary and paleo processes operating on different spatial and temporal scales in the Arabian Sea. The domain of research covered includes ocean circulation and water mass structure of the Arabian Sea; the behaviour of redox sensitive elements in response to suboxic and denitrifying conditions of the Arabian Sea water column; the temporal variation in Os isotopic composition of seawater on glacial-interglacial timescale; the role of climate and ocean circulation on the erosion, dispersal and deposition of sediments in the Arabian Sea.

Global ocean circulation helps in regulating the planet's heat budget by the interbasin transport of heat content. In addition, ocean circulation transports oxygen, nutrients etc form one ocean basin to another. The transport of these properties in the ocean by the means of water masses maintains a balance in terms of their demand and supply. Thus, by studying the water masses in the ocean, the rate and pattern of transport of properties within the ocean can be understood. Various trace elements and isotopes such as Cd, ¹⁴C and Nd have been used to track water masses in the ocean. Some of these tracers are affected by the biological activity; however, the distribution of Nd isotopes in the water column is independent of biology and is governed by mixing processes in the ocean. The residence time of Nd in the ocean is of the order of ocean mixing time making it a suitable proxy of ocean water circulation [*Frank*, 2002; *Goldstein and Hemming*, 2003; *Jeandel*, 1993; *Jeandel et al.*, 1998]. Thus, the distribution of Nd concentration and its isotopic composition (ε_{Nd}) serves as a coupled tracer of the origin and circulation of water masses both on the inter and intra oceanic scale [*Amakawa et al.*, 2000; *Frank*, 2002; *Goldstein and Hemming*, 2003; *Jeandel*, 1993; *Jeandel et al.*, 1998; *Peipgras and Wasserburg*, 1982; 1983]. The pattern and rate of ocean circulation generates spatial variation in the distribution of Nd isotopes which can be used to reconstruct the ocean circulation that brings about these variations. Therefore, the Nd isotopic composition of the water masses is one of the best proxies to study the ocean circulation owing to its suitable residence time and nature to acquire and preserve the source signature [*Goldstein and Hemming*, 2003]. The spatial variation in the ε_{Nd} of the ocean reflects the variation in the supply of Nd from the continent and/or its modification by mixing of different water masses [*Frank*, 2002; *Goldstein and Hemming*, 2003; *Lacan and Jeandel*, 2001; 2004a; 2005].

The application of the coupled Nd concentration- ε_{Nd} tracer for studying the water mass structure was mainly focussed in Arctic, Atlantic and the Pacific Oceans [*Jeandel*, 1993; *Lacan and Jeandel*, 2001; 2004b; 2005; *Peipgras and Wasserburg*, 1982; 1983; *Peipgras and Jacobson*, 1988; *Porcelli et al.*, 2009; *Rickli et al.*, 2010; *Shimizu et al.*, 1994; *Zimmermann et al.*, 2009]. Little is known about the water mass structure and various water masses forming in the Indian Ocean, particularly that of deeper waters in the northern Indian Ocean [*Amakawa et al.*, 2000; *Bertram and Elderfield*, 1993; *Nozaki and Alibo*, 2003]. The limited studies on Nd isotopic composition of seawater from the Indian Ocean suggest that it is intermediate to that of the Atlantic and the Pacific Oceans.

The shallow to intermediate water masses forming in the northern Indian Ocean have their origin in the Arabian Sea. These water masses are the Arabian Sea High Salinity Water (ASHSW), Persian Gulf Water (PGW) and Red Sea Water (RSW) [*Kumar and Li*, 1996; *Rochford*, 1964; *Shenoi et al.*, 1993; *Wyrtki*, 1973]. The studies on water mass structure of the Arabian Sea are mostly focussed on the shallow water masses, using potential temperature and salinity as proxies. There have been only limited studies on the deep water circulation in the northern Indian Ocean, especially in the Arabian Sea [*Mantyla and Reid*, 1995; *You*, 2000]. The applicability of potential temperature and salinity as water mass tracer in the Indian Ocean is hindered by the lack of variability of these parameters for deeper

waters of the basin. Other properties such as Cd, ¹⁴C, dissolved oxygen and nutrients are also not conservative in the Indian Ocean, especially in the Arabian Sea due to high productivity. In this regard, Nd isotopic composition of seawater is one such tool that can be applied as a conservative tracer of water masses in this basin. In this study an effort has been made to study the Nd concentration and its isotopic composition in the Arabian Sea. Further, Nd concentration and ε_{Nd} in conjunction with inverse modelling approach have been used to apportion and quantify the water masses in the Arabian Sea.

The Arabian Sea is a unique oceanic basin surrounded by continental landmass on its western, eastern and northern boundaries and connected to the Indian Ocean to the south. Being in the proximity of arid continental landmass with widespread deserts of Arabian Peninsula (Oman), Africa and western India, the aeolian supply of mineral dust contribute significantly to the dissolved trace elements budgets of the surface waters of the Arabian Sea. Annual supply of aeolian dust to the Arabian Sea is estimated to be ~100 million tons [*Goldberg and Griffin*, 1970; *Kolla et al.*, 1976; *Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989]. The supply of dust could impact the Nd budget of the surface ocean [*Tachikawa et al.*, 1999]. The surface water Nd content and its isotope composition of the Arabian Sea have been used to estimate the dust flux in this study.

The Arabian Sea is one of the highly productive oceanic basins; the productivity resulting from monsoonal upwelling brought about by seasonally reversing winds. Thus, the unique geographical setting of the Arabian Sea affects its circulation and biological productivity. During the South-West (SW) monsoon strong winds produce intense coastal upwelling in the Arabian Sea off Somalia, Yemen and Oman. These upwelled nutrient rich waters are transported hundreds of kilometres offshore enriching the entire euphotic zone with nutrients in these regions. These nutrients along with high aeolian dust flux results in high primary productivity. The North-East (NE) monsoon also causes convective mixing over a large area. The primary productivity during the NE monsoon is comparable with that during the SW monsoon [*Madhupratap et al.*, 1996]. High primary productivity is a

major factor responsible for prevalence of suboxic conditions in the Arabian Sea. The high productivity causes continuous rain of biogenic material through the water column. These debris during their transit are subject to combustion by dissolved oxygen in the water column, resulting in the formation of suboxic denitrification layer at intermediate depths, typically 200-1000m [Bange et al., 2005; Naqvi, 1994]. Further, the restricted supply of dissolved oxygen to intermediate depths also contributes to suboxic conditions. It is expected that the primary productivity in the Arabian Sea, its associated mid depth oxygen minima, denitrification and high rain rate of biogenic debris through the water column can have a measurable effect on the water column geochemistry of redox sensitive elements. Redox sensitive elements compose a suite of trace elements whose chemistry in seawater is directly influenced by changes in redox conditions of the water. Re, U and Mo are the redox sensitive trace elements that have found applications to study paleo-redox conditions of the ocean and determine chronology of marine deposits [Crusius et al., 1999; Henderson et al., 2001; Kendall et al., 2009; Morford et al., 2001; Nameroff and Balistrieri, 2002; Nameroff et al., 2004; Sarkar et al., 1993]. In addition, the role of Mo in marine biological processes is also known [Morel and Price, 2003].

The growing interest on the application of these elements as paleo-redox indicators of oceans requires better understanding of their geochemistry, which includes their sources, transport and internal cycling. Re, U and Mo are enriched in sediments that are rich in organic carbon [*Borole et al.*, 1982; *McManus et al.*, 2006; *Morford and Emerson*, 1999; *Morford et al.*, 2005; *Pattan and Pearce*, 2009; *Sarkar et al.*, 1993], suggesting that productivity and/or organic carbon burial may have a role in their removal from seawater. Such conditions are met in oceanic regions where the demand for oxygen for combustion of organic matter and respiration is not fulfilled (For example, in land locked seas and continental margins with restricted ventilation). Arabian Sea is one such oceanic basin where the demand of oxygen for combustion of organic matter is quite high. Thus the Arabian Sea basin provides ideal conditions of being a natural laboratory to study

the water column distribution of redox sensitive elements under suboxic/denitrifying conditions.

Further, the significant flux of particles through the water column of the Arabian Sea makes the case of removal of redox sensitive elements Re, U and Mo more susceptible. There have been only limited studies on the distribution of these redox sensitive elements in suboxic/reducing ocean water column to investigate their potential removal from seawater. The suboxic conditions of the Arabian Sea have been found to influence Mn and Fe cycling in the water column [*Saager et al.*, 1989]. These studies demonstrate the role of suboxic layers of the Arabian Sea in the mobilization of redox sensitive elements, Fe and Mn. One of the goals of the this study is to investigate the impact of the perennial Oxygen Minimum Zone (OMZ) and denitrification present in the water column of the Arabian Sea on the distribution of dissolved Re, U and Mo concentration.

Primary productivity in the Arabian Sea is in the range of 0.5 to 2.5 gC m⁻² d⁻¹ [*Madhupratap et al.*, 1996] suggesting significant surficial biological activity and rain of organic matter through the water column of the Arabian Sea. High productivity supplies large amounts of organic matter to the sediments creating anoxic condition at sediment water interface in the Arabian Sea. Redox sensitive elements such as Re, U, Mo, Os etc. are enriched in these sediments. For example, higher concentration of Re has been found in the surface sediments of the Arabian Sea [*Pattan and Pearce*, 2009]. Os is also a redox sensitive element and gets enriched in the reducing sediments from seawater. In this study, organic matter rich sediments from the Arabian Sea have been studied to track Os isotopic composition of the seawater and its temporal evolution.

The weathering of the hard rock continents is important in regulating the global carbon cycle and heat budget of the earth. Radiogenic isotopes in the ocean are sensitive to changes in the continental weathering and erosion. The variation in the isotopic composition of radiogenic isotopes in the ocean over the scales of time and space provides useful information on changes in the continental

weathering. Os is a very useful tracer of paleo-weathering intensity due to its residence time in the range of 8-40 ka [Oxburgh, 2001]. Global ocean receives Os from continents, hydrothermal inputs and cosmic dust. There is a large difference in terms of isotopic signature of Os derived from continental weathering $(^{187}\text{Os}/^{188}\text{Os} \sim 1.5)$ [Levasseur et al., 1999] and other sources, hydrothermal inputs $(^{187}\text{Os}/^{188}\text{Os})$ ~ 0.12) [Meisel et al., 2001] and dissolution of cosmic/micrometeoritic dust (187 Os/ 188 Os ~ 0.12-0.13) [Luck and Allègre, 1983; Walker and Morgan, 1989]. Thus, the study of Os isotopic composition evolution of seawater over the past has the potential to reveal the insights of continental paleo-weathering intensities over glacial-interglacial timescale. In this study, Os isotope composition of sediment core from the Arabian Sea, archiving the depositional history of about 30 ka, has been studied to reconstruct the seawater Os isotope signature during this period. The depositional duration of the sediments encompasses the well known event of Last Glacial Maximum (LGM). This event has been suggested to impact the seawater Os isotope composition by decreasing the continental weathering thereby decreasing the supply of radiogenic Os to the Seawater [Oxburgh, 1998; Oxburgh et al., 2007]. The aim of the present work is to study the temporal evolution in ¹⁸⁷Os/¹⁸⁸Os of Arabian seawater over changing glacial-interglacial climate scenario.

The process of continental erosion plays a key role in controlling the marine biogeochemical and sedimentary cycles. Thus, there is a need to understand the variations in continental erosion pattern in the past and their controlling factors. Continental erosion is enforced by the interplay between high frequency climate change (which vary on a decadal to ka time scale) and low frequency tectonic activity (varying over Ma time scale). Ocean sediments are good archives of the erosional history of the nearby continents. [*Ahmad et al.*, 2005; *Colin et al.*, 1999; *Kessarkar et al.*, 2003; *Tripathy et al.*, 2011] Sediments of the Arabian Sea receive terrigenous flux from the Himalaya, Deccan and peninsular India. The Arabian Sea annually receives ~400 million tons of suspended load from the Himalaya and Trans Himalaya [*Milliman et al.*, 1984] through the Indus river system, and ~100 million tons through the Narmada, Tapi and the rivers of the

Western Ghats [*Alagarsamy and Zhang*, 2005; *Chandramohan and Balchand*, 2007]. In addition, ~100 million tons of aeolian dust from the deserts of Oman, Africa and western India is deposited annually in the Arabian Sea, its contribution to the eastern Arabian Sea being only ~30 million tons, which further decreases towards the Indian peninsula [*Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989]. The sediments deposited in the Arabian Sea preserve in them the records of erosional patterns in their source regions, factors regulating them and the pathways of sediment dispersal in the sea [*Clift et al.*, 2008; *Rahaman et al.*, 2009]. Any temporal variation in the proportion of the sources can be tracked by studying these sediments. Tectonic activity is considered to be the prime cause for erosion with climate playing a secondary role [*Burbank et al.*, 2003]. However, some recent studies highlight the importance of climate in controlling erosion [*Clift et al.*, 2008; *Rahaman et al.*, 2009].

One of the key factors determining the erosion patterns of the drainage basins is the monsoon. The Indian subcontinent experiences two monsoons annually, the South-West (summer) and the North-East (winter) monsoons; the former being more pronounced at present. The intensities and patterns of these monsoons have varied during the past [Fleitmann et al., 2003; Gupta et al., 2003; Herzschuh, 2006]. These variations in turn, have affected the erosion pattern of drainage basins [Clift et al., 2008; Rahaman et al., 2009] and supply of sediments to the seas around India [Ahmad et al., 2005; Colin et al., 1999; Tripathy et al., 2011]. These variations, in addition to impacting erosion, also influence the surface water circulation in the Arabian Sea and the Bay of Bengal which determine the sediment dispersal and deposition in them. During the SW monsoon, surface water from the Arabian Sea flows to the Bay of Bengal; in contrast, during the NE monsoon, surface currents flow from the Bay of Bengal to the Arabian Sea [Schott and McCreary, 2001; Shankar et al., 2002]. There is evidence to suggest that the transport of low-salinity water from the Bay of Bengal to the Arabian Sea was enhanced during the Last Glacial Maximum (LGM) due to a more intense NE monsoon [Sarkar et al., 1990; Tiwari et al., 2005]. This study deals with unravelling the erosion history of the Himalaya and peninsular India and its

controlling factors highlighting the impact of monsoon variability and ocean surface currents on erosion patterns and dispersal of sediments in the eastern Arabian Sea for the last 40 ka.

1.2 OBJECTIVES OF THE THESIS

The basic objective of this thesis work is to study the trace elements and isotopes in the water column and the sediments of the Arabian Sea to understand the water mass structure, impact of denitrification on the water column cycling of trace elements and impact of varying climate and hydrography on the continental erosion and sediment dispersal.

In particular, the major objectives are to:

(i) study the water masses in the Arabian Sea using Nd isotopes in conjunction with an inverse modelling approach and estimate the dust flux to the surface waters.

(ii) study the distribution of redox sensitive elements (Re, U and Mo) in water column of the Arabian Sea and the processes controlling them.

(iii) track the temporal variation in Os isotopic record of Arabian seawater over the past 30 ka and assess the impact of climate in controlling it.

(iv) study the impact of monsoon variability and ocean surface circulation on erosion patterns and dispersal of sediments in the south-eastern Arabian Sea during the last ~40 ka.

1.3. STRUCTURE OF THE THESIS

Chapter 1: Introduction

This chapter introduces the topics that have been addressed in this thesis. The motive of this chapter is to highlight the present level of understanding of the topics and mark the existing research gaps in the knowledge pertaining to these topics. This chapter also provides the major objectives of this thesis.

Chapter 2: Materials and Methods

This chapter provides the details on the materials and the various analytical methodologies used to accomplish the goals of this thesis. This chapter has been divided into two parts. The former part of the chapter details the geographical location of the samples and the sampling procedures; the latter part of the chapter discusses the analytical techniques followed for the chemical and isotopic analysis of waters and sediments from the Arabian Sea.

Chapter 3: Nd concentration and isotopic composition of waters of the Arabian Sea: water mass analysis using inverse model approach

This chapter details the results and discussions on the study of Nd concentration and isotopic composition (ϵ_{Nd}) in the vertical profiles from the Arabian Sea. Further, this chapter describes the application of an inverse model to study water masses in the Arabian Sea and estimate the dust flux to the surface waters.

Chapter 4: Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea

This chapter presents the results and discussions pertaining to the distribution of redox sensitive elements Re, U and Mo in the suboxic and denitrifying water column of the Arabian Sea. In this chapter, the lateral and vertical distribution of Re, U and Mo in the Arabian Sea has been discussed in terms of their relations with salinity and oxygen content.

Chapter 5: Variations in ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater during past 30 ka

The contents of this chapter discuss the temporal variation in the Os isotopic records of the Arabian seawater over the past 30 ka. The data shows significant variation in the ¹⁸⁷Os/¹⁸⁸Os of seawater in Arabian Sea over glacial-interglacial cycle and has been discussed in terms of changes in the bottom water circulation and oxygen level over the past.

Chapter 6: Temporal variations in ⁸⁷Sr/⁸⁶Sr and ε_{Nd} in sediments of the south-eastern Arabian Sea: Impact of monsoon and surface water circulation This chapter deals with the study of Sr and Nd isotopic composition of sediments from two cores in the south-eastern Arabian Sea. The temporal variation in both ⁸⁷Sr/⁸⁶Sr and ε_{Nd} in the south-eastern Arabian Sea has been discussed in terms of changes in provenances of sediments related to climatic/monsoon conditions and surface water circulation over the past.

Chapter 7: Summary and future perspectives

This chapter summarises the major findings of this thesis and presents the future perspectives related to these studies.

CHAPTER 2

Materials and Methods

The major goal of this study is to investigate the spatio-temporal variations in the concentration and isotopic composition of selected trace elements in solution and solid phases of the Arabian Sea and exploit their applications to understand contemporary and paleo oceanographic processes operating in the region. Some of the topics investigated include ocean circulation, aeolian dust deposition, behaviour of redox sensitive trace elements and dispersal and deposition of sediments (in response to changing climate) in the northern Indian Ocean.

To fulfil these objectives, several water and sediments samples from the Arabian Sea and the rivers draining into it were collected and analyzed following various analytical methods.

The sampling and analytical details are described in the following sections.

2.1 MATERIALS

The samples used to address the various themes of this thesis are the sediment and seawater from the Arabian Sea. Further, to trace the sources of detrital sediments deposited at selected locations in the Arabian Sea, sediment samples from the west flowing rivers of India were also collected.

Scheme of sampling and initial processing of samples is shown in Fig. 2.1. The sampling locations for sediment and seawater samples are shown in Fig. 2.2.

2.1.1 Sediment samples

The sediments analyzed in the present study are from two sediment cores and from some of the west flowing rivers of India.

The following section details the sediment samples used for the work done in this thesis.



Fig 2.1: Scheme of sampling and initial processing of samples.

Sediments from the Arabian Sea

Sediment samples of the Arabian Sea are from an earlier collection by scientists of the Chemistry Lab., Physical Research Laboratory. The two gravity cores are; SS-3101G and SS-3104G (Fig. 2.2). These cores were collected from the eastern Arabian Sea during 1991-92 [*Agnihotri*, 2001]. The sediments were collected onboard FORV Sagar Sampada on oceanographic expeditions conducted by PRL.

The details of the sediment cores used in the present study are given in Table 2.1.

| Core | Lat. (°N) | Long. (°E) | Water depth (m) | Core length (cm) | Avg. accumulation rate (cm/ka) |
|----------|--------------|---------------|--------------------|---------------------|-----------------------------------|
| SS-3101G | 6.0 | 74.0 | 2766 | 150 | 4.6 |
| SS-3104G | 12.8 | 71.7 | 1680 | 150 | 3.5 |



Fig 2.2: Sampling locations for water and sediment samples in the Arabian Sea. The shaded region at the central eastern Arabian Sea marks the zone of active water column denitrification [*Naqvi*, 1994]. The closed circles (\bullet) show the locations of vertical profiles of seawater sampling and closed boxes (\blacksquare) mark the locations of the two sediment cores analyzed.

The cores were sub-sampled onboard into 1 or 2 cm slices, stored in clean plastic bags and sealed. In the laboratory, during this work a part of the sample was dried in an oven at 90 °C [*Agnihotri*, 2001].

The chronologies of these cores were established by ¹⁴C dating of planktonic formainiferal separates (>250 μ m) using Accelerator Mass Spectrometry (AMS). The measurements were made at the NSF Radiocarbon facility, Tucson, Arizona (USA). The details on the core and their chronology are discussed in earlier publications [*Agnihotri*, 2001; *Agnihotri et al.*, 2003; *Somayajulu et al.*, 1999]. The calibrated ages of the sediments from the cores SS-3101G and SS-3104G are given in Table 2.2. Chronology of the entire core length is developed based interpolation of these dated samples.

| Core | Depth (cm) | Calibrated Age (ka) |
|----------|------------|---------------------|
| SS-3101G | 1-2 | 1.93 ± 0.10 |
| | 11-12 | 4.68 ± 0.14 |
| | 26-27 | 10.61 ± 0.39 |
| | 38-39 | 13.49 ± 0.20 |
| | 53-54 | 18.32 ± 0.34 |
| | 71-72 | 20.56 ± 0.42 |
| | 87-88 | 21.72 ± 0.40 |
| | 102-104 | 24.52 ± 0.29 |
| | 132-134 | 28.98 ± 0.54 |
| SS-3104G | 2-3 | 1.36 ± 0.09 |
| | 9-10 | 3.31 ± 0.16 |
| | 19-20 | 6.47 ± 0.14 |
| | 34-35 | 14.63 ± 0.39 |
| | 52-53 | 19.59 ± 0.50 |
| | 68-69 | 20.82 ± 0.39 |
| | 84-85 | 26.13 ± 0.29 |
| | 99-100 | 28.43 ± 0.38 |
| | 120-122 | 35.58 ± 0.65 |
| | 142-144 | 41.09 ± 1.14 |

Table 2.2: Calibrated ¹⁴C ages of sediments of the two cores

The cores SS-3101G and SS-3104G archive depositional histories of ~30 and ~40 ka respectively. The average sediment accumulation rates were 4.6 and 3.5 cm/ka for the cores SS-3101G and SS-3104G respectively.



Fig. 2.3: ¹⁴C chronology of the cores SS-3101G and SS-3104G [Agnihotri, 2001; Agnihotri et al., 2003; Somayajulu et al., 1999].

Both the cores display temporal variations in sediment accumulation rates, with higher rates ~7.5 cm/ka and ~4.2 cm/ka prior to LGM which decreased to ~2.9 cm/ka and ~2.7 cm/ka for SS-3101G and SS-3104G respectively after the LGM (Fig. 2.3). Sedimentation rates for both these cores increased during LGM as has been discussed by earlier workers [*Agnihotri*, 2001; *Agnihotri et al.*, 2003; *Somayajulu et al.*, 1999].

The cores SS-3101G and SS-3104G were chosen to study the Sr and Nd isotopic composition of the silicate fraction of the sediments to assess their temporal variability and its causes particularly, in the provenance of these sediments. These two cores have been selected for this study as (i) their chronology is well established, based on ¹⁴C dating of planktonic foraminiferal separates [*Agnihotri*, 2001; *Agnihotri et al.*, 2003; *Somayajulu et al.*, 1999] representing depositional histories of ~30 and ~40 ka and (ii) they are strategically located to investigate the impact of SW/NE monsoon variability and its role on the transport of sediments from the Bay of Bengal to the Arabian Sea. The core SS-3101G lies east of the Chagos Laccadive ridge adjacent to a sill. Further, the location of the core is between two well studied cores [*Sarkar et al.*, 1990; *Tiwari et al.*, 2005] that have provided evidences for variations in the intensities of southwest/northeast monsoons.

In addition, the moderate to relatively high organic carbon content of the core SS-3101G (0.61 to 2.25%) [*Agnihotri*, 2001] hints at the possibility of incorporation of authigenic Os from seawater to the sediments. If this is indeed valid, the sediments of the cores offer a unique possibility to study the temporal evolution of Os isotopic composition in near equatorial seawater region. To explore this, sediments from the core SS-3101G were systematically analyzed to trace the evolution of seawater ¹⁸⁷Os/¹⁸⁸Os over last 30 ka.

River sediment samples

The Arabian Sea receives detrital sediments from several rivers. Sr and Nd isotopic composition of these river sediments can serve as tracers to track the

provenance of sediments in the Arabian Sea. The major source of sediments to the Arabian Sea is the Indus River. There is available data on the Sr and Nd isotopic composition of sediments supplied by the Indus River [*Clift et al.*, 2002; *Clift et al.*, 2008; *Clift et al.*, 2010]. Such data are unavailable for the rivers from the western India such as the Narmada, Tapi, Nethravathi, Periyar and those draining the Western Ghats (Vashishthi, Kajli, and Sukh). Therefore, sediments from these rivers were collected from locations close to their mouths. The details of sampling locations of the river sediments and lithology of the river basins are given in Table 2.3 and shown in Fig 2.4.

| River | Lithology drained | Sampling Month, Year | Lat. (°N) | Long. (°E) |
|----------------------|-----------------------|-------------------------|-----------|------------|
| Mahi | Aravalli Super Group, | March, 2011 | 22.44 | 73.08 |
| | Deccan basalts, | | | |
| | Alluvial deposits | | | |
| Narmada | Proterozoic rocks of | March, 2011 | 21.91 | 73.34 |
| | Vindhyan Supergroup, | | | |
| | Deccan basalts | | | |
| Tapti | Cretaceous-Eocene | March, 2011 | 21.29 | 73.04 |
| | Deccan Trap basalts | | | |
| Nethravathi* | Peninsular Granite | Apr, 2010 | 12.88 | 75.04 |
| | gneisses | Dec, 2010 | | |
| Periyar [†] | Peninsular Granite | Apr, 2011 | 10.06 | 76.28 |
| | gneisses | Apr, 2011 | 10.06 | 76.26 |
| Kajli | Deccan Basalts | Aug, 2001 | 16.93 | 73.51 |
| Sukh | Deccan Basalts | Aug, 2001 | 16.56 | 73.63 |
| Vashishthi | Deccan Basalts | Aug, 2001 | 17.53 | 73.54 |

 Table 2.3: Locations of sediment samples from the west flowing rivers of

 India

* Samples from Dr. K. Balakrishna, Manipal University.

[†] Samples from Dr. C. H. Sujatha, Cochin University of Science and technology (CUSAT). The geographical locations (Lat and Long) of these samples are taken from Google Maps, (<u>http://maps.google.co.in/maps</u>).

The Mahi River drains a multi-lithological terrain composed of sediments of the Vindhyan Super Group, metamorphic rocks of the Aravalli Super Group, the Deccan basalts and the alluvial deposits of the Pleistocene and the Holocene ages [*Sridhar*, 2008]. The Narmada is the largest river draining into the Arabian Sea

from the western India. It passes through the Vindhyan ranges and the Deccan basalts before plunging into the Arabian Sea at the Gulf of Cambay, near the town of Bharuch [*Gupta et al.*, 2011]. The Tapi River is the second largest west-flowing river; its drainage basin consists of the Deccan basalts and alluvial deposits. The Tapi enters the Arabian Sea at the Gulf of Cambay near the city of Surat [*Kale et al.*, 2003].



Fig. 2.4: Sampling locations of sediments from rivers Mahi, Narmada, Tapi, Nethravathi, Periyar and the three Western Ghat streams (Vashishthi, Kajli and Sukh). Broad lithology of the regions drained by these rivers and locations of cores SS-3101G and SS-3104G are also shown.

The Nethravathi River is a minor river flowing through the Western Ghats draining granites/gneisses of the peninsular India. It joins the Arabian Sea near the Mangalore. The Periyar River drains crystalline rocks of the Archaen age; sedimentary rocks of different ages and laterites capping them [*Chandramohan and Balchand*, 2007]. There are several small streams that drain the Deccan basalts on the Western Ghats. In the present study sediment samples from three of these streams (Vashishthi, Kajli, and Sukh) were also analyzed. These samples are from the collection of *Das et al.*, [2005].

2.1.2 Seawater samples

Seawater samples from various depths of the Arabian Sea were collected in Dec., 2007 (cruise SS-256); Nov., 2008 (cruise SS-259) and Dec., 2009 (cruise KH-09-5) during winter monsoon. The first two expeditions were onboard FORV Sagar Smapada of the Ministry of Earth Sciences (MoES), Government of India, while the third was done onboard R/V Hakuho Maru of the Japan Agency of Marine Science and Technology (JAMSTEC). The details of the stations for the seawater sampling in the Arabian Sea are given in Table 2.4.

| | | Lat. | Long. | Number of | Month, |
|---------|---------|-------|-------|--------------------|------------|
| Cruise | Station | (°N) | (°E) | samples in profile | Year |
| SS-256 | 0702 | 17.27 | 72.44 | 1 (RSE) | Dec., 2007 |
| SS-256 | 0703 | 18.00 | 72.00 | 3 (RSE) | Dec., 2007 |
| SS-256 | 0704 | 18.00 | 70.64 | 6 (RSE) | Dec., 2007 |
| SS-256 | 0705 | 18.00 | 68.50 | 10 (RSE) | Dec., 2007 |
| SS-256 | 0706 | 16.50 | 66.50 | 12 (RSE) | Dec., 2007 |
| SS-256 | 0707 | 15.00 | 68.49 | 11 (RSE) | Dec., 2007 |
| SS-256 | 0708 | 15.00 | 70.49 | 13 (RSE) | Dec., 2007 |
| SS-259 | 0802 | 14.42 | 69.42 | 20 (RSE); 14 (Nd) | Nov., 2008 |
| SS-259 | 0803 | 10.12 | 71.86 | 20 (RSE); 10 (Nd) | Nov., 2008 |
| SS-259 | 0805 | 6.01 | 77.48 | 20 (RSE); 13 (Nd) | Nov., 2008 |
| KH-09-5 | ER6 | 14.00 | 69.00 | 18 (RSE) | Dec., 2009 |

Table 2.4: Details of the sampling stations for seawater in the Arabian Sea

RSE: Samples for Redox Sensitive Elements Re, U and Mo.

Water samples were collected using 12 ℓ Niskin bottles on 12 position CTD rosette array (on SS-256 and SS-259) or a 24 position CTD rosette array (on KH-09-5). The seabird CTD was used in all the expeditions to measure conductivity, temperature and depth. On the KH-09-5 cruise, a clean CTD system was used which consisted of titanium hydrographic wire. After collection, water samples

for trace element analysis were further sub-sampled into pre-cleaned 2 ℓ carboys on SS-256 and SS-259 cruises and filtered onboard in clean lab through < 0.45 µm Millipore cellulose filter. In the KH-09-5 cruise, the water samples were filtered through 0.2 µm Acropak cartridge filters in a HEPA filtered clean air chamber. Filtered seawater samples were stored in pre-cleaned (by soaking in 2N HCl for several days and cleaning profusely with MilliQ water) polypropylene bottles. The samples were acidified to pH~2 using ultrapure quartz distilled HCl. These samples were brought to the lab for measuring the concentrations of Nd and redox sensitive elements Re, U and Mo in the water column of the Arabian Sea.

Further, to characterize the water masses in the Arabian Sea using Nd isotopes, about 5 to 10 ℓ of seawater samples were collected from depth profiles at three stations in the Arabian Sea (Fig. 2.2; stations 0802, 0803 and 0805) and processed onboard. Fig. 2.5 shows the composite images for one of the research vessels and various steps followed onboard for collection and processing of seawater samples.



Fig. 2.5: Composite image showing the research vessel, collection and processing of samples onboard. Clockwise from top left; Research vessel R/V Hakuho-Maru; sampling of seawater from Niskin bottles (mounted on CTD frame); onboard measurement of nutrients using autoanalyser; preconcentration of seawater samples for Nd using the C18 cartridges.
2.2 ANALYTICAL METHODOLOGY

This part of the chapter on materials and methods details the analytical methods adopted for various measurements. These methodologies used are detailed in Table 2.5 and Fig 2.6.

| Table 2.5: Techniques followed for | [,] analysis of | various | elemental | and | isotopic |
|------------------------------------|--------------------------|---------|-----------|-----|----------|
| compositions in seawater and sedin | nents | | | | |

| Sample | Parameter | Technique used | Instrument |
|-----------|----------------------|---|------------|
| Seawater | Re concentration | Isotope dilution, | Q-ICP-MS |
| _ | | column chemistry | |
| _ | U, Mo concentration | Isotope dilution | Q-ICP-MS |
| | Nd isotopes | REE extraction by C18 cartridges, | TIMS |
| _ | | column chemistry | MC-ICP-MS |
| _ | Nd concentration | Fe-hydroxide precipitation, | Q-ICP-MS |
| | | column chemistry | |
| Sediments | Os isotopes and | Isotope Dilution | N-TIMS |
| | concentration (bulk) | Carius tube digestion | |
| - | | solvent extraction | |
| | Os isotopes and | Isotope Dilution | N-TIMS |
| | concentration | Leaching with H ₂ O ₂ | |
| | (hydrogenous) | solvent extraction | |
| - | Re | Isotope dilution | Q-ICP-MS |
| _ | Sr, Nd isotopes and | Isotope dilution, decarbonated | TIMS |
| | concentration | samples, column chemistry | |

Q-ICP-MS: Quadrapole Inductively Coupled Plasma Mass Spectrometer

TIMS: Thermal Ionisation Mass Spectrometer

MC-ICP-MS: Multi Collector Inductively Coupled Plasma Mass Spectrometer

2.2.1 Nd concentration and isotopic composition of seawater samples

The Nd isotopic composition and concentration were measured in seawater samples from the Arabian Sea.

Protocols of chemical separation and pre-concentration of Nd from the seawater was set-up for the first time in the laboratory as a part of this thesis work. Brief description of these protocols is given in the following sections.



Fig 2.6: Analytical techniques for measurement of various elemental and isotopic proxies in seawater and sediments.

Nd concentration and isotopic composition measurements in seawater

For the measurement of Nd isotopic composition of seawater, about 5-10 ℓ seawater was collected and processed onboard. The water samples were filtered through 0.45 μ m Millipore cellulose filter and collected in pre-cleaned carboys.

The samples were subsequently acidified to pH~3.5 with ultrapure double distilled HCl.

Nd isotopic composition of seawater: pre-concentration and extraction by C18 cartridges

Nd from filtered seawater samples (5-10 ℓ) were pre-concentrated using C18 SepPak cartridges (WATERS Inc.) loaded with strong Rare Earth Element (REE) complexant: di(2-ethyl) hydrogen-phosphate (High Density Ethyl Hexyl Phosphate; HDEHP) [*Jeandel et al.*, 1998; *Shabani et al.*, 1992]. On loading the cartridge with the HDEHP, Nd and other REEs are efficiently retained in the cartridge when seawater sample is passed through it. The setup for the system is shown in Fig. 2.7. Various steps involved in the extraction and preconcentration of REEs using the C18 cartridges are shown in Fig. 2.8.



Fig. 2.7: The setup for the extraction of REEs from seawater sample using the C18 cartridges. About 5-10 ℓ of seawater was passed through the C18 cartridge pre-loaded with strong REE complexant di(2-ethyl) hydrogenphosphate. The preferential retention of REEs in the reagent allows their separation from the seawater.



Fig 2.8: Flow chart for the extraction of REEs using C18 cartridges.

Nd concentration measurement in seawater samples

Nd concentration was separately measured in the seawater samples. Towards this, about 0.5 ℓ of seawater sample was spiked with ¹⁵⁰Nd tracer to measure Nd concentration by isotope dilution technique. Then Fe carrier (purified by ether extraction) was added to sample. The sample was well shaken and kept 24 hrs for equilibration. Then, the pH of sample was raised to ~7.5 by adding ammonia to form iron hydroxide precipitate. The precipitate was then allowed to settle and separated from the liquid phase by centrifugation. The extracts were further processed for separation of Nd from Fe by column chromatography.

Column chromatography

After preconcentration of REEs from seawater using C18 cartridges and/or Fe coprecipitation, Nd was extracted from the samples following column chromatographic procedures. In the first step, REEs were separated from Ba and other elements (such as Fe) by passing the REE extracts dissolved in 2N HCl through 16.5 cm long column of AG 50W-X8 (200 to 400 mesh) resin. The REEs were retained in the column and subsequently eluted with 6N HCl. For Nd concentration measurement, this fraction was dried and redissolved in 0.4N HNO₃ for mass spectrometric analysis on Thermo X-Series II Q-ICP-MS.

For Nd isotopic measurements, the collected REE fraction was further passed through a Lanthanide specific resin column (LN-C50-B; Eichrom Company). Towards this, an 8 cm long column of LN-C50-B resin was calibrated for Nd and Sm separation. The result of Nd and Sm separation is shown in Fig. 2.9.



Fig 2.9: Separation of Nd from Sm by the Lanthanide specific resin. Distinct peaks for both Nd and Sm show that they are well separated.

Calibration of Nd spike

The concentration of Nd in the seawater samples was measured using the isotope dilution technique. For this, a suitable amount of Nd spike (enriched in ¹⁵⁰Nd isotope) was added to the samples. The abundances of Nd isotopes of the sample (natural) and spike are given in Table 2.6.

| Isotope | Natural (%) | Spike (%) |
|-------------------|-------------|-----------|
| ¹⁴² Nd | 27.06 | 0.67 |
| ¹⁴³ Nd | 12.22 | 0.30 |
| ¹⁴⁴ Nd | 23.83 | 0.66 |
| ¹⁴⁵ Nd | 8.30 | 0.28 |
| ¹⁴⁶ Nd | 17.20 | 0.61 |
| ¹⁴⁸ Nd | 5.76 | 0.41 |
| ¹⁵⁰ Nd | 5.63 | 97.08 |
| Atomic wt. | 144.2433 | 149.7660 |

 Table 2.6: Atomic abundances of Nd isotopes in the sample (natural) and the spike

A primary stock solution of Nd spike ($[Nd] = 1.8984 \ \mu g/g$) enriched in ¹⁵⁰Nd was available in the laboratory. This stock solution was diluted further to make a spike solution of suitable strength for seawater concentration. This diluted Nd spike was calibrated using the SPEX Nd standard ($[Nd] = 10.2 \ ng/g$). For this, five sets of precisely weighted aliquots of spike solution were mixed and equilibrated with known weights of Nd standard. The standard-spike solutions were diluted (using 0.4 N HNO₃) and measured on Q-ICP-MS. The calibrated concentration of Nd spike is given in Table 2.7.

| | Wt. Nd Std (g) | Wt. Nd spike (g) | Nd spike conc. (ng/g) |
|---------------|----------------|------------------|-----------------------|
| Nd spike cal1 | 0.60806 | 0.18294 | 10.20 |
| Nd spike cal2 | 0.60981 | 0.14896 | 10.31 |
| Nd spike cal3 | 0.60954 | 0.17411 | 10.26 |
| Nd spike cal4 | 0.60938 | 0.15390 | 10.35 |
| Nd spike cal5 | 0.60805 | 0.19077 | 10.26 |
| | | MEAN | 10.28 |
| | | STDEV (1o) | 0.057 |
| | | RSD (%) | 0.6 |

Table 2.7: Results of calibration of Nd Spike

Mass Spectrometric Analysis

The mass spectrometric analysis for Nd isotopic composition was done both on ISOPROBE-T TIMS and Thermo Finnigan-Neptune MC-ICP-MS. The samples

from the Arabian Sea (processed by C18 cartridges) were analyzed on TIMS while the samples for the GEOTRACES Intercalibration were analyzed for their Nd isotopic composition on MC-ICP-MS.

For analysis of samples on TIMS, the purified Nd was loaded on a Ta-Re-Ta triple filament assembly with Nd being loaded on one of the side filaments. The Nd on TIMS was analyzed as Nd⁺. Before loading the purified Nd fraction on the filaments, the filaments were heated under vacuum. For analysis on MC-ICP-MS, the extracted Nd (after column chemistry) was dried and redissolved in 2 ml of 0.4 N HNO₃. As the abundance of Nd in these samples is low, APEX desolvating nebuliser was used to feed the samples to the plasma of the mass spectrometer. The Nd isotopic composition of GEOTRACES intercalibration samples was measured on MC-ICP-MS.



Fig 2.10: Measurement of ¹⁴³Nd/¹⁴⁴Nd of JNdi-1 Nd standard (reported ¹⁴³Nd/¹⁴⁴Nd = 0.512115; [*Tanaka et al.*, 2000]) on TIMS. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.



Fig 2.11: Measurement of ¹⁴³Nd/¹⁴⁴Nd of JMC-321 Nd standard (reported ¹⁴³Nd/¹⁴⁴Nd = 0.511123; [Godard et al., 2006]) on MC-ICP-MS. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.

In both TIMS and MC-CP-MS, the analyses were made in static multi-collection mode. Mass fractionation corrections were made by normalizing ¹⁴⁶Nd/¹⁴⁴Nd ratios to 0.7219. For the analysis on TIMS, JNdi-1 Nd standard (typical load~100-200 ng) was measured several times which gave an average value of 0.512108 \pm 0.000011 (1 σ , n = 14; σ = Standard Deviation) for ¹⁴³Nd/¹⁴⁴Nd.

The JMC-321 Nd standard was measured on MC-ICP-MS. A solution of 15 ng/g concentration of this standard was run on the MC-ICP-MS, this yielded an average value of 0.511099 ± 0.000011 (1 σ , n = 25). The analysis of respective Nd standards on both TIMS and MC-ICP-MS are shown in Figs. 2.10 and 2.11.

The Nd concentration was measured by monitoring the ¹⁵⁰Nd/¹⁴⁴Nd ratio on Q-ICP-MS. Typical counts obtained for ¹⁴⁴Nd and ¹⁵⁰Nd were in excess of 5000 and 20000 cps respectively, much higher than the background counts (around 1 cps).

GEOTRACES Intercalibtration for Nd isotopic composition

PRL participated in the GEOTRACES intercalibration initiative for Nd isotope measurements in seawater. Two 10 ℓ aliquots of seawater samples (code named as LDEO Nd02 and Nd04) from unknown locations were sent to PRL from Lamont Doherty Earth Observatory (LDEO), USA. Nd was preconcentrated and separated from these samples following procedures discussed and the Nd isotopic composition of the Nd extracts was measured on MC-ICP-MS. The results of GEOTRACES intercalibration samples are given in Table 2.8 and compared with the results of other international laboratories in Fig. 2.12.

The Nd isotopic data is usually expressed in terms of standard ε notation,

$$\varepsilon_{Nd} = \left[\frac{{}^{143}Nd/{}^{144}Nd}{{}^{144}Nd_{CHUR}} - 1\right] \times 10^4$$
(2.1)

where, ¹⁴³Nd/¹⁴⁴Nd is the measured Nd isotopic composition of the sample and ¹⁴³Nd/¹⁴⁴Nd_{CHUR} is the present day ¹⁴³Nd/¹⁴⁴Nd value of CHUR (Chondritic Uniform Reservoir) which is 0.512638, [*Jacobsen and Wasserburg*, 1980].

Table 2.8: Nd isotopic composition of GEOTRACES intercalibration samples

| | | STD err | | err | Reported * | err |
|-------------------|--------------------------------------|----------|-----------------|-----|-------------------|-----|
| Sample | ¹⁴³ Nd/ ¹⁴⁴ Nd | (abs) | ٤ _{Nd} | 2σ | ٤ _{Nd} | 2σ |
| Nd02 | | | | | | |
| (BATS 2000m) | 0.511950 | 0.000011 | -13.4 | 0.4 | -13.1 | 0.6 |
| Nd04 | | | | | | |
| (BATS 15m) | 0.512145 | 0.000011 | -9.6 | 0.4 | -9.2 | 0.6 |
| * Reported by yan | do Eliordt ot al | [2012] | | | | |

* Reported by van de Flierdt et al., [2012]

Nd isotope composition of intercalibration samples measured in PRL are well within the recommended values based on measurements of other groups, lending confidence to the protocol followed for Nd isotope measurement in our laboratory.



Fig. 2.12: Nd isotopic composition of the "unknown" GEOTRACES intercalibration samples. PRL was assigned a laboratory number 13.

Nd concentration was also measured in these intercalibration samples. The Nd concentration was measured by isotope dilution following Fe-hydroxide extraction and measurement on Q-ICP-MS. The results of these measurements suggest that the Nd concentration measured in our lab for these intercalibration samples agree well with reported values [*van de Flierdt et al.*, 2012].

| Sample | | Nd (ng/kg) |
|--------|-----------|---------------|
| Nd02 | Measured | 2.6 ± 0.1 |
| | Reported* | 2.5 ± 0.2 |
| Nd04 | Measured | 2.2 ± 0.1 |
| | Reported* | 2.0 ± 0.2 |
| 4D 11 | 1 51 | 1 1 50010 |

 Table 2.9: Nd concentration measured in GEOTRACES intercalibration samples

*Reported by van de Flierdt et al., [2012]

As a part of Nd intercalibration, one Nd standard ([Nd] = 15 ng/g) of unknown isotopic composition was also measured to compare the performance of the mass spectrometer. This standard was run on the MC-ICP-MS along with the Nd standard JMC-321. The results of these measurements are given in Table 2.10 and Fig. 2.13, agreeing well with the recommended value of 0.511750 [*van de Flierdt et al.*, 2012]



Fig. 2.13: ¹⁴³Nd/¹⁴⁴Nd data of "unknown" GEOTRACES intercalibration standard. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.

| S. No. | ¹⁴³ Nd/ ¹⁴⁴ Nd | STD err (abs) | $\epsilon_{ m Nd}$ | err 2σ |
|----------|--------------------------------------|---------------|--------------------|--------|
| 1 | 0.511723 | 0.000008 | -17.8 | 0.3 |
| 2 | 0.511713 | 0.000007 | -18.0 | 0.3 |
| 3 | 0.511757 | 0.000012 | -17.2 | 0.5 |
| 4 | 0.511740 | 0.000007 | -17.5 | 0.3 |
| MEAN | 0.511733 | | -17.6 | |
| STDEV | 0.000019 | | 0.4 | |
| Reported | 0.511750 | 0.000029 | -17.3 | 0.5 |

Table2.10:NdisotopiccompositionofunknownGEOTRACESintercalibration standard

In addition to assessing the precision of the analysis, few samples for both Nd isotopic composition and Nd concentration were measured in replicates. The coefficient of variance CV(%) for replicate analysis was calculated based on the following equation.

$$CV(\%) = \sqrt{\sum_{i} \frac{1}{2n} \left(\frac{d_i}{\bar{x}}\right)^2} \times 100$$
(2.2)

where, n is the number of duplicate sets measured and d_i is the difference of the duplicates which have a mean value of \overline{x} .

The reproducibility as CV (%) was obtained to be 3.7 % for Nd concentration measurements based upon the replicate measurements (Table 2.11).

| S7 1.8 S7 R 1.9 S26 1.8 S26 R 1.7 S28 1.9 S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 R 2.3 | Sample | Nd (ng/kg) |
|--|------------|------------|
| S7 R 1.9 S26 1.8 S26 R 1.7 S28 1.9 S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 R 2.3 | S 7 | 1.8 |
| S26 1.8 S26 R 1.7 S28 1.9 S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 R 2.3 | S7 R | 1.9 |
| S26 R 1.7 S28 1.9 S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 2.2 2.3 | S26 | 1.8 |
| S28 1.9 S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 2.2 Nd04 R 2.3 | S26 R | 1.7 |
| S28 R 1.8 Nd02 2.6 Nd02 R 2.7 Nd04 2.2 Nd04 R 2.3 | S28 | 1.9 |
| Nd02 2.6 Nd02 R 2.7 Nd04 2.2 Nd04 R 2.3 | S28 R | 1.8 |
| Nd02 R 2.7 Nd04 2.2 Nd04 R 2.3 | Nd02 | 2.6 |
| Nd04 2.2 Nd04 R 2.3 | Nd02 R | 2.7 |
| Nd04 R 2.3 | Nd04 | 2.2 |
| | Nd04 R | 2.3 |

 Table 2.11: Replicate analysis for Nd concentration measurements

| | | err ¹⁴³ Nd/ ¹⁴⁴ Nd | | err e _{Nd} | |
|----------------|--------------------------------------|--|--------------------|---------------------|--|
| Sample | ¹⁴³ Nd/ ¹⁴⁴ Nd | (%) | $\epsilon_{ m Nd}$ | (2o) | |
| 0802 (3000m) | 0.51219 | 0.0019 | -8.8 | 0.4 | |
| 0802 (3000m) R | 0.51218 | 0.0021 | -8.9 | 0.4 | |
| 0803 (360m) | 0.51213 | 0.0021 | -9.8 | 0.4 | |
| 0803 (360m) R | 0.51217 | 0.0087 | -9.0 | 1.7 | |
| 0811 (300m) | 0.51200 | 0.0033 | -12.5 | 0.7 | |
| 0811 (300m) R | 0.51196 | 0.0018 | -13.2 | 0.4 | |

Table 2.12: Replicate analysis of the Nd isotopic composition

The isotopic composition of the Nd (143 Nd/ 144 Nd or ε_{Nd}) was also measured in replicates to determine the precision of these measurements (Table 2.12).

Based upon these replicate analyses, the average variation between sets of repeats was determined to be 0.3 ε_{Nd} units.

The total procedural blank was measured during the course of the work for the extraction and preconcentration of Nd by C18 cartridges. Three blanks were measured on TIMS. The total procedural blank measured for the method of extraction of Nd using C18 cartridges was found to be 588 ± 28 pg (average of three separate blank measurements). Similar blank level was also reported by *Lacan and Jeandel*, [2004] using the C18 cartridges.

The total procedural blank was also measured for the Fe co-precipitation method, determined to be~70 pg.

2.2.2 Re, U and Mo concentration measurements

The Re, U and Mo concentrations of seawater samples from the Arabian Sea were measured using the isotope dilution technique on Q-ICP-MS. For the measurement of Re, a method comprising of the isotope dilution and separation of Re (preconcentration) by column chromatography was followed, whereas for U and Mo, the samples were spiked and diluted before analyzing them on mass spectrometer.

Calibration of spikes

Calibration of Re spikes

For the measurement of Re, ¹⁸⁵Re enriched spike was used. The abundances of Re isotopes of the sample (natural) and spike are given in Table 2.13.

 Table 2.13: Atomic abundances of Re isotopes in the sample (natural) and spike

| Isotope | Natural (%) | Spike (%) |
|-------------------|-------------|-----------|
| ¹⁸⁵ Re | 37.40 | 94.50 |
| ¹⁸⁷ Re | 62.60 | 5.50 |
| Atomic wt. | 186.2067 | 185.0050 |

Two Re spikes (Re A and B) were prepared from stock Re spike and calibrated to estimate their concentrations accurately. For this, the spikes were calibrated against a Re standard of precisely known concentration ([Re] = 1.14146 ng/g) available in the lab. This standard was prepared by dissolving high purity Re metal (99.97%, procured from H. Cross Company) in 2N HNO₃.

Table 2.14: Calibration of Re spikes using Re standards

| | Wt. std (g) | Wt. spike (g) | Re conc. spike (ng/g) |
|--------|-------------|-------------------------|-----------------------|
| A Cal1 | 0.10215 | 0.02535 | 6.88 |
| A Cal2 | 0.09819 | 0.02962 | 7.02 |
| A Cal3 | 0.09995 | 0.03014 | 7.00 |
| | | MEAN | 6.97 |
| | | STDEV (1 ₅) | 0.07 |
| | | RSD (%) | 1.05 |
| | | | |
| | Wt. std (g) | Wt. spike (g) | Re conc. spike (ng/g) |
| B Cal1 | 0.09786 | 0.03308 | 6.51 |
| B Cal2 | 0.09526 | 0.0324 | 6.38 |
| B Cal3 | 0.11862 | 0.03544 | 6.40 |
| | | MEAN | 6.43 |
| | | STDEV (1 ₅) | 0.07 |
| | | DCD (0/) | 1 10 |

Three separate set of aliquots of precisely known weights of spike solution were equilibrated with known weight of this Re standard. The standard-spike solution were diluted and measured in Q-ICP-MS to obtain the Re strength of the spike solutions accurately. The calibrated concentrations of Re spikes are given in Table 2.14.

U and Mo spikes

The concentrations of U and Mo in the samples were also measured by the isotope dilution technique with enriched ²³⁶U and ¹⁰⁰Mo spikes. The abundances of U and Mo isotopes of the sample (natural) and spike are given in Tables 2.15 and 2.16 respectively.

Table 2.15: Atomic abundances of U isotopes in the sample (natural) and spike

| Isotope | Natural (%) | Spike (%) |
|------------------|-------------|-----------|
| ²³⁴ U | 0.01 | - |
| ²³⁵ U | 0.72 | < 0.004 |
| ²³⁶ U | - | 99.97 |
| ²³⁸ U | 99.27 | 0.02 |
| Atomic wt. | 238.0289 | 236.0460 |

 Table 2.16: Atomic abundances of Mo isotopes in the sample (natural) and spike

| Isotope | Natural (%) | Spike (%) |
|-------------------|-------------|-----------|
| ⁹² Mo | 14.84 | 0.60 |
| ⁹⁴ Mo | 9.25 | 0.23 |
| ⁹⁵ Mo | 15.92 | 0.40 |
| ⁹⁶ Mo | 16.68 | 0.81 |
| ⁹⁷ Mo | 9.55 | 0.36 |
| ⁹⁸ Mo | 24.13 | 1.69 |
| ¹⁰⁰ Mo | 9.63 | 95.90 |
| Atomic wt. | 95.9613 | 99.7386 |

The U and Mo spikes were calibrated against one composite standard comprising of U and Mo of known concentration. The standard used for the calibration of spikes was the reference material SLRS-4 of the National Research Council Canada ([U] = 0.05 ppb; [Mo] = 0.21 ppb).

| | Wt. std (g) | Wt. U spike (g) | Wt. Mo spike (g) | U conc. spike (ng/g) | Mo conc. spike (ng/g) |
|------------|----------------|--------------------|---------------------|-------------------------|--------------------------|
| U Mo Cal 1 | 10.62173 | 0.14138 | 0.11790 | 10.15 | 28.01 |
| U Mo Cal 2 | 10.58401 | 0.10420 | 0.12621 | 10.14 | 28.20 |
| U Mo Cal 3 | 11.04351 | 0.11165 | 0.11770 | 10.13 | 28.48 |
| | | | MEAN | 10.14 | 28.23 |
| | | | STDEV (1o) | 0.01 | 0.23 |
| | | | RSD (%) | 0.10 | 0.82 |

Table 2.17: Calibration of U and Mo spikes

For the calibration of both U and Mo spikes, precisely known weights of these spikes were mixed with a known weight of SLRS standard in a solution. The standard-spike solution (comprising U, Mo spikes and the standard) aliquots were diluted and measured in Q-ICP-MS to obtain the U and Mo strength of each of the spike solution. The calibrated concentrations of U and Mo spikes are given in Table 2.17.

2.2.2.1 Re concentration measurement of seawater samples

For Re measurements, a known weight of seawater (typically ~50g) was spiked with a known amount of ¹⁸⁵Re enriched (94.5%) tracer and stored at room temperature for at least 24h for sample-spike equilibration. Subsequently, the spiked samples were dried at 80 °C and digested with a few drops of quartz distilled HNO₃. The Re was extracted and purified from the residue by ion exchange separation methods [*Dalai et al.*, 2002; *Rahaman and Singh*, 2010; *Trivedi et al.*, 1999]. The purified Re was redissolved in 5 ml 0.4 N HNO₃.

The Re concentration in the acid solutions was determined by measuring their ¹⁸⁵Re/¹⁸⁷Re ratio on Thermo X-Series II Q-ICP-MS facility at PRL. Instrumental mass fractionation correction was done by measuring Re standard of natural

composition frequently. The sample counts were generally in excess of several thousand cps for both ¹⁸⁵Re and ¹⁸⁷Re, compared to 10 cps for the background.

| Station | Depth (m) | Re (pmol/kg) |
|---------|-----------|--------------|
| 0802 | 5 | 42.6 |
| | 5R | 42.3 |
| | 1500 | 40.7 |
| | 1500R | 40.0 |
| 0803 | 2400 | 40.4 |
| | 2400R | 40.0 |
| 0805 | 5 | 36.6 |
| | 5R | 36.8 |
| | 120 | 39.7 |
| | 120R | 39.8 |
| | 750 | 40.1 |
| | 750R | 40.0 |
| | 1100 | 39.6 |
| | 1100R | 39.7 |
| | 1250 | 38.9 |
| | 1250R | 39.9 |
| 0708 | 663 | 41.0 |
| | 663R | 40.6 |
| | 2200 | 40.4 |
| | 2000R | 40.7 |
| 0707 | 5 | 41.0 |
| | 5R | 41.7 |
| | 2000 | 39.1 |
| | 2000R | 38.7 |
| 0706 | 250 | 41.3 |
| | 250R | 40.0 |
| | 2100 | 38.9 |
| | 2100R | 40.0 |
| 0705 | 700 | 41.3 |
| | 700R | 40.1 |
| 0703 | 5 | 41.3 |
| | 5R | 41.9 |
| ER6 | 3000 | 39.0 |
| | 3000R | 39.2 |

 Table 2.18: Replicate analysis of Re concentration

In order to determine the analytical precision for the analysis of Re in the seawater samples, several samples were measured in duplicates. The results of these analyses are given in Table 2.18. Based upon the replicate analysis, the analytical precision (CV) was found out to be ~ 1 % for Re analysis of seawater samples.

Total procedural blank for Re measurement based on eight independent measurements was found to be 27 ± 10 femtomole. The blank level was found to be much lesser than the sample levels thus no correction for the blank was made.

2.2.2.2 U and Mo concentration measurement of seawater samples

U and Mo concentrations of seawater samples were measured by isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). For these measurements, about 0.25 g of precisely weighed sample was mixed with precisely known weights of ²³⁶U (99.27 %) and ¹⁰⁰Mo (95.9 %) enriched spikes. The sample spike mixture was allowed to equilibrate and diluted ~30 times using 0.4 N HNO₃ [*Klinkhammer and Palmer*, 1991].

The U and Mo concentrations in seawater samples were determined by measuring respectively the ${}^{236}\text{U}/{}^{238}\text{U}$ and ${}^{100}\text{Mo}/{}^{98}\text{Mo}$ ratios in the diluted samples on Q-ICP-MS. The sample counts were greater than 4000 for ${}^{98}\text{Mo}$ and greater than 15000 for ${}^{100}\text{Mo}$, ${}^{236}\text{U}$ and ${}^{238}\text{U}$. The background counts monitored during the runs were a few orders of magnitude lower than those for ${}^{98}\text{Mo}$, ${}^{100}\text{Mo}$, ${}^{236}\text{U}$ and ${}^{238}\text{U}$. The total procedural blank was also measured for both the U and Mo analysis. Based upon eight independent measurements, the total procedural blanks for U and Mo were 3.4 ± 0.8 femtomole and 1.0 ± 0.2 picomole respectively. As the U and Mo blank levels were much lesser than the sample concentrations, no corrections for the blanks were made in the samples.

Several samples were measured in replicates to determine the analytical precision of the U and Mo measurements in the seawater samples. The results of replicate analyses of samples have been given in Table 2.19. Based upon the replicate analyses, the analytical precision (CV) was determined to be 0.6 % and 0.8 % for U and Mo measurements respectively.

| Station | Depth (m) | U (nmol/kg) | Mo (nmol/kg) |
|---------|-----------|-------------|--------------|
| 0802 | 5 | 14.5 | 117 |
| | 5R | 14.3 | 116 |
| | 1000 | 13.8 | 113 |
| | 1000R | 14.0 | 111 |
| | 4040 | 13.8 | 111 |
| | 4040R | 13.7 | 111 |
| 0803 | 5 | 14.0 | 113 |
| | 5R | 13.9 | 114 |
| | 1200 | 13.8 | 112 |
| | 1200R | 13.8 | 113 |
| | 2200 | 13.8 | 112 |
| | 2200R | 13.7 | 110 |
| 0805 | 5 | 12.9 | 103 |
| | 5R | 12.7 | 103 |
| | 2250 | 13.9 | 111 |
| | 2250R | 13.6 | 110 |
| 0708 | 1400 | 13.8 | 114 |
| | 1400R | 13.8 | 111 |
| 0707 | 2000 | 13.7 | 112 |
| | 2000R | 13.7 | 111 |
| 0706 | 5 | 14.3 | 115 |
| | 5R | 14.3 | 116 |
| 0705 | 5 | 14.8 | 119 |
| | 5R | 14.7 | 118 |
| 0704 | 5 | 14.2 | 114 |
| | 5R | 14.3 | 113 |
| ER6 | 4140 | 13.8 | 113 |
| | 4140R | 13.9 | 114 |

 Table 2.19: Replicate analysis of U and Mo concentrations

Measurement of Re, U and Mo in SAFe water samples

Along with the measurement of Re, U and Mo in seawater samples, the concentration of these elements was also measured in SAFe (Sampling and Analysis of Fe) seawater samples. The results of the Re, U and Mo analysis in these samples are given in Table 2.20. The salinity normalised (at 35 salinity)

concentrations of Re, U and Mo in these SAFe water samples are 39.7 ± 0.7 , 14.0 \pm 0.1 and 112 \pm 2 respectively, nearly identical to their open ocean values [*Goswami et al.*, 2012a].

| SAFe water | | | | |
|------------|----------|--------------|-------------|--------------|
| Sample | Salinity | Re (pmol/kg) | U (nmol/kg) | Mo (nmol/kg) |
| D1-242 | 34.40 | 39.1 | 13.7 | 108 |
| D2-142 | 34.40 | 39.9 | 13.8 | 112 |
| S-107 | 34.90 | 39.4 | 14.0 | 111 |
| GD-31 | 34.98 | 40.6 | 13.9 | 113 |
| GS-149 | 36.65 | 40.7 | 14.6 | 116 |
| D1-242R | 34.40 | 39.0 | - | - |
| GS-149R | 36.65 | 40.7 | - | - |

Table 2.20: Concentration of Re, U and Mo in SAFe water samples

SAFe seawater samples provided by Prof. Kenneth Bruland, University of California, Santa Cruz. The salinity values given above were measured for profiles nearby the SAFe water samples collected at the same time.

2.2.3 Sr and Nd concentration and isotopic composition measurements in silicate fraction of sediments

The sediment samples from Arabian Sea cores and west flowing rivers of India were at first dried at 90 °C for a few days; powdered using an agate mortar and pestle to less than 100 μ m size and stored in pre-cleaned plastic containers.

Sr and Nd isotopic analyses were made on carbonate and organic matter free fraction of the sediments [*Singh et al.*, 2008]. The powdered sediment samples were first decarbonated by leaching with 0.6 N HCl at 80 °C for ~30 min with ultrasonic treatment. The slurry was centrifuged, residue washed with Milli-Q water, dried and ashed at ~600 °C to oxidize organic matter. A known weight (~100 mg) of the carbonate and organic matter free fraction of the sediment was transferred to Savillex[®] vial and digested repeatedly with HF-HNO₃-HCl at ~120 °C to bring the sediment to complete solution. The acid digestion step was repeated as needed to ensure that the entire sample was brought to complete solution. Sediments from the Arabian Sea were digested in the presence of ⁸⁴Sr and ¹⁵⁰Nd spikes whereas the river sediments were not spiked. Pure Sr and Nd

fractions were separated from the solution following standard ion exchange procedures [*Rahaman et al.*, 2009; *Singh et al.*, 2008]. The mass spectrometric analysis of samples from the Arabian Sea sediments was done on TIMS, whereas, the river sediment samples were analyzed on MC-ICP-MS.

For mass spectrometric analysis on TIMS, pure Sr was loaded on a vacuum baked Ta filament, whereas the purified fraction of Nd was loaded on the outer Ta filament of the Ta-Re-Ta triple filament assembly. In case of river sediment samples that were analyzed on MC-ICP-MS, the purified fractions of Sr and Nd were dried and then redissolved in 4 ml of 0.4 N HNO₃. The Sr and Nd analysis on both TIMS and MC-ICP-MS was done in static multicollection mode. The measured ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd were corrected for instrumental mass fractionation by normalizing measured ⁸⁶Sr/⁸⁸Sr and ¹⁴⁶Nd/¹⁴⁴Nd with respect to their natural values, *viz*. 0.1196 and 0.7219 respectively. The Sr and Nd elemental concentration for these samples were obtained through the isotope dilution method.

Along with samples, Sr and Nd standards were also routinely measured on both the mass spectrometers during the course of analysis. NBS-987 was measured as the Sr standard on both TIMS and MC-ICP-MS. The details of Nd standards run on TIMS and MC-ICP-MS have already been discussed in section 2.2.1 (Figs. 2.10 and 2.11). Sr standard NBS-987 was measured several times on TIMS (typical load ~500 ng) giving an average 87 Sr/ 86 Sr value of 0.710222 ± 0.000012 (1 σ , n = 22; σ = Standard Deviation). A solution of 50 ppb of NBS-987 Sr standard was measured several times on MC-ICP-MS, this yielded an average value of 0.710287 ± 0.000020 (1 σ , n = 15) for 87 Sr/ 86 Sr. The 87 Sr/ 86 Sr of the Sr NBS-987 standard measured on both TIMS and MC-ICP-MS has been given in Figs. 2.14 and 2.15. A few samples of sediments from the Arabian Sea were also measured in replicate for Sr and Nd concentration and isotopic composition to check the overall reproducibility of the Sr-Nd isotopic and concentration measurements. The result of the replicate analysis is shown in Table 2.21. Based on replicate measurements, the average variation between sets of repeats was determined to be 0.0002 and 0.2 for ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ϵ_{Nd} respectively.

| sample | ⁸⁷ Sr/ ⁸⁶ Sr | Sr (µg/g) | ¹⁴³ Nd/ ¹⁴⁴ Nd | 8 _{Nd} | Nd (µg/g) |
|-----------------|------------------------------------|-----------|--------------------------------------|-----------------|-----------|
| 3101(10-11) | 0.71459 | 139.5 | 0.51197 | -13.1 | 8.7 |
| 3101(10-11) R | 0.71501 | 133.1 | - | - | - |
| 3101(90-91) | 0.71950 | 101.2 | 0.51192 | -14.1 | 15.7 |
| 3101(90-91) R | 0.71956 | 101.9 | 0.51190 | -14.4 | 14.5 |
| 3104(23-24) | 0.71648 | 78.3 | 0.51213 | -9.9 | 9.9 |
| 3104(23-24) R | 0.71621 | 78.2 | 0.51213 | -9.9 | 10.9 |
| 3104(37-38) | 0.71642 | 100.1 | 0.51214 | -9.7 | 13.2 |
| 3104(37-38) R | 0.71649 | 100.1 | 0.51214 | -9.7 | 13.4 |
| 3104(41-42) | 0.71698 | 102.3 | 0.51212 | -10.1 | 14.0 |
| 3104(41-42) R | 0.71687 | 102.8 | 0.51213 | -9.9 | 14.8 |
| 3104(95-96) | 0.71708 | 92.7 | 0.51216 | -9.3 | 8.6 |
| 3104(95-96) R | 0.71693 | 92.1 | - | - | - |
| 3104(126-128) | 0.71727 | 112.6 | 0.51214 | -9.8 | 13.5 |
| 3104(126-128) R | 0.71721 | 110.9 | 0.51215 | -9.5 | 12.8 |

 Table 2.21: Reproducibility of elemental and isotopic composition of Sr and Nd for the sediment samples



Fig 2.14: Measurement of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ of NBS-987 Sr standard (reported ${}^{87}\text{Sr}/{}^{86}\text{Sr} = 0.710250$; [*Bralower et al.*, 2004]) on TIMS. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.



Fig 2.15: Measurement of 87 Sr/ 86 Sr of NBS-987 Sr standard on MC-ICP-MS. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.

The total procedural blank was also measured for Sr and Nd. The average based on four independent measurements was 3.2 ng and 1.6 ng respectively for Sr and Nd. These blanks are several orders of magnitude lower than typical total Sr and Nd loads analyzed and hence no corrections for blanks were made.

2.2.4 Os elemental and isotopic analysis of bulk and hydrogenous component of sediments from the Arabian Sea

The Os concentration and isotopic composition (187 Os/ 188 Os) was measured in the bulk and hydrogenous component of sediments from the Arabian Sea. Prior to analysis of the sediment samples, these were finely powdered using agate mortar and pestle and sieved using nylon mesh of 100 µm pore size. The coarser fractions were repowdered, mixed and homogenized with the <100 µM size sample.

Calibration of spike

The concentration of Os in the samples was measured using the isotope dilution technique. The abundances of Os isotopes of the sample (natural) and spike are given in Table 2.22.

| Isotope | Natural (%) | Spike (%) |
|-------------------|-------------|-----------|
| ¹⁸⁴ Os | 0.02 | 0.01 |
| ¹⁸⁶ Os | 1.60 | 0.02 |
| ¹⁸⁷ Os | 1.51 | 0.03 |
| ¹⁸⁸ Os | 13.29 | 0.52 |
| ¹⁸⁹ Os | 16.25 | 0.96 |
| ¹⁹⁰ Os | 26.37 | 96.57 |
| ¹⁹² Os | 40.96 | 1.90 |
| Atomic wt. | 190.2318 | 190.7775 |

 Table 2.22: Atomic abundances of Os isotopes in the sample (natural) and spike

The measurement of Os concentration using the isotope dilution technique involves addition of suitable amount of ¹⁹⁰Os spike (depending upon the Os concentration in the sample). The Os spikes available in the lab were previously used for the determination of concentration of Os in the black shale samples by *Tripathy*, [2011]. A new batch of Os spike was prepared by diluting the available Os stock solution of concentration 19.23 ng/g.

 Table 2.23: Calibration of osmium Spike using Os standard of known strength

| | Wt. std (g) | Wt. spike (g) | Os conc. spike (ng/g) |
|-------------|-------------|----------------|-----------------------|
| Os SPK Cal1 | 0.10437 | 0.53070 | 1.91 |
| Os SPK Cal2 | 0.10471 | 0.49891 | 1.91 |
| Os SPK Cal3 | 0.10560 | 0.55830 | 1.95 |
| | | MEAN | 1.92 |
| | | STDEV (1o) | 0.02 |
| | | RSD (%) | 1.14 |

The new batch of Os spike was calibrated against an Os standard (Os-STD B) with concentration of 16.25 ng/g, provided by Dr. L. Reisberg, CRPG, Nancy. Three aliquots of the precisely weighed Os standard were equilibrated with known amount of Os spike for 48 hrs. After equilibration, the Os isotopic composition for the standard-spike mixtures was measured using Thermal Ionization Mass

Spectrometer in negative mode. The calibrated concentration of Os spike is given in Table 2.23.

Sample digestion in Carius tube

For the Os analysis in the bulk sediments, the sediment samples from the Arabian Sea were digested in the Carius tube [*Shirey and Walker*, 1995], in presence of inverse aqua-regia (HNO₃:HCl::3:1) as the sample digestion medium. The Carius tubes used for the digestion were made of borosilicate glass. The length of the Carius tubes used was ~340 mm and wall thickness of the glass used for fabrication of the Carius tubes was ~3 mm. Before using the Carius tubes for the digestion of the samples, they were boiled in HNO₃ for ~6 hours and then washed profusely with Milli-Q water. The Carius tubes were then allowed to dry.



Fig 2.16: Sediment samples in inverse aqua-regia in the Carius tube kept in liquid nitrogen/acetone (-80 °C) slush prior to sealing the tube.

Around 1 to 1.5 g of sediment sample was weighed and transferred to the Carius tube. As the neck of the Carius tube is kept narrow (for easy sealing of the tube), proper care needs to be taken to transfer the sample to the Carius tube. ¹⁹⁰Os spike

was added to the powdered sediment sample in the Carius tube followed by 2 ml of HCl. The sample was let stand for ~5-6 hours. Then ¹⁸⁵Re spike was added to the sample (for Re concentration measurement in the sample). The addition of HCl decarbonates the samples. This decarbonation prevents pressure build-up inside the tube during dissolution of sample. The Carius tube (containing the sample) was then cooled by immersing it in a low temperature bath at -80 °C (liquid nitrogen/acetone slush; Fig. 2.16).

Once the contents of the Carius tube were cooled, 5 ml of HNO_3 was added. The cooling of the Carius tube and its contents is essential prior to the addition of HNO_3 to avoid any loss of Os. Following the acid addition, the Carius tube was evacuated using a hand vacuum pump and sealed using the LPG-oxygen mixture flame and annealed at ~550 °C for 6 hours while still keeping the sediment-acid slurry part of the tube in the cooling slush.

After annealing the Carius tube, it was placed inside an iron jacket and the assembly was kept in an oven at 240 °C for 24 hours for digesting the samples. The high temperature and pressure digestion of samples in the Carius tube brings Os from sediment sample to acid solution and ensures the sample-spike equilibration. The reaction mixture in the tube was then frozen by immersing the lower part of the tube in liquid nitrogen. The Carius tube was then opened and the liquid phase (oxic medium) was transferred to a Savillex[®] 60 ml PFA digestion vessel.

Hydrogenous Os leaching from sediments

For extraction of the hydrogenous component of Os from the sediment samples, a leaching procedure was adopted. About 1-1.5 g of dry sediment sample was taken in a clean 50 ml centrifuge tube. The sample was treated with 20 ml of 10% acetic acid in the first step to remove carbonate phases. Then, the sample was centrifuged and the leachate discarded. To the residue remaining in the centrifuge tube, 30 ml of leaching solution (Milli-Q water: H_2SO_4 (conc): H_2O_2 :: 45:1:1) was added. This mild leaching solution releases Os bound to the Fe-Mn oxide and

organic phases of the sediments sequestered directly from seawater [*Pegram et al.*, 1992]. The sample in centrifuge tube was subjected to ultrasonic treatment for ~30 minutes, after which it was let stand overnight. The sample was then carefully centrifuged and the leachate was transferred to a Savillex[®] 60 ml PFA digestion vessel and ¹⁹⁰Os spike was added to the sample. The digestion vessel containing the leachate was tightly closed and kept over a hot plate at ~60 °C for 24 hours. This step facilitates the sample-spike equilibration and also helps in breakdown of H₂O₂ present in the bomb. After 24 hours, the digestion vessel was kept in the freezer for 30 minutes. Then the vessel was opened and 1 ml of CrO₃ (in H₂SO₄) was added to its contents to make the medium oxidising. Thereafter, the separation of Os from the sample is done by solvent extraction and this procedure is same for both the bulk sediment analysis and hydrogenous phase analysis.

Solvent extraction for Os

To the Os extracts contained in the digestion vessel (from Carius tube digestion or hydrogen peroxide leaching), 1 ml of double distilled Br_2 liquid was added and the vessel was again closed by tightening the lid. The sample solution in the digestion vessel was kept on hot plate at 80 °C for 3 hours. This is a key step in the transfer of Os from the oxidising liquid phase to Br_2 . In the solvent extraction for Os, the use of Br_2 is beneficial in two ways; firstly, Os has an affinity to form osmium bromate complexes in oxic conditions and secondly, Br_2 is liquid which has a low boiling point (59 °C) and higher density than the liquid phase present in the Teflon bomb. So, Br_2 liquid boils and evaporates from bottom of the oxidising solution (containing Os) and passes through it, before condensing at the lid of the vessel. The Br_2 droplets forming at the lid again falls down to the bottom of the solution. This process takes place repeatedly and is called Br_2 refluxing (Fig. 2.17). During refluxing, Br_2 passes through the oxidising solution and captures Os from it. This process efficiently transfers the Os present in the oxidising liquid phase to the $Br_2[Birck et al., 1997]$.

After 3 hours of Br_2 refluxing, the vessel was taken off the hot plate and kept in the refrigerator to avoid volatilization of osmium. After sufficiently cooling down the contents of the vessel, the Br_2 was extracted and transferred to a Savillex[®] 7 ml Teflon vial containing 1-2 ml of cold water. The water was kept in the vial to minimize the loss of Br_2 by evaporation. The Br_2 refluxing and extraction step was repeated one more time to extract the remaining Os. Finally, the 7 ml Teflon vial containing 2 ml of Br_2 liquid contains the osmium.



Fig 2.17: Bromine refluxing in the Teflon bomb for extraction of Os from the sample [*Birck et al.*, 1997].

Microdistillation

Water from the top of the Br₂ layer in the 7 ml Teflon vial was carefully removed using a pipette out and discarded. To the Br₂ left in the Teflon vial, 0.5 ml of double distilled HBr was added to transfer Os present in volatile Br₂ to reducing HBr. In this condition, Os remains in $OsBr_6^{2-}$ form. The vial was then kept on hot plate at~80 °C to remove Br₂ and dry the HBr present in the vial to a small drop (<50 µl). The small drop of HBr was then transferred onto the lid of the Savillex[®] 5 ml Teflon conical vial and dried completely. About 20 µl of HBr was put to the conic section of the vial. Now, to the dried HBr (containing Os) on the lid of vial, 20 µl of CrO₃ (in H₂SO₄) was put. Then the conic section of the vial was put on the lid and tightened. The closed conical vial was wrapped with an aluminium foil leaving a gap on the top of conic section so that the HBr drop is not covered. The foil wrapped conical vial was kept on hot plate for 3 hours at a temperature of 80 °C. During this micro-distillation process, Os is volatilised from the cap of vial and is condensed onto the cooler HBr present at the conic section of the vial [*Birck et al.*, 1997]. After micro-distillation, the HBr containing the pure osmium is dried and used for isotopic and elemental analysis by thermal ionization mass spectrometer in its negative ionization mode.

Mass spectrometry for Os

The mass spectrometric analysis of Os was done in the negative mode Thermal Ionisation Mass Spectrometer (N-TIMS) with Os being analyzes as OsO_3^- species obtained by oxygen bleeding [*Creaser et al.*, 1991; *Volkening et al.*, 1991].

Sample loading: The extracted and purified Os from the sample was loaded on zone refined (99.999% purity, H. Cross Co.) platinum filament strip. Prior to deposition of Os on the filament, the Pt strip was heated by passing a current of~3 A for 30 minutes to oxidise any Os present on the filament surface. The filament was then kept idle for at least 24 hours before loading the Os. To load the purified Os, a current of~0.6 A was passed through the filament to slightly heat it. Os was dissolved in~1 μ l of HBr (using a Hamilton micro syringe) and slowly and steadily deposited at the centre of the filament. To the loaded Os on the filament, Ba(OH)₂ in 0.1 N NaOH was loaded as an ion enhancer [*Birck et al.*, 1997]. The ion enhancer (Ba(OH)₂ in 0.1 N NaOH) was prepared by refluxing a mixture of~0.1 g of NaOH, 0.7 g of Ba(OH)₂ and~30 ml H₂O in a vial for 3 hrs at 80 °C. This supersaturated solution can be used effectively for more than two months with minimal atmospheric exposure [*Luguet et al.*, 2008].

Mass spectrometric measurements of Os: The pure Os metal loaded on the Pt filament was analyzed for its isotopic compositions using the Isoprobe-T Thermal Ionization Mass Spectrometer in negative mode (N-TIMS) with oxygen bleeding. The isotopic measurements for Os were performed in OsO_3^- form in a peak jumping mode using a secondary electron multiplier (SEM) detector. A small amount of pure oxygen was purged into the source chamber of the mass spectrometer during the analysis. The pressure of the source chamber increased

to~ 2×10^{-7} mbar (from initial pressure of~ 3×10^{-8} mbar) due to oxygen bleeding. Osmium isotopic analysis was performed at this pressure level of the source chamber. Four isotopes of the Os (187 OsO₃, 188 OsO₃, 190 OsO₃ and 192 OsO₃) were measured with an integration time of 5 seconds each. The counting was repeated over 100 cycles to get precise isotopic composition of the sample. Among the four isotopes of Os, 187 Os being the least abundant, care was taken to ensure that it was measured at a count rate of at least 1000 cps for 5 seconds.

Further, during analysis, mass 233 was monitored for Re contamination (from ¹⁸⁵ReO₃). Only Os data from those samples was considered where the count rate at mass 233 was less than 10 cps. The samples with significantly high 233 mass count rate were not run for their Os isotopic analysis.

Data reduction: The Os isotope composition, as discussed earlier, was measured in its OsO_3^- form in peak jumping mode. To get a precise Os isotopic ratio from the measured OsO_3^- signals, these data have to be corrected for growth/decay (of signal) with time, instrumental mass fractionation, isobaric interference due to various OsO_3^- combinations and spike contribution. These corrections were done following standard data reduction procedure followed in our laboratory [*Singh et al.*, 1999; *Trivedi et al.*, 1999]. The measured isotopic ratios were normalized with respect to ¹⁸⁸Os/¹⁹²Os of 0.32439 [*Nier*, 1937] to correct for the instrumental mass dependent isotope fractionation.

Data precision and accuracy: An Os standard has been measured repeatedly for its isotopic composition over the duration of Os analysis in bulk sediments and hydrogenous fraction of sediments (Fig. 2.18). 50 to 1000 pg of Os standards were loaded on filaments to measure in N-TIMS, the average ¹⁸⁷Os/¹⁸⁸Os measurements for the standard has been found to be 0.1072 ± 0.0011 (1 σ , n=19), consistent with its reported value of 0.1069 ± 0.0024 [*Singh*, 1999] and 0.1069 ± 0.0009 [*Tripathy*, 2011].



Fig. 2.18: Measurement of ¹⁸⁷Os/¹⁸⁸Os of standard versus time. The dotted lines are the 2σ (σ = Standard deviation) spread of the data.

To check the precision and reproducibility of the measurements, some samples were measured in duplicates for both the bulk sediments as well as the hydrogenous fraction of the sediments. The details of these replicate measurements have been given in the Table 2.24.

| | Hydrogenou | Hydrogenous Fraction | | iments |
|-----------------|--------------------------------------|----------------------|--------------------------------------|-----------|
| Sample | ¹⁸⁷ Os/ ¹⁸⁸ Os | Os (pg/g) | ¹⁸⁷ Os/ ¹⁸⁸ Os | Os (pg/g) |
| 3101(68-69) | 1.033 | 186.9 | - | - |
| 3101(68-69) R | 1.025 | 201.9 | - | - |
| 3101(122-124) | 0.982 | 166.6 | - | - |
| 3101(122-124) R | 0.988 | 165.1 | - | - |
| 3101(130-132) | - | - | 0.736 | 317.7 |
| 3101(130-132) R | - | - | 0.742 | 296.5 |
| 3101(132-134) | 1.037 | 160.1 | - | - |
| 3101(132-134) R | 1.025 | 165.1 | - | - |

Table 2.24: Replicate analysis of Os and ¹⁸⁷Os/¹⁸⁸Os in samples

Based on replicate measurements done for the hydrogenous fraction of Os, the average variation between sets of repeats was determined to be 0.009 for 187 Os/ 188 Os (Table 2.24). The reproducibility for the Os concentration measurements of hydrogenous fraction was found to be 3.4 % (Table 2.24).

The replicate analysis for the Os concentration and isotopic composition for bulk sediment analysis was only done on one set (Table 2.24). But, Os concentration and ¹⁸⁷Os/¹⁸⁸Os was measured a number of times in the USGS SCo-1 Cody shale standard (bulk analysis). The data for ¹⁸⁷Os/¹⁸⁸Os measurements agrees well with that reported by *Meisel and Moser*, [2004].

Table 2.25: Measurement of Os and ¹⁸⁷Os/¹⁸⁸Os in USGS SCo-1 standard

| Standard | Measurement | ¹⁸⁷ Os/ ¹⁸⁸ Os | Os (pg/g) |
|------------------------------|----------------|--------------------------------------|-----------|
| SCo-1 | 1 | 1.50 | 74.00 |
| SCo-1 | 2 | 1.47 | 69.57 |
| SCo-1 | 3 | 1.50 | 78.33 |
| SCo-1 | 4 | 1.49 | 79.20 |
| | MEAN | 1.49 | 75.27 |
| | STDEV (1o) | 0.02 | 4.43 |
| | RSD (%) | 1.08 | 5.88 |
| Reported [#] | MEAN | 1.39 | 90 |
| | STDEV (1o) | 0.15 | 11.7 |
| | RSD (%) | 10.9 | 13 |

[#] Data from *Meisel and Moser*, [2004]

Os procedural blank

During the course of measurements, total procedural blank for Os was determined for both bulk sediment analysis and hydrogenous Os leaching methods. Towards this, the complete chemical procedure was carried out without the sample, but with the same amount of reagents. Os spike was also added as was done for the samples. The procedural blanks measured for Os has been found to be few orders lower compared to total Os processed from the samples and hence, no blank corrections was made in this work. The blank for the bulk sediment analysis is given in Table 2.26, while the blank for the hydrogenous Os leaching procedure is listed in Table 2.27.

 Table 2.26: Total procedural blank for Os measurements (bulk sediment analysis)

| Sample ID | Os, fg |
|---------------|-------------|
| BLK -1 | 1016 |
| BLK -2 | 2135 |
| BLK -3 | 310 |
| BLK -4 | 466 |
| MEAN | 982 ± 826 |
| fa: femtogram | |

fg: femtogram

 Table 2.27: Total procedural blank for Os measurements (Hydrogenous Os leaching)

| Sample ID | Os, fg |
|-----------|---------------|
| BLK -L1 | 832 |
| BLK -L2 | 664 |
| BLK-L3 | 411 |
| MEAN | 636 ± 212 |
| | |

fg: femtogram

Further, the blank was measured in all the individual reagents used for the hydrogenous Os leaching procedure. The results for the blank estimation of the reagents are given in Table 2.28.

 Table 2.28: Blank levels of reagents used for hydrogenous Os leaching procedure

| Reagent | Volume of Reagent | Os, fg |
|---|-------------------|--------|
| Double distilled water | 10 ml | 499 |
| Milli-Q water | 10 ml | 272 |
| CrO ₃ (in H ₂ SO ₄) | 1 ml | 91 |
| H_2SO_4 | 1 ml | 143 |
| H_2O_2 | 1 ml | 30 |
| for found a sugar | | |

fg: femtogram

2.2.5 Re concentration measurement in bulk sediments from the Arabian Sea The Re concentration in the sediment samples from the Arabian Sea core SS-3101G was measured in the bulk samples. After the solvent extraction for the Os isotopic analysis by Br₂ extraction, the Re was extracted from the residue left in the Teflon bomb. The residue in the bomb was completely dried. After drying the residue, 5 ml of 0.8 N HNO₃ was added. The slurry was then centrifuged and the supernatant liquid was loaded on an anion exchange resin (AG1X8, 100-200 mesh). The column was then washed with 0.8 N HNO₃ and Re was eluted from the column with 8 N HNO₃ [Dalai et al., 2002]. The extracted Re was dried and dissolved in 0.4 N HNO₃. The Re concentration in the acid solutions was determined by measuring their ¹⁸⁵Re/¹⁸⁷Re ratio on Thermo X-Series II Q-ICP-MS facility at PRL. Instrumental mass fractionation correction was done by measuring Re standard of natural composition frequently (after every 5 sample measurements). The background level of around 10 cps was found to be negligible in comparison to counts for both ¹⁸⁵Re and ¹⁸⁷Re (in excess of several thousand cps).

| Sample | Re (ng/g) |
|-----------------|-----------|
| 3101(0-1) | 0.26 |
| 3101(0-1) R | 0.26 |
| 3101(3-4) | 0.25 |
| 3101(3-4) R | 0.24 |
| 3101(32-33) | 0.44 |
| 3101(32-33) R | 0.45 |
| 3101(91-92) | 12.05 |
| 3101(91-92) R | 11.71 |
| 3101(104-106) | 2.26 |
| 3101(104-106) R | 2.30 |

Table 2.29: Replicate analysis of Re concentration in samples

In order to check the reproducibility and reliability of the Re concentration measurements, a few samples were measured in replicates. The replicate analysis of the samples is given in Table 2.29. Based upon the replicate analysis, the reproducibility (Coefficient of variance; CV) was obtained to be 2.3 %.

Re concentration was also measured in the USGS (United States Geological Survey) Cody shale standard SCo-1 (Table 2.30). The Re concentration measured in our laboratory in the SCo-1 standard agrees well with that reported by *Meisel and Moser*, [2004]

| Standard | Measurement | Re (ng/g) |
|------------------------------|-------------------------|-----------|
| SCo-1 | 1 | 1.04 |
| SCo-1 | 2 | 1.04 |
| SCo-1 | 3 | 1.06 |
| SCo-1 | 4 | 1.07 |
| SCo-1 | 5 | 1.04 |
| | MEAN | 1.05 |
| | STDEV (1 ₅) | 0.02 |
| | RSD (%) | 1.5 |
| Reported [#] | MEAN | 1.01 |
| | STDEV (1 ₅) | 0.06 |
| | RSD (%) | 6.2 |

Table 2.30: Measurement of Re concentration in USGS SCo-1 standard

[#] Data from *Meisel and Moser*, [2004]

Total procedural blank was also determined for Re (Table 2.31). Total procedural Re blank is order of magnitude lower than the total Re processed for the samples, so no blank correction was applied.

 Table 2.31: Total procedural blank level for Re measurements in bulk sediments

| Sample ID | Re, pg |
|-----------|------------|
| Re BLK1 | 31 |
| Re BLK2 | 34 |
| Re BLK3 | 30 |
| Re BLK4 | 38 |
| Re BLK5 | 35 |
| Re BLK6 | 36 |
| MEAN | 33 ± 3 |

CHAPTER **3**

Nd concentration and isotopic composition of waters of the Arabian Sea: water mass analysis using inverse model approach
3.1 Introduction

The distribution of Nd concentration and its isotopic composition (ε_{Nd}) serves as a coupled tracer of the origin and circulation of water masses both on the inter and intra oceanic [*Amakawa et al.*, 2000; *Frank*, 2002; *Goldstein and Hemming*, 2003; *Jeandel*, 1993; *Jeandel et al.*, 1998; *Peipgras and Wasserburg*, 1982; 1983]. This is primarily due to the oceanic residence time of Nd being comparable to the ocean mixing time [*Johannesson and Burdige*, 2007; *Nozaki and Alibo*, 2003; *Tachikawa et al.*, 1999]. The ε_{Nd} of the ocean reflects that of the nearby continents, thereby suggesting continental Nd as the dominant contributor of dissolved Nd into the ocean. Thus, the spatial variation in the ε_{Nd} of the ocean reflects the variation in the supply of Nd from the continent and/or modification of ε_{Nd} signature by mixing of different water masses [*Frank*, 2002; *Goldstein and Hemming*, 2003; *Lacan and Jeandel*, 2001; 2004a; b; 2005].

The potential of coupled Nd concentration- ε_{Nd} to track the water mass circulation in the ocean was realized in early eighties and since then a lot of such studies have been done in different basins such as Arctic, Atlantic and the Pacific Oceans [*Jeandel*, 1993; *Lacan and Jeandel*, 2001; 2004b; 2005; *Peipgras and Wasserburg*, 1982; 1983; *Peipgras and Jacobson*, 1988; *Porcelli et al.*, 2009; *Rickli et al.*, 2010; *Shimizu et al.*, 1994; *Zimmermann et al.*, 2009].

In the Indian Ocean, however, such studies on the Nd isotopic composition of water masses are limited [*Amakawa et al.*, 2000; *Bertram and Elderfield*, 1993; *Jeandel et al.*, 1998; *Nozaki and Alibo*, 2003]. The available studies on the Nd isotopic composition of Indian Ocean suggests that it is intermediate of that of the Pacific Ocean (with highly radiogenic ε_{Nd} values of between 0 and -4 for the surface and intermediate waters; and lower values of -3 to -6 for the deeper waters [*Peipgras and Jacobson*, 1988; *Shimizu et al.*, 1994]) and the Atlantic Ocean (which shows the most non-radiogenic ε_{Nd} values, as low as -26 in the North Atlantic near the Baffin Bay [*Stordal and Wasserburg*, 1986]).

As a consequence of mixing of Pacific waters with the Atlantic waters in the Southern Ocean, the water masses hence formed (Antarctic Intermediate Water, AAIW; Circumpolar Deep Water, CDW or Antarctic Bottom Water, AABW) have their ε_{Nd} between -7 and -9. Since, the Indian Ocean has no northern source of deep water masses, these waters with intermediate ε_{Nd} spreads northwards in the Indian Ocean and flush the intermediate to deeper waters in this oceanic basin. The shallow water masses forming in the northern Indian Ocean such as Arabian Sea High Salinity Water (ASHSW), Persian Gulf Water (PGW) and Red Sea Water (RSW) have their origin in the Arabian Sea. There have been no earlier efforts made for the quantification of water mass structure of the northern Indian Ocean especially in the Arabian Sea. The present study is an effort for the same using the Nd concentration and isotopic composition of waters from the Arabian Sea. Further, an inverse modelling approach has been applied for quantification of water mass fractions in the Arabian Sea.



Fig 3.1: Sampling stations in the Arabian Sea for Nd concentration and isotopic analysis. The red band encompassing the stations shows the direction/projection of the meridional section for the contour plots.

Arabian Sea is an oceanic basin that is bounded by arid continental mass to its eastern, western and northern boundaries. Around 100 million tons of aeolian dust from the deserts of Arabian Peninsula (Oman), Africa and western India is deposited annually in the Arabian Sea [*Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989]. Aeolian dust is an important and direct source of nutrients to the surface ocean. With Arabian Sea in the proximity of arid (desert) continental landmass, the dust deposition flux in the Arabian Sea can be fairly significant. Estimated dust flux in the Arabian Sea based on various approaches range between 1.5 and 13 g m⁻² y⁻¹ [*Duce et al.*, 1991; *Measures and Vink*, 1999; *Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989]. In the present study an effort has been made to estimate the dust flux into the surface waters of the Arabian Sea using Nd content in these waters.

3.2 Northern Indian Ocean: water mass structure

The northwestern part of Indian Ocean which composes of Arabian Sea exhibits distinct lateral salinity gradients in the upper 1000m [*Wyrtki*, 1973] due to marked differences in the rate of evaporation over precipitation and the influx of less saline waters from the Bay of Bengal through its southeastern corner. In addition, the Persian Gulf and the Red Sea contribute high salinity waters to the Arabian Sea at depths of about 200 m and 500 m respectively. Thus, the upper 1000 m water column of the Arabian Sea is composed of three characteristic water masses, the Arabian Sea High Salinity Water (ASHSW), the Persian Gulf Water (PGW) and the Red Sea Water (RSW).

The upper water masses viz. ASHSW, PGW and RSW progress southwards and mix to form the North Indian Intermediate water (NIIW) below the upper 1000m water column of Arabian Sea, which also travels southwards. On its southward progression, NIIW mixes with the northward moving polar waters and forms the North Indian Deep water (NIDW). The deeper water masses in the Arabian Sea primarily compose of Modified North Atlantic Deep water (MNADW) and Antarctic Bottom water (AABW) [*Kumar and Li*, 1996]. The North Atlantic Deep Water (NADW) forms in the northern Atlantic by cooling and sinking of water in the Baffin Bay and Norwegian Sea. Then NADW travels southwards in the Atlantic Ocean and enters the Indian Ocean to the south of African peninsula. In the ocean near the Antarctica, the NADW mixes with the Antarctic Surface Water

(ASW) and the Weddell Sea Bottom Water (WSDW). This results in lowering of the salinity and potential temperature of the NADW and transformation of NADW into the Modified North Atlantic Deep Water (MNADW). Hence transformed, the MNADW travels in the Indian Ocean northwards. The deepest and the bottom water mass AABW reaching the northern Indian Ocean has its origin in the Weddell Sea [*Mantyla and Reid*, 1995]. The role of bottom topography of the ocean basin is significant in deciding the progression of these deeper water masses in the Arabian Sea.

The bottom water movement in the Indian Ocean is quite different to that in other oceanic basins; Atlantic and Pacific Oceans. In the Atlantic and Pacific Oceans, dense deeper waters from Antarctica spread northward on the western sides of the ocean. In the Indian Ocean, these waters spread northwards both in the west and east. Both the western and eastern entry points of deeper waters in the Indian Ocean have different sources of waters. The deeper waters in the Arabian Sea are sourced from the western route in the Indian Ocean. In the western Indian Ocean, the deeper waters enter the basin through the discordance zone in the Southwest Indian Ridge at about 30°S, 60°E [*Warren*, 1978]. The deeper waters in the Indian Ocean then reach the Madagascar basin and the Mascarene basin. From the Mascarene basin, the deeper waters enter the Somali basin via the narrow Amirante passage (at ~10°S, 53°E) [*Johnson and Damuth*, 1979; *Johnson et al.*, 1991]. The deeper waters then propagate to the Arabian Sea from the Somali basins through the Owen fracture zone [*Mantyla and Reid*, 1995].

Further, warm and low salinity surface and intermediate waters of the Pacific origin enter the Indian Ocean at its eastern boundary via the Indonesian throughflow [*Jeandel et al.*, 1998]. The Indonesian seas (Java Sea, Banda Sea, and Molucca Sea) are mostly filled with Pacific waters. But, the dynamics through the Indonesian seas results in a vertical mixing of the different water masses to such a degree that when they leave the Indonesian seas Pacific waters are no more recognizable, and these "renewed waters" are called Indonesian Waters. Characteristic water masses of the Indonesian Seas that are transported westwards

from the Indonesian throughflow are the Indonesian throughflow surface Waters (IW) that is the surface layer water mass and the Indonesian throughflow Intermediate Water (IIW) [*Jeandel et al.*, 1998].

3.3 Results and discussion

The Nd concentration and isotopic composition were measured in three vertical profiles from the Arabian Sea (Chapter 2). Fig. 3.1 shows the stations for the study of vertical profile of Nd concentration and ε_{Nd} in the Arabian Sea. The red band encompassing the stations in Fig. 3.1 shows the direction/projection of the meridional section for the contour plots.

Table 3.1: Salinity, potential temperature (0), Nd concentration and ϵ_{Nd} in the profiles from the Arabian Sea

| Depth (m) | Salinity | θ (°C) | Nd (pmol/kg) | ٤ _{Nd} | err ɛ _{Nd} | | |
|-------------------------|----------|--------|--------------|-----------------|---------------------|--|--|
| 0802 (14.42°N, 69.42°E) | | | | | | | |
| 5 | 36.7 | 28.9 | 15.8 | -7.7 | 0.4 | | |
| 65 | 36.5 | 26.3 | 14.0 | -7.1 | 0.5 | | |
| 120 | 35.8 | 20.0 | 14.3 | -8.5 | 0.4 | | |
| 230 | 35.7 | 14.6 | 12.5 | -11.4 | 0.5 | | |
| 400 | 35.5 | 12.3 | 12.7 | -8.5 | 0.3 | | |
| 500 | 35.5 | 11.7 | 13.5 | -9.0 | 0.3 | | |
| 700 | 35.5 | 10.3 | - | -8.6 | 1.8 | | |
| 1000 | 35.3 | 8.0 | 20.2 | -9.4 | 0.3 | | |
| 1500 | 35.0 | 5.1 | 16.9 | -8.3 | 2.1 | | |
| 2100 | 34.8 | 2.7 | 17.5 | -10.7 | 0.3 | | |
| 3000 | 34.7 | 1.6 | 23.1 | -8.8 | 0.4 | | |
| 3600 | 34.7 | 1.4 | 25.3 | -9.0 | 0.3 | | |
| 3900 | 34.7 | 1.4 | 24.6 | -8.4 | 0.3 | | |
| 4040 | 34.9 | 1.4 | 34.3 | -9.4 | 0.3 | | |
| 0803 (10.12°N, 71.86°E) | | | | | | | |
| 5 | 35.5 | 28.9 | 20.1 | -7.8 | 0.7 | | |
| 35 | 36.4 | 28.8 | 15.4 | -7.1 | 0.6 | | |
| 130 | 35.1 | 16.4 | 15.6 | - | - | | |
| 210 | 35.2 | 13.3 | - | -9.9 | 0.6 | | |
| 300 | 35.2 | 12.1 | 13.3 | -11.2 | 0.5 | | |
| 360 | - | 11.5 | 13.3 | -9.9 | 0.4 | | |
| 465 | 35.3 | 10.9 | 14.2 | -9.4 | 0.5 | | |

| 600 | 35.2 | 10.3 | 14.4 | -8.8 | 0.6 | |
|---------------|----------|------|------|-------|-----|--|
| 900 | 35.2 | 8.4 | 16.6 | -9.9 | 0.3 | |
| 1200 | 35.0 | 6.4 | 18.6 | - | - | |
| 1600 | 34.9 | 4.2 | 19.7 | -9.3 | 0.6 | |
| 2400 | 34.8 | 1.9 | 22.5 | -10.2 | 0.6 | |
| 0805 (6.01°N, | 77.48°E) | | | | | |
| 5 | 32.4 | 29.1 | 27.8 | - | - | |
| 60 | 35.3 | 28.0 | 16.5 | - | - | |
| 120 | 35.0 | 21.8 | - | -12.1 | 0.7 | |
| 200 | 35.0 | 14.1 | 19.3 | -10.7 | 0.7 | |
| 300 | 34.9 | 11.6 | 18.0 | -12.4 | 0.4 | |
| 580 | 35.0 | 9.4 | 18.1 | - | - | |
| 650 | 34.8 | 9.0 | 19.5 | -14.7 | 1.4 | |
| 845 | 35.0 | 7.8 | 21.0 | -11.3 | 0.4 | |
| 1000 | 35.0 | 6.9 | 22.0 | -10.9 | 0.4 | |
| 1150 | 34.9 | 6.0 | 21.9 | - | - | |
| 1450 | 34.9 | 4.6 | 22.8 | -12.6 | 0.5 | |
| 1850 | 34.8 | 3.1 | 23.5 | -10.1 | 0.3 | |
| 2250 | 34.8 | 2.3 | 25.7 | -10.6 | 0.4 | |

-: Not measured.

The Nd concentration in the waters of the Arabian Sea varies from 12.5 to 34.3 pmol/kg (n=36, Table 3.1). The Nd concentration in the surface waters of the Arabian Sea show an increase from north to south. The surface waters of the northern station 0802 (14.42°N, 69.42°E) show the minimum concentration ([Nd] = 15.8 pmol/kg) as compared to the stations 0803 (10.12°N, 71.86°E) ([Nd] = 20.1 pmol/kg) and southern station 0805 (6.01°N, 77.48°E) ([Nd] = 27.8 pmol/kg) (Fig 3.2a).

In the southern station 0805 which lies between the Arabian Sea and Bay of Bengal, the Nd concentrations are higher by 4 to 6 pmol/kg at all the corresponding depth compared to northern stations 0802 and 0803 (Fig. 3.2). Higher concentration in water of the southern station indicates the contribution of enriched Nd water from the Bay of Bengal. Nd concentrations in the Bay of Bengal water are significantly higher due to its release from particulates [*Nozaki and Alibo*, 2003; *Singh et al.*, 2012].



Fig 3.2: The distribution of (a) Nd concentration and (b) isotopic composition (ϵ_{Nd}) in the vertical profiles from the Arabian Sea. The Nd concentration shows a nutrient like profile but displays enrichment at the surface. The ϵ_{Nd} in the vertical profiles from the Arabian Sea shows a north-south gradient with the southern station having more non-radiogenic Nd.

In all profiles, the Nd concentration trend is similar displaying nutrient like profile, a minimum value between 200 to 400 m depth and increasing Nd in deeper sections. Sub-surface minima in these profiles are due to removal of Nd from these waters by adsorption onto sinking particles in the Arabian Sea. Studies based upon the sediment trap deployment in the Arabian Sea have shown that the rain rate of particles through the water column of the Arabian Sea is quite high with values ranging from 25–30 g m⁻² y⁻¹ [*Ramaswamy and Nair*, 1994] with significant lithogenic and biogenic fluxes. These conditions make Arabian Sea conducive for removal of rare earth element (Nd) from its surface and sub-surface waters. In all the three profiles Nd concentration in the surface waters are higher, compared to that of sub-surface. This is due to supply of Nd from particulate matters. These particulate matters could be either aeolian or fluvial in nature.

The Nd concentration in the vertical profile from the Arabian Sea has been measured earlier by *Bertram and Elderfield*, [1993] at a station (1605; 14.43°N, 66.92°E). This station is near to the northern station 0802 occupied in the present study. The general trend for the Nd concentration in the profile 1605 in the central

Arabian Sea is similar to the Nd concentration in the station 0802. The Nd concentration in the station 1605 shows a very slight enrichment in the surface ([Nd] = 11.4 pmol/kg). Nd concentration trend in the profile 0802, though is similar to that of station 1605, concentrations are marginally higher. Similar trend of higher Nd concentration in the surface and sub-surface waters is also reflected by the station 0803 in the Arabian Sea. The Nd concentration was also measured by *Bertram and Elderfield*, [1993] in the northern Arabian Sea in the Gulf of Oman. The Nd profile measured in the Gulf of Oman shows a similar trend to the Arabian Sea profile 0802, but the Nd concentration in the 0802 profile are higher by ~3 pmol/kg as compared to the vertical profiles in the Gulf of Oman.

The ε_{Nd} in the vertical profiles from the Arabian Sea shows large variability varying from -7.1 to -14.7 (n=33, Table 3.1). The vertical profiles 0802 and 0803 in the Arabian Sea show more radiogenic values with ε_{Nd} ranging from -10 to -7 (Fig 3.2b), whereas in the southern station 0805 which is near the periphery of Bay of Bengal, the ε_{Nd} is more non-radiogenic (more negative) ranging from -15 to -10 (Fig 3.2b). The ε_{Nd} has been previously measured in the western Indian Ocean by *Bertram and Elderfield*, [1993] in the Somali, Mascarene and Madagascar basins. The ε_{Nd} in the Somali basin was measured in vertical profile up to a depth of ~4900 m. The vertical profile of Nd isotopic composition measured in the Arabian Sea profiles 0802 and 0803 in this study shows similar values to that of measured in the Somali basin. This similarity, however, breaks down in the sub-surface waters (100-250m) where the ε_{Nd} in the Arabian Sea is more non-radiogenic (Fig 3.2b).

The ε_{Nd} was also measured in the surface waters of the Bay of Bengal at a station PA-9 (8.02°N, 88.99°E) which showed a non-radiogenic value of -11.2 [*Amakawa et al.*, 2000]. The Nd isotopic composition was not measured in the surface waters of the southern station 0805 (near the Bay of Bengal), but the ε_{Nd} in this station at a depth of 120 m shows a non-radiogenic value of -12.1 (Fig 3.2b). The lesser radiogenic ε_{Nd} and the high Nd content in the Bay of Bengal surface waters (PA-

9) and that of the station 0805 suggest the supply of non-radiogenic Nd to the Bay of Bengal from the Himalaya through the Ganga-Brahmaputra river system.

3.3.1 Water masses in the Arabian Sea: quantification by inverse modelling approach

The distribution of dissolved Nd concentration and isotopic composition in the Arabian Sea is an intricate mixture of Nd contributed by various water masses and its supply from aeolian dust, contribution from sinking particulate matter and/or from sediment water interactions. In the present work, an inverse modelling approach [*Tarantola*, 2005; *Tripathy and Singh*, 2010] has been applied for the quantification of these various contributions resulting in the observed Nd distributions.

The inverse modelling approach is based on set of mass balance equations that relates the observed data (data space) with the model parameters (model space). In this approach, the contributions from various sources (end-members) are estimated by iteratively solving a set of mass balance equations based on the observed parameters. The inverse model calculates not only the contribution of various sources to the observed quantity (parameter) but also provides the best estimates for that parameter of the end-members. In the current context, in order to find out the contribution of Nd from various water masses (sources) in the waters of the Arabian Sea, the parameters that have been considered are; (i) Potential temperature, (ii) Salinity, (iii) Nd concentration and (iv) Nd isotopic composition (ϵ_{Nd}).

The inverse model calculation provides the best values of these properties (Potential temperature, salinity, Nd concentration and ε_{Nd}) of the various endmembers and computes the contribution of various water masses present in the Arabian Sea. The calculations are based upon a set of mass balance equations which relate the observed data and the model parameters. These mass balance equations are as follows:

$$X_m = \sum_{i=1}^n X_i \times f_{im} \tag{3.1}$$

Where, X = Potential temperature and Salinity of the water mass (source/end-member).

For Nd concentration and ε_{Nd} , the mass balance equations have been written as follows:

$$Nd_m = Nd_m^{excess} + \sum_{i=1}^n Nd_i \times f_{im}$$
(3.2)

$$\left(\varepsilon_{Nd}\right)_{m} = \frac{\left(\varepsilon_{Nd}\right)_{m}^{excess} \times Nd_{m}^{excess} + \sum_{i=1}^{n} Nd_{i} \times \left(\varepsilon_{Nd}\right)_{i} \times f_{im}}{Nd_{m}^{excess} + \sum_{i=1}^{n} Nd_{i} \times f_{im}}$$
(3.3)

Here, m denotes a sample or observation point. In equations (3.2) and (3.3), extra terms have been used for Nd_m^{excess} and $(\varepsilon_{Nd})_m^{excess}$. These terms arise from the Nd contribution in the water column apart from the water masses (sources) considered in the present problem. The excess of Nd can come from the aeolian supply of dust or by the release from the sinking particles [*Jeandel et al.*, 1995; *Tachikawa et al.*, 1999].

In this study, a total of 9 water masses/sources (thus, n=9) were considered. The details of these water masses have been given in the section 3.3.1.1.

 f_{im} is the fraction contributed by the ith water mass/source on the mth observation/data point, and

$$\sum_{i=1}^{n} f_{im} = 1$$
(3.4)

In general, the above equations (3.1-3.4) can be written as d = G(m), where d and m are the data and model spaces respectively. G is the function that relates the data and model spaces. The model spaces are assumed to follow log-normal probability distribution. A non-linear weighted fit of equations (3.1-3.4) was obtained using the Quasi-Newton method [*Tarantola*, 2005], which provided the

best possible set for the model parameters and the covariance (i.e. uncertainties) associated with them.

The reliability of the inverse model used in the present study was ensured by running this model on the published river data [*Tripathy and Singh*, 2010] by estimating contributions from different sources.

3.3.1.1 *A priori* values of the source water masses (end-members)

The inverse modelling approach for the quantification of various sources (endmembers) requires an initial knowledge of the parameters (potential temperature (θ), salinity, Nd concentration and ε_{Nd} in the present case) of the possible sources. This basic and initial information on the contributing sources is called the "*a priori*" information of these sources. The water mass structure of the surface and subsurface waters in the Northern Indian Ocean have been studied earlier by several authors [*Kumar and Li*, 1996; *Rochford*, 1964; *Shenoi et al.*, 1993; *You and Tomczak*, 1993; *You*, 2000].

A total of nine water masses (sources/end-members; n = 9; Table 3.2) have been considered in this study. The source/end-member properties (potential temperature, salinity, Nd concentration and ε_{Nd}) among these nine water masses are assumed to contribute to the potential temperature, salinity dissolved Nd (concentration and isotopic composition) of waters of the region. These water masses/sources are, (1) Riverine supply to the Arabian Sea; (2) Bay of Bengal (BoB) waters; (3) Arabian Sea High Salinity Water (ASHSW); (4) North Indian Intermediate Water (NIIW); (5) North Indian Deep Water (NIDW) (6) Indonesian throughflow surface Water (IW); (7) Indonesian throughflow Intermediate Water (IIW); (8) Modified North Atlantic Deep Water (MNADW); and (9) Antarctic Bottom Water (AABW). The *a priori* information on potential temperature, salinity, dissolved Nd and ε_{Nd} for these water masses are given in Table 3.2. In the present study, Antarctic Intermediate Water (AAIW) was not considered as a significant water mass in the Arabian Sea as its influence in the western Indian Ocean has been found to be limited to ~5°S only [*Kumar and Li*, 1996].

| Water Mass | θ (°C) | salinity | Nd (pmol/kg) | ٤ _{Nd} |
|---------------------------|------------------|------------------|----------------|-----------------|
| <u>a priori values</u> | | | | |
| Riverine supply | 28.000 ± 0.001 | 0.000 ± 0.001 | 6.6 ± 0.2 | -15.7 ± 0.3 |
| BoB waters | 11.475 ± 0.001 | 35.032 ± 0.001 | 23.7 ± 0.8 | -14.6 ± 0.3 |
| ASHSW | 28.877 ± 0.001 | 36.694 ± 0.001 | 10.2 ± 0.4 | -8.5 ± 0.3 |
| NIIW | 11.677 ± 0.001 | 35.506 ± 0.001 | 13.5 ± 0.5 | -9.0 ± 0.3 |
| NIDW | 2.717 ± 0.001 | 34.813 ± 0.001 | 17.5 ± 0.6 | -10.7 ± 0.3 |
| IW | 29.700 ± 0.001 | 33.970 ± 0.001 | 7.4 ± 0.3 | -4.1 ± 0.3 |
| IIW | 4.470 ± 0.001 | 34.612 ± 0.001 | 17.6 ± 0.7 | -3.6 ± 0.3 |
| MNADW | 1.774 ± 0.001 | 34.738 ± 0.001 | 18.0 ± 0.6 | -8.5 ± 0.3 |
| AABW | 0.000 ± 0.001 | 34.659 ± 0.001 | 34.0 ± 1.2 | -8.0 ± 0.3 |
| <u>a posterior values</u> | | | | |
| Riverine supply | 28.000 ± 0.001 | 0.000 ± 0.001 | 6.6 ± 0.2 | -15.7 ± 0.3 |
| BoB waters | 11.475 ± 0.001 | 35.032 ± 0.001 | 23.2 ± 0.8 | -14.9 ± 0.8 |
| ASHSW | 28.877 ± 0.001 | 36.694 ± 0.001 | 9.8 ± 0.3 | -8.6 ± 0.3 |
| NIIW | 11.677 ± 0.001 | 35.506 ± 0.001 | 12.1 ± 0.4 | -9.2 ± 0.3 |
| NIDW | 2.717 ± 0.001 | 34.813 ± 0.001 | 16.2 ± 0.5 | -11.3 ± 0.3 |
| IW | 29.700 ± 0.001 | 33.970 ± 0.001 | 7.3 ± 0.3 | -4.1 ± 0.3 |
| IIW | 4.470 ± 0.001 | 34.612 ± 0.001 | 17.0 ± 0.7 | -3.7 ± 0.3 |
| MNADW | 1.774 ± 0.001 | 34.738 ± 0.001 | 16.3 ± 0.6 | -8.8 ± 0.3 |
| AABW | 0.000 ± 0.001 | 34.659 ± 0.001 | 29.8 ± 1.0 | -9.0 ± 0.3 |

 Table 3.2: A priori and a posterior values of the water mass end-members

 used in the inverse model computations

Source of the data:

Riverine supply: [Goldstein and Jacobson, 1987; Allègre et al., 2010; Goswami et al., 2012b].

BoB waters: [Singh et al., 2012]; station 0811 0811; 16.76°N, 86.996°E

ASHSW: Present study, station 0802 (14.42°N, 69.42°E), 5 m depth.

NIIW: Present study, station 0802 (14.42°N, 69.42°E), 500 m depth.

NIDW: Present study, station 0802 (14.42°N, 69.42°E), 2100 m depth.

IW: [Jeandel et al., 1998], station # 10, 59 m depth.

IIW: [Jeandel et al., 1998], station # 33, 800 m depth.

MNADW: [*Bertram and Elderfield*, 2003], station # 1507 (06.15°S, 50.56°E), 2000 m depth.

AABW: θ and salinity by Kumar and Li, [1996] (GEOSECS station 430 (59.98°S,

60.98°E), 4709 m depth; Nd concentration by Zieringer et al., [2011]; ε_{Nd} by *Frank*, [2002]

The *a priori* data for the riverine discharge in the Arabian Sea was taken with zero salinity and a temperature of 28°C (Table 3.2). The Nd concentration of the riverine supply was taken to be 6.65 pmol/kg, similar to that of the Indus River [*Goldstein and Jacobson*, 1987] considering a 70% removal of Nd in the estuary.

Estimation of Nd isotopic composition of the riverine end-member (source) is based on ε_{Nd} of sediments from the Indus, Narmada, Tapti, Mahi and rivers flowing through the Deccan basalts and peninsular India, covering majority of rivers draining into the Arabian Sea [*Allègre et al.*, 2010; *Goswami et al.*, 2012b]. The flux weighted ε_{Nd} of -15.7 was taken as the *a priori* information for the Nd isotopic composition of the riverine supply into the Arabian Sea.

The parameters for ASHSW, NIIW and NIDW, water masses forming in the Arabian Sea [*Kumar and Li*, 1996; *Wyrtki*, 1973] are taken from the samples measured in the present study from station 0802 (14.42°N, 69.42°E). The potential temperature and salinity for the ASHSW is taken as that of the surface waters of the station 0802. Nd concentration and isotopic composition of the surface water of the Arabian Sea could be modified by Nd supplied by particulates. Hence, *a priori* Nd concentration of the ASHASW was estimated based on the Nd concentration of 120m deep water in station 0802 after correcting for the excess Nd supplied by particulates. The ε_{Nd} of ASHSW is taken to be similar to that of the water at 120m depth at station 0802. The *a priori* information for the parameters of NIIW was taken as the same for the sample measured at depth of 500m at the profile 0802. Similarly, the *a priori* data for the water mass NIDW was taken as that of the measurements on a sample in the profile 0802 at a depth of 2100m.

The *a priori* information of potential temperature, salinity, Nd concentration and ε_{Nd} for the Bay of Bengal waters has been taken from the measurement of these properties by Singh et al., [2012] (Station 0811; 16.76°N, 86.996°E). The values of these properties for the IW and IIW are those reported from the Indonesian throughflow straits [*Jeandel et al.*, 1998].

The data for MNADW has been taken from the measurement of the properties (salinity, potential temperature, Nd concentration and ε_{Nd}) at a depth of 2000 m in the profile CD-1507 (06.15°S, 50.56°E) in the Somali basin [*Bertram and Elderfield*, 1993]; thus properties of this water represent that of MNADW just

before it enters the Arabian Sea. The *a priori* information on potential temperature and salinity data for AABW has been to be the same as those reported for water from a depth of 4709 m at GEOSECS station 430 [*Kumar and Li*, 1996]. The ε_{Nd} and dissolved Nd concentration data for AABW has been taken from *Frank*, [2002], *Jeandel et al.* [1993] and *Zieringer et al.*, [2011]

The Arabian Peninsula and the Indian subcontinent can contribute significant amount of dust to the surface Arabian Sea. The Nd isotopic composition of aeolian dust over the western Arabian Sea is characterized by radiogenic Nd (ε_{Nd} = -6) [*Sirocko*, 1995]. This has been taken as the *a priori* information for the Nd isotopic composition of the excess or additionally added Nd to the ocean ((ε_{Nd})_m^{excess} term in eq. 3.2 and 3.3). Further, the difference between the surface water Nd concentration of 0802 profile and the Nd concentration of the ASHSW was taken as the *a priori* value for the Nd concentration of the excess or additionally added Nd to the ocean (Nd_m^{excess} term in eq. 3.2 and 3.3). As the Nd concentration and isotopic composition of the externally added Nd can vary a lot, the uncertainties associated for Nd concentration and that for the ε_{Nd} were taken to be 100% and 2 ε_{Nd} units respectively in the source covariance matrix for the inverse model computations.

3.3.1.2 *A posterior* values of the source water masses (end-members)

The *a posterior* or the best fit values of potential temperature, salinity, Nd concentration and ε_{Nd} the source water masses (end-members) computed based on the inverse model calculations are given in Table 3.2. Based upon the model calculations, the results of the various water mass (source) fractions calculated for the observed parameters in the Arabian Sea have been shown in Fig. 3.3.

3.3.1.3 Contribution of different water masses in the Arabian Sea.

The contribution of riverine flux form the Indus River and the west flowing rivers of India (Narmada, Tapti Rivers and those flowing through the Western Ghats and peninsular India) was calculated by the inverse modelling approach and the results have been shown in Fig. 3.3a. The results of the inverse model computations

suggest that riverine flux is not a significant contributor to the surface waters of the Arabian Sea. Further, the salinity in the surface waters of the Arabian Sea vertical profiles 0802 and 0803 is very high (>36). Such high salinity of surface waters hints to the lack of fresh water input to the surface waters of the Arabian Sea.

The contribution of the Bay of Bengal waters in the Arabian Sea shows a decreasing trend from south to north (Fig. 3.3b). The contribution of Bay of Bengal waters is maximum in the southern station 0805 which lies near the boundary of the Bay of Bengal. The core of this water mass lies in the southern station in the surface and sub-surface waters. During winter/north-east monsoon season over the northern Indian Ocean, the surface currents transfer waters from the Bay of Bengal to the Arabian Sea. Thus, the observed contribution of Bay of Bengal waters at the southern stations 0805 is consistent with the entrance of low salinity Bay of Bengal waters in the Arabian Sea during the winter monsoon months (Nov-Feb) [*Schott and McCreary*, 2001; *Wyrtki*, 1973]. The impact of Bay of Bengal waters is reduced significantly to the north in the Arabian Sea and by ~14.5°N; the effect of this water mass is almost absent.

The contribution of ASHSW in the waters of the Arabian Sea has been shown in Figs 3.3c. In the surface and sub-surface waters of the Arabian Sea, the ASHSW is the dominant water mass with contributions in excess of 90% in the surface waters of the station 0802 (~14.5°N). The ASHSW forms in the Arabian Sea due to excess of evaporation over precipitation. The production rate of this water mass is maximum during May-Jul and minimum during Feb-Apr. The production of this water mass in the Arabian Sea during winter months is quite significant [*Shenoi et al.*, 1993; *Rochford*, 1964]. Within the core of this water mass, the salinity can be in excess of 36.7, similar to the surface waters of the station 0802.

The NIIW is a mixture of characteristic water masses of the Northern Indian Ocean (Arabian Sea). This water mass form by the mixing of the Persian Gulf Water (PGW) and the Red Sea Water (RSW) with the ASHSW. The NIIW forms

in the north-western Indian Ocean in the Arabian Sea and moves southwards [*Kumar and Li*, 1993]. In the Arabian Sea, the distribution of NIIW shows a north-south gradient suggesting more production of this water mass in the north (Fig. 3.3d). As the water mass moves to the south, it loses its identity by mixing with other water masses. The contribution of this water mass in the Arabian Sea waters is as high as ~50% in the intermediate waters (200-1000 m) at station 0802. The contribution reduces to the south and is around 10-20% at the southern station 0805.









Fig. 3.3: Meridional and vertical distribution (in %) of various water masses in the Arabian Sea: (a) Riverine supply; (b) BoB waters; (c) ASHSW; (d) NIIW; (e) NIDW; (f) IW; (g) IIW; (h) MNADW and (i) AABW. Refer to Fig. 3.1 for the direction/projection of the meridional section of the contour plots.

In the northern Indian Ocean, NIDW forms by the sinking and mixing of NIIW (a mixture of PGW and RSW) with circumpolar waters [*Kumar and Li*, 1993]. In the Arabian Sea waters, the core layer of NIDW forms at around 8°N (Fig. 3.3e). The influence of NIDW is seen more on the southern station 0805 rather than northern station 0802 and 0803 in the Arabian Sea. This confirms the formation of NIDW by mixing of NIIW with northern moving polar waters. In the intermediate to deep waters in the Arabian Sea (600-1800 m), the contribution of NIDW in the northern waters of the Arabian Sea (north of 8°N) is ~ 30%, whereas to the south, especially at the southern station 0805, the contribution of NIDW is as high as 50% at around 1500 m depth. The formation of NIIW and NIDW in the northern Indian Ocean prevents the northward propagation of Central Indian Water (CIW) [*Kumar and Li*, 1993].

The distribution of IW in the Arabian Sea show the entrance of Indonesian surface waters (IW; Fig. 3.3f) in the Arabian Sea with the contribution of this water greater than 30% at ~ 10° N (station 0803). The propagation of IW to the Arabian Sea can take place from the Bay of Bengal by the entrance of Bay of Bengal waters to the Arabian Sea during the sampling month in winter monsoon. The intermediate depth water mass of the Indonesian origin, IIW is a minor component of water mass structure of this basin (Fig. 3.3g).

The deeper waters in the Arabian Sea are constituted with the MNADW and AABW. The stations used in the present study lie across the Chagos-Laccadive ridge in the Arabian Sea (Fig. 3.1). The stations 0802 and 0803 lie on the western side of this ridge while, the station 0805 lies to its east. Thus, the bottom topography due to the presence of this ridge in the Arabian Sea can also influence the propagation of deeper water masses in these stations. The distribution of MNADW shows a north-south gradient with its higher contribution to the north (Fig. 3.3h). In the Arabian Sea, the distribution of MNADW at ~14°N shows a contribution of >40% in 1500-2500 m water depth range. The contribution of MNADW in the Arabian Sea at ~10°N is reduced to 30-40% and reduces further south. Similarly, the fractional contribution of AABW, the deepest water mass, shows a north-south gradient. The deepest layers of the Arabian Sea at ~14°N show a dominant abundance of AABW with contribution in excess of 50% below a depth of 3000m. The contribution of this water mass in the south and across the Chagos-Laccadive ridge gets reduced in the shallower waters (<40%; Fig. 3.3i). You, [2000] suggested that the influence of MNADW in the Arabian Sea is limited to ~10°N at a longitude of 70°E based on the modelling of potential temperature, salinity, oxygen content and nutrient content data from the Indian Ocean. The north-south gradient in the distribution of MNADW and AABW (Figs. 3.3h and 3.3i) suggests that once these deeper water masses enter the Arabian Sea they travel to the north of 14.5°N and then they retreat to the south. On their return to the south these deeper water masses (MNADW and AABW) travel to the west of Chagos-Laccadive ridge as their influence is very limited to

the south of 8° N. The presence of shallow Chagos-Laccadive ridge (shallowest depth ~ 1500 m) cuts down the contribution of deeper waters across to the Bay of Bengal. The result of this study suggests that during their southward movement, deeper waters (MNADW and AABW) stick to the western flange of the Chagos-Laccadive ridge. This separates the deeper water structure of the Arabian Sea and the Bay of Bengal.

3.3.1.4 Excess Nd and its ϵ_{Nd}

Using the inverse modelling approach, the Nd contributed by all the nine water masses to individual samples have been estimated. The aggregated contribution of Nd from these water masses range from 44% to 100% of the measured Nd in the three profiles analyzed in the Arabian Sea.

At the northern station, the surface and sub-surface waters show deficit (in the aggregated Nd content based on end-member water mass contributions only) from observed data by 60 to 80%. At the station 0803, in the surface and sub-surface waters, the aggregated Nd from the water masses is as low as 49 to 65% whereas in the southern station 0805, much of the profile shows depleted contribution of Nd from water masses as compared to observed Nd (by 77 to 96%). The observation that all the nine water masses does not sum up to provide 100% measure Nd requires the additional Nd. This could be supplied to the Arabian Seawater by release of Nd from particulate matters.

| Depth | Nd _{excess} | err (Nd _{excess}) | $(\varepsilon_{\rm Nd})_{\rm excess}$ | $err(\epsilon_{Nd})_{excess}$ |
|-------------------------|----------------------|-----------------------------|---------------------------------------|-------------------------------|
| 0802 (14.42°N, 69.42°E) | | | | |
| 5 | 6.0 | 0.8 | -6.6 | 1.6 |
| 65 | 3.5 | 0.8 | -4.5 | 1.9 |
| 120 | 1.9 | 1.1 | -5.8 | 2.8 |
| 230 | 0.6 | 0.5 | -8.0 | 4.0 |
| 400 | 0.7 | 0.6 | -5.7 | 2.8 |
| 500 | 0.9 | 0.7 | -6.0 | 2.9 |
| 1000 | 3.1 | 2.2 | -6.9 | 3.2 |

Table 3.3: Excess Nd (Nd_{excess}, in pmol/kg) and its ε_{Nd} in the Arabian Sea waters calculated from the inverse modelling of the data

| 1500 | 1.3 | 1.0 | -5.8 | 2.9 | | | |
|------------------------|---------------|-----|-------|-----|--|--|--|
| 2100 | 1.0 | 0.9 | -9.0 | 4.4 | | | |
| 3000 | 1.2 | 1.1 | -5.9 | 2.9 | | | |
| 3600 | 1.4 | 1.2 | -6.1 | 3.0 | | | |
| 3900 | 1.4 | 1.2 | -5.5 | 2.7 | | | |
| 4040 | 7.5 | 2.2 | -9.2 | 2.4 | | | |
| 0803 (10.12 | 2°N, 71.86°E) | | | | | | |
| 5 | 11.0 | 0.9 | -8.1 | 1.5 | | | |
| 35 | 5.8 | 0.8 | -5.6 | 1.8 | | | |
| 300 | 0.7 | 0.6 | -7.6 | 3.8 | | | |
| 465 | 0.9 | 0.8 | -6.3 | 3.1 | | | |
| 600 | 1.0 | 0.8 | -5.9 | 2.9 | | | |
| 900 | 1.4 | 1.1 | -6.7 | 3.3 | | | |
| 1600 | 2.0 | 1.7 | -6.3 | 3.1 | | | |
| 2400 | 1.3 | 1.2 | -7.2 | 3.5 | | | |
| 0805 (6.01°N, 77.48°E) | | | | | | | |
| 200 | 3.2 | 1.8 | -7.8 | 3.7 | | | |
| 300 | 1.3 | 1.0 | -8.2 | 4.0 | | | |
| 650 | 1.7 | 1.4 | -9.1 | 4.5 | | | |
| 845 | 3.4 | 2.3 | -10.9 | 4.7 | | | |
| 1000 | 4.1 | 2.6 | -10.9 | 4.5 | | | |
| 1450 | 5.6 | 2.2 | -14.6 | 3.5 | | | |
| 1850 | 2.9 | 2.3 | -10.1 | 4.2 | | | |
| 2250 | 3.4 | 2.3 | -13.9 | 5.0 | | | |

Based on the measured and estimated Nd (from nine water masses), additionally required Nd, Nd_{excess}, was estimated for each sample (Table 3.3). The Nd_{excess} represents the externally supplied Nd apart from that contributed by the nine water masses. The Nd_{excess} distribution in the Arabian Sea shows high values in the surface waters of stations 0802 and 0803 (Table 3.3, Fig. 3.4a) and bottom water of station 0802. In the surface waters of the northern station the excess Nd contribution is 6.0 ± 0.8 pmol/kg, whereas in the station 0803, the excess Nd in the surface waters is 11.0 ± 0.9 pmol/kg (Table 3.3). Modelled Nd isotopic composition, ε_{Nd} of this excess Nd in the surface waters of the Arabian Sea are - 6.6 ± 1.6 for the surface waters of 0802 and -8.1 ± 1.5 for the surface waters of 0803; (Table 3.3; Fig. 3.4b). This is similar to the ε_{Nd} of dust supplied over the Arabian Sea [-6.0; *Sirocko*, 1995]. This indicates that additional Nd to the surface water of the Arabian Sea is delivered by the dust. This can be due to the significant dust contribution to the surface waters of the Arabian Sea from the nearby landmass. Further, the bottom water (depth 4040 m) of profile 0802 has significant amount of Nd_{excess} (Table 3.3, Fig. 3.4a) with ε_{Nd} , -9.2 indicating release of large amount of Nd from the bottom sediments. The core-top (most recent) sediments from a nearby sediment core in the Arabian Sea also show similar Nd isotopic composition of -9.4.

The additional Nd (Nd_{excess}) is observed through the water column of the southern profile 0805 (Table 3.3, Fig. 3.4a). The ε_{Nd} of Nd_{excess} in the southern station shows more non-radiogenic (Table 3.3, Fig. 3.4b). The non-radiogenic Nd_{excess} in station 0805 could be due to the significant release of Nd from the Ganga-Brahmaputra (G-B) particles of the Himalayan origin. The Bay of Bengal receives an annual supply of ~10¹² kg of riverine particles [*Galy and France-Lanord*, 2001; *Unger et al.*, 2003] from these rivers. The ε_{Nd} of Nd_{excess} of the surface water at station 0805 is -8. This indicates the release of Nd both from dust with radiogenic Nd and riverine sediments with non radiogenic Nd. Even the surface water of station 0803, the Nd_{excess} could have been influenced by riverine particles from the Bay of Bengal as ε_{Nd} of Nd_{excess} is -8.1, marginally lower compared to ε_{Nd} of dust.

The Nd_{excess} of the surface waters of the Arabian Sea, particularly of station 0802 which is only influenced by the contribution from the dust, can be used to estimate the dust flux over this oceanic region. The rate of deposition of dust in the surface waters (dust flux) can be estimated in an inverse approach by investigating the dissolved Nd signal in the surface waters. In this regard, the magnitude of the additional Nd signature (Nd_{excess}) in the surface waters can be used to estimate the magnitude of dust deposition in the ocean. For the estimation of dust flux, four factors control the magnitude of excess Nd signature in the surface waters: the relative abundance of Nd in the aeolian dust; fractional solubility of Nd in the surface ocean; depth of the mixed layer into which the dust is deposited and the residence time of Nd in the mixed layer of the ocean.



Fig. 3.4: Distribution of (a) Nd_{excess} and its corresponding (b) ε_{Nd} in the waters of the Arabian Sea computed form the inverse model application.

The Nd_{excess} in the surface waters of the ocean can be used to estimate the dust flux as it has a suitable residence time of ~2.5 years in the surface ocean mixed layer [*Amakawa et al.*, 2000]. Thus, the relatively shorter residence time of Nd in the mixed layer of the ocean is ideal to capture the integrated dust flux into the ocean during ~2.5 years. Further, like Al and unlike Fe and Mn, Nd is also biologically inert in the surface waters of the ocean and encounters only passive scavenging by particles. The Nd_{excess} signature is assumed to be in steady state in the mixed layer of the ocean. Considering these assumptions, the dust flux depositing over the ocean surface can be estimated by the eq. (3.5).

$$F_{Dust} = \frac{Nd_{excess} \times M \times S \times \rho_{SW}}{f \times C_{Nd}} \times 100$$
(3.5)

In the previous relation (eq. 3.5), F_{Dust} is the estimated dust flux into the surface ocean (in g m⁻² y⁻¹); Nd_{excess} is the excess Nd content (in unit of pg/kg) of the

surface ocean due to the dust deposition; *M* is mixed layer depth in meters; *S* is the scavenging factor which is 0.4 y⁻¹ based upon a Nd residence time of 2.5 years in the surface ocean [*Amakawa et al.*, 2000]; ρ_{SW} is the density of seawater (in g cm⁻³). *f* is the fractional solubility of Nd in the surface ocean from dust which is assumed to be 5%, similar to that of Al [*Measures and Vink*, 2000]; C_{Nd} is the concentration of Nd in the dust in units of $\mu g g^{-1}$.

For the estimation of dust flux into the surface ocean, the mixed layer depth of the ocean was taken to be 30m. The factor C_{Nd} i.e. the concentration of Nd in the dust was taken to be Nd concentration in the upper continental crust (26.5 μ g g⁻¹) [Taylor and McLennan, 1995]. The term Nd_{dust} in eq. (3.5) has been obtained by the Nd_{excess} in the surface waters of station 0802 by the inverse model calculations (Table 3.3). By substituting all the parameters in eq. 3.5, the estimated dust flux in the Arabian Sea is 8 ± 2 g m⁻² y⁻¹ at the stations 0802 in the Arabian Sea. Duce et al., [1991] estimated the aeolian supply of dust flux into the surface waters of the Northern Indian Ocean to be $\sim 7 \text{ g m}^{-2}\text{y}^{-1}$ with large uncertainty based on the modelling of trace element concentrations in dust, dry deposition velocities, precipitation scavenging ratios and precipitation amounts. Sirocko and Sarntherin, [1989] estimated the dust flux in the Arabian Sea to be ranging from 5-13 g $m^{-2}v^{-1}$ based on the study of lithogenic fraction of sediments in the Arabian Sea near the Oman margin and modelling the satellite data. Measures and Vink, [1999] estimated the dust deposition flux in the Arabian Sea to be ranging from 2.2 to 7.4 g m⁻² y⁻¹ in the north-eastern Arabian Sea using dissolved Al as the proxy. These estimates are comparable to dust flux estimate of this study.

3.4 Conclusions

The vertical distribution of dissolved Nd concentration and its ε_{Nd} in the waters of the Arabian Sea exhibit significant lateral and vertical variations. Dissolved Nd content in the southern profile is higher compared to those from the northern profiles, indicating the contribution of Bay of Bengal waters at this station. In the Arabian Sea, at ~14.5°N, the vertical profile of Nd isotopic composition shows radiogenic values of -7 to -10. Similar ε_{Nd} values were observed at ~10°N. Contrary to this, the vertical profile of ε_{Nd} in the southern station 0805 (in the periphery of Bay of Bengal), showed quite non-radiogenic values. This suggests that contribution of Nd at station 0805 is from the Bay of Bengal, influenced by non-radiogenic Nd supply from Ganga-Brahmaputra river system by the weathering of Himalaya.

Inverse model estimates a small contribution of Nd from riverine supply to the Arabian Sea surface waters. Model suggests the supply of water from the Bay of Bengal to the Arabian Sea. The Intermediate waters in the Arabian Sea are significantly composed of NIIW and NIDW. The contribution of NIIW is more significant in the Arabian Sea north of 10°N, while the existence of NIDW is more significant in the Arabian Sea south of 8°N. The deeper waters in the Arabian Sea, MNADW and AABW both show a north-south transport in the Arabian Sea after their entry from the Somali basin. The return of these deeper water masses towards south takes place along the western flange of the Chagos-Laccadive ridge. The presence of Chagos-Laccadive ridge significantly reduces the flow of deeper water masses (MNADW and AABW) from the Arabian Sea to the Bay of Bengal.

The Nd excess in the Arabian Sea computed from the inverse modelling of data shows significant additional inputs of Nd (other than that from the mixing of water masses) to the surface waters at the location of stations 0802 and 0803 and bottom water of station 0802 in the Arabian Sea. The ε_{Nd} of this excess Nd is ~-6, similar to that of dust depositing over the Arabian Sea. This result highlights the significance of dust deposition in the Arabian Sea from the nearby landmass in supplying the dissolved Nd to the Arabian Sea. Based on the Nd_{excess} content in surface waters of the Arabian Sea at station 0802, the dust deposition flux in this oceanic basin was estimated to be 8 ± 2 g m⁻² y⁻¹. Nd_{excess} with less radiogenic ε_{Nd} was observed through the entire water column of profile 0805. This was attributed to the release of Nd from sinking particles of G-B origin from the Bay of Bengal.

CHAPTER 4

Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea

4.1 Introduction

Re, U and Mo compose a set of redox sensitive trace elements that have found applications to study paleo-redox conditions of the ocean and determine chronology of marine deposits [*Crusius et al.*, 1999; *Henderson et al.*, 2001; *Kendall et al.*, 2009; *Morford et al.*, 2001; *Nameroff and Balistrieri*, 2002; *Nameroff et al.*, 2004; *Sarkar et al.*, 1993]. In addition, Mo is associated with marine biological processes [*Morel and Price*, 2003], acting as metal cofactor in enzymatically catalyzed process of denitrification. The growing attention on the applications of these elements as paleo-redox indicators would be better served through a more detailed understanding of their marine geochemistry that includes their sources, sinks and internal cycling in the ocean. Re, U and Mo are enriched in sediments rich in organic carbon [*Borole et al.*, 1982; *McManus et al.*, 2006; *Morford and Emerson*, 1999; *Pattan and Pearce*, 2009; *Sarkar et al.*, 1993], suggesting that productivity and/or organic carbon burial may have a role in their removal from seawater.

The distribution of Re, U and Mo in well oxygenated oceanic regions shows conservative behavior [Anbar et al., 1992; Collier, 1985; Ku et al., 1977; Singh et al., 2011; Sohrin et al., 1999]. In these well oxygenated oceanic zones, these trace elements interact weakly with particles and maintain a relatively constant ratio to salinity. In well oxygenated oceanic regions, Re, U and Mo occur in their higher oxidation states as oxyanions, $\text{Re}^{\text{VII}}\text{O}_4^-$, $U^{\text{VI}}\text{O}_2(\text{CO}_3)_3^{4-}$ and $\text{Mo}^{\text{VI}}\text{O}_4^{2-}$ respectively. The high stability and unreactive nature of these oxyanions is reflected in their long oceanic residence times, of the order of $\sim 10^5 - 10^6$ y [Bruland and Lohan, 2003]. Under reducing conditions the oxidation states of these elements become Re^{IV}, U^{IV} and Mo^{IV}, making them particle reactive and susceptible for removal from dissolved to particle phases by adsorption onto sinking particles. Thus, the reducing conditions formulate the removal of these redox sensitive elements more efficient from seawater. Such reducing conditions are met in oceanic regions where the demand for oxygen for combustion of organic matter and respiration is not fulfilled (For e.g. in land locked seas and continental margins with restricted ventilation). There have been only limited

studies on the distribution of these redox sensitive elements in suboxic/reducing ocean water column to investigate their potential removal from seawater.

In this context, earlier studies of Re, U and Mo in anoxic/suboxic basins have highlighted the role of their diffusion from overlying seawater to pore waters to facilitate their removal followed by their uptake at the oxic-anoxic boundary [*Anderson et al.*, 1989; *Colodner et al.*, 1995; *Crusius et al.*, 1996; *Emerson and Huested*, 1991; *Klinkhammer and Palmer*, 1991; *Nameroff and Balistrieri*, 2002]. More recent study [*Vorlicek and Helz*, 2002] however has shown that the presence of mineral surfaces catalyses the reduction of redox sensitive elements into particle reactive species, thus making their removal from seawater more efficient. For example, Re, U and Mo measurements in the Black Sea have demonstrated their removal from seawater in the euxinic deeper waters; the mechanism of their removal, however still remains to be fully understood [*Anderson et al.*, 1989; *Colodner et al.*, 1995]. On the basis of EXAFS study of Mo rich black shales and Mo scavenging experiments in the laboratory, it was proposed that a critical precursory step in Mo scavenging is conversion of MoO₄²⁻ to MoS₄²⁻ [*Helz et al.*, 1996].

In contrast to investigations of Re, U and Mo in sediments, there are only limited studies on their behavior in suboxic/anoxic water column. Investigation on the distribution of U in the Cariaco trench doesn't indicate any detectable removal from the suboxic/reducing water column; in contrast, its distribution in the Arabian Sea water column has hinted towards its possible removal from the oxygen minimum zone (OMZ) [*Rengarajan et al.*, 2003]. A recent study by *Helz et al.*, [2011] indicated the removal of Mo from the waters of euxinic basins under specific combination of H₂S concentration and pH in presence of reactive Fe. Such studies on the distribution of these redox sensitive elements in the suboxic/anoxic water column are important to address issues pertaining to their potential removal from water column to sediments.

The oceanic zones with high water column productivity and organic matter rich sediments are suggested as a major sink for seawater Re, U and Mo. Such oceanic zones though constitute only 0.3% of the world's ocean, they account for $\sim 50\%$ removal of Re from the oceans [Colodner et al., 1993]. Recent studies of Re in estuaries show that it behaves conservatively in the river-ocean transit zone, though its supply in some estuaries is highly perturbed due to anthropogenic activities [Colodner et al., 1995; Rahaman and Singh, 2010] . Recent studies of U in sediments led to the conclusion that the shelf and margin sediments act as sinks for the removal of U from seawater [Anderson et al., 1989; Klinkhammer and Palmer, 1991]. These studies also suggested that the dominant mechanism for the removal of U from seawater is the diffusion of U^{VI} from bottom waters to the anoxic layers of sediments where it gets reduced as U^{IV} and gets trapped. The role of Mo as a cofactor of enzymes in the marine nitrogen cycle has been well known. As the amount of Mo required as the cofactor of these enzymes is negligible compared to concentration of Mo in seawater, its biological uptake does not influence its distribution in the ocean [Bruland and Lohan, 2003; Morel and Price, 2003].

The goal of the present study is to investigate the impact of the perennial Oxygen Minimum Zone (OMZ) and denitrification present in the water column of the Arabian Sea on the distribution of dissolved Re, U and Mo concentration. The suboxic conditions of the Arabian Sea have been found to influence Mn and Fe cycling in the water column [*Saager et al.*, 1989]. Vertical profiles of Mn in the Arabian Sea, within the core of denitrification zone, show maxima in its concentration coinciding with the secondary nitrite maxima [*Lewis and LutherIII*, 2000]. Similarly, significant enrichment of dissolved Fe was reported in the depth range of 200-400m relative to overlying and underlying waters, with up to 50% of dissolved Fe present as Fe^{II}. The maxima of Fe enrichment was also found to coincide with the secondary nitrite maxima [*Moffett et al.*, 2007]. These studies demonstrate the role of suboxic layers of the Arabian Sea in determining the mobilization of redox sensitive elements, Fe and Mn. This raises the question of whether the distribution of the dissolved concentration of redox sensitive

elements, Re, U and Mo are also impacted by the denitrifying layer of the Arabian Sea. The work carried out in the present study addresses this question.

Furthermore, while the present work was in progress, the distributions of Re, U and Mo were reported from the waters of the Bay of Bengal [*Singh et al.*, 2011], another basin in the northern Indian Ocean characterized by high river water and particulate flux. The results of the present study are compared with the Bay of Bengal data to learn about the relative behavior of these elements in the two basins, both with high particulate flux, one with high biogenic flux (Arabian Sea) and the other with high detrital flux (Bay of Bengal). Thus, in order to understand the effect of suboxic and denitrifying conditions in the Arabian Sea water on the water column geochemistry of redox sensitive elements Re, U and Mo, water samples from the Arabian Sea were collected within the core of intense denitrification and outside it (Refer chapter 2 of this thesis for details on the sampling locations and sample collection).

4.2. The Arabian Sea and its suboxic water column

The Arabian Sea is a unique oceanic basin surrounded by continental landmass on its western, eastern and northern boundaries and connected to the Indian Ocean to the south. The Arabian Sea is one of the highly productive ocean basins; the productivity resulting from monsoonal upwelling brought about by seasonally reversing winds. The high productivity causes continuous rain of biogenic material through the water column. These debris during their transit are subject to combustion by dissolved oxygen in the water column, resulting in the formation of intense oxygen minimum and suboxic denitrification layer at intermediate depths, typically 200-1000m [*Bange et al.*, 2005; *Naqvi*, 1994]. Denitrification process is a perennial feature of the Arabian Sea water column. The restricted ventilation of the basin also contributes to the suboxic conditions of the Arabian Sea.

In the suboxic waters of the Arabian Sea, occurrence of dissolved H_2S has not been observed, though the presence of sulfides as metal complexes has been reported [*Theberge et al.*, 1997]. Further, measurable sea-air fluxes of methane from the upper layers of the Arabian Sea have been explained in terms of reducing micro environments [*Lal et al.*, 1996; *Owens et al.*, 1991]. In addition to suboxic conditions at intermediate waters, the Arabian Sea is a region of high particle flux through its water column (25-50 g m⁻²y⁻¹) [*Ramaswamy and Nair*, 1994]. These features make Arabian Sea a suitable basin to study the behavior of redox sensitive elements such as Re, U and Mo in the water column. In contrast to the water column, signatures of reducing (anoxic) environment are more wide spread in the Arabian Sea sediments. For example, the high abundances of organic matter, authigenic uranium in the margin and shelf sediments of the Arabian Sea has been attributed to presence of reducing environments [*Borole et al.*, 1982].

The riverine supply to the Arabian Sea is mainly contributed by the Indus River. The Indus River is the largest river flowing into Arabian Sea, supplying 9×10^{13} ℓ of water and 400 million tons of sediments to the Arabian Sea annually, though in recent decades, its flow has been restricted considerably due to construction of dams [*Garzanti et al.*, 2005]. In addition, there are several medium and minor rivers draining into the Arabian Sea; the Narmada, Tapi, Mahi and several rivers flowing through the Western Ghats of India. Altogether these rivers supply ~ 8 × 10^{13} ℓ of water and ~100 million tons of sediments annually. Also, being in the proximity of Asian landmass with widespread deserts, aeolian transport of dust is also a significant source of sediments to the Arabian Sea; contributing ~ 100 million tons of sediments [*Goldberg and Griffin*, 1970; *Kolla et al.*, 1976; *Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989].

The Arabian Sea exhibits distinct lateral salinity gradients in the upper 1000m [*Wyrtki*, 1971; 1973] due to marked differences in the rate of evaporation over precipitation and the influx of less saline waters from the Bay of Bengal through its southeastern corner. In addition, the Persian Gulf and the Red Sea contribute high salinity waters to the Arabian Sea at depths of about 200 m and 500 m respectively. Thus, the upper 1000 m water column of the Arabian Sea is composed of three characteristic water masses, the Arabian Sea High Salinity

Water (ASHSW), the Persian Gulf Water (PGW) and the Red Sea Water (RSW) [*Kumar and Li*, 1996; *Rochford*, 1964; *Shenoi et al.*, 1993; *Wyrtki*, 1973].

Below the 1000m water column of Arabian Sea, the upper water masses viz. ASHSW, PGW and RSW mix to form the North Indian Intermediate Water (NIIW), which moves southwards. On its southward progression, NIIW mixes with the northward moving polar waters and forms the North Indian Deep Water (NIDW). The deeper water masses in the Arabian Sea compose of North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW) [*Kumar and Li*, 1996].

4.3 Results

4.3.1 General Observations

All the basic parameters such as salinity, dissolved oxygen (DO) and nitrite concentration of the samples were measured onboard on all three expeditions in which samples were collected for this study (SS-256, SS-259, KH-09-5; Chapter2). Salinity was determined by measuring the conductivity of the samples using a salinometer. Dissolved oxygen was measured by the winkler's titration method and the nitrite content using an autoanalyzer. The salinity, DO and nitrite data are given in Table 4.1 along with the other measured parameters. Fig. 4.1 shows two typical θ -S (potential temperature vs. salinity) plots from the stations investigated in the present study. The ASHSW is found in all the stations excluding the station lying in the southern Arabian Sea in proximity of the western edge of the Bay of Bengal (station 0805). The water masses PGW and RSW are also shown with their core densities (σ_{θ}) 26.5 and 27.25 respectively.

Fig. 4.2 shows significant difference in the water column structure of the Arabian Sea basin, indicating marked distinction in water column from north to south. The most significant feature is the drop in the salinity for the station 0805 (southern station at 6.01°N, 77.48°E). This is due to entrance of less saline waters into the Arabian Sea from its south-eastern margin with Bay of Bengal during the winter monsoon (North-East monsoon).



Fig. 4.1: Representative θ -S plots for two of the stations from the Arabian Sea. The plots show significant difference in the water column structure of the Arabian Sea from north to south. The σ_{θ} contours are also shown along with the characteristic water masses in the Arabian Sea. The plot for the station 0805 shows a lower salinity for the surface waters due to entrance of low salinity waters from the Bay of Bengal.

The temperature profile in the Arabian Sea shows well stratified layers with higher temperatures (25-30°C) at the surface (Fig. 4.2a). The salinity in the Arabian Sea shows higher values (35-37) in the surface and sub-surface waters which are prominent north of 10°N (Fig 4.3b). This is due to excess of evaporation over precipitation in the Arabian Sea basin, with Arabian Sea being a negative water body. Near the southernmost station at ~6°N, the surface water salinity is much lower. The depth of penetration of high salinity waters is more towards the north (Fig. 4.2b).

North of 12°N, dissolved oxygen shows a very prominent minimum between 100 to 1200m (Fig. 4.2c). The high surface productivity coupled with restricted ventilation contributes to extreme depletion of dissolved oxygen in these waters. This, as mentioned earlier, creates widespread oxygen minimum zone (OMZ) with active water column denitrification [*Bange et al.*, 2005; *Naqvi*, 1994], as evidenced from secondary nitrite maxima (SNM) in the upper 500 m of water column (Fig. 4.2d). The redox conditions prevailing in the intermediate waters of

Arabian Sea significantly influence the vertical distribution of suite of trace elements especially Fe and Mn [*Lewis and LutherIII*, 2000; *Moffett et al.*, 2007; *Saager*, 1994].



Fig. 4.2: Latitudinal variation in (a) temperature (°C), (b) salinity, (c) dissolved oxygen (μ M), (d) Nitrite (μ M), (e) Re (pmol/kg), (f) U (nmol/kg) and (g) Mo (nmol/kg) in the Arabian Sea. North of 12°N, the water column of the Arabian Sea shows the zone of intense oxygen minima. All the plots were made using the ocean data view (ODV) program [*Schlitzer*, 2010].

4.3.2 Re, U and Mo distributions

The Re, U and Mo concentrations of the samples along with the salinity, dissolved oxygen (DO) and nitrite concentration are listed in Table 4.1 and presented in Fig. 4.3. The Re, U and Mo concentrations vary from 37 to 43 pmol/kg, 12.9 to 14.8 nmol/kg and 103 to 119 nmol/kg respectively, covering a salinity range from 32.4 to 36.7 and a wide range of dissolved oxygen levels from 2.2 μ M to 212 μ M.

Most of the stations sampled fall under the zone of active water column denitrification experience water column denitrifying conditions, the exceptions being stations 0803, 0805 and the shallow stations 0702 and 0703. The Re, U and Mo concentrations in four nearby profiles viz. 0802, 0708, 0707 and ER6 (within \pm 1° latitude and longitude) are quite similar overlapping within analytical uncertainties (Table 4.1, Fig. 4.3).

The water samples on the KH-09-5 were collected using a clean CTD system that consisted of titanium hydrographic wire. The observation that the concentrations of Re, U and Mo are nearly identical in samples collected by conventional sampling system (on SS-256 and SS-259 cruises) and clean sampling technique onboard KH-09-5 (station ER6) suggests that for these elements conventional sampling system does not introduce discernible contamination during sampling and thus the conventional sampling system can be used for seawater sample collection for redox sensitive elements Re, U and Mo without any flaw.





Fig. 4.2 (continued).

The distribution of Re, U and Mo (Fig. 4.2e–4.2g) show a correlation with salinity (Fig 4.2b), rather than with the dissolved oxygen (Fig. 4.2c) in the Arabian Sea. The distribution of Re, U and Mo in the water column of the Arabian Sea unlike dissolved oxygen (Fig. 4.2c), does not show any removal from the intermediate waters of the basin. On the contrary concentration of Re, U and Mo shows an enrichment akin to salinity in the northern intermediate waters of the Arabian Sea.
The common feature shared by salinity and Re, U and Mo concentrations is an increase towards higher latitudes in the Arabian Sea.

| Denth(m) | Salinity | Temp | O_2 | NO_2 | Re (pmel/kg) | U (nmel/kg) | Mo (nmol/kg) |
|------------------|-----------------------|------------------------|--------------|--------|-----------------|----------------|-----------------|
| | 30NI 60 1201 | (U) F) | (μινι) | (µ101) | (pinoi/kg) | (mnoi/kg) | (mnoi/kg) |
| 0002 (14.4. F | 2°1N, 09.42°1 26 7 | E) 28.0 | 200.0 | 0.1 | 12 6 | 145 | 117 |
|) (5 | 36.7 | 28.9 | 209.0 | 0.1 | 42.6 | 14.5 | 11/ |
| 65 | 36.5 | 26.3 | 1/1.0 | 0.5 | 42.3 | 14.6 | 11/ |
| 120 | 35.8 | 20.0 | 12.9 | 0.4 | 41.6 | 14.2 | 116 |
| 230 | 35.7 | 14.6 | 8.9 | 3.3 | 41.7 | 14.1 | 114 |
| 330 | 35.5 | 12.7 | 4.3 | 0.3 | 40.8 | 14.0 | 113 |
| 400 | 35.5 | 12.3 | 5.2 | 0.1 | 40.7 | 14.2 | 111 |
| 500 | 35.5 | 11.7 | 8.3 | 0.4 | 41.2 | 14.0 | 113 |
| 550 | 35.5 | 11.4 | 4.6 | 0.4 | 40.9 | 14.0 | 112 |
| 600 | 35.5 | 11.0 | 6.3 | 0.9 | 40.8 | 14.0 | 113 |
| 700 | 35.5 | 10.3 | 6.4 | 0.9 | 40.7 | 13.9 | 115 |
| 800 | 35.4 | 9.6 | 7.1 | 1.6 | 40.9 | 13.9 | 112 |
| 900 | 35.3 | 8.8 | 10.3 | 0.0 | 40.4 | 14.0 | 111 |
| 1000 | 35.3 | 8.0 | 16.5 | 0.0 | 41.0 | 13.8 | 113 |
| 1500 | 35.0 | 5.1 | 51.6 | 0.1 | 40.7 | 13.9 | 111 |
| 2100 | 34.8 | 2.7 | 109.1 | 0.0 | 40.1 | 13.7 | 111 |
| 2700 | 34.8 | 1.8 | 139.4 | 0.0 | 39.6 | 13.8 | 111 |
| 3000 | 34.7 | 1.6 | 147.3 | 0.0 | 39.9 | 13.7 | 111 |
| 3600 | 34.7 | 1.4 | 154.5 | 0.0 | 40.0 | 13.8 | 110 |
| 3900 | 34.7 | 1.4 | 145.9 | 0.0 | 40.0 | 13.7 | 112 |
| 4040 | 34.9 | 1.4 | 148.9 | 0.0 | 40.4 | 13.8 | 111 |
| 0803 (10.12 | 2°N, 71.86°I | E) | | | | | |
| 5 | 35.5 | 28.9 | 202.3 | 0.0 | 40.6 | 14.0 | 113 |
| 35 | 36.4 | 28.8 | 201.6 | 0.0 | 42.0 | 14.3 | 115 |
| 75 | 35.9 | 23.9 | 53.8 | 0.2 | 41.4 | 14.1 | 114 |
| 130 | 35.1 | 16.4 | _ | 0.0 | 40.3 | 13.8 | 112 |
| 210 | 35.2 | 13.3 | 36.6 | 0.0 | 40.7 | 13.9 | 113 |
| 300 | 35.2 | 12.1 | 27.3 | 0.0 | 41.1 | 13.9 | 112 |
| 360 | 35.2 | 11.5 | 33.5 | 0.0 | 40.9 | 13.9 | 114 |
| 465 | 35.3 | 10.9 | 20.3 | 0.0 | 41.2 | 14.0 | 111 |
| 600 | 35.2 | 10.3 | 20.0 17 1 | 0.0 | 40.8 | 13.8 | 112 |
| 700 | 35.2 | 94 | 195 | 0.0 | 40.3 | 14.0 | 112 |
| 800 | 35.2 | 2. 1 8 7 | 17.5 24 5 | 0.0 | 41.1 | 14.0 | 113 |
| 900 | 35.2 | 84 | 25.8 | 0.0 | 41.1 | 13.9 | 111 |

| 10 | 000 | 35.1 | 7.7 | 34.4 | 0.0 | 41.1 | 13.8 | 112 |
|------|------------|-------------|------|-------|-----|------|------|-----|
| 12 | 200 | 35.0 | 6.4 | 43.9 | 0.0 | 40.6 | 13.8 | 112 |
| 14 | 400 | 35.0 | 5.2 | 64.3 | 0.0 | 40.0 | 13.8 | 112 |
| 1 | 600 | 34.9 | 4.2 | 85.1 | 0.0 | - | 13.8 | 111 |
| 1 | 800 | 34.8 | 3.3 | 101.9 | 0.0 | 40.2 | 13.7 | 111 |
| 20 | 000 | 34.8 | 2.6 | 127.3 | 0.0 | - | 13.8 | 113 |
| 22 | 200 | 34.8 | 2.2 | 129.8 | 0.0 | 39.9 | 13.8 | 112 |
| 2 | 400 | 34.8 | 1.9 | 144.5 | 0.0 | 40.4 | 13.8 | 111 |
| 080 | 5 (6.01°N | , 77.48°E) | | | | | | |
| | 5 | 32.4 | 29.1 | 211.6 | 0.0 | 36.6 | 12.9 | 103 |
| (| 60 | 35.3 | 28.0 | 187.8 | 0.3 | 40.1 | 14.0 | 113 |
| 1 | 20 | 35.0 | 21.8 | 49.9 | 0.0 | 39.7 | 13.9 | 111 |
| 2 | 200 | 35.0 | 14.1 | 20.1 | 0.0 | 39.6 | 14.0 | 115 |
| 3 | 300 | 34.9 | 11.6 | 19.6 | 0.0 | 39.8 | 13.8 | 113 |
| 4 | 100 | 35.1 | 10.7 | 28.4 | 0.0 | 39.5 | 13.9 | 113 |
| 4 | 190 | 35.1 | 10.2 | 25.9 | 0.0 | 40.0 | 13.8 | 111 |
| 5 | 580 | 35.0 | 9.4 | 24.1 | 0.0 | 39.0 | 13.9 | 113 |
| 6 | 550 | 34.8 | 9.0 | - | 0.0 | 39.6 | 13.7 | 114 |
| 7 | 750 | 35.0 | 8.4 | 34.3 | 0.0 | 40.1 | 14.0 | 114 |
| 8 | 345 | 35.0 | 7.8 | 34.8 | 0.0 | 39.4 | 13.8 | 112 |
| 8 | 390 | 35.0 | 7.7 | 38.9 | 0.0 | 39.7 | 13.9 | 113 |
| 10 | 000 | 35.0 | 6.9 | 45.5 | 0.0 | 40.1 | 13.7 | 115 |
| 1 | 100 | 34.9 | 6.0 | 52.7 | 0.0 | 39.6 | 13.7 | 112 |
| 12 | 250 | 34.9 | 5.6 | 65.1 | 0.0 | 38.9 | 13.9 | 112 |
| 14 | 450 | 34.9 | 4.6 | 81.0 | 0.0 | 38.8 | 13.7 | 113 |
| 1 | 650 | 34.9 | 3.8 | 96.8 | 0.0 | 39.0 | 13.7 | 112 |
| 1 | 850 | 34.8 | 3.1 | 115.1 | 0.0 | 38.9 | 13.7 | 113 |
| 20 | 050 | 34.8 | 2.6 | 128.2 | 0.0 | 39.2 | 13.7 | 111 |
| 2 | 250 | 34.8 | 2.3 | 133.2 | 0.0 | 39.1 | 13.9 | 111 |
| 0708 | 8 (15.00°) | N, 70.49°E) | | | | | | |
| | 6 | 36.0 | 28.1 | 201.8 | 0.0 | 41.3 | 14.1 | 116 |
| (| 67 | 36.3 | 26.2 | 146.8 | 0.3 | 40.9 | 14.3 | 118 |
| 1 | 68 | 35.5 | 15.9 | 11.4 | 1.9 | - | - | - |
| 2 | 200 | 35.3 | 14.9 | 4.5 | 0.0 | 40.3 | 13.9 | 114 |
| 3 | 350 | 35.5 | 12.6 | 7.7 | 0.0 | 40.3 | 13.9 | 115 |
| 5 | 500 | 35.4 | 11.6 | 10.1 | 0.0 | 41.0 | 13.8 | 114 |
| 6 | 563 | 35.5 | 10.9 | 7.3 | 0.0 | 41.0 | 14.1 | 115 |
| 8 | 300 | 35.4 | 9.8 | 23.2 | 0.0 | 40.4 | 14.0 | 115 |
| 10 | 000 | 35.3 | 8.4 | 11.6 | 0.0 | 40.4 | 14.0 | 114 |
| 14 | 400 | 35.1 | 5.9 | 43.8 | 0.0 | 40.9 | 13.8 | 114 |
| 1 | 800 | 34.9 | 3.7 | 82.6 | 0.0 | 40.5 | 13.7 | 111 |
| 20 | 000 | 34.8 | 3.0 | 97.7 | 0.0 | 40.4 | - | 112 |
| 22 | 200 | 34.8 | 2.5 | 109.7 | 0.0 | 40.4 | 13.7 | 111 |

0707 (15.00°N, 68.49°E)

| 5 | 36.2 | 27.7 | 195.5 | 0.0 | 41.0 | 14.1 | 118 |
|------------|-------------|------|-------|-----|------|------|-----|
| 70 | 36.4 | 27.2 | 184.9 | 0.2 | 42.3 | 14.3 | 117 |
| 220 | 35.7 | 14.9 | 5.1 | 4.1 | 40.8 | 13.9 | 113 |
| 380 | 35.6 | 12.4 | 5.3 | 0.5 | 40.3 | 14.1 | 114 |
| 500 | 35.5 | 11.7 | 6.6 | - | 41.2 | 14.1 | 114 |
| 550 | 35.5 | 11.4 | 11.4 | 1.0 | 40.9 | 14.0 | 111 |
| 600 | 35.5 | 11.0 | 11.4 | 0.0 | 41.0 | 14.0 | 115 |
| 900 | 35.4 | 8.8 | 14.0 | 0.0 | 41.0 | 14.0 | 115 |
| 1200 | 35.2 | 6.8 | 31.7 | 0.0 | 40.6 | 13.9 | 113 |
| 1600 | 35.0 | 4.6 | 64.3 | 0.0 | 40.4 | 13.8 | 111 |
| 2000 | 34.8 | 3.0 | 101.8 | 0.0 | 39.1 | 13.7 | 112 |
| 0706 (16.5 | 0°N, 66.50° | N) | | | | | |
| 5 | 36.3 | 26.3 | 177.6 | 0.4 | 41.4 | 14.3 | 115 |
| 110 | 36.0 | 21.3 | 4.4 | 0.1 | 41.3 | 14.4 | 116 |
| 250 | 35.9 | 15.2 | 6.0 | 4.8 | 41.3 | 14.0 | 114 |
| 380 | 35.7 | 12.9 | 20.4 | 0.0 | 40.9 | 14.2 | 115 |
| 520 | 35.6 | 11.8 | 10.2 | 0.0 | 40.7 | 14.2 | 114 |
| 600 | 35.5 | 11.2 | 3.2 | 0.1 | 40.6 | - | - |
| 700 | 35.5 | 10.7 | 10.4 | 0.0 | 40.8 | 13.9 | 115 |
| 800 | 35.5 | 9.9 | 4.8 | 0.0 | 40.5 | 14.0 | 112 |
| 1000 | 35.3 | 8.2 | 16.2 | 0.0 | 39.5 | 13.8 | 110 |
| 1400 | 35.1 | 5.9 | 38.2 | 0.0 | 39.1 | 13.9 | 111 |
| 1800 | 34.9 | 3.7 | 73.2 | 0.0 | 38.9 | 13.8 | 112 |
| 2100 | 34.9 | 2.8 | 95.4 | 0.0 | 38.9 | 13.7 | 113 |
| 0705 (18.0 | 0°N, 68.50° | E) | | | | | |
| 5 | 36.7 | 27.0 | 200.9 | 0.1 | 42.6 | 14.8 | 119 |
| 190 | 35.8 | 15.8 | 5.4 | 6.5 | 41.1 | 14.4 | 116 |
| 340 | 35.5 | 12.9 | 6.5 | 0.1 | 40.6 | 14.4 | 116 |
| 530 | 35.6 | 11.8 | 8.7 | 0.0 | 41.0 | 14.8 | 117 |
| 700 | 35.6 | 10.9 | 9.8 | 0.1 | 41.3 | 14.3 | 115 |
| 800 | 35.5 | 10.1 | 7.6 | 0.1 | 41.0 | 14.4 | 117 |
| 1000 | 35.3 | 8.6 | 11.9 | 0.1 | 40.3 | 14.6 | 117 |
| 1800 | 35.0 | 3.8 | 102.1 | 0.3 | 39.6 | 14.2 | 116 |
| 2100 | 34.8 | 2.7 | 98.8 | 0.0 | 40.0 | 14.1 | 114 |
| 2250 | 34.8 | 2.4 | 115.1 | 0.0 | 40.1 | 14.4 | 117 |
| 0704 (18.0 | 0°N, 70.64° | E) | | | | | |
| 5 | 35.6 | 27.7 | 207.4 | 0.0 | 40.7 | 14.2 | 114 |
| 180 | 35.6 | 17.7 | 16.3 | 5.2 | 40.7 | 14.2 | 116 |
| 325 | 35.7 | 14.0 | 10.9 | 4.3 | 40.8 | 14.1 | 114 |
| 400 | 35.7 | 13.1 | 9.8 | 2.1 | 41.4 | 14.1 | 115 |
| 550 | 35.6 | 12.3 | 2.2 | - | 41.3 | 14.1 | 114 |
| 800 | 35.5 | 10.0 | 16.3 | 0.2 | 40.9 | 13.9 | 114 |
| 0703 (18.0 | 0°N, 72.00° | E) | | | | | |
| 5 | 35.5 | 28.3 | 191.1 | 0.0 | 41.3 | 14.0 | 114 |
| | | | | | | | |

| 55 | 36.3 | 28.5 | 183.5 | 0.1 | - | 14.4 | 117 | |
|-------------------------|------|------|-------|------|------|------|-----|--|
| 85 | 35.5 | 23.4 | 27.1 | 0.0 | - | 14.2 | 115 | |
| 0702 (17.27°N, 77.44°E) | | | | | | | | |
| 2 | 35.1 | - | 209.6 | 0.0 | 40.2 | 14.0 | 113 | |
| ER6 (14.00°N, 69.00°E) | | | | | | | | |
| 10 | 36.3 | 28.5 | 199.0 | 0.1 | 42.3 | 14.3 | 117 | |
| 25 | 36.7 | 28.7 | 199.1 | 0.1 | 42.1 | 14.5 | 119 | |
| 50 | 36.6 | 28.3 | 191.3 | 0.4 | 42.1 | 14.4 | 117 | |
| 60 | 36.6 | 28.1 | 185.7 | 0.7 | 41.7 | 14.4 | 117 | |
| 100 | 36.0 | 22.3 | 22.0 | 0.1 | 40.9 | 14.3 | 118 | |
| 150 | 35.8 | 18.3 | 3.9 | 13.9 | 41.2 | 14.1 | 116 | |
| 200 | 35.7 | 15.8 | 2.5 | 7.9 | 40.8 | 14.1 | 115 | |
| 250 | 35.5 | 13.4 | 2.5 | 7.3 | 39.7 | 13.9 | 116 | |
| 400 | 35.5 | 12.3 | 2.8 | 0.0 | 40.4 | 14.1 | 115 | |
| 600 | 35.5 | 11.1 | 5.1 | 0.0 | 40.3 | 14.1 | 113 | |
| 800 | 35.4 | 9.5 | 9.7 | 0.0 | 39.1 | 14.1 | 114 | |
| 1250 | 35.1 | 6.4 | 37.0 | 0.0 | 39.3 | 13.7 | 111 | |
| 2000 | 34.8 | 3.0 | 103.0 | 0.0 | 39.3 | 13.8 | 111 | |
| 2500 | 34.8 | 2.0 | 132.6 | 0.0 | 39.6 | 13.9 | 114 | |
| 3000 | 34.7 | 1.6 | 151.3 | 0.0 | 39.0 | - | - | |
| 3500 | 34.7 | 1.4 | 158.0 | 0.0 | 38.7 | 13.9 | 114 | |
| 4000 | 34.7 | 1.4 | 146.7 | 0.0 | 39.2 | 13.8 | 113 | |
| 4140 | 34.7 | 1.4 | 145.9 | 0.0 | 38.8 | 13.8 | 113 | |

-: Not measured.









Fig. 4.3: Depth profiles of dissolved Re, U and Mo concentration in the Arabian Sea along with the salinity (blue), dissolved oxygen (DO; red) and nitrite (green) profiles in (a) 0802, (b) 0803, (c) 0805, (d) 0708, (e) 0707, (f) 0706, (g) 0705, (h) 0704, (i) ER6. The bars shown at the bottom right of the plots show the analytical uncertainties in the measurement of Re, U and Mo. The concentrations of Re, U and Mo show a marked correlation with salinity rather than dissolved oxygen levels.

4.4 Discussion

4.4.1 Re, U and Mo in the water column of the Arabian Sea

The vertical profiles for Re, U and Mo in the Arabian Sea are shown in Fig. 4.3 (a - i), along with profiles for DO, nitrite and salinity. The data show that within

analytical uncertainties, the dissolved Re, U and Mo concentrations within each profile and among the profiles are independent of the dissolved oxygen concentration. However, the distribution of dissolved Re, U and Mo concentrations in the Arabian show a correlation with salinity.

The Re, U and Mo concentrations do not exhibit any significant correlation with the dissolved oxygen in the water column (Table 4.2, Fig. 4.4). The average Re (n = 11), U (n = 10) and Mo (n = 10) in the samples with DO concentration less than 5 μ M are 40.7 \pm 1.0 pmol/kg, 14.1 \pm 0.3 nmol/kg and 114 \pm 3 nmol/kg respectively (Table 4.2). The errors given along with the numbers are the 2σ uncertainties of the data. This is nearly identical to the average Re (n = 41), U (n = 42) and Mo (n = 42) concentrations of 40.4 \pm 2.6 pmol/kg, 14.0 \pm 1.0 nmol/kg and 114 \pm 6 nmol/kg respectively, in samples with DO concentration greater than 100 μ M (Table 4.2). The larger scatter in the data in samples with DO > 100 μ M is due to salinity variations. The near identical concentrations of dissolved Re, U and Mo in samples with DO <5 μ M and DO >100 μ M (Table 4.2) suggest that, the abundances of these redox sensitive elements are not affected by the suboxic conditions in the water column. This inference is also reaffirmed by the frequency distribution plots for Re, U and Mo concentrations for different dissolved oxygen levels (Figs. 4.4a, 4.4b and 4.4c).

Table 4.2: Statistics of Re, U and Mo concentration with different dissolved oxygen levels in the waters of the Arabian Sea. The associated errors given with the Re, U and Mo concentrations are the 2σ uncertainties of the data. The Re, U and Mo concentrations in the waters of the Arabian Sea overlap with within the uncertainty for different dissolved oxygen levels

| | n | Re | 2σ | n | \mathbf{U} | 2σ | n | Мо | 2σ |
|-----------------|------|-----------|------|-----|--------------|-----|------|-----------|------|
| DO (μ M) | (Re) | (pmol/kg) | (Re) | (U) | (nmol/kg) | (U) | (Mo) | (nmol/kg) | (Mo) |
| <5 | 11 | 40.7 | 1.0 | 10 | 14.1 | 0.3 | 10 | 114 | 3 |
| 5-10 | 20 | 40.8 | 1.1 | 20 | 14.1 | 0.5 | 20 | 114 | 3 |
| <10 | 31 | 40.8 | 1.1 | 30 | 14.1 | 0.4 | 30 | 114 | 3 |
| >10 | 96 | 40.3 | 2.0 | 98 | 14.0 | 0.5 | 99 | 113 | 5 |
| >100 | 41 | 40.4 | 2.6 | 42 | 14.0 | 1.0 | 42 | 114 | 6 |
| All | 127 | 41.1 | 1.9 | 128 | 14.0 | 0.5 | 129 | 114 | 5 |



Fig. 4.4: Frequency distribution of (a) Re, (b) Mo and (c) U in the samples analysed. It is evident that the concentration of these elements in samples with $DO < 5\mu M$ and $DO > 100 \mu M$ are the same within errors; the scatter in the data is due to variation in salinity.

The nitrite profiles (Figs. 4.2d, 4.3) show the presence of secondary nitrite maxima (SNM) in the upper water column (200-600m) north of 12°N, in stations 0802, 0708, 0707, 0706, 0705, 0704 and ER6, whereas, in stations 0803 and 0805

SNM is not seen, suggesting that these two stations lie outside the active water column denitrification zone. The near identical concentrations of Re, U and Mo in samples from the denitrification zone and outside it further suggests that denitrification also does not impact their distribution in the water column of the Arabian Sea (Table 4.1).

The two shallow stations (0702 and 0703) occupied during the cruise SS-256 (Dec, 2007) lie on the western Indian shelf in the zone where intense seasonal hypoxia and water column H₂S have been reported [*Naqvi et al.*, 2000]. Dissolved H₂S was not measured during the sampling, but considering that local seasonal hypoxia occurs during October, it is likely that it waned by the time samples were collected in December for the present work from these locations. The measurable DO levels (DO ~ 27 μ M) support this contention. The Re, U and Mo concentrations in the surface sample at station 0702 are 40.2 pmol/kg, 14.0 nmol/kg and 113 nmol/kg respectively, quite similar to the open ocean values. At station 0703, where three samples were collected in the vertical profile up to a depth of 85m (water depth 98m), the U and Mo concentrations show nearly constant values 14.2 ± 0.2 and 115 ± 2 respectively. Re concentration was measured only in the surface sample which had a value of 40.2 pmol/kg; nearly the same as the value for the open ocean (Table 4.1). These results suggest that the impact of dissolved H₂S, if any on the abundances of these elements also waned away by the time of sampling.

The Re, U and Mo concentrations in the Arabian Sea show good correlation with the salinity with correlation coefficients of 0.96, 0.93 and 0.96 respectively (Fig. 4.5). The data for the SAFe waters (Pacific Ocean; this study), Bay of Bengal [*Singh et al.*, 2011] and Pacific Ocean [*Anbar et al.*, 1992; *Chen et al.*, 1986] are also shown (Fig. 4.5). The Re, U and Mo in the Arabian Sea, Bay of Bengal and Pacific Ocean show a good correlation with salinity. This covariation is a strong indication that salinity is the dominant factor governing the distribution of these three redox sensitive elements in the ocean water column. This makes physical process such as evaporation and mixing of water masses more significant in

deciding the Re, U and Mo concentrations in the ocean rather than the biogeochemical processes.

The concentrations of Re, U and Mo in surface waters of the Arabian Sea are generally high which are attributable to high salinity of these waters. In contrast, in the surface water of station 0805 (6.01°N, 77.48°E), which lies in the southern Arabian Sea, the Re concentration is as low as 36.6 pmol/kg. The U and Mo concentrations are also lower in this water with values of 12.9 nmol/kg and 103 nmol/kg respectively. These low values are consistent with low salinity of this water (32.4). The lower salinity in this surface sample is due to influx of less saline water from the Bay of Bengal into the Arabian Sea during winter monsoon (North-East monsoon). During this season north-easterly winds in the Bay of Bengal set up the East Indian Coastal Current (EICC) as a southward western boundary current which runs parallel to the Indian peninsula carrying low salinity waters from the Bay of Bengal. This low salinity surface water, characterised by lower concentrations of Re, U and Mo [Singh et al., 2011] enters the Arabian Sea via the West Indian Coastal Current [Schott and McCreary, 2001; Shankar et al., 2002; Wyrtki, 1973]. This coupling between Re, U and Mo abundances and salinity suggests that these elements can serve as tracers of water masses in the Arabian Sea and the Bay of Bengal.

Comparison of Re profile in the Arabian Sea with that reported for the Pacific Ocean [*Anbar et al.*, 1992] shows a distinct difference. In the Pacific, the data showed enrichment of Re in surface waters which was unexplained by salinity variations. The high Re content in the surface waters of Pacific Ocean was attributed to possible input of anthropogenic Re to the surface ocean via the atmosphere. In the surface waters of Arabian Sea, no such enrichment is observed in the concentration of Re (Fig. 4.3). Thus the role of atmospheric/aeolian input of Re to the surface waters of Arabian Sea is insignificant.

Table 4.3 is a comparison of Re, U and Mo concentrations in the Arabian Sea, Bay of Bengal, Pacific Ocean and Atlantic Ocean in waters of 35 salinity. The data show that Re, U and Mo concentrations in these basins are same within uncertainties and suggest that the Re, U and Mo distribution in the ocean is uniform. Further considering that the settling particles in the Bay of Bengal are dominated by river detritus whereas those in the Arabian Sea by biogenic material produced in the surface water [*Ramaswamy and Nair*, 1994], it can be inferred that the composition and nature of settling particles also does not influence the water column distribution of these elements.



Fig. 4.5: Concentration of (a) Re, (b) U and (c) Mo vs. Salinity in the Arabian Sea. The measured concentration for each tenth of salinity (e.g.: 34.9, 35.0, 35.1, etc) are averaged to minimize the clutter in data. Data show a good correlation with salinity suggesting that salinity is dominant factor governing the distribution of these elements in the water column. The concentration of Re is in the units of pmol/kg while the concentrations of U and Mo are in the units of nmol/kg. The data from the Bay of Bengal and Pacific Ocean are also plotted.

| | Re | 1σ | U | 1σ | Mo | 1σ |
|----------------------------|-----------------------|----------------------|--------------------|------------------|------------------|----------------|
| Region | (pmol/kg) | (Re) | (nmol/kg) | (U) | (nmol/kg) | (Mo) |
| Arabian Sea [†] | 39.8 | 0.7 | 13.8 | 0.1 | 114 | 1 |
| Bay of Bengal [#] | 41.0 | 0.8 | 13.9 | 0.1 | 112 | 1 |
| Pacific Ocean | 40.1 ^{&} | 1.1 ^{&} | 13.7 ^{\$} | $0.1^{\$}$ | 107 [£] | 3^{f} |
| Atlantic Ocean | 40.1 [€] | 0.4€ | 13.6 [¥] | 0.4^{F} | 109 [§] | 9 [§] |

Table 4.3: Dissolved Re, U and Mo in Arabian Sea and other oceanic basins(at 35 salinity)

[†]This study, [#] [Singh et al., 2011], [&][Anbar et al., 1992], [§][Chen et al., 1986], [£][Collier, 1985], [€][Colodner et al., 1993], [¥][Ku et al., 1977], [§][Morris, 1975]

4.4.2 Re, U and Mo in the Arabian Sea sediments

There have been a few studies on the abundance and distribution of Re, U and Mo in the sediments of the Arabian Sea [*Borole et al.*, 1982; *Pattan and Pearce*, 2009; *Sirocko et al.*, 2000]. These studies show that these elements are enriched in sediments associated with high organic carbon. For example, in the organic carbon rich surface sediments of the Arabian Sea, up to 50 times enrichment in the Re/Al ratio [*Pattan and Pearce*, 2009] has been reported over the upper continental crust (UCC; Table 4.4) [*Taylor and McLennan*, 1995; *Viers et al.*, 2009]. Similarly, U/Al and Mo/Al are also enriched in the surface sediments with ratios up to 8 and 4 times over the UCC value (Table 4.4).

| | Re/Al (ppb/%) | U/Al (ppm/%) | Mo/Al (ppm/%) |
|-----------------------|------------------|--------------------|--------------------|
| UCC [†] | 0.06 | 0.35 | 0.37 |
| Arabian Sea sediments | 3.11€ | 2.68 ^{\$} | 1.36 ^{\$} |
| | | 2.88^{F} | |
| Enrichment | 50 | 8 | 4 |

 Table 4.4: Enrichment of Re, U and Mo in the sediments of the Arabian Sea

 relative to upper continental crust (UCC)

[†] [Taylor and McLennan, 1995]; [€] [Pattan and Pearce, [2009];

^{\$} [Sirocko et al., 2000]; [¥] [Borole et al., 1982]

These data indicate that the organic matter plays an important role in sequestering these elements in sediments of the Arabian Sea. Thus, the Arabian Sea basin is an important site for the removal of redox sensitive elements Re, U and Mo. The mechanism and sites of such removal are still poorly understood. As has been discussed in the present work, the removal of these elements from the water column of the Arabian Sea is not a favoured phenomenon.

Primary productivity was not measured during this study. However, available data show that primary productivity is quite high and is in the range of 0.5 to 2.5 gC m⁻ ²d⁻¹ in the Arabian Sea surface water during winter [Madhupratap et al., 1996]. The primary productivity during the months of winter monsoon in the Arabian Sea results from surface cooling driven convection process that inject nutrients up into the surface waters of the Arabian Sea. Further, results of sediment trap deployment in the eastern and central Arabian Sea showed that settling flux of particles is in the range of 25-30 g m⁻²y⁻¹, with ~6 % of organic carbon [Ramaswamy and Nair, 1994]. These studies suggest that there is significant primary productivity and rain of organic matter through the water column of the Arabian Sea. This high productivity and biogenic particle rain through the water column do not seem to have any discernible impact on the dissolved profile of Re, U and Mo as evidenced from their uniform lateral and vertical distribution. Therefore the enrichment of Re, U and Mo observed in organic matter rich sediments seems to be due to their removal at the sediment-water interface. Investigations on the pore water abundances of Re, U and Mo in the sediments are required to better understand and characterize the mechanism of removal of these elements from the waters of the Arabian Sea.

4.5 Conclusions

The dissolved Re, U and Mo concentrations from the oxic and suboxic layers of the Arabian Sea show that these elements behave conservatively in the water column, i.e. there is no discernable removal of Re, U or Mo from the suboxic and denitrifying layers of the Arabian Sea. The concentrations of Re, U and Mo in the water column of the Arabian Sea vary as a function of salinity showing good correlations with correlation coefficients of 0.96, 0.93 and 0.96 respectively. Comparison of the concentrations of Re, U and Mo in the water column of the Arabian Sea with data from other oceanic regions show that they overlap with each other for the same salinity suggesting that salinity exerts a dominant control on their concentration and that Re, U and Mo behave conservatively in the water column. The similarity of dissolved Re, U and Mo concentrations in the water column of Arabian Sea (high biogenic debris through the water column) and the Bay of Bengal (high detrital flux through the water column) suggest that even the high flux and/or nature of particles through the water column do not affect the water column distribution of these elements with no removal from the water column. The salinity-concentration link further supports that the distribution of these elements is governed by physical processes of advection and mixing between water masses and evaporation and not by biogeochemical processes operating in the water column. The salinity dependence of Re, U and Mo concentrations hints at the possibility of using their distributions to track water masses in the ocean.

CHAPTER 5

Variations in ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater during past 30 ka

5.1 Introduction

Continental chemical weathering regulates the global carbon and exogenic cycles of various elements and heat budget of the Earth. The impact of chemical weathering on carbon cycle regulates global climate on long time scales [*Ruddiman*, 1997]. In turn, global climate significantly influences continental weathering as chemical erosion depends on temperature, rainfall and glaciation. Climate variability can induce variation in the intensity of chemical weathering, records of which are archived in marine sediments. Radiogenic isotopes in the ocean track the history of continental erosion variation and its rate, intensity and pattern. A number of radiogenic isotopes in the ocean, ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ¹⁸⁷Os/¹⁸⁸Os serve as tracers to investigate past variations in the continental erosion and sediment provenances [*Goswami et al.*, 2012b; *Tripathy et al.*, 2011].

Among the various radiogenic isotope proxies, Os has a residence time of 8-40 ka in the ocean [Oxburgh, 2001], long enough to homogenise its isotopic signature in the global ocean but at the same time, short enough to track the variations in its supply on glacial – interglacial time scale. Os isotopes in the ocean has three sources, continental, hydrothermal input and extra terrestrial dust. Among these three, Os derived from continental weathering has a highly radiogenic isotopic composition (¹⁸⁷Os/¹⁸⁸Os ~ 1.5) [Levasseur et al., 1999] compared to the two other sources of Os, hydrothermal inputs (¹⁸⁷Os/¹⁸⁸Os ~ 0.12) [Meisel et al., 2001] and dissolution of cosmic/micrometeoritic dust ($^{187}Os/^{188}Os \sim 0.12-0.13$) [Luck and Allegre, 1983; Walker and Morgan, 1989]. Any variation in the relative proportion of Os supplied to the ocean from these radiogenic and non-radiogenic sources would reflect in the ¹⁸⁷Os/¹⁸⁸Os of seawater. Os isotope studies from East pacific Rise [Oxburgh, 1998], Cariaco Basin [Oxburgh et al., 2007], Santa Barbara Basin [Williams and Turekian, 2004] and Japan Sea [Dalai et al., 2005] indicate the variation in ¹⁸⁷Os/¹⁸⁸Os sea water over glacial-interglacial time scale, with lower ¹⁸⁷Os/¹⁸⁸Os during glacial periods, particularly during the Last Glacial Maxima (LGM). Lower oceanic ¹⁸⁷Os/¹⁸⁸Os during the LGM has been attributed to reduced supply of radiogenic Os from continents. This was due to reduced continental weathering and decreased continental runoff resulting from lower temperature. The occurrence of this trend in the Atlantic and the Pacific oceans has prompted to consider the dip in the Os isotopic composition during the LGM as a global signature [*Oxburgh et al.*, 2007], though it is yet to be verified in the Indian Ocean.

Organic matter rich marine sediments are known to sequester redox sensitive elements e.g. U, Mo, Re and Os from seawater. Re and Os behave conservatively in seawater and shows similar behaviour to U and Mo [Goswami et al., 2012a; Levasseur et al., 1998; Singh et al., 2011]. Re and Os are removed from seawater to sediments generally at or near the sediment-water interface via their diffusion through pore water to depths where the redox conditions of sediments are conducive to their sequestration. This often leads to their enrichment in anoxic/suboxic marine sediments [Crusius et al., 1996]. The degree of removal of Re from seawater to sediments via pore water has been found to be more than U and Mo. The Re enrichment in the anoxic/suboxic marine sediments is greater than many other redox sensitive elements (including U and Mo) due to the high ratio of [Re]_{seawater}/[Re]_{crust} which reflects the high solubility of the perrhenate ion ReO_4 in seawater. The Os concentration in the detrital material of sediment is quite low. Therefore its budget in the organic matter rich sediment is dominated by authigenic Os and hence the Os isotopic composition of organic matter rich sediments by and large represents the Os isotopic signature of the seawater [Dalai et al., 2005; Oxburgh et al., 2007] at the time of their deposition.

In this study, Re, Os concentrations and ¹⁸⁷Os/¹⁸⁸Os have been analysed in organic matter rich sediments taken from a core (SS-3101G, Figure 2.2) raised from the south-eastern Arabian Sea. The basic objective of this study is to reconstruct the Os isotope composition of seawater from the Arabian Sea over last 30 ka. This study will provide an opportunity to compare the temporal evolution of the Os isotopic composition in the Northern Indian Ocean to those reported for the Atlantic and the Pacific Oceans and to assess whether the Os isotopic variations of seawater over glacial – interglacial time scale represents a global phenomenon.

5.2 Results and discussion

5.2.1 Os concentration and its isotope composition of bulk sediments

Organic carbon content of the sediments of the core SS-3101G analysed in this study range from 0.61 to 2.25 wt% [*Agnihotri*, 2001]. Organic matter rich marine sediments are known to sequester Os from the seawater. The Os in the organic matter rich marine sediments is known to be scavenged by marine organic matter under reducing bottom water conditions. Thus, the Os isotopic composition of organic matter rich sediments at a time represents that of the seawater [*Dalai et al.*, 2005]. The relatively high concentration of organic carbon in these sediments prompted the measurement of ¹⁸⁷Os/¹⁸⁸Os in bulk sediments with the premise that these sediments would record the seawater Os isotopic composition. The Os concentration and its isotopic composition derived from bulk sediments are given in Table 5.1 and plotted in Fig. 5.1.

The Os concentrations in bulk sediments of the core vary from 119 to 321 pg/g, with higher concentrations during the LGM (Fig. 5.1). The Os isotopic composition (187 Os/ 188 Os) of the bulk sediments from the Arabian Sea ranges from 0.69 to 1.00. It shows four excursions towards lower values during ~2.5 ka, ~8 ka, ~20 ka and ~29 ka. The Os isotopic composition of bulk sediments display lower values compared to the contemporary seawater value. The most recent sample with age of 2.2 ka shows a 187 Os/ 188 Os of 0.96 which is significantly lower compared to contemporary seawater 187 Os/ 188 Os value of 1.06 ± 0.01 [*Levasseur et al.*, 1998].

Further during the LGM, the ¹⁸⁷Os/¹⁸⁸Os of bulk sediments of the Arabian Sea is quite less radiogenic compared to those observed during same time in other ocean basins [*Oxburgh et al.*, 2007]. The ¹⁸⁷Os/¹⁸⁸Os of the bulk sediments from the Arabian Sea display much lower values than the records available for the Os isotopic composition from other oceanic basins (in the records of seawater basin from Pacific and Atlantic basins, the seawater ¹⁸⁷Os/¹⁸⁸Os varies only between 0.91 and 1.06 for the last 200 ka) [*Oxburgh*, 1998; *Oxburgh et al.*, 2007, *Williams and Turekian*, 2004].

| Sample [*] | Age (ka) | ¹⁸⁷ Os/ ¹⁸⁸ Os | Os (pg/g) |
|---------------------|----------|--------------------------------------|-----------|
| 3101(2-3) | 2.2 | 0.960 | 119 |
| 3101(3-4) | 2.5 | 0.693 | 196 |
| 3101(6-7) | 3.3 | 0.941 | 199 |
| 3101(12-13) | 5.1 | 0.907 | 153 |
| 3101(16-17) | 6.7 | 0.871 | 141 |
| 3101(19-20) | 7.8 | 0.718 | 202 |
| 3101(22-23) | 9.0 | 1.004 | 255 |
| 3101(25-26) | 10.2 | 0.948 | 235 |
| 3101(32-33) | 12.0 | 0.975 | 141 |
| 3101(39-40) | 13.8 | 0.986 | 197 |
| 3101(45-46) | 15.7 | 0.934 | 258 |
| 3101(61-62) | 19.3 | 0.963 | 276 |
| 3101(67-68) | 20.1 | 0.736 | 321 |
| 3101(77-78) | 21.0 | 0.970 | 235 |
| 3101(85-86) | 21.6 | 0.994 | 260 |
| 3101(91-92) | 22.4 | 0.877 | 262 |
| 3101(95-96) | 23.2 | 0.889 | 260 |
| 3101(114-116) | 26.3 | 0.822 | 269 |
| 3101(126-128) | 28.1 | 0.847 | 251 |
| 3101(130-132) | 28.7 | 0.744 | 318 |

Table 5.1: Os concentration and $^{187}\mathrm{Os}/^{188}\mathrm{Os}$ of bulk sediments from the core SS-3101G

* Numbers in parenthesis are depth intervals in cm.

For calibrated ¹⁴C ages of the sediments refer to Table 2.2 (Chapter 2)

These lines of evidences suggest that bulk sediments of the Arabian Sea analysed in this study do not strictly record the seawater Os isotope composition. In addition to seawater Os, significant fraction of detrital Os is also present in these core sediments and hence these sediments are providing the mixed signature of seawater and detrital Os. Detrital material responsible for non-radiogenic Os in these sediments could be the sediments from the Trans-Himalaya delivered by the Indus River, Deccan Basalts and aeolian dust from African and Arabian Peninsula.



Fig. 5.1: Temporal variation in the ¹⁸⁷Os/¹⁸⁸Os and Os concentration in bulk sediments of core SS-3101G from the Arabian Sea

It is evident from the above results and discussion that the application of Os isotope composition of the bulk sediments of the core SS-3101G to study the evolution of Os isotopic composition of Arabian seawater over the past is difficult. Therefore, to investigate the temporal evolution of ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater, the hydrogenous component of Os from the sediments has to be separated and analyzed. This was done by leaching these sediments with mild acidic peroxide solution. The leaching of sediments with acidified hydrogen peroxide solution efficiently releases the hydrogenous Os from ferromanganese oxyhydroxide and organic matter phases, presumed to contain the sea water Os [*Pegram et al.*, 1992; *Pegram and Turekian*, 1999; *Williams and Turekian*, 2004].

5.2.2 Re concentration of bulk sediments

The temporal variation in Re concentration of the bulk SS-3101G sediments core is listed in Table 5.2. Re concentrations of the bulk sediments of the SS-3101G core are lower during the Holocene (last 10 ka; Fig. 5.2). In the most recent sample of the strata, the Re concentration is 0.26 ng/g. This is slightly lower than the average continental crust value of 0.4 ng/g [*Taylor and McLennan*, 1995].

These sediments contains significant fraction of CaCO₃, varying from ~60% in the most recent sediments to ~20% in sediments deposited during the LGM [Agnihotri, 2001].

| Sample | Age (ka) | Re (ng/g) |
|---------------|----------|-----------|
| 3101(0-1) | 1.7 | 0.26 |
| 3101(3-4) | 2.5 | 0.25 |
| 3101(6-7) | 3.3 | 0.27 |
| 3101(12-13) | 5.1 | 0.68 |
| 3101(16-17) | 6.7 | 1.58 |
| 3101(17-18) | 7.1 | 3.90 |
| 3101(22-23) | 9.0 | 2.97 |
| 3101(25-26) | 10.2 | 1.89 |
| 3101(27-28) | 10.9 | 0.62 |
| 3101(32-33) | 12.1 | 0.44 |
| 3101(39-40) | 13.8 | 0.73 |
| 3101(45-46) | 15.7 | 4.74 |
| 3101(46-47) | 16.1 | 11.02 |
| 3101(53-54) | 18.3 | 29.91 |
| 3101(58-59) | 18.9 | 13.90 |
| 3101(62-63) | 19.4 | 16.51 |
| 3101(66-67) | 19.9 | 7.40 |
| 3101(77-78) | 21.0 | 3.41 |
| 3101(85-86) | 21.6 | 15.10 |
| 3101(91-92) | 22.4 | 12.05 |
| 3101(95-96) | 23.2 | 13.98 |
| 3101(100-102) | 24.2 | 11.54 |
| 3101(104-106) | 24.8 | 2.26 |
| 3101(114-116) | 26.3 | 2.15 |
| 3101(126-128) | 28.1 | 10.02 |
| 3101(130-132) | 28.7 | 25.98 |

Table 5.2: Re concentration in bulk sediments of core SS-3101G

* Numbers in parenthesis are depth intervals in cm. For calibrated ¹⁴C ages of the sediments refer to Table 2.2 (Chapter 2)

The calcium carbonate fraction contains very little Re (< 0.05 ng/g) as Re is not incorporated into the calcite shells [Colodner et al., 1993]. Correcting for carbonate dilution, the Re concentration in the most recent sediments from the core SS-3101G would be ~0.65 ng/g, marginally higher than the continental crust value. Carbonate dilution correction would further increase Re contents in the sediments deposited during LGM. Higher concentration of Re in the sediments of the Arabian Sea during LGM suggest increased bottom water reducing conditions in the basin. The productivity in this basin was lower during the LGM [*Agnihotri et al.*, 2003]; hence the bottom water reducing conditions could be due to the poor supply of oxygen in the deeper water. These will be discussed in details in later section of this chapter.



Fig. 5.2: Temporal variation in Re concentration of bulk sediments of core SS-3101G

5.2.3 Os concentration and isotopic composition of hydrogenous fraction of core SS-3101G

To avoid the Os contamination from detrital material, Os was analysed in the hydrogenous fraction of the sediments. The hydrogenous fraction of the sediments was extracted by mild acidic peroxide leaching. The isotopic composition of the hydrogenous Os fraction is measured to track the Os isotopic evolution of Arabian seawater.

The results of the temporal variation in the Os concentration and its isotopic composition in hydrogenous fraction of sediments from the Arabian Sea are given in Table 5.3 and plotted in Fig. 5.3.

| Sample [*] | age (ka) | ¹⁸⁷ Os/ ¹⁸⁸ Os | Os (pg/g) |
|---------------------|----------|--------------------------------------|-----------|
| 3101(1-2) | 1.9 | 1.040 | 102 |
| 3101(6-7) | 3.3 | 1.023 | 86 |
| 3101(17-18) | 7.1 | 1.033 | 81 |
| 3101(19-20) | 7.8 | 1.009 | 72 |
| 3101(23-34) | 9.4 | 1.032 | 132 |
| 3101(33-34) | 12.3 | 0.992 | 69 |
| 3101(42-43) | 14.8 | 1.009 | 103 |
| 3101(46-47) | 16.1 | 0.982 | 201 |
| 3101(51-52) | 17.7 | 1.018 | 144 |
| 3101(54-55) | 18.4 | 1.029 | 257 |
| 3101(66-67) | 19.9 | 1.004 | 166 |
| 3101(68-69) | 20.2 | 1.033 | 187 |
| 3101(78-79) | 21.1 | 1.032 | 175 |
| 3101(90-91) | 22.3 | 1.038 | 250 |
| 3101(100-102) | 24.2 | 1.030 | 141 |
| 3101(110-112) | 25.7 | 1.012 | 101 |
| 3101(122-124) | 27.5 | 0.982 | 167 |
| 3101(130-132) | 28.7 | 1.007 | 147 |
| 3101(132-134) | 29.0 | 1.037 | 160 |

Table 5.3: Os concentration and $^{187}\mathrm{Os}/^{188}\mathrm{Os}$ of hydrogenous fraction of core SS-3101G

* Numbers in parenthesis are depth intervals in cm.

For calibrated ¹⁴C ages of the sediments refer to Table 2.2 (Chapter 2)

The Os concentration in the leachable fraction of sediments varies from ~ 80 pg/g in the recent samples to ~ 250 pg/g for samples representing the LGM, suggesting an increase in the authigenic fraction of Os to the sediments deposited during LGM, like Re enrichment in sediments during the LGM. The ¹⁸⁷Os/¹⁸⁸Os of seawater (as represented by the hydrogenous component) in the most recent sample has a value of 1.04 ± 0.01 , close to the Os isotopic composition of present day seawater (1.06 ± 0.01) [*Levasseur et al.*, 1998]. The Os isotopic composition of the Arabian seawater shows lowest value of 0.982 at ~16 ka just after the LGM, and also at ~27.5 ka prior to the LGM (Table 5.3). Between these two lowest values, ¹⁸⁷Os/¹⁸⁸Os shows a hump with higher values during LGM. The ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater during LGM is nearly identical to the contemporary seawater.



Fig 5.3: Temporal variation in Os concentration and ¹⁸⁷Os/¹⁸⁸Os of hydrogenous fraction of core SS-3101G. Os concentrations are higher during the LGM.

5.2.3.1 Os concentration variations in the leachable fraction of SS-3101G

The temporal variation in the Os concentration of the leachable phase from the sediments of the core SS-3101G is plotted along with Re concentration (in bulk sediments) and organic carbon content of the core SS-3101G in Fig. 5.4.

The Os concentration of the leachable fraction of the sediments shows higher values during the LGM. This increase in the Os concentration is also associated with an increase in the Re concentration of bulk sediments and an increase in the organic carbon content (Fig. 5.4). Re and Os are known to be redox sensitive elements that are removed from the seawater to sediments under reducing conditions.

Re is a useful proxy for deciphering the past redox changes of the oceanic basin [*Colodner et al.*, 1995]. *Pattan and Pearce*, [2009] and *Sarkar et al.*, [1993] observed higher concentrations of Re and U in the Arabian Sea sediments deposited during the LGM which was attributed to anoxic/suboxic bottom water

conditions in the region during that time. In addition, the organic carbon content of the sediments are also higher during LGM, which could be attributed to better preservation of organic carbon owing to the lower oxygen content of the water column of the Arabian Sea. The high organic carbon can also result from higher productivity during the LGM, however, this has been ruled out based on distribution of other productivity proxies [*Agnihotri et al.*, 2003].



Fig. 5.4: Temporal variations in the Os concentration of leachable fraction of the sediments, Re concentration of the bulk sediments and organic carbon content of the sediments of the core SS-3101G. The organic carbon content of the sediments is from *Agnihotri*, [2001]. The Re concentration in the bulk sediments and the Os concentration of the leachable fraction of the sediments show an increase during the LGM along with higher organic carbon content of the core during that time.

The accumulation fluxes of Re, Os and organic carbon were calculated using the linear sedimentation rate (LSR) and dry bulk density (DBD) of the sediments of the core. The accumulation fluxes were calculated using the following relation:

$$F = C \times LSR \times d \tag{5.1}$$

where, F is the accumulation flux (in $g \text{ cm}^{-2} \text{ka}^{-1}$)

C is the concentration of Re, Os and organic carbon in the sediments LSR is the linear sedimentation rate (obtained from the ages and depths of the overlying and underlying samples)

d is the dry bulk density taken to be 0.85 (in g cm⁻³)

The mass accumulation rate of organic carbon in the core is generally low up to ~17.5 ka (varying only from 0.003 to 0.053 g cm⁻²ka⁻¹). During the LGM, the accumulation rate of organic carbon increased to a high value ranging from 0.061 to 0.266 g cm⁻²ka⁻¹. This increase in the accumulation rate of organic carbon was due to better preservation of organic carbon during the LGM. The accumulation rates for Re and Os show a behaviour similar to that of the organic carbon. The accumulation rates range from 0.07 to 29.10 ng cm⁻²ka⁻¹ for Re and 0.07 to 0.53 ng cm⁻²ka⁻¹ for Os during 2 - 17.5 ka. During the LGM, the Re and Os accumulation rates showed an increase with values ranging from 50.46 to 178.43 ng cm⁻²ka⁻¹ for Re and 1.13 to 2.07 ng cm⁻²ka⁻¹ for Os. This increase in the accumulation rates of Re and Os in the sediments during the LGM is associated to higher accumulation rate of the organic carbon during that time. This suggests the association/linkage of organic carbon in sequestering the Re and Os from the seawater into the sediments.

5.2.3.2 Temporal variation in ¹⁸⁷Os/¹⁸⁸Os of seawater from the Arabian Sea

The ¹⁸⁷Os/¹⁸⁸Os of leachable fraction of sediments (representing seawater Os) from the core SS-3101G varies between 0.982 and 1.040 (Table 5.3). ¹⁸⁷Os/¹⁸⁸Os of the hydrogenous Os from the most recent sediment sample is nearly identical to the contemporary seawater value confirming that leachable fraction does represent the seawater Os isotope composition. The ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater

shows an increase in the Holocene towards the present (Fig. 5.3). Further, the Os isotopic composition of seawater shows an excursion towards higher values during the LGM.

The Os entering the ocean is derived from three different sources. These are the continental source with isotopic composition, $^{187}Os/^{188}Os \sim 1.5$ [*Levasseur et al.*, 1999], the micrometeoric/cosmic dust with $^{187}Os/^{188}Os$ of ~ 0.12 [*Meisel et al.*, 2001] and the hydrothermal input with $^{187}Os/^{188}Os$ of ~ 0.12 [*Luck and Allegre*, 1983; *Walker and Morgan*, 1989]. Thus the Os isotopic composition of the dissolved Os in the ocean, at a given time, is the resultant of combination and relative proportions of these sources. Any change in the Os isotopic composition and/or flux of Os from these sources can result in the variation in the Os isotopic composition of the seawater over the past.

The variation in the range for the isotopic composition of the Os derived from the mantle (via hydrothermal vents) and micrometeoric/cosmic dust is small (these sources have ${}^{187}\text{Os}/{}^{188}\text{Os}$ very close to 0.12). Thus, it is the flux of these sources that would require varying in order to influence the seawater Os isotopic composition. The flux of extraterrestrial dust (cosmic dust) has been studied from the Indian Ocean and found to remain fairly constant over the last 200 ka [Marcantonio et al., 1999]. Additionally the study based on the Antarctic ice core, the supply of extraterrestrial material has been found to be stable for the last 30 ka [Winckler and Fischer, 2006], which provides an additional argument for the support of the stability of extraterrestrial input. Further, for the time span covered by the sediments of the core (~30 ka), there has not been any major event of sea floor spreading which would result in the increase in the supply of mantle derived Os into the ocean [Oxburgh, 1998]. Thus, the variation in the Os isotopic composition of seawater recorded by the SS-3101G core from south-eastern Arabian Sea is not due to change in the Os isotopic composition and/or Os flux from the cosmic dust and hydrothermal inputs. The measured changes in the seawater Os isotopic composition therefore has to result from changes in the Os isotopic composition and/or Os flux from the continental source.

The oceanic inventory of Os is considered to be well mixed and thus the Os isotopic composition of seawater at any time would reflect the global signature in the ocean. There have been a few studies on the record of Os isotopic composition of seawater over the past; from the East Pacific Rise, Pacific Ocean [*Oxburgh*, 1998]; Cariaco basin, Atlantic Ocean [*Oxburgh et al.*, 2007]; Santa Barbara Basin [*Williams and Turekian*, 2004] and Japan Sea [*Dalai et al.*, 2005]. The temporal evolution of Os isotopic composition of seawater from the Arabian Sea measured in the present study is compared with some of these global records in Fig. 5.5.



Fig. 5.5: Comparison of the temporal variation in the Os isotopic composition of the Arabian seawater (present work) with reported ¹⁸⁷Os/¹⁸⁸Os variations from the East Pacific Rise (Pacific Ocean) [*Oxburgh*, 1998] and Cariaco basin (Atlantic Ocean) [*Oxburgh et al.*, 2007]. The black curve is the 3-point running average (used as a response filter to suppress the high frequency fluctuation in the data) of ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater. The Os isotopic trend from the Arabian Sea and other oceanic basins show a similar trend for the last ~16 ka with gradual increase in the ¹⁸⁷Os/¹⁸⁸Os of seawater towards the present day seawater value of 1.06 ± 0.01 . During the LGM, the ¹⁸⁷Os/¹⁸⁸Os of seawater from the Arabian Sea shows major departure from other records with a hump in contrast to lower values for the other oceanic regions

As the flux and isotope composition of non-radiogenic sources of Os to seawater have remained constant during last 200 ka, the excursions in the ¹⁸⁷Os/¹⁸⁸Os of the seawater reflect variations in the flux and/or isotopic composition of dissolved Os reaching the oceans from the continents. The possibility of the variation in the Os

isotopic composition of the riverine supply to the ocean has been discussed and discarded by *Oxburgh*, [1998] based on very limited variation in the ¹⁸⁷Os/¹⁸⁸Os (1.3 to 1.4) of the deltaic sediments from a number of world's large rivers relative to wide range of ¹⁸⁷Os/¹⁸⁸Os values (1.2 to 3.6) reported for the continental rocks. The seawater Os isotope composition therefore would vary due to variation in the flux of continental Os.

In general, the trend of Os isotope evolution of the Arabian seawater (Fig. 5.5) resembles with those observed in other global basins, such as the East Pacific Rise [Oxburgh, 1998] and Cariaco Basin [Oxburgh et al., 2007] during 2 -16 ka, whereas, during the LGM, i.e. between 17 and 26 ka, they differ drastically. Earlier studies have observed higher concentrations of redox sensitive elements U and Re in the sediments of the Arabian during LGM [Pattan and Pearce, 2009; Sarkar et al., 1993]. The sediments of the core SS-3101G also exhibit higher content of Re and Os during the LGM (Fig. 5.4). These evidences suggest that the redox sensitive elements Re, U and Os were more efficiently incorporated into the sediments of the Arabian Sea during the LGM. This was due to the reduced oxygen content of the deeper waters in the Arabian Sea [Pattan and Pearce, 2009; Sarkar et al., 1993]. The reduced oxygen content in the deeper waters of the Arabian Sea and anoxic/suboxic conditions at the bottom could be ascribed to poor ventilation of the basin due to reduced supply of polar waters the LGM [Pattan and Pearce, 2009; Piotrowski et al., 2009; Sarkar et al., 1993; Schmiedl and Leuschner, 2005]. Reduction in the flow of North Atlantic Deep Water (NADW) to the northern Indian Ocean has been reported by *Piotrowski et al.*, 2009. The NADW flows in the depth range of 2000 to 3800m in the Arabian Sea [Piotrowski et al., 2009]. The core SS-3101G in the Arabian Sea is situated at a water depth of 2766m, lying in the domain of the NADW water depth. The reduced flow of NADW partially isolated the Arabian Sea basin from other oceanic basins during the LGM. Consequently, the non radiogenic Os signature of global ocean (with 187 Os/ 188 Os ~ 0.98; [Oxburgh et al., 2007]) was unable to influence the Os isotopic composition of Arabian seawater. The Arabian Sea was restricted to get the supply of non-radiogenic Os delivered by the intense weathering of East Indies, Papua New Guinea, the Philippines and ophiolite section of the circum-Pacific region to the global ocean during LGM [*Williams and Turekian*, 2004]. Radiogenic signature of Os in the Arabian Sea during LGM is local in nature and it is derived from the weathering of the Himalayan and Peninsular lithologies. Contribution from the Deccan Basalt weathering would not have been significant as their Os content is quite low [*Allègre et al.*, 1999]. Further, low salinity water with higher ¹⁸⁷Os/¹⁸⁸Os from the Bay of Bengal entered the Arabian Sea due to intensification of North-East monsoon during the LGM [*Sarkar et al.*, 1990]. This will also increase the Os isotope composition of the Arabian Sea water during LGM. Higher fluxes of aeolian dust during LGM could also increase the Os isotope composition of dust over the Arabian Sea.

5.3 Conclusions

The Os isotopic composition of the organic matter rich bulk sediments from the Arabian Sea show significant amount of detrital contamination. This hinders the applicability of the bulk sediments from the Arabian Sea in tracking the temporal variation in 187 Os/ 188 Os of the Arabian seawater.

The ¹⁸⁷Os/¹⁸⁸Os of the seawater and Os concentration of the leachable fraction of sediments from the Arabian Sea show a correlation with climate with both the Os isotopic composition as well as the concentration showing an excursion towards higher values during the LGM. The ¹⁸⁷Os/¹⁸⁸Os of seawater from Arabian Sea shows a similar trend to the records of the Os isotopic composition from the other global basins, displaying increase in the ¹⁸⁷Os/¹⁸⁸Os from 16 ka to 2 ka approaching towards the present day seawater ¹⁸⁷Os/¹⁸⁸Os of 1.06 \pm 0.01. The ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater shows a decoupling from other records during LGM, experiencing an excursion towards higher values. Also, the Re content of the sediments as well as the Os concentration of the leachable fraction of the sediments was also higher during the LGM. These are due to anoxic conditions in the bottom waters of the Arabian Sea caused by the reduced transport of NADW

into the Arabian Sea, resulting in its partial isolation from rest of the oceans during the LGM.

CHAPTER 6

Temporal variations in $^{87}Sr/^{86}Sr$ and ϵ_{Nd} in sediments of the south-eastern Arabian Sea: Impact of monsoon and surface water circulation

6.1 Introduction

The Arabian Sea annually receives ~400 million tons of suspended load from the Himalaya and Transhimalaya [*Milliman et al.*, 1984] through the Indus river system, and ~100 million tons through the Narmada, Tapi and the rivers of the Western Ghats [*Alagarsamy and Zhang*, 2005; *Chandramohan and Balchand*, 2007]. In addition, ~100 million tons of aeolian dust from the deserts of Oman, Africa and western India is deposited annually in the Arabian Sea, its contribution to the eastern Arabian Sea being only ~30 million tons, which further decreases towards the Indian peninsula [*Ramaswamy and Nair*, 1994; *Sirocko and Sarnthein*, 1989]. The sediments deposited in the Arabian Sea preserve in them the records of erosional patterns in their source regions, factors regulating them and the pathways of sediment dispersal in the sea [*Clift et al.*, 2008; *Rahaman et al.*, 2009].

One of the key factors determining the erosion patterns of the drainage basins is the monsoon. The Indian subcontinent experiences two monsoons annually, the South-West (summer) and the North-East (winter) monsoons; the former being more pronounced at present. The intensities and patterns of these monsoons have varied during the past [*Fleitmann et al.*, 2003; *Gupta et al.*, 2003; *Herzschuh*, 2006], these in turn, have affected the erosion distribution of drainage basins [*Clift et al.*, 2008; *Rahaman et al.*, 2009] and supply of sediments to the seas around India [*Ahmad et al.*, 2005; *Colin et al.*, 1999; *Tripathy et al.*, 2011]. These variations, in addition to impacting erosion, also influence the surface water circulation in the Arabian Sea and the Bay of Bengal which determine the sediment dispersal and deposition in them.

During the SW monsoon, surface water from the Arabian Sea flows to the Bay of Bengal; in contrast, during the NE monsoon, surface currents flow from the Bay of Bengal to the Arabian Sea [*Schott and McCreary*, 2001; *Shankar et al.*, 2002]. There is evidence to suggest that the transport of low-salinity water from the Bay of Bengal to the Arabian Sea was enhanced during the Last Glacial Maximum

(LGM) due to a more intense NE monsoon [Sarkar et al., 1990; Tiwari et al., 2005].

Clay mineralogy and radiogenic isotopes of Sr and Nd have been used to investigate spatial variations in the provenance of sediments in the Arabian Sea and the Bay of Bengal and their causative factors. For example, investigations of surface sediments in the Arabian Sea suggest that supply from the Himalaya, Transhimalaya and Karakorum ranges brought via the Indus dominate in the northern and central regions [*Garzanti et al.*, 2005], whereas the sediments off the shelf and slope regions of the eastern Arabian Sea are sourced mainly from peninsular India [*Chauhan and Gujar*, 1996; *Chauhan et al.*, 2010; *Kessarkar et al.*, 2003; *Kolla et al.*, 1976; *Rao and Rao*, 1995]. There is also evidence based on clay mineral studies of sediments from the southwestern slope of India that suggest long range transport of Ganga-Brahmaputra sediments to the tip of Indian peninsula by surface currents [*Chauhan and Gujar*, 1996; *Chauhan et al.*, 2010].

The radiogenic isotopes of Sr and Nd in silicate phases are commonly used as proxies for sediment provenances. The Sr (⁸⁷Sr/⁸⁶Sr) and Nd (¹⁴³Nd/¹⁴⁴Nd) isotopic composition of continental source rocks depend on their Rb/Sr and Sm/Nd ratios and their ages. Terrigenous sediments in the ocean are weathering products of continental rocks that have wide range of Sr and Nd isotope ratios. Thus, the Sr and Nd isotopic composition of detrital marine sediments provide a means to trace their sources and their variations in space and time [*Innocent et al.*, 2000; *Rutberg et al.*, 2005].

The samples used for this work are the sediments from the Arabian Sea cores (SS-3104G and SS-3101G) and the west flowing rivers of India. Details of the sediments have been given in chapter 2 of this thesis. Fig. 6.1 shows the location of the sediment cores (in the Arabian Sea) along with major rivers draining into the Arabian Sea and Bay of Bengal.

The objective of this work is to track the temporal variation in the provenance of sediments deposited in the eastern region of the Arabian Sea during the last ~40 ka and assess the impact of climate and surface water circulation in determining their source(s) and dispersal. This work also addresses the issue of long range transport of sediments from the Bay of Bengal to the Arabian Sea during the LGM due to intensification of NE monsoon.



Fig. 6.1: Locations of the two sediment cores analyzed in the study. Various rivers draining into the Arabian Sea and the Bay of Bengal are also shown. Core SS-3101G lies between the present day limits of the Indus and Bengal Fans. Core SS-3104G lies in the present day Deccan basaltic provenance zone and outside the limit of Indus Fan. The location of the core SS-3101G lies between the limit of Bay of Bengal fans.

6.2 Results

6.2.1 River sediments

The Sr and Nd isotopic composition in silicate fraction of river sediments are given in Table 6.1 and plotted in Fig. 6.2.
| Sample code | River | ⁸⁷ Sr/ ⁸⁶ Sr | ¹⁴³ Nd/ ¹⁴⁴ Nd | 8 _{Nd} |
|---------------|------------------|------------------------------------|--------------------------------------|-----------------|
| MH | Mahi | 0.73051 | 0.51160 | -20.3 |
| NM | Narmada | 0.72126 | 0.51203 | -11.9 |
| NM R | Narmada (Repeat) | 0.72121 | 0.51205 | -11.5 |
| TP-1 | Tapi | 0.70947 | 0.51235 | -5.7 |
| TP-2 | Tapi | 0.70961 | 0.51233 | -5.9 |
| NETHRAVATHI-1 | Nethravathi | 0.72176 | 0.51054 | -40.8 |
| NETHRAVATHI-2 | Nethravathi | 0.71507 | 0.51097 | -32.6 |
| PERIYAR-1 | Periyar | 0.72379 | 0.51130 | -26.2 |
| PERIYAR-2 | Periyar | 0.72176 | 0.51119 | -28.2 |
| KJL/2K1/M | Kajli | 0.70529 | 0.51275 | 2.2 |
| SUKH/2K1/M | Sukh | 0.70885 | 0.51257 | -1.3 |
| SUKH/2K1/M R | Sukh (Repeat) | 0.70888 | 0.51258 | -1.2 |
| VAT/2K1/M | Vashishthi | 0.70636 | 0.51258 | -1.2 |

Table 6.1: Sr and Nd isotopic composition of silicate fraction of river sediments †

[†] Sampling location details are given in Table 2.3 (Chapter 2).

The isotopic composition of river sediments, as expected, reflects those of lithologies of the region. Sediment from the Mahi river is the most radiogenic in Sr (87 Sr/ 86 Sr = 0.73051) while its ε_{Nd} is quite unradiogenic (-20.3), consistent with the lithology of the Mahi River basin that comprises of metamorphic rocks of the Aravalli Super Group, the Deccan basalts and the alluvial deposits of Pleistocene and Holocene ages. The 87 Sr/ 86 Sr and ε_{Nd} of the Narmada sediments are 0.72126 and -11.9 respectively, indicating contribution of radiogenic Sr from the Vindhyan Super Group along with unradiogenic Sr from Deccan basalts.

The Deccan basalts comprise of various formation that are distinct in their Sr and Nd isotopic composition. The northern part of the Deccan basalts consists of Poladpur, Bushe and Jawhar-Igatpuri formations that show evidence of contamination with upper crustal material. The 87 Sr/ 86 Sr of these formations range from 0.705 to 0.720, whereas the ε_{Nd} varies from -5 to -20 [*Mahoney et al.*, 2000; *Peng et al.*, 1998]. The central and south-western parts of the Deccan basalts are composed of the Ambenali and Mahabaleshwar formations that have less degree of crustal contamination. The 87 Sr/ 86 Sr and ε_{Nd} of these formations vary from

0.703 to 0.708 and +5 to -10 respectively [*Mahoney et al.*, 2000; *Peng et al.*, 1998]. The river Tapi flows through the northern areas of Deccan basalts; the Poladpur, Bushe and Jawhar-Igatpuri formations that are higher in 87 Sr/ 86 Sr and lower in ε_{Nd} . The two samples from the Tapi River yield 87 Sr/ 86 Sr of 0.70947, 0.70961 and ε_{Nd} of -5.9, -5.7; consistent with the isotopic composition of the dominant Deccan basalt formations in its drainage.



Fig. 6.2: Sr-Nd isotope plot of contemporary river sediments (silicate fraction) draining into the Arabian Sea. The isotopic composition of major end-members is also given.

The Nethravathi sediments collected in April, 2010 (Tables 6.1) have Sr isotopic composition (0.72176) and ε_{Nd} (-40.8) that are distinctively different from those in the sample collected in December, 2010 (87 Sr/ 86 Sr 0.71507; ε_{Nd} -32.6; Table 6.1). These seasonal differences can arise from variations in mixing proportions of sediments from tributaries during different seasons.

The isotopic composition of sediments of the Periyar River (87 Sr/ 86 Sr 0.72379 and 0.72176; ε_{Nd} -26.2 and -28.2; Table 6.1) is also close to that of the Nethravathi River, not unexpected considering that both of them drain Peninsular granites/gneisses. The Sr and Nd isotopic composition of sediments from the three Western Ghats streams are least radiogenic in 87 Sr/ 86 Sr (0.70529 to 0.70885) and most radiogenic in ε_{Nd} (-1.3 to 2.2), within the range reported for Deccan basalts.

6.2.2 Arabian Sea sediments

Sr and Nd concentrations and their isotopic compositions in the silicate fraction of sediments from SS-3104G and SS-3101G cores are given in Tables 6.2 and 6.3. The temporal variation in Sr and Nd concentrations and their isotopic compositions in silicate phases of cores SS-31014G and SS-3101G are shown in Figs. 6.3 and 6.4 respectively.

| Sample* | Age (ka) | \mathbf{Sr}^{\dagger} | ⁸⁷ Sr/ ⁸⁶ Sr [§] | \mathbf{Nd}^{\dagger} | 143 Nd/ 144 Nd $^{\$}$ | 8 _{Nd} |
|--------------|----------|-------------------------|---|-------------------------|----------------------------------|-----------------|
| 3104(2-3) | 1.4 | 127.4 | 0.71416 | 15.5 | 0.51216 | -9.4 |
| 3104(6-7) | 1.6 | 84.3 | 0.71689 | 25.6 | 0.51198 | -12.9 |
| 314(9-10) | 3.3 | 88.7 | 0.71667 | - | - | - |
| 3104(11-12) | 3.9 | 105.8 | 0.71521 | - | - | - |
| 3104(14-15) | 4.9 | - | - | 14.4 | 0.51209 | -10.7 |
| 3104(17-18) | 5.8 | 86.9 | 0.71651 | 12.1 | 0.51213 | -10.0 |
| 3104(19-20) | 6.5 | 85.7 | 0.71658 | 11.1 | 0.51214 | -9.6 |
| 3104(21-22) | 7.6 | 88.6 | 0.71647 | 12.3 | 0.51213 | -9.9 |
| 3104(23-24) | 8.6 | 78.4 | 0.71648 | 9.9 | 0.51213 | -9.9 |
| 3104(23-24)R | 8.6 | 78.2 | 0.71621 | 10.9 | 0.51213 | -9.9 |
| 3104(24-25) | 9.2 | 111.3 | 0.71434 | 10.2 | 0.51219 | -8.8 |
| 3104(26-27) | 10.3 | 83.5 | 0.71702 | 12.3 | 0.51215 | -9.5 |
| 3104(28-29) | 11.4 | 86.5 | 0.71779 | 7.4 | 0.51207 | -11.0 |
| 3104(30-31) | 12.5 | 83.2 | 0.71748 | 9.3 | 0.51212 | -10.2 |
| 3104(31-32) | 13.0 | 94.1 | 0.71596 | - | - | - |
| 3104(32-33) | 13.5 | 99.3 | 0.71671 | 13.5 | 0.51215 | -9.5 |
| 3104(37-38) | 15.5 | 100.1 | 0.71642 | 13.2 | 0.51214 | -9.7 |
| 3104(37-38)R | 15.5 | 100.1 | 0.71649 | 13.4 | 0.51214 | -9.7 |
| 3104(41-42) | 16.6 | 102.3 | 0.71698 | 14.0 | 0.51212 | -10.1 |
| 3104(41-42)R | 16.6 | 102.8 | 0.71687 | 14.8 | 0.51213 | -9.9 |

Table 6.2: Sr and Nd concentration and isotopic composition of core SS-3104G silicates

| 3104(44-45) | 17.4 | 96.6 | 0.71719 | 13.7 | 0.51211 | -10.3 |
|----------------|------|-------|---------|------|---------|-------|
| 3104(48-49) | 18.5 | 101.6 | 0.71773 | 14.3 | 0.51208 | -10.8 |
| 3104(52-53) | 19.6 | 98.5 | 0.71754 | 13.7 | 0.51210 | -10.5 |
| 3104(61-62) | 20.3 | 95.2 | 0.71745 | 12.6 | 0.51212 | -10.0 |
| 3104(68-69) | 20.8 | 93.6 | 0.71759 | 14.2 | 0.51214 | -9.8 |
| 3104(71-72) | 21.8 | 94.6 | 0.71788 | 12.8 | 0.51213 | -9.9 |
| 3104(74-75) | 22.8 | - | - | 14.7 | 0.51214 | -9.7 |
| 3104(77-78) | 23.8 | - | - | 13.8 | 0.51212 | -10.2 |
| 3104(80-81) | 24.8 | 91.4 | 0.71793 | 11.5 | 0.51211 | -10.2 |
| 3104(82-83) | 25.5 | - | - | 13.8 | 0.51209 | -10.6 |
| 3104(84-85) | 26.1 | 94.1 | 0.71840 | 14.0 | 0.51214 | -9.8 |
| 3104(88-89) | 26.7 | 93.8 | 0.71764 | 12.6 | 0.51213 | -10.0 |
| 3104(95-96) | 27.8 | 92.7 | 0.71708 | 8.6 | 0.51216 | -9.3 |
| 3104(95-96)R | 27.8 | 92.1 | 0.71693 | - | - | - |
| 3104(100-102) | 28.9 | 111.2 | 0.71680 | - | - | - |
| 3104(102-104) | 29.6 | 93.9 | 0.71768 | 13.9 | 0.51215 | -9.6 |
| 3104(106-108) | 30.9 | 94.9 | 0.71778 | 14.0 | 0.51214 | -9.8 |
| 3104(114-116) | 33.6 | 92.3 | 0.71785 | 13.4 | 0.51214 | -9.8 |
| 3104(116-118) | 34.3 | 112.2 | 0.71714 | - | - | - |
| 3104(122-124) | 36.1 | 98.3 | 0.71649 | 14.4 | 0.51216 | -9.3 |
| 3104(126-128) | 37.1 | 112.6 | 0.71727 | 13.5 | 0.51214 | -9.8 |
| 3104(126-128)R | 37.1 | 111.0 | 0.71721 | 12.8 | 0.51215 | -9.5 |
| 3104(132-134) | 38.6 | 94.5 | 0.71702 | 13.4 | 0.51217 | -9.0 |

-: not analysed

R: Replicate analysis

* Numbers in parenthesis are depth intervals in cm.

[†]Sr, Nd concentrations in $\mu g/g$

[§] The errors on the Sr and Nd isotopic data are better than 10 ppm ($1\sigma_{\mu}$).

In SS-3104G, which lies in the northeastern Arabian Sea off Mangalore (Fig. 6.1) the Sr and Nd concentrations range from 78 to 127 μ g/g and 7 to 26 μ g/g respectively and are generally lower than that in sediments of SS-3101G.

The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of SS-3104G (Table 6.2, Fig. 6.3) vary in a narrower range compared to SS-3101G, with most samples having ⁸⁷Sr/⁸⁶Sr between 0.716 to 0.718 and ε_{Nd} between -10.5 to -9.0. These ratios are within the range of isotopic compositions of slope sediments of west coast of India [*Kessarkar et al.*, 2003].

| Sample* | Age (ka) | \mathbf{Sr}^{\dagger} | ⁸⁷ Sr/ ⁸⁶ Sr [§] | \mathbf{Nd}^{\dagger} | 143 Nd/ 144 Nd $^{\$}$ | ٤ _{Nd} |
|---------------|----------|-------------------------|---|-------------------------|----------------------------------|-----------------|
| 3101(1-2) | 1.9 | 117.1 | 0.71631 | 19.8 | 0.51197 | -13.0 |
| 3101(6-7) | 3.3 | 156.4 | 0.71412 | 6.0 | 0.51213 | -9.8 |
| 3101(10-11) | 4.4 | 139.5 | 0.71459 | 8.7 | 0.51197 | -13.1 |
| 3101(10-11)R | 4.4 | 133.1 | 0.71501 | - | - | - |
| 3101(13-14) | 5.5 | 112.7 | 0.71686 | 13.4 | 0.51194 | -13.7 |
| 3101(16-17) | 6.7 | 98.5 | 0.71838 | 12.7 | 0.51193 | -13.8 |
| 3101(18-19) | 7.5 | 95.7 | 0.71755 | 6.5 | 0.51192 | -14.1 |
| 3101(21-22) | 8.6 | 88.0 | 0.71930 | 12.5 | 0.51190 | -14.4 |
| 3101(23-24) | 9.4 | 107.9 | 0.71768 | 12.9 | 0.51190 | -14.3 |
| 3101(26-27) | 10.6 | 96.3 | 0.71677 | 11.7 | 0.51208 | -10.9 |
| 3101(30-31) | 11.6 | 203.3 | 0.71690 | 20.0 | 0.51206 | -11.3 |
| 3101(34-35) | 12.5 | 94.1 | 0.71830 | 13.7 | 0.51204 | -11.8 |
| 3101(38-39) | 13.5 | 98.3 | 0.71753 | 45.7 | 0.51218 | -9.0 |
| 3101(41-42) | 14.5 | 100.2 | 0.71685 | 12.8 | 0.51206 | -11.2 |
| 3101(43-44) | 15.1 | 109.1 | 0.71721 | 12.3 | 0.51204 | -11.7 |
| 3101(46-47) | 16.1 | 97.9 | 0.71776 | 19.6 | 0.51203 | -11.8 |
| 3101(50-51) | 17.4 | 95.9 | 0.71906 | 13.7 | 0.51200 | -12.4 |
| 3101(53-54) | 18.3 | 117.2 | 0.71773 | - | - | - |
| 3101(59-60) | 19.1 | 101.1 | 0.72069 | 14.6 | 0.51189 | -14.6 |
| 3101(62-63) | 19.4 | 82.5 | 0.71949 | 13.4 | 0.51186 | -15.2 |
| 3101(70-71) | 20.4 | 90.4 | 0.71854 | 18.3 | 0.51196 | -13.3 |
| 3101(86-87) | 21.6 | 86.7 | 0.71920 | 17.4 | 0.51192 | -14.0 |
| 3101(90-91) | 22.3 | 101.2 | 0.71950 | 15.8 | 0.51192 | -14.1 |
| 3101(90-91)R | 22.3 | 101.9 | 0.71956 | 14.5 | 0.51190 | -14.4 |
| 3101(94-95) | 23.0 | 135.4 | 0.71805 | - | - | - |
| 3101(98-99) | 23.7 | 113.0 | 0.71864 | 13.9 | 0.51194 | -13.6 |
| 3101(102-104) | 24.5 | 101.1 | 0.71752 | 11.3 | 0.51209 | -10.7 |
| 3101(108-110) | 25.4 | 102.8 | 0.71828 | 14.6 | 0.51206 | -11.3 |
| 3101(116-118) | 26.6 | 102.9 | 0.71779 | 13.1 | 0.51210 | -10.6 |
| 3101(122-124) | 27.5 | 94.7 | 0.71850 | 13.2 | 0.51208 | -10.8 |
| 3101(126-128) | 28.1 | 96.9 | 0.71860 | 13.8 | 0.51206 | -11.3 |
| 3101(132-134) | 29.0 | 95.2 | 0.71707 | 10.4 | 0.51206 | -11.2 |

Table 6.3: Sr and Nd concentration and isotopic composition of core SS-**3101G silicates**

-: not analysed

R: Replicate analysis

* Numbers in parenthesis are depth intervals in cm. [†]Sr, Nd concentrations in μg/g

[§] The errors on the Sr and Nd isotopic data are better than 10 ppm ($1\sigma_{\mu}$).



Fig. 6.3: Temporal variation in ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ϵ_{Nd} of sediments from SS-3104G. Sr and Nd isotope composition of these sediments display a narrow range, suggesting that their sources and the mixing proportions have remained nearly the same during the last 40 ka. The markers along the x-axis of the plots show age control points in the core. The lines represent 3-point moving average of the data.

In SS-3101G, from the near equatorial region (Fig. 6.1) the Sr and Nd concentrations range from 94 to 200 μ g/g and 6 to 45 μ g/g respectively (Table 6.3). Both ⁸⁷Sr/⁸⁶Sr (0.71412 to 0.72069) and ε_{Nd} (-15.2 to -9.0) show variations with depth but with opposite trends (Figs. 6.4a, b).

The concomitant temporal changes in both 87 Sr/ 86 Sr and ε_{Nd} in SS-3101G (Figs. 6.4a, b) and the observation that their range is much larger than the average analytical uncertainty leads to infer that these variations represent source variability and/or their mixing proportions. Therefore, the data from these two cores serve as a proxy to track variations in their provenance.



Fig. 6.4: ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of sediments of core SS-3101G. The data show significant temporal variation which correlate with known climatic/monsoon variability (c) [*Herzschuh*, 2006]. Sr and Nd isotope compositions of these sediments display two excursions during ~20 and ~9 ka coinciding with LGM and intensified SW monsoon respectively. The lines in (a) and (b) are 3-point moving average of the data respectively and the markers along the x-axis of the plots show age control points in the core. Line in (d) is 3-point moving average of ε_{Nd} values form the Indus delta [*Clift et al.*, 2008].

6.3 Discussion

The Sr and Nd isotopic composition of river sediments supplied to the Arabian Sea are given in Fig. 6.2. The data demonstrate the impact of various lithologies drained by these rivers in determining the isotopic composition of their sediments. The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} values of the two Arabian Sea cores along with those of their potential sources, the Deccan basalts, the higher and lesser Himalaya, the Vindhyan Super Group and the Peninsular granites/gneisses are presented in an isotopic mixing diagram (Fig. 6.5). Sr and Nd isotopic composition of these sources (Fig. 6.5, Table 6.4) are from published literature [*Ahmad et al.*, 2009; *Chakrabarti et al.*, 2007; *Clift et al.*, 2002 ; *Clift et al.*, 2008; *Clift et al.*, 2010 ; *Harris et al.*, 1994; *Peucat et al.*, 1989; *Singh et al.*, 2008 ; *Tripathy et al.*, 2011; *Tripathy*, 2011].



Fig. 6.5: Sr and Nd isotope compositions of SS-3101G and SS-3104G sediments and their potential sources in two isotope mixing plot. Sediments of the core SS-3104G show very limited variation. Sr and Nd isotopic composition of SS-3101G sediments show wider range. Various lithologies used as end-members are: D, Deccan basalts; V, Vindhyan Super Group; P, Peninsular granites/gneisses; HHC, Higher Himalayan Crystalline; LHS, Lesser Himalayan Silicates.

| | ⁸⁷ Sr/ ⁸⁶ Sr | | | E _{Nd} | | | |
|-------------------------------------|------------------------------------|------|---------|-----------------|-----|---------|--|
| Endmembers | Rar | nge | Typical | Ra | nge | Typical | |
| <u>Himalaya</u> | | | | | | | |
| \mathbf{TSS}^{\dagger} | 0.72 | 0.74 | 0.73 | -15 | -12 | -13 | |
| \mathbf{HHC}^{\dagger} | 0.73 | 0.79 | 0.76 | -16 | -14 | -15 | |
| LH silicate [†] | 0.76 | 0.94 | 0.85 | -25 | -24 | -25 | |
| Siwaliks [†] | 0.72 | 0.76 | 0.74 | -18 | -16 | -17 | |
| <u>Peninsular India</u> | | | | | | | |
| Deccan Basalt † | 0.70 | 0.72 | 0.71 | -13 | 5 | -5 | |
| Vindhyan ^{€¥} | | | 0.90 | -34 | -14 | -19 | |
| Peninsular Gneiss ^{# §} | 0.70 | 0.73 | 0.71 | -8 | -45 | -29 | |
| Contemporary River sedin | nents | | | | | | |
| West flowing ^{††} | | | | | | | |
| Mahi | | | 0.73 | | | -20 | |
| Narmada | | | 0.72 | | | -12 | |
| Тарі | | | 0.71 | | | -6 | |
| Nethravathi | | | 0.72 | -41 | -33 | -37 | |
| Periyar | | | 0.72 | -26 | -28 | -27 | |
| Kajli | | | 0.71 | | | 2 | |
| Sukh | | | 0.71 | | | -1 | |
| Vashishthi | | | 0.71 | | | -1 | |
| East flowing [*] | | | | | | | |
| Pennar | | | 0.76 | -24 | -22 | -23 | |
| Godavari | | | 0.72 | -18 | 15 | -16 | |
| Krishna | | | 0.72 | -13 | 12 | -12 | |
| <u>Himalayan</u> | | | | | | | |
| Indus ^{##} §§ €€ | | | 0.72 | | | -15 | |
| Brahmaputra ^{†††} | | | 0.73 | | | -14 | |
| Ganga [†] | | | 0.76 | | | -16 | |
| Marine Sediments | | | | | | | |
| Bengal Fan sediments ^{§§§} | | | 0.74 | | | -16 | |
| Western Bay of Bengal ^{\$} | | | | | | | |
| Glacial | | | 0.73 | | | -14 | |
| Holocene IMP | | | 0.74 | | | -16 | |

Table 6.4: 87 Sr/ 86 Sr and ϵ_{Nd} of potential end members

The role of Indus as the source of sediments in the eastern Arabian Sea is debated. Based on clay mineralogical study, *Kessarkar et al.*, [2003] suggest that the penetration of Indus sediments is restricted to the north of Saurashtra (~20°N), whereas, *Ramaswamy and Nair*, [1989] suggests that longshore current helps Indus sediments to be transported to the south of Mangalore.

In addition to riverine particulates, another source of sediments to the Arabian Sea is aeolian dust from the deserts of Arabia [*Kolla et al.*, 1976; *Sirocko and Sarnthein*, 1989]. The magnitude of supply of dust has been reported to vary with time with enhanced contribution during the LGM [*Harrison et al.*, 2001; *Petit et al.*, 1999; *Reichart et al.*, 1997; *Sirocko et al.*, 2000]. The Sr and Nd isotopic composition of aeolian dust over the western Arabian Sea is characterized by unradiogenic Sr (87 Sr/ 86 Sr = 0.709) and radiogenic Nd ($\epsilon_{Nd} = -6$) [*Sirocko*, 1995]. The Sr and Nd isotopic composition of dust falls within the range of Deccan basalts and if dust with such isotopic composition also deposits over the eastern Arabian Sea it is difficult to differentiate between aeolian dust and sediments sourced from basalts and assess their contribution. However, there have been earlier studies in the eastern Arabian Sea which suggest that aeolian dust is not a significant contributor of sediments to this area [*Kessarkar et al.*, 2003; *Kolla et al.*, 1976; *Sirocko and Sarnthein*, 1989].

6.3.1 Core SS-3104G

The sediments of SS-3104G have 87 Sr/ 86 Sr and ε_{Nd} within a narrow range defined by the contemporary sediments of the Indus, Narmada, Tapi and other Western Ghats streams suggesting that all these rivers are potential sources of silicate sediments to this core site Despite the proximity of Nethravathi River to the SS-3104G core site, its contribution and hence that from the Peninsular granites/gneisses to this core site seems minor. This inference is based upon the highly depleted ε_{Nd} values of the Nethravathi sediments and the observation that at present the Nethravathi River supplies only ~1 million tons of sediments annually to the Arabian Sea [*Panda et al.*, 2011]. The limited range in Sr and Nd isotopic composition throughout the length of this core covering a time span of ~40 ka also leads us to infer that the provenance of sediments and their mixing proportion have remained nearly the same during this period. The reason for the lower 87 Sr/ 86 Sr in the (2-3) cm and ε_{Nd} in the (6-7) cm sections of SS-3104G (Table 6.2), however, is unclear.

6.3.2 Core SS-3101G

The Sr and Nd isotopic composition of SS-3101G silicates displays wider range than those in SS-3104G with two excursions at ~9 ka and ~20 ka (Figs. 6.4a, b). The lower bound of ⁸⁷Sr/⁸⁶Sr (i.e. the lowest values of ⁸⁷Sr/⁸⁶Sr) and the upper bound of ε_{Nd} (i.e. the most radiogenic values of ε_{Nd}) of SS-3101G is similar to that observed for the core SS-3104G. Thus, the ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of core SS-3104G can be considered to represent the baseline values of Sr and Nd isotopic composition of SS-3101G sediments. This in turn would suggest that Deccan basalts and the Vindhyan Super Group are the dominant sources of sediments to this core, delivered through the Narmada and the Tapi rivers. In addition, there has to be enhanced relative contribution of sediments with more radiogenic Sr and unradiogenic Nd to account for the excursion in its isotopic composition during ~9ka and ~20ka (Fig. 6.4).

The excursions in the Sr and Nd isotopic composition of SS-3101G core overlaps with the known climatic (monsoon) variations in the Asian region (Fig. 6.4c), [*Herzschuh*, 2006]. The timing of the first excursion in the Sr and Nd isotopic data at ~20 ka corresponds to the well known Last Glacial Maximum (LGM) whereas the excursion at ~9 ka overlaps with the known intensification of SW monsoon precipitation [*Fleitmann et al.*, 2003; *Herzschuh*, 2006; *Prell and Kutzbach*, 1987; *Sinha et al.*, 2005]. It is clear from the observed interrelations between Sr-Nd isotopic composition and monsoon variations (Fig. 6.4), that climate exerts a significant control on the erosion patterns and sediment fluxes from different sources depositing at this core location and their mixing proportions.

6.3.2.1 Provenance of sediments during Last Glacial Maximum (LGM)

The Sr and Nd isotopic composition in SS-3101G during LGM show a peak in 87 Sr/ 86 Sr and a dip in ε_{Nd} (Figs. 6.4a, b) with values similar to that from sediments of the western Bay of Bengal during LGM [*Tripathy et al.*, 2011]. Potential sources that can contribute to the Sr and Nd excursions during LGM are relative increase in (i) Himalayan sediments and/or (ii) Peninsular granites/gneisses, both of which are characterized by higher radiogenic Sr and low ε_{Nd} composition.

It is known that during LGM there was decrease in SW monsoon precipitation and increase in NE monsoon [*Herzschuh*, 2006]. The intensification of NE monsoon with concomitant decrease in SW monsoon during LGM would promote strengthening of southwestward East Indian Coastal Current (EICC) in the Bay of Bengal. This in turn would enhance the flow of waters from the Bay of Bengal to the Arabian Sea [*Schott and McCreary*, 2001; *Shankar et al.*, 2002]. Such enhanced transport of Bay of Bengal waters to the south eastern Arabian Sea during LGM is documented in the oxygen isotopic composition of foraminifera deposited during this period [*Sarkar et al.*, 1990; *Tiwari et al.*, 2005].

The observation that the isotopic composition of LGM stratum in SS-3101G is similar to those in western Bay of Bengal [*Tripathy et al.*, 2011], that there is enhanced flow of low salinity water from Bay of Bengal to southeastern Arabian Sea during this period and that the existence of sediment plumes in the coastal and open Bay of Bengal [*Sridhar et al.*, 2008a,b; *Rajawat et al.*, 2005] is an indication that sediments from the western Bay of Bengal may be transported to this core site. However, clay mineral studies of sediments from southeastern Arabian Sea have yielded divergent conclusions; *Kessarkar et al.* [2003] suggest that the sediments of the southeastern Arabian Sea largely represent hinterland flux and are not influenced by sediments transported from the Bay of Bengal waters during the intensification of NE monsoon. In contrast, *Chauhan and Gujar* [1996] and *Chauhan et al.* [2010] argue in favour of sediment transport from Bay of Bengal during intensification of NE monsoon.

If sediments from the western Bay of Bengal are indeed the cause of Sr and Nd isotopic excursion, then based on a two end-member mixing model, it can be estimated that during LGM about one-fifth of sediments in SS-3101G are from western Bay of Bengal, the balance being of SS-3104G composition.



Fig. 6.6: The surface currents in the Arabian Sea during the monsoon. The arrows indicate the direction of surface currents during the intensification of (a) North-East monsoon and (b) South-West monsoon; [Schott and McCreary, 2001; Shankar et al., 2002; Wyrtki, 1973]. NMC, North-East Monsoon Current; SMC, South-West Monsoon Current; EICC, East India Coastal Current; WICC, West India Coastal Current.

Alternatively, considerably enhanced contribution of sediments sourced from Peninsular granites/gneisses (e.g. through the Nethravathi, Periyar rivers) can also explain the isotopic excursions. This however seems unlikely considering that at present these rivers account for only a very small fraction of sediments to the south-eastern region of the Arabian Sea [*Chandramohan and Balchand*, 2007, *Nair et al.*, 2003, *Panda et al.*, 2011] and the observation of *Ramaswamy and Nair*, [1989] that much of sediments from the peninsular rivers are retained in the western shelf of India peninsula.

6.3.2.2 Provenance of sediments during Holocene Intensified Monsoon Phase (IMP)

The core SS-3101G shows a second excursion in Sr and Nd isotopic composition during ~9 ka, coinciding with higher SW monsoon precipitation phase commonly known as the Holocene Intensified Monsoon Phase (IMP) [Fleitmann et al., 2003; Herzschuh, 2006; Prell and Kutzbach, 1987]. Based on the mixing diagram (Fig. 6.5), this excursion also require enhanced contribution of sediments with more radiogenic Sr and unradiogenic Nd analogous to that needed to explain the LGM data. This requirement is intriguing considering that the monsoon trend was opposite during the two periods; SW monsoon being intense during ~9 ka whereas, NE monsoon was more pronounced during ~20 ka. More intense SW monsoon during Holocene IMP would constrain the North-East monsoon current (Fig. 6.6) and therefore ensuing flow of water from the Bay of Bengal to the Arabian Sea. In such a case, supply of sediments from the Bay of Bengal to the Arabian Sea to account for the isotopic excursion at ~9 ka would also be restricted. Further, as was the case during LGM, peninsular rivers as a major source also seems unlikely unless their sediment flux during Holocene IMP was significantly higher and the sediments were transported efficiently to the core site. Two lines of evidence based on contemporary information indicate that these requirements may not be fulfilled. These are (i) during Holocene IMP, the sea level was similar to that at present, therefore, the efficiency of shelf storage of sediments is expected to be similar to that of today [Siddall et al., 2003] and (ii) the clay mineralogy of sediment trap samples indicate that sediments from west flowing peninsular rivers are by and large retained in the shelf region of the Arabian Sea [*Ramaswamy and Nair*, 1989]. The Narmada and Tapi rivers are the other major suppliers of sediments to the Arabian Sea. The discharge of these rivers is dictated by SW monsoon and therefore they could transport more sediment during intensification of SW monsoon. However, these sediments cannot explain the observed magnitude in isotopic excursion if their isotopic composition was the same as those measured in this study (Table 6.6); the ε_{Nd} values of the Narmada and Tapi sediments are about -11.5 and -5.8 respectively, which are significantly more radiogenic than the values for core SS-3101G at Holocene IMP (-14).

The Sr and Nd isotopic composition of SS-3101G display variations similar to those reported for the Indus delta during the past ~14 ka (ε_{Nd} ; Fig. 6.4d) [Clift et al., 2008; Clift et al., 2010] with both of them showing excursions in ⁸⁷Sr/⁸⁶Sr and ε_{Nd} during ~9 ka. The similarity in the Sr and Nd isotopic composition and their temporal pattern hints at the possibility of supply of Indus delta sediments to the SS-3101G core site. The more radiogenic 87 Sr/ 86 Sr and lesser ε_{Nd} during ~9 ka in the core SS-3101G can be explained in terms of enhanced sediment supply through the Himalayan tributaries of the Indus. This can result from intensification of SW monsoon precipitation over the Himalaya during this period [Clift et al., 2008; Clift et al., 2010]. The intensification of SW monsoon during ~9 ka resulted in stronger surface currents in the southeast direction from the Arabian Sea to the Bay of Bengal (Fig. 6.6). The strengthening of this current would result in enhanced southeastward transport of water and sediments from the Arabian Sea to Bay of Bengal. The core SS-3101G lies to the east of Chagos-Laccadive ridge with the presence of sill adjacent to the core location that can facilitate transfer of sediments across the ridge by surface currents. Thus, Sr and Nd isotopic excursions observed during ~9 ka in the core SS-3101G can be a result of increased sediment supply from the Himalayan sources by the Indus tributaries. Based on the Nd isotopic data of sediments of the Indus delta, and that of the Arabian Sea sediments and two endmember mixing calculation, it can be estimated that during the Holocene IMP, about 15% of sediments at the SS-3101G

location are derived from the Indus delta. This interpretation, however, rests on the premise that the sediment flux from the peninsular rivers during ~9 ka was the same as that at present and that much of the flux is retained in the shelf. If such a premise is proven to be invalid then the isotopic excursion in SS-3101G during ~9 ka may also result from sediment supply of peninsular rivers.

Such a contribution from Indus at ~9 ka to core SS-3104G can be ruled out on the basis that presently, the location of the core SS-3104G is dominated by sediments brought by the Narmada and Tapi River from the Deccan basalts and Vindhyan ranges [*Kolla et al.*, 1976]. Even during the intensification of SW monsoon during ~9 ka the Deccan contribution at the core site would increase due to more rainfall on the Western Ghats and the transfer of sediments to the location of core SS-3104G.

It is clear from the above discussion that in addition to climate, ocean circulation also plays an important role in sediment dispersal and their deposition as has been documented in the deposition of Meiji drift in the Pacific Ocean [*VanLaningham et al.*, 2009].

6.4 Conclusions

Temporal variations in Sr and Nd isotopic composition of silicate component of two well dated sediment cores from the eastern Arabian Sea have been determined. Sr and Nd isotopic compositions of sediments from the more northern core (SS-3104G) display narrow ranges indicating only minor variations in their source proportion since last ~40 ka. Even the flux of aeolian dust has changed very little over the eastern Arabian Sea during last ~40 ka remaining almost consistent during this time. In contrast, the results of the southeastern Arabian Sea core (SS-3101G) exhibit two excursions in the isotopic composition coinciding with two major climate change events; LGM and Holocene Intensified Monsoon Phase (IMP). This correlation suggests significant control of climate/monsoon on erosion pattern and sedimentation. Sediment supply is controlled by climatic variability whereas its dispersal is controlled by circulation pattern of the surface

ocean. The Sr and Nd isotopic excursion at ~20 ka is attributed to enhanced sediment contribution from the Bay of Bengal resulting from strengthened NE monsoon which boosts N-S coastal current in the western Bay of Bengal, transporting water and sediments, the later with higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} . In contrast, intensified SW monsoon precipitation during ~9 ka enhanced sediment transfer from the Indus delta to the southeastern Arabian Sea enabling sediment transfer from the Arabian Sea to Bay of Bengal. This work demonstrates that the Sr and Nd isotopic composition in the silicate fraction of the Arabian Sea sediments has the potential to track the variation in the intensity and pattern of the Indian monsoon system.

CHAPTER 7

Summary and future perspectives

The major goals of this thesis were to study the processes related to ocean circulation, aeolian dust deposition, behaviour of redox sensitive elements and dispersal of sediments in the northern Indian Ocean, especially the Arabian Sea. These goals were accomplished by the studying the spatio-temporal variations in the concentration and isotopic composition of trace elements in the aqueous and sedimentary reservoirs of the Arabian Sea. Nd concentration and its isotopic composition (ε_{Nd}) in the water column of the Arabian Sea along with inverse modelling approach were used to quantify the water masses in the Arabian Sea. Further, lateral and vertical distribution of the dissolved redox sensitive elements Re, U and Mo was studied from several vertical profiles within and outside the zone of intense denitrification in the Arabian Sea. The focus of this work was to assess the role of suboxic/denitrifying water column of the Arabian Sea in influencing the water column distribution of these elements. In addition, the temporal evolution of ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater was studied to assess the impact of paleo-weathering and ocean circulation in influencing the Os isotopic inventory of the Arabian Sea on a glacial-interglacial timescale. Efforts were also made to use the Sr-Nd isotopic composition of silicate fraction of sediments from the south-eastern Arabian Sea to reconstruct temporal variation in their provenances, and their controlling factors. The major outcomes of this thesis have been summarized in the following section.

7.1 Nd and ε_{Nd} of waters from Arabian Sea: quantification of water masses and estimation of dust flux using inverse model approach

The distribution of dissolved Nd concentration and its ε_{Nd} in the waters of the Arabian Sea exhibit significant lateral and vertical variations. In the Arabian Sea, at ~14.5°N, the vertical profile of Nd isotopic composition shows radiogenic values of -7 to -10. Similar ε_{Nd} values were observed at ~10°N. Contrary to this, the ε_{Nd} of the waters from southern station 0805 (in the periphery of Bay of Bengal), are quite non-radiogenic. This suggests a significant contribution of Nd from Bay of Bengal indicating the inter-basin exchange of water between the Arabian Sea and Bay of Bengal at the south-eastern periphery.

Inverse model calculation of Nd concentration, ε_{Nd} , salinity and temperature data of the waters of the Arabian Sea suggest transport of low salinity waters from the Bay of Bengal to the Arabian Sea during the sampling period. The Intermediate waters in the Arabian Sea are significantly composed of NIIW and NIDW. The contribution of NIIW is more significant in the Arabian Sea north of 10°N, while the existence of NIDW is more representative of intermediate waters in the Arabian Sea at around 8°N. The deeper waters in the Arabian Sea, MNADW and AABW both show a transport from north to south in the Arabian Sea waters, suggesting a more northward progression of these water masses in the Arabian Sea after their entry in the basin from the Somali basin. The return of these deeper water masses towards the south in the Arabian Sea takes place along the western flange of the Chagos-Laccadive ridge. The presence of Chagos-Laccadive ridge significantly reduces the flow of deeper water masses (MNADW and AABW) from the Arabian Sea to the Bay of Bengal.

The Nd_{excess} (Nd content of water other than that from the mixing of water masses) in the Arabian Sea computed from the inverse modelling shows significant additional input of Nd to the surface waters at the location of stations 0802 and 0803 in the Arabian Sea. The ε_{Nd} of this Nd_{excess} supply was obtained to be around -6 at stations 0802, similar to that of the dust depositing over the Arabian Sea. This inference highlights the significance of dust deposition from the nearby landmass in modifying the Nd content and isotopic composition of surface waters of the Arabian Sea. Based upon Nd_{excess} signature in surface waters of the Arabian Sea, the dust deposition flux in this oceanic basin was estimated to be 8 ± 2 g m⁻² y⁻¹. Nd distribution in the water column of station 0805 is affected by release from sinking particles of the Bay of Bengal origin.

7.2 Distribution of Re, U and Mo in the Arabian Sea

The concentration of redox sensitive elements was measured in the water columns of the Arabian Sea. The dissolved Re, U and Mo concentrations from the oxic and suboxic layers of the Arabian Sea show that these elements behave conservatively in the water column. The findings of this study suggest that there is no discernable removal of Re, U or Mo from the suboxic and denitrifying layers of the Arabian Sea. Rather, the distribution of Re, U and Mo in the waters of the Arabian Sea show a dominant control of salinity. The concentrations of Re, U and Mo in the water column of the Arabian Sea vary as a function of salinity. Comparison of the concentrations of Re, U and Mo in the water column of the Arabian Sea with data from other oceanic regions shows that they overlap with each other for the same salinity. This suggests that the distribution of Re, U and Mo behave conservatively in the water columns of the Arabian Sea, even in the oxygen minimum zone. The similarity of dissolved Re, U and Mo concentrations in the water column of Arabian Sea (with high biogenic debris through the water column) and the Bay of Bengal (with high detrital flux through the water column) suggest that even the high flux and/or nature of particles do not affect the distribution of these elements. The salinity-concentration link further supports that the distribution of these elements is governed by the physical processes of advection and mixing between water masses and evaporation and not by biogeochemical processes related to denitrification operating in the water column.

7.3 Temporal evolution of ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater

The Os isotopic composition of Arabian seawater over the past shows a correlation with the climate. The ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater is similar to that of the global oceans since last 30 ka except during the LGM. The ¹⁸⁷Os/¹⁸⁸Os of the Arabian seawater decouples from other oceanic records during LGM, experiencing an excursion towards higher values. Further, the Re content of the sediments as well as the Os concentration of the leachable fraction of the sediments was also higher during the LGM. The observed increase in Re and Os contents during the LGM are due to anoxic/suboxic conditions in the deeper waters of the Arabian Sea basin during that time. As the productivity in the Arabian Sea was lower during the LGM, the anoxic/suboxic conditions were caused by the decrease in the oxygen content of the deep Water (NADW) into the Arabian Sea.

7.4 Temporal variation in $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} of the sediments of eastern Arabian Sea

As a part of this thesis work, sediments from two well dated cores from the eastern Arabian Sea have been analyzed to study their Sr and Nd isotopic compositions in silicate phases. Sr and Nd isotopic compositions of sediments from the more northern core (SS-3104G; 12.8°N, 71.7°E) display narrow ranges indicating only minor variations in their source proportion since last ~40 ka. Even the flux of aeolian dust has changed very little over the eastern Arabian Sea for the last ~40 ka. In contrast, the results on the Sr and Nd isotopic composition in the south-eastern Arabian Sea core (SS-3101G; 6.0°N, 74.0°E) exhibit two excursions in these isotopic composition coinciding with two major climate change events; the LGM and the Holocene Intensified Monsoon Phase (IMP). This correlation suggests significant control of climate/monsoon on erosion pattern and deposition of sediments in the Arabian Sea. Sediment supply to the ocean is controlled by climatic variability whereas its dispersal is controlled by circulation pattern of the surface ocean.

The Sr and Nd isotopic excursion at ~20 ka has been linked to enhanced sediment contribution from the Bay of Bengal resulting from strengthened NE monsoon. This resulted in strengthening of N-S coastal current in the western Bay of Bengal, transporting water and sediments, the later with higher 87 Sr/ 86 Sr and lower ϵ_{Nd} from Bay of Bengal to the Arabian Sea. In contrast, intensified SW monsoon precipitation during ~9 ka enhanced sediment transfer from the Indus delta to the southeastern Arabian Sea enabling sediment transfer from the Arabian Sea to Bay of Bengal. The Sr and Nd isotopic variations in the sediments from the Arabian Sea and their association with the climatic changes demonstrate that the Sr and Nd isotopic composition of these sediments have the potential to track the variation in the intensity and pattern of the Indian monsoon system.

7.5 Future Perspectives

Studies carried out towards this thesis have addressed the issues related to ocean circulation, aeolian dust deposition, behaviour of redox sensitive trace elements

and, Os isotope evolution and dispersal and deposition of sediments in the Arabian Sea. Results of this thesis indicate few interesting scientific problems which need to be addressed in future. These have been listed as follows:

(i) In this thesis, the Nd concentration and its isotopic composition were analyzed in the water columns of the eastern Arabian Sea. Very little information is available regarding the Nd budget in the western Arabian Sea. A detail study of Nd concentration and its isotope composition in water column of the western and central Arabian Sea will be required to study the pathways of deep and bottom water (NADW and AABW) in the Arabian Sea.

(ii) The Re, U and Mo distribution in the water column of the Arabian Sea shows a conservative nature with no removal from the intermediate suboxic layers. However, the sediments of the Arabian Sea are found to be enriched in these elements. Further investigations on the pore water abundances of Re, U and Mo are required to better understand and characterize the mechanism of their removal from waters to the sediments of the Arabian Sea. A large area on the western shelf of India develops an intense seasonal hypoxia with the presence of H₂S [*Naqvi et al.*, 2000]. In this region, presence of H₂S in the water column has been detected. Behavior of redox sensitive elements needs to be characterized in such regions of the Arabian Sea.

(iii) This study displays the conservative nature of Mo in the OMZ of the Arabian Sea despite the fact that it acts as a metal cofactor in marine biological cycles. It could be due to high concentration of Mo in seawater. Mo isotopes should be studied in the OMZ of the Arabian Sea to understand its internal cycling.

(iv) The Sr and Nd isotopic composition of sediments from the core SS-3101G in the south-eastern Arabian Sea show significant provenance changes during the LGM and the Holocene IMP, confirming an erosion-climate link over a millennial timescale. As the majority of detrital material/sediments are carried to the ocean by rivers; it is logical to expect a similar change in provenance of sediments in river basins draining multi-lithological terrains. Further investigations on the temporal variations in the Sr and Nd isotopic compositions of river sediments would provide insights of the changes in provenance of riverine sediments. Thus, in future, it will be interesting to employ Sr and Nd isotopes to reconstruct the past changes in provenances of river sediments, particularly that of the Ganga, Brahmaputra, Indus and the Godavari Rivers close to their mouths.

REFERENCES

- Agnihotri, R. (2001), Chemical and isotopic studies of sediments from the Arabian Sea and Bay of Bengal, *PhD. Thesis*, MLSU.
- Agnihotri, R., M. M. Sarin, B. L. K. Somayajulu, A. J. T. Jull, and G. S. Burr (2003), Late-Quaternary biogenic productivity and organic carbon deposition in the eastern Arabian Sea, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 197, 43-60.
- Ahmad, S. M., G. A. Babu, V. M. Padmakumari, A. M. Dayal, B. S. Sukhija, and P. Nagabhushanam. (2005), Sr, Nd isotopic evidence of terrigenous flux variations in the Bay of Bengal: Implications of monsoons during the last 34,000 years, *Geophys. Res. Lett.*, 32.
- Ahmad, S. M., V. M. Padmakumari, and G. A. Babu (2009), Strontium and neodymium isotopic compositions in sediments from Godavari, Krishna and Pennar rivers, *Curr. Sci.*, 97, 1766-1769.
- Alagarsamy, R., and J. Zhang (2005), Comparative studies on trace metal geochemistry in Indian and Chinese rivers, *Curr. Sci.*, 89, 299-309.
- Allègre, C. J., J. L. Birck, F. Capmas, and V. Courtillot (1999), Age of the Deccan traps using ¹⁸⁷Re-¹⁸⁷Os systematics, *Earth Planet Sci. Lett.*, 170, 197-204.
- Allègre, C. J., P. Louvat, J. Gaillardet, L. Meynadier, S. Rad, and F. Capmas (2010), The fundamental role of island arc weathering in the oceanic Sr isotope budget, *Earth Planet Sci. Lett.*, 292, 51-56.
- Amakawa, H., D. S. Alibo, and Y. Nozaki (2000), Nd isotopic composition and REE pattern in the surface waters of the eastern Indian Ocean and its adjacent seas, *Geochim. Cosmochim. Acta*, 64, 1715–1727.
- Anbar, A. D., R. A. Creaser, D. A. Papanstassiou, and G. J. Wasserburg (1992), Rhenium in seawater: confirmation of generally conservative behavior, *Geochim. Cosmochim. Acta*, 56, 4099-4104.
- Anderson, R. F., M. Q. Fleisher, and A. P. LeHuray (1989), Concentration, oxidation state, and particluate flux of uranium in the Black Sea, *Geochim. Cosmochim. Acta*, 53, 2215-2224.

- Bange, H. W., S. W. A. Naqvi, and L. A. Codispoti (2005), The nitrogen cycle in the Arabian Sea, *Prog. Oceanogr.*, 65, 145-158.
- Bertram, C. J., and H. Elderfield (1993), The geochemical balance of the rare earth elements and neodymium isotopes in the oceans, *Geochim. Cosmochim. Acta*, 57, 1957-1986.
- Birck, J. L., M. Roy Barman, and F. Capmas (1997), Re-Os isotopic measurements at the Femtomole level in natural samples, *Geostand. Newslett.*, 20, 19-27
- Borole, D. V., S. Krishnaswami, and B. L. K. Somayajulu (1982), Uranium isotopes in rivers, estuaries and adjacent coastal sediments of eastern India: their weathering, transport and oceanic budget, *Geochim. Cosmochim. Acta*, 46, 125-137.
- Bralower, T. J., P. D. Fullagar, T. A. McCay, K. G. MacLeod, J. Bergen, and E. Zapata (2004), Strontium isotope stratigraphy of Crataceous sediments at sites 1183 and 1186, Ontong Java plateau, in *Proceedings of the Ocean Drilling Program, Scientific Results* edited by J. G. Fitton, et al., pp. 1-19.
- Bruland, K. W., and M. C. Lohan (2003), Controls of Trace Metals in Seawater, in *Treatise on Geochemistry: The Oceans and Marine Geochemistry*, edited by H. Elderfield, Elsevier Pergamon.
- Burbank, D. W., A. E. Blythe, J. Putkonen, B. Pratt-Sitaula, E. Gabet, M. Oskin, A. Barros, and T. P. Ojha (2003), Decoupling of erosion and precipitation in the Himalayas, *Nature*, 426, 652-655.
- Chakrabarti, R., A. R. Basu, and A. Chakrabarti (2007), Trace element and Ndisotopic evidence for sediment sources in the mid-Proterozoic Vindhyan Basin, central India, *Precamb. Res.*, 159, 260-274.
- Chandramohan, T., and A. N. Balchand (2007), Regional sediment yield pattern for the west flowing rivers of Kerala state, India, *RMZ Mater*. *Geoenviron.*, 54, 501–511.
- Chauhan, O. S., A. M. Dayal, N. Basavaiah, and U. Syed Abdul Kader (2010), Indian summer monsoon and winter hydrographic variations over past millennia resolved by clay sedimentation, *Geochem. Geophys. Geosyst.*, 11, Q09009.
- Chauhan, O. S., and A. R. Gujar (1996), Surficial clay mineral distribution on the southwestern continental margin of India: Evidence of input from the Bay of Bengal, *Cont. Shelf Res.*, 16, 321-333.

- Chen, J.H., R. L. Edwards, G. J. Wasserburg (1986), ²³⁸U, ²³⁴U and ²³²Th in seawater, *Earth Planet. Sci. Lett.*, 80, 241–251.
- Clift, P. D., J. I. Lee, P. Hildebrand, N. Shimizu, G. D. Layne, J. Blusztajn, J. D. Blum, E. Garzanti, and A. A. Khan (2002), Nd and Pb isotope variability in the Indus River System: implications for sediment provenance and crustal heterogeneity in the Western Himalaya, *Earth Planet. Sci. Lett.*, 200, 91-106.
- Clift, P. D., L. Giosan, A. Carter, E. Garzanti, V. Galy, A. R. Tabrez, M. Pringle, I. H. Campbell, C. France-Lanord, J. Blusztajn, C. Allen, A. Alizai, A. Lückage, M. Danish, and M. M. Rabbani (2010), Monsoon control over erosion patterns in the Western Himalaya: possible feed-back into the tectonic evolution, *in Monsoon Evolution and Tectonics–Climate Linkage in East Asia*, edited by P. D. Clift, R. Tada, and H. Zheng, pp. 185-218, Geological Society of London (special publication), London.
- Clift, P. D., L. Giosan, J. Blusztajn, H. Campbell, C. Allen, M. Pringle, A. R. Tabrez, M. Danish, M. M. Rabbani, A. Alizai, A. Carter, and A. Lückage (2008), Holocene erosion of Lesser Himalaya triggered by intensified summer monsoon, *Geology*, 36, 79-82.
- Colin, C., L. Turpin, J. Bertaux, A. Desprairies, and C. Kissel (1999), Erosional history of the Himalayan and Burman ranges during the last two glacialinterglacial cycles, *Earth Planet. Sci. Lett.*, 171, 647-660.
- Collier, R. W. (1985), Molybdenum in the Northeast Pacific Ocean, *Limnol. Oceanogr.*, 30(6), 1351-1354.
- Colodner, D., J. Edmond, and E. Boyle (1995), Rhenium in the Black Sea: comparison with molybdenum and uranium, *Earth Planet Sci. Lett.*, 131, 1-15.
- Colodner, D., J. Sachs, G. Ravizza, K. Turekian, J. Edmond, and E. Boyle (1993), The geochemical cycle of rhenium: a reconnaissance, *Earth Planet Sci. Lett.*, 117, 205-221.
- Creaser, R. A., D. A. Papanastassiou, and G. J. Wasserburg (1991), Negative thermal ion mass spectrometry of osmium, rhenium and iridium, *Geochim. Cosmochim. Acta*, 55, 397-401
- Crusius, J., S. Calve, T. Pedersen, and D. Sage (1996), Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition, *Earth Planet Sci. Lett.*, 145, 65-78.

- Crusius, J., T. F. Pedersen, S. E. Calvert, G. L. Cowie, and T. Oba (1999), A 36 kyr geochemical record from the Sea of Japan of organic matter flux variations and changes in intermediate water oxygen concentrations, *Paleoceanography*, 14, 248-259.
- Dalai, T. K., K. Suzuki, M. Minagawa, and Y. Nozaki (2005), Variations in seawater osmium isotope composition since the last glacial maximum: A case study from the Japan Sea, *Chem. Geo.*, 220 303-314.
- Dalai, T. K., S. K. Singh, J. R. Trivedi, and S. Krishnaswami (2002), Dissolved rhenium in the Yamuna River System and the Ganga in the Himalaya: role of black shale weathering on the budgets of Re, Os, and U in rivers and CO₂ in the atmosphere, *Geochim. Cosmochim. Acta*, 66, 29-43.
- Das, A., S. Krishnaswami, M. M. Sarin, and K. Pande (2005), Chemical weathering in the Krishna Basin and Western Ghats of the Deccan Traps, India: Rates of basalt weathering and their controls, *Geochim. Cosmochim. Acta*, 69, 2067-2084.
- Duce, R. A., P. S. Liss, J. T. Merrill, E. L. Atlas, P. Buat-Menard, B. B. Hicks, J. M. Miller, J. M. Prospero, R. Arimoto, T. M. Church, W. Ellis, J. N. Galloway, L. Hansen, T. D. Jickells, A. H. Knap, K. H. Reinhardt, B. Schneider, A. Soudine, J. J. Tokos, S. Tsunogi, R. Wollast, and M. Zhou (1991), The atmospheric input of trace species to the world ocean, *Global Biogeochemical cycles*, 5, 193-259.
- Emerson, S. R., and S. S. Huested (1991), Ocean anoxia and the concentration of molybdenum and vanadium in seawater, *Mar. Chem.*, 34, 177-196.
- Fleitmann, D., S. J. Burns, M. Mudelsee, U. Neff, J. Kramers, A. Mangini, and A. Matter (2003), Holocene Forcing of the Indian Monsoon Recorded in a Stalagmite from Southern Oman, *Science*, 300, 1737.
- France-Lanord, C., L. Derry, and A. Michard (1993), Evolution of the Himalaya since Miocene time: isotopic and sedimentological evidences from the Bengal fan, *in Himalayan Tectonics* edited by Treloar P.J. and Searle M. P., 74, 603-621.
- Frank, M. (2002), Radiogenic isotopes: Tracers of past ocean circulation and erosional input, *Rev. Geophys.*, 40, 1-38.
- Galy, A., and C. France-Lanord (2001), Higher erosion rates in the Himalaya: Geochemical constraints on riverine fluxes, *Geology*, 29, 23-26.

- Garzanti, E., G. Vezzoli, S. Andò, P. Paparella and P. D. Clift (2005), Petrology of Indus River sands: a key to interpret erosion history of the Western Himalayan Syntaxis, *Earth Planet. Sci. Lett.*, 229, 287–302.
- Godard, M., D. Bosch, and F. Einaudi (2006), A MORB source for low-Ti magmatism in the Semail ophiolite, *Chem. Geo.*, 234, 58–78.
- Goldberg, E. D., and J. J. Griffin (1970), The sediments of the northern Indian Ocean, *Deep-Sea Res.*, 17, 513-537.
- Goldstein, S. L., and S. R. Hemming (2003), Long-lived Isotopic Tracers in Oceanography, Paleoceanography, and Ice-sheet Dynamics, *in Treatise on Geochemistry: The Oceans and Marine Geochemistry*, edited by H. Elderfield, p. 453, Elsevier Pergamon.
- Goldstein, S. J., and J. Jacobsen (1987), The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater, *Chem. Geo.*, *66*, 245-272.
- Goswami, V., S. K. Singh, and R. Bhushan (2012a), Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea, *Chem. Geo.*, 291, 256-268.
- Goswami, V., S. K. Singh, R. Bhushan, and V. K. Rai (2012b), Temporal variations in ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} in sediments of the southeastern Arabian Sea: Impact of monsoon and surface water circulation, *Geochem. Geophys. Geosyst.*, 13(Q01001).
- Gupta, A. K., D. M. Anderson, and J. T. Overpeck (2003), Abrupt changes in the Asian southwest monsoon during the Holocene and their links to the North Atlantic Ocean, *Nature*, 421, 354-356.
- Gupta, H., G. J. Chakrapani, K. Selvaraj, and S.-J. Kao (2011), The fluvial geochemistry, contributions of silicate, carbonate and saline-alkaline components to chemical weathering flux and controlling parameters: Narmada River (Deccan Traps), India, *Geochim. Cosmochim. Acta*, 75, 800-824.
- Harris, N. B. W., M. Santosh, and, P. N. Taylor (1994), Crustal evolution in South India: Constraints from Nd isotopes, *J. Geol.*, 102, 139-150.
- Harrison, S. P., K. E. Kohfeld, C. Roelandt, and T. Claquin (2001), The role of dust in climate changes today, at the last glacial maximum and in the future, *Earth Sci. Rev.*, 54, 43-80.

- Helz, G. R., C. V. Miller, J. M. Charnock, J. F. W. Mosselmans, R. A. D. Pattrick, C. D. Garner, and D. J. Vaughan (1996), Mechanism of Molybdenum removal from the sea and its concentration in black shales: EXAFS evidence, *Geochim. Cosmochim. Acta*, 60, 3631-3642.
- Henderson, G. M., N. C. Slowey, and M. Q. Fleisher (2001), U-Th dating of carbonate platform and slope sediments, *Geochim. Cosmochim. Acta*, 65, 2757-2770.
- Herzschuh, U. (2006), Palaeo-moisture evolution in monsoonal Central Asia during the last 50,000 years, *Quat. Sci. Rev.*, 25, 163-178.
- Innocent, C., N. Fagel, and C. Hillaire-Marcel (2000), Sm-Nd isotope systematics in deep-sea sediments: Clay-size versus coarser fractions, *Geochim. Cosmochim. Acta*, 168, 79–87.
- Jacobsen, S. B., and G. J. Wasserburg (1980), Sm-Nd isotopic systematics of chondrites and achondrites, *Meteoritics*, 15, 307–308.
- Jeandel, C. (1993), Concentration and isotopic composition of Nd in the South Atlantic Ocean, *Earth Planet Sci. Lett.*, 117, 581-591.
- Jeandel, C., D. Thouron, and M. Fieux (1998), Concentrations and isotopic compositions of neodymium in the eastern Indian Ocean and Indonesian straits, *Geochim. Cosmochim. Acta*, 62, 2597-2607.
- Jeandel, C., J. K. Bishop and A. Zindler (1995), Exchage of neodymium and its isotopes between seawater and small and large particles in the Sargasso Sea, *Geochim. Cosmochim. Acta*, 59, 535-547.
- Johannesson, K. H., and D. J. Burdige (2007), Balancing the global oceanic neodymium budget: Evaluating the role of groundwater, *Earth Planet Sci. Lett.*, 253, 129-142.
- Johnson, D. A., and J. E. Damuth (1979), Deep thermohaline flow and current controlled sedimentation in the Amrante Passage: Western Indian Ocean, *Geochim. Cosmochim. Acta*, 33, 1-44.
- Johnson, G. C., B. A. Warren, and D. B. Olson (1991), Flow of bottom water in the Somali Basin, *Deep-Sea Res.*, 38, 637-652.
- Kale, V. S., S. Mishra, and V. R. Baker (2003), Sedimentary records of palaeofloods in the bedrock gorges of the Tapi and Narmada rivers, central India, *Curr. Sci.*, 84, 1072-1079.

- Kendall, B., R. A. Creaser, and D. Selby (2009), ¹⁸⁷Re-¹⁸⁷Os geochronology of Precambrian organic-rich sedimentary rocks, *in Global Neoproterozoic Petroleum Systems: The Emerging Potential in North Africa*, edited by J. Craig, et al., pp. 85-107, Geological Society of London (Special Publications), London.
- Kessarkar, P. M., V. Purnachandra Rao, S. M. Ahmad, and G. Anil Babu (2003), Clay minerals and Sr-Nd isotopes of the sediments along the western margin of India and their implication for sediment provenance, *Geochim. Cosmochim. Acta*, 202, 55-69.
- Klinkhammer, G. P., and M. R. Palmer (1991), Uranium in the oceans: Where it goes and why?, *Geochim. Cosmochim. Acta*, 55.
- Kolla, V., L. Henderson, and P. E. Biscaye (1976), Clay minerology and sedimentation in the Western Indian Ocean, *Deep-Sea Res.*, 23, 949-961.
- Ku, T.-L., K. G. Kanuss, and G. G. Mathieu (1977), Uranium in open ocean: concentration and isotopic composition, *Deep-Sea Res.*, 24, 1005-1017.
- Kumar, M. D., and Y.-H. Li (1996), Spreading of water masses and regeneration of silica and ²²⁶Ra in the Indian Ocean, *Deep-Sea Res.*, 43, 83-110.
- Lacan, F., and C. Jeandel (2001), Tracing Papua New Guinea imprint on the central Equatorial Pacific Ocean using neodymium isotopic compositions and Rare Earth Element patterns, *Earth Planet Sci. Lett.*, 186, 497-512.
- Lacan, F., and C. Jeandel (2004a), Denmark Strait water circulation traced by heterogeneity in neodymium isotopic compositions, *Deep-Sea Res.*, 51, 71–82.
- Lacan, F., and C. Jeandel (2004b), Subpolar Mode Water formation traced by neodymium isotopic composition, *Geophys. Res. Lett.*, 31.
- Lacan, F., and C. Jeandel (2005), Neodymium isotopes as a new tool for quantifying exchange fluxes at the continent–ocean interface, *Earth Planet Sci. Lett.*, 232, 245–257.
- Lal, S., P. K. Patra, S. Venkatramni, M. M. Sarin, (1996), Distribution of nitrous oxide and methane in the Arabian Sea, *Curr. Sci.* 71 (Special section: JGOFS India), 894-890.
- Levasseur, S., J. L. Birck, and C. J. Allegre (1998), Direct measurement of femtomoles of Osmium and ¹⁸⁷Os/¹⁸⁸Os ration in seawater, *Science*, 282 272-274.

- Levasseur, S., J. L. Birck, and C. J. Allegre (1999), The osmium riverine flux and the oceanic mass balance of osmium, *Earth Planet Sci. Lett.*, 174, 7-23.
- Lewis, B. L., and G. W. LutherIII (2000), Processes controlling the distribution and cycling of manganese in the oxygen minimum zone of the Arabian Sea, *Deep-Sea Res.*, 47, 1541-1561.
- Luck, J. M., and C. J. Allègre (1983), ¹⁸⁷Re-¹⁸⁷Os systematics in meteorites and cosmochemical consequences, *Nature*, 302, 130-132.
- Luguet, A., G. Nowell, and D. Pearson (2008), ¹⁸⁴Os/¹⁸⁸Os and ¹⁸⁶Os/¹⁸⁸Os measurements by Negative Thermal Ionisation Mass Spectrometry (NTIMS): Effects of interfering element and mass fractionation corrections on data accuracy and precision, *Chem. Geo.*, 248, 342-362
- Madhupratap, M., S. P. Kumar, P. M. A. Bhattathiri, M. D. Kumar, S. Raghukumar, K. K. C. Nair, and N. Ramaiah (1996), Mechanism of the biological response to winter cooling in the northeastern Arabian Sea, *Nature*, 384, 549-551.
- Mahoney, J. J., H. C. Sheth, D. Chandrasekharam, and Z. X. Peng (2000), Geochemistry of flood basalts of the Toranmal section, northern Deccan traps, India: implications for regional Deccan stratigraphy, *J. Petrol.*, 41, 1099-1120.
- Mantyla, A. W., and J. L. Reid (1995), On the origins of deep and bottom waters of the Indian Ocean, *J. Geophys. Res.*, 100, 2417-2243.
- Marcantonio, F., K. Turekian, K., S. Higgins, R. F. Anderson, M. Stute, and P. Schlosser (1999), The accretion rate of extraterrestrial ³He based on oceanic ²³⁰Th flux and the relation to Os isotope variation over the past 200,000 years in an Indian Ocean core, *Earth Planet Sci. Lett.*, 170, 157-168.
- McManus, J., W. M. Berelson, S. Severmann, R. L. Poulson, D. E. Hammond, G. P. Klinkhammer, and C. Holm (2006), Molybdenum and Uranium geochemistry in continental margin sediments: Paleoproxy potential, *Geochim. Cosmochim. Acta*, 70, 4643-4662.
- Measures, C. I., and S. Vink (1999), Seasonal variations in the distribution of Fe and Al in the surface waters of the Arabian Sea, *Deep-Sea Res.*, 46, 1597-1622.

- Measures, C. I., and S. Vink (2000), On the use of dissolved aluminum in surface waters to estimate dust deposition to the ocean, *Global Biogeochem. cycles*, 14, 317-327
- Meisel, T., and J. Moser (2004), Platinum-group element and rhenium concentrations in low abundance reference materials, *Geostand. Geoanal. Res.*, 28, 133-250.
- Meisel, T., R. J. Walker, A. J. Irving, and J.-P. Lorand (2001), Osmium isotopic compositions of mantle xenoliths: a global perspective, *Geochim. Cosmochim. Acta*, 65, 1311–1323.
- Milliman, J. D., G. S. Quraishee, and, M. A. A. Beg (1984), Sediment discharge from the Indus river to the ocean: past, present and furture, *in Marine Geology and Oceanography of Arabian Sea and Coastal Pakistan*, edited by B. U. Haq and J. D. Milliman, pp. 65-70, Van Nostrand Reinhold/Scientific and Academic Editions, New York.
- Moffett, J. W., T. J. Goepferta, and S. W. A. Naqvi (2007), Reduced iron associated with secondary nitrite maxima in the Arabian Sea, *Deep-Sea Res.*, 54, 1341–1349.
- Morel, F. M. M., and N. M. Price (2003), The Biogeochemical Cycles of Trace Metals in the Oceans, *Science*, 300, 944-947.
- Morford, J. L., A. D. Russell, and S. Emerson (2001), Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, Saanich Inlet, BC, *Geochim. Cosmochim. Acta*, 174, 355-369.
- Morford, J. L., S. Emerson, E. J. Breckel, and S. K. Kim (2005), Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin, *Geochim. Cosmochim. Acta*, 69, 5021-5032.
- Morford, J., and S. Emerson (1999), The geochemistry of redox sensitive trace metals in sediments, *Geochim. Cosmochim. Acta*, 63, 1735-1750.
- Morris, A.W., (1975), Dissolved molybdenum and vanadium in the northeast Atlantic Ocean, *Deep-Sea Res.*, 22, 49–54.
- Nair, M., T. Joseph, K. K. Balachandran, K. K. C. Nair, and J. S. Paimpillii (2003), Arsenic enrichment in estuarine sediments-impact of iron and manganese mining, in *Fate of arsenic in the environment (Int. Symp. on Fate of Arsenic in the Environment*), edited by M. F. Ahmed, M. A. Ali, M. A., Z. Adeel, pp. 57-67, Dhaka.

- Nameroff, T. J., and L. S. Balistrieri (2002), suboxic trace metal geochemisrty in the tropical North Pacific, *Geochim. Cosmochim. Acta*, 66, 1139-1158.
- Nameroff, T. J., S. E. Calvert, and J. W. Murray (2004), Glacial-interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals, *Paleoceanography*, 19(PA1010).
- Naqvi, S. W. A. (1994), Denitrification processes in the Arabian Sea, *Proc. Indian Acad. Sci. (Earth Planet Sci.)*, 103, 279-300.
- Naqvi, S. W. A., D. A. Jayakumar, P. V. Narvekar, H. Naik, V. V. S. S. Sarma, W. D'Souza, S. Joseph, and M. D. George (2000), Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf, *Nature*, 408, 346-349.
- Nier, A. (1937), The isotopic constitution of osmium, Phys. Rev. 52, 885-885
- Nozaki, Y., and D. S. Alibo (2003), Importance of vertical geochemical processes in controlling the oceanic profiles of dissolved rare earth elements in the northeastern Indian Ocean, *Earth Planet Sci. Lett.*, 205, 155-172.
- Oxburgh, R. (1998), Variations in the Osmium isotope composition of sea water over the past 200,000 years, *Earth Planet Sci. Lett.*, 159, 183-191.
- Oxburgh, R. (2001), Residence time of osmium in the oceans, Geochem. Geophys. Geosyst., 2.
- Oxburgh, R., A.-C. Pierson-Wickmann, L. Reisberg, and S. Hemming (2007), Climate-correlated variations in seawater ¹⁸⁷Os/¹⁸⁸Os over the past 200,000 yr: Evidence from the Cariaco Basin, Venezuela, *Earth Planet Sci. Lett.*, 263, 246–258.
- Owens, N. J. P., C. S. Law, R. F. C. Mantoura, P. H. Burkill, C. A. Llewellyn, (1991), Methane flux to the atmosphere from the Arabian Sea, Nature. 354, 293-295.
- Panda, D. K., A. Kumar, and S. Mohanty (2011), Recent trends in sediment load of the tropical (Peninsular) river basins of India, *Global Planet. Change*, 75, 108-118.
- Pattan, J. N., and N. J. G. Pearce (2009), Bottom water oxygenation history in southeastern Arabian Sea during the past 140 ka: Results from redoxsensitive elements, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 280, 396– 405.

- Pegram, W. J., and K. K. Turekian (1999), The osmium isotopic composition change of Cenozoic sea water as inferred from a deep-sea core corrected for meteoritic contributions, *Geochim. Cosmochim. Acta*, 63, 4053–4058.
- Pegram, W. J., S. Krishnaswami, G. E. Ravizza, and K. K. Turekian (1992), The record of seawater ¹⁸⁷Os/¹⁸⁶Os variation through the Cenozoic, *Earth Planet Sci. Lett.*, 113, 569-576
- Peipgras, D. J., and G. J. Wasserburg (1982), Isotopic composition of neodymium in waters from the Drake Passage, *Science*, 217, 207-217.
- Peipgras, D. J., and G. J. Wasserburg (1983), Influence of the Mediterranean outflow on the isotopic composition of neodymium in the waters of North Atlantic, *J. Geophys. Res.*, 88, 5997-6006.
- Peipgras, D. J., and S. B. Jacobson (1988), The isotopic composition of neodymium in the North Pacific, *Geochim. Cosmochim. Acta*, 52, 1373-1381.
- Peng, Z. X., J. J. Mahoney, P. R. Hooper, J. D. Macdougall, and P. Krishnamurthy (1998), Basalts of the northeastern Deccan Traps, India: Isotopic and elemental geochemistry and relation to southwestern Deccan stratigraphy, J. Geophys. Res., 103, 29,843-29,865.
- Petit, J. R., J. Jouzel, D. Reynaud, N. I. Barkov, J. M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, M. Delmotte, V. M. Kotyakov, M. Legrand, V. Y. Lepyakov, C. Lorius, L. Pepin, C. Ritz, E. Saltman, and M. Stievenard (1999), Climate and atmospheric history of the past 420,000 years from the vostok ice core, Antarctica, *Nature*, 399, 429-436.
- Peucat, J. J., P. Vidal, J. Bernard-Griffiths, and K. C. Condie (1989), Sr, Nd, and Pb isotopic systematics in the Archean low to high-grade transition zone of southern India: Synaccretion vs. Post-accretion granulites, J. Geol., 97, 537-550.
- Piotrowski, A. M., V. K. Banakar, A. E. Scrivner, H. Elderfield, A. Galy, and A. Dennis (2009), Indian Ocean circulation and productivity during the last glacial cycle, *Earth Planet Sci. Lett.*, 285, 179–189.
- Porcelli, D., P. S. Andersson, M. Baskaran, M. Frank, G. Björk, and I. Semiletov (2009), The distribution of neodymium isotopes in Arctic Ocean basins, *Geochim. Cosmochim. Acta*, 73, 2645–2659.

- Prell, W. L., and J. E. Kutzbach (1987), Monsoon variability over the past 150,000 years, J. Geophys. Res., 92, 8411-8425.
- Rahaman, W., and S. K. Singh (2010), Rhenium in rivers and estuaries of India: Sources, transport and behaviour, *Mar. Chem.*, 118, 1-10.
- Rahaman, W., S. K. Singh, R. Sinha, and S. K. Tandon (2009), Climate control on erosion distribution over the Himalaya during the past ~100 ka, *Geology*, 37, 559-562.
- Rajawat A. S., Y. Gupta, Y. Pradhan, A.V. Thomaskutty and S. Nayak (2005), Coastal Processes along the Indian Coast - case studies based on synergistic use of IRS - P4 OCM IRS - 1C/1D data, *Indian J. Mar. Sci.*, 34, 459-472.
- Ramaswamy, V., and R. R. Nair (1989), Lack of Cross-shelf Transport of Sediments on the Western Margin of India: Evidence from Clay Mineralogy, J. Coastal Res., 5, 541-546.
- Ramaswamy, V., and R. R. Nair (1994), Fluxes of material in the Arabian Sea and Bay of Bengal - Sediment trap studies, *in Biogeochemistry of the Arabian Sea: Present information and gaps*, edited by Lal, D. Proc. Indian Acad. Sci. (Earth Planet. Sci.) Indian Acad. of Sci.; Bangalore; India., 103(2), 189-210.
- Rao, V. P., and B. R. Rao (1995), Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India, *Cont. Shelf Res.*, 15, 1757-1771.
- Reichart, G. J., M. d. Dulk, H. J. Visser, C. H. v. d. Weijden, and W. J. Zachariasse (1997), A 225 kyr record of dust supply, paleoproductivity and the oxygen minimum zone from the Murray Ridge (northern Arabian Sea), *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 134, 149-169.
- Rengarajan, R., M. M. Sarin, and S. Krishnaswami (2003), Uranium in the Arabian Sea: role of denitrification in controlling its distribution., *Oceanol. Acta*, 26, 687-693.
- Rickli, J., M. Frank, A. R. Baker, S. Aciego, G. d. Souza, R. B. Georg, and A. N. Halliday (2010), Hafnium and neodymium isotopes in surface waters of the eastern Atlantic Ocean: Implications for sources and inputs of trace metals to the ocean, *Geochim. Cosmochim. Acta*, 74, 540–557.
- Rochford, D. J. (1964), Salinity maxima in the upper 1000 meters of the North Indian Ocean, Aust. J. Mar. Freshw. Res., 15, 1-24.
- Ruddiman, W. F. (1997), Tectonic Uplift and Climate Change, Plenum, New York.
- Rutberg, R. L., S. L. Goldstein, S. R. Hemming, and R. F. Anderson (2005), Sr isotope evidence for sources of terrigenous sediments in the southeast Atlantic Ocean: Is there increased available Fe for enhanced glacial productivity?, *Paleoceanography*, 20, PA1018.
- Saager, P. M. (1994), The biogeochemical distribution of trace elements in the Indian Ocean., *Proc Indian Acad Sci (Earth Planet Sci.)*, 103, 237–278.
- Saager, P. M., H. J. W. De Baar, and P. H. Burkill (1989), Manganese and Iron in Indian Ocean waters, *Geochim. Cosmochim. Acta*, 53, 2259-2267.
- Sarkar, A., R. Ramesh, S. K. Bhattacharya, and G. Rajagopalan (1990), Oxygen isotope evidence for a stronger winter monsoon current during the last glaciation, *Nature*, 343, 549-551.
- Sarkar, A., S. K. Bhattacharya, and M. M. Sarin (1993), Geochemical evidence for anoxic deep water in the Arabian Sea during the last glaciation, *Geochim. Cosmochim. Acta*, 57, 1009-1016.
- Schlitzer, R., (2010), Ocean Data View, http://odv.awi.de.
- Schmiedl, G., and D. C. Leuschner (2005), Oxygenation changes in the deep western Arabian Sea during last 190,000 years: Productivity versus deepwater circulation, *Paleoceanography*, 20(PA2008).
- Schott, F. A., and J. P. McCreary, Jr (2001), The monsoon circulation of the Indian Ocean, *Prog. Oceanogr.*, 51, 1-123.
- Shabani, M. B., T. Akagi, and A. Masuda (1992), Preconcentration of trace Rare-Earth elements in seawater by complexation with Bis(2-ethylhexyl) Hydrogen Phosphate and 2-Ethylhexyl dihydrogen phosphate adsorbed on a C18 cartridge and determination by inductively coupled Plasma Mass Spectrometry, Anal. Chem., 64, 737-743.
- Shankar, D., P. N. Vinayachandran, and A. S. Unnikrishnan (2002), The monsoon currents in the north Indian Ocean, *Prog. Oceanogr.*, 52, 63-120.
- Shenoi, S. S. C., S. R. Shetye, A. D. Gouveia, and G. S. Michael (1993), Salinity Extrema in the Arabian Sea, *Mitt. Geol.-Palaeont*. Inst. Univ. Hamburg SCOPE/UNEP Sonderband, 76, 37-49.

- Shimizu, H., K. Tachikawa, A. Masuda, and Y. Nozaki (1994), Cerium and Nd isotope ratios and REE patterns in seawater from the North Pacific ocean, *Geochim. Cosmochim. Acta*, 58, 323–333.
- Shirey, S. B., and R. J. Walker (1995), Carius tube digestion for low-blank rhenium-osmium analysis, *Anal. Chem.*, 67, 2136-2141.
- Siddall, M., E. J. Rohling, A. Almogi-Labin, Ch. Hemleben, D. Meischner, I. Schmelzer, and D. A. Smeed (2003), Sea-level fluctuations during the last glacial cycle, *Nature*, 423, 853-857.
- Singh, S. K. (1999), Isotopic and geochemical studies of the Lesser Himalayan sedimentaries *Ph.D. Thesis*, M.S. University of Baroda
- Singh, S. K., J. R. Trivedi, and S. Krishnaswami (1999), Re-Os isotope systematics in black shales from the Lesser Himalaya: Their chronology and role in the ¹⁸⁷Os/¹⁸⁸Os evolution of seawater, *Geochim. Cosmochim. Acta*, 63, 2381-2392
- Singh, S. K., and C. France-Lanord (2002), Tracing the distribution of erosion in the Brahmaputra watershed from isotopic compositions of stream sediments, *Earth Planet. Sci. Lett.*, 202, 645-662.
- Singh, S. K., S. K. Rai, and S. Krishnaswami (2008), Sr and Nd isotopes in river sediments from the Ganga Basin: Sediment provenance and spatial variability in physical erosion, *J. Geophys. Res.*, 113.
- Singh, S. P., S. K. Singh, and R. Bhushan (2011), Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal, *Mar. Chem.*, 126, 76-88.
- Singh, S. P., S. K. Singh, V. Goswami, R. Bhushan, and V. K. Rai (2012), Spatial distribution of dissolved neodymium and ɛNd in the Bay of Bengal: Role of particulate matter and mixing of water masses, *Geochim. Cosmochim. Acta*, (Under Review).
- Sinha, A., K. G. Cannariato, L. D. Stott, and H.-c. Li (2005), Variability of Southwest Indian summer monsoon precipitation during the Bølling-Allerød, *Geology*, 33, 813-816.
- Sirocko, F. (1995), Abrupt change in monsoonal climate: Evidence from the geochemical composition of Arabian sea sediments, *Habilitation thesis*, University of Kiel.

- Sirocko, F., and M. Sarnthein (1989), Wind-borne deposits in the northwestern Indian Ocean: Record of Holocene sediments versus modern satellite data, in Paleoclimatology and Paleometeorology:Modern and past patterns of global atmospheric transport (NATO ASI series), edited by M. Leinen and M. Sarnthein, pp. 401-433, Kluwer Academic Publishers, Dordrecht.
- Sirocko, F., D. G. Schonberg, and C. Devey (2000), Processes controlling trace element geochemistry of Arabian Sea sediments during the last 25,000 years, *Global Planet. Change*, 26, 217-303.
- Sohrin, Y., M. Matsui, and E. Nakayam (1999), Contrasting behavior of tungsten and molybdenum in the Okinawa Trough, the East China Sea and the Yellow Sea, *Geochim. Cosmochim. Acta*, 63, 3457–3466.
- Somayajulu, B. L. K., R. Bhushan, A. Sarkar, G. S. Burr, and A. J. T. Jull (1999), Sediment deposition rates on the continental margins of the eastern Arabian Sea using ²¹⁰Pb, ¹³⁷Cs and ¹⁴C, *Sci. Total Environ.*, 237/238, 429-439.
- Sridhar P. N., M. M. Ali, P. Vedamony, M. T. Babu, I. V. Ramana, and, B. Jayakumar (2008a), Seasonal occurrence of unique sediment plume in the Bay of Bengal, *Eos AGU*, 89, 22-23.
- Sridhar P. N., I. V. Ramana, M. M. Ali and B. Veeranarayana (2008b) Understanding the suspended sediment dynamics in the coastal waters of the Bay of Bengal using high resolution ocean colour data, *Curr. Sci.*, 94, 1499-1502.
- Sridhar, A. (2008), Evidence of a late-medieval mega flood event in the upper reaches of the Mahi River basin, Gujarat, *Curr. Sci.*, 96, 1517-1520.
- Stordal, M. C., and G. J. Wasserburg (1986), Neodymium isotopic study of Baffin bay water: Sources of REE from very old terranes, *Earth Planet Sci. Lett.*, 77, 259–272.
- Tachikawa, K., C. Jeandel, and M. Roy-Barman (1999), A new approach to the Nd residence time in the ocean: the role of atmospheric inputs, *Earth Planet Sci. Lett.*, 170, 433-446.
- Tanaka, T., S. Togashi, H. Kamioka, H. Amakawa, H. Kagami, T. Hamamoto, M. Yuhara, Y. Orihashi, S. Yoneda, H. Shimizu, T. Kunimaru, K. Takahashi, T. Yanagi, T. Nakano, H. Fujimaki, R. Shinjo, Y. Asahara, M. Tanimizu, and C. Dragusanu (2000), JNdi-1: a neodymium isotopic reference in consistency with LaJolla neodymium, *Chem. Geo.*, 168, 279–281.

- Tarantola, A. (2005), The least square criterion. In: Inverse problem theory and methods for model parameter estimation, *Society for Industrial and Applied Mathematics* (Philadelphia).
- Taylor, S. R., and S. M. McLennan (1995), The geochemical evolution of the continental crust, *Rev. Geophys.*, 33, 241-265.
- Theberge, S. M., G. W. Luther III, and A. M. Farrenkopf (1997), On the existence of free and metal complexed sulfide in the Arabian Sea and its oxygen minimum zone, *Deep-Sea Res.*, 44, 1381-1390.
- Tiwari, M., R. Ramesh, B. L. K. Somayajulu, A. J. T. Jull, and G. S. Burr (2005), Early deglacial (~19–17 ka) strengthening of the northeast monsoon, *Geophys. Res. Lett.*, 32 L19712.
- Tripathy, G. R. (2011), Isotope geochemistry of black shales and recent marine sediments, *PhD. Thesis*, MLSU.
- Tripathy, G. R., and S. K. Singh (2010), Chemical erosion rates of river basins of the Ganga system in the Himalaya: Reanalysis based on inversion of dissolved major ions, Sr, and ⁸⁷Sr/⁸⁶Sr, Geochem. Geophys. Geosyst., 11(Q03013).
- Tripathy, G. R., S. K. Singh, R. Bhushan, and V. Ramaswamy (2011), Sr-Nd isotope composition of the Bay of Bengal Sediments: Impact of Climate on Erosion in the Himalaya, *Geochem. J.*, 45, 175-186.
- Trivedi, J. R., S. K. Singh, and S. Krishnaswami (1999), ¹⁸⁷Re-¹⁸⁷Os in Lesser Himalayan sediments: Measurement techniques and preliminary results, *Proc Indian Acad Sci. (Earth Planet. Sci.)*, 108, 179-187.
- Unger, D., V. Ittekkot, P. Schäfer, J. Tiemann, and S. Reschke (2003), Seasonality and interannual variability of particle fluxes to the deep Bay of Bengal: influence of riverine input and oceanographic processes, *Deep-Sea Res.*, 50, 897-923.
- van de Flierdt, T., K. Pahnke, H. Amakawa, P. Andersson, C. Basak, C. Colin, K. Crocket, M. Frank, N. Frank, S. L. Goldstein, V. Goswami, B. A. Haley, E. C. Hathorne, S. R. Hemming, G. M. Henderson, C. Jeandel, K. Jones, K. Kreissig, F. Lacan, E. E. Martin, D. R. Newkirk, L. Pena, A. M. Piotrowski, C. Pradoux, H. D. Scher, H. Schöberg, S. K. Singh, H. Tazoe, D. Vance, and J. J. Yang (2012), GEOTRACES intercalibration of neodymium isotopes and rare earth elements in seawater and marine particulates Part 1: international intercomparison, *Limnology and Oceanography: Methods* (Under review).

- VanLaningham, S., N. G. Pisias, R. A. Duncan, and P. D. Clift (2009), Glacialinterglacial sediment transport to the Meiji Drift, northwest Pacific Ocean: Evidence for timing of Beringian outwashing, *Earth Planet. Sci. Lett.*, 277, 64-72.
- Viers, J., B. Dupré, and J. Gaillardet (2009), Chemical composition of suspended sediments in World Rivers: New insights from a new database, *Sci. Total Environ.*, 407, 853-868.
- Volkening, J., T. Walczyk, and K. Heumann (1991), Osmium isotope ratio determinations by negative thermal ionization mass spectrometry, *Int. J. Mass Spectrom. Ion Processes*, 105, 147-159.
- Vorlicek, T. P., and G. R. Helz (2002), Catalysis by mineral surfaces: Implication for Mo geochemistry in anoxic environments, *Geochim. Cosmochim. Acta*, 66, 3679-3692.
- Walker, R. J., and J. W. Morgan (1989), Rhenium–osmium isotope systematics of carbonaceous chondrites, *Science*, 243, 519– 522.
- Warren, B. A. (1978), Bottom water transport hrought he Southwest Indian Ridge, *Deep-Sea Res.*, 25, 315-321.
- Williams, G. A., and K. K. Turekian (2004), The glacial interglacial variation of seawater osmium isotopes as recorded in Santa Barbara Basin., *Earth Planet Sci. Lett.*, 228, 379-389.
- Winckler, G., and H. Fischer (2006), 30,000 years of cosmic dust in Antarctic ice, *Science*, 228, 379-389.
- Wyrtki, K. (1971), Oceanographic Atlas of the International Indian Ocean Expedition., *National Science Foundation*, Washington, DC 531 pp.
- Wyrtki, K. (1973), Physical oceanography of the Indian Ocean, *in The biology of the Indian Ocean*, edited by B. Zeitschel, pp. 18-36, Springer-Verlag, Berlin.
- You, Y., and M. Tomczak (1993), Thermocline circulation and ventilation in the Indian Ocean derived from water mass analysis, *Deep-Sea Res.*, 40, 13-56.
- You, Y. (2000), Implications of the deep circulation and ventilation of the Indian Ocean on the renewal mechanism of North Atlantic Deep Water, J. Geophys. Res., 105, 23,895-823,926.

- Zieringer, M., T. Stichel, and M. Frank (2011), The hafnium and neodymiujm isotopic composition of seawater in the tropical Atlantic Ocean, *Mineralog. Mag.*, 75, 2286.
- Zimmermann, B., D. Porcelli, M. Frank, J. Rickli, D.-C. Lee, and A. N. Halliday (2009), The hafnium isotope composition of Pacific Ocean water, *Geochim. Cosmochim. Acta*, 73, 91–101.

LIST OF PUBLICATIONS

- G. R. Tripathy, V. Goswami, S. K. Singh, G. J. Chakrapani (2010) Temporal variations in Sr and ⁸⁷Sr/⁸⁶Sr of the Ganga headwaters: Estimates of dissolved Sr flux to the mainstream. *Hydrological processes*, 24, 1159– 1171, doi: 10.1002/hyp.7572.
- V. Goswami, S. K. Singh, R. Bhushan (2012) Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea, *Chemical Geology*, 291, 256–268, doi: 10.1016/j.chemgeo.2011.10.021.
- 3) V. Goswami, S. K. Singh, R. Bhushan, V. K. Rai (2012) Temporal variations in ⁸⁷Sr/⁸⁶Sr and e_{Nd} in sediments of the southeastern Arabian Sea: Impact of monsoon and surface water circulation, *Geochemisty Geophysics Geosystems*, 13, Q01001, doi:10.1029/2011GC003802.
- A. Kumar, A. K. Sudheer, V. Goswami, R. Bhushan (2012) Influence of continental outflow on aerosol chemical characteristics over the Arabian Sea during winter, *Atmospheric Environment*, doi: 10.1016/j.atmosenv.2011.12.040 (article in press).
- 5) T. van de Flierdt, K. Pahnke, H. Amakawa, P. Andersson, C. Basak, C. Colin, K. Crocket, M. Frank, N. Frank, S. L. Goldstein, V. Goswami, B. A. Haley, E. C. Hathorne, S. R. Hemming G. M. Henderson, C. Jeandel, K. Jones, K. Kreissig, F. Lacan, E. E. Martin, D. R. Newkirk, L. Pena, A. M. Piotrowski, C. Pradoux, H. D. Scher, H. Schöberg, S. K. Singh, H. Tazoe, D. Vance, J. Yang (2012) GEOTRACES intercalibration of neodymium isotopes and rare earth elements in seawater and marine particulates Part 1: international intercomparison. (Under review in *Limnology and Oceanography: Methods*)

6) S. P. Singh, S. K. Singh, V. Goswami, R. Bhushan, V. K. Rai (2012) Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses. (Under review in *Geochimica et Cosmochimica Acta*)

Abstracts (Conferences/Symposium)

- V. Goswami, S. K. Singh, R. Bhushan. Variation in Osmium isotopic composition of seawater over past 26 ka recorded in organic matter rich sediments of Arabian Sea. Physical Research Laboratory Diamond jubilee conference "Terrestrial planets: evolution through time" at Physical Research Laboratory (PRL) Jan. 22-25, 2008.
- G. R. Tripathy, V. Goswami, S. K. Singh, G. J. Chakrapani. Seasonal variations in the major ions, Sr and ⁸⁷Sr/⁸⁶Sr in Ganga headwaters. Physical Research Laboratory Diamond jubilee conference "Terrestrial planets: evolution through time" at Physical Research Laboratory (PRL) Jan. 22-25, 2008.
- 3) V. Goswami, S. K. Singh and R. Bhushan. Impact of OMZ on the distribution of redox sensitive trace elements in Arabian Sea. 7th annual AOGS (Asia Oceania Geosciences Society) meeting at Hyderabad International Convention Centre, Hyderabad, July 5-9, 2010.
- 4) V. Goswami, S. K. Singh, R. Bhushan, Sr and Nd isotopic composition of sediments from the eastern Arabian Sea: impact of climate and surface water circulation. 7th International Conference on Asian Marine Geology at National Institute of Oceanography, Goa, Oct. 11-14, 2011.

Chemical Geology 291 (2012) 256-268

Contents lists available at SciVerse ScienceDirect



Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Research paper

Dissolved redox sensitive elements, Re, U and Mo in intense denitrification zone of the Arabian Sea

Vineet Goswami *, Sunil K. Singh, Ravi Bhushan

Geosciences Division, Physical Research Laboratory, Ahmedabad, India

ARTICLE INFO

Article history: Received 13 July 2011 Received in revised form 25 October 2011 Accepted 27 October 2011 Available online 4 November 2011

Editor: J.D. Blum

Keywords: Re U Mo Arabian Sea Denitrification GEOTRACES

ABSTRACT

The concentrations of redox sensitive elements rhenium, uranium and molybdenum have been measured in the suboxic water column of the Arabian Sea to determine their response (behavior) to intense oxygen minima and denitrifying conditions in the water column. North of 12°N, within the core of the intense oxygen minimum zone (OMZ) of the Arabian Sea, the dissolved oxygen levels drop to values as low as $<5 \,\mu$ M accompanied by the presence of secondary nitrite maxima (SNM) indicating the occurrence of denitrification in the water column. The distributions of Re. U and Mo in the Arabian Sea show that their dissolved concentrations in the suboxic layer are indistinguishable from those in the overlying and underlying oxic waters suggesting that there is no discernible removal of these elements from the suboxic denitrifying layers. In contrast, the lateral and vertical distribution of dissolved Re, U and Mo concentrations vary as a function of salinity suggesting their conservative behavior. The salinity normalized (35) Re, U and Mo concentrations in the Arabian Sea are 40 pmol/kg, 13.8 nmol/kg and 114 nmol/kg respectively. These concentrations are nearly identical to their abundances in the Bay of Bengal, a basin adjacent to the Arabian Sea characterized by high freshwater influx and fluvial sediments. The similarity in concentration suggests that the large variability in the biogenic and detrital particulate fluxes and the suboxic/denitrifying conditions between these two oceanic regions do not affect the concentrations of Re, U and Mo and that the prevailing biogeochemical conditions in these regions are inadequate for their removal from the water column.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Re, U and Mo constitute a suite of redox sensitive trace elements that have found applications to investigate paleo-redox conditions of the ocean and determine chronology of marine deposits (Sarkar et al., 1993; Crusius et al., 1999; Henderson et al., 2001; Morford et al., 2001; Nameroff et al., 2002, 2004; Kendall et al., 2009). In addition, Mo is associated with marine biological processes (Morel and Price, 2003). The growing interest on the applications of these elements as paleo-redox indicators would be better served through a more detailed understanding of their marine geochemistry that includes their sources, sinks and internal cycling in the ocean. Re, U and Mo are enriched in sediments rich in organic carbon (Borole et al., 1982; Sarkar et al., 1993; Morford and Emerson, 1999; Morford et al., 2005; McManus et al., 2006; Pattan and Pearce, 2009), suggesting that productivity and/or organic carbon burial may have a role in their removal from seawater.

The distribution of Re, U and Mo in well oxygenated oceanic regions shows conservative behavior (Ku et al., 1977; Collier, 1985; Anbar et al., 1992; Sohrin et al., 1999; Singh et al., 2011). In these oceanic regions, Re, U and Mo occur in their higher oxidation states as oxyanions, $\text{Re}^{\text{VII}}O_4^-$, $\text{U}^{\text{VI}}O_2(\text{CO}_3)_3^{4-}$ and $\text{Mo}^{\text{VI}}O_4^{2-}$ respectively. The high stability and unreactive nature of these oxyanions is reflected in their long oceanic residence times, of the order of ~10⁵– 10⁶ y (Bruland and Lohan, 2003). Under reducing conditions the oxidation states of these elements become Re^{IV} , U^{IV} and Mo^{IV} , making them particle reactive and susceptible for removal from dissolved to particle phases. Such reducing conditions are met in oceanic regions where the demand for oxygen for combustion of organic matter and respiration is not fulfilled. There have been only limited studies on the distribution of these redox sensitive elements in suboxic/reducing ocean water column to investigate their potential removal from seawater.

In this context, earlier studies of Re, U and Mo in anoxic/suboxic basins have highlighted the role of their diffusion from overlying seawater to pore waters to facilitate their removal followed by their uptake at the oxic–anoxic boundary (Anderson et al., 1989; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Colodner et al., 1995; Crusius et al., 1996; Nameroff et al., 2002). More recent study (Vorlicek and Helz, 2002) however has shown that the presence of mineral surfaces catalyzes the reduction of redox sensitive elements into particle reactive species, thus making their removal from seawater more efficient. For example, Re, U and Mo measurements in the Black Sea have demonstrated their removal from seawater in

^{*} Corresponding author. Tel.: +91 79 2631 4313; fax: +91 79 2631 4900.

E-mail addresses: vineetg@prl.res.in (V. Goswami), sunil@prl.res.in (S.K. Singh), bhushan@prl.res.in (R. Bhushan).

^{0009-2541/\$ –} see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.chemgeo.2011.10.021

V. Goswami et al. / Chemical Geology 291 (2012) 256-268



Fig. 1. Location of sampling stations in the Arabian Sea. The shaded region in the center of the Arabian Sea is the intense Oxygen minimum zone (OMZ). The stations 0702, 0703, 0704, 0705, 0706, 0707 and 0708 were occupied during the SS-256 cruise (Dec, 2007) and the three stations 0802, 0803 and 0805 were sampled during the cruise SS-259 (Nov, 2008). The station ER6 was occupied during KH-09-5 cruise (Dec, 2009).

the euxinic deeper waters; the mechanism of their removal, however still remains to be fully understood (Anderson et al., 1989; Colodner et al., 1995). In contrast to investigations of Re, U and Mo in sediments, there are only limited studies on their behavior in suboxic/ anoxic water column. Investigation on the distribution of U in the Cariaco trench doesn't indicate any detectable removal from the suboxic/reducing water column (Anderson, 1987); in contrast, its distribution in the Arabian Sea water column has hinted toward its possible removal from the oxygen minimum zone (OMZ; Rengarajan et al., 2003). A recent study (Helz et al., 2011) indicated the removal of Mo from the waters of euxinic basins under specific combination of H₂S concentration and pH in presence of reactive Fe. Such studies on the distribution of these redox sensitive elements in the suboxic/ anoxic water column are important to address issues pertaining to their potential removal from water column to sediments.

The goal of the present study is to investigate the impact of the perennial OMZ and denitrification present in the water column of the Arabian Sea on the distribution of dissolved Re, U and Mo. The suboxic conditions of the Arabian Sea have been found to influence Mn and Fe cycling in the water column (Saager et al., 1989). Vertical profiles of Mn in the Arabian Sea, within the core of denitrification zone, show maxima in its concentration coinciding with the secondary nitrite maxima (Lewis and Luther, 2000). Similarly, significant enrichment of dissolved Fe was reported in the depth range of 200–400 m relative to overlying and underlying waters, with up to 50% of

| Table 1 | | |
|----------------|----------|----------|
| Details of the | sampling | stations |

| Cruise | Month, year | Station | Lat (°N) | Long(°E) | Research vessel |
|---------|-------------|---------|----------|----------|-----------------|
| SS-256 | Dec, 2007 | 0702 | 17.27 | 72.44 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0703 | 18.00 | 72.00 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0704 | 18.00 | 70.64 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0705 | 18.00 | 68.50 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0706 | 16.50 | 66.50 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0707 | 15.00 | 68.49 | Sagar Sampada |
| SS-256 | Dec, 2007 | 0708 | 15.00 | 70.49 | Sagar Sampada |
| SS-259 | Nov, 2008 | 0802 | 14.42 | 69.42 | Sagar Sampada |
| SS-259 | Nov, 2008 | 0803 | 10.12 | 71.86 | Sagar Sampada |
| SS-259 | Nov, 2008 | 0805 | 6.01 | 77.48 | Sagar Sampada |
| KH-09-5 | Dec, 2009 | ER6 | 14.00 | 69.00 | Hakuho-Maru |

dissolved Fe present as Fe^{II}. The maxima of Fe enrichment was also found to coincide with the secondary nitrite maxima (Moffett et al., 2007). These studies demonstrate the role of suboxic layers of the Arabian Sea in determining the mobilization of redox sensitive elements, Fe and Mn. This raises the question of whether the distribution of the dissolved concentration of redox sensitive elements, Re, U and Mo are also impacted by the denitrifying layer of the Arabian Sea. The

| Table | 2a |
|-------|----|
|-------|----|

| Replicate ana | lysis of | Re | concentrat | ion |
|---------------|----------|----|------------|-----|
|---------------|----------|----|------------|-----|

| Station | Depth (m) | Re (pmol/kg) |
|---------|-----------|--------------|
| 0802 | 5 | 42.6 |
| | 5R | 42.3 |
| | 1500 | 40.7 |
| | 1500R | 40.0 |
| 0803 | 2400 | 40.4 |
| | 2400R | 40.0 |
| 0805 | 5 | 36.6 |
| | 5R | 36.8 |
| | 120 | 39.7 |
| | 120R | 39.8 |
| | 750 | 40.1 |
| | 750R | 40.0 |
| | 1100 | 39.6 |
| | 1100R | 39.7 |
| | 1250 | 38.9 |
| | 1250R | 39.9 |
| 0708 | 663 | 41.0 |
| | 663R | 40.6 |
| | 2200 | 40.4 |
| | 2000R | 40.7 |
| 0707 | 5 | 41.0 |
| | 5R | 41.7 |
| | 2000 | 39.1 |
| | 2000R | 38.7 |
| 0706 | 250 | 41.3 |
| | 250R | 40.0 |
| | 2100 | 38.9 |
| | 2100R | 40.0 |
| 0705 | 700 | 41.3 |
| | 700R | 40.1 |
| 0703 | 5 | 41.3 |
| | 5R | 41.9 |
| ER6 | 3000 | 39.0 |
| | 3000R | 39.2 |

Author's personal copy

V. Goswami et al. / Chemical Geology 291 (2012) 256-268

| Table 2b |
|--|
| Replicate analysis of U and Mo concentrations. |

Table 4

Salinity, temperature, DO, $\rm NO_2^-$ and Re, U and Mo concentration in the profiles from the Arabian Sea.

| Station | Depth (m) | U (nmol/kg) | Mo (nmol/kg) |
|---------|-----------|-------------|--------------|
| 0802 | 5 | 14.5 | 117 |
| | 5R | 14.3 | 116 |
| | 1000 | 13.8 | 113 |
| | 1000R | 14.0 | 111 |
| | 4040 | 13.8 | 111 |
| | 4040R | 13.7 | 111 |
| 0803 | 5 | 14.0 | 113 |
| | 5R | 13.9 | 114 |
| | 1200 | 13.8 | 112 |
| | 1200R | 13.8 | 113 |
| | 2200 | 13.8 | 112 |
| | 2200R | 13.7 | 110 |
| 0805 | 5 | 12.9 | 103 |
| | 5R | 12.7 | 103 |
| | 2250 | 13.9 | 111 |
| | 2250R | 13.6 | 110 |
| 0708 | 1400 | 13.8 | 114 |
| | 1400R | 13.8 | 111 |
| 0707 | 2000 | 13.7 | 112 |
| | 2000R | 13.7 | 111 |
| 0706 | 5 | 14.3 | 115 |
| | 5R | 14.3 | 116 |
| 0705 | 5 | 14.8 | 119 |
| | 5R | 14.7 | 118 |
| 0704 | 5 | 14.2 | 114 |
| | 5R | 14.3 | 113 |
| ER6 | 4140 | 13.8 | 113 |
| | 4140R | 13.9 | 114 |

work carried out in the present study addresses this question. In addition, while this work was in progress, the distributions of Re, U and Mo were reported from the waters of the Bay of Bengal (Singh et al., 2011), another basin in the northern Indian Ocean characterized by high river water and particulate flux. The results of the present study are compared with the Bay of Bengal data to learn about the relative behavior of these elements in the two basins, both with high particulate flux, one with high biogenic flux (Arabian Sea) and the other with high detrital flux (Bay of Bengal).

2. Study area

The Arabian Sea is a unique oceanic basin surrounded by continental landmass on its west, east and northern boundaries and connected to the Indian Ocean to the south. The Arabian Sea is one of the highly productive ocean basins; the productivity resulting from monsoonal upwelling brought about by seasonally reversing winds. The high productivity causes continuous rain of biogenic material through the water column. These debris during their transit are subject to combustion by dissolved oxygen in the water column, resulting in the formation of suboxic denitrifying layer at intermediate

| Table 3 | | | | |
|-----------|------|----|------|--------|
| Re, U and | l Mo | in | SAFe | water. |

| SAFe water sample | Salinity | Re (pmol/kg) | U (nmol/kg) | Mo (nmol/kg) |
|-------------------|----------|--------------|-------------|--------------|
| D1-242 | 34.40 | 39.1 | 13.7 | 108 |
| D2-142 | 34.40 | 39.9 | 13.8 | 112 |
| S-107 | 34.90 | 39.4 | 14.0 | 111 |
| GD-31 | 34.98 | 40.6 | 13.9 | 113 |
| GS-149 | 36.65 | 40.7 | 14.6 | 116 |
| D1-242R | 34.40 | 39.0 | - | - |
| GS-149R | 36.65 | 40.7 | - | - |

SAFe (sampling and analysis of Fe) samples are the seawater samples provided by Prof. Kenneth Bruland, University of California, Santa Cruz.

The salinity values given above were measured for profiles nearby the SAFe water samples collected at the same time.

| Depth(m) | Salinity | Temp | O_2 | NO_2^- | Re (pmol/kg) | U (nmol/kg) | Mo (pmol/kg) |
|-------------|--------------|--------------|----------------|----------|-----------------|----------------|-----------------|
| | | () | (µvi) | (μινι) | (pmol/kg) | (nmol/kg) | (nmol/kg) |
| 0802 (14.42 | 2°N, 69.42° | Έ) | | | 10.0 | | |
| 5 | 36.7 | 28.9 | 209.0 | 0.1 | 42.6 | 14.5 | 117 |
| 05 120 | 30.5 | 26.3 | 1/1.0 | 0.5 | 42.3 | 14.6 | 117 |
| 230 | 35.7 | 14.6 | 89 | 33 | 41.0 | 14.2 | 114 |
| 330 | 35.5 | 12.7 | 4.3 | 0.3 | 40.8 | 14.0 | 113 |
| 400 | 35.5 | 12.3 | 5.2 | 0.1 | 40.7 | 14.2 | 111 |
| 500 | 35.5 | 11.7 | 8.3 | 0.4 | 41.2 | 14.0 | 113 |
| 550 | 35.5 | 11.4 | 4.6 | 0.4 | 40.9 | 14.0 | 112 |
| 600 | 35.5 | 11.0 | 6.3 | 0.9 | 40.8 | 14.0 | 113 |
| /00 | 35.5 | 10.3 | 6.4 7.1 | 0.9 | 40.7 | 13.9 | 115 |
| 800 900 | 35.4 | 9.0 8.8 | 7.1 10.3 | 1.6 | 40.9 | 13.9 | 112 |
| 1000 | 35.3 | 8.0 | 16.5 | 0.0 | 41.0 | 13.8 | 111 |
| 1500 | 35.0 | 5.1 | 51.6 | 0.1 | 40.7 | 13.9 | 111 |
| 2100 | 34.8 | 2.7 | 109.1 | 0.0 | 40.1 | 13.7 | 111 |
| 2700 | 34.8 | 1.8 | 139.4 | 0.0 | 39.6 | 13.8 | 111 |
| 3000 | 34.7 | 1.6 | 147.3 | 0.0 | 39.9 | 13.7 | 111 |
| 3600 | 34.7 | 1.4 | 154.5 | 0.0 | 40.0 | 13.8 | 110 |
| 3900 | 34.7 | 1.4 | 145.9 | 0.0 | 40.0 | 13.7 | 112 |
| 4040 | 34.9 | 1.4 | 148.9 | 0.0 | 40.4 | 13.8 | 111 |
| 0803 (10.13 | 2°N 71.86 | °) | | | | | |
| 5 | 35.5 | 28.9 | 202.3 | 0.0 | 40.6 | 14.0 | 113 |
| 35 | 36.4 | 28.8 | 201.6 | 0.0 | 42.0 | 14.3 | 115 |
| 75 | 35.9 | 23.9 | 53.8 | 0.2 | 41.4 | 14.1 | 114 |
| 130 | 35.1 | 16.4 | - | 0.0 | 40.3 | 13.8 | 112 |
| 210 | 35.2 | 13.3 | 36.6 | 0.0 | 40.7 | 13.9 | 113 |
| 300 | 35.2 | 12.1 | 27.3 | 0.0 | 41.1 | 13.9 | 112 |
| 360 | 35.2 | 11.5 | 33.5 | 0.0 | 40.9 | 13.9 | 114 |
| 465 | 35.3 | 10.9 | 20.3 | 0.0 | 41.2 | 14.0 | 111 |
| 600 | 35.2 | 10.3 | 17.1 | 0.0 | 40.8 | 13.8 | 112 |
| 200 | 35.2 | 9.4 | 19.5 | 0.0 | 40.3 | 14.0 | 113 |
| 900 | 35.2 | 8.7 8.4 | 24.J 25.8 | 0.0 | 41.1 | 13.0 | 115 |
| 1000 | 35.1 | 7.7 | 34.4 | 0.0 | 41.1 | 13.8 | 112 |
| 1200 | 35.0 | 6.4 | 43.9 | 0.0 | 40.6 | 13.8 | 112 |
| 1400 | 35.0 | 5.2 | 64.3 | 0.0 | 40.0 | 13.8 | 112 |
| 1600 | 34.9 | 4.2 | 85.1 | 0.0 | - | 13.8 | 111 |
| 1800 | 34.8 | 3.3 | 101.9 | 0.0 | 40.2 | 13.7 | 111 |
| 2000 | 34.8 | 2.6 | 127.3 | 0.0 | - | 13.8 | 113 |
| 2200 | 34.8 | 2.2 | 129.8 | 0.0 | 39.9 | 13.8 | 112 |
| 2400 | 54.0 | 1.9 | 144,5 | 0.0 | 40.4 | 15.0 | 111 |
| 0805 (6.01 | °N, 77.48°E | E) | | | | | |
| 5 | 32.4 | 29.1 | 211.6 | 0.0 | 36.6 | 12.9 | 103 |
| 60 | 35.3 | 28.0 | 187.8 | 0.3 | 40.1 | 14.0 | 113 |
| 120 | 35.0 | 21.8 | 49.9 | 0.0 | 39.7 | 13.9 | 111 |
| 200 | 35.0 | 14.1 | 20.1 | 0.0 | 39.6 | 14.0 | 115 |
| 300 | 34.9 | 11.6 | 19.6 | 0.0 | 39.8 | 13.8 | 113 |
| 400 | 35.I | 10.7 | 28.4 | 0.0 | 39.5 | 13.9 | 113 |
| 490 580 | 35.0 | 0 / | 23.9 | 0.0 | 40.0 30.0 | 13.0 | 111 |
| 650 | 34.8 | 9.4 | - | 0.0 | 39.6 | 13.5 | 114 |
| 750 | 35.0 | 8.4 | 34.3 | 0.0 | 40.1 | 14.0 | 114 |
| 845 | 35.0 | 7.8 | 34.8 | 0.0 | 39.4 | 13.8 | 112 |
| 890 | 35.0 | 7.7 | 38.9 | 0.0 | 39.7 | 13.9 | 113 |
| 1000 | 35.0 | 6.9 | 45.5 | 0.0 | 40.1 | 13.7 | 115 |
| 1100 | 34.9 | 6.0 | 52.7 | 0.0 | 39.6 | 13.7 | 112 |
| 1250 | 34.9 | 5.6 | 65.1 | 0.0 | 38.9 | 13.9 | 112 |
| 1450 | 34.9 | 4.6 | 81.0 | 0.0 | 38.8 | 13.7 | 113 |
| 1650 | 34.9 | 3.8 | 96.8 | 0.0 | 39.0 | 13./ | 112 |
| 2050 | 34.ð 34.9 | 5.1 2.6 | 110.1 100 0 | 0.0 | 20.9 20.2 | 13./ 13.7 | 115 111 |
| 2050 | 34.8 | 2.0 | 133.2 | 0.0 | 39.1 | 13.9 | 111 |
| | | | | | | | |
| 0708 (15.00 | 0°N, 70.49° | °Ε) | | | | | |
| 6 | 36.0 | 28.1 | 201.8 | 0.0 | 41.3 | 14.1 | 116 |
| 67 | 36.3 | 26.2 | 146.8 | 0.3 | 40.9 | 14.3 | 118 |
| 168 | 35.5 | 15.9 | 11.4 | 1.9 | - | - | - |
| 200 | 35.3 25 F | 14.9 12.6 | 4.5 7.7 | 0.0 | 40.3 | 13.9 | 114 |
| 500 | 354 | 12.0 11.6 | 7.7 10 1 | 0.0 | 41.0 | 13.9 | 115 |
| 663 | 35.5 | 10.9 | 7.3 | 0.0 | 41.0 | 14.1 | 115 |
| | | | | | | | - |

258

| Table 4 | (continu | ed) |
|---------|----------|-----|
|---------|----------|-----|

| able I (com | maca) | | | | | | |
|-------------|-------------------------|--------------|------------------------|-------------------------|-----------------|----------------|-----------------|
| Depth(m) | Salinity | Temp (°C) | Ο ₂ (μΜ) | NO ₂ (μM) | Re (pmol/kg) | U (nmol/kg) | Mo (nmol/kg) |
| 000 | 25.4 | 0.0 | 22.2 | 0.0 | 40.4 | 140 | 115 |
| 800 | 35.4 | 9.8 | 23.2 | 0.0 | 40.4 | 14.0 | 115 |
| 1000 | 30.3 | 8.4 5.0 | 11.0 | 0.0 | 40.4 | 14.0 | 114 |
| 1400 | 24.0 | 5.9 | 45.0 | 0.0 | 40.9 | 12.0 | 114 |
| 1800 | 24.9 | 3.7 | 02.0 | 0.0 | 40.3 | 15.7 | 111 |
| 2000 | 24.0 | 5.0 | 97.7 | 0.0 | 40.4 | - 127 | 112 |
| 2200 | 54.0 | 2.5 | 109.7 | 0.0 | 40.4 | 15.7 | 111 |
| 0707 (15.00 | 0°N, 68.49° | °E) | | | | | |
| 5 | 36.2 | 27.7 | 195.5 | 0.0 | 41.0 | 14.1 | 118 |
| 70 | 36.4 | 27.2 | 184.9 | 0.2 | 42.3 | 14.3 | 117 |
| 220 | 35.7 | 14.9 | 5.1 | 4.1 | 40.8 | 13.9 | 113 |
| 380 | 35.6 | 12.4 | 5.3 | 0.5 | 40.3 | 14.1 | 114 |
| 500 | 35.5 | 11.7 | 6.6 | - | 41.2 | 14.1 | 114 |
| 550 | 35.5 | 11.4 | 11.4 | 1.0 | 40.9 | 14.0 | 111 |
| 600 | 35.5 | 11.0 | 11.4 | 0.0 | 41.0 | 14.0 | 115 |
| 900 | 35.4 | 8.8 | 14.0 | 0.0 | 41.0 | 14.0 | 115 |
| 1200 | 35.2 | 6.8 | 31.7 | 0.0 | 40.6 | 13.9 | 113 |
| 1600 | 35.0 | 4.6 | 64.3 | 0.0 | 40.4 | 13.8 | 111 |
| 2000 | 34.8 | 3.0 | 101.8 | 0.0 | 39.1 | 13.7 | 112 |
| 0706 (16.50 | 0°N, 66.50° | °N) | | | | | |
| 5 | 36.3 | 26.3 | 177.6 | 0.4 | 41.4 | 14.3 | 115 |
| 110 | 36.0 | 21.3 | 4.4 | 0.1 | 41.3 | 14.4 | 116 |
| 250 | 35.9 | 15.2 | 6.0 | 4.8 | 41.3 | 14.0 | 114 |
| 380 | 35.7 | 12.9 | 20.4 | 0.0 | 40.9 | 14.2 | 115 |
| 520 | 35.6 | 11.8 | 10.2 | 0.0 | 40.7 | 14.2 | 114 |
| 600 | 35.5 | 11.2 | 3.2 | 0.1 | 40.6 | - | - |
| 700 | 35.5 | 10.7 | 10.4 | 0.0 | 40.8 | 13.9 | 115 |
| 800 | 35.5 | 9.9 | 4.8 | 0.0 | 40.5 | 14.0 | 112 |
| 1000 | 35.3 | 8.2 | 16.2 | 0.0 | 39.5 | 13.8 | 110 |
| 1400 | 35.1 | 5.9 | 38.2 | 0.0 | 39.1 | 13.9 | 111 |
| 1800 | 34.9 | 3.7 | 73.2 | 0.0 | 38.9 | 13.8 | 112 |
| 2100 | 34.9 | 2.8 | 95.4 | 0.0 | 38.9 | 13.7 | 113 |
| 0705 (18.00 | 0°N, 68.50° | °Ε) | | | | | |
| 5 | 36.7 | 27.0 | 200.9 | 0.1 | 42.6 | 14.8 | 119 |
| 190 | 35.8 | 15.8 | 5.4 | 6.5 | 41.1 | 14.4 | 116 |
| 340 | 35.5 | 12.9 | 6.5 | 0.1 | 40.6 | 14.4 | 116 |
| 530 | 35.6 | 11.8 | 8.7 | 0.0 | 41.0 | 14.8 | 117 |
| 700 | 35.6 | 10.9 | 9.8 | 0.1 | 41.3 | 14.3 | 115 |
| 800 | 35.5 | 10.1 | 7.6 | 0.1 | 41.0 | 14.4 | 117 |
| 1000 | 35.3 | 8.6 | 11.9 | 0.1 | 40.3 | 14.6 | 11/ |
| 1800 | 35.0 | 3.8 | 102.1 | 0.3 | 39.6 | 14.2 | 116 |
| 2100 | 34.8 | 2.7 | 98.8 | 0.0 | 40.0 | 14.1 | 114 |
| 2250 | 34.8 | 2.4 | 115.1 | 0.0 | 40.1 | 14.4 | 117 |
| 0704 (18.00 | 0°N, 70.64° | °E) | | | | | |
| 5 | 35.6 | 27.7 | 207.4 | 0.0 | 40.7 | 14.2 | 114 |
| 180 | 35.6 | 17.7 | 16.3 | 5.2 | 40.7 | 14.2 | 116 |
| 325 | 35.7 | 14.0 | 10.9 | 4.3 | 40.8 | 14.1 | 114 |
| 400 | 35./ | 13.1 | 9.8 | 2.1 | 41.4 | 14.1 | 115 |
| 550 | 35.0 | 12.3 | 2.2 | - | 41.3 | 14.1 | 114 |
| 800 | 35.5 | 10.0 | 10.3 | 0.2 | 40.9 | 13.9 | 114 |
| 0703 (18.00 |)°N, 72.00° | °E) | | | | | |
| 5 | 35.5 | 28.3 | 191.1 | 0.0 | 41.3 | 14.0 | 114 |
| 55 | 36.3 | 28.5 | 183.5 | 0.1 | - | 14.4 | 117 |
| 85 | 35.5 | 23.4 | 27.1 | 0.0 | - | 14.2 | 115 |
| 0702 (17.27 | ^{7°} N, 77.44° | °E) | | | | | |
| 2 | 35.1 | - | 209.6 | 0.0 | 40.2 | 14.0 | 113 |
| ER6 (14.00° | °N, 69.00°E | E) | | | | | |
| 10 | 36.3 | 28.5 | 199.0 | 0.1 | 42.3 | 14.3 | 117 |
| 25 | 36.7 | 28.7 | 199.1 | 0.1 | 42.1 | 14.5 | 119 |
| 50 | 36.6 | 28.3 | 191.3 | 0.4 | 42.1 | 14.4 | 117 |
| 60 | 36.6 | 28.1 | 185.7 | 0.7 | 41.7 | 14.4 | 117 |
| 100 | 36.0 | 22.3 | 22.0 | 0.1 | 40.9 | 14.3 | 118 |
| 150 | 35.8 | 18.3 | 3.9 | 13.9 | 41.2 | 14.1 | 116 |
| 200 | 35.7 | 15.8 | 2.5 | 7.9 | 40.8 | 14.1 | 115 |
| 250 | 35.5 | 13.4 | 2.5 | 7.3 | 39.7 | 13.9 | 116 |
| 400 | 35.5 | 12.3 | 2.8 | 0.0 | 40.4 | 14.1 | 115 |
| 600 | 35.5 | 11.1 | 5.1 | 0.0 | 40.3 | 14.1 | 113 |
| 800 | 35.4 | 9.5 | 9.7 | 0.0 | 39.1 | 14.1 | 114 |
| 1250 | 35.1 | 6.4 | 37.0 | 0.0 | 39.3 | 13./ | 111 |

(continued on next page)

| l'at | able 4 (continued) | | | | | | | | |
|------|--------------------|----------|--------------|------------------------|-------------------------------------|-----------------|----------------|-----------------|--|
| D | Depth(m) | Salinity | Temp (°C) | Ο ₂ (μΜ) | NO ₂ (μΜ) | Re (pmol/kg) | U (nmol/kg) | Mo (nmol/kg) | |
| 2 | 000 | 34.8 | 3.0 | 103.0 | 0.0 | 39.3 | 13.8 | 111 | |
| 2 | 500 | 34.8 | 2.0 | 132.6 | 0.0 | 39.6 | 13.9 | 114 | |
| 3 | 000 | 34.7 | 1.6 | 151.3 | 0.0 | 39.0 | - | - | |
| 3 | 500 | 34.7 | 1.4 | 158.0 | 0.0 | 38.7 | 13.9 | 114 | |
| 4 | 000 | 34.7 | 1.4 | 146.7 | 0.0 | 39.2 | 13.8 | 113 | |
| 4 | 140 | 34.7 | 1.4 | 145.9 | 0.0 | 38.8 | 13.8 | 113 | |

-: not measured.

depths, typically 200-1000 m (Naqvi, 1994; Bange et al., 2005). Denitrification process is a perennial feature of the Arabian Sea water column (Fig. 1). In these suboxic layers, occurrence of dissolved H₂S has not been observed, though the presence of sulfides as metal complexes has been reported (Theberge et al., 1997). Further, measurable sea-air fluxes of methane from the upper layers of the Arabian Sea have been explained in terms of reducing micro environments (Owens et al., 1991; Lal et al., 1996). In addition to suboxic conditions at intermediate waters, the Arabian Sea is a region of high particle flux through its water column (25–50 g m⁻² y⁻¹; Ramaswamy and Nair, 1994). These features make Arabian Sea a suitable basin to study the behavior of redox sensitive elements such as Re, U and Mo in the water column. In contrast to the water column, signatures of reducing (anoxic) environment are more wide spread in the Arabian Sea sediments. For example, the high abundances of organic matter, authigenic uranium in the margin and shelf sediments of the Arabian Sea has been attributed to presence of reducing environments (Borole et al., 1982).

The Indus River is the largest river flowing into Arabian Sea, supplying 9×10^{13} l of water and 400 million tons of sediments to the Arabian Sea annually, though in recent decades, its flow has been restricted considerably due to construction of dams (Garzanti et al., 2005). In addition, there are several medium and minor rivers draining into the Arabian Sea; the Narmada, Tapi, Mahi and several rivers flowing through the Western Ghats of India. Altogether these rivers supply ~8 × 10¹³ l of water and ~100 million tons of sediments annually. Also, being in the proximity of Asian landmass with widespread deserts, aeolian transport of dust is also a significant source of sediments to the Arabian Sea; contributing ~100 million tons of sediments (Goldberg and Griffin, 1970; Kolla et al., 1976; Sirocko and Sarnthein, 1989; Ramaswamy and Nair, 1994).

The Arabian Sea exhibits distinct lateral salinity gradients in the upper 1000 m (Wyrtki, 1971, 1973) due to marked differences in the rate of evaporation over precipitation and the influx of less saline waters from the Bay of Bengal through its southeastern corner. In addition, the Persian Gulf and the Red Sea contribute high salinity waters to the Arabian Sea at depths of about 200 m and 500 m



Fig. 2. Representative θ -S (potential temperature vs. salinity) plots for the stations in the Arabian Sea. The σ_{θ} contours are also shown along with the characteristic water masses in the Arabian Sea. The plot for the station 0805 shows a lower salinity for the surface waters. This is due to entrance of low salinity waters from the Bay of Bengal.

Author's personal copy

V. Goswami et al. / Chemical Geology 291 (2012) 256-268

respectively. Thus, the upper 1000 m water column of the Arabian Sea is composed of three characteristic water masses, the Arabian Sea High Salinity Water (ASHSW), the Persian Gulf Water (PGW) and the Red Sea Water (RSW) (Rochford, 1964; Wyrtki, 1973; Shenoi et al., 1993; Kumar and Li, 1996).

3. Methods

Seawater samples were collected during three cruises in the Arabian Sea; SS-256 (Dec, 2007) and SS-259 (Nov, 2008) onboard

FORV Sagar Sampada and GEOTRACES oceanographic expedition KH-09-5 (Dec, 2009) onboard R/V Hakuho Maru of the Japan Agency of Marine Science and Technology (JAMSTEC). The sampling locations are shown in Fig. 1 and the details of the sampling stations are given in Table 1. Water samples were collected using 12 l Niskin bottles on 12 position CTD rosette array (on SS-256 and SS-259) or a 24 position CTD rosette array (on KH-09-5). The seabird CTD was used in all of the oceanographic expeditions to measure conductivity, temperature and depth. On the KH-09-5 cruise, a clean CTD system was used which consisted of titanium hydrographic wire. After collection,



Fig. 3. Latitudinal variation in (a) temperature (°C), (b) salinity, (c) dissolved oxygen (μ M), (d) nitrite (μ M), (e) Re (pmol/kg), (f) U (nmol/kg) and (g) Mo (nmol/kg) in the Arabian Sea. All the plots were made using the ocean data view (ODV) program (Schlitzer, 2010).

V. Goswami et al. / Chemical Geology 291 (2012) 256-268



water samples for trace element analysis were further sub-sampled into clean 2 l carboys on SS-256 and SS-259 cruises and filtered in onboard clean lab through 0.45 µm Millipore cellulose filter. In the KH-09-5 cruise, the water samples were filtered through 0.2 µm Acropak cartridge filters in a HEPA filtered clean air chamber. Filtered seawater samples were stored in precleaned (by soaking in 2 N HCl for several days and cleaning profusely with MilliQ water) polypropylene bottles. The samples were acidified to pH~2 using ultrapure quartz distilled HCl. For Re measurements, a known weight of seawater (typically ~50 g) was spiked with a known amount of ¹⁸⁵Re enriched (94.5%) tracer and stored at room temperature for at least 24 h for sample-spike equilibration. Subsequently, the spiked samples were dried at 80 °C and digested with a few drops of quartz distilled HNO₃. The Re was extracted and purified from the residue by ion exchange separation methods (Trivedi et al., 1999; Dalai et al., 2002; Rahaman and Singh, 2010). The purified Re was redissolved in 5 ml 0.4 N HNO₃. The Re concentration in the acid solutions was determined by measuring



their ¹⁸⁵Re/¹⁸⁷Re ratio on Thermo X-Series II Q-ICP-MS facility at PRL. Instrumental mass fractionation correction was done by measuring Re standard of natural composition frequently. The sample counts were generally in excess of several thousand cps for both ¹⁸⁵Re and ¹⁸⁷Re, compared to 10 cps for the background.

U and Mo concentrations were also measured by isotope dilution inductively coupled plasma mass spectrometry. For these measurements, about 0.25 g of precisely weighed sample was mixed with precisely known weights of 236 U (99.97%) and 100 Mo (95.9%) enriched spikes. The sample spike mixture was allowed to equilibrate and diluted ~30 times using 0.4 N HNO₃ (Klinkhammer and Palmer, 1991). The 236 U/ 238 U and 100 Mo/ 98 Mo ratios were determined on the diluted samples. The sample counts were greater than 4000 for 98 Mo and greater than 15,000 for 100 Mo, 236 U and 238 U. The background counts monitored during the runs were a few orders of magnitude lower than those for 98 Mo, 100 Mo, 236 U and 238 U.

Total procedural blank levels were also measured for all the three elements. The average blank based on eight independent measurements was found to be 5 ± 2 pg for Re; 0.8 ± 0.2 pg for U and 100 ± 20 pg for Mo. As these blanks were much lower than the sample levels, no corrections for blanks were made. Several samples were measured in replicates to determine the analytical precision; the results of these analyses are given in Tables 2a and 2b. Analytical precision (CV%), determined based on the replicate analyses are ~1%, 0.6% and 0.8% for Re, U and Mo measurements respectively.

Along with the samples, a few SAFe (Sampling and Analysis of Fe) samples were also analyzed for Re, U and Mo. Their salinity normalized concentrations are similar to their open ocean values (Table 3; Collier, 1985; Chen et al., 1986; Anbar et al., 1992; Colodner et al., 1993; Singh et al., 2011).

Salinity, dissolved oxygen (DO) and nitrite concentration of the samples were measured onboard on all three expeditions. Salinity was determined by measuring the conductivity of the samples using a salinometer. Dissolved oxygen was measured by the Winkler's titration method and the nitrite content using an autoanalyzer. The salinity, DO and nitrite data are given in Table 4 along with the other measured parameters.

4. Results

4.1. General observations

Fig. 2 shows two typical θ -S (potential temperature vs. salinity) plots from the stations investigated in the present study. The ASHSW is found in all the stations excluding the station lying in the southern

Arabian Sea in proximity of the western edge of the Bay of Bengal (station 0805). The water masses PGW and RSW are also shown.

The temperature profile in the Arabian Sea shows well stratified layers with higher temperatures (25-30 °C) at the surface (Fig. 3a). The salinity in the Arabian Sea shows higher values (35-37) in the surface and sub-surface waters which are prominent north of 10 °N (Fig. 3b). Near the southernmost station at ~6 °N, the surface water salinity is much lower. The depth of penetration of high salinity waters is more toward the north (Fig. 3b).

North of 12 °N, dissolved oxygen shows a very prominent minimum between 100 and 1200 m (Fig. 3c). The high surface productivity coupled with restricted ventilation contributes to extreme depletion of dissolved oxygen in these waters. This, as mentioned earlier, creates widespread oxygen minimum zone (OMZ) with active water column denitrification (Naqvi, 1994; Bange et al., 2005), as evidenced from secondary nitrite maxima (SNM) in the upper 500 m of water column (Fig. 3d). The redox conditions prevailing in the intermediate waters of Arabian Sea significantly influence the vertical distribution of suite of trace elements especially Fe and Mn (Saager, 1994; Lewis and Luther, 2000; Moffett et al., 2007).

4.2. Re, U and Mo distributions

The Re, U and Mo concentrations of the samples along with the salinity, dissolved oxygen and nitrite concentration are listed in Table 4 and presented in Fig. 4. The Re, U and Mo concentrations vary from 37 to 43 pmol/kg, 12.9 to 14.8 nmol/kg and 103 to 119 nmol/kg respectively, covering a salinity range from 32.4 to 36.7 and a wide range of dissolved oxygen levels from 2.2 µM to 212 µM. Most of the stations sampled experience active water column denitrification (Fig. 1), the exceptions being stations 0803, 0805 and the shallow stations 0702 and 0703. The Re, U and Mo concentrations in four nearby profiles viz. 0802, 0708, 0707 and ER6 (within $\pm\,1^\circ$ latitude and longitude) are quite similar overlapping within analytical uncertainties (Table 4, Fig. 4). The observation that the concentrations of Re, U and Mo are nearly identical in samples collected by conventional sampling system and clean sampling technique onboard KH-09-5 (station ER6) suggests that for these elements conventional sampling system does not introduce discernible contamination during sampling.

The distribution of Re, U and Mo (Fig. 3e–g) shows a correlation with salinity (Fig. 3b), rather than with the dissolved oxygen (Fig. 3c) in the Arabian Sea. The common feature shared by salinity and Re, U and Mo concentrations is an increase toward higher latitudes in the Arabian Sea.



Fig. 4. Depth profiles of dissolved Re, U and Mo concentrations in the Arabian Sea along with the salinity (blue), dissolved oxygen (DO; red) and nitrite (green) profiles in (a) 0802, (b) 0803, (c) 0805, (d) 0708, (e) 0707, (f) 0706, (g) 0705, (h) 0704, and (i) ER6. The bars shown at the bottom right of the plots show the analytical uncertainties in the measurement of Re, U and Mo.

5. Discussion

5.1. Re, U and Mo in the water column of the Arabian Sea

The vertical profiles for Re, U and Mo in the Arabian Sea are shown in Fig. 4 (a to i), along with profiles for DO, nitrite and salinity. The data show that within analytical uncertainties, the dissolved Re, U and Mo

concentrations within each profile and among the profiles are independent of the dissolved oxygen concentration, but covary with the salinity. The Re, U and Mo concentrations do not exhibit any significant correlation with the dissolved oxygen in the water column (Fig. 5). The average Re (n=11), U (n=10) and Mo (n=10) in the samples with DO concentration less than 5 μ M are 40.7 \pm 1.0 pmol/kg, 14.1 \pm 0.3 nmol/kg and 114 \pm 3 nmol/kg respectively (Table 5, Fig. 5). The errors given



are 2σ spread in the data. This is nearly identical to the average Re (n=41), U (n=42) and Mo (n=42) concentrations of $40.4 \pm 2.6 \text{ pmol/kg}$, $14.0 \pm 1.0 \text{ nmol/kg}$ and $114 \pm 6 \text{ nmol/kg}$ respectively, in samples with DO concentration greater than 100 μ M (Table 5). The larger scatter in the data of samples with DO > 100 μ M is due to salinity variations. The near identical concentrations of dissolved Re, U and Mo in samples with DO <5 μ M and DO > 100 μ M (Table 5) suggest

that, the abundances of these redox sensitive elements are not affected by the suboxic conditions in the water column. This inference is also reaffirmed by the frequency distribution plots for Re, U and Mo concentrations for different dissolved oxygen levels (Fig. 5a, b and c).

The nitrite profiles (Figs. 3d, 4) show the presence of secondary nitrite maxima (SNM) in the upper water column (200–600 m) north of 12 °N, in stations 0802, 0708, 0707, 0706, 0705, 0704 and



ER6, whereas, in stations 0803 and 0805 SNM is not seen, suggesting that these two stations lie outside the active water column denitrification zone. The near identical concentrations of Re, U and Mo in samples from the denitrification zone and outside it further suggests that denitrification also does not impact the distribution of these three redox sensitive elements in the water column of Arabian Sea (Table 4).

The two shallow stations (0702 and 0703) occupied during the cruise SS-256 (Dec, 2007) lie on the western Indian shelf in the

zone where intense seasonal hypoxia and water column H_2S have been reported (Naqvi et al., 2000). Dissolved H_2S was not measured during the sampling, but considering that local seasonal hypoxia occurs during October, it is likely that it waned by the time samples were collected in December for the present work from these locations. The measurable DO levels (DO ~ 27 μ M) support this contention. The Re, U and Mo concentrations in the surface sample at station 0702 are 40.2 pmol/kg, 14.0 nmol/kg and 113 nmol/kg respectively, quite similar to the open ocean values. At station 0703, where three



Fig. 5. Frequency distribution of (a) Re, (b) Mo and (c) U in the samples analyzed. It is evident that the concentration of these elements in samples with DO $<5 \,\mu$ M and DO $>100 \,\mu$ M is the same within errors; the scatter in the data is due to variation in salinity.

samples were collected in the vertical profile up to a depth of 85 m (water depth 98 m), the U and Mo concentrations show nearly constant values of 14.2 ± 0.2 and 115 ± 2 respectively. Re concentration was measured only in the surface sample which had a value of 40.2 pmol/kg; nearly the same as the value for the open ocean (Table 4). These results suggest that the impact of dissolved H₂S, if

Table 5Statistics of Re, U and Mo concentration with oxygen.

| DO (µM) | n (Re) | Re (pmol/kg) | 2σ (Re) | n (U) | U (nmol/kg) | 2σ (U) | n (Mo) | Mo (nmol/kg) | 2σ (Mo) |
|------------|-----------|-----------------|------------|----------|----------------|-----------|-----------|-----------------|------------|
| <5 | 11 | 40.7 | 1.0 | 10 | 14.1 | 0.3 | 10 | 114 | 3 |
| 5-10 | 20 | 40.8 | 1.1 | 20 | 14.1 | 0.5 | 20 | 114 | 3 |
| <10 | 31 | 40.8 | 1.1 | 30 | 14.1 | 0.4 | 30 | 114 | 3 |
| >10 | 96 | 40.3 | 2.0 | 98 | 14.0 | 0.5 | 99 | 113 | 5 |
| >100 | 41 | 40.4 | 2.6 | 42 | 14.0 | 1.0 | 42 | 114 | 6 |
| All | 127 | 41.1 | 1.9 | 128 | 14.0 | 0.5 | 129 | 114 | 5 |

any on the abundances of these elements also waned away by the time of sampling.

The Re, U and Mo concentrations in the Arabian Sea show good correlation with the salinity with correlation coefficients of 0.96, 0.93 and 0.96 respectively (Fig. 6). The data for the SAFe waters (Pacific Ocean; this study), Bay of Bengal (Singh et al., 2011) and Pacific Ocean (Chen et al., 1986; Anbar et al., 1992) are also shown (Fig. 6). The Re, U and Mo in the Arabian Sea, Bay of Bengal and Pacific Ocean show a good correlation with salinity. This covariation is a strong indication that salinity is the dominant factor governing the distribution of these three redox sensitive elements in the ocean water column. This makes physical process such as evaporation and mixing of water masses more significant in deciding the Re, U and Mo distributions in the ocean rather than the biogeochemical processes. The concentrations of Re, U and Mo in surface waters of the Arabian Sea are generally high which are attributable to high salinity of these waters. In contrast, in the surface water of station 0805 (6.01°N, 77.48°E), which lies in the southern Arabian Sea, the Re concentration is as low as 36.6 pmol/kg. The U and Mo concentrations are also lower in this water with values of 12.9 nmol/kg and 103 nmol/kg respectively. These low values are consistent with low salinity of this water (32.4). The lower salinity in this surface sample is due to influx of less saline water from the Bay of Bengal into the Arabian Sea during winter monsoon (North-East monsoon). During this season north-easterly winds in the Bay of Bengal set up the East Indian Coastal Current (EICC) as a southward western boundary current which runs parallel to the Indian peninsula carrying low salinity waters from the Bay of Bengal. This low salinity surface water, characterized by lower concentrations of Re, U and



Fig. 6. Concentration of (a) Re, (b) U and (c) Mo vs. salinity in the Arabian Sea. The measured concentrations for each tenth of salinity (e.g.: 34.9, 35.0, 35.1, etc.) are averaged to minimize the clutter in data. Data show a good correlation with salinity suggesting that salinity is a dominant factor governing the distribution of these elements in the water column. The concentration of Re is in the units of pmol/kg while the concentrations of U and Mo are in the units of nmol/kg. The data from the Bay of Bengal and Pacific Ocean are also plotted.

Mo (Singh et al., 2011) enters the Arabian Sea via the West Indian Coastal Current (Wyrtki, 1973; Schott and McCreary, 2001; Shankar et al., 2002). This coupling between Re, U and Mo abundances and salinity suggests that these elements can serve as tracers of water masses in the Arabian Sea and the Bay of Bengal.

Comparison of Re profile in the Arabian Sea with that reported for the Pacific Ocean (Anbar et al., 1992) show a distinct difference. In the Pacific, the data showed enrichment of Re in surface waters which was unexplained by salinity variations. The high Re content in the surface waters of Pacific Ocean was attributed to possible input of anthropogenic Re to the surface ocean via the atmosphere. In the surface waters of Arabian Sea, no such enrichment is observed in the concentration of Re (Fig. 4). Thus the role of atmospheric/aeolian input of Re to the surface waters of Arabian Sea is insignificant.

Table 6 is a comparison of Re, U and Mo concentrations in the Arabian Sea, Bay of Bengal, Pacific Ocean and Atlantic Ocean in waters of 35 salinity. The data show that Re, U and Mo concentrations in these basins are same within uncertainties and suggest that the Re, U and Mo distribution in the ocean is uniform. Further considering that the settling particles in the Bay of Bengal are dominated by river detritus whereas those in the Arabian Sea by biogenic material produced in the surface water (Ramaswamy and Nair, 1994), it can be inferred that the composition and nature of settling particles also do not influence the water column distribution of these elements.

5.2. Re, U and Mo in the Arabian Sea sediments

There have been a few studies on the abundance and distribution of Re, U and Mo in the sediments of the Arabian Sea (Borole et al., 1982; Sirocko et al., 2000; Pattan and Pearce, 2009). These studies show that these elements are enriched in sediments with high organic carbon. For example, in the organic carbon rich surface sediments of the Arabian Sea, up to 50 times enrichment in the Re/Al ratio (Pattan and Pearce, 2009) has been reported over the upper continental crust (UCC, Taylor and McLennan, 1985; Viers et al., 2009). Similarly, U/Al and Mo/Al are also enriched in the surface sediments with ratios up to 8 and 4 times over the UCC value. These data indicate that the organic matter plays an important role in sequestering these elements in sediments.

Primary productivity was not measured during this study. However, available data show that primary productivity is in the range of 0.5 to $2.5 \text{ g C m}^{-2} \text{ d}^{-1}$ in the Arabian Sea surface water during winter (Madhupratap et al., 1996). Further, results of sediment trap deployment in the eastern and central Arabian Sea showed that settling flux of particles is in the range of 25–30 g m⁻² y⁻¹, with ~6% of organic carbon (Ramaswamy and Nair, 1994). These studies suggest that there is significant primary productivity and rain of organic matter through the water column of the Arabian Sea. This high productivity and biogenic particle rain through the water column do not seem to have any discernible impact on the dissolved profile of Re, U and Mo as evidenced from their uniform lateral and vertical distribution. Therefore the enrichment of Re, U and Mo observed in organic matter rich sediments seems to be due to their removal at the sediment–water interface. Investigations on

| Table | 6 |
|-------|---|
|-------|---|

| Region | Re (pmol/ | 1σ | U (nmol/ | 1σ | Mo (nmol/ | 1σ |
|---|-------------------|------------------|--------------------|-------------------|------------------|----------------|
| | kg) | (Re) | kg) | (U) | kg) | (Mo) |
| Arabian Sea [†] Bay of Bengal [#] | 39.8 41.0 | 0.7 0.8 | 13.8 13.9 | 0.1 0.1 | 114 112 | 1 1 |
| Pacific Ocean | 40.1 [*] | 1.1 [*] | 13.7 ^{\$} | 0.1 ^{\$} | 107 [£] | 3£ |
| Atlantic Ocean | 40.1 [€] | 0.4 [€] | 13.6 [¥] | 0.4 [¥] | 109 [§] | 9 [§] |

[†]This study, [#]Singh et al., 2011, ^{*}Anbar et al., 1992, ^{\$}Chen et al., 1986, [£]Collier 1985, [€]Colodner et al., 1993, [¥] Ku et al., 1977, [§]Morris, 1975. the pore water abundances of Re, U and Mo in the sediments are required to better understand and characterize the mechanism of removal of these elements from the waters of the Arabian Sea.

6. Conclusions

The dissolved Re, U and Mo concentrations from the oxic and suboxic layers of the Arabian Sea show that these elements behave conservatively in the water column, i.e. there is no discernible removal of Re, U or Mo from the suboxic and denitrifying layers of the Arabian Sea. The concentrations of Re, U and Mo in the water column of the Arabian Sea vary as a function of salinity with good correlation. Comparison of the concentrations of Re, U and Mo in the water column of the Arabian Sea with data from other oceanic regions show that they overlap with each other for the same salinity suggesting that salinity exerts a dominant control on their concentration and that Re, U and Mo behave conservatively in the water column. The salinity-concentration link further supports that the distribution of these elements is governed by physical processes of advection and mixing between water masses and evaporation and not by biogeochemical processes operating in the water column. The salinity dependence of Re, U and Mo concentrations hints at the possibility of using their distributions to track water masses.

Acknowledgments

We are grateful to the captain, crew and scientific party of FORV Sagar Sampada cruise No. 256, 259 and the GEOTRACES oceanographic expedition onboard RV Hakuho Maru (cruise No. KH-09-5; Eridanus expedition). We thank chief scientist Prof. T. Gamo, and the scientific party of the Eridanus expedition for their help during sampling and the Director and staff of CMLRE for logistic support for the expeditions onboard FORV Sagar Sampada. We sincerely thank Ministry of Earth Sciences, Government of India for financial support. Discussions with Prof. S. Krishnaswami and his comments were helpful and constructive on improving this manuscript. We thank Mr. J.P. Bhavsar, Mr. B. Srinivas, Mr. Satinder Pal Singh and Ms. Jayati Chatterjee for their assistance during various onboard sampling and measurements. Re, U and Mo concentrations were measured using the ICP-MS facility of the PLANEX program; we thank Prof. S. V. S. Murty for providing the instrument time and Mr. Durga Prasad for help during the measurements. We thank the two anonymous reviewers and Prof. Joel D. Blum, co-editor in chief, for their fruitful reviews.

References

- Anbar, A.D., Creaser, R.A., Papanstassiou, D.A., Wasserburg, G.J., 1992. Rhenium in seawater: confirmation of generally conservative behavior. Geochimica et Cosmochimica Acta 56, 4099–4104.
- Anderson, R.F., 1987. Redox behavior of uranium in an anoxic marine basin. Uranium 3, 145–164.
- Anderson, R.F., Fleisher, M.Q., LeHuray, A.P., 1989. Concentration, oxidation state, and particulate flux of uranium in the Black Sea. Geochimica et Cosmochimica Acta 53, 2215–2224.
- Bange, H.W., Naqvi, S.W.A., Codispoti, L.A., 2005. The nitrogen cycle in the Arabian Sea. Progress in Oceanography 65, 145–158.

Borole, D.V., Krishnaswami, S., Somayajulu, B.L.K., 1982. Uranium isotopes in rivers, estuaries and adjacent coastal sediments of eastern India: their weathering, transport and oceanic budget. Geochimica et Cosmochimica Acta 46, 125–137.

Bruland, K.W., Lohan, M.C., 2003. Controls of trace metals in seawater. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry: the Oceans and Marine Geochemistry. 6. Elsevier Pergamon. Oxford. pp. 23–47

istry, 6. Elsevier Pergamon, Oxford, pp. 23–47. Chen, J.H., Edwards, R.L., Wasserburg, G.J., 1986. ²³⁸U, ²³⁴U and ²³²Th in seawater. Earth and Planetary Science Letters 80, 241–251.

Collier, R.W., 1985. Molybdenum in the Northeast Pacific Ocean. Limnology and Oceanography 30, 1351–1354.

Colodner, D., Sachs, J., Ravizza, R., Turekian, K., Edmond, J., Boyle, E., 1993. The geochemical cycle of rhenium: a reconnaissance. Earth and Planetary Science Letters 117, 205–221.

Colodner, D., Edmond, J., Boyle, E., 1995. Rhenium in the Black Sea: comparison with molybdenum and uranium. Earth and Planetary Science Letters 131, 1–15.

Author's personal copy

V. Goswami et al. / Chemical Geology 291 (2012) 256-268

- Crusius, J., Calvert, S., Pedersen, T., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. Earth and Planetary Science Letters 145, 65–78.
- Crusius, J., Pedersen, T.F., Calvert, S.E., Cowie, G.L., Oba, T., 1999. A 36 kyr geochemical record from the Sea of Japan of organic matter flux variations and changes in intermediate water oxygen concentrations. Paleoceanography 14, 248–259.
- Dalai, T.K., Singh, S.K., Trivedi, J.R., Krishnaswami, S., 2002. Dissolved rhenium in the Yamuna River System and the Ganga in the Himalaya: role of black shale weathering on the budgets of Re, Os, and U in rivers and CO₂ in the atmosphere. Geochimica et Cosmochimica Acta 66, 29–43.
- Emerson, S.R., Huested, S.S., 1991. Ocean anoxia and the concentration of molybdenum and vanadium in seawater. Marine Chemistry 34, 177–196.
- Garzanti, E., Vezzoli, G., Andò, S., Paparella, P., Clift, P.D., 2005. Petrology of Indus River sands: a key to interpret erosion history of the Western Himalayan Syntaxis. Earth and Planetary Science Letters 229, 287–302.
- Goldberg, E.D., Griffin, J.J., 1970. The sediments of the northern Indian Ocean. Deep Sea Research 17, 513–537.
- Helz, G.R., Bura-Nakić, E., Mikac, N., Ciglenečki, I., 2011. New model for molybdenum behavior in euxinic waters. Chemical Geology 284, 323–332.
- Henderson, G.M., Slowey, N.C., Fleisher, M.Q., 2001. U-Th dating of carbonate platform and slope sediments. Geochimica et Cosmochimica Acta 65, 2757-2770.
- Kendall, B., Creaser, R.A., Selby, D., 2009. ¹⁸⁷Re⁻¹⁸⁷Os geochronology of Precambrian organic-rich sedimentary rocks. In: Craig, J., Thurow, J., Thusu, B., Whitham, A., Abutarruma, Y. (Eds.), Global Neoproterozoic Petroleum Systems: the Emerging Potential in North Africa: Geological Society (London) Special Publications, 326, pp. 85–107.
- Klinkhammer, G.P., Palmer, M.R., 1991. Uranium in the oceans: where it goes and why. Geochimica et Cosmochimica Acta 55, 1799–1806.
- Kolla, V., Henderson, L., Biscaye, P.E., 1976. Clay minerology and sedimentation in the Western Indian Ocean. Deep Sea Research 23, 949–961.
- Ku, T.-L., Knauss, K.G., Mathieu, G.G., 1977. Uranium in open ocean: concentration and isotopic composition. Deep Sea Research 24, 1005–1017.
- Kumar, M.D., Li, Y.-H., 1996. Spreading of water masses and regeneration of silica and 226Ra in the Indian Ocean. Deep Sea Research 43, 83–110.
- Lal, S., Patra, P.K., Venkatramni, S., Sarin, M.M., 1996. Distribution of nitrous oxide and methane in the Arabian Sea. Current Science 71, 894–899 (Special section: JGOFS India).
- Lewis, B.L., Luther III, G.W., 2000. Processes controlling the distribution and cycling of manganese in the oxygen minimum zone of the Arabian Sea. Deep Sea Research 47, 1541–1561.
- Madhupratap, M., Prasanna kumar, S., Bhattathiri, P.M.A., Kumar, M.D., Raghukumar, S., Nair, K.K.C., Ramaiah, N., 1996. Mechanism of the biological response to winter cooling in the northeastern Arabian Sea. Nature 384, 549–551.
- McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E., Klinkhammer, G.P., Holm, C., 2006. Molybdenum and uranium geochemistry in continental margin sediments: paleoproxy potential. Geochimica et Cosmochimica Acta 70, 4643–4662.
- Moffett, J.W., Goepfert, T.J., Naqvi, S.W.A., 2007. Reduced iron associated with secondary nitrite maxima in the Arabian Sea. Deep Sea Research 54, 1341–1349.
- Morel, F.M.M., Price, N.M., 2003. The biogeochemical cycles of trace metals in the oceans. Science 300, 944–947.
- Morford, J.L., Emerson, S., 1999. The geochemistry of redox sensitive trace metals in sediments. Geochimica et Cosmochimica Acta 63, 1735–1750.
- Morford, J.L., Russell, A.D., Emerson, S., 2001. Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, Saanich Inlet, BC. Marine Geology 174, 355–369.
- Morford, J.L., Emerson, S., Breckel, E.J., Kim, S.K., 2005. Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin. Geochimica et Cosmochimica Acta 69, 5021–5032.
- Morris, A.W., 1975. Dissolved molybdenum and vanadium in the northeast Atlantic Ocean. Deep Sea Research 22, 49–54.
- Nameroff, T.J., Balistrieri, L.S., Murray, J.W., 2002. Suboxic trace metal geochemistry in the Eastern Tropical North Pacific. Geochimica et Cosmochimica Acta 66, 1139–1158.
- Nameroff, T.J., Calvert, S.E., Murray, J.W., 2004. Glacial-interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals. Paleoceanography 19, PA1010.
- Naqvi, S.W.A., 1994. Denitrification processes in the Arabian Sea. Proceedings of the Indian Academy of Sciences – Earth and Planetary Sciences 103, 279–300.

- Naqvi, S.W.A., Jayakumar, D.A., Narvekar, P.V., Naik, H., Sarma, V.V.S.S., D'Souza, W., Joseph, S., George, M.D., 2000. Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf. Nature 408, 346–349.
- Owens, NJ.P., Law, C.S., Mantoura, R.F.C., Burkill, P.H., Llewellyn, C.A., 1991. Methane flux to the atmosphere from the Arabian Sea. Nature 354, 293–295.
- Pattan, J.N., Pearce, N.J.G., 2009. Bottom water oxygenation history in southeastern Arabian Sea during the past 140 ka: results from redox-sensitive elements. Palaeogeography, Palaeoclimatology, Palaeoecology 280, 396–405.
- Rahaman, W., Singh, S.K., 2010. Rhenium in rivers and estuaries of India: sources, transport and behaviour. Marine Chemistry 118, 1–10.
- Ramaswamy, V., Nair, R.R., 1994. Fluxes of material in the Arabian Sea and Bay of Bengal – sediment trap studies. In: Lal, D. (Ed.), Biogeochemistry of the Arabian Sea: Indian Academy of Sciences, Proceedings of the Indian National Science Academy, Bangalore, pp. 189–210.
 Rengarajan, R., Sarin, M.M., Krishnaswami, S., 2003. Uranium in the Arabian Sea: role of
- Rengarajan, R., Sarin, M.M., Krishnaswami, S., 2003. Uranium in the Arabian Sea: role of denitrification in controlling its distribution. Oceanologica Acta 26, 687–693.
- Rochford, D.J., 1964. Salinity maxima in the upper 1000 meters of the North Indian Ocean. Australian Journal of Marine and Freshwater Research 15, 1–24.
- Saager, P.M., 1994. The biogeochemical distribution of trace elements in the Indian Ocean. In: Lal, D. (Ed.), Biogeochemistry of the Arabian Sea: Indian Academy of Sciences, Proceedings of the Indian National Science Academy, Bangalore, pp. 237–278.
- Saager, P.M., De Baar, H.J.W., Burkill, P.H., 1989. Manganese and iron in Indian Ocean waters. Geochimica et Cosmochimica Acta 53, 2259–2267.
- Sarkar, A., Bhattacharya, S.K., Sarin, M.M., 1993. Geochemical evidence for anoxic deep water in the Arabian Sea during the last glaciation. Geochimica et Cosmochimica Acta 57, 1009–1016.
- Schlitzer, R., 2010. Ocean Data View. http://odv.awi.de.
- Schott, F.A., McCreary Jr., J.P., 2001. The monsoon circulation of the Indian Ocean. Progress in Oceanography 51, 1–123.
- Shankar, D., Vinayachandran, P.N., Unnikrishnan, A.S., 2002. The monsoon currents in the north Indian Ocean. Progress in Oceanography 52, 63–120.
- Shenoi, S.S.C., Shetye, S.R., Gouveia, A.D., Michael, G.S., 1993. Salinity extrema in the Arabian Sea. Mitteilungen des Geologisch-Paläontologischen Instituts der Universität Hamburg SCOPE/UNEP Sonderband., 76, pp. 37–49.
- Singh, S.P., Singh, S.K., Bhushan, R., 2011. Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal. Marine Chemistry 126, 76–88.
- Sirocko, F., Sarnthein, M., 1989. Wind-borne deposits in the northwestern Indian Ocean: record of Holocene sediments versus modern satellite data. In: Leinen, M., Sarnthein, M. (Eds.), Paleoclimatology and Paleometerology: Modern and Past Patterns of Global Atmospheric Transport, pp. 401–433.
- Sirocko, F., Schonberg, D.G., Devey, C., 2000. Processes controlling trace element geochemistry of Arabian Sea sediments during the last 25,000 years. Global and Planetary Change 26, 217–303.
- Sohrin, Y., Matsui, M., Nakayam, E., 1999. Contrasting behavior of tungsten and molybdenum in the Okinawa Trough, the East China Sea and the Yellow Sea. Geochimica et Cosmochimica Acta 63, 3457–3466.
- Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: its Composition and Evolution. Blackwell, Oxford.
- Theberge, S.M., Luther III, G.W., Farrenkopf, A.M., 1997. On the existence of free and metal complexed sulfide in the Arabian Sea and its oxygen minimum zone. Deep Sea Research 44, 1381–1390.
- Trivedi, J.R., Singh, S.K., Krishnaswami, S., 1999. ¹⁸⁷Re-¹⁸⁷Os in Lesser Himalayan sediments: measurement techniques and preliminary results. Proceedings of the Indian Academy of Sciences – Earth and Planetary Sciences 108, 179–187.
- Viers, J., Dupré, B., Gaillardet, J., 2009. Chemical composition of suspended sediments in World Rivers: new insights from a new database. Science of the Total Environment 407, 853–868.
- Vorlicek, T.P., Helz, G.R., 2002. Catalysis by mineral surfaces: implication for Mo geochemistry in anoxic environments. Geochimica et Cosmochimica Acta 66, 3679–3692.
- Wyrtki, K., 1971. Oceanographic Atlas of the International Indian Ocean Expedition. National Science Foundation, Washington, DC. 531 pp.
- Wyrtki, K., 1973. Physical oceanography of the Indian Ocean. In: Zeitschel, B. (Ed.), The Biology of the Indian Ocean. Springer-Verlag, Berlin, pp. 18–36.





Published by AGU and the Geochemical Society

Temporal variations in 87 Sr/ 86 Sr and ε_{Nd} in sediments of the southeastern Arabian Sea: Impact of monsoon and surface water circulation

Vineet Goswami, Sunil K. Singh, Ravi Bhushan, and Vinai K. Rai

Physical Research Laboratory, Ahmedabad 380 009, India (vineetg@prl.res.in; sunil@prl.res.in; bhushan@prl.res.in; rai@prl.res.in)

[1] Sr and Nd isotopic composition of silicate fractions of sediments have been measured in two well dated gravity cores from the eastern Arabian Sea archiving a depositional history of ~29 and ~40 ka. The 87 Sr/ 86 Sr and ε_{Nd} in the northern core (SS-3104G; 12.8°N, 71.7°E) ranges from 0.71416 to 0.71840 and -8.8 to -12.8; these variations are limited compared to those in the southeastern core (SS-3101G; 6.0° N, 74.0°E), in which they vary from 0.71412 to 0.72069 and -9.0 to -15.2 respectively. This suggests that the variation in the relative proportions of sediments supplied from different sources to the core SS-3104G are limited compared to core SS-3101G. The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} profiles of SS-3101G exhibit two major excursions, ca. 9 ka and 20 ka, coinciding with periods of Holocene Intensified Monsoon Phase (IMP) and the Last Glacial Maximum (LGM) respectively with more radiogenic 87 Sr/ 86 Sr and lower ε_{Nd} during these periods. These excursions have been explained in terms of changes in the erosion patterns in the source regions and surface circulation of the Northern Indian Ocean resulting from monsoon intensity variations. The intensification of North-East (NE) monsoon and associated strengthening of the East Indian Coastal Current in southwest direction during LGM transported sediments with higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} from the western Bay of Bengal to the Arabian Sea. In contrast, enhanced South-West (SW) monsoon at \sim 9 ka facilitated the transport of sediments from the northern Arabian Sea, particularly Indus derived, to the southeastern Arabian Sea. This study thus highlights the impact of monsoon variability on erosion patterns and ocean surface currents on the dispersal of sediments in determining the Sr and Nd isotopic composition of sediments deposited in the eastern Arabian Sea during the last ~40 ka.

Components: 8600 words, 6 figures, 3 tables.

Keywords: Arabian Sea; Sr-Nd isotopes; climate; erosion; monsoon.

Index Terms: 1040 Geochemistry: Radiogenic isotope geochemistry; 1051 Geochemistry: Sedimentary geochemistry; 4863 Oceanography: Biological and Chemical: Sedimentation (1861).

Received 19 July 2011; Revised 8 November 2011; Accepted 17 November 2011; Published 6 January 2012.

Goswami, V., S. K. Singh, R. Bhushan, and V. K. Rai (2012), Temporal variations in 87 Sr/ 86 Sr and ε_{Nd} in sediments of the southeastern Arabian Sea: Impact of monsoon and surface water circulation, *Geochem. Geophys. Geosyst.*, 13, Q01001, doi:10.1029/2011GC003802.

1. Introduction

[2] The Arabian Sea annually receives ~400 million tons of suspended load from the Himalaya and

Transhimalaya [*Milliman et al.*, 1984] through the Indus river system, and ~100 million tons through the Narmada, Tapi and the rivers of the Western Ghats [*Alagarsamy and Zhang*, 2005; Chandramohan and Balchand, 2007]. In addition, \sim 100 million tons of aeolian dust from the deserts of Oman, Africa and western India is deposited annually in the Arabian Sea, its contribution to the eastern Arabian Sea being only \sim 30 million tons, which further decreases toward the Indian peninsula [Ramaswamy and Nair, 1994; Sirocko and Sarnthein, 1989]. The sediments deposited in the Arabian Sea preserve in them the records of erosional patterns in their source regions, factors regulating them and the pathways of sediment dispersal in the sea [Clift et al., 2008; Rahaman et al., 2009].

Geochemistry

Geophysics Geosystems

[3] One of the key factors determining the erosion patterns of the drainage basins is the monsoon. The Indian subcontinent experiences two monsoons annually, the South-West (summer) and the North-East (winter) monsoons; the former being more pronounced at present. The intensities and patterns of these monsoons have varied during the past [Fleitmann et al., 2003; Gupta et al., 2003; Herzschuh, 2006], these in turn, have affected the erosion distribution of drainage basins [Clift et al., 2008; Rahaman et al., 2009] and supply of sediments to the seas around India [Ahmad et al., 2005; Colin et al., 1999; Tripathy et al., 2011]. These variations, in addition to impacting erosion, also influence the surface water circulation in the Arabian Sea and the Bay of Bengal which determine the sediment dispersal and deposition in them. During the SW monsoon, surface water from the Arabian Sea flows to the Bay of Bengal; in contrast, during the NE monsoon, surface currents flow from the Bay of Bengal to the Arabian Sea [Schott and McCreary, 2001; Shankar et al., 2002]. There is evidence to suggest that the transport of lowsalinity water from the Bay of Bengal to the Arabian Sea was enhanced during the Last Glacial Maximum (LGM) due to a more intense NE monsoon [Sarkar et al., 1990; Tiwari et al., 2005].

[4] Clay mineralogy and radiogenic isotopes of Sr and Nd have been used to investigate spatial variations in the provenance of sediments in the Arabian Sea and the Bay of Bengal and their causative factors. For example, investigations of surface sediments in the Arabian Sea suggest that supply from the Himalaya, Transhimalaya and Karakorum ranges brought via the Indus dominate in the northern and central regions [*Garzanti et al.*, 2005], whereas the sediments off the shelf and slope regions of the eastern Arabian Sea are sourced mainly from peninsular India [*Chauhan and Gujar*, 1996; *Chauhan et al.*, 2010; *Kessarkar et al.*, 2003; *Kolla et al.*, 1976; *Rao and Rao*, 1995]. There is also evidence based on clay mineral studies of sediments from the southwestern slope of India that suggest long range transport of Ganga-Brahmaputra sediments to the tip of Indian peninsula by surface currents [*Chauhan and Gujar*, 1996; *Chauhan et al.*, 2010].

[5] The radiogenic isotopes of Sr and Nd in silicate phases are commonly used as proxies for sediment provenances. The Sr (⁸⁷Sr/⁸⁶Sr) and Nd (¹⁴³Nd/¹⁴⁴Nd) isotopic composition of continental source rocks depend on their Rb/Sr and Sm/Nd ratios and their ages. Terrigenous sediments in the ocean are weathering products of continental rocks that have wide range of Sr and Nd isotope ratios. Thus, the Sr and Nd isotopic composition of detrital marine sediments provide a means to trace their sources and their variations in space and time [*Innocent et al.*, 2000; *Rutberg et al.*, 2005].

[6] The objective of this work is to track the temporal variation in the provenance of sediments deposited in the eastern region of the Arabian Sea during the last \sim 40 ka and assess the impact of climate and surface water circulation in determining their source(s) and dispersal. This work also addresses the issue of long range transport of sediments from the Bay of Bengal to the Arabian Sea during the LGM due to intensification of NE monsoon.

2. Study Area, Materials and Methods

2.1. Details of the Sediment Cores and Their Chronology

[7] Sediments from two gravity cores; SS-3101G and SS-3104G, raised from the southeastern Arabian Sea (Figures 1 and 2 and Table S1 in the auxiliary material) onboard FORV Sagar Sampada during 1991-92 [Somayajulu et al., 1999] are investigated for their Sr and Nd isotopes of silicate phases in this study.¹ These cores have been studied in detail earlier to retrieve records of paleoproductivity and monsoon using a multiproxy approach [Agnihotri et al., 2003; Sarkar et al., 2000]. These two cores have been selected for this study as (1) their chronology is well established based on AMS ¹⁴C dating of planktonic foraminiferal separates (Table S2) [Agnihotri, 2001; Agnihotri et al., 2003; Somayajulu et al., 1999], which show that they represent depositional histories of ~29 and ~ 40 ka and (2) they are strategically located to investigate the impact of SW/NE monsoon variations on the transport of sediments from the Bay of Bengal

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GC003802.



Geochemistry

Geophysics Geosystems

Figure 1. Locations of the two sediment cores analyzed in the study. Various rivers draining into the Arabian Sea and the Bay of Bengal are also shown. Core SS-3101G lies between the present-day limits of the Indus and Bengal Fans. Core SS-3104 lies in the present-day Deccan basaltic provenance zone and outside the limit of Indus Fan. The arrows indicate the direction of surface currents during the intensification of (a) North-East monsoon and (b) South-West monsoon; [*Schott and McCreary*, 2001; *Shankar et al.*, 2002; *Wyrtki*, 1973]. NMC, North-East Monsoon Current; SMC, South-West Monsoon Current; EICC, East India Coastal Current; WICC, West India Coastal Current.

to the Arabian Sea. The core SS-3101G is located east of Chagos Laccadive Ridge adjacent to a sill and is in the pathway of water exchange between the Bay of Bengal and the Arabian Sea due to monsoon pattern reversal (Figure 1). The average sediment accumulation rates of these cores are 4.6 and 3.5 cm/ka respectively, with higher rates 7.5 and 4.2 cm/ka prior to LGM which decreased to 2.9 and 2.7 cm/ka after the LGM (Figure S1). The sedimentation rates of both these cores were higher during LGM [*Agnihotri*, 2001; *Agnihotri et al.*, 2003; *Somayajulu et al.*, 1999].

2.2. River Sediments

[8] The Arabian Sea receives detrital sediments from several rivers. Sr and Nd isotopic composition of these river sediments can serve as tracers to track the provenance of sediments in the Arabian Sea. Such data are unavailable for the rivers from the western India such as the Narmada, Tapi, Nethravathi, Periyar and those draining the Western Ghats (Vashishthi, Kajli, and Sukh). Therefore, sediments from these rivers were collected and analyzed for Sr and Nd isotopic composition. The river sediments were generally collected from locations close to their mouths. The details of sampling locations of the river sediments and lithology of the river basins are given in Table S3.

[9] The sampling of the Mahi, Narmada and Tapi sediments was done in March, 2011; whereas for the Nethravathi, it was done during two different seasons, April and December, 2010. Samples of Periyar River sediments were collected from two locations, Cheranellur and Chennur (near Kochi), in April, 2011. The samples from the minor streams Vashishthi, Kajli, and Sukh flowing through the Western Ghats are from the collection of *Das et al.* [2005].



Figure 2. Sampling locations of sediments from rivers Mahi, Narmada, Tapi, Nethravathi, Periyar and the three Western Ghats streams Vashishthi, Kajli and Sukh. Broad lithology of the regions drained by these rivers and locations of cores SS-3101G and SS-3104G are also shown.

[10] The Mahi River drains a multilithological terrain composed of sediments of the Vindhvan Super Group, metamorphic rocks of the Aravalli Super Group, the Deccan basalts and the alluvial deposits of Pleistocene and Holocene ages [Sridhar, 2008]. The Narmada is the largest river draining into the Arabian Sea from western India. It passes through the Vindhyan ranges and Deccan basalts before plunging into the Arabian Sea at the Gulf of Cambay, near the town of Bharuch [Gupta et al., 2011]. The Tapi River is the second largest westflowing river; its drainage basin consists of Deccan basalts and alluvial deposits. The Tapi enters the Arabian Sea at the Gulf of Cambay near the city of Surat [Kale et al., 2003]. The Nethravathi River is a minor river flowing through the Western Ghats draining granites/gneisses of peninsular India. It joins the Arabian Sea near Mangalore. The Periyar River drains crystalline rocks of Archaen age; sedimentary rocks of different ages and laterites capping them [Chandramohan and Balchand, 2007]. There are several small streams that drain Deccan basalts on the Western Ghats. In the present study sediment samples from three of these streams (Vashishthi, Kajli, and Sukh) were analyzed [Das et al., 2005].

Geochemistry

Geophysics Geosystems

2.3. Measurement of Sr, Nd Concentrations and Isotopic Composition

[11] In the laboratory, the sediment samples were dried at 90°C for a few days, powdered using an agate mortar and pestle to less than 100 μ m size and stored in pre-cleaned plastic containers.

[12] Sr and Nd isotopic analyses were made on carbonate and organic matter free fraction of the sediments [Singh et al., 2008]. The powdered sediment samples were first decarbonated by leaching with 0.6 N HCl at 80°C for ~30 min with ultrasonic treatment. The slurry was centrifuged, residue washed with Milli-Q water, dried and ashed at ~600°C to oxidize organic matter. A known weight (~100 mg) of the carbonate and organic matter free fraction of the sediment was transferred to Savillex® vial and digested repeatedly with HF-HNO₃-HCl at \sim 120°C to bring the sediment to complete solution. The acid digestion step was repeated as needed to ensure that the entire sample was brought to complete solution. Sediments from the Arabian Sea were digested in the presence of ⁸⁴Sr and ¹⁵⁰Nd spikes whereas the river sediments were not spiked. Pure Sr and Nd fractions were separated from the solution following standard ion exchange procedures [Rahaman et al., 2009; Singh et al., 2008].

[13] Sr and Nd concentrations and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ${}^{143}\text{Nd}/{}^{144}\text{Nd}$ of the Arabian Sea sediments were measured on an Isoprobe-T TIMS and that of river sediments on a Finnigan Neptune MC-ICP-MS at PRL. The analyses were made in static multicollection mode. Mass fractionation corrections for Sr and Nd were made by normalizing ⁸⁶Sr/⁸⁸Sr to 0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd to 0.7219 respectively. During the course of analyses, NBS987 Sr standard was measured on both TIMS and MC-ICP-MS, these yielded values of 0.710227 \pm 0.000014 (1 σ , n = 110; σ = Standard Deviation) and 0.710287 ± 0.000020 (1 σ , n = 15) respectively for ⁸⁷Sr/⁸⁶Sr. For Nd, JNdi-1 Nd standard was measured on TIMS which gave an average value of $0.512108 \pm$ $0.000008 (1\sigma, n = 35)$ for ¹⁴³Nd/¹⁴⁴Nd, while JMC-321 standard was measured on MC-ICP-MS, this yielded an average value of 0.511095 ± 0.000007 $(1\sigma, n = 13).$

[14] The internal reproducibility of measurements was better than 10 ppm $(1\sigma_{\mu})$ for both Sr and Nd isotopic ratios. Based on replicate measurements, the average variation between sets of repeats was determined to be 0.0002 and 0.00001 for ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd respectively. The Nd isotopic data is expressed in terms of standard ε notation,

$$\varepsilon_{Nd} = \left[\frac{\frac{143}{Nd}}{\frac{143}{Nd}} - 1\right] \times 10^4$$

where ¹⁴³Nd/¹⁴⁴Nd is the measured Nd isotopic composition of the sample and ¹⁴³Nd/¹⁴⁴Nd_{CHUR} is the present-day ¹⁴³Nd/¹⁴⁴Nd value of CHUR (Chondritic Uniform Reservoir) which is 0.512638 [*Jacobsen and Wasserburg*, 1980]. The average variation between sets of repeats for $\varepsilon_{\rm Nd}$ was 0.2.

[15] Several total procedural blanks for Sr and Nd were also processed during the analysis. These blanks are several orders of magnitude lower than typical total Sr and Nd loads analyzed and hence no corrections for blanks were made.

3. Results

3.1. River Sediments

[16] The Sr and Nd isotopic composition in silicate fraction of river sediments are given in Table 1 and plotted in Figure 3. The isotopic composition of river sediments, as expected, reflects those of lithologies of the region. Sediment from the Mahi river is the most radiogenic in Sr (87 Sr/ 86 Sr = 0.73051) while its ε_{Nd} is quite unradiogenic (-20.3), consistent with the lithology of the Mahi

| Sample Code | River | ⁸⁷ Sr/ ⁸⁶ Sr | ¹⁴³ Nd/ ¹⁴⁴ Nd | $\varepsilon_{ m Nd}$ |
|---------------|------------------|------------------------------------|--------------------------------------|-----------------------|
| MH | Mahi | 0.73051 | 0.51160 | -20.3 |
| NM | Narmada | 0.72126 | 0.51203 | -11.9 |
| NM R | Narmada (Repeat) | 0.72121 | 0.51205 | -11.5 |
| TP-1 | Tapi | 0.70947 | 0.51235 | -5.7 |
| TP-2 | Tapi | 0.70961 | 0.51233 | -5.9 |
| NETHRAVATHI-1 | Nethravathi | 0.72176 | 0.51054 | -40.8 |
| NETHRAVATHI-2 | Nethravathi | 0.71507 | 0.51097 | -32.6 |
| PERIYAR-1 | Periyar | 0.72379 | 0.51130 | -26.2 |
| PERIYAR-2 | Periyar | 0.72176 | 0.51119 | -28.2 |
| KJL/2K1/M | Kajli | 0.70529 | 0.51275 | 2.2 |
| SUKH/2K1/M | Sukh | 0.70885 | 0.51257 | -1.3 |
| SUKH/2K1/M R | Sukh (Repeat) | 0.70888 | 0.51258 | -1.2 |
| VAT/2K1/M | Vashishthi | 0.70636 | 0.51258 | -1.2 |

Table 1. Sr and Nd Isotopic Composition of Silicate Fraction of River Sediments^a

^aSampling location details are given in Table S3.

Geochemistry

Geophysics Geosystems

River basin that comprises of metamorphic rocks of the Aravalli Super Group, the Deccan basalts and the alluvial deposits of Pleistocene and Holocene ages. The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} of the Narmada sediments are 0.72126 and -11.9 respectively, indicating contribution of radiogenic Sr from the Vindhyan Super Group along with unradiogenic Sr from Deccan basalts. The Deccan basalts comprise of various formation that are distinct in their Sr and Nd isotopic composition. The northern part of the Deccan basalts consists of Poladpur, Bushe and Jawhar-Igatpuri formations that show evidence of contamination with upper crustal material. The ⁸⁷Sr/⁸⁶Sr of these formations range from 0.705 to 0.720, whereas the $\varepsilon_{\rm Nd}$ varies from -5 to -20 [Mahoney et al., 2000; Peng et al., 1998]. The central and southwestern parts of the Deccan basalts are composed of the Ambenali and Mahabaleshwar formations that have less degree of crustal contamination. The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} of these formations vary from 0.703 to 0.708 and +5 to -10 respectively [Mahoney et al., 2000; Peng et al., 1998]. The river Tapi flows through the northern areas of Deccan basalts; the Poladpur, Bushe and Jawhar-Igatpuri formations that are higher in ⁸⁷Sr/⁸⁶Sr and lower in $\varepsilon_{\rm Nd}$. The two samples from the Tapi River yield ⁸⁷Sr/⁸⁶Sr of 0.70947, 0.70961 and $\varepsilon_{\rm Nd}$ of -5.9, -5.7; consistent with the isotopic composition of the dominant Deccan basalt formations in its drainage. The Nethravathi sediments collected in April, 2010 (Tables 1 and S3) have Sr isotopic composition (0.72176) and $\varepsilon_{\rm Nd}$ (-40.8) that are distinctively different from those in the sample collected in December, 2010 (87 Sr/ 86 Sr 0.71507; ε_{Nd} -32.6; Table 1). These seasonal differences can arise from variations in mixing proportions of sediments from tributaries during different seasons. The isotopic composition of sediments of the Periyar River $({}^{87}\text{Sr}/{}^{86}\text{Sr} 0.72379 \text{ and } 0.72176; \varepsilon_{\text{Nd}} -26.2 \text{ and}$

-28.2; Table 1) is also close to that of the Nethravathi River, not unexpected considering that both of them drain Peninsular granites/gneisses. The Sr and Nd isotopic composition of sediments from the three Western Ghats streams are least radiogenic in ⁸⁷Sr/⁸⁶Sr (0.70529 to 0.70885) and most radiogenic in ε_{Nd} (-1.3 to 2.2), within the range reported for Deccan basalts.

3.2. Arabian Sea Sediments

[17] Sr and Nd concentrations and their isotopic compositions in the silicate fraction of sediments from SS-3104G and SS-3101G cores are given in Tables 2 and 3 and Figures 4 and 5 respectively. In SS-3104G, which lies in the northeastern Arabian Sea off Mangalore (Figures 1 and 2) the Sr and Nd concentrations range from 78 to 127 μ g/g and 7 to 26 μ g/g respectively and are generally lower than that in sediments of SS-3101G. The ⁸⁷Sr/⁸⁶Sr and



Figure 3. Sr-Nd isotope plot of contemporary river sediments (silicate fraction) draining into the Arabian Sea. The isotopic composition of major end-members is also given.

| Sample ^b | Age (ka) | Sr ^c | ${}^{87}{ m Sr}/{}^{86}{ m Sr}^{ m d}$ | Nd ^c | 143 Nd/ 144 Nd ^d | $\varepsilon_{ m Nd}$ |
|---------------------|----------|-----------------|--|-----------------|---------------------------------------|-----------------------|
| 3104(2-3) | 1.4 | 127.4 | 0.71416 | 15.5 | 0.51216 | -9.4 |
| 3104(6-7) | 1.6 | 84.3 | 0.71689 | 25.6 | 0.51198 | -12.9 |
| 314(9–10) | 3.3 | 88.7 | 0.71667 | - | - | - |
| 3104(11–12) | 3.9 | 105.8 | 0.71521 | - | - | - |
| 3104(14–15) | 4.9 | - | - | 14.4 | 0.51209 | -10.7 |
| 3104(17-18) | 5.8 | 86.9 | 0.71651 | 12.1 | 0.51213 | -10.0 |
| 3104(19-20) | 6.5 | 85.7 | 0.71658 | 11.1 | 0.51214 | -9.6 |
| 3104(21-22) | 7.6 | 88.6 | 0.71647 | 12.3 | 0.51213 | -9.9 |
| 3104(23-24) | 8.6 | 78.4 | 0.71648 | 9.9 | 0.51213 | -9.9 |
| 3104(23–24)R | 8.6 | 78.2 | 0.71621 | 10.9 | 0.51213 | -9.9 |
| 3104(24-25) | 9.2 | 111.3 | 0.71434 | 10.2 | 0.51219 | -8.8 |
| 3104(26-27) | 10.3 | 83.5 | 0.71702 | 12.3 | 0.51215 | -9.5 |
| 3104(28-29) | 11.4 | 86.5 | 0.71779 | 7.4 | 0.51207 | -11.0 |
| 3104(30-31) | 12.5 | 83.2 | 0.71748 | 9.3 | 0.51212 | -10.2 |
| 3104(31-32) | 13.0 | 94.1 | 0.71596 | - | - | - |
| 3104(32-33) | 13.5 | 99.3 | 0.71671 | 13.5 | 0.51215 | -9.5 |
| 3104(37–38) | 15.5 | 100.1 | 0.71642 | 13.2 | 0.51214 | -9.7 |
| 3104(37–38)R | 15.5 | 100.1 | 0.71649 | 13.4 | 0.51214 | -9.7 |
| 3104(41-42) | 16.6 | 102.3 | 0.71698 | 14.0 | 0.51212 | -10.1 |
| 3104(41-42)R | 16.6 | 102.8 | 0.71687 | 14.8 | 0.51213 | -9.9 |
| 3104(44-45) | 17.4 | 96.6 | 0.71719 | 13.7 | 0.51211 | -10.3 |
| 3104(48-49) | 18.5 | 101.6 | 0.71773 | 14.3 | 0.51208 | -10.8 |
| 3104(52-53) | 19.6 | 98.5 | 0.71754 | 13.7 | 0.51210 | -10.5 |
| 3104(61-62) | 20.3 | 95.2 | 0.71745 | 12.6 | 0.51212 | -10.0 |
| 3104(68-69) | 20.8 | 93.6 | 0.71759 | 14.2 | 0.51214 | -9.8 |
| 3104(71-72) | 21.8 | 94.6 | 0.71788 | 12.8 | 0.51213 | -9.9 |
| 3104(74-75) | 22.8 | - | - | 14.7 | 0.51214 | -9.7 |
| 3104(77-78) | 23.8 | - | - | 13.8 | 0.51212 | -10.2 |
| 3104(80-81) | 24.8 | 91.4 | 0.71793 | 11.5 | 0.51211 | -10.2 |
| 3104(82–83) | 25.5 | - | - | 13.8 | 0.51209 | -10.6 |
| 3104(84-85) | 26.1 | 94.1 | 0.71840 | 14.0 | 0.51214 | -9.8 |
| 3104(88–89) | 26.7 | 93.8 | 0.71764 | 12.6 | 0.51213 | -10.0 |
| 3104(95–96) | 27.8 | 92.7 | 0.71708 | 8.6 | 0.51216 | -9.3 |
| 3104(95–96)R | 27.8 | 92.1 | 0.71693 | _ | - | - |
| 3104(100-102) | 28.9 | 111.2 | 0.71680 | - | - | - |
| 3104(102-104) | 29.6 | 93.9 | 0.71768 | 13.9 | 0.51215 | -9.6 |
| 3104(106-108) | 30.9 | 94.9 | 0.71778 | 14.0 | 0.51214 | -9.8 |
| 3104(114–116) | 33.6 | 92.3 | 0.71785 | 13.4 | 0.51214 | -9.8 |
| 3104(116-118) | 34 3 | 112.2 | 0 71714 | - | - | - |
| 3104(122-124) | 36.1 | 98.3 | 0.71649 | 14.4 | 0.51216 | -93 |
| 3104(126-128) | 37.1 | 112.6 | 0.71727 | 13.5 | 0.51210 | -9.8 |
| 3104(126–128)R | 37.1 | 111.0 | 0.71721 | 12.8 | 0.51215 | -9.5 |
| 3104(132-134) | 38.6 | 94.5 | 0.71702 | 13.4 | 0.51217 | -9.0 |
| 2131(132 131) | 20.0 | 1.5 | 0.71702 | 10.1 | 0.01217 | 2.0 |

Table 2. Sr and Nd Concentration and Isotopic Composition of Core SS-3104G Silicates^a

^aAbbreviations and symbols: -: not analyzed; R: Replicate analysis.

^bNumbers in parenthesis are depth intervals in cm.

^cSr, Nd concentrations in μ g/g.

Geochemistry

Geophysics Geosystems

^dThe errors on the Sr and Nd isotopic data are better than 10 ppm $(1\sigma_{\mu})$.

 $\varepsilon_{\rm Nd}$ of SS-3104G (Table 2 and Figure 4) vary in a narrower range compared to SS-3101G, with most samples having ${}^{87}{\rm Sr/}^{86}{\rm Sr}$ between 0.716 to 0.718 and $\varepsilon_{\rm Nd}$ between -10.5 to -9.0. These ratios are within the range of isotopic compositions of slope sediments of west coast of India [*Kessarkar et al.*, 2003].

[18] In SS-3101G, from the near equatorial region (Figures 1 and 2) the Sr and Nd concentrations range from 94 to 200 μ g/g and 6 to 45 μ g/g

respectively. Both $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ (0.71412 to 0.72069) and $\varepsilon_{\rm Nd}$ (-15.2 to -9.0) show variations with depth but with opposite trends (Figures 5a and 5b).

^[19] The concomitant temporal changes in both ⁸⁷Sr/⁸⁶Sr and ε_{Nd} in SS-3101G and the observation that their range is much larger than the average analytical uncertainty leads to infer that these variations represent source variability and/or their mixing proportions. Therefore, the data from these

| Sample ^b | Age (ka) | Sr ^c | ⁸⁷ Sr/ ⁸⁶ Sr ^d | Nd ^c | 143 Nd/ 144 Nd ^d | $\varepsilon_{\rm Nd}$ |
|---------------------|----------|-----------------|---|-----------------|---------------------------------------|------------------------|
| 3101(1-2) | 1.9 | 117.1 | 0.71631 | 19.8 | 0.51197 | -13.0 |
| 3101(6-7) | 3.3 | 156.4 | 0.71412 | 6.0 | 0.51213 | -9.8 |
| 3101(10-11) | 4.4 | 139.5 | 0.71459 | 8.7 | 0.51197 | -13.1 |
| 3101(10–11)R | 4.4 | 133.1 | 0.71501 | - | - | - |
| 3101(13–14) | 5.5 | 112.7 | 0.71686 | 13.4 | 0.51194 | -13.7 |
| 3101(16-17) | 6.7 | 98.5 | 0.71838 | 12.7 | 0.51193 | -13.8 |
| 3101(18-19) | 7.5 | 95.7 | 0.71755 | 6.5 | 0.51192 | -14.1 |
| 3101(21-22) | 8.6 | 88.0 | 0.71930 | 12.5 | 0.51190 | -14.4 |
| 3101(23-24) | 9.4 | 107.9 | 0.71768 | 12.9 | 0.51190 | -14.3 |
| 3101(26-27) | 10.6 | 96.3 | 0.71677 | 11.7 | 0.51208 | -10.9 |
| 3101(30-31) | 11.6 | 203.3 | 0.71690 | 20.0 | 0.51206 | -11.3 |
| 3101(34–35) | 12.5 | 94.1 | 0.71830 | 13.7 | 0.51204 | -11.8 |
| 3101(38–39) | 13.5 | 98.3 | 0.71753 | 45.7 | 0.51218 | -9.0 |
| 3101(41-42) | 14.5 | 100.2 | 0.71685 | 12.8 | 0.51206 | -11.2 |
| 3101(43-44) | 15.1 | 109.1 | 0.71721 | 12.3 | 0.51204 | -11.7 |
| 3101(46-47) | 16.1 | 97.9 | 0.71776 | 19.6 | 0.51203 | -11.8 |
| 3101(50-51) | 17.4 | 95.9 | 0.71906 | 13.7 | 0.51200 | -12.4 |
| 3101(53-54) | 18.3 | 117.2 | 0.71773 | - | - | - |
| 3101(59-60) | 19.1 | 101.1 | 0.72069 | 14.6 | 0.51189 | -14.6 |
| 3101(62–63) | 19.4 | 82.5 | 0.71949 | 13.4 | 0.51186 | -15.2 |
| 3101(70-71) | 20.4 | 90.4 | 0.71854 | 18.3 | 0.51196 | -13.3 |
| 3101(86-87) | 21.6 | 86.7 | 0.71920 | 17.4 | 0.51192 | -14.0 |
| 3101(90-91) | 22.3 | 101.2 | 0.71950 | 15.8 | 0.51192 | -14.1 |
| 3101(90–91)R | 22.3 | 101.9 | 0.71956 | 14.5 | 0.51190 | -14.4 |
| 3101(94-95) | 23.0 | 135.4 | 0.71805 | - | - | - |
| 3101(98–99) | 23.7 | 113.0 | 0.71864 | 13.9 | 0.51194 | -13.6 |
| 3101(102–104) | 24.5 | 101.1 | 0.71752 | 11.3 | 0.51209 | -10.7 |
| 3101(108–110) | 25.4 | 102.8 | 0.71828 | 14.6 | 0.51206 | -11.3 |
| 3101(116-118) | 26.6 | 102.9 | 0.71779 | 13.1 | 0.51210 | -10.6 |
| 3101(122–124) | 27.5 | 94.7 | 0.71850 | 13.2 | 0.51208 | -10.8 |
| 3101(126–128) | 28.1 | 96.9 | 0.71860 | 13.8 | 0.51206 | -11.3 |
| 3101(132–134) | 29.0 | 95.2 | 0.71707 | 10.4 | 0.51206 | -11.2 |

Table 3. Sr and Nd Concentration and Isotopic Composition of Core SS-3101G Silicates^a

^aAbbreviations and symbols: -: not analyzed; R: Replicate analysis.

^bNumbers in parenthesis are depth intervals in cm.

^cSr, Nd concentrations in μ g/g.

Geochemistry

Geophysics Geosystems

^dThe errors on the Sr and Nd isotopic data are better than 10 ppm $(1\sigma_{\mu})$.

two cores serve as a proxy to track variations in their provenance.

4. Discussion

[20] The Sr and Nd isotopic composition of river sediments supplied to the Arabian Sea are given in Figure 3. The data demonstrate the impact of various lithologies drained by these rivers in determining the isotopic composition of their sediments. The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} values of the two Arabian Sea cores along with those of their potential sources, the Deccan basalts, the higher and lesser Himalaya, the Vindhyan Super Group and the Peninsular granites/ gneisses are presented in an isotopic composition of these sources (Figure 6 and Table S4) are from published literature [*Ahmad et al.*, 2009; *Chakrabarti et al.*, 2007; *Clift et al.*, 2002, 2008,

2010; Harris et al., 1994; Peucat et al., 1989; Singh et al., 2008; Tripathy et al., 2011; Tripathy, 2011].

[21] The role of Indus as the source of sediments in the eastern Arabian Sea is debated. Based on clay mineralogical study, *Kessarkar et al.* [2003] suggest that the penetration of Indus sediments is restricted to the north of Saurashtra (~20°N), whereas *Ramaswamy and Nair* [1989] suggest that longshore current helps Indus sediments to be transported to the south of Mangalore.

[22] In addition to riverine particulates, another source of sediments to the Arabian Sea is aeolian dust from the deserts of Arabia [*Kolla et al.*, 1976; *Sirocko and Sarnthein*, 1989]. The magnitude of supply of dust has been reported to vary with time with enhanced contribution during the LGM [*Harrison et al.*, 2001; *Petit et al.*, 1999; *Reichart et al.*, 1997; *Sirocko et al.*, 2000]. The Sr and Nd isotopic composition of aeolian dust over the GOSWAMI ET AL.: SR, ND ISOTOPES OF ARABIAN SEA SEDIMENTS 10.1029/2011GC003802



Geochemistry

Geophysics Geosystems

Figure 4. Temporal variation in ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} of sediments from SS-3104G. Sr and Nd isotope composition of these sediments display a narrow range, suggesting that their sources and the mixing proportions have remained nearly the same during the last 40 ka. The markers along the *x* axis of the plots show age control points in the core. The lines represent 3-point moving average of the data.

western Arabian Sea is characterized by unradiogenic Sr (87 Sr/ 86 Sr = 0.709) and radiogenic Nd ($\varepsilon_{Nd} = -6$) [*Sirocko*, 1995]. The Sr and Nd isotopic composition of dust falls within the range of Deccan basalts and if dust with such isotopic composition also deposits over the eastern Arabian Sea it is difficult to differentiate between aeolian dust and sediments sourced from basalts and assess their contribution. However, there have been earlier studies in the eastern Arabian Sea which suggest that aeolian dust is not a significant contributor of sediments to this area [*Kessarkar et al.*, 2003; *Kolla et al.*, 1976; *Sirocko and Sarnthein*, 1989].

4.1. Core SS-3104G

[23] The sediments of SS-3104G have ⁸⁷Sr/⁸⁶Sr and ε_{Nd} within a narrow range defined by the contemporary sediments of the Indus, Narmada, Tapi and other Western Ghats streams suggesting that all these rivers are potential sources of silicate sediments to this core site. Despite the proximity of Nethravathi River to the SS-3104G core site, its contribution and hence that from the Peninsular granites/gneisses to this core site seems minor. This inference is based upon the highly depleted ε_{Nd} values of the Nethravathi sediments and the observation that at present the Nethravathi River supplies only ~1 million tons of sediments annually to the Arabian Sea [*Panda et al.*, 2011]. The limited range in Sr and Nd isotopic composition throughout the length of this core covering a time span of ~40 ka also leads us to infer that the provenance of sediments and their mixing proportion have remained nearly the same during this period. The reason for the lower ⁸⁷Sr/⁸⁶Sr in the (2–3) cm and $\varepsilon_{\rm Nd}$ in the (6–7) cm sections of SS-3104G (Table 2), however, is unclear.



Figure 5. ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of sediments of core SS-3101G. The data show significant temporal variation which correlate with (c) known climatic/monsoon variability [*Herzschuh*, 2006]. Sr and Nd isotope compositions of these sediments display two excursions during ~20 and ~9 ka coinciding with LGM and intensified SW monsoon. (a, b) The lines are 3-point moving average of the data respectively and the markers along the *x* axis of the plots show age control points in the core. (d) The line is 3-point moving average of ε_{Nd} values form the Indus delta [*Clift et al.*, 2008].

GOSWAMI ET AL.: SR, ND ISOTOPES OF ARABIAN SEA SEDIMENTS 10.1029/2011GC003802



Geochemistry

Geophysics Geosystems

Figure 6. Sr and Nd isotope compositions of SS-3101G and SS-3104G sediments and their potential sources in two isotope mixing plot. Sediments of the core SS-3104G show very limited variation. Sr and Nd isotopic composition of SS-3101G sediments show wider range. Various lithologies used as end-members are: D, Deccan basalts; V, Vindhyan Super Group; P, Peninsular granites/gneisses; HHC, Higher Himalayan Crystalline; LHS, Lesser Himalayan Silicates.

4.2. Core SS-3101G

[24] The Sr and Nd isotopic composition of SS-3101G silicates displays wider range than those in SS-3104G with two excursions at ~9 ka and ~20 ka (Figures 5a and 5b). The lower bound of ⁸⁷Sr/⁸⁶Sr (i.e., the lowest values of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$) and the upper bound of $\varepsilon_{\rm Nd}$ (i.e., the most radiogenic values of $\varepsilon_{\rm Nd}$) of SS-3101G is similar to that observed for the core SS-3104G. Thus, the 87 Sr/ 86 Sr and ε_{Nd} of core SS-3104G can be considered to represent the baseline values of Sr and Nd isotopic composition of SS-3101G sediments. This in turn would suggest that Deccan basalts and the Vindhyan Super Group are the dominant sources of sediments to this core, delivered through the Narmada and the Tapi rivers. In addition, there has to be enhanced relative contribution of sediments with more radiogenic Sr and unradiogenic Nd to account for the excursions in its isotopic composition during ~9 ka and ~20 ka (Figure 5).

[25] The excursions in the Sr and Nd isotopic composition of SS-3101G core overlap with the known climatic (monsoon) variations in the Asian region (Figure 5c) [*Herzschuh*, 2006]. The timing of the first excursion in the Sr and Nd isotopic data at ~20 ka corresponds to the well known Last Glacial Maximum (LGM) whereas the excursion at ~9 ka overlaps with the known intensification of SW monsoon precipitation [*Fleitmann et al.*, 2003;

Herzschuh, 2006; *Prell and Kutzbach*, 1987; *Sinha et al.*, 2005]. It is clear from the observed interrelations between Sr-Nd isotopic composition and monsoon variations (Figure 5) that climate exerts a significant control on the erosion patterns and sediment fluxes from different sources depositing at this core location and their mixing proportions.

4.2.1. Provenance of Sediments During Last Glacial Maximum (LGM)

[26] The Sr and Nd isotopic composition in SS-3101G during LGM show a peak in ⁸⁷Sr/⁸⁶Sr and a dip in ε_{Nd} (Figures 5a and 5b) with values similar to that from sediments of the western Bay of Bengal during LGM [*Tripathy et al.*, 2011]. Potential sources that can contribute to the Sr and Nd excursions during LGM are relative increase in (1) Himalayan sediments and/or (2) Peninsular granites/gneisses, both of which are characterized by higher radiogenic Sr and low ε_{Nd} composition.

[27] It is known that during LGM there was decrease in SW monsoon precipitation and increase in NE monsoon [*Herzschuh*, 2006]. The intensification of NE monsoon with concomitant decrease in SW monsoon during LGM would promote strengthening of southwestward East Indian Coastal Current (EICC) in the Bay of Bengal. This in turn would enhance the flow of waters from the Bay of Bengal to the Arabian Sea [*Schott and McCreary*, 2001; *Shankar et al.*, 2002]. Such enhanced transport of Bay of Bengal waters to the southeastern Arabian Sea during LGM is documented in the oxygen isotopic composition of foraminifera deposited during this period [*Sarkar et al.*, 1990; *Tiwari et al.*, 2005].

[28] The observation that the isotopic composition of LGM stratum in SS-3101G is similar to those in western Bay of Bengal [Tripathy et al., 2011], that there is enhanced flow of low salinity water from Bay of Bengal to southeastern Arabian Sea during this period and that the existence of sediment plumes in the coastal and open Bay of Bengal [Sridhar et al., 2008a, 2008b; Rajawat et al., 2005] is an indication that sediments from the western Bay of Bengal may be transported to this core site. However, clay mineral studies of sediments from southeastern Arabian Sea have yielded divergent conclusions; Kessarkar et al. [2003] suggest that the sediments of the southeastern Arabian Sea largely represent hinterland flux and are not influenced by sediments transported from the Bay of Bengal waters during the intensification of NE monsoon. In contrast, Chauhan and Gujar [1996]

and *Chauhan et al.* [2010] argue in favor of sediment transport from Bay of Bengal during intensification of NE monsoon.

Geochemistry

Geophysics Geosystems

[29] If sediments from the western Bay of Bengal are indeed the cause of Sr and Nd isotopic excursion, then based on a two end-member mixing model, it can be estimated that during LGM about one-fifth of sediments in SS-3101G are from western Bay of Bengal, the balance being of SS-3104G composition.

[30] Alternatively, considerably enhanced contribution of sediments sourced from Peninsular granites/gneisses (e.g., through the Nethravathi, Periyar rivers; Table 1) can also explain the isotopic excursions. This however seems unlikely considering that at present these rivers account for only a very small fraction of sediments to the southeastern region of the Arabian Sea [*Chandramohan and Balchand*, 2007, *Nair et al.*, 2003, *Panda et al.*, 2011] and the observation of *Ramaswamy and Nair* [1989] that much of sediments from the peninsular rivers are retained in the western shelf of India peninsula.

4.2.2. Provenance of Sediments During Holocene Intensified Monsoon Phase (IMP)

[31] The core SS-3101G shows a second excursion in Sr and Nd isotopic composition during ~9 ka, coinciding with higher SW monsoon precipitation phase commonly known as the Holocene Intensified Monsoon Phase (IMP) [Fleitmann et al., 2003; Herzschuh, 2006; Prell and Kutzbach, 1987]. Based on the mixing diagram (Figure 6), this excursion also require enhanced contribution of sediments with more radiogenic Sr and unradiogenic Nd analogous to that needed to explain the LGM data. This requirement is intriguing considering that the monsoon trend was opposite during the two periods; SW monsoon being intense during ~ 9 ka whereas, NE monsoon was more pronounced during ~ 20 ka. More intense SW monsoon during Holocene IMP would constrain the North-East monsoon current (Figure 1) and therefore ensuing flow of water from the Bay of Bengal to the Arabian Sea. In such a case, supply of sediments from the Bay of Bengal to the Arabian Sea to account for the isotopic excursion at \sim 9 ka would also be restricted. Further, as was the case during LGM, peninsular rivers as a major source also seems unlikely unless their sediment flux during Holocene IMP was significantly higher and the sediments were transported efficiently to the core site. Two lines of evidence based on contemporary information indicate that these requirements may not be fulfilled. These are (1) during Holocene IMP, the sea level was similar to that at present, therefore, the efficiency of shelf storage of sediments is expected to be similar to that of today [Siddall et al., 2003] and (2) the clay mineralogy of sediment trap samples indicate that sediments from west flowing peninsular rivers are by and large retained in the shelf region of the Arabian Sea [Ramaswamy and Nair, 1989]. The Narmada and Tapi rivers are the other major suppliers of sediments to the Arabian Sea. The discharge of these rivers is dictated by SW monsoon and therefore they could transport more sediment during intensification of SW monsoon. However, these sediments cannot explain the observed magnitude in isotopic excursion if their isotopic composition was the same as those measured in this study (Table 1); the $\varepsilon_{\rm Nd}$ values of the Narmada and Tapi sediments are about -11.5 and -5.8 respectively, which are significantly more radiogenic than the values for core SS-3101G at Holocene IMP (-14).

[32] The Sr and Nd isotopic composition of SS-3101G display variations similar to those reported for the Indus delta during the past ~14 ka ($\varepsilon_{\rm Nd}$; Figure 5d) [Clift et al., 2008, 2010] with both of them showing excursions in $^{87}{\rm Sr}/^{86}{\rm Sr}$ and $\varepsilon_{\rm Nd}$ during ~9 ka. The similarity in the Sr and Nd isotopic composition and their temporal pattern hints at the possibility of supply of Indus delta sediments to the SS-3101G core site. The more radiogenic ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and lesser ε_{Nd} during ~9 ka in the core SS-3101G can be explained in terms of enhanced sediment supply through the Himalayan tributaries of the Indus. This can result from intensification of SW monsoon precipitation over the Himalaya during this period [Clift et al., 2008, 2010]. The intensification of SW monsoon during \sim 9 ka resulted in stronger surface currents in the southeast direction from the Arabian Sea to the Bay of Bengal (Figure 1). The strengthening of this current would result in enhanced southeastward transport of water and sediments from the Arabian Sea to Bay of Bengal. The core SS-3101G lies to the east of Chagos-Laccadive ridge with the presence of sill adjacent to the core location that can facilitate transfer of sediments across the ridge by surface currents. Thus, Sr and Nd isotopic excursions observed during ~9 ka in the core SS-3101G can be a result of increased sediment supply from the Himalayan sources by the Indus tributaries. Based on the Nd isotopic data of sediments of the Indus delta, and that of the Arabian Sea sediments and two end-member mixing calculation, it can be estimated that during the Holocene IMP, about



15% of sediments at the SS-3101G location are derived from the Indus delta. This interpretation, however, rests on the premise that the sediment flux from the peninsular rivers during \sim 9 ka was the same as that at present and that much of the flux is retained in the shelf. If such a premise is proven to be invalid then the isotopic excursion in SS-3101G during \sim 9 ka may also result from sediment supply of peninsular rivers.

Geochemistry

Geophysics Geosystems

[33] Such a contribution from Indus at ~9 ka to core SS-3104G can be ruled out on the basis that presently, the location of the core SS-3104G is dominated by sediments brought by the Narmada and Tapi River from the Deccan basalts and Vindhyan ranges [*Kolla et al.*, 1976]. Even during the intensification of SW monsoon during ~9 ka the Deccan contribution at the core site would increase due to more rainfall on the Western Ghats and the transfer of sediments to the location of core SS-3104G.

[34] It is clear from the above discussion that in addition to climate, ocean circulation also plays an important role in sediment dispersal and their deposition as has been documented in the deposition of Meiji drift in the Pacific Ocean [*VanLaningham et al.*, 2009].

5. Conclusions

[35] Temporal variations in Sr and Nd isotopic composition of silicate component of two well dated sediment cores from the eastern Arabian Sea have been determined. Sr and Nd isotopic compositions of sediments from the more northern core (SS-3104G) display narrow ranges indicating only minor variations in their source proportion since last ~40 ka. Even the flux of aeolian dust has changed very little over the eastern Arabian Sea during last ~40 ka remaining almost consistent during this time. In contrast, the results of the southeastern Arabian Sea core (SS-3101G) exhibit two excursions in the isotopic composition coinciding with two major climate change events; LGM and Holocene Intensified Monsoon Phase (IMP). This correlation suggests significant control of climate/ monsoon on erosion pattern and sedimentation. Sediment supply is controlled by climatic variability whereas its dispersal is controlled by circulation pattern of the surface ocean. The Sr and Nd isotopic excursion at ~20 ka is attributed to enhanced sediment contribution from the Bay of Bengal resulting from strengthened NE monsoon which boosts N-S coastal current in the western Bay of Bengal, transporting water and sediments, the later with higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} . In contrast, intensified SW monsoon precipitation during ~9 ka enhanced sediment transfer from the Indus delta to the southeastern Arabian Sea enabling sediment transfer from the Arabian Sea to Bay of Bengal. This work demonstrates that the Sr and Nd isotopic composition in the silicate fraction of the Arabian Sea sediments has the potential to track the variation in the intensity and pattern of the Indian monsoon system.

Acknowledgments

[36] We thank J. P. Bhavsar and K. Damodar Rao for help during the field campaigns. Discussions with S. Krishnaswami and his comments were helpful and constructive in improving the manuscript. We thank K. Balakrishna and C. H. Sujatha for the sediment samples of the Nethravathi and Periyar Rivers and Anirban Das for sediment samples from Western Ghats streams. The suggestions of the Editor Louis Derry and the reviews of Sidonie Revillon and an anonymous reviewer were useful in improving the quality of this paper.

References

- Agnihotri, R. (2001), Chemical and isotopic studies of sediments from the Arabian Sea and Bay of Bengal, PhD thesis, Mohan Lal Sukhadia Univ., Rajasthan, India.
- Agnihotri, R., M. M. Sarin, B. L. K. Somayajulu, A. J. T. Jull, and G. S. Burr (2003), Late-Quaternary biogenic productivity and organic carbon deposition in the eastern Arabian Sea, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 197, 43–60, doi:10.1016/S0031-0182(03)00385-7.
- Ahmad, S. M., G. A. Babu, V. M. Padmakumari, A. M. Dayal, B. S. Sukhija, and P. Nagabhushanam (2005), Sr, Nd isotopic evidence of terrigenous flux variations in the Bay of Bengal: Implications of monsoons during the last 34,000 years, *Geophys. Res. Lett.*, 32, L22711, doi:10.1029/2005GL024519.
- Ahmad, S. M., V. M. Padmakumari, and G. A. Babu (2009), Strontium and neodymium isotopic compositions in sediments from Godavari, Krishna and Pennar rivers, *Curr. Sci.*, 97, 1766–1769.
- Alagarsamy, R., and J. Zhang (2005), Comparative studies on trace metal geochemistry in Indian and Chinese rivers, *Curr. Sci.*, *89*, 299–309.
- Chakrabarti, R., A. R. Basu, and A. Chakrabarti (2007), Trace element and Nd-isotopic evidence for sediment sources in the mid-Proterozoic Vindhyan Basin, central India, *Precambrian Res.*, *159*, 260–274, doi:10.1016/j.precamres.2007. 07.003.
- Chandramohan, T., and A. N. Balchand (2007), Regional sediment yield pattern for the west flowing rivers of Kerala state, India, *RMZ Mater. Geoenviron.*, *54*, 501–511.
- Chauhan, O. S., and A. R. Gujar (1996), Surficial clay mineral distribution on the southwestern continental margin of India: Evidence of input from the Bay of Bengal, *Cont. Shelf Res.*, *16*, 321–333, doi:10.1016/0278-4343(95)00015-S.
- Chauhan, O. S., A. M. Dayal, N. Basavaiah, and U. Syed Abdul Kader (2010), Indian summer monsoon and winter

hydrographic variations over past millennia resolved by clay sedimentation, *Geochem. Geophys. Geosyst.*, *11*, Q09009, doi:10.1029/2010GC003067.

Geochemistry

Geophysics Geosystems

- Clift, P. D., J. I. Lee, P. Hildebrand, N. Shimizu, G. D. Layne, J. Blusztajn, J. D. Blum, E. Garzanti, and A. A. Khan (2002), Nd and Pb isotope variability in the Indus River System: Implications for sediment provenance and crustal heterogeneity in the Western Himalaya, *Earth Planet. Sci. Lett.*, 200, 91–106, doi:10.1016/S0012-821X(02)00620-9.
- Clift, P. D., et al. (2008), Holocene erosion of Lesser Himalaya triggered by intensified summer monsoon, *Geology*, *36*, 79–82, doi:10.1130/G24315A.1.
- Clift, P. D., et al. (2010), Monsoon control over erosion patterns in the Western Himalaya: Possible feed-back into the tectonic evolution, in *Monsoon Evolution and Tectonics– Climate Linkage in East Asia*, edited by P. D. Clift, R. Tada, and H. Zheng, *Geol. Soc. Spec. Publ.*, 342, 185–218.
- Colin, C., L. Turpin, J. Bertaux, A. Desprairies, and C. Kissel (1999), Erosional history of the Himalayan and Burman ranges during the last tow glacial-interglacial cycles, *Earth Planet. Sci. Lett.*, 171, 647–660, doi:10.1016/S0012-821X (99)00184-3.
- Das, A., S. Krishnaswami, M. M. Sarin, and K. Pande (2005), Chemical weathering in the Krishna Basin and Western Ghats of the Deccan Traps, India: Rates of basalt weathering and their controls, *Geochim. Cosmochim. Acta*, 69, 2067–2084, doi:10.1016/j.gca.2004.10.014.
- Fleitmann, D., S. J. Burns, M. Mudelsee, U. Neff, J. Kramers, A. Mangini, and A. Matter (2003), Holocene forcing of the Indian monsoon recorded in a stalagmite from southern Oman, *Science*, *300*, 1737–1739, doi:10.1126/science. 1083130.
- Garzanti, E., G. Vezzoli, S. Andò, P. Paparella, and P. D. Clift (2005), Petrology of Indus River sands: A key to interpret erosion history of the Western Himalayan Syntaxis, *Earth Planet. Sci. Lett.*, 229, 287–302, doi:10.1016/j.epsl.2004. 11.008.
- Gupta, A. K., D. M. Anderson, and J. T. Overpeck (2003), Abrupt changes in the Asian southwest monsoon during the Holocene and their links to the North Atlantic Ocean, *Nature*, *421*, 354–357, doi:10.1038/nature01340.
- Gupta, H., G. J. Chakrapani, K. Selvaraj, and S.-J. Kao (2011), The fluvial geochemistry, contributions of silicate, carbonate and saline–alkaline components to chemical weathering flux and controlling parameters: Narmada River (Deccan Traps), India, *Geochim. Cosmochim. Acta*, 75, 800–824, doi:10.1016/j.gca.2010.11.010.
- Harris, N. B. W., M. Santosh, and P. N. Taylor (1994), Crustal evolution in South India: Constraints from Nd isotopes, J. Geol., 102, 139–150, doi:10.1086/629659.
- Harrison, S. P., K. E. Kohfeld, C. Roelandt, and T. Claquin (2001), The role of dust in climate changes today, at the last glacial maximum and in the future, *Earth Sci. Rev.*, *54*, 43–80, doi:10.1016/S0012-8252(01)00041-1.
- Herzschuh, U. (2006), Palaeo-moisture evolution in monsoonal Central Asia during the last 50,000 years, *Quat. Sci. Rev.*, 25, 163–178, doi:10.1016/j.quascirev.2005.02.006.
- Innocent, C., N. Fagel, and C. Hillaire-Marcel (2000), Sm-Nd isotope systematics in deep-sea sediments: Clay-size versus coarser fractions, *Mar. Geol.*, 168, 79–87, doi:10.1016/ S0025-3227(00)00052-9.
- Jacobsen, S. B., and G. J. Wasserburg (1980), Sm-Nd isotopic systematics of chondrites and achondrites, *Meteoritics*, *15*(4), 307–308.

- Kale, V. S., S. Mishra, and V. R. Baker (2003), Sedimentary records of palaeofloods in the bedrock gorges of the Tapi and Narmada rivers, central India, *Curr. Sci.*, 84, 1072–1079.
- Kessarkar, P. M., V. Purnachandra Rao, S. M. Ahmad, and G. Anil Babu (2003), Clay minerals and Sr-Nd isotopes of the sediments along the western margin of India and their implication for sediment provenance, *Mar. Geol.*, 202, 55–69, doi:10.1016/S0025-3227(03)00240-8.
- Kolla, V., L. Henderson, and P. E. Biscaye (1976), Clay minerology and sedimentation in the Western Indian Ocean, *Deep Sea Res.*, 23, 949–961.
- Mahoney, J. J., H. C. Sheth, D. Chandrasekharam, and Z. X. Pemg (2000), Geochemistry of flood basalts of the Toranmal section, northern Deccan traps, India: Implications for regional Deccan stratigraphy, *J. Petrol.*, 41, 1099–1120, doi:10.1093/petrology/41.7.1099.
- Milliman, J. D., G. S. Quraishee, and M. A. A. Beg (1984), Sediment discharge from the Indus river to the ocean: Past, present and furture, in *Marine Geology and Oceanography* of *Arabian Sea and Coastal Pakistan*, edited by B. U. Haq and J. D. Milliman, pp. 65–70, Van Nostrand Reinhold, New York.
- Nair, M., T. Joseph, K. K. Balachandran, K. K. C. Nair, and J. S. Paimpillii (2003), Arsenic enrichment in estuarine sediments-impact of iron and manganese mining, in *Fate of Arsenic in the Environment (International Symposium on Fate of Arsenic in the Environment)*, edited by M. F. Ahmed, M. A. Ali, and Z. Adeel, pp. 57–67, Dhaka, Bangladesh.
- Panda, D. K., A. Kumar, and S. Mohanty (2011), Recent trends in sediment load of the tropical (Peninsular) river basins of India, *Global Planet. Change*, 75, 108–118, doi:10.1016/j.gloplacha.2010.10.012.
- Peng, Z. X., J. J. Mahoney, P. R. Hooper, J. D. Macdougall, and P. Krishnamurthy (1998), Basalts of the northeastern Deccan Traps, India: Isotopic and elemental geochemistry and relation to southwestern Deccan stratigraphy, J. Geophys. Res., 103, 29,843–29,865, doi:10.1029/98JB01514.
- Petit, J. R., et al. (1999), Climate and atmospheric history of the past 420,000 years form the vostok ice core, Antarctica, *Nature*, *399*, 429–436, doi:10.1038/20859.
- Peucat, J. J., P. Vidal, J. Bernard-Griffiths, and K. C. Condie (1989), Sr, Nd, and Pb isotopic systematics in the Archean low to high-grade transition zone of southern India: Synaccretion vs. Post-accretion granulites, J. Geol., 97, 537–549, doi:10.1086/629333.
- Prell, W. L., and J. E. Kutzbach (1987), Monsoon variability over the past 150 000 years, J. Geophys. Res., 92, 8411–8425, doi:10.1029/JD092iD07p08411.
- Rahaman, W., S. K. Singh, R. Sinha, and S. K. Tandon (2009), Climate control on erosion distribution over the Himalaya during the past ~100 ka, *Geology*, 37, 559–562, doi:10.1130/ G25425A.1.
- Rajawat, A. S., Y. Gupta, Y. Pradhan, A. V. Thomaskutty, and S. Nayak (2005), Coastal Processes along the Indian Coast— Case studies based on synergistic use of IRS-P4 OCM IRS-1C/1D data, *Indian J. Mar. Sci.*, 34, 459–472.
- Ramaswamy, V., and R. R. Nair (1989), Lack of cross-shelf transport of sediments on the western margin of India: Evidence from clay mineralogy, J. Coastal Res., 5, 541–546.
- Ramaswamy, V., and R. R. Nair (1994), Fluxes of material in the Arabian Sea and Bay of Bengal—Sediment trap studies, in *Biogeochemistry of the Arabian Sea: Present Information and Gaps*, vol. 103, edited by D. Lal, pp. 189–210, Indian Acad. of Sci., Bangalore.

Rao, V. P., and B. R. Rao (1995), Provenance and distribution of clay minerals in the sediments of the western continental shelf and slope of India, *Cont. Shelf Res.*, 15, 1757–1771, doi:10.1016/0278-4343(94)00092-2.

Geochemistry

Geophysics Geosystems

- Reichart, G. J., M. den Dulk, H. J. Visser, C. H. d. Weijden, and W. J. Zachariasse (1997), A 225 kyr record of dust supply, paleoproductivity and the oxygen minimum zone from the Murray Ridge (northern Arabian Sea), *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 134, 149–169, doi:10.1016/ S0031-0182(97)00071-0.
- Rutberg, R. L., S. L. Goldstein, S. R. Hemming, and R. F. Anderson (2005), Sr isotope evidence for sources of terrigenous sediments in the southeast Atlantic Ocean: Is there increased available Fe for enhanced glacial productivity?, *Paleoceanography*, 20, PA1018, doi:10.1029/ 2003PA000999.
- Sarkar, A., R. Ramesh, S. K. Bhattacharya, and G. Rajagopalan (1990), Oxygen isotope evidence for a stronger winter monsoon current during the last glaciation, *Nature*, 343, 549–551, doi:10.1038/343549a0.
- Sarkar, A., R. Ramesh, B. L. K. Somayajulu, R. Agnihotri, A. J. T. Jull, and G. S. Burr (2000), High resolution Holocene monsoon record from the eastern Arabian Sea, *Earth Planet. Sci. Lett.*, 177, 209–218, doi:10.1016/S0012-821X(00) 00053-4.
- Schott, F. A., and J. P. McCreary Jr. (2001), The monsoon circulation of the Indian Ocean, *Prog. Oceanogr.*, *51*, 1–123, doi:10.1016/S0079-6611(01)00083-0.
- Shankar, D., P. N. Vinayachandran, and A. S. Unnikrishnan (2002), The monsoon currents in the north Indian Ocean, *Prog. Oceanogr.*, 52, 63–120, doi:10.1016/S0079-6611(02) 00024-1.
- Siddall, M., E. J. Rohling, A. Almogi-Labin, C. Hemleben, D. Meischner, I. Schmelzer, and D. A. Smeed (2003), Sea-level fluctuations during the last glacial cycle, *Nature*, 423, 853–858, doi:10.1038/nature01690.
- Singh, S. K., S. K. Rai, and S. Krishnaswami (2008), Sr and Nd isotopes in river sediments from the Ganga Basin: Sediment provenance and spatial variability in physical erosion, *J. Geophys. Res.*, 113, F03006, doi:10.1029/2007JF000909.
- Sinha, A., K. G. Cannariato, L. D. Stott, and H.-C. Li (2005), Variability of Southwest Indian summer monsoon precipitation during the Bølling-Allerød, *Geology*, 33, 813–816, doi:10.1130/G21498.1.
- Sirocko, F. (1995), Abrupt change in monsoonal climate: Evidence from the geochemical composition of Arabian sea sediments, habilitation thesis, Univ. of Kiel, Kiel, Germany.
- Sirocko, F., and M. Sarnthein (1989), Wind-borne deposits in the northwestern Indian Ocean: Record of Holocene sedi-

ments versus modern satellite data, in *Paleoclimatology* and *Paleometeorology:Modern and Past Patterns of Global Atmospheric Transport, NATO ASI Ser., Ser. C*, edited by M. Leinen and M. Sarnthein, pp. 401–433, Kluwer Acad., Dordrecht, Netherlands.

- Sirocko, F., D. G. Schonberg, and C. Devey (2000), Processes controlling trace element geochemistry of Arabian Sea sediments during the last 25,000 years, *Global Planet. Change*, 26, 217–303, doi:10.1016/S0921-8181(00)00046-1.
- Somayajulu, B. L. K., R. Bhushan, A. Sarkar, G. S. Burr, and A. J. T. Jull (1999), Sediment deposition rates on the continental margins of the eastern Arabian Sea using ²¹⁰Pb, ¹³⁷Cs and ¹⁴C, *Sci. Total Environ.*, 237–238, 429–439, doi:10.1016/S0048-9697(99)00155-2.
- Sridhar, A. (2008), Evidence of a late-medieval mega flood event in the upper reaches of the Mahi River basin, Gujarat, *Curr. Sci.*, 96, 1517–1520.
- Sridhar, P. N., M. M. Ali, P. Vedamony, M. T. Babu, I. V. Ramana, and B. Jayakumar (2008a), Seasonal occurrence of unique sediment plume in the Bay of Bengal, *Eos Trans. AGU*, 89(3), 22, doi:10.1029/2008EO030002.
- Sridhar, P. N., I. V. Ramana, M. M. Ali, and B. Veeranarayana (2008b), Understanding the suspended sediment dynamics in the coastal waters of the Bay of Bengal using high resolution ocean colour data, *Curr. Sci.*, 94, 1499–1502.
- Tiwari, M., R. Ramesh, B. L. K. Somayajulu, A. J. T. Jull, and G. S. Burr (2005), Early deglacial (~19–17 ka) strengthening of the northeast monsoon, *Geophys. Res. Lett.*, 32, L19712, doi:10.1029/2005GL024070.
- Tripathy, G. R. (2011), Isotope geochemistry of black shales and recent marine sediments, PhD thesis, Mohan Lal Sukhadia Univ., Rajasthan, India.
- Tripathy, G. R., S. K. Singh, R. Bhushan, and V. Ramaswamy (2011), Sr-Nd isotope composition of the Bay of Bengal sediments: Impact of climate on erosion in the Himalaya, *Geochem. J.*, 45, 175–186.
- VanLaningham, S., N. G. Pisias, R. A. Duncan, and P. D. Clift (2009), Glacial–interglacial sediment transport to the Meiji Drift, northwest Pacific Ocean: Evidence for timing of Beringian outwashing, *Earth Planet. Sci. Lett.*, 277, 64–72, doi:10.1016/j.epsl.2008.09.033.
- Wyrtki, K. (1973), Physical oceanography of the Indian Ocean, in *The Biology of the Indian Ocean*, edited by B. Zeitschel, pp. 18–36, Springer, Berlin, doi:10.1007/978-3-642-65468-8 3.