U, Re, Mo and isotopic studies of Boron in water and sediments of the northern Indian Ocean: Implications to Contemporary and Paleo-Biogeochemical processes.

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by

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Dedicated to

Meenal, Mahin and the family

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ABSTRACT

This thesis deals with the spatio-temporal variations in abundances and isotope compositions of selected trace elements in the northern Indian Ocean to learn about their geochemistry, water mass structure and past oceanic chemistry. The U, Mo and Re abundances in surface waters of the Bay of Bengal (BoB) are controlled by fresh water supply from the Ganga–Brahmaputra (G–B) Rivers. Subsurface abundances of these elements are not affected by the prevailing suboxic conditions but show a salinity control suggestive of their conservative behavior. Further, water mass structure of the BoB, as constructed by inversion of Nd abundance, ε_{Nd} and hydrographic data, suggests that its less saline surface waters are composed primarily of G-B fresh water and Indonesian Throughflow surface waters, whereas the bottom waters are dominated by Antarctic Bottom Waters. The REEs content and ε_{Nd} in the bay hint at their significant supply by *in* situ release from G–B particles and from the margin sediments in the entire bay. The Nd contribution from G–B particulates, which characterizes the bay waters as less-radiogenic compared to rest of the Indian Ocean and the Pacific Ocean, diminishes in intermediate waters at about 1500 km away from mouth of the G-B River. Furthermore, a globally significant influx of dissolved Ba from the G-B river system to surface layer (top ~100 m) of the BoB is removed completely through the sinking particulate matter, about 95 % of which is regenerated in deep waters and at sediment-water interface. The temporal variations in $\delta^{11}B$ of G. Sacculifer are used to reconstruct the paleo-pH since last ~14 ka in surface waters of the Arabian Sea. The unrealistic pH, as low as \sim 7.1, in surface waters is due to a potential contamination by the detritus locked inside the forams.

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Chapter 1

Introduction

1.1 Introduction

Trace elements and their isotopes (TEIs) are both regulators and diagnostic of various marine biogeochemical processes and perturbations caused by human activity (SCOR, 2007). TEIs in marine deposits faithfully record the temporal variations in oceanic processes and environments such as hydrographical conditions, ocean chemistry, circulation, productivity and sedimentation. Due to ocean–climate coupling, these temporal records of TEIs provide us significant information about past climate and oceanographic processes and further predict the future global change. The growing interest on the applications of TEIs as indicators of various past marine biogeochemical processes requires better understanding of their geochemistry, which includes better knowledge of their sources, transport, chemical speciation, internal cycling and sinks. The geochemistry of TEIs can be well understood by exploring their distributions in diverse environments of the contemporary oceans and by ascertaining the factors regulating these distributions.

The northern Indian Ocean is comprised of two vast oceanic basins around the Indian Peninsula, namely the Arabian Sea (AS) and the Bay of Bengal (BoB). Both of these basins though face similar atmospheric forcing being situated geographically at same latitudes, their freshwater forcing are different-the AS has excess evaporation over the precipitation in contrast to the BoB receiving a net freshwater input of ~ 4050 km³/v (Sengupta et al., 2006). Further, the Bay of Bengal is one of the oceanic basins receiving the world's largest flux of particulate matter ~ 10^{12} kg (Galy and France-Lanord, 2001; Milliman and Mead, 1983). These fresh water and particulate fluxes are significant means to deliver the continental input of various TEIs to the Bay of Bengal and beyond to the global oceans through the water circulation. Besides the fresh water and particulate matter, the hydrographical conditions such as temperature, salinity, dissolved oxygen (Chappaz et al., 2010; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Zheng et al., 2002a, b) and continent-ocean interface (boundary exchange) put additional constraints on the water column distribution pattern of various TEIs (Arsouze et al., 2009; Jeandel et al., 2011; Jeandel et al., 1998; Lacan and Jeandel, 2005; Rempfer et al., 2011). Boundary processes are most

crucial to establish the paleo-hydrology using the extensively utilized TEIs of marine deposits (Wilson et al., 2012). Even in the contemporary oceans, boundary processes compromise the use of these TEIs (such as relative abundance pattern of Rare Earth Elements, (REEs) and neodymium isotope composition (ε_{Nd})) as water mass tracers by altering their signatures. Therefore, the Bay of Bengal serves as a natural laboratory to investigate the role of fresh water and suspended matter on the water column distribution of various TEIs and to demarcate the limit from these spatial distributions beyond which these tracers can be used reliably. At present, the Arabian Sea is a significant source of potential green house gas, CO₂ to the atmosphere (Sarma et al., 2000; Sarma, 2003; Takahashi et al., 2002; Takahashi et al., 2009). However, little is known about its role in the past. The knowledge on the natural variations in pH of surface oceans can be used to put better constraints on recent increase in anthropogenic CO₂, which is a potential threat to our environment due to the global warming.

Several studies have focused on the paleo-redox state of the oceanic basins using sedimentary archives of redox sensitive elements (RSEs) such as U, Mo and Re (Calvert and Pedersen, 1993; Crusius et al., 1996; Pattan and Pearce, 2009; Sarkar et al., 1993). Among the various RSEs, U, Mo and Re have been preferentially exploited in paleo-oceanographic research as these elements get enriched to a greater extent in sediments compared to many other RSEs due to their higher [metal]_{seawater}/[metal]_{crust} ratio. The homogenized abundances of these elements in open oceans (Collier, 1985; Colodner, 1993; Ku et al., 1977; Miyake, 1970; Owens et al., 2011) reflect their passive behavior under well oxygenated water conditions due to formation of their oxyanions and show long residence times, of the order of $\sim 10^5$ years (Dunk et al., 2002; Miller et al., 2011; Rahaman and Singh, 2010). However, their behavior under reducing conditions is prone to reduction and subsequent removal (Anderson, 1987; Anderson et al., 1989; Bertine, 1972; Colodner, 1993; Colodner et al., 1995; Emerson and Huested, 1991; Mckee and Todd, 1993; Rengarajan et al., 2003), but mode of their removal from the water column is still a matter of debate.

Although, U is known to form organo-metallic complexes, its contribution as a removal phase depends on bottom water oxygenation condition and seems to contribute to shallow coastal zone only (Anderson, 1982; Chappaz et al., 2010; Zheng et al., 2002a, b). On the other hand, coagulation and resuspension of its colloidal phase is invoked to explain its removal/addition from river–sea mixing zone on shelf area of the Amazon River (Swarzenski et al., 1995) but its significant contribution to offshore waters is challenged (Guo et al., 2007).

Molybdenum is well known cofactor in the enzymes and thus participates actively in marine biology (Falkowski, 1983) but this process does not seem to affect Mo abundance in seawater (Bruland and Lohan, 2003). Earlier studies have highlighted the formation of particle reactive thiomolybdates (Erickson and Helz, 2000; Vorlicek and Helz, 2002; Vorlicek et al., 2004) or transient Mo(V) (Wang et al., 2011) for removal of Mo in euxinic waters. In contrast, Helz et al., (2011) proposed the precipitation of Fe(II)–Mo(VI)–S(II) phase under the unique pH and H₂S conditions from euxinic basins.

Further, Helz and Dolor, (2012) suggest that both molybdenum and rhenium are thiolated at surfaces of the colloidal phase Fe(II)-Mo(VI)-S(II) phase and subsequently co-precipitate. Thus, Re is removed by co-precipitation rather than reduction or particle reactive thiolated products.

These studies although conducted in sulphidic environments, highlight the preferential role of the mineral surfaces in removing these elements from the water column under reducing conditions (both suboxic as well as anoxic), which is further corroborated by enhanced enrichment of these elements in sediments from the suboxic/anoxic basins (Pattan and Pearce, 2009; Sarkar et al., 1993). Thus, even in the absence of dissolved H₂S, organic matter bound sulphur can have a potential for sequestration of these elements from the water column. Therefore, the BoB characterized by high sediment load and intense suboxic conditions is a potential site to test this hypothesis.

Apart from RSEs, the relative abundance pattern of REEs and radiogenic isotopes of Nd have found extensive applications. Their direct measurement in

dissolved phase is used to trace the global water circulation and the continental input (Alibo and Nozaki, 2004; Bertram and Elderfield, 1993; Jeandel et al., 1998; Nozaki and Alibo, 2003a, b). On the other hand, REEs and isotope composition of Nd in authigenic phases hold promise for reconstructions of past ocean circulation pattern (Ling et al., 1997; Martin and Scher, 2006; Piotrowski et al., 2009; Piotrowski et al., 2004, 2005; Von Blanckenburg, 1999) and continental weathering (Burton and Vance, 2000; Gourlan et al., 2008; Gourlan et al., 2010; Le Houedec et al., 2012; Ling et al., 2005; Stoll et al., 2007; Von Blanckenburg and Nägler, 2001), whereas those in the detrital phases are used for the provenance determination (Albarède et al., 1997; Colin et al., 1999; Frank, 2002; Frank et al., 1999; Goldstein and Hemming, 2003; Goswami et al., 2012; Rahaman et al., 2009; Tripathy et al., 2011).

The short oceanic residence time of REEs with predominant continental supply from local landmasses (having distinct relative abundance and isotope signatures) and the non-reactivity in marine biological activity (hampering the other potential proxies for paleo-oceanographic reconstructions, such as $\delta^{13}C$ or Cd/Ca) make the REEs relative abundance pattern and radiogenic neodymium isotope composition (ε_{Nd}) as excellent water mass tracers on an ocean-wide scale (Alibo and Nozaki, 2004; Amakawa et al., 2000; Frank, 2002; Goldstein and Hemming, 2003 and references therein; Nozaki and Alibo, 2003a; Zhang and Nozaki, 1996). Despite a significant continental supply of REEs to oceans, the exact mode of this supply is controversial (Nozaki and Alibo, 2003b; Rempfer et al., 2011; Siddall et al., 2008; Tachikawa et al., 1999; Wilson et al., 2012). Earlier studies (Lacan and Jeandel, 2005; Tachikawa et al., 2003), have highlighted the role of continent-ocean interface as a net dominant source of REEs. Since margin sediments can act as source as well as sink, this process is termed as Boundary Exchange. A vertical migration and the boundary exchange (Arsouze et al., 2009; Jeandel et al., 1998; Lacan and Jeandel, 2005; Rempfer et al., 2011; Wilson et al., 2012) complicate the use of both the relative abundance pattern of REEs and ε_{Nd} as proxies for water circulation. The degree of fractionation caused by these processes alters the REEs pattern to a greater extent compared to ε_{Nd} (German et al., 1995; Jeandel, 1993; Jeandel et al., 1998; Nozaki and Alibo, 2003a), which makes the later a better proxy of initial source waters and hence to trace the global ocean circulation.

The radiogenic ε_{Nd} signature is well resolved for the recognized voluminous water masses of the world's ocean (Amakawa et al., 2009; Andersson et al., 2008; Bertram and Elderfield, 1993; Jeandel, 1993; Jeandel et al., 1998; Piepgras and Jacobsen, 1988; Piepgras and Wasserburg, 1980, 1982; Piepgras and Wasserburg, 1983, 1987; Piepgras et al., 1979; Porcelli et al., 2009; Rickli et al., 2009; Shimizu et al., 1994; Spivack and Wasserburg, 1988; Stordal and Wasserburg, 1986). However, the radiogenic ε_{Nd} signature in the northern Indian Ocean, where various surface and intermediate water masses are formed (Wyrtki, 1973) and transported southward to the central Indian Ocean is not yet known.

Hitherto, radiogenic neodymium isotope composition of the Indian Ocean (Amakawa et al., 2000; Bertram and Elderfield, 1993; Jeandel et al., 1998; Tazoe et al., 2011) was believed to be intermediate between the less radiogenic Atlantic and the more radiogenic Pacific Ocean values (Bertram and Elderfield, 1993; Frank, 2002). Further, the limited available pattern for Nd abundance and its isotope composition in surface waters of the northeastern Indian Ocean (Amakawa et al., 2000) and significantly high Nd content throughout the depth profile, PA-9 (Nozaki and Alibo, 2003b) in the Bay of Bengal hint at significant contribution of REEs from particles in the Bay of Bengal. However, impact of dissolution of these particulate matters, which is most likely sourced from the Himalaya characterized by unradiogenic neodymium (Robinson et al., 2001; Singh and France-Lanord, 2002; Singh et al., 2008) and delivered to the north Indian Ocean by the Ganga, Brahmaputra, Irrawaddy and the Indus Rivers, on the ε_{Nd} signatures of various water masses present in the northern Indian Ocean is not known. Therefore, the Bay of Bengal receiving a globally significant flux of particulate matter is an ideal geographical region to learn about the geochemistry of REEsto evaluate the role of particulate matter in supplying REEs to the water column and modifying the ε_{Nd} signature of various water masses and to demarcate the boundary beyond which such perturbations become negligible enough to use the quasi-conservative ε_{Nd} as a reliable water mass tracer.

Boundary exchange and vertical migrations are restricted not only to the REEs but other particle reactive elements as well. The particle reactive nature of dissolved barium is conspicuous from its oceanic distribution as typical of nutrients (Hoppema et al., 2010; Jacquet et al., 2007; Jacquet et al., 2004; Jeandel et al., 1996; Ostlund et al., 1987), the only difference being its concentration is not totally extinct in surface waters. In contrast to this behavior, the dissolved Ba data collected in the GEOSECS program (Ostlund et al., 1987) show an excess in surface waters of the northeastern Indian Ocean most probably derived from the G–B river system. Since boundary processes significantly modify the net influxes of particle reactive TEIs to the global oceans, this globally significant influx of dissolved barium from the Ganga-Brahmaputra river system (Carroll et al., 1993; Moore, 1997) is prone to modification by higher particulate sinking fluxes in the Bay of Bengal. Further, it is well established that the particulate barium is mostly (~99 %) regenerated in the deeper waters and at the sediment-water interface (Paytan and Kastner, 1996; Rubin et al., 2003). Thus, it is worth exploring the Ba cycle in the Bay of Bengal, a region characterized by higher particulate fluxes and large influx of dissolved Ba from the G–B river system, to quantify the net lateral outflow of dissolved Ba to the global oceans.

Boron isotope composition of carbonate shells secreted by surface dwellers (planktonic foraminifera) fingerprints the paleo-pH of surface oceans, which can track the paleo-pCO₂ of the atmosphere on the geological time scale (Hemming and Hanson, 1992; Hemming et al., 2007 and references therein; Honisch et al., 2009; Hönisch and Hemming, 2005; Palmer et al., 2010; Sanyal et al., 1997; Sanyal et al., 1995). It has capability to establish the role of an oceanic basin as a source or sink of potential green house gas (CO₂) to the atmosphere on the millennial time scale by comparing pCO_2 levels of contemporaneous atmosphere and surface oceans.

The Arabian Sea belongs to the category of world's most productive oceanic basins. The oxidation of sinking organic matter results in high dissolved inorganic carbon (DIC) in subsurface waters of the Arabian Sea. Intense upwelling and lateral advection of these waters offshore the Somalia, Yemen,

Oman and the west coast of India resulting from wind forcing during the strong South–West monsoon create the seasonal differences in pCO_2 levels of the AS surface waters (Sarma, 2003; Takahashi et al., 2009). Despite the seasonal differences in pCO_2 levels of the surface waters, the AS acts as a perennial source of carbon dioxide to the atmosphere. However, due to past changes in the atmospheric CO_2 , sea surface temperature, and monsoon strength (hence the upwelling), the surface pCO_2 content of the AS has been varied. Thus, it is interesting to explore the paleo- pCO_2 information in the recent past to better understand the natural variations and human perturbation of anthropogenic CO_2 .

In the present thesis, the spatial distributions of abundances of dissolved redox sensitive elements (U, Mo and Re), Ba and REEs along with isotope composition of Nd have been explored in the Bay of Bengal to learn about their spatial variations, causative factors and water mass structure of the basin. The water mass structure of a basin helps us to understand the internal biogeochemical cycling of various TEIs having a short residence time due to their incomplete homogenization over the ocean mixing period. Briefly, the role of fresh water, particulate matter, *in situ* hydrographical conditions and boundary exchange on the distribution pattern of above selected TEIs are evaluated among the various causative factors. In addition, an attempt is made to track the temporal variations in boron isotope composition in planktonic foraminifera from the southeastern Arabian Sea to trace the paleo-pH of surface waters in the region over the last few thousand years.

1.2 Objectives

- 1. To determine the distribution of selected TEIs namely, U, Mo, Re, Ba, REEs and ε_{Nd} in water column of the BoB and factors regulating their distributions.
- **2.** Use radiogenic Nd isotopes to explore the Nd geochemistry and the water mass structure in the BoB.
- **3.** Establishing the chemical extraction of Boron from the environmental samples and its isotope determination by MC–ICPMS at PRL for the first time and explore the potential of boron isotope systematics to estimate paleo-pH in surface waters of the Arabian Sea.

1.3 Anatomy of the thesis

Chapter 1: Introduction

This chapter sets the basic framework of the thesis and highlights the research gaps in current understanding of geochemistry of selected trace elements and their isotopes (TEIs) acquired from earlier studies and deals with relatively unexplored geographical region, the northern Indian Ocean. Basic objectives set here offer new insights about the geochemistry of selected TEIs and significance of the northern Indian Ocean to global oceans as well as the atmosphere.

Chapter 2: Materials and Methods

The chapter deals with the strategy adopted for sampling and their analytical processing to accomplish the objectives set in chapter 1. Brief details regarding the locations of sampling sites, the preliminary sample preparation, analysis onboard the sampling vessel and further analytical processing in the laboratory are also discussed in this chapter.

Chapter 3: Behavior of dissolved redox sensitive elements (U, Mo and Re) in water column of the Bay of Bengal

The main objective of this chapter is to determine the role of external forcing (enormous amount of freshwater and particulate matter input) and *in situ* hydrographical conditions (such as dissolved oxygen, salinity) on distributions of three redox sensitive elements (uranium, molybdenum and rhenium) in water column of the Bay of Bengal.

Chapter 4: Rare earth elements (REEs) in water column of the Bay of Bengal

This chapter is focused on the geochemistry of REEs in the Bay of Bengal. Special emphasis is given on the mechanisms responsible for the spatial distributions of both absolute and relative abundance pattern of REEs.

Chapter 5: Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses

The chapter evaluates the role of the Ganga–Brahmaputra river system in delivering the non-radiogenic Nd to the Bay of Bengal. The spatial distribution of
dissolved Nd concentration and ε_{Nd} along with that of conventional water mass tracers, potential temperature and salinity is processed through *an inverse modeling approach* to explore the water mass structure in the BoB and excess non-radiogenic Nd supplied by the G–B river system. The spatial distribution of the excess Nd in the BoB helps us to gaze the lateral extent from the mouth of the G–B River, where radiogenic Nd isotope composition is unaffected by the boundary exchange and can be used to reconstruct the water circulation both in contemporary as well as past oceans.

Chapter 6: Internal cycling of dissolved barium in water column of the Bay of Bengal

This chapter is on the spatial distributions dissolved barium in water column of the Bay of Bengal. Attempts are made using a two box model, under the assumption of steady state conditions, to balance various internal (particle regeneration) and external (dissolved) fluxes of barium and to quantify the net dissolved Ba outflow from the BoB to the global oceans.

Chapter 7: Temporal variations in boron isotope composition of planktonic foraminifera from the southeastern Arabian Sea: Implications to paleo-pCO₂ levels of the surface oceans

In this study, attempts are made to measure the boron isotope composition using MC–ICPMS. In this chapter, boron isotope composition in the foraminiferal carbonate shells handpicked from the core sediments archiving information since past ~14 ka are utilized to reconstruct the paleo-pH in surface waters of the southeastern Arabian Sea.

Chapter 8: Summary and future directions

This chapter summarizes the major outcomes of this thesis and set directions towards the future work.

Chapter 2

Materials and methods

The prime objective of this study is focused on determination of the contemporary distributions of selected trace elements and isotopes (TEIs) namely, U, Mo, Re, Ba, REEs and ε_{Nd} in water column of the Bay of Bengal and factors regulating these distributions. This objective leads to the ultimate goal of the international GEOTRACES program that focuses on the oceanic distributions of selected TEIs and their causative factors. Subsidiary objective is to study the temporal variations of paleo-pCO₂ in surface waters of the Arabian Sea by using boron isotope composition of carbonate shells produced by surface dwellers. These temporal variations help us to establish the role of the Arabian Sea as a source or sink of the major green house gas (CO₂) to the atmosphere during past few thousand years.

To accomplish these objectives several samples of seawater and a sediment core were taken from the Bay of Bengal (BoB) and the Arabian Sea (AS), respectively. The details regarding the locations of sampling sites and their preliminary sample preparation and analysis onboard the sampling vessel and further analytical processing in our laboratory are discussed in the following sections.

2.1 Materials

For the contemporary distribution of TEIs in water column of the Bay of Bengal, seawater samples were collected during November, 2008, onboard FORV Sagar Sampada on cruise SS259. Whereas for the boron isotope studies, sediment core 3101G (archived at PRL) was collected earlier from the southeastern Arabian Sea during 1994, onboard FORV Sagar Sampada on cruise SS117.

2.1.1 Seawater samples

Seawater samples from the surface and various depths down to the sea floor characterized by oxic and suboxic conditions in water column of the Bay of Bengal were collected at eight stations (Fig. 2.1). The sampling was covering a large transect (GIO1 section of the international GEOTRACES program) along 87° E meridian from ~21^{\circ}N to ~6^{\circ}N. Several seawater samples were also collected near mouths of the Ganga–Brahmaputra river system. Details of the







Fig. 2.2: FORV Sagar Sampada (left) and Niskin sampling bottles over the rosette carrying a Seabird CTD (right) used in seawater sampling.

sampling locations collected at each station are given in Table 2.1. The depth profiles of seawater samples were collected using 12 L Niskin bottles mounted on a 12 bottle rosette with a Seabird CTD (Fig. 2.2). A few surface water samples were also collected using a plastic bucket while the ship was moving (Table 2.1).

Onboard sample processing and analysis

Selected hydrographic and chemical properties of samples were measured onboard. The preliminary data on temperature and salinity was taken from the CTD profiles. The pH of the samples was measured using a pH-meter (Radiometer, PHM 84). Dissolved oxygen was measured by the Winkler's method (Knap, 1996; Strickland and Parsons, 1968). The precision of pH measurements based on repeats was better than 0.02 pH units, whereas the CV % of dissolved oxygen based on repeat measurements of the different samples (n = 4) over wide range of its concentrations was \sim 7 %.

For the TEIs studies, ~2 L of seawater samples were sub-sampled into precleaned plastic carboys, filtered through 0.45 μ m Millipore filters onboard soon after their recovery, acidified to pH ~2 with quartz double distilled 6 N HCl and stored in acid cleaned LDPE bottles for further analysis. The trace element concentration and isotope composition determined in these 0.45 μ m filtered water samples were treated as dissolved phase measurements. For the determination of Nd isotope composition, Nd was pre-concentrated onboard from ~10 L of

Station	Latitude ([°] N)	Longitude ([°] E)	Sampling Depth (m)
SS259-0806	5.813	86.997	5–3800
SS259-08-S1	6.990	86.938	Surface
SS259-08-S2	8.021	86.990	Surface
SS259-0807	8.494	87.007	5–3550
SS259-08-S3	9.974	86.805	Surface
SS259-0808	11.270	86.990	5-3200
SS259-08-S4	12.405	86.994	Surface
SS259-0809	13.769	87.004	5–2900
SS259-08-S5	14.572	88.066	Surface
SS259-08-S6	15.373	89.104	Surface
SS259-0810	16.420	90.498	5–2350
SS259-08-S7	16.457	89.471	Surface
SS259-08-S8	16.697	87.420	Surface
SS259-0811	16.759	86.993	5-2500
SS259-0812	18.759	86.997	5-2000
SS259-0813	20.047	87.262	5–640
SS259-0814	20.537	87.476	4–45
SS259-0815	20.975	87.778	4–30
SS259-0816	20.571	88.107	4–30
SS259-0817	20.836	88.492	5–70
SS259-0818	21.003	88.996	5–60
SS259-0819	20.576	88.753	5–110
SS259-0820	20.585	88.249	5

 Table 2.1: Details of sampling locations in the Bay of Bengal

seawater using the Fe co-precipitation protocol (Amakawa et al., 2000) for stations 0807, 0809, 0810, 0812 and 0813 and from \sim 5–8 L of seawater following the C18 cartridge method (Jeandel et al., 1998; Shabani et al., 1992) for stations 0806, 0808 and 0811 (c.f. section 2.2).

2.1.2 Sediment samples

To ascertain the role of the Arabian Sea as a source or sink to the atmospheric CO₂ since last ~14 ka, a well dated sediment core 3101G from the region was selected. This gravity core was raised from a water depth of 2766 m in the southeastern Arabian Sea (6.0°N, 74.0°E; Fig. 2.1). Chronology of the core was established by Agnihotri, (2001) using ¹⁴C content of handpicked planktonic foraminifera (> 250 μ m) determined by Accelerator Mass Spectrometry. Carbonate shells from these sedimentary samples were collected following the standard procedure (Hastings et al., 1996). Further, the shells of planktonic

Sample	Parameter	Technique	Instrument
	U and Mo concentration	Isotope Dilution technique	Q-ICPMS
Seawater	Re concentration	Isotope Dilution technique followed by Column Chromatography	Q-ICPMS
	REEs concentration	Isotope Dilution technique followed by Column Chromatography	Q-ICPMS
	Nd isotope composition	Onboard pre-concentration followed by Column Chromatography	MC-ICPMS
	Ba concentration	External calibration	Q-ICPMS
nate shells	Boron isotope composition	Standard–sample–standard bracketing after purification by micro-sublimation	MC-ICPMS
Carbor	Trace elements concentration	External calibration	Q-ICPMS

Table 2.2: Analytical techniques and instruments used for analysis of selected parameters

Q–ICPMS: Quadrupole Inductively Coupled Plasma Mass Spectrometer MC–ICPMS: Multi Collector Inductively Coupled Plasma Mass Spectrometer

for aminifera, the Globigerinoides Sacculifer in size fraction $>425~\mu m$ were handpicked for the selected trace elements and boron isotope analysis.

2.2 Analytical methodology

This section deals with analytical methodology adopted for analysis of selected TEIs (Table 2.2) in seawater. The 'nmol/kg' level concentrations of U, Mo and Ba were measured directly on adequately diluted samples to reduce the sample matrix. Whereas, the 'pmol/kg' level concentrations of REEs and Re were measured on pre-concentrated samples after their purification by ion chromatography. Barium concentration was measured by external calibration. On the other hand, the concentrations of redox sensitive elements (U, Mo and Re) and REEs after their pre-concentration were determined using Isotope Dilution technique and calculated as given in equation 2.1.



Fig. 2.3: The analytical scheme for analysis of selected TEIs in seawater of the Bay of Bengal.

$$C_{Sample} = \frac{C_{Spike} \times W_{Spike} \times M_{Sample}}{W_{Sample} \times M_{Spike}} \times \left(\frac{X_{Spike} - R_{Mixture} \times Y_{Spike}}{R_{Mixture} \times Y_{Sample} - X_{Sample}}\right) (2.1)$$

where C, W and M are concentration, weight and atomic weight; R is ratio of abundance of isotope X to that of Y. The elemental concentrations were analyzed

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Fig. 2.4: Analytical scheme for trace elements and boron isotope analysis in foraminiferal carbonate samples.

on Quadrupole ICPMS (Thermo X-series-II), whereas isotope compositions of B and Nd were analyzed on MC–ICPMS (Thermo Finnigan–Neptune). Isotope composition of B was measured after their chemical purification from foraminiferal samples through micro-sublimation, whereas neodymium isotope composition from pre-concentrated and stored seawater samples by ion chromatography. An overall analytical scheme adopted for analysis of selected TEIs in seawater and carbonate samples is given in Figs. 2.3 and 2.4, respectively.

Station	Depth	Ва	U	Мо	Re
Station	(m)		(nmol/kg)	(pmol/kg)	
0806	60	40.0	14.0	116	40.0
	60R	39.1	14.2	115	40.7
	1200	73.6	14.0	114	41.1
	1200R	71.9	13.9	113	_
	2000	96.6	13.9	113	41.3
	2000R	95.8	14.0	116	40.8
	3200	106.4	14.1	114	40.9
	3200R	105.9	14.1	116	_
0807	5	43.2	13.4	108	39.3
	5R	44.2	13.4	108	39.4
	400	49.5	14.1	113	40.7
	400R	50.4	14.0	114	41.0
	1500	94.9	14.0	114	41.7
	1500R	95.7	14.0	112	40.9
	3550	131.6	14.0	114	41.4
	3550R	132.4	14.0	113	_
0808	70	32.5	13.8	114	_
	70R	-	14.1	113	-
	175	40.6	14.0	113	41.2
	175R	42.0	14.0	114	40.5
	380	45.8	14.2	114	40.3
	380R	45.6	14.1	114	40.5
	900	68.9	14.0	113	40.3
	900R	67.2	13.9	_	-
	2300	98.2	14.0	113	40.3
	2300R	101.2	14.0	—	39.9
0809	180	39.5	13.8	113	41.6
	180R	38.5	13.8	114	41.5
	700	56.0	13.9	113	42.5
	700R	56.8	_	115	_
	1400	78.1	13.8	114	42.2
	1400R	83.4	13.8	114	42.2
	2900	107.5	13.8	112	41.6
	2900R	107.2	13.8	114	
0810	5	42.6	12.9	105	37.2
	5R	43.8	12.9	104	37.3
	500	44.7	13.8	113	40.6
	500R	48.8	-	114	-
	1000	57.7	13.8	114	41.0
	1000R	61.7	14.1	113	40.7
	1700	87.6	13.8	113	39.7
0011	1700R	-	-	-	40.0
0811	5	36.8	13.5	109	45.0
	5K		-	110	-
	180	44.5	13.8	113	41.6
	INUK	41.1	13.7	113	41.4

Table 2.3: Reproducibility of Ba, U, Mo and Re concentration measurements from analysis of duplicate samples

	400	46.6	13.9	114	39.8
	400R	_	_	-	41.1
	1100	69.6	13.9	113	42.0
	1100R	70.8	13.8	113	41.0
0812	110	39.6	13.8	112	40.4
	110R	_	14.0	112	40.8
	600	57.1	14.0	114	39.6
	600R	56.9	14.0	113	40.9
	1200	82.4	14.0	114	39.8
	1200R	82.5	14.1	114	_
	2000	109.5	13.9	115	40.6
	2000R	109.8	14.0	113	-
0813	70	33.8	13.7	114	40.2
	70R	_	13.7	-	41.3
	250	43.9	13.8	114	40.4
	250R	44.9	-	115	_
	550	52.5	14.0	115	40.5
	550R	51.0	14.0	113	40.9
0816	30	49.9	12.6	100	36.3
	30R	52.5	12.6	101	-
0818	60	37.2	13.5	110	39.1
	60R	37.6	13.6	110	-
0820	5	47.8	13.1	104	37.0
	5R	47.3	13.1	105	37.5
08–S1	surface	26.2	13.2	107	38.5
	surface	26.1	13.3	108	38.9
08–S5	surface	26.6	13.6	108	39.3
	surface	25.7	13.5	108	-
08–S7	surface	33.3	13.0	103	37.2
	surface	34.3	13.0	103	37.4
CV (%)		2	1	2	1

- : not measured; R : analysis of duplicate samples

2.2.1 Measurement of U and Mo concentrations

The concentration of dissolved U and Mo were measured using isotope dilution technique. A known weight of seawater samples (~0.5 g) were diluted precisely (typically 20–25 times) with 0.4 N HNO₃ to decrease the matrix level and spiked with ²³⁶U (atomic abundance ~99.97 %) and ¹⁰⁰Mo (atomic abundance ~95.90 %) tracers. The details regarding calibration of these spikes are given by Goswami (2012). After equilibration of the sample and spike, the intensities of ²³⁸U, ²³⁶U, ⁹⁸Mo and ¹⁰⁰Mo were measured using a quadrupole ICPMS. The concentrations of U and Mo in samples were calculated from ratios of these measured intensities, ²³⁶U/²³⁸U and ¹⁰⁰Mo/⁹⁸Mo. Total procedural blanks for U and Mo were 1.0 ± 0.8 pg (n = 2) and 170 ± 20 pg (n = 3), respectively, which were



Fig. 2.5: Comparison of U, Mo and Re concentrations in the reference materials.

significantly lower than signal and hence no blank correction was made. The coefficient of variation (CV %) based on several measurements (Table 2.3) of duplicate samples are 1 and 2 % for U and Mo, respectively.

Along with the seawater samples of the BoB, international standards of seawater NASS-5 and estuarine water SLEW-3 supplied by National Research Council, Canada, a coral, PR-16 and a few SAFe (Sampling and Analysis of Fe) reference samples were also analyzed. The SAFe samples were seawater samples provided by Prof. Ken Bruland, University of California, Santa Cruz. U and Mo concentrations of these reference samples are consistent within uncertainty with the expected values based on their salinities (Fig. 2.5) attesting to the accuracy of the measurements.

2.2.2 Measurement of Re concentration

For the measurement of Re concentration, Re was extracted from a known weight of seawater (typically 30–60 grams) following the protocol used in our laboratory (Rahaman and Singh, 2010). Briefly, samples were spiked with ¹⁸⁵Re (atomic abundance ~94.50 %) tracer and allowed to equilibrate in oxidizing medium, dried and taken in 0.8 N HNO₃. The details regarding calibration of the tracer are given by Rahaman (2010). Re was separated from the sample through anion exchange chromatography using the resin AG 1–X8 (100–200 mesh). Re was eluted from the resin with 8 N HNO₃, dried and the pure Re fraction was dissolved in 0.4 N HNO₃. Re concentrations were determined by measuring the ratio of intensity of ¹⁸⁵Re to that of ¹⁸⁷Re in the solution using ICP–MS. The coefficient of variation (CV %) based on measurement of duplicate samples (Table 2.3) was ~1 %. Re was also measured in the SAFe samples. Similar to U and Mo, concentration of Re in these reference samples is similar to that expected based on their salinities, attesting to the accuracy of the measurements (Fig. 2.5).

2.2.3 Measurement of REEs concentrations

The concentrations of various REEs are determined indirectly by external calibration technique by assuming their total chemical extraction efficiency similar to that of Nd, which is determined by isotope dilution technique using Q–ICPMS. For the purpose, we required a suitable Nd tracer of known concentration

Isotono	Atomic	Atomic A	bundance
isotope	Mass	Natural	Tracer
¹⁴² Nd	141.90772	0.2706	0.0067
¹⁴³ Nd	142.90981	0.1222	0.0030
¹⁴⁴ Nd	143.91008	0.2383	0.0066
¹⁴⁵ Nd	144.91257	0.0830	0.0028
¹⁴⁶ Nd	145.91311	0.1720	0.0061
¹⁴⁸ Nd	147.91689	0.0576	0.0041
¹⁵⁰ Nd	¹⁵⁰ Nd 149.92089		0.9708
Atomic Weight		144.2433	149.7660

Table 2.4: Atomic abundances and atomic weight of the ¹⁵⁰Nd tracer

 Table 2.5: Calibration of the diluted ¹⁵⁰Nd tracer with respect to Nd_{Spex} standard solution

	Wt. of Nd standard	Wt. of Nd tracer	Concentration of Nd _{Spike}
	(g)		(ng/g)
Nd-Cal-1	0.50920	0.92392	8.314
Nd-Cal-2	0.50960	0.86044	8.307
Nd-Cal-3	0.50892	0.83617	8.291
Nd-Cal-4	0.50930	0.85941	8.266
Nd-Cal-5	0.50870	0.84714	8.243
Nd-Cal-6	0.54173	1.10819	8.111
Nd-Cal-7	0.53832	1.07915	8.339
Nd-Cal-8	0.53883	1.07783	8.368
Nd-Cal-9	0.53783	1.07754	8.286
Nd-Cal-10	0.53753	1.07852	8.347
		Average	8.287
		RSD (%)	0.9

and isotope composition (Table 2.4), which was prepared by diluting the calibrated stock solution (~665.10 ng/g). This diluted tracer was calibrated (Table 2.5) with respect to the Nd standard solution (from *SPEX*) of known concentration (~10.154 ng/g).

To determine the REEs concentration in seawater samples, precisely weighed aliquots (~500 g) of the filtered and acidified samples were spiked with known amount of ¹⁵⁰Nd tracer. After 24 hours of sample and spike equilibration, the REEs were pre-concentrated from these samples using Fe co-precipitation and purified by cation exchange separation (Amakawa et al., 2000; Tachikawa et al.,

Ctotion.	Depth	Pr	Nd	Sm	Eu	Gd	Dy				
Station	(m)	(m) (pmol/kg)									
0806	2000	8.0	29.2	5.4	1.5	3.5	-				
	2000R	8.5	30.3	5.9	1.7	3.8	-				
	3500	10.8	39.8	6.6	1.5	4.4	0.1				
	3500R	11.4	40.6	6.8	1.5	4.0	0.0				
0807	400	4.4	21.5	4.3	1.4	6.0	6.3				
	400R	4.0	21.4	4.2	1.1	5.8	5.8				
0808	380	4.1	20.5	4.0	1.1	5.4	5.0				
	380R	4.4	21.4	4.2	1.3	5.8	5.9				
	2900	7.6	38.5	7.2	2.0	9.5	8.6				
	2900R	8.2	40.4	7.6	2.1	9.9	9.1				
0809	2600	7.7	36.8	7.1	2.1	9.3	7.7				
	2600R	8.3	38.5	7.5	2.2	9.6	7.5				
0810	2350	7.7	35.5	7.3	2.4	9.6	8.3				
	2350R	6.8	36.5	7.3	2.3	9.8	9.7				
0811	1900	7.3	34.7	6.8	2.0	9.1	8.0				
	1900R	7.3	35.5	7.1	2.0	9.3	8.5				
0812	1700	7.1	37.2	6.8	1.6	9.4	8.9				
	1700R	6.6	35.6	6.8	1.6	9.4	9.0				
CV (%)		5.4	2.5	3.4	8.0	3.8	6.7				

 Table 2.6: Reproducibility of Nd concentration measurements from analysis of duplicate samples

- : not measured; R : analysis of duplicate samples

1999) on resin AG 50W–X8 (200–400 mesh) (c.f. Sections 2.2.4.1 and 2.2.4.3). These extracts were further analyzed on Q–ICPMS for the intensities of REEs at masses 141, 144, 146, 147, 150, 151, 157. True Nd concentrations were calculated from the ratio of intensity at mass 150 to that at 144 (i.e. using the ¹⁵⁰Nd/¹⁴⁴Nd in equation 2.1) after the Sm correction estimated from intensity at mass 147. Nd extraction efficiency is estimated by ratio of this true concentration as determined by isotope dilution technique to Nd concentration estimated by external calibration at mass 146. The concentration of REEs estimated by external calibration were corrected for this extraction efficiency. To check for accuracy of the measurements, the REEs data from the station 0807 were compared to that reported earlier by Nozaki and Alibo (2003) from a nearby station PA-9 (8.000°N, 88.995°E). However, the measured concentrations of Pr, Nd, Sm, Eu, Gd and Dy only among the REEs were found in agreement (\pm 20 %) with the reported concentrations from PA-9, and hence discussed in the present thesis. The total procedural blanks of Pr, Nd and Sm for their concentration determination



Fig. 2.6: The purification scheme of Fe-carrier from crude ferric chloride hexahydrate.

based on two measurements were 8 ± 2 , 30 ± 5 and 5 ± 1 pg, whereas it was 15 ± 1 pg for those of Eu, Gd and Dy. The coefficient of variation (CV %) for dissolved concentrations of Pr, Nd, Sm, Eu, Gd and Dy based on repeat measurements (Table 2.6) of nine different samples covering a wide range of their concentrations were determined to be 5.4, 2.5, 3.4, 8.0, 3.8, 6.7 %, respectively.

2.2.4 Measurement of Nd isotope composition

For Nd isotope composition, REEs was pre-concentrated onboard from \sim 5–10 L of seawater samples using either the Fe co-precipitation protocol (Amakawa et al., 2000) or following the C18 cartridge method (Jeandel et al., 1998; Shabani et al., 1992) and stored in acid cleaned LDPE bottles until their analysis. The details of the pre-concentrated procedures followed onboard are discussed briefly as follow:

2.2.4.1 REEs pre-concentration by Fe co-precipitation

In this method, ~1 mL of Fe-carrier (pre-purified by isopropyl ether extraction; Fig. 2.6) containing ~25 mg of Fe³⁺ was added to ~10 L of filtered and acidified (pH ~2) seawater samples taken into pre-cleaned plastic carboys. The solution was left overnight after stirring vigorously. The pH of the solution was further raised to ~8 using NH₄OH, stirred vigorously and left overnight again to settle the precipitate, Fe(OH)₃ that co-precipitates the REEs. The excess water over the precipitates was decanted off and precipitates were collected over 8 inch *WHATMAN* filter paper (whereas in case REEs concentration determination precipitates were collected by centrifugation in ~50 mL centrifuge tubes). The REEs extracts from these precipitates were taken in 50 ml 6 N HCl and stored in acid cleaned LDPE bottles until their further processing in our laboratory.

2.2.4.2 REEs pre-concentration by C18 cartridges

In this method, an organic sorbent bis(2–ethylhexyl) hydrogen–phosphate (HDEHP from *SIGMA–ALDRICH*) was adsorbed onto strongly hydrophobic silica based bonded phase of commercially available C18 cartridges (from *WATERS*). The sorbent with high affinity toward REEs (III) extracted these elements from seawater during sorbent–sample phase interaction. Briefly, \sim 5–8 L of filtered and acidified (pH \sim 3.5) seawater samples were passed through these C18 cartridges preloaded with HDEHP at a controlled flow rate (\sim 20 mL/min) with the help of a peristaltic pump. These Nd extracts from the C18 cartridges were eluted with quartz double distilled \sim 50 mL of 6N HCl at a flow rate of \sim 10 mL/min and collected in 60 mL LDPE bottles for further chemical processing in laboratory.





2.2.4.3 Purification of Nd for its isotope composition determination

Nd from the pre-concentrated REEs extracts was separated following the protocol used in our laboratory (Goswami, 2012). Briefly, the stored REEs extracts were dried and re-dissolved in 2 N HCl. The re-dissolved solution was loaded on a cation exchange resin, AG 50W–X8 (200–400 mesh), which was initially calibrated to separate REEs from other ions (Fig. 2.7). The REEs were eluted with 6 N HCl after removing other ions with 2 N HCl. The solution containing REEs was evaporated to dryness, and re-dissolved in 0.16 N HCl. The Nd was separated from REEs by loading the solution onto a reverse phase chromatographic column (Ln Resin, LN–B50–S in a quartz column) that was previously calibrated by Goswami (2012). The Nd was eluted using 0.25 N HCl from this resin. The purified Nd was dried and re-dissolved in 0.4 N HCl to measure its isotope composition.

2.2.4.4 Nd isotope composition determination on MC-ICPMS

The Nd isotope composition of the purified Nd extracts was determined by MC-ICPMS (Neptune) using a PFA100 nebulizer with an APEX introduction system as Nd⁺ in static multi-collection mode by measuring the intensities at masses 143, 144 and 146 for 40 cycles. Sm correction, if any, was done by measuring the intensity at mass 147. Amplifiers connected to Faraday cups were rotated after every 10 cycles to eliminate amplifier efficiency variations. The signal intensity of Nd at mass 144 in the samples depended on their Nd concentration, and typical values were in the range 0.2–0.6 V. Instrumental mass bias was corrected using an exponential law relative to ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. To check the accuracy and precision of measurements, an international standard, JMC321 was repeatedly run during the period of analysis. The measured average 143 Nd/ 144 Nd of JMC321 was 0.511024 ± 0.000016 (2 σ , n = 9; Fig. 2.8) against the reported value of 0.511123 ± 0.000012 (Barrat and Nesbitt, 1996). The measured ¹⁴³Nd/¹⁴⁴Nd of JMC321 was lower compared to its reported value and hence the ¹⁴³Nd/¹⁴⁴Nd in samples was corrected by normalization to the reported ¹⁴³Nd/¹⁴⁴Nd of JMC321. Total procedural blank for Nd isotope determination was 70 ± 2 pg (n = 2) based on the iron co-precipitation method and $\sim 600 \pm 50$ pg (n =



Fig. 2.8: Nd isotope composition of the reference material, JMC-321.

2) for Nd extraction using C18 cartridge similar to earlier reported blank levels (Lacan and Jeandel, 2004).

2.2.5 Measurement of Ba concentration

The filtered and acidified seawater samples (~ 0.5 g) were diluted suitably (25–30 times) with 0.4 N HNO₃ to decrease the matrix level and dissolved barium was measured by multi–block external calibration method. Two isotopes of barium, ¹³⁵Ba and ¹³⁷Ba free from isobaric interferences were determined in peak jumping mode at standard resolution. Ba concentration was calculated using the more abundant ¹³⁷Ba isotope intensity. In a few samples, Ba was measured by both external calibration and standard addition methods, the results were in agreement (Table 2.7) within \pm 5 %. The background counts of Ba in washing solution (MilliQ water) passed in between Ba analysis of each pair of two samples was less than 1 % of the typical sample intensities thereby ruling out any possible memory effect during the measurement. The total procedural blank for Ba was ~150 \pm 100 pg (n = 3). The precision of Ba data expressed as coefficient of variation from analysis of duplicate samples (Table 2.3) was ~2 %.

Sample ID	Ba _{ext. cal.} (nmol/kg)	Ba _{std.add.} (nmol/kg)
0808-70 m	34.2	35.2
0808-1200 m	77.9	74.4
0808-2900 m	111.4	112.7

 Table 2.7: Comparison of Ba measurements by external calibration and standard addition method

2.2.6 Measurement of trace elements and B isotope composition in carbonate shells

Analytical scheme adopted for processing of carbonate samples for trace elements and boron isotope analysis is given in the Fig. 2.4. The carbonate shells of a planktonic foraminifera, Globigerinoides sacculifer in the size fraction > 425 μ m were separated from bulk sediments of the core 3101G archiving the information since last ~14 ka using the standard protocol (Hastings et al., 1996).

2.2.6.1 Purification of boron for its isotope composition determination

For the boron isotope composition analysis, ~50–80 shells of above separated forams were gently crushed between two glass plates and cleaned rigorously following the protocol for the clay removal (Barker et al., 2003). The organic matter in samples was oxidised for ~24 hours with 5 % NaOCl solution (Hönisch and Hemming, 2005) and samples were transferred to clean vials. Any of adsorbed boron during the earlier cleaning steps was removed with a weak acid (0.001 N HNO₃) leach (Barker et al., 2003). The cleaned samples were finally dissolved in Teflon distilled 0.3 N HNO₃. After dissolution of carbonates as indicated by ceasing of CO₂ bubbling, these samples were centrifuged and ~10 % aliquots of the supernatant solution were kept for the trace element analysis, while rest of the solution was purified directly by sublimation at 98°C for ~24 hours (Wang et al., 2010) for its isotope composition determination.

2.2.6.2 Boron isotope composition determination on MC–ICPMS

The boron isotope composition of the purified solution (~100 ppb of B) was determined by the ratio of simultaneously measured boron intensities at two



Fig. 2.9: Boron isotope composition of sublimated SRM-951.

Faraday cups aligned at the masses 10 and 11 on MC–ICPMS. The solution was aspirated into the plasma using a PFA-50 nebuliser with a quartz single chamber as introduction system to homogenize the sample aerosols for the stable signal. Typical signal intensity in purified samples varied as 0.35-0.5 V. The instrumental drift is corrected using the matrix and concentration matched STANDARD–SAMPLE–STANDARD bracketing. The boron isotope composition (δ^{11} B) of the sample is reported as given in equation 2.2.

$$\delta^{11}B(\%_{0}) = \left[\frac{2 \times \left(\frac{11B_{Sample} - 11B_{Bkg}}{10B_{Sample} - 10B_{Bkg}}\right)}{\left(\frac{11B_{Std 1} - 11B_{Bkg}}{10B_{Std 1} - 10B_{Bkg}}\right) + \left(\frac{11B_{Std 2} - 11B_{Bkg}}{10B_{Std 2} - 10B_{Bkg}}\right)} - 1\right] \times 1000$$
(2.2)

Where *Std 1* and *std 2* correspond to standard intensities analyzed before and after the *Sample*. The preceding backgrounds (B_{bkg}) of each sample and standard are determined in the 0.3 N HNO₃ and these backgrounds are subtracted from their intensities as shown in equation 2.2. No isotope fractionation during the chemical extraction step is confirmed by measuring the boron isotope composition of the standard SRM-951 processed through same chemical extraction procedure (Fig. 2.9). Total procedural boron blank is ~1.5–3.5 ng. The external precision (2 σ) of boron isotope composition determination is ~0.67 ‰.

2.2.6.3 Trace elements analysis

At first, calcium concentrations in the small aliquots were measured on ICP–AES and rest of the solutions were suitably diluted to make their Ca concentration ~10 ppm. A multi-element stock solution (with suitable concentrations) was prepared from the single element ICP standards (~1000 ppm). Standards for external calibration were prepared by suitable dilution of this stock solution keeping a final calcium concentration of ~10 ppm. Trace element/Calcium ratios (Al/Ca, Mg/Ca, Mn/Ca) in above aliquots were measured using these matrix matched standards for external calibration following the protocol established by Yu et al., (2005) on Q–ICPMS. The precision (RSD %) of ratio (Al/Ca, Mg/Ca, Mn/Ca) measurements based on repeat analysis of same standard was 5.3, 4.3 and 4.5 %.

Chapter 3

Behavior of dissolved redox sensitive elements (U, Mo and Re) in water column of the Bay of Bengal

3.1 Introduction

The concentrations and the distributions of redox sensitive elements (RSEs), Fe, Mn, U, Mo, Re and V in sediments, have been used extensively to investigate contemporary and past oceanographic conditions (Calvert and Pedersen, 1993; Crusius et al., 1999; Morford et al., 2001; Nameroff et al., 2002; Nameroff et al., 2004; Pattan and Pearce, 2009; Sarkar et al., 1993; Schenau et al., 2002). The growing interest on the applications of these elements as paleo-redox indicators of oceans requires better understanding of their geochemistry, which includes their sources, transport, internal cycling and sinks. Among the various RSEs, the behavior of U, Mo and Re has been investigated in greater detail as these elements get enriched to a greater extent in sediments compared to many other RSEs due to their higher [metal]_{Seawater}/[metal]_{Crust} ratio; this has led to their preferential exploitation in paleo-oceanographic research. In the case of Mo, in addition to studies on its abundance, its isotope systematics have provided better insight into its oceanic budget (Neubert et al., 2008; Poulson et al., 2006; Siebert et al., 2006; Voegelin et al., 2009). Mo isotopes fractionate significantly during their removal from sea water onto Fe–Mn nodules (i.e. oxic sinks), compared to minor or no fractionation from Mo isotope composition of seawater during their removal into euxinic sediments (i.e. euxinic sinks) (Anbar, 2004; Barling and Anbar, 2004; Barling et al., 2001; McManus et al., 2002). Investigations on the isotopic composition of Mo holds promise for the reconstructions of global ocean paleo-anoxicity and assessing the areal extent of reducing conditions in the oceans on million year time scales (Anbar, 2004; Arnold et al., 2004; Siebert et al., 2003).

The distributions of dissolved U, Mo and Re in well oxygenated oceanic regions show their conservative behavior. In these regions, they occur in their higher oxidation states, $U^{VI}O_2(CO_3)_3^{4-}$, $Mo^{VI}O_4^{2-}$, and $Re^{VII}O_4^{-}$. The relatively passive nature of these oxy-anions in oxic seawater is reflected in their long residence times, estimated to be in the range of ~10⁵–10⁶ y (Colodner et al., 1993; Dunk et al., 2002; Emerson and Huested, 1991; Rahaman and Singh, 2010). The onset of reducing conditions, particularly anoxic conditions can lower their oxidation states to U^{IV} , Mo^{IV} , and Re^{IV} , which are amenable for sequestrations

from dissolved to particulate phases (Bertine, 1972; Colodner et al., 1995; Colodner et al., 1993; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). Such reducing conditions are generally associated with oceanic regions that do not meet the oxygen demand for combustion of organic matter such as land locked seas/channels or continental margins with restricted ventilation. The chemical speciation of U, Mo and Re in reducing oceanic water column is not well constrained compared to that in oxygenated waters and the processes promoting their removal from such regions are still debated. Among these three elements, Mo actively participates in bio-geochemical processes, being a cofactor in enzymes (Falkowski, 1983), however its distribution in the water column does not seem to be affected by its involvement in these processes (Bruland et al., 2003). In contrast, there is no evidence to suggest active participation of U and Re in bio-geochemical processes; though, U is known to form organo-metallic complexes. These complexes can contribute to its authigenic deposition in coastal and margin environments, the preservation of which depends on bottom water oxygen concentration (Anderson, 1982; Chappaz et al., 2010; Zheng et al., 2002).

There have been studies on the removal of these three redox sensitive elements from the seawater to sediments, particularly to sediments underlying suboxic/anoxic waters, such as the Arabian Sea, Black Sea, Cariaco Trench, Saanich Inlet and the eastern tropical North Pacific (Anderson et al., 1989b; Barnes and Cochran, 1990; Colodner et al., 1995; Colodner et al., 1993; Crusius et al., 1996; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). These studies have brought out the role of diffusion in pore waters and various carrier phases (Dellwig et al., 2010; Nealson et al., 1991; Tebo, 1991) in sequestering these elements to sediments. Some of these studies also have underscored the importance of element dependent microbial processes in their reduction and sequestration, for example in the reduction of U compared to that of Mo and Re (McKee and Todd, 1993; Morford et al., 2009).

Studies in the Black Sea (Anderson et al., 1989a; Colodner et al., 1995; Emerson and Huested, 1991), demonstrated that all these three elements are depleted in the euxinic deeper waters; suggesting their removal from the water column. The mechanism(s) and sites of their removal, however, remain to be fully established. In case of Mo, inter-conversion of molybdates to more particle reactive intermediate thio-molybdates when H₂S exceeds a threshold value has been suggested as a mechanism for its removal in sediments (Erickson and Helz, 2000; Vorlicek and Helz, 2002; Vorlicek et al., 2004). In contrast to investigation of these elements in sediments, there are, however only limited studies on their behavior in suboxic/reducing water columns. Study in the Cariaco Trench (Anderson, 1987) does not indicate any measurable variation of U concentration in oxygen minimum zone (OMZ) compared to that in oxygenated waters. However, uranium distribution in the water columns of the Arabian Sea and Framvaren Fjord and sediment trap studies in BoB (Bay of Bengal) hinted towards its possible removal from the OMZ (McKee and Todd, 1993; Rengarajan et al., 2003; Sarin et al., 2000). Studies pertaining to Mo and Re distribution in the water columns associated with OMZ are limited.

The present study is on the distribution and behavior of U, Mo and Re in water column of the Bay of Bengal. This investigation is motivated by two principle considerations; (1) the BoB is an oceanic region that receives a large quantity of fresh water and suspended matter, 1887 km³/year and 2.1×10^{12} kg/year, respectively, from various rivers, the Ganga-Brahmaputra, Godavari, Irrawaddy, Salween, Krishna, Cauveri, and the Mahanadi (Bird et al., 2008; http://www.cciw.ca/atlas-gwq/table3-e.html). Sediment trap studies in the deep and shallow BoB have reported total particulate matter flux ranging from 29 to 63 g $m^{-2} v^{-1}$ with lithogenic fraction varying from 15 % at the distal southernmost site to 46 % at the site near the continental margin (Ramaswamy and Gaye, 2006; Unger et al., 2003). The particulate matter flux shows significant seasonal and inter-annual variations. The bay, therefore serves as a natural laboratory to investigate the role of fresh water and suspended matter in governing the distribution of various elements and (2) the intermediate water of the bay is suboxic (Rao et al., 1994; Sardessai et al., 2007; Wyrtki, 1971). This provides an opportunity to investigate the role of suboxicity and high particulate input in determining the behavior of RSEs in the water column.

The fresh water discharge into the bay leads to the formation of a thick low salinity water lens over the denser saline water in the BoB causing salinity stratification and inhibiting wind driven vertical mixing in the surface layers. Nutrients supplied by riverine discharge enhance the primary productivity in the coastal region (Ramaswamy and Nair, 1994). The oxidation of sinking organic matter that is contributed by marine and terrigenous sources results in an oxygen minimum zone at intermediate depths of 200–800 m in the northern BoB (Rao et al., 1994; Sardessai et al., 2007; Wyrtki, 1971). The suboxic conditions in the BoB show seasonal variations, with models suggesting overall oxygen minimum conditions sustained throughout the year by the physical and biological pumps (Sarma, 2002). The abundance and distributions of the redox sensitive elements in oxic and suboxic waters experiencing high particulate fluxes provides a handle to learn about their behavior in these conditions.

3.2 Results

The concentrations of U, Mo and Re in filtered (< 0.45 μ m) seawater samples collected from surface and various depths in water column of the Bay of Bengal are measured as described in Chapter 2. These data along with other onboard measured properties (temperature, salinity, pH and dissolved oxygen) are presented in Table 3.1. Details of the sampling locations for seawater samples collected at each station are also given in Chapter 2.

Table 3.1 Temperature, pH, salinity, DO and concentrations of dissolved U,Mo and Re in seawater from surface and depth profiles of the Bayof Bengal

Otation	Depth	Temperature		Colinity	DO	U	Мо	Re
Station	(m)	(°C)	рн	Salinity	(µmol/l)	(nmo	ol/kg)	(pmol/kg)
0806	5	29.3	8.36	33.4	217.2	13.5	109	39.4
	60	27.5	7.82	35.0	27.7	14.0	116	40.0
	130	18.6	7.97	34.8	50.2	14.0	114	40.2
	200	13.8	7.87	35.0	24.9	13.9	115	40.8
	290	11.8	7.83	35.1	23.3	14.0	114	41.0
	380	11.1	7.83	35.1	38.8	14.0	114	40.8
	460	10.4	7.81	35.0	24.0	14.1	114	40.5
	520	10.1	7.80	35.0	23.2	-	-	_
	600	9.5	7.79	35.0	26.7	14.0	115	40.5
	700	8.9	7.80	35.0	34.0	_	_	_

Dissolved U, Mo and Re in water column of the BoB

	800	8.1	7.80	35.0	34.8	14.0	114	40.7
	900	7.4	7.80	35.0	44.9	-	_	-
	1000	6.7	7.81	34.9	56.2	14.0	114	40.8
	1200	5.8	7.82	34.9	62.4	14.0	114	41.1
	1400	5.0	7.81	34.9	76.9	13.9	114	40.6
	1700	3.5	7.83	34.8	100.1	14.1	114	40.3
	2000	2.7	7.85	34.8	123.5	13.9	113	41.3
	2300	2.3	7.87	34.8	130.6	13.9	112	40.3
	2600	2.0	7.87	34.7	145.7	14.0	112	40.4
	2900	1.8	7.88	34.7	156.4	14.0	113	40.3
	3200	1.6	7.88	34.7	162.5	14.1	114	40.9
	3500	1.5	7.89	34.7	167.8	13.9	113	40.4
	3800	1.4	7.91	34.7	168.6	13.9	113	40.9
0807	5	29.2	8.38	33.3	208.6	13.4	108	39.3
	70	27.3	8.20	34.9	110.6	13.9	114	41.2
	110	21.9	7.94	34.9	27.3	-	-	-
	160	16.5	7.88	35.0	24.1	14.0	114	40.7
	220	14.2	7.87	35.1	26.9	-	-	-
	300	12.2	7.83	35.1	15.6	14.1	114	41.2
	400	10.9	7.79	35.0	19.1	14.1	113	40.7
	500	10.0	7.79	35.0	19.2	-	-	-
	600	9.1	7.80	35.0	27.8	14.0	114	41.1
	800	7.9	7.79	35.0	36.5	14.1	114	41.0
	900	7.2	7.79	35.0	45.8	14.0	115	40.6
	1000	6.7	7.80	34.9	50.4	14.0	116	40.4
	1100	6.2	7.82	34.9	52.9	-	_	-
	1300	5.3	7.82	34.9	73.7	14.1	115	41.9
	1500	4.4	7.84	34.8	86.4	14.0	114	41.7
	1800	3.2	7.85	34.8	104.4	-	_	-
	2100	2.6	7.86	34.8	117.9	14.0	113	41.0
	2400	2.2	7.86	34.8	137.7	-	-	-
	2700	1.9	7.88	34.7	146.0	14.0	114	41.4
	3000	1.7	7.89	34.7	155.2	-	-	-
	3300	1.6	7.90	34.7	186.5	13.9	114	41.4
	3550	1.4	7.91	34.7	169.7	14.0	114	41.4
0808	5	28.8	8.35	33.3	205.1	13.5	108	38.9
	70	25.7	8.10	34.9	72.2	13.8	114	-
	175	14.8	7.86	34.9	3.2	14.0	113	41.2
	280	11.6	7.81	35.0	9.6	14.0	115	40.6
	380	10.6	7.79	35.0	14.4	14.2	114	40.3
	495	9.6	7.79	35.0	14.5	14.1	113	41.6
	600	8.9	7.79	35.0	22.1	14.1	116	40.8
	700	8.2	7.78	35.0	36.3	-	_	40.4
	800	7.6	7.79	34.9	36.9	-	114	-
	900	7.0	7.78	34.9	42.8	14.0	113	40.3

Dissolved U, Mo and Re in water column of the BoB

	1000	6.4	7.78	34.9	55.4	_	113	_
	1200	5.5	7.79	34.9	66.3	14.0	_	40.6
	1400	4.7	7.82	34.8	79.2	_	112	_
	1700	3.4	7.81	34.8	99.7	13.8	_	40.2
	2000	2.7	7.83	34.8	109.9	_	113	_
	2300	2.2	7.83	34.8	133.8	14.0	113	40.3
	2600	2.0	7.86	34.7	146.8	_	112	_
	2900	1.8	7.85	34.7	147.7	13.9	_	40.6
	3200	1.6	7.86	34.7	151.0	14.0	113	40.5
0809	5	28.7	8.35	33.2	207.5	13.3	109	39.6
	85	25.3	8.10	35.0	80.7	13.9	113	41.7
	180	15.0	7.84	35.0	9.1	13.8	113	41.6
	300	11.6	7.79	35.0	8.0	14.0	114	41.5
	400	10.6	7.79	35.0	8.0	14.0	114	41.2
	500	9.8	7.79	35.0	9.9	13.9	113	41.8
	600	9.1	7.79	35.0	31.8	13.9	114	42.1
	700	8.3	7.79	35.0	23.5	13.9	113	42.5
	800	7.8	7.79	35.0	28.1	13.8	114	42.4
	900	7.3	7.79	35.0	37.8	13.8	113	43.5
	1000	6.6	7.80	34.9	47.2	13.8	114	41.7
	1200	5.7	7.79	34.9	63.1	_	_	_
	1400	4.9	7.81	34.9	74.4	13.8	114	42.2
	1700	3.6	7.81	34.8	98.8	-	_	_
	2000	2.8	7.83	34.8	119.1	13.8	113	40.9
	2300	2.3	7.84	34.8	131.2	-	_	_
	2600	2.0	7.85	34.7	138.1	13.9	113	41.4
	2900	1.7	7.86	34.7	158.9	13.8	112	41.6
0810	5	28.4	8.36	32.1	218.3	12.9	105	37.2
	40	28.9	8.36	33.5	213.8	13.3	107	39.2
	140	20.7	7.94	34.6	14.1	13.7	113	40.6
	200	14.3	7.85	35.0	4.1	13.7	114	40.5
	300	11.5	7.81	35.0	9.0	13.8	114	40.9
	400	10.6	7.80	35.0	12.6	13.9	114	40.7
	500	10.0	7.80	35.0	12.6	13.8	113	40.6
	600	9.3	7.80	35.0	16.7	13.8	113	40.1
	700	8.6	7.80	35.0	22.9	13.9	114	40.5
	800	7.9	7.80	35.0	28.0	13.8	112	40.1
	1000	6.7	7.81	34.9	41.6	13.8	114	41.0
	1200	5.7	7.82	34.9	59.6	13.9	112	40.8
	1400	4.9	7.82	34.9	72.3	13.9	113	40.9
	1700	3.6	7.83	34.8	99.2	13.8	113	39.7
	2000	2.7	7.85	34.8	121.6	13.9	112	41.6
	2200	2.4	7.86	34.8	129.4	13.8	113	40.8
	2350	2.2	7.87	34.8	133.4	13.9	112	40.0
0811	5	28.3	8.38	33.9	207.2	13.5	109	45.0

Dissolved U, Mo and Re in water column of the BoB

	70	23.8	7.97	34.7	13.6	13.7	112	42.0
	110	19.8	7.93	34.9	10.9	13.8	114	43.7
	180	15.5	7.86	35.0	5.7	13.8	113	41.6
	300	11.6	7.80	35.0	9.3	13.8	115	39.8
	400	10.6	7.80	35.0	6.8	13.9	114	39.8
	500	9.8	7.81	35.0	6.1	13.8	113	42.2
	600	9.0	7.81	35.0	18.6	13.8	113	43.3
	700	8.5	7.01	35.0	18.0	13.8	113	40.7
	000	0.5	7.01	25.0	20.0	12.0	110	40.7
	900	7.3	7.02	35.0	50.0	13.9	114	41.0
	1100	6.3	7.83	34.9	52.9	13.9	113	42.0
	1300	5.4	7.83	34.9	64.5	13.9	114	42.2
	1500	4.6	7.84	34.9	85.3	13.8	117	41.1
	1700	3.7	7.84	34.8	103.1	13.8	113	41.0
	1900	3.1	7.85	34.8	111.6	13.7	113	40.6
	2100	2.6	7.85	34.8	118.7	13.7	113	40.3
	2300	2.3	7.85	34.8	131.5	13.7	113	41.2
	2500	2.0	7.84	34.7	139.6	13.8	113	40.8
0812	5	27.6	8.36	32.0	216.4	13.0	103	37.6
	50	25.9	8.04	34.3	31.2	13.8	112	41.8
	110	18.7	7.91	34.9	6.0	13.8	112	40.4
	200	13.3	7.87	35.0	4.9	14.0	114	40.6
	300	11.5	7.83	35.0	4.7	14.0	114	40.2
	400	10.6	7.81	35.0	5.3	14.0	114	40.6
	500	9.9	7.81	35.0	7.6	14.1	114	40.7
	600	9.3	7.80	35.0	10.7	14.0	114	39.6
	800	8.1	7.80	35.0	28.4	14.0	114	40.3
	1000	6.7	7.80	34.9	42.1	14.1	115	40.5
	1200	5.6	7.81	34.9	60.0	14.0	114	39.8
	1400	4.7	7.81	34.9	75.9	14.0	113	_
	1700	3.4	7.83	34.8	98.4	14.0	114	40.5
	2000	2.5	7.86	34.8	124.2	13.9	115	40.6
0813	5	27.7	8.37	32.7	214.5	13.1	106	38.6
	70	24.0	7.99	34.7	8.4	13.7	114	40.2
	150	17.1	7.89	34.9	3.6	13.8	114	40.5
	250	12.4	7.88	35.0	3.4	13.8	114	40.4
	350	11.1	7.82	35.0	12.4	14.0	114	40.6
	440 550	10.4	7.00	35.0	1.3	14.1	114	41.1
	550 640	9.5	7.01	35.0	0.0 12.6	14.0	110	40.5
0814	4	27.3	8.43	29.6	217.9	12.3	97	34.9
0014	45	28.3	8.41	32.5	213.8	13.0	102	37.3
0815	4	26.7	8.43	29.0	216.3	12.0	95	35.1
	30	28.1	8.41	31.5	207.1	12.5	101	35.5
0816	4	26.5	8.51	24.5	254.2	11.0	82	29.7
	30	28.3	8.38	30.9	183.5	12.6	100	36.3
0817	5	26.7	8.42	29.1	211.0	12.4	99	34.9
	70	27.6	8.19	33.7	105.6	13.5	108	40.2
0818	5	26.3	8.42	28.1	216.8	11.6	93	34.3

	60	26.5	8.19	34.0	92.2	13.5	110	39.1
0819	5	26.8	8.42	30.7	217.7	13.0	102	37.2
	110	20.9	7.97	34.8	3.5	13.8	113	40.3
0820	5	27.7	8.40	32.2	214.6	13.1	104	37.0
08-S1	Surface	_	-	_	-	13.2	107	38.5
08-S2	Surface	_	-	_	-	13.3	108	39.7
08-S3	Surface	_	-	_	-	13.4	108	38.9
08-S4	Surface	_	-	_	-	13.4	107	38.9
08-S5	Surface	_	-	_	-	13.6	108	39.3
08-S6	Surface	_	-	_	-	13.4	107	39.1
08-S7	Surface	_	-	_	-	13.0	103	37.2
08-S8	Surface	_	_	_	_	13.5	107	38.9

- not measured

3.2.1 General observations

The surface water temperatures show a North-South gradient with the lowest temperature (26.3°C) at the northernmost station, 0818, while the equatorial station, 0806 shows the maximum temperature (29.3°C; Fig. 3.1a). Surface waters of shallow coastal stations have pH 8.3-8.4. Salinity (reported on Practical Salinity Scale) contours show a North–South gradient due to fresh water supply from the Ganga–Brahmaputra (G–B) river system (Fig. 3.1b); the surface water sample salinity ranges from 24.0 to 34.9, with lower values in the northern stations increasing southward (Table 3.1). Both dissolved oxygen and pH show lower values in intermediate waters (Fig. 3.1c and d). In general, dissolved oxygen decreases drastically in the depth interval 200–800 m at all stations sampled in the Bay of Bengal. It becomes suboxic (DO < 10 μ mol/l and as low as 3 μ mol/l) at stations north of 11°N (Fig. 3.1d) consistent with that reported earlier during the fall inter-monsoon season. The OMZ in the BoB is due to remineralization of sinking organic particles and surface water stratification inhibiting vertical mixing (Gupta and Naqvi, 1984; Rao et al., 1994). The entire OMZ in the BoB shows lower pH as a consequence of remineralization of sinking organic debris (Fig. 3.2).

3.2.2 The distribution of dissolved U, Mo and Re

The dissolved concentrations of U, Mo and Re measured in the water columns of the Bay of Bengal are given in Table 3.1. In the surface water (depth \leq 5 m), concentrations of U, Mo and Re increase steadily from a minimum of 11.0


Fig. 3.1: Distribution of (a) temperature; (b) salinity; (c) pH and (d) dissolved oxygen in the BoB waters along the 87°E transect. Please Note: All the contours are plotted in ODV4 software (Schlitzer, 2010). Whereas Bathymetry data for section contours was taken along the cruise track using GMRT grid (http://www.geomapapp.org; Ryan et al., 2009).



Fig. 3.2: Scatter plot of dissolved oxygen versus pH. Both decrease with water depth with a minimum in the range of 200–800 m (shown by red squares) due to remineralization of sinking organic particles. Arrow points along increasing depth.

nmol/kg, 82 nmol/kg and 29.7 pmol/kg at the northernmost station, 0816, to 13.5 nmol/kg, 109 nmol/kg and 39.4 pmol/kg, respectively at the southernmost station, 0806 (Fig. 3.3 and Table 3.1). The increase parallels that of salinity, resulting from North–South decrease in the mixing proportion of river water and seawater. The concentrations of U, Mo and Re in the shallow and deep waters generally vary within a narrow range, 13.7–14.2 nmol/kg, 112–116 nmol/kg and 39.6–43.5 pmol/kg for the salinity and dissolved oxygen ranges of 34.6–35.1 and 3.2–186.5 µmol/l, respectively (Table 3.1). The only exception to the trend is surface waters of station 0811, which shows a slightly higher concentration of Re (~45 pmol/kg). Table 3.2 show that the concentration ranges of U, Mo and Re in the BoB are similar to those reported for other oceanic basins (Anbar et al., 1992; Chen et al., 1986; Collier, 1985; Colodner et al., 1993; Ku et al., 1977; Morris, 1975; Nameroff et al., 2002; Rengarajan et al., 2003; Sarin et al., 1994).

3.3 Discussion

3.3.1 Dissolved U, Mo and Re in surface waters

The concentrations of dissolved U, Mo and Re in surface waters of the BoB show a North–South gradient mimicking that of salinity (Fig. 3.3).



Fig. 3.3: Salinity and dissolved concentrations of U, Mo and Re in surface waters of the BoB along 87°E transect. The data show north-south gradient due to river water-seawater mixing with dominant water supply from the G-B river system.

This trend can be attributed to dilution from supply of river water, particularly from the G–B, with lower concentrations of these elements. The large influx of fresh water from several major and medium rivers into the BoB significantly influences its salinity and U, Mo and Re distributions in surface waters. The annual input of fresh water to the Bay of Bengal (area ~ 2.2×10^6 km²; average depth ~ 3 km) is 1.89×10^{15} 1 (Bird et al., 2008; http://www.cciw.ca/atlas-gwq/table3-e.html; Sarin et al., 1990), compared to the volume ~ 6.6×10^{18} 1 of the bay. Thus, the residence time of water in the bay relative to river input is only ~ 3.5×10^3 years compared to the global average value of ~ 3.8×10^4 years. This shorter residence time of water in the bay relative to fresh water input highlights the importance of riverine discharge on the properties and distributions of these elements in the bay.

The concentrations of U, Mo and Re in the surface water samples covary with salinity (Fig. 3.4a). The strong positive correlations between the abundances



Fig. 3.4: Scatter plots of U, Mo and Re dissolved concentrations with salinity (a) for surface waters (depth < 5 m) and (b) for samples from depths > 5 m. The strong linear correlations indicate control of salinity on these concentrations. Note that the data point in the red circle (Fig. 3.4a) is excluded from the regression analysis. Figures in insets are for higher salinity samples that are enlarged for clarity. The black, green and red symbols represent samples with DO concentration > 10, 5–10, < 5 µmol/l, respectively. It is evident from these plots that oxygen concentrations in seawater do not affect the distributions of U, Mo and Re.

Oceanic Basin	U (nmol/kg)	Mo (nmol/kg)	Re (pmol/kg)	References
Antarctic Ocean	13.4 ± 0.2			(Ku et al., 1977)
Arabian Sea	13.5 ± 0.8			(Sarin et al., 1994)
	13.1 ± 0.8			(Rengarajan et al., 2003)
Arctic Ocean	14.1 ± 0.2			(Ku et al., 1977)
Atlantic Ocean	13.8 ± 0.4			(Ku et al., 1977)
	13.14 ± 0.03			(Chen et al., 1986)
		109.0 ± 8.7		(Morris, 1975)
			40.1 ± 0.4^{a}	(Colodner et al., 1995; 1993)
Bay of Bengal	14.0 ± 0.1	114 ± 2	41.0 ± 0.4	This study
East China Sea and Yellow Sea		104 ± 6		(Sohrin et al., 1999)
Pacific Ocean	13.8 ± 0.4			(Ku et al., 1977)
	13.7 ± 1.1			(Miyake, 1970)
	13.43 ± 0.03			(Chen et al., 1986)
	13.4 ± 0.3	103.4 ± 2.1	40.8 ± 0.8	(Nameroff et al., 2002)
		105 ± 5		(Collier, 1985)
			39.8 ± 0.2	(Anbar et al., 1992)
			39.5 ± 0.6^{a}	(Colodner et al., 1995; 1993)

Table 3.2 Salinity (35) normalized U, Mo and Re concentrations in various oceanic basins

^a Re values published in Colodner et al., 1993 are modified here by 10 % as corrected in Colodner et al., 1995

of these elements and salinity, as mentioned earlier, suggest that their distributions are dominated by river–seawater mixing. The concentrations of U, Mo and Re in seawater end-member (salinity 35) calculated from the regression lines of concentration–salinity scatter plots for samples from depth \leq 5 m (Fig. 3.4a) are 14.0 ± 0.9 nmol/kg, 113 ± 6 nmol/kg and 41.0 ± 2.4 pmol/kg, respectively. These values are consistent with those reported for open ocean samples from other regions (Table 3.2) and those measured in this study for deeper BoB waters with salinities close to 35. The concentrations in the riverine end-member also deduced from these lines (Fig. 3.4a), are 3.85 ± 0.53 nmol/kg, 11.54 ± 4.04 nmol/kg and 4.90 ± 1.70 pmol/kg for U, Mo and Re respectively. These end-member values overlap within errors to those reported for the Meghna (combined Ganga– Brahmaputra, G–B) in Bangladesh, 3.15 nmol U/kg (Chabaux et al., 2001), and the Hooghly River in India, 13.8 nmol Mo/kg and 6.6 pmol Re/kg (Rahaman and Singh, 2010; Rahaman et al., 2010). The agreement between the riverine endmember estimated in this study with that reported in literature indicates that among the rivers the G–B system is the dominant contributor of these elements to the BoB.

Among the various stations sampled, the Re concentration in surface waters of station 0811, is 45.0 pmol/kg (Table 3.1) about 13 %, higher than that expected from the salinity of this water, 33.9. Further the data seems to show a systematic decrease in Re concentration up to 300 m (c.f. section 3.3.2) in contrast to concentrations observed in other stations from this region, but similar to the trend reported in the Pacific Ocean (Anbar et al., 1992). Although, the higher Re concentration in surface waters of this station and its distribution in the upper layer seems consistent with its supply via atmospheric deposition (Chappaz et al., 2008; Colodner et al., 1995; Colodner et al., 1993; Rauch et al., 2003), it seems unlikely as nearby stations do not show elevated Re in surface water. One likely source for this high [Re] in surface water can be the Godavari River that enters the BoB about 400 km west of this station. This river has Re concentration about 3 times higher than dissolved Re in seawater (Rahaman et al., 2012). The Re, thus introduced by the Godavari has to be transported to the station, 0811; a mechanism for this could be clockwise gyres that develop in surface waters of the BoB, offshore the Godavari River during early winter (Unger et al., 2003) when these samples were collected. Alternatively, strong eddies present in the BoB (Sasamal, 1990) could also transport water eastward from the Godavari to station 0811. The role of the Godavari in determining the Re distribution in surface water of the BoB, can be better assessed through more systematic measurements of Re from the Godavari coast to mid BoB. If the results of this study and the hypothesis to interpret these are confirmed through more systematic studies of Re distribution in the BoB, then dissolved Re can be used to track the movement of Godavari river water in the BoB, as the Re concentration of this particular river is significantly higher than seawater.

3.3.2 Depth profiles of U, Mo and Re in OMZ

The concentration-salinity plots of U, Mo and Re in all samples other than those collected near the surface are presented in Fig. 3.4b. The elemental concentrations show good linear correlations with salinity; however the



Fig. 3.5: Distributions of (a) U; (b) Mo and (c) Re in the water columns of BoB. The waters in BoB seem to have nearly uniform concentrations of these elements; the marginal variations being governed by salinity. For Re, there may be anomalous supply from the Godavari River.

correlation coefficients are lower for Re compared to those for the surface samples (Fig. 3.4a). This seems to result from scatter in the concentration data in the high



Fig. 3.6: Depth profiles of U, Mo, Re, dissolved oxygen (black line) and salinity (blue line). DO decreases in the depth range of 200-800 m at all stations, with pronounced low values (< 10 μmol/l) at stations north of 11°N (gray bands). The distributions of U, Mo and Re in the water columns follow salinity variations and are independent of DO. Uncertainties on U, Mo and Re measurements are shown by horizontal bar for the station, 0806.



Fig. 3.6: Continued...

salinity samples, where both salinity and Re concentrations are within restricted range. The U, Mo and Re concentrations of the samples at all the stations with salinity 35 are in the range of 13.7 to 14.2 nmol/kg (av. 14.0 ± 0.1), 112 to 116

nmol/kg (av. 114 ± 2) and 39.6 to 43.5 pmol/kg (av. 41.0 ± 0.4), respectively. The ranges in U and Mo concentration at salinity 35 are ~4 %, whereas Re has a wide range, ~10 % (insets in Fig. 3.4b). The cause for the wider range in Re abundance is puzzling and needs to be investigated further. The mean U, Mo and Re concentrations at salinity 35 are consistent within errors with those reported for other oceanic regions (Table 3.2).

It is borne out from the foregoing discussion that the dominant factor controlling dissolved U, Mo and Re concentrations in the BoB samples is salinity (Figs. 3.1b, 3.4b and 3.5). Considering that all the three elements are redox sensitive, attempts were also made to look for the impact of dissolved oxygen concentration on their distribution. Dissolved oxygen concentration decreases with depth in all the profiles sampled; with minimum DO concentration in the depth range of 200–800 m (Figs. 3.1d and 3.6). This decrease attains very low values, < 10 μ mol/l in stations north of 11°N. Comparison of dissolved oxygen concentration contours (Fig. 3.1d) with U, Mo and Re contours (Fig. 3.5) show that U, Mo and Re concentrations do not show any measurable change with DO, even within the OMZ prevalent north of 11°N (Fig. 3.6). The U, Mo and Re concentrations even in waters of extreme suboxicity (DO < 5 μ mol/l; e.g. 175 m depth in station 0808, salinity ~ 34.9), are 14.0 nmol/kg, 113 nmol/kg and 40.5 pmol/kg, respectively, indistinguishable from those in waters with significantly higher DO concentration.

Fig. 3.4b is a scatter plot of U, Mo and Re concentrations with salinity in samples of > 5 m depth. The plot includes samples with a wide range of DO concentration, < 5 μ mol/l to > 250 μ mol/l. The plots show significant linear correlations with salinity and do not seem to be impacted by the DO levels in the samples. It is obvious from insets in Fig. 3.4b that even samples having oxygen content < 5 μ mol/l have U, Mo and Re concentrations overlapping with those of others with much higher oxygen content. This leads to the conclusion that observed variations in the concentrations of U, Mo and Re in the Bay of Bengal is not dependent on dissolved oxygen (Figs. 3.4b and 3.6), and are mainly due to salinity variations.

The lack of dependence of U, Mo and Re concentrations on DO in BoB waters inference is consistent with the earlier reports from other suboxic oceanic regions, e.g. the eastern tropical North Pacific (Nameroff et al., 2002). It must be added here that the distribution of uranium in H₂S rich waters of the Black Sea and the Cariaco basin (Anderson, 1987; Anderson et al., 1989a), show divergent behavior with former showing its significant removal, which in the latter basin is nearly conservative. These results suggest that even in addition to H₂S, there must be additional factors that control the removal of uranium. The BoB though has a large particulate flux, the absence of H₂S in its water column, inhibits the formation of more particle reactive Mo-complexes resulting in its removal.

The U, Mo and Re distributions in water column of the BoB are conservative despite the presence of strong suboxic layer in the intermediate waters and large particulate flux. The dominant factor regulating the distributions of these three RSEs is salinity.

3.4 Conclusions

The dissolved concentrations of U, Mo, Re, and salinity exhibit a North-South gradient in surface waters of the Bay of Bengal due to mixing of seawater with fresh water supplied by various rivers, the dominant being the Ganga-Brahmaputra river system. The U, Mo and Re concentrations of both surface and deeper waters covary with salinity, displaying their conservative behavior in the entire Bay of Bengal. A few samples from the surface and upper water columns from the central Bay of Bengal seem to have Re concentration disproportionately higher than that expected from salinity. This higher concentration, if confirmed through more systematic measurements, may be a result of supply from the Godavari River, which has Re concentrations three times higher than seawater. Suboxic conditions (DO < 10 μ mol/l) in intermediate waters (200–800 m) were found north of 11°N along meridian 87°E in the Bay of Bengal. The distributions of U, Mo and Re in water column of the BoB are independent of the suboxic conditions prevailing at the intermediate depths. Similarly, the high flux of suspended material including detrital organic matter does not seem to regulate the abundances and distributions of U, Mo and Re in the water column.

Chapter 4

Rare Earth Elements in the Bay of Bengal

4.1 Introduction

The Rare Earth Elements (REEs), lanthanum (La) to lutetium (Lu) have progressive filling of their valence electrons to same inner 4f shell and hence show a coherent change in their physico-chemical behavior corresponding to their atomic numbers (Nozaki, 2010). For example, their degree of complexation with organic and/or inorganic ligands varies systematically from La (atomic number, z = 57) to Lu (z = 71), which causes their gradual retention in solution phase from La to Lu (Alibo and Nozaki, 1999; Bertram and Elderfield, 1993; Sholkovitz et al., 1994). Thus, lighter REEs are more particle reactive compared to heavy REEs. This particle reactive nature of REEs (except for cerium) is responsible for oceanic distribution typical of nutrients, i.e., their abundances increase both along advective paths of water masses and vertically with depth (De Baar et al., 1983; De Baar et al., 1985a; De Baar et al., 1985b; Elderfield and Greaves, 1982). REEs exist in their natural oxidation state (III) in seawater, however, the redox sensitive REEs, cerium and europium show anomalous behavior due to either oxidation (Ce^{III} to Ce^{IV}) or reduction (Eu^{III} to Eu^{II}). Generally, the seawater abundance of Ce is low due to its oxidative scavenging (Bertram and Elderfield, 1993; Klinkhammer et al., 1983; Nozaki and Alibo, 2003; Stichel et al., 2012; Tachikawa et al., 1999) but shows a typical maximum at intermediate water depths having intense oxygen minimum conditions (Alibo and Nozaki, 2000; De Baar et al., 1988; German and Elderfield, 1990; Schijf, 1992). On the other hand, Eu shows both anomalous (positive as well as negative) and normal behavior in seawater profiles (Alibo and Nozaki, 1999, 2000, 2004; Amakawa et al., 2000; Bayon et al., 2011; Bertram and Elderfield, 1993; De Baar et al., 1985a; De Baar et al., 1988; German et al., 1995; Nozaki and Alibo, 2003). These special features (anomalies) in abundance pattern of REEs in seawater can provide better insights into their internal cycling.

Earlier studies (Amakawa et al., 2000; Nozaki and Alibo, 2003), have highlighted the enrichment of middle REEs (Pr to Dy) compared to rest of lanthanides in waters of the Bay of Bengal. Despite a similar dissolved phase enrichment in the entire eastern Indian Ocean and other nearby oceanic basins (Alibo and Nozaki, 2000, 2004; Nozaki et al., 1999; Zhang and Nozaki, 1996), the



Fig. 4.1: Locations of sampling sites (red circles) in the BoB during the cruise SS259. Pink triangles represent the sampling locations of PA-9 and PA-10 (Nozaki and Alibo, 2003), and the yellow squares are sediment trap locations (Unger et al., 2003).

REEs pattern in the BoB is unique (with more enrichment of light REEs) and hints at a possible influence of the Indian sub-continent through riverine dissolved as well as particulate phases. In this study, the spatial distribution of relative abundance pattern of dissolved middle REEs is explored to learn about their geochemistry and to elucidate the role of the Ganga, Brahmaputra, Irrawaddy and the peninsular rivers of India in supplying dissolved and labile particulate phases of REEs to the Bay of Bengal.

4.2 Results and discussion:

The concentrations of dissolved REEs in water column of the BoB have been measured in seawater samples collected along an 87°E transect. The details regarding the seawater sample locations and methodology adopted for the measurements of REEs are given in Chapter 2.

Station	Depth	Pr	Nd	Sm	Eu	Gd	Dy	Sm/Nd	Eu _{anomaly} a	
	(m)			(pmo	ol/kg)					
0806	5	4.3	22.1	4.9	1.2	6.9	6.3	0.22	0.95	
	60	3.6	18.6	3.8	1.0	5.2	4.9	0.20	0.97	
	130	3.3	16.8	3.6	0.9	4.9	4.1	0.21	0.93	
	200	3.4	18.1	3.7	1.0	5.1	5.0	0.20	1.02	
	290	3.8	19.7	4.0	1.0	5.2	4.6	0.20	0.99	
	380	3.4	17.0	3.5	1.0	4.8	4.0	0.21	1.13	
	460	4.7	21.4	5.8	3.5	8.2	11.0	0.27	2.28	
	600	4.4	21.1	4.7	1.8	6.2	6.5	0.22	1.49	
	800	4.4	21.2	4.7	1.8	6.4	6.4	0.22	1.47	
	1000	4.0	21.5	4.1	1.1	5.7	5.0	0.19	1.00	
	1200	4.8	24.3	4.6	1.3	6.4	5.2	0.19	1.07	
	1400	4.8	25.4	5.0	1.3	6.7	6.0	0.20	1.03	
	1700	7.7	27.7	4.8	1.0	2.9	_	0.17	7 1.16 9 1.51	
	2000	8.0	29.2	5.4	1.5	3.5	_	0.19		
	2300	8.8	30.3	5.0	1.0	3.0	_	- 0.16 1.16		
	2600	8.6	30.9	4.9	1.1	3.0	_	0.16	0.16 1.25	
	2900	8.8	33.8	5.8	1.2	3.9	_	0.17	1.15	
	3200	9.7	36.5	6.5	1.6	4.7	_	0.18	1.34	
	3500	10.8	39.8	6.6	1.5	4.4	_	0.17	1.21	
	3800	10.4	38.2	6.5	1.5	4.3	—	0.17	1.26	
0807	5	3.6	24.2	5.8	1.6	9.0	11.6	0.24	0.97	
	70	3.8	17.8	3.7	1.0	5.1	6.1	0.21	0.98	
	160	3.9	18.8	3.7	1.0	5.0	6.0	0.19	1.07	
	300	5.1	22.7	4.4	1.2	5.9	6.3	0.20	1.01	
	400	4.4	21.5	4.3	1.4	6.0	6.3	0.20	1.22	
	600	4.1	22.1	4.5	1.5	6.4	7.5	0.20	1.22	
	800	4.5	23.3	4.6	1.3	6.2	5.8	0.20	1.07	
	900	4.7	24.8	5.0	1.4	6.6	6.1	0.20	1.08	
	1000	4.4	23.5	4.7	1.3	6.5	6.1	0.20	1.09	
	1300	5.7	27.5	5.4	1.5	7.2	5.8	0.20	1.08	
	1500	6.9	33.2	6.5	1.8	8.2	7.5	0.20	1.10	
	2100	6.8	32.6	6.4	1.8	8.5	7.1	0.20	1.09	
	2700	7.4	35.2	6.7	2.0	9.0	6.8	0.19	1.13	
	3300	8.2	40.5	7.5	2.0	9.8	8.9	0.19	1.04	
	3550	7.3	36.4	6.6	1.8	8.9	8.3	0.18	1.04	
0808	5	7.2	34.5	7.4	1.9	10.0	9.3	0.21	1.01	
	70	5.5	24.8	5.0	1.3	6.4	5.6	0.20	0.99	
	175	4.5	22.7	4.3	1.1	6.0	5.4	0.19	1.01	
	280	4.3	21.1	4.2	1.1	5.8	5.1	0.20	1.01	
	380	4.1	20.5	4.0	1.1	5.4	5.0	0.19	1.01	

Table 4.1: Depth profiles of middle REEs, Sm/Nd and Eu_{anomaly} in the BoB.

Dissolved REEs in water column of the BoB

	495	6.6	29.9	5.8	1.5	7.3	5.4	0.19	1.01
	600	5.1	24.2	4.9	1.6	6.8	7.3	0.20	1.25
	700	4.5	23.1	4.4	1.2	6.1	5.6	0.19	1.06
	900	5.1	26.1	5.1	1.6	7.0	6.7	0.19	1.21
	1200	5.8	29.0	5.5	1.5	7.5	7.2	0.19	1.07
	1700	6.0	29.9	5.7	1.6	7.6	6.9	0.19	1.09
	2300	7.2	43.3	6.6	1.8	9.1	7.9	0.15	1.07
	2900	7.6	38.5	7.2	2.0	9.5	8.6	0.19	1.06
	3200	8.4	41.2	7.5	2.2	10.1	9.1	0.18	1.11
0809	5	7.6	35.6	7.8	2.2	10.5	9.8	0.22	1.11
	85	3.0	14.8	3.1	1.0	4.4	4.6	0.21	1.24
	180	4.8	22.2	4.6	1.4	6.1	5.0	0.21	1.18
	300	4.7	21.5	4.4	1.4	5.8	4.7	0.20	1.27
	400	4.9	23.1	4.6	1.4	6.2	5.4	0.20	1.19
	500	5.2	23.8	4.8	1.4	6.2	4.6	0.20	1.14
	600	5.1	23.9	4.9	1.5	6.5	5.7	0.20	1.18
	700	5.0	24.5	4.9	1.5	6.6	6.5	0.20	1.21
	800	6.8	33.1	7.5	2.2	9.9	9.7	0.23	1.12
	900	5.3	25.9	5.1	1.6	7.0	6.6	0.20	1.17
	1000	5.3	25.6	5.1	1.5	6.9	5.9	0.20	1.16
	1400	5.7	27.8	5.6	1.7	7.5	7.2	0.20	1.20
	2000	7.1	34.1	6.7	2.0	9.0	7.3	0.20	1.18
	2600	7.7	36.8	7.1	2.1	9.3	7.7	0.19	1.19
	2900	7.4	35.2	6.7	2.0	9.0	6.7	0.19	1.15
0810	5	9.4	43.1	9.6	2.7	13.3	10.3	0.22	1.08
	40	7.1	32.9	7.1	2.0	9.8	7.9	0.21	1.09
	140	4.4	21.0	4.5	1.2	6.3	5.8	0.22	1.04
	200	4.8	22.6	4.7	1.4	6.5	6.0	0.21	1.13
	300	4.8	23.0	4.7	1.3	6.5	5.8	0.21	1.06
	400	5.1	23.7	4.8	1.4	6.6	5.6	0.20	1.11
	500	4.9	23.3	4.8	1.4	6.5	5.6	0.21	1.11
	600	5.3	23.4	5.1	1.7	6.8	5.2	0.22	1.31
	700	5.3	24.2	5.1	1.7	6.9	5.8	0.21	1.26
	800	5.7	25.8	5.4	1.9	7.3	5.7	0.21	1.34
	1000	6.5	28.5	6.1	2.1	7.8	5.1	0.21	1.34
	1200	6.5	29.0	6.2	2.1	8.1	6.3	0.21	1.32
	1400	6.6	30.4	6.3	2.1	8.5	7.3	0.21	1.29
	1700	6.6	31.4	6.5	2.2	8.8	7.5	0.21	1.32
	2000	7.4	34.4	7.3	2.3	9.5	7.9	0.21	1.26
	2200	7.6	34.8	7.3	2.3	9.4	7.6	0.21	1.26
	2350	7.7	35.5	7.3	2.4	9.6	8.3	0.20	1.31
0811	5	7.4	34.0	7.3	1.9	9.9	8.4	0.21	1.02
	70	5.6	26.5	5.5	1.5	7.3	6.9	0.21	1.08
	110	4.9	23.1	4.7	1.3	6.3	5.6	0.21	1.04

Dissolved REEs in water column of the BoB

	180	5.1	23.7	4.7	1.2	6.3	5.5	0.20	1.03
	300	5.0	23.7	4.7	1.3	6.3	5.4	0.20	1.05
	400	5.2	24.7	5.0	1.3	6.7	6.2	0.20	1.04
	500	5.8	26.8	5.3	1.4	6.9	5.4	0.20	1.07
	600	5.6	26.8	5.3	1.5	7.0	6.2	0.20	1.08
	700	5.9	27.4	5.5	1.5	7.2	6.3	0.20	1.06
	900	5.7	26.4	5.3	1.5	7.0	5.3	0.20	1.10
	1100	6.1	28.9	5.9	1.6	7.7	6.1	0.20	1.09
	1300	6.3	30.2	6.1	1.7	8.0	7.4	0.20	1.09
	1500	6.6	31.9	6.4	1.8	8.4	7.3	0.20	1.10
	1700	6.8	32.9	6.5	1.8	8.4	7.6	0.20	1.08
	1900	7.3	34.7	6.8	2.0	9.1	8.0	0.20	1.11
	2100	8.0	38.5	7.8	2.2	10.2	8.4	0.20	1.11
	2300	7.5	35.8	7.0	2.0	9.1	7.8	0.20	1.14
	2500	8.1	37.7	7.3	2.1	9.6	7.2	0.19	1.11
0812	5	9.4	45.4	9.6	2.3	13.2	11.0	0.21	0.90
	50	6.0	31.0	6.4	1.5	9.4	9.2	0.21	0.87
	110	4.2	22.5	4.2	0.8	5.9	5.8	0.19	0.75
	200	4.9	25.8	4.9	1.0	6.8	6.7	0.19	0.79
	300	4.9	26.3	4.8	1.0	6.6	6.2	0.18	0.79
	400	5.1	30.0	4.9	1.0	6.8	5.8	0.16	0.79
	500	4.8	25.7	4.8	0.9	6.6	6.4	0.19	0.75
	600	5.4	28.3	5.3	1.0	7.1	6.1	0.19	0.76
	800	5.4	28.0	5.2	1.1	7.0	6.4	0.19	0.85
	1000	5.8	29.4	5.4	1.1	7.4	6.4	0.18	0.79
	1200	6.0	31.1	5.7	1.2	7.7	5.9	0.18	0.83
	1400	6.3	32.0	6.1	1.4	8.1	6.7	0.19	0.90
	1700	7.1	37.2	6.8	1.6	9.4	8.9	0.18	0.87
	2000	7.4	38.8	7.4	1.8	10.3	9.8	0.19	0.92
0813	5	9.4	46.4	10.3	3.1	14.5	12.3	0.22	1.13
	70	4.8	24.4	5.4	1.7	7.5	7.2	0.22	1.21
	150	4.5	22.5	4.9	1.6	6.9	6.2	0.22	1.22
	250	5.5	25.3	5.8	2.2	7.6	5.7	0.23	1.50
	350	5.0	24.8	5.0	1.6	7.0	5.9	0.20	1.25
	440	5.3	27.0	5.8	1.8	7.6	6.9	0.21	1.25
	550	5.4	27.3	5.7	1.8	7.7	7.0	0.21	1.21
2	640	8.8	30.4	7.9	3.7	9.4	7.2	0.26	1.89

^a $Eu_{anomaly} = Eu_{norm}/(Sm_{norm} \times Gd_{norm})^{0.5}$

The data of dissolved REEs concentrations, Sm/Nd and Eu anomaly are given in Table 4.1. Nozaki and Alibo (2003) have reported Nd concentration–depth profile at a station (PA-9; Fig. 4.1) near to station 0807 measured in this study. The Nd concentration–depth profiles at these stations are similar, but the



Fig. 4.2: Distributions of middle REEs in BoB surface waters.

Nd concentrations measured in this study are systematically higher by ~ 10 % than those reported for PA-9. The cause for this difference is unclear; it could be due to spatial variability and/or calibration uncertainties.

4.2.1 Surface waters (depth $\leq 5 m$)

Spatial distribution of concentrations of dissolved REEs in surface waters of the Bay of Bengal is shown in Fig. 4.2. North–South decreasing trends in concentrations of REEs are conspicuous in BoB surface waters. Measured



Fig. 4.3: Variations in concentrations of REEs with salinity in surface waters.

concentrations of Pr, Nd, Sm, Eu, Gd and Dy in surface waters vary as 3.6–9.4, 22.1–46.4, 4.9–10.3, 1.2–3.1, 6.9–14.5 and 6.3–12.3 pmol/kg, respectively. Higher concentrations of these REEs close to mouths of the Ganga–Brahmaputra Rivers hint at possible contributions from the riverine fresh water supply. However, non-linear concentration–salinity plots (Fig. 4.3) reflect non-

conservative behavior of these REEs in BoB surface waters. Such a nonconservative behavior can be caused by their removal by sinking particles and/or their addition through particle release (Alibo and Nozaki, 1999; Greaves et al., 1999; Greaves et al., 1994; Jacobson and Holmden, 2006; Lacan and Jeandel, 2005; Sholkovitz et al., 1994). The sources of these biotic as well as abiotic particles can be either atmospheric or riverine. However, riverine lithogenic fraction dominates over eolian dust in the BoB (Galy and France-Lanord, 2001; Srinivas et al., 2011). Thus, the non-conservative behavior of dissolved REEs in the BoB brings out the role of river particulates in causing the observed concentrations of REEs in surface waters of the region, which was speculated in earlier studies with limited data from the surface waters (Amakawa et al., 2000; Nozaki and Alibo, 2003; Obata et al., 2004). Therefore, major contributors of dissolved REEs to the bay are the dissolved and particulate phases of the G-B and the Irrawaddy Rivers along with inputs from the large peninsular rivers, the Godavari and the Krishna. Unfortunately, there is no published data on concentrations of dissolved REEs in these rivers falling into the Bay of Bengal. However, considering the freshwater and particulate supply of these rivers and circulation pattern of BoB surface waters (Shankar et al., 2002), it can be inferred that the Ganga-Brahmaputra river system presumably dominates over the Irrawaddy and the peninsular rivers in terms of their contribution to the dissolved REEs budget in the BoB surface waters along the 87°E transect.

Fig. 4.4a shows the relative abundance pattern of REEs in surface waters of the BoB. In earlier studies (Alibo and Nozaki, 1999; Bertram and Elderfield, 1993; Elderfield and Greaves, 1982; Tachikawa et al., 1999), such relative abundance pattern of REEs in seawater was discussed, based on the shale normalization. More recently (Alibo and Nozaki, 2000, 2004; Amakawa et al., 2000; Nozaki et al., 1999), the shale has been replaced by North Pacific Deep Water (NPDW) as a reference, to avoid any experimental artifact during processing of sample and reference due to difference in their physical states. Following this practice, the REEs data have been normalized to the reference NPDW in this study. A general North–South trend of the REEs pattern (Fig. 4.4a), similar to that of absolute abundances of individual REEs (Fig. 4.2), is obvious



Fig. 4.4: The relative abundance pattern of REEs in surface waters of (a) the BoB at stations, 0806–13, and the Chao Phraya River (salinity ~0.1) and (b) 0807 and PA-9 in the BoB and PA-10 in the Andaman Sea.

with stronger enrichments of REEs in northern profiles compared to that in the southern profiles. The REEs pattern at 0807 (Fig. 4.4b) is similar to that obtained earlier from the nearby profile PA-9 in the Bay of Bengal and PA-10 in the Andaman Sea by Nozaki and Alibo (2003). This similarity indicates either similar sources of REEs or exchange of water masses across the Andaman–Nicobar ridge at these locations. Otherwise, REEs input (both particulate and dissolved phases) from the G–B river system can support the North–South trend obtained for both absolute as well as relative abundance pattern of REEs in BoB surface waters.

Although, there is scarcity of riverine dissolved REEs data of G–B system, but earlier studies from the world's major and minor estuarine systems (Åström et al., 2012; Nozaki et al., 2000; Sholkovitz and Szymczak, 2000; Sholkovitz, 1993), have confirmed that the abundances and pattern of dissolved REEs of river water is significantly modified during the estuarine transit. Nevertheless, for the sake of simplicity, the abundance pattern of dissolved REEs in the Chao Phraya River in Thailand (Nozaki et al., 2000) at salinity ~ 0.1 is taken into consideration to mimic the composition of the G–B Rivers as these rivers drain similar lithology (Obata et al., 2004). Similar REEs patterns in surface seawater and river water samples with enrichment of Sm, Eu and Gd and with generally high abundances in river water indicate strong influence by the fluvial sources on REEs budget of BoB surface waters.

4.2.2 Subsurface waters (depth > 5 m)

4.2.2.1 Depth contours of REEs

The depth contours of measured concentrations of REEs along the 87°E transect are shown in Fig. 4.5. Depth profiles of the REEs typically show a higher concentration in surface waters that decreases to a minimum at depths ~ 50-200 m and follows a gradual increase with depth (Table. 4.1). The steady increase in the concentration of dissolved REEs with depth can result from its release from sinking particles as they transit through the water column. Alternatively, the supply of REEs to bottom waters from sediment pore waters (benthic flux) and its subsequent upward diffusion can also generate profiles similar to those observed. The presence of hot-spots of dissolved REEs (Fig. 4.5) near the sediment-water interface indicates possibility of such sources in BoB bottom waters. The importance of pore water as a source of dissolved REEs to bottom waters is however still debated. The results of Haley et al. (2004) and Bayon et al. (2011) from the California margin, off Peru and the Niger delta for the stations away from cold seeps support the hypothesis, whereas the data of Nozaki and Alibo (2003) for station PA-9 in the BoB and that of Carter et al. (2012) for two stations in the eastern Pacific Sector of the Southern Ocean, seem to indicate potential removal in the benthic boundary layer rather than their release. The relative



Fig. 4.5: Distributions of REEs in water column of the BoB.

significance of REEs release from the sinking particles vis-à-vis benthic supply can be assessed only when data on dissolved REEs concentration in sediment pore waters become available.



4.2.2.2 Fractional solubility of REEs in surface layer (top $\approx 100 \text{ m}$)

High concentration of REEs in BoB surface waters is typical of many other elements that include Al, Pb etc. (Bruland and Lohan, 2003 and references therein; Measures and Vink, 1999, 2000; Obata et al., 2004) as observed in

Parameter	Station	Pr	Nd	Sm	Eu	Gd	Dy
	0806	65	285	90	20	120	125
ol/m²)	0807	10	300	100	25	190	320
	0808	170	780	180	45	240	225
Ĕ	0809	170	800	190	50	250	275
dd (l	0810	255	1160	270	75	375	290
ЧШ	0811	140	600	150	40	210	190
R	0812	265	1180	280	75	385	330
	0813	420	1350	385	190	475	385
2	0806	0.34	1.26	0.25	0.05	0.19	0.18
m²/	0807	0.63	2.32	0.45	0.09	0.35	0.32
lon	0808	0.89	3.28	0.64	0.12	0.50	0.46
url)	0809	0.80	2.93	0.58	0.11	0.44	0.41
Jenic	0810	0.92	3.40	0.67	0.13	0.51	0.47
ithog	0811	0.92	3.40	0.67	0.13	0.51	0.47
REE	0812	1.15	4.25	0.83	0.16	0.64	0.59
	0813	1.15	4.25	0.83	0.16	0.64	0.59
(%	0806	7	10	14	15	25	29
у ^а (0807	1	5	9	11	21	39
oilit	0808	8	10	11	15	19	20
alut	0809	9	11	13	18	23	27
Š	0810	11	14	16	24	29	24
ona	0811	6	7	9	12	16	16
acti	0812	9	11	13	19	24	22
Fr	0813	15	13	18	47	29	26

Table 4.2: Additional content, lithogenic fluxes and fractional solubility ofREEs in surface layer (top ~100 m) of the BoB.

^a Fractional Solubility (%) = REE_{Add}/REE_{Lithogenic} × 40

various oceanic regions. These enhanced concentrations in surface waters, particularly in open ocean regions, have been interpreted in terms of their release from eolian dust as it interacts with surface waters. As discussed before (Section 4.2.1), the high surface concentrations of REEs in the BoB, on the other hand, are most likely due to dissolved and particulate phases of the G–B Rivers. The subsurface minimum seems to be an artifact of the net surface addition of REEs. In absence of such addition, the concentration–depth profiles of REEs would likely to be similar to that typical of nutrients—REEs depletion in surface waters, followed by a gradual increase in their concentrations with depth in subsurface waters. These surface additions (REE_{Add}) have been calculated from the difference



Fig. 4.6: NPDW normalized REEs composition of various source rocks.



Fig. 4.7: Fractional solubility of REEs in BoB surface layer (top ≈ 100 m).

in area between the measured REE concentration-depth profile and that of extrapolated profile from its minimum to the sea surface (Table 4.2). These additions (REE_{Add}) show overall North-South decreasing trends with significant

scatter. The trends are similar to that reported for settling lithogenic particle flux (Unger et al., 2003), suggestive of their inter-relation. The calculated REE_{Add} allows us to constrain the fractional solubility (labile fraction) of these elements from particulate phases, if data on REEs abundance in particles, their fluxes and residence time of dissolved REEs are available. The calculation of these labile fractions is based on two principle assumptions; (1) the REEs composition of nascent particulate phases is same as that of G-B shelf sediments (Anne-Catherine, 2000) since the G-B rivers are the dominant suppliers of sediments to the Bay of Bengal. The REEs composition of other source rocks (Fig. 4.6; Kurian et al., 2008; Mahoney et al., 2000; Mclennan, 1989; Mclennan, 2001; Nance and Taylor, 1976; Whitford et al., 1979) resulted in unrealistically higher fractional solubility. Thus, the absolute numbers of fractional solubility calculated here are subject to large uncertainty. Further, the settling fluxes of these particles are estimated from the shallow sediment traps data in the region (Ramaswamy and Gaye, 2006; Unger et al., 2003) and (2) these elements have an identical residence time of ~2.5 year in BoB surface waters as that reported for Nd by Amakawa et al. (2000). Fractional solubility (which includes both *in situ* particle dissolution and estuarine release) calculated here for Nd (~5-14 %) is similar to that reported earlier by Tachikawa et al., (1999). Fractional solubility pattern shows a general increasing trend (Fig. 4.7) from ~5 % (Pr) to ~30 % (Dy) following their particle reactive nature (Bertram and Elderfield, 1993; Sholkovitz et al., 1994), except the station 0813. The northernmost station (0813) shows relatively higher fractional solubility of Eu. Such anomalous behavior cannot be anticipated simply from its particle reactive nature. This indicates either the source rock signature is different from G–B shelf sediment composition as this coastal shallow station 0813 falls in the vicinity of the Mahanadi River or its preferential fractionation during the estuarine release and/or the shelf sediment efflux (Aubert et al., 2001; Shibata et al., 2006).

4.2.2.3 Relative abundance pattern of REEs of depth profiles

The REEs patterns obtained at eight depth profiles, stations 0806–13, in the Bay of Bengal are shown in Fig. 4.8. The abundance and pattern of REEs in surface waters of each profile are already discussed earlier (c.f. Section 4.2.1).



Fig. 4.8: The abundance pattern of REEs in water column of the BoB. For comparison, REEs pattern in seafloor sediments (scaled down by a factor of 10^7) from nearby locations are also shown by KL-series.

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Fig. 4.8: Continued.....



Fig. 4.8: Continued.....

The REEs pattern in subsurface waters is significantly different from the surface samples. Divergence of the REEs patterns at depths ~1400–1700 m in the southernmost profile 0806 indicates the presence of different water masses above and below these depths. REEs remineralization from higher particulate fluxes could have masked this observation at other stations further north in the BoB. The depth profiles of REEs typically show a similar pattern characterized by more enrichment of lighter elements (Pr, Nd and Sm) compared to their heavy counterparts (Gd and Dy). This observation is similar to the REEs pattern of BoB seafloor bulk sediments (KL–series, Anne-Catherine, 2000) reported from the nearby locations (Fig. 4.8a, c and f–h). Furthermore, there is similarity in REEs



Fig. 4.9: Sm/Nd (solid squares) and europium anomaly (hollow squares) in the water column of the BoB.

pattern of these bulk sediments with that of G–B (with no prominent Eu anomaly) compared to that of basaltic sources (Deccan traps, MORB, Indonesian Sunda Basalt; Figs. 4.6 and 4.8). Therefore, both dissolved and particulate REEs are mostly derived from the G–B river systems as expected. In contrast, Eu shows spectacular features (a strong positive anomaly) at depths ~ 400–800 m in

Parameter	Station	Pr	Nd	Sm	Eu	Gd	Dy
	0806	0.0	0.0	0.0	0.0	0.0	0.0
kg)	0807	0.4	1.6	-0.1	0.2	0.5	0.2
/lor	0808	0.7	4.1	0.1	0.2	0.8	0.9
ud)	0809	0.8	2.7	0.3	0.4	0.9	0.4
cess	0810	1.3	4.0	0.9	0.7	1.6	0.9
ů Ľ	0811	1.5	5.5	0.9	0.4	1.5	1.0
RE	0812	1.3	7.6	0.9	0.0	1.7	1.8
	0813	1.8	6.3	1.7	0.9	2.2	1.8

Table 4.3: Excess REEs in sub-surface waters (below ~100 m) of the BoB.

^a based on Nozaki and Alibo (2003)

southern stations 0806–08 and in bottom waters of the northernmost station 0813. These Eu anomalies show interesting positive correlations with Sm/Nd (Fig. 4.9). Sm and Nd being neighboring REEs are tightly coupled in seawater and show narrow but systematic decrease from the Atlantic to the Pacific Ocean (Bertram and Elderfield, 1993). Thus, Sm/Nd is less affected by fractionation process and can be used to trace their source signatures. The REEs data from the Arabian Sea show a remarkable higher Sm/Nd and a strong positive Eu anomaly (Goswami et al., personal communication). Therefore, overlapping spikes in depth distributions of Sm/Nd and Eu_{anomaly} (Fig. 4.9) at intermediate depths of 0806–08 can be signatures of different water mass. This is also corroborated by overlapping higher salinity, Eu anomaly and Sm/Nd at these depths. On the other hand, those spikes in bottom waters of the northernmost shallow station 0813 indicate possible benthic sources.

4.2.2.4 Excess REEs in subsurface waters and the remineralization (J) fluxes

The REEs data from similar depths (Table 4.1) show a general decreasing North–South trend in abundances of REEs throughout the water column, similar to that in BoB surface waters. Further, except for the southernmost station 0806, the REEs patterns in the entire Bay of Bengal seem to be affected by their contributions from additional sources (c.f. Section 4.2.2.3). Therefore, the amount of excess REEs (REE_{Excess}) in subsurface waters (depth > 100 m) at various stations have been calculated with respect to the REEs distributions observed at station 0806 by considering the density stratification in the BoB. The calculated

Parameter	Station	Pr	Nd	Sm	Eu	Gd	Dy
	0806	0.05	0.13	0.03	0.01	0.02	0.02
	0807	0.05	0.14	0.02	0.01	0.02	0.01
(Y)B	0808	0.05	0.15	0.02	0.01	0.03	0.02
j/k	0809	0.04	0.14	0.02	0.01	0.02	0.02
buo	0810	0.05	0.14	0.03	0.01	0.03	0.02
J) (0811	0.05	0.13	0.03	0.01	0.03	0.02
	0812	0.06	0.17	0.03	0.01	0.03	0.03
	0813	0.41	0.32	0.16	0.14	0.10	0.05

Table 4.4: The particle remineralization (J) fluxes in the BoB.

^a based on Nozaki and Alibo (2003)

amount for each REE show a clear North–South decreasing trend (Table 4.3). This observation hints at additional sources (*in situ* release from riverine particulate matter as well as from margin sediments) in the subsurface waters of the northern BoB. The parallel North–South feature of both REE_{Excess} and settling lithogenic fluxes (Unger et al., 2003) is an indication of REEs release from settling particles, analogous to the observation of Nozaki and Alibo (2003) in the Bay of Bengal and the Andaman Sea.

To quantify the release of REEs during particle–seawater interaction, the remineralization J fluxes of these REEs have been calculated using a one dimensional vertical advection–diffusion–scavenging model (Nozaki and Alibo, 2003). The particle remineralization fluxes, J (pmol/kg/y) can be estimated from equation (4.1).

$$K_{z} \begin{pmatrix} \partial^{2}C_{d} \\ \partial z^{2} \end{pmatrix} + w \begin{pmatrix} \partial C_{d} \\ \partial z \end{pmatrix} = R$$
(4.1)

where, R is a function of J flux, the concentration of REE in various particle classes and their aggregation-disaggregation coefficients; K_z is the eddy diffusion coefficient; w is the advection velocity; C_d is the REE concentration in the dissolved phase and z is vertical depth below the sea surface. The solution of this equation with various parameters drawn from Nozaki and Alibo (2003) predicts a linearly increasing trend of dissolved REE concentration with depth. The slope of this trend is a measure of the J flux. The J fluxes calculated here (Table 4.4) from



Fig. 4.10: Total remineralization (J) flux of REEs in water column of the BoB.

the slopes of linear fit of C_d (anomalously high C_d at top ~100 m are excluded from the regression) and depth (*z*) of profiles and various parameters used for profile PA-9 (Nozaki and Alibo, 2003) are given in Fig. 4.10. For each REE, the J flux is almost similar throughout the Bay of Bengal, the only exception being the northernmost coastal shallow station 0813. This similarity in J fluxes for each REE suggests that the collective behavior of particles and their properties in the Bay of Bengal is similar. The J fluxes at the station 0813 become progressively higher from Dy to Pr and in case of light REEs are order of magnitude higher compared to rest of the Bay of Bengal. This is similar to laboratory based observation of preferential release of light REEs during seawater–particle interaction (Sholkovitz, 1995).

In contrast to homogeneous particle remineralization in the entire BoB (Table 4.4), there are gradually enhanced contributions of REE_{Excess} (Table 4.3) northward in the bay. This observation further corroborates that *in situ* particle dissolution is not the only cause of excess REEs in the BoB. Therefore, the release of REEs from the northern margin sediments can be another potential source, which is being facilitated by solution of Fe–Mn oxyhydroxide coatings on the
grains but this requires suboxic conditions. Concurrent measurements of dissolved Fe, Mn, REEs and DO would help in testing this hypothesis.

4.3 Conclusions

Both the absolute and relative abundance pattern of dissolved REEs show significant variations in water column of the Bay of Bengal along an 87°E transect. The gradual North–South decrease in abundances of REEs is attributed to their enhanced additions in the northern region of the BoB. The sources of these additions are *in situ* release from particulate matter supplied by the Ganga–Brahmaputra Rivers and possible benthic sources from the margin sediments. However, the distributions of REEs at the southernmost station 0806 seem to be unaffected by such releases.

Chapter 5

Spatial distribution of dissolved neodymium and ϵ_{Nd} in the Bay of Bengal:

Role of particulate matter and mixing of water masses

5.1 Introduction

The distribution of dissolved Nd in seawater, along with its radiogenic isotope composition serves as a water mass tracer on an ocean-wide scale. The radiogenic Nd isotope composition is a function of time of evolution and Sm/Nd of source rock exposed over the earth surface and usually expressed as ε_{Nd} with reference to ${}^{143}Nd/{}^{144}Nd$ of the Chondritic Uniform Reservoir (CHUR), i.e. 0.512638 (Jacobsen and Wasserburg, 1980) as given below (Eq. 5.1).

$$\mathcal{E}_{Nd} = \begin{bmatrix} \begin{bmatrix} 143 & Nd \\ & 144 & Nd \end{bmatrix}_{Sample} \\ \hline \begin{bmatrix} 143 & Nd \\ & 144 & Nd \end{bmatrix}_{CHUR} -1 \\ \times 10^4$$
(5.1)

The oceanic residence time of neodymium, though not well established, is known to be of the order of the ocean mixing time (Broecker and Peng, 1982; Jeandel et al., 1995; Johannesson and Burdige, 2007; Tachikawa et al., 2003; Tachikawa et al., 1999). This leads to the dispersal of continental Nd in the global oceans through water circulation. The ε_{Nd} data of different oceanic regions reflect those of its sources, predominantly continental supply, and their subsequent modification by water mass mixing and boundary exchange (Frank, 2002; Goldstein and Hemming, 2003; Jeandel, 1993; Lacan and Jeandel, 2005; Piepgras and Wasserburg, 1987).

There have been a number of studies that have utilized Nd isotopes to investigate water mass mixing in the Arctic, Atlantic and the Pacific Oceans (Amakawa et al., 2009; Andersson et al., 2008; Carter et al., 2012; Piepgras and Wasserburg, 1987; Porcelli et al., 2009; Rickli et al., 2010; Rickli et al., 2009). Similar studies in the Indian Ocean, however, are sparse (Amakawa et al., 2000; Bertram and Elderfield, 1993; Jeandel et al., 1998; Tazoe et al., 2011). The limited available results show that ε_{Nd} values of the Indian Ocean are intermediate between the less radiogenic Atlantic and the more radiogenic Pacific Ocean values

(Bertram and Elderfield, 1993; Frank, 2002; Jeandel et al., 1998). These findings are based primarily on results obtained from the equatorial and southern Indian Ocean. There have been only a few studies on the northern Indian Ocean, particularly in the Bay of Bengal and the Arabian Sea, both of which receive significant input of fresh water and particulate matter from rivers draining the Himalaya. These rivers, the Ganga, Brahmaputra, Irrawaddy and the Indus all drain terrains in the Himalaya characterized by unradiogenic neodymium (Robinson et al., 2001; Singh and France-Lanord, 2002; Singh et al., 2008). This study focuses on the measurements of dissolved Nd concentration and its isotope composition in waters of the Bay of Bengal, which receives large quantities of fresh water and particulate matter through the Ganga–Brahmaputra (G–B) and the Irrawaddy river systems draining the Himalaya.

The Bay of Bengal (BoB) covers an area of $\sim 2.2 \times 10^6$ km² in the northern Indian Ocean, with an average depth of \sim 3 km. The G–B river system contributes $\sim 1000 \text{ km}^3$ of freshwater to the bay, corresponding to $\sim 25 \%$ of the annual input of fresh water to the BoB (Sarin et al., 1989; Sengupta et al., 2006). The annual delivery of fresh water to the BoB accounts for about 0.06 % of the total inventory of water in the bay. This large influx of fresh water is also responsible for the stratification of the upper water column commonly observed in the bay (Gopalakrishna et al., 2002; Murty et al., 1992). The water mass structure of the bay has been characterized (Dileep Kumar and Li, 1996; Rao et al., 1996; Sastry et al., 1985; You, 1997, 2000) and circulation of the upper water column has been shown to be prone to monsoon-driven seasonal changes (Colborn, 1975; Schott and Mccreary, 2001; Shankar et al., 2002; Shenoi et al., 1999; Shetye et al., 1996; Wyrtki, 1973; You, 1997). In the present study, the concentrations as well as isotope composition of dissolved Nd in the BoB water column have been measured to characterize the water masses, to learn about geochemical cycling of Nd in the region, particularly to assess the role of particulate Nd in modifying the abundance of dissolved Nd and its isotope signature in different water masses. The latter objective becomes significant in the BoB, as it is one of the oceanic regions receiving the world's largest flux of particulate matter, $\sim 10^{12}$ kg/y (Galy and France-Lanord, 2001; Milliman and Mead, 1983).



Fig. 5.1: Depth profiles (red circles) acquired for dissolved Nd and ε_{Nd} in the BoB.

5.2 Results and discussion

Several samples of seawater from eight depth profiles (0806–13, Fig. 5.1) along the 87°E transect of the BoB have been analyzed for Nd concentration and its radiogenic isotope composition as described in Chapter 2. These data along with CTD data of salinity and potential temperature are given in Table 5.1. For the convenience of interpretation, the data are sub-grouped into the southern BoB (stations 0806–07; south of 10°N), central BoB (stations 0808–11; 10°N–17°N) and the northern BoB (stations 0812–0813; north of 17°N).

Table 5.1 Depth profiles of potential temperature, salinity, dissolved Nd and
Nd isotope composition in the Bay of Bengal

Station	Depth	Pot. Temp.	Salinity	Nd	٤ _{Nd}	2σ
	(m)	(°C)		(pmol/kg)		20
0806	5	29.252	33.351	22.1	-8.0	1.2
	60	27.523	35.034	18.6	-8.7	0.7
	130	18.541	34.807	16.8	_	_
	200	13.818	35.027	18.1	-11.3	0.5

	290	11.766	35.061	19.7	-12.1	0.2	
	380	11.038	35.082	17.0	-	-	
	420	10.707	35.066	-	-10.8	0.2	
	460	10.376	35.050	21.4	-	-	
	600	9.454	35.030	21.1	-11.4	0.4	
	800	8.035	34.989	21.2	-11.4	0.4	
	1000	6.634	34.936	21.5	-10.0	0.3	
	1200	5.738	34.903	24.3	-	-	
	1400	4.893	34.871	25.4	-10.2	0.3	
	1700	3.397	34.813	27.7	-10.5	0.2	
	2000	2.577	34.777	29.2	-10.2	0.3	
	2300	2.082	34.755	30.3	_	_	
	2600	1.772	34.742	30.9	-10.0	0.1	
	2900	1.542	34.734	33.8	- 0.7	_	
	3500	1.385	34.728	30.5	-9.7	0.2	
	3800	1.211	34.723	39.8	-	-	
0807	5	29.211	34.719	<u>38.2</u> 24.2	<u> </u>	0.2	_
0007	70	23.211	34 878	17.8	_12.8	0.0	
	160	16 446	3/ 000	18.8	-12.0	0.9	
	300	10.440	35 052	22.7	_13.0 _13.1	0.0	
	400	10.857	35.052	22.7	_12.8	0.0	
	600	9.053	35.030	21.0	-12.0	0.0	
	800	7 820	3/ 080	22.1	_12.5	0.0	
	900	7.020	34.900	23.5	-11.2	0.1	
	1000	6 6 2 9	24.900	24.0	12.5	0.2	
	1300	5 100	24.950	23.5	11.2	0.3	
	1500	4 206	24.000	27.0	-11.5	0.5	
	1800	4.290	34.049	33.Z	-	-	
	2100	3.097	34.000	-	-11.2	0.4	
	2400	2.420	34.771	52.0	-	-	
	2700	1.969	34.732	- 25 0	-11.0	0.3	
	3000	1.670	34.739	50.Z	-	-	
	3300	1.500	34.732	— 40 F	-10.6	0.2	
	3550	1.305	34.720	40.5	-	-	
0808	5	28 796	34.721	30.4	_13.0	0.3	_
0000	70	25.730	3/ 9/7	24.8	-13.6	0.4	
	175	14 793	34 947	24.0	-12.3	0.0	
	280	11 583	35 032	22.7	-12.5	0.4	
	380	10 588	35 032	20.5	_10.5	0.4	
	495	0.500	35 002	20.5	_10.5 _12.8	0.0	
	600	9.000 8 807	3/ 026	29.9 24.2	_12.0 _11 G	0.4	
	700	0.021 Q 1/2	34 062	24.2 22.1	_11.0 _12.1	0.4	
	900	6 002	34.045	20.1	-12.1	0.4	
	1200	5 201	31 956	20.1 20.0	-12.0	0.0	
		0.094	54.000	∠J.U	-13.0	0.4	

Dissolved Nd and $\epsilon_{Nd}\, in$ water column of the BoB

	1700	3.306	34.775	29.9	-11.6	0.4
	2300	2.072	34.755	43.3	-11.7	0.3
	2900	1.549	34.727	38.5	-11.0	0.3
	3200	1.324	34.727	41.2	-11.0	0.2
0809	5	28.671	33.207	35.6	-14.8	0.2
	85	25.232	34.961	14.8	-14.0	0.3
	180	14.938	34.966	22.2	-16.3	0.2
	300	11.604	35.038	21.5	-13.9	0.3
	400	10.537	35.035	23.1	-13.4	0.2
	500	9.768	35.027	23.8	-14.5	0.4
	600	9.012	35.010	23.9	-13.9	0.4
	700	8.242	34.988	24.5	-14.8	0.2
	800	7.720	34.973	33.1	-14.3	0.4
	900	7.172	34.954	25.9	_	_
	1000	6.475	34.929	25.6	-10.9	0.3
	1400	4.764	34.864	27.8	-14.2	0.2
	2000	2.617	34.778	34.1	-10.6	0.5
	2600	1.793	34.743	36.8	-10.1	0.2
	2900	1.524	34.733	35.2	-10.5	0.2
0810	5	28.389	32.117	43.1	-13.7	0.2
	40	28.882	33.541	32.9	-13.3	0.3
	140	20.670	34.650	21.0	-13.6	0.5
	200	14.306	34.959	22.6	-13.0	0.3
	300	11.445	35.031	23.0	-10.3	0.4
	400	10.549	35.030	23.7	-11.8	0.3
	500	9.917	35.024	23.3	-12.9	0.3
	600	9.222	35.012	23.4	-12.5	0.3
	700	8.511	34.992	24.2	-12.5	0.4
	800	7.791	34.971	25.8	-11.7	0.4
	1000	6.574	34.930	28.5	-16.4	0.4
	1200	5.594	34.894	29.0	-11.0	0.3
	1400	4.783	34.864	30.4	-11.0	0.3
	1700	3.493	34.814	31.4	-11.8	0.3
	2000	2.587	34.777	34.4	-11.6	0.2
0044	2200	2.246	34.762	34.8	-12.2	0.4
0811	5 70	28.327	33.856	34.0	-15.0	0.3
	110	23.162	34.747	26.5	-14.5	0.3
	190	19.491	34.874	23.1	-14.5	0.3
	200	14.670	34.960	23.7	-14.8	0.4
	400	11.475	35.032	23.7	-14.6	0.4
	500	10.550	35.033	24.7	-14.0	0.4
	600	9.776	35.024	20.8 20.0	-13.4	0.4
	700	9.049	35.009	∠0.8	-14.1	0.4
	000	8.4/3	34.993	27.4	-13.3	0.5
	900	7.235	34.954	26.4	-12.1	0.4

Dissolved Nd and ϵ_{Nd} in water column of the BoB

	1100	6.181	34.917	28.9	_	_
	1300	5.328	34.886	30.2	_	_
	1500	4.488	34.854	31.9	-11.0	0.3
	1700	3.590	34.818	32.9	_	_
	1900	2.920	34.791	34.7	-11.7	0.4
	2100	2.422	34.770	38.5	_	_
	2300	2.169	34.759	35.8	-12.0	0.4
	2500	1.859	34.746	37.7	-11.9	0.3
0812	5	27.497	32.049	45.4	-14.5	0.3
	50	25.633	34.311	31.0	-13.9	0.3
	110	18.693	34.875	22.5	-13.4	0.3
	200	13.249	34.991	25.8	-14.0	0.4
	300	11.472	35.028	26.3	-13.3	0.3
	400	10.564	35.030	30.0	-14.0	0.4
	500	9.885	35.024	25.7	-13.2	0.5
	600	9.232	35.012	28.3	-14.2	0.2
	800	7.986	34.979	28.0	-11.8	0.3
	1000	6.634	34.934	29.4	-13.1	0.3
	1200	5.506	34.892	31.1	-13.0	0.3
	1400	4.552	34.855	32.0	-12.7	0.2
	1700	3.225	34.803	37.2	-12.2	0.2
	2000	2.351	34.766	38.8	-11.7	0.2
0813	5	27.652	32.668	46.4	-15.0	0.3
	70	23.952	34.661	24.4	-13.9	0.3
	150	17.110	34.895	22.5	-16.0	0.3
	250	12.411	35.008	25.3	-13.1	0.2
	350	11.053	35.029	24.8	-13.3	0.3
	440	10.350	35.028	27.0	-12.6	0.3
	550	9.411	35.016	27.3	-13.5	0.3
	640	8.824	35.003	30.4	-11.7	0.3

not measured

The Nd concentration in the water column along the 87°E transect of the BoB covers a wide range, from 14.8 to 46.4 pmol/kg (Table 5.1). The concentration of Nd in surface waters of the BoB decreases from north to south, while the subsurface value exhibits a minimum at a water depth of around 100 m (Chapter 4). A cursory look at the Nd concentration data (Fig. 5.2a) in waters from the upper water column (~100 m to ~2000 m) of the northern and central BoB show that they are higher (about two fold) than those reported for similar depths from other oceanic basins (Amakawa et al., 2004; Amakawa et al., 2012; Jeandel et

al., 1998; Nozaki and Alibo, 2003a, b; Porcelli et al., 2009; Rickli et al., 2009; Stordal and Wasserburg, 1986).

 ε_{Nd} in the Bay of Bengal displays large variability, from -16.4 to -8 (Table 5.1), with one sample from station 0807 (depth \approx 800 m) having a highly unradiogenic value of -19.1 possibly contributed by rivers draining the peninsular India. Surface and intermediate waters of the northern and central bay have lower ε_{Nd} compared to waters from similar depths of the southern bay (c.f. Sections 5.2.1 and 5.2.2). ε_{Nd} in the southern BoB compares well with the available data for a few samples from this region (Amakawa et al., 2000). The ε_{Nd} of the northern and central BoB waters (Fig. 5.2b) is less radiogenic compared to those reported from other regions of the Indian Ocean (Amakawa et al., 2000; Bertram and Elderfield, 1993; Jeandel et al., 1998; Tazoe et al., 2011), and also the rest of global oceans; the only exceptions being Baffin Bay, the North Atlantic Subpolar Gyre and the Niger delta margin (Amakawa et al., 2004; Amakawa et al., 2009; Bayon et al., 2011; Bertram and Elderfield, 1993; Carter et al., 2012; Jeandel et al., 1998; Porcelli et al., 2009; Rickli et al., 2009; Stordal and Wasserburg, 1986). It is interesting to note that the ε_{Nd} values of bottom waters in the profiles 0806–09 south of 15°N (-9 to -11) and in profiles 0810-0813 north of 15°N (-11 to -13) overlap with reported ε_{Nd} values of Holocene sediments from the region (Colin et al., 1999). The close resemblance of ε_{Nd} values of bottom waters and Holocene sediments is indicative of the role that sediments of the BoB play as sources or sinks of dissolved Nd to bottom waters. More recently, Piotrowski et al. (2009) have utilized the Nd isotope composition of sedimentary Fe-Mn oxyhydroxides to trace deep water circulation in the Indian Ocean. The composition of core top ϵ_{Nd} values of those Fe–Mn phases shows good agreement with ε_{Nd} of bottom water measured in this study from similar depths at adjacent locations (depth ~ 3800 m at station 0806), which re-affirms the application of Nd isotope composition of Fe-Mn oxyhydroxides as a proxy of Nd isotope composition of deep waters.

5.2.1 Surface waters

Samples from depths \leq 5 m are considered as surface samples. The salinity of surface waters in the northern Bay of Bengal is generally low due to a large



Fig. 5.2: A comparison of dissolved Nd and ε_{Nd} in the BoB with the global data.

influx of fresh water from the Ganga–Brahmaputra river system. Similarly, the contribution of less saline Indonesian Throughflow water through an eastward Equatorial Jet (EJ), generally encountered during the fall inter-monsoon (Shenoi et al., 1999), decreases the salinity in surface waters of the southern BoB. In the



Fig. 5.3: The distribution of (a) salinity; (b) dissolved Nd concentration and (c) ε_{Nd} in surface waters along 87°E transect. The salinity increases southward, except at station 0811 where it is higher compared to the rest of the BoB surface waters. The Nd concentration shows a North–South decreasing trend with more negative ε_{Nd} values in the northern BoB compared to that in the southern BoB. The high Nd concentration and lower ε_{Nd} in the northern and central BoB reflect dissolved Nd sourced from the G–B river system.



Fig. 5.4: Scatter plots of (a) salinity versus Nd concentration and (b) 1/Nd versus ε_{Nd} in surface waters of the BoB. The salinity versus Nd concentration plot shows decreasing trend albeit significant scatter. The 1/Nd versus ε_{Nd} also exhibits an overall linear trend, with data for the northern and central BoB scattering around the mixing line.

central BoB, the salinity of surface waters at station 0811 is marginally higher compared to those of the northern and southern bay (Fig. 5.3a). This could be due to eddy pumping of more saline subsurface water from 50–100 m depth in the region (Murty et al., 1992). In contrast to salinity, the concentration of dissolved Nd in surface waters of the BoB shows a North–South decreasing trend (Fig. 5.3b), ranging from 46.4 to 22.1 pmol/kg, albeit with significant scatter. The plot of Nd concentration in surface waters with salinity (Fig. 5.4a) shows an overall decreasing trend, although the data points do not fall on the theoretical mixing line. This suggests that in addition to water mixing, other processes also influence the dissolved Nd abundance and distribution in these surface waters as earlier

discussed in Chapter 4. Similar to dissolved Nd abundance in surface waters of the bay, ε_{Nd} also shows a North–South trend (Fig. 5.3c), with less radiogenic values $(\epsilon_{Nd} \approx -15)$ at station 0813 in the northernmost surface waters, compared to that in surface waters of the southernmost station 0806 ($\epsilon_{Nd} \approx -8$). The dissolved Nd in surface waters of the northern and central BoB has ε_{Nd} values in range of -14 ± 1 (Fig. 5.3c). The North–South trend in ε_{Nd} values can be explained in terms of source functions of Nd to the bay. The major contributors of dissolved Nd to the bay are the dissolved and particulate phases of the G-B and the Irrawaddy Rivers along with inputs from the peninsular rivers, the Godavari and the Krishna. Yet, there is no published data of dissolved ε_{Nd} in these Rivers. However, Goldstein and Jacobsen (1987) have shown a close resemblance of ε_{Nd} data of dissolved and particulate phases of the world's rivers. Chatterjee et al. (personal communication) have measured dissolved ε_{Nd} values of -16 for the Ganga River, similar to or slightly more radiogenic compared to that of its particulate load (~-16 to ~-18; Singh et al., 2008). The isotope composition of dissolved Nd of the Brahmaputra River is not available, but it supplies sediments with $\varepsilon_{Nd} \approx -14$ (Galy and France-Lanord, 2001; Singh and France-Lanord, 2002), more radiogenic than the Ganga River. The combined flow of the Ganga–Brahmaputra, therefore, is likely to supply dissolved Nd with $\varepsilon_{Nd} \approx -15 \pm 1$ to the BoB. Given the likely similarity in ε_{Nd} values of particulates of the G–B and the peninsular rivers (Ahmad et al., 2005; Ahmad et al., 2009), and considering that freshwater and particulate matter discharge of the peninsular rivers is orders of magnitude lower than that of the G-B river system, it seems unlikely that the contribution of the peninsular rivers to the budget of Nd and the ε_{Nd} of the BoB would be significant. This inference however needs to be attested through direct measurements of dissolved Nd concentration and its ε_{Nd} in the peninsular rivers and their estuaries. Similarly, the dominance of Nd contribution from the G-B River over that of the Irrawaddy River (as discussed based on surface water circulation in Chapter 4) is also indicated in the ε_{Nd} value of surface waters of station 0810 (Fig. 5.1). This station in the eastern BoB along the track of the Irrawaddy mouth has $\varepsilon_{Nd} \approx -13.7$, significantly less radiogenic than the river value ($\varepsilon_{Nd} \approx -10$; Allègre, 2010). Thus the available data seem to indicate that the Ganga-Brahmaputra river system

dominates over the Irrawaddy and the peninsular rivers in terms of their contribution to the dissolved Nd budget in the BoB surface waters along the 87°E transect.

Another potential source of low radiogenic Nd to surface waters of the northern BoB is its release from particulate matter supplied by the G–B Rivers and/or from the shelf sediments of the bay, which are also dominated by contributions from the G–B Rivers. Such a release can also support the non-conservative behavior of dissolved Nd in BoB surface waters. Thus, the supply of Nd to the BoB from the G–B river system both as dissolved and particulate phases can account for the measured ε_{Nd} in the northern bay. On the other hand, the more radiogenic ε_{Nd} in surface waters of the southern BoB (Fig. 5.3c), could be a result of mixing of the Indonesian Throughflow surface water (IW), having $\varepsilon_{Nd} \sim -4.1$ (Amakawa et al., 2000; Jeandel et al., 1998), with surface waters of the central bay ($\varepsilon_{Nd} \approx -14 \pm 1$), a proposition corroborated by the salinity data.

Fig. 5.4b is a plot of 1/Nd versus ε_{Nd} in surface waters. The data show an overall mixing trend with data points from the northern and central BoB scattering around the mixing line. This overall trend, though indicative of two endmember mixing in surface waters of the BoB, also suggests that, analogous to dissolved Nd concentration, the behavior of ε_{Nd} in these waters is also not strictly conservative due to possible Nd release from particulate matter. The North–South features of dissolved Nd and its isotope composition in surface waters bring out the roles of dissolved and particulate phases of the G–B river system and the Indonesian Throughflow waters in determining their distribution (Fig. 5.4a and b).

5.2.2 Subsurface waters

The contours of dissolved Nd concentration and ε_{Nd} in the Bay of Bengal are shown in Fig. 5.5a and b. The distributions of Nd abundance and its isotope composition in subsurface waters show a North–South feature similar to that in surface waters. At a first glance, the low Nd concentration at intermediate depths (blue patch; Fig. 5.5a) seems to be a result of intrusion of different water mass. High salinity and low concentration of Nd at these depths hints at upper water



Fig. 5.5: The distribution of dissolved Nd (a) concentration and (b) isotope composition Nd in water column of the Bay of Bengal along 87°E transect.

column of the Arabian Sea as a source of this water mass. Alternatively, the particle reactive nature of Nd along with its additions from the G–B river system (Chapter 4) to the surface and subsurface waters of the BoB could produce the similar pattern of Nd concentration. These additions cause high Nd concentrations characterized by less radiogenic ε_{Nd} in the northern BoB compared to those in the central and southern bay (Figs. 5.6 and 5.7).

On the other hand, the distribution of ε_{Nd} in the upper water column of the BoB (Fig. 5.5b) shows a wide range from -8 to -15; however, this range becomes narrow (-9 to -12) in the deep waters. This mutation of ε_{Nd} in BoB deep waters could be due to mixing of G–B sourced unradiogenic neodymium with more



Fig. 5.6: The dissolved Nd concentration-depth profiles in water column of the northern, central and southern BoB along the 87°E transect. Note the increase in water column depth from north to south. The data show a North-South decreasing trend (shift in the grey band representing Nd concentration in the depth interval ~100 to ~2000 m). The Nd concentrations in the bottom waters of the southern BoB show a marginal decrease similar to the trend reported for PA-9 (Nozaki and Alibo, 2003).

radiogenic Nd in deep waters of the Indian Ocean. Therefore, the spatial variations of ε_{Nd} in the Bay of Bengal are attributable to multiple sources of dissolved Nd



Fig. 5.7: The dissolved ε_{Nd} -depth profiles in water column of the northern, central and southern BoB along the 87°E transect. Note the increase in water column depth from north to south. The data show a North–South increasing trend (shift in the grey band representing ε_{Nd} in the depth interval ~100 to ~2000 m).

with their distinct ε_{Nd} signatures. In the following section an effort has been made to estimate the additional Nd and its source signature using an inverse modeling approach.

5.2.3 Dissolved Nd supply from various water masses and from particulate phases in the Bay of Bengal

5.2.3.1 Inverse modeling

The lateral and vertical distributions of dissolved Nd concentration and its isotope composition in the BoB waters are the result of a complex mixture of Nd contributions from various water masses, sinking particulate matter and sediment–water interactions with their characteristic ε_{Nd} values. An inverse modeling (Tarantola, 2005; Tripathy and Singh, 2010) approach has been used to determine the contributions from these sources, particularly release from particulate matter. For an under-determined system such as considered in this study, an inverse model provides the most probable estimates of the fraction of various water masses and the amount of excess dissolved Nd along with their uncertainties based on the mass balance equations of salinity, temperature, Nd concentration and its radiogenic isotope composition.

The inversion method used in this study relies on the following set of mass balance equations for the ' i^{th} ' water mass and the ' j^{th} ' water sample.

$$\sum_{i=1}^{9} f_{ij} = 1$$
(5.2)

$$\sum_{i=1}^{9} f_{ij} x_i = x_j$$
(5.3)

$$\sum_{i=1}^{9} f_{ij} N d_i + N d_j^{excess} = N d_j$$
(5.4)

$$\sum_{i=1}^{9} f_{ij} N d_i \varepsilon_{Nd_i} + N d_j^{excess} \varepsilon_{Nd_j^{excess}} = N d_j \varepsilon_{Nd_j}$$
(5.5)

where, f_{ij} is the water mass fraction of the 'ith, water mass in 'jth, sample, x_i and x_j are either potential temperature or salinity of the 'ith, water mass and 'jth, sample, and Nd_j^{excess} is the dissolved Nd in 'jth, sample in excess of the sum of contributions from different water masses. These equations are written in a matrix form i.e., d = g(v), where "d" and "v" form the measured and unknown parametric

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matrices associated by a transformation matrix "g". In this approach, it has been assumed that the variables (elements of matrix "v") follow the log normal probability distributions for the constraint of positivity and the data set (elements of matrix "d") is a linear (quasi-linear) combination of these variables. The quasi-Newton method (Tarantola, 2005) has been used to find the most probable set of variables (v) along with their uncertainties by minimizing the misfit between the matrices, "d" and "g(v)". Considering the under-determination of the problem and lower sampling frequency at deeper depths, the entire data set is dealt with collectively to seek the most probable solution of the problem.

A priori information

The application of inverse modeling requires a priori knowledge of various water mass endmembers contributing Nd to a given sample, their Nd concentration and ε_{Nd} values. The prominent water masses present in the surface and subsurface layers of the BoB have been discussed previously by several authors (Dileep Kumar and Li, 1996; Rao et al., 1996; Sastry et al., 1985; You, 1997, 2000). Among these, nine water masses are assumed to contribute dissolved Nd to the region of this study (Table 5.3). These are, (1) G–B dominated Bay of Bengal Low Salinity Water (GB-BBLS); (2) Bay of Bengal Subsurface Water (BBSS); (3) Arabian Sea High Salinity Water (ASHS); (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 5.3. These data for GB-BBLS and BBSS are taken to be the same as those measured in this study for surface waters of station 0812, and for the sample from a water depth of 70 m from the central BoB profile at 0811 since its occasional shoaling can measurably alter salinity, Nd and ε_{Nd} in the BoB surface waters. These parameters for ASHS, NIIW and NIDW, water masses forming in the Arabian Sea (Dileep Kumar and Li, 1996; Wyrtki, 1973) are based on unpublished results from station 0802 (14.419°N, 69.418°E; Goswami et al., in preparation) in the eastern Arabian Sea. The values of these properties for the IW and IIW are

Water Mass	Pot. Temp. (°C)	Salinity	Nd (pmol/kg)	٤ _{Nd}
A priori values				
GB–BBLS	27.497 ± 0.001	32.049 ± 0.001	45.4 ± 1.1	-14.5 ± 0.3
BBSS	23.162 ± 0.001	34.747 ± 0.001	26.5 ± 0.7	-14.5 ± 0.3
ASHS	26.347 ± 0.001	36.514 ± 0.001	14.0 ± 0.4	-7.1 ± 0.3
NIIW	11.677 ± 0.001	35.506 ± 0.001	13.5 ± 0.3	-9.0 ± 0.3
NIDW	2.717 ± 0.001	34.813 ± 0.001	17.5 ± 0.4	-10.7 ± 0.3
IW	29.700 ± 0.001	33.970 ± 0.001	7.4 ± 0.2	-4.1 ± 0.3
IIW	4.470 ± 0.001	34.612 ± 0.001	17.6 ± 0.4	-3.6 ± 0.3
MNADW	1.774 ± 0.001	34.738 ± 0.001	24.9 ± 0.6	-8.5 ± 0.3
AABW	-0.615 ± 0.001	34.659 ± 0.001	34.0 ± 0.9^{a}	-8.6 ± 0.3^{b}
A posteriori va	lues			
GB–BBLS	27.521 ± 0.001	32.020 ± 0.001	44.7 ± 1.0	-14.8 ± 0.2
BBSS	23.162 ± 0.001	34.747 ± 0.001	25.5 ± 0.7	-17.1 ± 0.3
ASHS	26.347 ± 0.001	36.514 ± 0.001	12.8 ± 0.4	-8.1 ± 0.3
NIIW	11.677 ± 0.001	35.506 ± 0.001	13.0 ± 0.3	-9.8 ± 0.3
NIDW	2.717 ± 0.001	34.814 ± 0.001	16.5 ± 0.4	-13.8 ± 0.3
IW	29.738 ± 0.001	33.912 ± 0.001	7.1 ± 0.2	-4.5 ± 0.3
IIW	4.470 ± 0.001	34.612 ± 0.001	17.2 ± 0.4	-3.9 ± 0.3
MNADW	1.774 ± 0.001	34.739 ± 0.001	24.0 ± 0.6	-9.2 ± 0.3
AABW	-0.615 ± 0.001	34.665 ± 0.001	32.3 ± 0.8	-8.7 ± 0.2

Table 5.2 A priori and a posteriori values of the water mass endmembers

Data Source

GB–BBLS; this study; station 0812 (18.76°N, 87.00°E), depth $\approx 5 m$ BBSS; this study; station 0811 (16.76°N, 86.99°E), depth \approx 70 m ASHS; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth ≈ 65 m NIIW; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth ≈ 500 m NIDW; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth ≈ 2100 m IW; (Amakawa et al., 2000); station PA–7 (9.99°S, 101.98°E), depth ≈ 5 m IIW; (Jeandel et al., 1998); station 20 (11.50°S, 115.95°E), depth ≈ 1099 m MNADW; (Bertram and Elderfield, 1993); station 1504 (27.01°S, 56.97°E), depth ≈ 3100 m AABW; (Dileep Kumar and Li, 1996); station GEOSECS 430 (59.98°S, 60.98°E), depth ≈ 4709 m ^a (Zieringer et al., 2011) ^b (Frank, 2002; Jeandel, 1993)

those reported from the Indonesian straits (Amakawa et al., 2000; Jeandel et al., 1998). The data for MNADW are taken to be the same as that measured at a depth of 3100 m in the profile CD-1504 (27.01°S, 56.97°E) in the Madagascar basin (Bertram and Elderfield, 1993). The potential temperature and salinity data for AABW are assumed to be the same as those reported for water from a depth of 4709 m at GEOSECS station 430 (Dileep Kumar and Li, 1996). The ε_{Nd} and dissolved Nd data for AABW are taken from Frank (2002), Jeandel et al. (1993) and Zieringer et al. (2011).

A posteriori values

The best fit endmember values of potential temperature, salinity, Nd concentration and ε_{Nd} of different water masses calculated based on the inverse



Fig. 5.8: An excellent agreement is seen between measured and reproduced Nd concentration and ε_{Nd} by inverse model.

model are also given in Table 5.2. Excellent agreement was found between the measured Nd and ε_{Nd} with their model reproduced values (Fig. 5.8). The model sensitivity is checked by varying Nd input of concentrations by ~20 % and ~2 units of ε_{Nd} for GB–BBLS and AABW, which are the dominant contributors of dissolved Nd to BoB waters. The model results are found insensitive to these variations in *a priori values*. The uncertainty on water mass fractions estimated from model calculations for the dominant water masses like GB–BBLS, IW and AABW is less than 15 %. The average uncertainties on various water mass fractions are ~25 % which are lower for higher fractions and vice versa. The proportions of various water masses contributing to the Nd concentration and its isotope composition at different depths along 87°E transect are shown in Fig. 5.9. The model derived Nd contributions from various water masses to the measured Nd abundance at selected depths in stations 0806 and 0812 are presented in Fig. 5.10.

5.2.3.2 Nd contribution from different water masses

In surface waters, as would be expected, GB–BBLS makes significant contribution to the water mass budget ($f_{GB-BBLS} > 5$ %) along the entire 87°E







transect (Fig. 5.9a) with its maximum value ($f_{GB-BBLS} > 80$ %) at station 0812 in the northern Bay of Bengal. The Nd contributed by the GB–BBLS decreases generally southward from > 95 % at the northern station 0812 to ~10 % at the southernmost station 0806, and drastically below a depth of ~50 m ($f_{GB-BBLS}$ 10 %



or less; Figs. 5.9a and 5.10). On the other hand, the Nd contribution of IW decreases from ~30 % in surface waters at station 0806 to ~10 % at ~50 m depth at station 0812 (Fig. 5.10). The depth of penetration of IW also decreases northward (Fig. 5.9b); it has Nd contribution of > 5 % at depths of ~200 m in the



Fig. 5.10: The Nd contribution from different water masses for the southernmost station, 0806 and northern station, 0812. The sum of Nd contributed (Σ Nd_{mixing} (%)) by the various water masses at various depths are also given. It seems that Σ Nd_{mixing} (%) do not account for the measured dissolved Nd concentrations at several depths in the profiles suggesting the need for additional Nd source(s).

southernmost profile (~6°N). These two water masses, GB–BBLS and IW by and large account for almost 100 % of salinity but only ~40 to ~95 % of dissolved Nd in BoB surface waters, with lower values in the southern region. This suggests that the surface water salinity of the BoB in the latitude belt ~20°N–6°N is determined by the Ganga–Brahmaputra in the north (characterized by GB–BBLS) and the Indonesian Throughflow water in the south. For dissolved Nd, in addition to these two water masses additional source(s) is required to balance the budget. This finding is consistent with earlier observations based on Nd–Salinity and ε_{Nd} – 1/Nd relation (c.f. Section 5.2.1).

Below the surface layer, significant water mass fractions (~30 %) of ASHS and BBSS waters are noticed north and south of 13°N respectively, without any discernible signature of their upwelling (Fig. 5.9c and d). The results indicate that the ASHS water mass enters the southern BoB at a depth interval of ~50-100 m and spreads northward consistent with the finding of Murty et al. (1992) and Sastry et al. (1985). The Nd contribution of ASHS is maximum (~30 %) at 60 m depth at station 0806, and decreases both northward as well as with depth to values of ~5 % at ~800 m depth (Fig. 5.10). On the other hand, Nd contribution of BBSS is ~15 % at 200 m depth at station 0812, decreasing both above and below this depth. IW is the dominant source of surface waters of the southern and central BoB. In contrast, intermediate water from the Indonesian straits (IIW) is only minor ($f_{IIW} \sim 5$ %) along the 87°E transect (Fig. 5.9e). This fraction accounts for \sim 5–10 % of Nd in the depth range of 200–1400 m at station 0806 (Fig. 5.10). The NIIW, a mixture of Persian Gulf Water (PGW) and Red Sea Water (RSW) with ASHS water, enters the southern Bay of Bengal from the Arabian Sea, contributing a maximum of ~25 % Nd at ~400 m depth at station 0806 (Figs. 5.9f and 5.10). The Nd contribution (> 10 %) of NIIW shows a South–North gradient in the depth range ~200 to ~1400 m. This high salinity water mass (NIIW) is present throughout the BoB at an intermediate depth interval of 300-500 m (Dileep Kumar and Li, 1996; Wyrtki, 1973), and is responsible for the high salinity at these depths along the entire 87°E transect in the bay. Below this high saline water mass, NIDW, MNADW and AABW constitute the BoB deep waters (Fig. 5.9g, h and i). The average depth (~900 m for NIDW and ~1700 m for

MNADW) of appearance of both NIDW and MNADW in the BoB (Fig. 5.9g and h) are shallower compared to their depths of occurrence in the Arabian Sea (at station 0802) and the Madagascar Basin (at station 1504), respectively (Bertram and Elderfield, 1993). This result hints at shoaling of the waters sourced from the Atlantic Ocean due to mixing during their transport to the BoB. In contrast to NIDW and MNADW, AABW seems to be the major contributor of Nd in the BoB deeper waters with its Nd contribution varying from ~80 % to the bottom waters (depth ~ 3800 m at station 0806) to ~20 % at depths ~800 m (Fig. 5.10). Nd concentration at depths shallower than ~800 m is determined by roughly similar contributions from the NIIW, NIDW and MNADW (Fig. 5.10).

5.2.3.3 Excess Nd and its isotope composition

The inverse model results have provided estimates of dissolved Nd contribution from the nine water masses to the samples analyzed. The sum of these contributions (Σ Nd_{mixing} (%)) to the measured dissolved Nd content of various profiles is in the range of 35 to 99 %. For example, in the northern profile from station 0812 (Fig. 5.10) there is excellent balance between the measured Nd concentrations and that estimated from the model for the surface waters (i.e., Σ Nd_{mixing} (%)), whereas in samples from 50 m and below the estimated contribution makes up only two thirds of the measured value. In contrast, in the southernmost profile from station 0806 (Fig. 5.10), there is good agreement between measured and modeled dissolved Nd concentration values for the intermediate waters (~200–2900 m), whereas in the surface and deeper waters the modeled values are deficient. The deficiency in the modeled values brings out the need for additional sources to balance the budget. The need for excess Nd persists even if the measured Nd concentrations of all samples are reduced by 10 % to account for potential overestimation of Nd abundance due to measurement uncertainty if any (Chapter 4). The excess Nd (i.e., Nd_{measured} - Nd_{calculated}) contribution to the samples ranges from ~ 1 to ~ 65 % of the measured Nd concentration (Fig. 5.11a), with ~85 % of total number of samples requiring in excess of 10 % of measured Nd to balance its budget. The ε_{Nd} values of excess Nd ~ -16.0 ± 2.0 (Fig. 5.11b) overlap with that of the G-B and peninsular river sediments, in contrast to eolian dust with $\varepsilon_{Nd} \approx -13.8$ (Goldstein et al., 1984). Considering that the G–B fluvial



Fig. 5.11: The BoB water column distribution of (a) excess Nd concentration and (b) isotope composition of excess Nd as calculated from the inverse model. The "hot-spots" of Nd release in the northern slope region is indicative of a source of these elements from margin sediments (see text). The ε_{Nd} of \sim -16.0 ± 2.0 for the excess Nd overlaps with that of the G–B particles hinting that the excess Nd is very likely sourced from the G–B Rivers.

sediment flux is orders of magnitude more than that from the peninsular rivers, it is tempting to attribute this excess Nd to its release from G–B particles and sediments depositing on the margins of the northern bay. However, earlier discussion (Chapter 4) based on the J fluxes has invoked the need for source(s) other than *in situ* particle remineralization to account for the measured concentrations in the northern Bay of Bengal.

Furthermore, the observation that there are "hot-spots" of modeled excess Nd (orange patch, Fig. 5.11a) near the sediment–water interface of the continental margin hints at possibility of a sediment source of Nd in this region. Thus, the release of Nd from margin sediments can be an important process (Boundary Exchange) controlling the dissolved Nd budget of the Bay of Bengal similar to earlier studies from other oceanic regions (Arsouze et al., 2009; Jeandel et al., 1998; Lacan and Jeandel, 2005; Wilson et al., 2012).

The excess Nd from sinking particles and/or from margin sediments contributes significantly to the dissolved Nd budget of coastal and remote regions of a basin receiving a large sediment flux. Considering the average J flux of ~ 0.14 pmol/kg/y, the average excess Nd content (~7.5 pmol/kg) in the water column of the BoB can be built up in \sim 50 years only, in comparison to the residence time of Nd, ~200 years in the bay (Nozaki and Alibo, 2003b). The ε_{Nd} of the water column resulting from the mixing of different water masses is altered due to the addition of this excess Nd and exhibits non-conservative behavior. Thus, it would be difficult to use ε_{Nd} of the water column to track water masses in the presence of the excess Nd derived from particulates. It is therefore important to know the geographical extent to which this process could be significant in a basin in order to use ε_{Nd} as a water mass tracer. In the case of the BoB, receiving a huge sediment influx from the Ganga-Brahmaputra river system, the only station that seems to be free from excess Nd is 0806. For the entire water column, except at the surface and at the bottom of station 0806, the excess Nd is negligible. Hence based on the example of BoB, it can be estimated that the impact of particulate Nd is diminished, and the conservative nature of ε_{Nd} in the water column could be retrieved, at about 1500 km away from the source of the particulates. However, this will vary from basin to basin and will depend on the source strength and flow direction in the basin.

5.3 Conclusions and implication

The lateral and vertical distribution of dissolved Nd and ε_{Nd} in the water column of the Bay of Bengal along 87°E transect exhibits significant lateral and depth variations. The results show that GB–BBLS (Ganga Brahmaputra – Bay of Bengal Low Salinity Water) and AABW (Antarctic Bottom Water) are the dominant sources of dissolved Nd to the surface and deeper waters of the Bay of Bengal. On the other hand, NIIW (North Indian Intermediate Water), NIDW (North Indian Deep Water) and MNADW (Modified North Atlantic Deep Water) make significant Nd contributions to intermediate waters. However, the budget calculations show that the sums of Nd contributions from all the different water masses are inadequate to balance the measured Nd abundances, underscoring the need for an additional source. The source is inferred to be release of Nd from particulate matter delivered by the G–B river system bearing $\varepsilon_{Nd} \sim -16.0 \pm 2.0$. Calculations based on an inverse model bring out the existence of "hot-spots" of "Nd excess" along the northern margin sediment–water interface. This excess is most likely a result of Nd release from margin sediments, probably through dissolution of Fe–Mn oxyhydroxide coatings enriched in REEs (Nd) on the nascent settled particles. Consistent with other modeling studies, this study highlights the importance of particle–water interaction in estuaries and sediment–water interaction in margins in regulating the spatial distribution of dissolved Nd and its ε_{Nd} .

The dominant role of GB–BBLS and AABW in regulating Nd and ε_{Nd} distribution in the water column suggests that variations in their fluxes to the BoB would influence the Nd and ε_{Nd} in the bay and global oceans through water circulation. Further, significant variations in the supply of particulate matter from the G–B river system and/or sediment water exchange can modify the ε_{Nd} of surface and bottom waters of the bay. Investigations of these records can provide insight into these processes and their causative factors. The studies of Burton and Vance (2000), Gourlan et al. (2010), Piotrowski et al. (2009) and Stoll et al. (2007) attest to this application.

Chapter 6

Internal cycling of dissolved barium in water column of the Bay of Bengal

6.1 Introduction

The study on Ba, an alkaline earth element, in the seawater is being motivated by its use as a tracer of productivity and hence organic carbon remineralization (Cardinal et al., 2005; Dehairs et al., 2008; Gingele and Dahmke, 1994; Jeandel et al., 2000; Paytan and Griffith, 2007; Sternberg et al., 2008). Water column distribution of dissolved Ba in seawater resembles those of dissolved Si, ²²⁶Ra and alkalinity, which promote its use as a water mass tracer (Guay et al., 2009; Hoppema et al., 2010; Jacquet et al., 2005; Jacquet et al., 2007a; Jeandel et al., 1996). Dissolved barium profiles in seawater are characterized by its depletions at the surface and relative enrichment at deeper depths, typical of nutrients profile. The depletion of Ba from surface water occurs due to its adsorption onto sinking authigenic as well as detrital particulate matter (Dehairs et al., 2008 and references therein); incorporation in calcareous skeletons (Lea and Spero, 1992; Schroeder et al., 1997); bio-precipitation of barite in well saturated micro-environments of decaying organic matter as well as acantharian skeletons and their uptake by protozoan (Bernstein et al., 1992; Bernstein et al., 1998; Bishop, 1988; Dehairs et al., 1980; Ganeshram et al., 2003; Gooday and Nott, 1982; Sternberg et al., 2007; Stroobants et al., 1991). The "scavengers" of Ba (Gonneea and Paytan, 2006 and references therein) dissolve at different depths in seawater due to dependence of their solubility on pressure, thereby releasing Ba to dissolved phase. These processes pertaining to Ba cycle have already been studied earlier in global oceans (Falkner et al., 1993; Jeandel et al., 1996; Lin et al., 2010; Mcquay et al., 2008; Moore and Dymond, 1991; Paytan and Kastner, 1996). Role of dissolved Ba as water mass tracer and as hydrographical fronts marker in southern region of the Indian Ocean have attracted significant attention (Dehairs et al., 1997; Hoppema et al., 2010; Jacquet et al., 2005; Jacquet et al., 2007a; Jacquet et al., 2004; Jeandel et al., 1996). A few depth profiles of dissolved Ba in the northern Indian Ocean have been measured earlier during the GEOSECS program. The available results from the Bay of Bengal (BoB) show a higher inventory of barium in its deeper waters compared to rest of the Indian Ocean (Ostlund et al., 1987) that highlights the importance of the internal cycling in its water column over the water mass mixing. Furthermore, the surface waters of the



Fig. 6.1: Locations of seawater sampling (red circles and white squares representing depth profiles collected in this study and GEOSECS program, respectively) and one sediment core 4032 (yellow triangle) in the BoB.

BoB show anomalous Ba enrichment in contrast to its nutrient like behavior. Barium has been studied in surface waters of the BoB near mouths of the Ganga-Brahmaputra river system to explore the role of large flux of particulates and submarine ground water discharge (SGD) in supplying the surplus Ba to its surface waters. Higher Ba concentration found at mouths of the Ganga-Brahmaputra (G–B) river system is attributed to its supply from SGD and particulate Ba desorption (Carroll et al., 1993; Moore, 1997). Supply of Ba from the G-B river system, the presence of a meridional variety of Ba scavengers (Gonneea and Paytan, 2006; Ramaswamy and Gaye, 2006; Unger et al., 2003) and an exceptional near saturation level with respect to barite of deeper waters in the Bay of Bengal (Monnin and Cividini, 2006; Monnin et al., 1999; Rushdi et al., 2000) make the bay as an interesting site to explore the biogeochemical processes regulating dissolved Ba distribution in this oceanic region. In this study, the dissolved Ba concentrations have been measured in the BoB to explore the spatial redistribution (internal cycling) of its large influx from the G-B point source. Attempts are also made using mass balance approach to quantify the net lateral
Station	Depth	Salinity	Ba	Station	Depth	Salinity	Ba
	(m)		(nmoi/kg)		(m)		(nmol/kg)
0806	5	33.4	34.9		2700	34.7	117.1
	60	35	40		3000	34.7	-
	130	34.8	34.2		3300	34.7	127.2
	200	35	37.1		3550	34.7	131.6
	290	35.1	45.4	0808	5	33.3	39.7
	380	35.1	43		70	34.9	32.5
	460	35	44.9		175	34.9	40.6
	520	35	-		280	35	43.7
	600	35	47.8		380	35	45.8
	700	35	_		495	35	50.3
	800	35	55.9		600	35	54.4
	900	35	_		700	35	59.5
	1000	34.9	68		800	34.9	_
	1200	34.9	73.6		900	34.9	68.9
	1400	34.9	79.1		1000	34.9	_
	1700	34.8	87.7		1200	34.9	78.7
	2000	34.8	96.6		1400	34.8	_
	2300	34.8	100		1700	34.8	88
	2600	34.7	101.5		2000	34.8	_
	2900	34.7	101.4		2300	34.8	98.2
	3200	34.7	106.4		2600	34.7	_
	3500	34.7	110.1		2900	34.7	108
	3800	34.7	109.1		3200	34.7	108.5
0807	5	33.3	43.2	0809	5	33.2	40.4
	70	34.9	40.8		85	35	32.4
	110	34.9	-		180	35	39.5
	160	35	42.9		300	35	41.2
	220	35.1	_		400	35	45.6
	300	35.1	48.7		500	35	47.6
	400	35	49.5		600	35	51.4
	500	35	_		700	35	56
	600	35	62		800	35	59.8
	800	35	70		900	35	65.6
	900	35	74.8		1000	34.9	67.5
	1000	34.9	79.2		1200	34.9	_
	1100	34.9	_		1400	34.9	78.1
	1300	34.9	89.8		1700	34.8	_
	1500	34.8	94.9		2000	34.8	94.3
	1800	34.8	_		2300	34.8	_
	2100	34.8	111.1		2600	34.7	103.5
	2400	34.8	_		2900	34.7	107.5

 Table 6.1 Depth profiles of salinity and Ba in seawater of the BoB

Dissolved Ba in water column of the BoB

0810	5	32.1	42.6	0812	5	32	53.8
	40	33.5	35.6		50	34.3	37.4
	140	34.6	32.2		110	34.9	39.6
	200	35	41.2		200	35	43.7
	300	35	40.3		300	35	46.5
	400	35	42.3		400	35	48.6
	500	35	44.7		500	35	51.4
	600	35	48.2		600	35	57.1
	700	35	53		800	35	63.7
	800	35	54.8		1000	34.9	72.6
	1000	34.9	57.7		1200	34.9	82.4
	1200	34.9	74.3		1400	34.9	91.2
	1400	34.9	78.7		1700	34.8	103.9
	1700	34.8	87.6		2000	34.8	109.5
	2000	34.8	95.3	0813	5	32.7	48.5
	2200	34.8	100.9		70	34.7	33.8
	2350	34.8	99		150	34.9	39.1
0811	5	33.9	36.8		250	35	43.9
	70	34.7	32.4		350	35	45.5
	110	34.9	33.7		440	35	47.1
	180	35	44.5		550	35	52.5
	300	35	43.9		640	35	55.3
	400	35	46.6	0814	4	29.6	53.3
	500	35	50.1		45	32.5	44.4
	600	35	52	0815	4	29	56.6
	700	35	54.2		30	31.5	52.9
	900	35	62.9	0816	4	24.5	112.8
	1100	34.9	69.6		30	30.9	49.9
	1300	34.9	75.8	0817	5	29.1	50.7
	1500	34.9	82.3		70	33.7	40.6
	1700	34.8	88.6	0818	5	28.1	57.2
	1900	34.8	91.5		60	34	37.2
	2100	34.8	97.3	0819	5	30.7	46.7
	2300	34.8	98.6		110	34.8	34.4
	2500	34.7	129.6	0820	5	32.2	47.8

outflow of dissolved Ba through surface layer of the Bay of Bengal to the global oceans and the total remineralization rates of particulate Ba in deeper waters of the bay.



Fig. 6.2: Distribution of (a) dissolved Ba concentration and (b) salinity in surface waters (depth ≤ 5 m).

6.2 Results and discussion

This chapter is on the distributions of dissolved Ba in surface and deep waters of the Bay of Bengal. Towards this, dissolved Ba concentration in filtered (< 0.45 μ m) seawater samples, from surface and depth profiles along with those collected near mouths of the Ganga–Brahmaputra river system (Fig. 6.1), is measured as described in Chapter 2. These data along with salinity are presented in Table 6.1.

6.2.1 Surface waters (depth $\leq 5 m$)

Ba concentration shows a North-South decreasing trend in BoB surface waters, whereas salinity indicates increasing trend (Fig. 6.2). Surface waters from the shallowest coastal station 0816, which is close to mouths of the Hooghly estuary, show a minimum of salinity (~ 24.5) due to fresh water supply mostly from the Hooghly River (Fig. 6.2b). Maximal dissolved Ba (~112.8 pmol/kg) measured in this study (station 0816), is about three times higher than its concentration in open ocean surface waters but similar to those reported earlier at similar salinity from other channels of the G-B and world's major estuarine systems (Carroll et al., 1993; Coffey et al., 1997; Hanor and Chan, 1977; Li and Chan, 1979; Moore, 1997; Nozaki et al., 2001; Wang et al., 2009). These estuarine studies have attributed such higher Ba content to particulate desorption and SGD contribution along with dissolved riverine input. Recently, Rahaman and Singh (submitted) have demonstrated that behavior of dissolved Ba in the Hooghly estuary is non-conservative and overall Ba "excess" in the estuary estimated from river- seawater mixing proportion is about 2.5 times the riverine dissolved input. Besides the station 0816, surface waters at the northern latitudes (north of 18°N) with salinity < 32 show dissolved barium concentrations ~ 25 % higher than those observed further south in the BoB and can be attributed to same sources as well. Although, Ba concentration along the eastern coast of India is not measured, its contribution from the peninsular rivers, having fresh water and sediment discharge (Mckee et al., 2004) an order of magnitude lower compared to that of the G-B Rivers and draining mostly the basaltic lithology with low Ba mobility (Das and Krishnaswami, 2006), is presumably low. Further, Nd isotope signatures of surface waters (Chapter 5) rule out influence of the Irrawaddy river system to the BoB. Therefore, the G-B river system can be considered as a dominant riverine source of dissolved Ba to surface waters of the Bay of Bengal.

6.2.2 Depth profiles

The Ba concentration-depth profiles for the stations 0806–13 are given in Fig. 6.3. Dissolved Ba concentrations measured in this study at station 0807 are in good agreement with reported values (Ostlund et al., 1987) from a nearby station



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Fig. 6.4: Barium profile at the southernmost station 0806. Higher Ba concentrations (red and blue kinks) most probably reflect different water masses.

GEOSECS-445 (Figs. 6.1 and 6.3). Typically, these Ba profiles show a higher concentration in surface waters that decreases to a minimum and then increases with depth in deep waters, similar to a typical behavior of REEs as observed in the BoB (Chapter 4). However, the southernmost station 0806 is an exception to this behavior. This station shows two kinks toward higher concentrations in the Ba profile, one at depth ~60 m and other at ~290 m. Higher Ba concentrations at these depths (Fig. 6.4) most probably reflect two different water masses (Chapter 5); Arabian Sea High Salinity Water (ASHS) and North Indian Intermediate Water (NIIW).

6.2.2.1 Shallow waters (depth = 0-200 m)

The section contours of barium and salinity in shallow waters are shown in Figs. 6.5a and 6.6a. Low salinity and high Ba concentration (hot-spots) found close to mouths of the G–B river system (north of 18° N) are diffused southward in BoB shallow waters. Generally, Ba shows a depletion along the entire transect in depth interval ~ 50 to ~ 150 m (Fig. 6.5a), which appears to be a permanent feature resulting from biogeochemical processes printed over hydrographic conditions as observed earlier (Ostlund et al., 1987) for two Ba concentration–



Fig. 6.5: Depth contours of dissolved Ba in (a) top ~200 m and (b) below ~200 m of water column of the BoB.

depth profiles at GEOSECS stations 445 (8.6°N, 86.1°E) and 446 (12.6°N, 84.6°E) in the BoB. Besides this general depletion of Ba, a pronounced minimum is seen from similar depths at mid latitudes (10°N to 18°N) probably due to enhanced productivity as evidenced by higher settling fluxes of both opaline silica and coccolith carbonate from the central Bay of Bengal (Ramaswamy and Gaye, 2006; Unger et al., 2003). This suggests that barium is removed efficiently from water column at a depth interval 50–150 m either through their involvement in marine productivity or by adsorption onto the sinking particulate matter as learned from earlier studies (Bernstein et al., 1992; Bishop, 1988; Dehairs et al., 1980; Gooday and Nott, 1982; Schroeder et al., 1997; Stroobants et al., 1991).

Despite the efficient removal of Ba, its concentrations, unlike those of nutrients, are not totally extinct at the sea surface. High Ba concentrations in



Fig. 6.6: Depth contours of salinity in (a) top ~200 m and (b) below ~200 m of water column of the BoB.

surface waters similar to those of REEs are resulted by their net additions from either *in situ* particle dissolution or the estuarine release from the G–B river system over their removal onto the sinking particles. These Ba additions in surface layer (top ≈ 100 m) at stations 0806–13 can be calculated from difference in area between observed Ba concentration–depth profile and extrapolated profile from its minima to sea surface as done earlier in Chapter 4. In case of station 0806, area is calculated by neglecting the influence of ASHS at a depth of ~60 m and thus ascribed to addition from the G–B fluvial source only. The surface additions of Ba and Nd show a North–South decreasing trend and a good positive correlation (R² = 0.76; Fig. 6.7a). These surface additions of Ba and Nd are supposed to show 1:1 correlation, if both elements are derived from same sources, assuming their identical residence times of ~2.5 year in surface waters of the BoB. But the slope



Fig. 6.7: A comparison of Ba and Nd for their (a) additional amount and (b) fractional solubility in surface layer of the BoB.

is greater than 1 that hints at additional sources of Nd. To constrain these additions by *in situ* particle release, the fractional solubility of Ba and Nd has been determined from the sinking lithogenic particulate fluxes (Unger et al., 2003) in the region by assuming their elemental composition similar to those of G–B shelf sediments (Anne-Catherine, 2000). The unrealistically higher Ba fractional solubility (Fig. 6.7b) and its poor correlation with Nd fractional solubility indicate



Fig. 6.8: Ba concentration-salinity relation for (a) salinity ≤ 34.6 (Top ~ 200 m) and (b) salinity > 34.6.

an insignificant *in situ* particle release of Ba. Therefore, the surface additions of Ba can be attributed entirely to the estuarine release from the G–B river system. This is also corroborated with a good but inverse Ba concentration–salinity correlation ($R^2 = 0.79$; Fig. 6.8a) in shallow waters for salinity < 34.6, indicating the riverine sources of Ba. Further, it can be inferred from the slope of Ba_{Add}– Nd_{Add} plot (Fig. 6.7a) that *in situ* particle release can account for ~40 % of the Nd_{Add} in surface waters of the BoB, which is comparable to the average excess Nd (particle release) in deep waters of the bay. Hence, the G–B river system acts as a point source of Ba, while Nd is significantly added from *in situ* particle release to the surface water of the BoB.

6.2.2.2 Deep waters (depth > 200 m)

The overall variations of barium and salinity in water column of the BoB are 32.2-131.6 nmol/kg and 34.6-35.1, respectively (Table 1). The "hot-spots" of barium in deep waters are clearly discernible at latitudinal zones $\sim 8-10^{\circ}$ N (Figs. 6.5b) and hint at possible influence from benthic fluxes. On the other hand, except for the surface waters close to mouths of the G–B, no "hot-spot" of Ba was found on the continental slope that could be ascribed to intrusion of SGD derived Ba. This is in contrast with deep SGD contribution of Ba found earlier at a depth of 600 m from the Pingtung coastal zone, Southern Taiwan (Lin et al., 2010).

Ba abundances in deep waters correlated with salinity by two linear trends (Fig. 6.8b), however, cannot be explained simply from the water mass structure (Chapter 5) of the region. This is due to the fact that the observed Ba concentration in BoB deep waters is significantly higher compared to maximum Ba concentration reported for the various water mass constituents (Ostlund et al., 1987) and highlights the importance of vertical cycling of Ba in the region. Furthermore, below the shallow waters, barium concentration shows a steady increase with depth while salinity increases to a maximum followed by a decrease (Figs. 6.5b and 6.6b). Therefore, the observed Ba concentration–salinity correlations in BoB deep waters are resulted from their spatial coherence only.

6.2.3 Ba cycle in water column of the BoB

Barium cycle in the Bay of Bengal can be easily understood by a two box model approach (Fig. 6.9). Top box consists of surface layer (depth ~ 0–100 m) whereas bottom box covers the deep waters (depth > 100 m). The area of each box is considered as equal to total area of the Bay of Bengal (~ 2.2×10^{12} m²). Top box receives a major input of dissolved Ba from the G–B point source. Direct quantification of this influx is cumbersome due to non-conservative behavior of Ba (i.e., its concentration at low to mid salinity exceeds that of the riverine as well as seawater end-member) in the G–B estuarine region. Although, additional endmembers with high Ba concentration such as ground water and/or suspended particles (Dalai et al., 2002; Dalai et al., 2004; Dowling et al., 2003) can account for the observed concentration, direct quantification of Ba fluxes from these



Fig. 6.9: The Ba cycle in the Bay of Bengal. Top box has a vertical depth ~100 m and high riverine influence. Black and white arrows indicate particulate and dissolved Ba fluxes. The numbers (bracketed numbers) represent Ba inventory (fluxes) in mol (mol/year) unless specified.

sources is very difficult. Although, the magnitude of this influx is supposed to be season dependent, Carroll et al., (1993) attempted earlier to calculate annual Ba fluxes ($\sim 5.3 \times 10^8$ mol/year) from the G–B river system to the BoB by considering only the desorption from the annual sediment delivery. Later, Moore (1997) found that even for low discharge (water as well as sediment) period, Ba content in the shelf region (~ 10 m isobaths) is comparable to that during peak discharge and



Fig. 6.10: The $C_{org'}/Ba_{Bio}$ -depth relationship is determined from the sediment trap data in the Arabian Sea (Balakrishnan Nair et al., 2005).

attributed this to a large contribution from the SGD. Assuming steady state conditions and considering Ba inventory and the residence time (~5-45 days) of water in the shelf region, Moore (1997) calculated net offshore Ba fluxes as $\sim 1-10$ $\times 10^6$ mol/d. In the present study conducted soon after the peak discharge period (November) when higher Ba fluxes are expected, we have considered the upper limit, $\sim 3.6 \times 10^9$ mol/year, of Ba flux as proposed by Moore (1997). Further, Ba release from the particles (Ba_{Add}) to the surface layer (top box) is negligible compared to this large influx (Ba_{G-B}) from the G-B point source (c.f. Section 6.2.2.1). Furthermore, the BoB surface layer is characterized by less saline water lens throughout the year that inhibits the vertical mixing between surface and deep waters. Therefore, on the first order approximation, direct exchange of dissolved Ba between these waters (top and bottom boxes) can be neglected. However, the Ba addition to the bottom box is allowed through regeneration of sinking biogenic barium (Ba_{Bio}) that is formed initially in the top box. The calculation of this sinking flux is challenging due to scarcity of particulate barium data from the region. There have been several studies that have utilized the sedimentary accumulation of Ba_{Bio} to reconstruct paleo-productivity of the surface oceans

(Chow and Goldberg, 1960; Dehairs et al., 2000; Dymond and Collier, 1996; Dymond et al., 1992; Francois et al., 1995; Goldberg and Arrhenius, 1958; Pfeifer et al., 2001; Schenau et al., 2001). Such reconstructions are based on the observed relation between depth and C_{org}/Ba_{Bio} of settling particulate matter obtained from sedimentary trap data in different oceanic basins. This relation (a power function of depth) is based on the hypothesis that biogenic barium (mostly the marine barite) is supposed to form by organic matter degradation with depth. Although, such data is restricted to depths greater than ~1000 m, Weinstein and Moran (2005) reconstructed similar particulate C_{org}/Ba_{Bio} ratio from fluxes of these species in top ~250 m based on 234 Th/ 238 U disequilibrium and 234 Th supported contents in sinking particles.

Conversely, BaBio fluxes in this study are determined from the export production in the Bay of Bengal by using a similar Corg/BaBio-depth relationship (Fig. 6.10) obtained from the sediment trap data in the Arabian Sea (Balakrishnan Nair et al., 2005), considering similar annual Corg fluxes in these two oceanic basins (Prasanna Kumar et al., 2007 and references therein). The particulate Ba_{Bio} sinking out of top box is approximated by dividing the annual export production (P_{Export}) ~6.6 mol/m²/year (Gauns et al., 2005; Kumar and Ramesh, 2005; Kumar et al., 2004) by the ratio $C_{org}/Ba_{Bio} \sim 4.5 \times 10^3$ mol/mol calculated at ~100 m (Fig. (6.10) and multiplying with area of the box. The sinking flux of Ba_{Bio} is estimated to be ~3.2 \times 10⁹ mol/year, which is comparable to the dissolved Ba flux (~3.6 \times 10⁹ mol/year) from the G-B point source, which indicates that there is no net outflow of dissolved Ba from the surface layer of the BoB to the global oceans (Fig. 6.9). Further, dividing the total Ba inventory ($\sim 8.1 \times 10^9$ mol) in top box by this sinking flux, a residence time of ~2.5 year is resulted, which is same as assumed earlier (c.f. Section 6.2.2.1) and that of other particle reactive elements (Amakawa et al., 2000; Measures and Vink, 1999, 2000; Obata et al., 2004).

The sinking particulate barium is regenerated both during its transit in water column and at sediment–water interface. The total regeneration of Ba_{Bio} , $Ba_{Regeneration}$ can be calculated as the difference between the sinking biogenic Ba flux from top box and accumulation of biogenic barium ($Ba_{Bio-Accumulation}$) in BoB deep sea sediments as given (Eq. 6.1).

$$Ba_{\text{Regeneration}} = Ba_{Bio} - Ba_{Bio-Accumulation} \tag{6.1}$$

To calculate the accumulation of biogenic barite, $Ba_{Bio-Accumulation}$, a sediment core 4032 (13.35°N, 88.90°E; water depth ~3000 m) is selected from the central Bay of Bengal (Bhushan, 2008). The sedimentation rate at the location is ~1.168 cm/ka. Biogenic barium concentration in the core top sediments is calculated by subtracting lithogenic fraction from the measured concentration of Ba (Eq. 6.2). Lithogenic Ba in core top sediments is estimated from the measured Ti concentration and Ba/Ti ratio of detrital phases that is assumed to be similar to the Post-Archean average Australian shale (PAAS) composition as used by Balakrishnan Nair et al., (2005) to establish the C_{Org}/Ba_{Bio}–Depth relationship for settling particulates in the Arabian Sea.

$$Ba_{Bio-Core\,top} = Ba_{Core\,top} - \left(\frac{Ba}{Ti}\right)_{PAAS} \times Ti_{Core\,top} \tag{6.2}$$

Ba_{Bio-Accumulation} is calculated by multiplying this biogenic Ba concentration (Ba_{Bio-Core top} ~560 ppm) with sedimentation rate (~1.168 cm/ka), dry bulk density (~1.5 g/cm³) and total area of the Bay of Bengal (~ 2.2×10^{16} cm²), which turns out to be ~ 1.6×10^8 mol/year.

Bottom box clearly demonstrates a significant (~95 %) remineralization of biogenic barium (Ba_{Regeneration} ~ 3.1×10^9 mol/year) in BoB deep waters (depth ~100–3000 m), which is similar to earlier reports (Klump et al., 2001; Mcmanus et al., 1999; Mcmanus et al., 1998; Paytan and Griffith, 2007 and references therein). The remineralization estimate made in this study is a lower limit since a significant portion of Ba_{bio} is precipitated as marine barite at deeper depths ~100–1000 and contributes significantly to its accumulation in marine sediments (Bishop, 1988; Dehairs et al., 1992; Dehairs et al., 1980; Jacquet et al., 2011; Jacquet et al., 2007b; Stroobants et al., 1991; Van Beek et al., 2007).

Further, the rain of nascent Ba particulates (Ba_{Bio-Deposition}; Fig. 6.10), to the seafloor can be calculated from the ratio of the C_{org} rain to the C_{org}/Ba_{bio} of settling particles at depth ~3000 m, similar to that calculated at depth ~100 m, the bottom of top box. The C_{org} rain (~8.2 × 10¹¹ mol/year) near the sea floor is calculated from the export production (P_{Export}) and water column depth by using algorithm (Eq. 6.3) provided by Sarnthein et al. (1988).

$$C_{Org} (gm^{-2} year^{-1}) = 20.5631 \times \left(P_{Export} (gm^{-2} year^{-1})\right)^{0.6648} \times \left(depth(m)\right)^{-0.5537}$$
(6.3)

These calculations result into a flux, $\sim 7.6 \times 10^8$ mol/year of nascent biogenic barium to the seafloor, where these particles are further prone to dissolution before getting buried completely. This dissolution can be expressed as either sedimentary efflux of dissolved Ba to the bottom waters, Ba_{Efflux} (Eq. 6.4) or preservation of biogenic barium into buried sediments, Ba_{Preservation} (Eq. 6.5).

$$Ba_{Efflux} = Ba_{Bio-Deposition} - Ba_{Bio-Accumulation}$$
(6.4)

$$Ba_{\Pr eservation} = \frac{Ba_{Bio-Accumulation}}{Ba_{Bio-Deposition}}$$
(6.5)

Mass balance (Eq. 6.4) at the sediment–water interface resulted into an average benthic flux of ~ 6.0×10^8 mol/year, which is comparable to the sedimentary Ba efflux in the Weddell Gyre (~ 4.0×10^8 mol/year) having surface area (~ 1×10^{12} m²) about half of the BoB (Hoppema et al., 2010). The Ba_{Efflux} in the BoB corresponds to ~20 % preservation of Ba_{bio} in the seafloor sediments of the BoB similar to earlier reports from other open ocean regions (Paytan and Kastner, 1996; Schenau et al., 2001). Further, the ~95 % regeneration of particulate barium corresponds to ~175 year residence time of Ba in the BoB deep waters, which is an upper limit since other sources (contribution from various water masses) of dissolved Ba to deep waters are neglected. This upper limit of residence time of Ba in BoB deep waters is orders of magnitude shorter compared to ~ 10^4 year in global oceans (Paytan and Kastner, 1996). Therefore, deep waters receiving a large influx of dissolved Ba through particle release in relatively short span of time have a potential to act as a major source of Ba to deep waters of the Indian Ocean.

6.3 Conclusions

Barium concentration shows a North–South non-linear decreasing trend in surface waters of the Bay of Bengal due to its enormous supply from the Ganga–

Brahmaputra estuarine zone. This supply masks the particle reactive nature of Ba in surface layer of the BoB. On the other hand, two subsurface Ba maximal values at depths ~60 m and ~290 m in the southernmost station indicate intrusion of Arabian Sea High Saline Water and North Indian Intermediate Water sourced from the Arabian Sea. In contrast, a much localized Ba minimum is found at depths ~50–150 m in the central BoB most probably resulting from high productivity in the region. Ba concentration in deep waters increases steadily with depth up to a factor of three compared to that in surface waters indicating substantial regeneration of particulate barium in deep waters.

Ba cycle in the Bay of Bengal is well described by a two box model dealing separately with surface and deep waters. Mass balance under the steady state conditions indicates that on an annual scale there is no net lateral outflow of dissolved Ba to the Indian Ocean from top \sim 100 m of the BoB despite a large influx from the G–B river system. This Ba influx leaves the surface layer through sinking particulate to the deep waters, where \sim 95 % of this large particulate flux of Ba is regenerated again to the dissolved phase. Therefore, deep waters of the Bay of Bengal receiving a large influx of dissolved Ba through particle remineralization with short residence time can be a significant source to the Indian Ocean.

Chapter 7

Temporal variations in boron isotope composition of planktonic foraminifera from the southeastern Arabian Sea

7.1 Introduction

At present, the Arabian Sea is one of the largest oceanic sources of the potential green house gas, CO₂ to the atmosphere (Sarma, 2003; Takahashi et al., 2002; Takahashi et al., 2009), due to high thermo-chemical driving potential, the Δ pCO₂ which is a difference of partial pressure of CO₂ between surface seawater and the contemporaneous atmosphere. Numerous factors are responsible to increase the partial pressure of CO₂ in surface oceans, such as carbonate precipitation, solar insolation, geographical region and upwelling of subsurface waters with high DIC. Temporal changes in productivity, solar insolation and the Asian Monsoon, regulating primarily the upwelling in the Arabian Sea (Agnihotri et al., 2002; Clemens and Prell, 2003; Reichart et al., 1997), have been modifying the pCO_2 levels in surface waters of the Arabian Sea. Palmer et al., (2010) has reconstructed the paleo-pCO₂ in surface waters of the northern Arabian Sea and suggested it as a continuous source of CO_2 in the last 5–29 ka with an intensification (Average Δ pCO₂~140 ppmv) at about 11–17 ka. This seems to be an upper limit since strong South-West monsoon causes intense upwelling and lateral advection of subsurface waters with high DIC offshore the Somalia, Yemen, Oman compared to the west coast of India (Swallow, 1984; Wyrtki, 1973). Therefore, to establish the role of entire basin as a source or sink of CO_2 , one should account the spatial differences in pCO₂ levels in surface waters (Sarma et al., 2000; Sarma, 2003; Takahashi et al., 2009). In this study, an attempt is made to exploit boron isotope composition of the planktonic foraminifera to reconstruct the paleo-pCO₂ of the southeastern Arabian Sea showing a large seasonality in surface pCO₂ (Sarma, 2003) due to proximity of intense upwelling at the south–west coast of India and fresh water discharge from the Bay of Bengal.

Boron isotope composition of carbonate shells of surface dwellers (planktonic foraminifera) is the best archive to record the temporal changes in pH that can be easily correlated to CO_2 levels of the surface oceans (Hemming and Hanson, 1992; Hönisch and Hemming, 2005). Boron has two isotopes, ¹⁰B and ¹¹B and occurs in seawater as two major species; trigonal boric acid, B(OH)₃ and tetrahedral borate ion, B(OH)₄⁻. The relative fraction and boron isotope composition of these two species depends on both temperature (through



Fig. 7.1: The sampling locations in the Arabian Sea.

dissociation constant of boric acid, K_B^*) and pH of seawater but B(OH)₃ is always isotopically heavier than B(OH)₄⁻ due to difference in their coordination controlled vibrational energy (Klochko et al., 2006; Zeebe and Wolf-Gladow, 2001 and references therein). Similar boron isotope composition of modern marine carbonates and tetrahedral borate ion in seawater suggests that only borate ion is incorporated in calcium carbonate precipitation (Hemming and Hanson, 1992). Therefore, pH of seawater (Pearson et al., 2009) can be calculated from $\delta^{11}B_{Borate}$ – pH curve by substituting $\delta^{11}B_{Borate}$ with the measured boron isotope composition of carbonates ($\delta^{11}B_C$) as given in equation 7.1.

$$pH = pK_B^* - \log\left(-\frac{\delta^{11}B_{SW} - \delta^{11}B_C}{\delta^{11}B_{SW} - \alpha_B \times \delta^{11}B_C - \varepsilon_B}\right)$$
(7.1)

where pH is on the total scale; K_B^* is dissociation constant of boric acid at given salinity and paleo-temperature reconstructed from Mg/Ca ratio (Anand et al., 2003; Dickson, 1990); $\delta^{11}B_{SW}$ is boron isotope composition of seawater (39.5 ‰); α_B and ε_B are fractionation factor (1.0272) and total fractionation (27.2) for boron isotope exchange between boric acid and borate ion (Klochko et al., 2006).

Table	1.1 Chronology, measured data of boron isotope composition and
	trace element/Ca ratios of G. Sacculifer tests from the core
	3101G along with reconstructed temperature and pH of surface
	waters of the AS

Sample	Calibrated Age	δ ¹¹ Β	Al/Ca	Mn/Ca	Mg/Ca	Temperature		
	(ka)	(‰)	(µmol/mol)		(mmol/mol)	(°C)	рн⊤	
CC-1	2.7	10.1	1550	873	10	37.2	-	
CC-2	3.5	11.3	1500	679	12	38.5	-	
CC-3	4.1	11.3	1859	785	14	40.3	-	
CC-4	4.9	9.5	2138	934	15	41.3	-	
CC-5	6.0	11.2	2394	531	21	45.4	-	
CC-6	7.0	8.0	1553	603	14	40.3	-	
CC-7	9.8	10.6	1530	396	14	40.5	-	
CC-8	10.3	10.0	2326	460	15	41.1	-	
CC-9	10.6	16.5	717	83	6	31.9	7.82	
CC-10	10.8	12.9	904	276	7	32.9	7.06	
CC-11	11.1	18.5	530	181	6	30.5	8.04	
CC-12	11.5	15.9	678	105	6	30.8	7.77	
CC-13	11.7	16.4	599	240	6	31.5	7.82	
CC-14	12.0	13.7	441	219	7	33.0	7.33	
CC-15	12.3	13.5	2633	261	9	35.1	7.26	
CC-16	13.9	17.5	996	188	6	32.0	7.93	

However, earlier studies (Rollion-Bard and Erez, 2010; Sanyal, 1996; Sanyal et al., 2000) have documented both inter as well as intra-species boron isotope composition offset due to vital effect of altering the pH of their microenvironment by biomineralization process. Intra-species variations are averaged out in bulk analysis and reflect pH of the seawater. Boron isotope composition of the Globigerinoides Sacculifer, a more refractory planktonic foraminifera with shell size > 425 μ m, is widely used for paleo-pH proxy since boron isotope fractionation arises by partial dissolution and with different shell sizes (Cullen and Prell, 1984; Hönisch and Hemming, 2004). Sampling site of the core 3101G (6°N, 74°E; water column depth ~ 2766 m; Fig. 7.1) on the Chagos–Laccadive Ridge is above the foraminiferal lysocline in the Arabian Sea (Cullen and Prell, 1984) and rules out any significant partial dissolution.

7.2 Results and discussion

In this study, for each sample \sim 50–80 carbonate shells of planktonic foraminifera, Globigerinoides Sacculifer were cleaned to remove detrital, organic



Fig. 7.2: (a) Temporal variations in $\delta^{11}B$ at core 3101G (\circ —this study) and at NIOP464 (\Box —Palmer et al., 2010) whereas (b) Inverse correlation between the trends of three point averages of $\delta^{11}B$ and Al/Ca (Δ) represented by red and black solid lines at core 3101G.

as well as adsorbed contaminants using the standard protocols (Chapter 2). The cleaned forams were dissolved in Teflon distilled 0.3 N HCl and centrifuged. Supernatant solution was used to measure B isotope composition and selected trace element concentrations. Boron isotope composition ($\delta^{11}B$) and trace element ratios (Al/Ca, Mg/Ca, Mn/Ca) of these samples of the core sediments archiving information since last ~14 ka were measured on MC–ICPMS and Q–ICPMS, respectively (Table 7.1). The $\delta^{11}B$ values measured in this study are unexpectedly low (Fig. 7.2a) and correspond to unrealistically low pH in surface waters of the

region (Table 7.1). Further, the trend line formed by three point running averages of δ^{11} B shows an inverse correlation with that of Al/Ca ratios (Fig. 12b) and hints at potential contamination of cleaned samples by the continental detritus having δ^{11} B ~-13 to -8 ‰ (Ishikawa and Nakamura, 1993). The detrital contamination is further indicated by high Al/Ca and Mn/Ca (Al/Ca > 120 µmol/mol and Mn/Ca > 50 µmol/mol; Foster, 2008; Ni et al., 2010; Yu et al., 2007), which is also reflected in unrealistic high sea surface temperature reconstructed from Mg/Ca thermometer (Table 7.1). Thus, the current data set is not suitable to reconstruct paleo-pCO₂ levels of the surface oceans.

Chapter 8

Summary and future directions

8.1 Summary

The ultimate objective of this thesis was focused on exploring the spatial and temporal distributions of abundances and isotope compositions of selected trace elements in the relatively unexplored northern Indian Ocean. Such distributions of these TEIs, which have already been utilized extensively in literature to study various marine biogeochemical processes and environments, help us to learn about their geochemistry by studying their causative factors and are tracers of the past oceanic conditions. In this study, the role of fresh water, particulate matter, in situ hydrographical conditions and boundary processes on the spatial distributions of abundances of RSEs, Ba, REEs and isotope composition of Nd in BoB seawater are evaluated among various other causative factors. This study is motivated as the Bay of Bengal receives a globally significant flux of these elements through riverine dissolved and particulate phases that are amenable to modification by in situ hydrographical conditions and boundary processes. Attempts are made using the modeling approaches to quantify net influences (if any) of these fluxes on the oceanic distributions of these TEIs. On the other hand, the temporal variations of boron isotope composition of handpicked foraminiferal carbonates from a sediment core of the southeastern Arabian Sea are determined to put constraints on past oceanic chemistry of the region. The past variations in pH of surface seawater (an index of its pCO₂ levels) are determined using B isotopes in this study. Major findings of the present thesis are summarized in subsequent sections.

8.1.1 Behavior of dissolved redox sensitive elements (U, Mo and Re) in water column of the Bay of Bengal

The dissolved concentrations of redox sensitive elements, U, Mo and Re have been measured in the water column of the Bay of Bengal to track their distributions and behavior in its suboxic layers at the intermediate depths. The dissolved oxygen content in the intermediate waters (200–800 m) north of ~11°N decreases to values as low as ~3 μ mol/L. The distribution of U, Mo and Re in BoB surface waters along the 87°E transect shows a north–south gradient with significant correlation with salinity, underscoring the dominant influence of the

Ganga-Brahmaputra (G-B) Rivers in controlling the geochemical budgets of these three elements. The concentrations of these three elements in surface and deep waters of the BoB are governed by salinity suggestive of their conservative behavior. On a macro-scale, there is no discernable removal of U, Mo, or Re from the suboxic layer in the BoB water column, consistent with earlier studies in the suboxic zones of other oceanic regions. Further, their conservative behavior in the bay, suggest that the annual delivery of $\sim 10^9$ tons of suspended matter rich in organic matter by the G-B and other rivers do not have any measurable impact in determining their distributions. This study suggests that the suboxic conditions and high particulate flux prevailing in water column of the Bay of Bengal do not affect the conservative behavior of U, Mo and Re. The dissolved Re concentrations in the upper layers of the central BoB seem to be marginally higher compared to that expected based on their salinities. This seems to be contributed from the Godavari River, which drains into the BoB and has dissolved Re three times higher than seawater. The higher Re concentrations in the central Bay of Bengal suggest that mixing process by local gyre and/or eddies in the BoB transports riverine dissolved material to ~400 km offshore.

8.1.2 Rare earth elements in the Bay of Bengal

Spatial distributions of dissolved concentrations of REEs in the Bay of Bengal have been explored to learn about their geochemistry and water mass structure in the region. These distributions in BoB surface waters (except at the station 0807) along an 87°E transect show a gradual North–South decreasing trend in both the absolute and relative abundance pattern of dissolved REEs. This trend is most probably resulted from *in situ* particle and/or estuarine release of REEs on the northern (G–B) shelf area. However, REEs pattern in surface waters at station 0807 is similar to that of the Andaman Sea at PA-10, which indicates a possible water mass exchange across the Andaman–Nicobar ridge between the two basins. The typical REE concentration–depth profile show a higher concentration in surface waters that reaches a minimum value at depths (~50–200 m) and increase further with depth in subsurface waters. On the other hand, subsurface samples show a similar relative abundance pattern of REEs that is characterized by an enrichment of light REEs (Pr, Nd and Sm) compared to Gd and Dy. This pattern is

similar to those of seafloor sediments of the BoB and G–B shelf sediments, which indicates a direct influence of these particulates. The distinct abundance pattern of REEs in a few subsurface samples from the southernmost station 0806 indicates the presence of different water masses. However, such distinction is less obvious further north in the BoB due to additions of REEs by enhanced particle remineralization and possible benthic sources in the northern region of the BoB.

8.1.3 Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses

The concentration and isotope composition of dissolved Nd have been measured in water column of the Bay of Bengal to investigate the effect of water mass mixing and Nd release from particulate matter in determining these properties. The concentration of Nd in surface waters of the BoB shows a North-South decreasing non-linear trend with salinity, whereas its depth profiles typically show a high value in surface waters, a minimum in the shallow subsurface (depth ~50–200 m), followed by a gradual increase with depth. The Nd concentration of BoB waters is generally higher than that in nearby oceanic basins. On the other hand, the ε_{Nd} values in the BoB are less radiogenic compared to those reported for other regions of the global oceans (except Baffin Bay, the North Atlantic Subpolar Gyre and the Niger delta margin), and show a greater variation in the upper water column. Surface waters of the southernmost profile (~6°N) show a more radiogenic ε_{Nd} value -8, which decreases to -15 in the northernmost profile (~20°N), close to the values for dissolved and particulate phases of the Ganga-Brahmaputra (G-B) Rivers. This latitudinal trend is most likely a result of variations in mixing proportion between the more radiogenic Indonesian Throughflow surface waters (IW) and un-radiogenic BoB low salinity waters-the former's signature being more clearly discernible in surface waters of the two southernmost profiles ($\sim 6^{\circ}N$ and $\sim 8.5^{\circ}N$).

Attempts to balance the Nd budget in the water column based on an inversion model, suggest that in addition to water masses other source(s) is required, the strength of which is estimated to vary from 1% to 65% of the measured Nd concentration. The calculations also show that the ε_{Nd} of this

additional source(s) has to be in the range of $\sim -16 \pm 2$, typical of G–B river sediments. These observations, coupled with the North–South distribution of dissolved Nd and ε_{Nd} , indicate that this additional source is release from particulate phases supplied by the G–B river system. The calculations also bring out the presence of "hot-spots" of Nd release (excess Nd) near the sediment–water interface along the northern slope of the bay, indicating supply of Nd from continental margin sediments. Such perturbations caused by the excess Nd seem to be negligible at about 1500 km from the G–B source, where sinking lithogenic particle flux is $\sim 4 \text{ g/m}^2/\text{d}$. Thus, ε_{Nd} can be used as a reliable proxy in the open ocean where lithogenic particulate fluxes are less than $\sim 4 \text{ g/m}^2/\text{d}$.

8.1.4 Internal cycling of dissolved barium in water column of the Bay of Bengal

Spatial distributions of dissolved barium concentration in water column of the BoB have been measured to explore the redistribution of its large influx from the G-B river system. Dissolved Ba concentration shows a North-South decreasing trend in surface waters of the Bay of Bengal due to its enormous supply from the Ganga-Brahmaputra estuarine zone. On the other hand, subsurface waters at depths ~60 m and ~290 m in the southernmost station 0806 show Ba maximal values due to intrusion of high saline water masses (Arabian Sea High Saline Water and North Indian Intermediate Water) sourced from the Arabian Sea. The signatures of these water masses further north in the BoB are masked by the Ba supply from the G-B river system. In contrast to these advective controls of Ba, a much localized Ba minimum is found at depths ~50-150 m in the central BoB most probably resulting from high productivity in the region that favors the particle reactive nature of Ba in surface layer of the BoB. Ba concentration in deep waters increases steadily with depth up to three fold compared to that in surface waters indicating substantial regeneration of particulate barium in deep waters.

Considering a two box model under steady state conditions, mass balance calculations on an annual scale resulted into no net lateral outflow of dissolved Ba to the global oceans from top ~ 100 m of the BoB, despite its large influx from the G–B river system. This Ba influx leaves the surface layer in sinking particulate

form to the deep waters, where ~ 95 % of this large particulate flux of Ba is regenerated again to the dissolved phase. Therefore, deep waters of the Bay of Bengal receiving a large Ba influx through particle remineralization can be a significant source of dissolved Ba to the Indian Ocean.

8.1.5 Temporal variations in boron isotope composition of planktonic foraminifera from the southeastern Arabian Sea

Temporal variations in boron isotope composition of the G. Sacculifer (planktonic foraminifera) have been measured to reconstruct the paleo-pH levels in the southeastern Arabian Sea. However, due to potential contamination of these samples by continental detritus the reconstructed paleo-pH is too low (~7.3) reflecting unrealistically high pCO₂ levels. Thus, the current data set of δ^{11} B is not suitable for paleo-reconstructions of the pCO₂ of the Arabian Sea surface waters.

8.2 Future directions

High resolution data of selected TEIs collected in this study has led us to interesting aspects about their macro-scale geochemistry and the water mass structure of the Bay of Bengal. The results obtained in this thesis lead to interesting research topics to better understand the various bio-geochemical processes occurring in a natural oceanic system, which can be pursued in future. These are appended below:

- 1. Spatial distributions of U, Mo and Re concentrations in oxic as well as suboxic conditions indicate no discernible removal of these elements, despite a high particulate matter sinking to the seafloor. However, the authigenic enrichment of these elements in suboxic sediments of various oceanic basins argues in favor of their removal from the water column. Further investigation of these elements in dissolved and particulate (both sinking as well as suspended) phases under diverse marine oxygenation conditions (oxic, suboxic, anoxic, euxinic) are required to resolve the issue.
- 2. Limited data of Re concentration from surface layer of the central Bay of Bengal show its high value that is probably contributed by the fresh water

supply from the Godavari River. More data of Re concentration in the surface layer of the BoB extending up to the river mouth is required to confirm this and to use Re as a tracer of fresh water plume of the Godavari River in the BoB.

- 3. The dissolved REEs concentrations and isotope composition of Nd in water column of the Bay of Bengal hints at possible supply of these TEIs by sediment efflux from the northern region in the vicinity of the G–B river system. Sediment pore water data of REEs and ε_{Nd} is required to apportion their contributions from *in situ* particle regeneration and benthic fluxes in controlling REEs budget in the Bay of Bengal.
- 4. The contribution of dissolved TEIs to the surface waters of the Bay of Bengal from the peninsular rivers of India is presumably neglected considering their low sediment as well as water discharge. However, as observed in studies pertaining to this thesis, the net influxes of particle reactive trace elements are usually modified in the estuarine regions. Thus, direct measurement of these TEIs in the estuarine regions of major and medium rivers is required to learn about their contributions to the surface oceans.
- 5. Barium cycle in the Bay of Bengal is investigated under the basic assumption that particulate biogenic Ba fluxes in the region is similar to that in the Arabian Sea. This assumption has to be tested by direct measurement of particulate biogenic Ba determination in the sinking particulate matter collected from various depths throughout the region.
- 6. Temporal variations of boron isotope composition of carbonate shells of planktonic foraminifera from the eastern Arabian Sea are required to better constrain the lower limit on past pCO₂ levels of the region. For the purpose, more rigorous cleaning of carbonate shells from detrital phases is required.

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1. Singh S.P., Singh S.K. and Bhushan R. (2011). Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal, Marine Chemistry, volume 126, pages 76–88, doi:10.1016/j.marchem.2011.04.001

2. Singh S.P., Singh S.K., Goswami V., Bhushan R. and Rai V.K. (2012). Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses. Geochimica et Cosmochimica Acta, volume 94, pages 38–56, doi:10.1016/j.gca.2012.07.017

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Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal

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ABSTRACT

The dissolved concentrations of redox sensitive elements, U, Mo and Re have been measured in the water column of the Bay of Bengal (BoB) to track their distributions and behavior in its suboxic layers at the intermediate depths. The dissolved oxygen content in the intermediate waters (200-800 m) north of ~11°N decreases to values as low as ~3 µmol/. The distribution of U, Mo and Re in the surface waters along the 87°E transect shows a north-south gradient with significant correlation with salinity, underscoring the dominant influence of the Ganga-Brahmaputra (G-B) Rivers in controlling the geochemical budgets of these three elements. The concentrations of these three elements in surface and deep waters of the BoB are governed by salinity suggestive of their conservative behavior. On a macroscale, there is no discernable removal of U, Mo, or Re from the suboxic layer in the BoB water column, consistent with earlier studies in the suboxic zones of other oceanic regions. Further, their conservative behavior in the bay, suggest that the annual delivery of $\sim 10^9$ tons of suspended matter rich in organic matter by G–B and other rivers do not have any measurable impact in determining their distributions. This study suggests that the suboxic conditions and high particulate flux prevailing in the water column of the Bay of Bengal do not affect the conservative behavior of U, Mo and Re. The dissolved Re concentrations in the upper layers in the central BoB seem to be marginally higher compared to that expected based on their salinities. This seems to be contributed from the Godavari River, which drains into the BoB and has dissolved Re three times higher than seawater. The higher Re concentrations in the central Bay of Bengal suggest that mixing process by local gyre and/or eddies in the BoB transports riverine dissolved material to ~400 km offshore. More detailed transects of Re from the Godavari coast to central bay are needed to confirm this.

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1. Introduction

The concentrations and the distributions of redox sensitive elements (RSEs), Fe, Mn, U, Mo, Re and V in sediments, have been used extensively to investigate contemporary and paleo-oceanographic conditions (Calvert and Pedersen, 1993; Crusius et al., 1999; Morford et al., 2001; Nameroff et al., 2002; Nameroff et al., 2004; Pattan and Pearce, 2009; Sarkar et al., 1993; Schenau et al., 2002). The growing interest on the applications of these elements as paleo-redox indicators of oceans requires better understanding of their geochemistry, which includes their sources, transport, internal cycling and sinks. Among the various RSEs, the behavior of U, Mo and Re has been investigated in greater detail as these elements get enriched to a greater extent in sediments compared to many other RSEs due to their higher [metal]_{seawater}/[metal]_{crust} ratio; this has led to their preferential exploitation in paleo-oceanographic research. In the case of Mo, in addition to studies on its

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abundance, its isotope systematics have provided better insight into its oceanic budget (Neubert et al., 2008; Poulson et al., 2006; Siebert et al., 2006; Voegelin et al., 2009). Mo isotopes fractionate significantly during their removal from sea water onto Fe–Mn nodules (i.e. oxic sinks), compared to minor or no fractionation from Mo isotope composition of sea water during their removal into euxinic sediments (i.e. anoxic sinks) (Anbar, 2004; Barling and Anbar, 2004; Barling et al., 2001; McManus et al., 2002). Investigations on the isotopic composition of Mo holds promise for the reconstructions of global ocean paleo-anoxicity and assessing the areal extent of reducing conditions in the oceans on million year time scales (Anbar, 2004; Arnold et al., 2004; Siebert et al., 2003).

The distributions of dissolved U, Mo and Re in well oxygenated oceanic regions show their conservative behavior. In these regions, they occur in their higher oxidation states, $U^{VI}O_2(CO_3)_3^{4-}$, $MO^{VI}O_4^{2-}$, and $Re^{VII}O_4^{-}$. The relatively passive nature of these oxy-anions in oxic seawater is reflected in their long residence times, estimated to be in the range of ~ 10^5 – 10^6 y (Colodner et al., 1993; Dunk et al., 2002; Emerson and Huested, 1991; Rahaman and Singh, 2010). The onset of reducing conditions, particularly anoxic conditions can lower their oxidation states to U^{IV}, Mo^{IV}, and Re^{IV} which are amenable for

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Fig. 1. Sampling locations for dissolved U, Mo and Re in the Bay of Bengal during the cruise SS-259 onboard FORV Sagar Sampada. Please Note: All the contours in this and subsequent figures are plotted in ODV4 software (Schlitzer, 2010). Whereas Bathymetry data for section contours was taken along the cruise track using GMRT grid (http://www.geomapapp.org; Ryan et al., 2009).

sequestrations from dissolved to particulate phases (Bertine, 1972; Colodner et al., 1995; Colodner et al., 1993; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). Such reducing conditions are generally associated with oceanic regions that do not meet the oxygen demand for combustion of organic matter such as land locked seas/channels or continental margins with restricted ventilation. The chemical speciation of U, Mo and Re in reducing oceanic water column is not well constrained compared to that in oxygenated waters and the processes promoting their removal from such regions are still debated. Among these three elements, Mo actively participates in bio-geochemical processes, being a cofactor in enzymes (Falkowski, 1983), however its distribution in the water column does not seem to be affected by its involvement in these processes (Bruland et al., 2003). In contrast, there is no evidence to

Table 1	1
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Details of sampling locations in the Bay of Bengal.

Station	Latitude ([°] N)	Longitude ([°] E)	Sampling depth (m)	No. of samples
SS259-0806	5.813	86.997	5-3800	21
SS259-08-S1	6.990	86.938	Surface	1
SS259-08-S2	8.021	86.990	Surface	1
SS259-0807	8.494	87.007	5-3550	16
SS259-08-S3	9.974	86.805	Surface	1
SS259-0808	11.270	86.990	5-3200	15
SS259-08-S4	12.405	86.994	Surface	1
SS259-0809	13.769	87.004	5-2900	15
SS259-08-S5	14.572	88.066	Surface	1
SS259-08-S6	15.373	89.104	Surface	1
SS259-0810	16.420	90.498	5-2350	17
SS259-08-S7	16.457	89.471	Surface	1
SS259-08-S8	16.697	87.420	Surface	1
SS259-0811	16.759	86.993	5-2500	18
SS259-0812	18.759	86.997	5-2000	14
SS259-0813	20.047	87.262	5-640	8
SS259-0814	20.537	87.476	4-45	2
SS259-0815	20.975	87.778	4-30	2
SS259-0816	20.571	88.107	4-30	2
SS259-0817	20.836	88.492	5-70	2
SS259-0818	21.003	88.996	5-60	2
SS259-0819	20.576	88.753	5-110	2
SS259-0820	20.585	88.249	5	1

suggest active participation of U and Re in bio-geochemical processes; though, U is known to form organo-metallic complexes. These complexes can contribute to its authigenic deposition in coastal and margin environments, the preservation of which depends on bottom water oxygen concentration (Anderson, 1982; Chappaz et al., 2010; Zheng et al., 2002).

There have been studies on the removal of these three redox sensitive elements from the seawater to sediments, particularly to sediments underlying suboxic/anoxic waters, such as the Arabian Sea, Black Sea, Cariaco Trench, Saanich Inlet and the eastern tropical North Pacific (Anderson et al., 1989b; Barnes and Cochran, 1990; Colodner et al., 1995; Colodner et al., 1993; Crusius et al., 1996; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). These studies have brought out the role of diffusion in pore waters and various carrier phases (Dellwig et al., 2010; Nealson et al., 1991; Tebo, 1991) in sequestering these elements to sediments. Some of these studies also have underscored the importance of element dependent microbial processes in their reduction and sequestration, for example in the reduction of U compared to that of Mo and Re (McKee and Todd, 1993; Morford et al., 2009).

Studies in the Black Sea (Anderson et al., 1989a; Colodner et al., 1995; Emerson and Huested, 1991), demonstrated that all these three elements are depleted in the euxinic deeper waters; suggesting their removal from the water column. The mechanism(s) and sites of their removal, however, remain to be fully established. In case of Mo, interconversion of molybdates to more particle reactive intermediate thiomolybdates when H₂S exceeds a threshold value has been suggested as a mechanism for its removal in sediments (Erickson and Helz, 2000; Vorlicek and Helz, 2002; Vorlicek et al., 2004). In contrast to investigation of these elements in sediments, there are, however only limited studies on their behavior in suboxic/reducing water columns. Study in the Cariaco Trench (Anderson, 1987) does not indicate any measurable variation of U concentration in oxygen minimum zone (OMZ) compared to that in oxygenated waters. However, uranium distribution in the water columns of the Arabian Sea and Framvaren Fjord and sediment trap studies in BoB (Bay of Bengal) hinted towards its possible removal from the OMZ (McKee and Todd, 1993; Rengarajan et al., 2003; Sarin et al., 2000). Studies pertaining to Mo and Re distribution in the water columns associated with OMZ are limited.

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Table 2 (continued)

Temp pH

Salinity DO

U

Мо

Re

40.6

40.2

40.3 39.9

40.6

40.5

39.6

41.7

41.6

41.5

41.5

41.2

41.8

42.1

42.5

42.4

43.5

41.7

42.2

42.2

40.9

41.4

41.6

37.2

37.3

39.2

40.6

40.5

40.9

40.7

40.6

40.1

40.5

40.1

41.0 40.7

40.8

40.9 39.7

40.0

41.6

40.8

40.0

45.0

42.0

43.7

41.6 41.4

39.8

39.8

41.1

42.2 43.3

40.7

41.0

42.0

41.0

42.2

_

(pmol/kg)

Depth (m)

Table 2

Temperature, pH, salinity, DO and concentrations of dissolved U, Mo and Re in seawater from surface and depth profiles of the Bay of Bengal.

UIII SUITACE all	ia aeptn	proni	es of the	Bay of Ber	igal.				(°C)			(µmol/l)	(nmol/kg)	(nmol/kg)
Depth (m)	Temp	pН	Salinity	DO	U	Мо	Re	SS259-0808						
	(°C)			(µmol/l)	(nmol/kg)	(nmol/kg)	(pmol/kg)	1200	5.5	7.79	34.9	66.3	14.0	-
SS259-0806								1400	4.7	7.82	34.8	79.2	-	112
5	29.3	8.36	33.4	217.2	13.5	109	39.4	1700	3.4	7.81	34.8	99.7	13.8	-
60	27.5	7.82	35.0	27.7	14.0	116	40.0	2000	2.7	7.83	34.8	109.9	-	113
60R	-	-	-	-	14.2	115	40.7	2300	2.2	7.83	34.8	133.8	14.0	113
130	18.6	7.97	34.8	50.2	14.0	114	40.2	2300R	-	-	-	-	14.0	-
200	13.8	7.87	35.0	24.9	13.9	115	40.8	2600	2.0	7.80	34.7 24.7	140.8	-	112
290	11.8	7.83	35.1	23.3	14.0	114	41.0	2900	1.0	7.65	34.7 34.7	147.7	13.9	- 112
380	11.1	7.83	35.1	38.8	14.0	114	40.8	5200	1.0	7.00	54.7	151.0	14.0	115
460	10.4	7.81	35.0	24.0	14.1	114	40.5	\$\$259-0809						
520	10.1	7.80	35.0	23.2	-	-	-	5	28.7	8.35	33.2	207.5	13.3	109
500	9.5	7.79	35.0	26.7	14.0	115	40.5	85	25.3	8.10	35.0	80.7	13.9	113
200	8.9 9 1	7.80	35.0	34.0 24.9	-	-	-	180	15.0	7.84	35.0	9.1	13.8	113
900	7.4	7.80	35.0	J4.0 11 Q	14.0	-	40.7	180R	-	-	-	-	13.8	114
1000	67	7.80	34.9	56.2	14.0	114	40.8	300	11.6	7.79	35.0	8.0	14.0	114
1200	5.8	7.82	34.9	62.4	14.0	114	41.1	400	10.6	7.79	35.0	8.0	14.0	114
1200R	-	-	-	-	13.9	113	-	500	9.8	7.79	35.0	9.9	13.9	113
1400	5.0	7.81	34.9	76.9	13.9	113	40.6	600	9.1	7.79	35.0	31.8	13.9	114
1700	3.5	7.83	34.8	100.1	14.1	114	40.3	700	8.3	7.79	35.0	23.5	13.9	113
2000	2.7	7.85	34.8	123.5	13.9	113	41.3	700R	-	-	-	-	-	115
2000D	2.7	7.87	34.8	121.4	14.0	116	40.8	800	7.8	7.79	35.0	28.1	13.8	114
2300	2.3	7.87	34.8	130.6	13.9	112	40.3	900	7.3	7.79	35.0	37.8	13.8	113
2600	2.0	7.87	34.7	145.7	14.0	112	40.4	1000	6.6	7.80	34.9	47.2	13.8	114
2900	1.8	7.88	34.7	156.4	14.0	113	40.3	1200	5.7	7.79	34.9	63.1	-	-
3200	1.6	7.88	34.7	162.5	14.1	114	40.9	1400	4.9	7.81	34.9	74.4	13.8	114
3200R	-	-	-	-	14.1	116	-	1400K	-	-	-	-	13.8	114
3500	1.5	7.89	34.7	167.8	13.9	113	40.4	1700	3.0	7.01	34.8	98.8	-	-
3800	1.4	7.91	34.7	168.6	13.9	113	40.9	2000	2.0	7.05	24.0	121.2	15.0	115
								2500	2.5	7.04	24.0	120.1	-	- 112
SS259-0807								2000	2.0	7.85	34.7	158.0	13.9	115
5	29.2	8.38	33.3	208.6	13.4	108	39.3	2900R	- 1.7	-	-	-	13.8	112
5R	-	-	-	-	13.4	108	39.4	25000					15.0	114
70	27.3	8.20	34.9	110.6	13.9	114	41.2	\$\$259-0810						
110	21.9	7.94	34.9	27.3	-	-	-	5	284	8 36	32.1	218 3	12.9	105
160	16.5	7.88	35.0	24.1	14.0	114	40.7	5R	-	-	-	-	12.9	104
220	14.2	7.87	35.I	26.9	-	-	-	40	28.9	8.36	33.5	213.8	13.3	107
300	12.2	7.83	35.1	15.0	14.1	114	41.2	140	20.7	7.94	34.6	14.1	13.7	113
400	10.9	7.79	25.0	19.1	14.1	115	40.7	200	14.3	7.85	35.0	4.1	13.7	114
400D 500	10.9	7.80	35.0	- 10.2	14.0	-	41.0	300	11.5	7.81	35.0	9.0	13.8	114
600	9.1	7.80	35.0	27.8	14.0	114	41.1	400	10.6	7.80	35.0	12.6	13.9	114
800	7.9	7.79	35.0	36.5	14.1	114	41.0	500	10.0	7.80	35.0	12.6	13.8	113
900	7.2	7.79	35.0	45.8	14.0	115	40.6	500R	-	-	-	-	-	114
1000	6.7	7.80	34.9	50.4	14.0	116	40.4	600	9.3	7.80	35.0	16.7	13.8	113
1100	6.2	7.82	34.9	52.9	-	-	-	700	8.6	7.80	35.0	22.9	13.9	114
1300	5.3	7.82	34.9	73.7	14.1	115	41.9	800	7.9	7.80	35.0	28.0	13.8	112
1500	4.4	7.84	34.8	86.4	14.0	114	41.7	1000	6.7	7.81	34.9	41.6	13.8	114
1500R	-	-	-	-	14.0	112	40.9	1000R	-	-	-	-	14.1	113
1800	3.2	7.85	34.8	104.4	-	-	-	1200	5.7	7.82	34.9	59.6	13.9	112
2100	2.6	7.86	34.8	117.9	14.0	113	41.0	1400	4.9	7.82	34.9	72.3	13.9	113
2400	2.2	7.86	34.8	137.7	-	-	-	1700 1700R	3.0	7.83	34.8	99.2	13.8	113
2700	1.9	7.88	34.7	146.0	14.0	114	41.4	1700K	-	- 7.95	-	-	-	- 112
3000	1.7	7.89	34.7	155.2	-	-	-	2000	2.7	7.05	34.0	121.0	13.9	112
3300	1.6	7.90	34.7	186.5	13.9	114	41.4	2200	2.4	7.80	34.8	123.4	13.0	115
3550	1.4	7.91	34.7	169.7	14.0	114	41.4	2550	2,2	7.07	54.0	155.4	13.5	112
3550R	-	-	-	-	14.0	113	-	\$\$259-0811						
66250 0000								5	283	8 38	33.9	207.2	13.5	109
55259-0808	20.0	0.25	22.2	205.1	10.5	100	20.0	5R	-	-	-	-	-	110
5	28.8	8.35	33.3	205.1	13.5	108	38.9	70	23.8	7.97	34.7	13.6	13.7	112
70	25.7	8.10	34.9	72.2	13.8	114	-	110	19.8	7.93	34.9	10.9	13.8	114
70D	23.7	8.07	34.9	2.00	14.1	113	-	180	15.5	7.86	35.0	5.7	13.8	113
175 175D	14.8	7.80	34.9	3.2	14.0	113	41.2	180R	-	-	-	-	13.7	113
1/JK 280	-	- 7 0 1	-	- 0.6	14.0	114	40.5	300	11.6	7.80	35.0	9.3	13.8	115
200 380	10.6	7.01 7.70	35.0	9.0 14.4	14.0	11J 11/	-10.0	400	10.6	7.80	35.0	6.8	13.9	114
3800	10.0	7.79	35.0 35.0	14.4	14.2 1 <u>/</u> 1	114	40.5	400R	-	-	-	-	-	-
495	0.0	7 70	35.0	14.4	14.1 14.1	114	41.6	500	9.8	7.81	35.0	6.1	13.8	113
-99 600	9.0	7 70	35.0	14.J 22.1	14.1	116	40.8	600	9.1	7.81	35.0	18.6	13.8	113
700	80.9	778	35.0	26.2	-	-	40.0	700	8.5	7.81	35.0	18.9	13.8	113
,00	0.2 7.6	7.70	34.0	36.0	-	- 114	-101	900	7.3	7.82	35.0	38.0	13.9	114
XIIII	1.0	1.19	J-1.J	10.9	-	117	40.2	1100	6.3	7.83	34.9	52.9	13.9	113
900	70	7 7 2	34.4	4)×	1411	115	40.3							
900 900R	7.0	7.78 -	34.9	42.8	14.0	-	40.3	1100R	-	-	-	-	13.8	113

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Table 2 (continued)

SS29-0811UUUUU15003.77.843.4310.3113.811.711.341.019003.17.853.4811.1613.711.340.621002.07.853.4811.513.711.340.225002.07.843.4811.513.711.341.225002.07.843.4813.213.811.241.811018.77.913.496.013.811.240.820001.57.835.04.94.011.440.620011.57.835.05.01.4111.440.760011.57.805.07.61.4111.440.760029.97.815.07.501.4111.440.760037.83.505.31.4011.440.5120047.67.803.94.211.4111.540.5120055.67.813.497.591.4011.440.7120047.47.833.489.841.4011.440.5120055.57.843.421.331.1440.5120067.17.833.507.31.3110.63.8120067.17.833.507.31.3110.63.8120077.47.831.341.341.1	Depth (m)	Temp (°C)	pН	Salinity	DO (µmol/l)	U (nmol/kg)	Mo (nmol/kg)	Re (pmol/kg)
1500 4.6 7.84 34.9 85.3 13.8 11.7 41.1 1900 3.1 7.84 34.8 10.1 13.8 11.7 11.3 40.6 2100 2.6 7.85 34.8 11.6 13.7 11.3 40.3 2300 2.0 7.84 34.8 13.15 13.7 11.3 40.3 2500 2.0 7.84 34.7 13.96 13.8 11.2 40.8 SX259-0817 - - 14.0 11.2 40.8 12.2 40.4 110 18.7 7.91 34.9 6.00 13.8 11.2 40.4 110 1.5 7.83 35.0 4.9 14.0 11.4 40.2 200 1.3 7.80 35.0 4.9 14.0 11.4 40.6 110 1.6 7.81 35.0 7.6 14.1 11.4 40.7 600 1.1 11.4 11.4 11.4 40.5 12.0 12.0 12.5 7.86 3.0 1	SS259-0811							
1700 3.7 7.84 34.8 11.6 13.7 113 40.6 2100 2.6 7.85 34.8 11.6 13.7 113 40.3 2200 2.0 7.84 34.7 13.9 11.3 41.2 2500 2.0 7.84 34.7 13.9 11.3 40.8 S2259-0812 - - - 10.0 13.8 112 40.8 50 25.9 8.04 34.3 31.2 13.8 112 40.4 100 18.7 7.91 34.9 6.0 13.8 112 40.4 100 15.7 7.83 35.0 4.7 14.0 114 40.6 200 13.3 7.87 35.0 7.6 14.1 114 40.6 500 9.9 7.81 35.0 7.6 14.1 114 40.6 600 1.4 11.1 14.0 11.4 36.6 36.8 12.0 13.8 114 40.6 12000 - -	1500	4.6	7.84	34.9	85.3	13.8	117	41.1
1900 3.1 7.85 3.48 111.6 13.7 113 40.6 2300 2.0 7.85 3.48 113.5 13.7 113 40.3 2300 2.0 7.85 3.48 113.5 13.7 113 40.3 S259-0812 - - 13.8 112 40.4 110 13.7 7.85 3.49 6.0 13.8 112 40.4 110 13.7 7.87 35.0 4.9 14.0 114 40.6 200 13.3 7.80 35.0 7.41 114 40.4 400 10.6 7.81 35.0 7.6 14.1 114 40.7 600R - - - 14.0 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 1200 7.7 8.37 3.4 13.1 10.6 20.6 1200	1700	3.7	7.84	34.8	103.1	13.8	113	41.0
2100 2.6 7.85 34.8 113.7 113 40.3 2500 2.0 7.84 34.7 139.6 13.8 113 40.8 SS259-0812 5 2.6 3.3 32.0 2.16.4 13.0 103 37.6 50 2.5 8.04 34.3 11.2 13.8 112 40.4 110 1.8.7 7.91 34.9 6.0 13.8 112 40.4 200 13.3 7.87 35.0 4.9 14.0 114 40.6 300 1.5 7.83 35.0 7.6 14.1 114 40.6 500 9.3 7.80 35.0 16.0 114 40.3 6000 8.1 7.80 35.0 2.44 14.0 114 40.3 1000 6.7 7.80 34.9 7.60 14.0 114 40.3 1100 3.4 7.83 34.8 94.4 14.0 </td <td>1900</td> <td>3.1</td> <td>7.85</td> <td>34.8</td> <td>111.6</td> <td>13.7</td> <td>113</td> <td>40.6</td>	1900	3.1	7.85	34.8	111.6	13.7	113	40.6
2300 2.3 7.85 34.8 131.5 13.7 113 41.2 2500 2.0 7.84 34.7 139.6 13.8 113 40.8 SS259-0812 5 27.6 8.36 32.0 216.4 13.0 103 37.6 50 25.8 8.04 34.3 50.0 13.8 112 40.4 100 13.7 7.87 35.0 4.9 14.0 114 40.6 300 1.5 7.83 35.0 7.6 14.1 114 40.7 600R - - - 14.0 114 40.3 1000 6.7 7.80 35.0 7.6 14.1 114 40.7 1000 6.7 7.80 34.9 6.00 14.0 114 40.3 1000 6.7 7.83 34.8 9.8 14.0 114 40.5 2000 2.5 7.83 34.8 9.8	2100	2.6	7.85	34.8	118.7	13.7	113	40.3
2500 2.0 7.84 34.7 139.6 13.8 113 40.8 SS259-0812 5 2.6 8.04 3.1 13.8 112 41.8 110 18.7 7.91 34.9 6.0 13.8 112 40.4 200 13.3 7.87 35.0 4.9 14.0 114 40.6 300 11.5 7.83 35.0 4.7 14.0 114 40.6 500 9.9 7.81 35.0 7.6 14.1 114 40.6 6000 8.1 7.80 35.0 10.7 14.0 114 40.9 6000 8.1 7.80 34.9 42.1 14.1 115 40.5 12000 5.6 7.81 34.9 60.0 14.0 114 49.5 2000R - - - 14.1 114 40.5 2000R - 7.83 34.9 84.14.0 114	2300	2.3	7.85	34.8	131.5	13.7	113	41.2
SS259-0812 V V V 5 27.6 8.36 32.0 21.6.4 13.0 103 37.6 50 25.5 8.04 34.3 31.2 13.8 112 40.4 110R - - - 14.0 112 40.8 200 13.7 7.80 35.0 4.7 14.0 114 40.6 300 1.5 7.83 35.0 4.7 14.0 114 40.6 500 9.9 7.81 35.0 7.6 14.1 114 40.6 600R - 14.0 113 40.9 800R 8.1 7.80 35.0 2.84 14.0 114 40.3 1000 5.6 7.81 34.9 6.00 14.0 113 -0 1000 5.6 7.81 34.9 8.4 14.0 114 40.5 2000 2.5 7.83 34.8 124.2 13.9 115 40.6 2000 2.5 7.83 34.8 124.2 13.9 114 40.5 2000 2.5 7.81 35.0 7.3 13.1 104	2500	2.0	7.84	34.7	139.6	13.8	113	40.8
Solution 27.6 8.36 32.0 21.64 13.0 103 37.6 50 25.9 8.04 34.3 31.2 13.8 112 40.4 110 1.7 7.91 34.9 6.0 13.8 112 40.4 100 1.3 7.87 35.0 4.9 14.0 114 40.6 300 1.15 7.83 35.0 7.6 1.1 11.4 40.7 600 9.9 7.81 35.0 7.6 1.41 11.4 40.7 6000 6.7 7.80 34.9 60.0 1.0 1.14 40.3 1200 5.6 7.81 34.9 60.0 1.0 1.1 40.5 1200 2.5 7.80 34.9 60.0 1.0 1.1 1.40 1.33 - 1200 2.5 7.83 34.8 98.4 14.0 11.4 40.5 20000 2.5 7.83	SS259-0812							
50 25.9 8.04 34.3 31.2 13.8 112 41.8 110 18.7 7.91 3.49 6.0 13.8 112 40.4 200 13.3 7.87 35.0 4.9 14.0 114 40.6 300 11.5 7.83 35.0 7.6 14.1 114 40.7 400 10.6 7.81 35.0 7.6 14.1 114 40.7 600 8.0 7.80 35.0 10.7 14.0 113 40.9 800 8.1 7.80 34.9 42.1 14.1 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 113 - 1200 5.5 7.81 34.9 60.0 14.0 114 40.5 2000 2.5 7.86 34.8 94.4 13.0 114 40.5 2000 2.5 7.86 34.3 12.4	5	27.6	8.36	32.0	216.4	13.0	103	37.6
110 1.8.7 7.91 34.9 6.0 13.8 112 40.4 110R - - 1.40 112 40.8 200 13.3 7.87 35.0 4.7 14.0 114 40.2 300 10.5 7.81 35.0 7.6 14.1 114 40.6 600 9.9 7.81 35.0 7.6 14.1 114 40.6 600R - - - 14.0 114 40.5 1000 6.7 7.80 34.9 42.1 14.1 114 40.5 1200 5.6 7.81 34.9 9.6.0 14.0 114 40.5 1200 5.6 7.81 34.9 9.6.0 14.0 114 40.5 1200 5.6 7.81 34.9 9.6.0 14.0 114 40.5 1200 7.7 8.37 3.2.7 14.1 114 40.5 2000R - - - 13.3 114 40.5 2000R	50	25.9	8.04	34.3	31.2	13.8	112	41.8
110R - - - 14.0 112 408 200 13.3 7.87 35.0 4.9 14.0 114 40.6 300 11.5 7.83 35.0 5.3 14.0 114 40.6 400 10.6 7.81 35.0 7.61 14.1 114 40.7 600R - - - 14.0 114 40.3 600R - - - - 14.0 114 40.3 1000 6.7 7.80 34.9 42.1 14.1 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 1200 4.7 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 124.2 13.9 115 40.6 2000R - 7.83 3.7 14.4 14.0 14.4 40.2 2000R - 7.83 3.7 14.3 114 40.4 40.6<	110	18.7	7.91	34.9	6.0	13.8	112	40.4
200 13.3 7.87 35.0 4.9 14.0 114 40.6 300 11.5 7.83 35.0 4.7 14.0 114 40.6 500 9.9 7.81 35.0 7.6 14.1 114 40.7 600 9.3 7.80 35.0 2.8.4 14.0 114 40.3 600 6.1 7.80 35.0 2.8.4 14.0 114 40.3 1000 6.7 7.80 34.9 4.0.0 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.1 106 38.6 70 24.0 7.99 34.7 8.4 13.7 - 41.3 110 7.4 7.83 35.0 12.4 14.0	110R	-	-	-	-	14.0	112	40.8
300 11.5 7.83 35.0 4.7 14.0 114 40.2 400 10.6 7.81 35.0 7.6 14.1 114 40.7 600 9.3 7.80 35.0 1.0.7 14.0 113 40.9 600R - - 14.0 114 40.7 600R - - 14.0 114 40.7 800 6.7 7.80 34.9 60.0 14.0 114 40.5 1200 5.6 7.81 34.9 75.9 14.0 114 40.5 1200 4.7 7.81 34.9 75.9 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000 2.5 7.83 32.7 214.5 13.1 106 38.6 70 2.40 7.99 34.7 8.4 13.7 114 40.2 7	200	13.3	7.87	35.0	4.9	14.0	114	40.6
400 10.6 7.81 35.0 7.3 14.0 114 40.6 500 9.3 7.80 35.0 10.7 14.0 114 40.7 600R - - - 14.0 113 40.9 600R - - - 14.0 114 40.3 600R - - - 14.1 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 1200R - - - 14.1 114 - - 1200R 2.5 7.86 34.8 124.2 13.9 115 40.6 2000 2.5 7.86 34.8 13.7 114 40.2 2000 2.4 7.89 34.7 13.8 114 40.7 2000 1.7 7.83 35.0 12.4 14.0 114 40.7 500 1.1 7.82<	300	11.5	7.83	35.0	4.7	14.0	114	40.2
500 9.9 7.81 35.0 7.6 1.4.1 1.14 40.7 600 14.0 113 40.9 800 8.1 7.80 35.0 28.4 14.0 114 40.3 1000 6.7 7.80 34.9 42.1 14.1 115 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 40.5 1200 5.6 7.81 34.9 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 98.4 14.0 114 40.5 2000R - - - 13.7 115 40.6 2000R - - - 13.1 106 38.6 70R - 8.7 8.4 13.2 114 40.4 250 12.4 7.80 35.0 3.4 13.8 114 40.6 440	400	10.6	7.81	35.0	5.3	14.0	114	40.6
600 9.3 7.80 35.0 10.7 14.0 114 39.6 600R - - - 14.0 113 40.9 800 6.1 7.80 34.9 62.1 14.1 114 40.3 1000 6.7 7.80 34.9 60.0 14.0 114 40.5 1200 5.6 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000 2.5 7.86 34.8 124.2 13.9 114 40.5 2000 2.5 7.86 34.8 13.2 114 40.2 2000 2.5 7.86 35.0 7.3 13.1 116 40.5 250 17.1 7.80 35.0 12.4 14.0 114 <	500	9.9	7.81	35.0	7.6	14.1	114	40.7
600R - - - 14.0 113 40.9 800 8.1 7.80 35.0 28.4 14.0 114 40.5 1200 5.6 7.81 34.9 60.0 14.0 114 39.8 1200R - - - 14.1 114 - - 1400 4.7 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - 14.0 113 - S259-0813 - - 14.0 113 40.2 70R - - - 113 40.2 70R - - - 114 40.4 250 1.1 7.8 35.0 12.4 13.0 <td< td=""><td>600</td><td>9.3</td><td>7.80</td><td>35.0</td><td>10.7</td><td>14.0</td><td>114</td><td>39.6</td></td<>	600	9.3	7.80	35.0	10.7	14.0	114	39.6
800 8.1 7.80 35.0 28.4 14.0 114 40.3 1000 6.7 7.80 34.9 60.0 14.0 114 39.8 1200R - - - 14.1 114 - 1400 4.7 7.81 34.9 75.9 14.0 114 40.5 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000R - - - 14.0 113 - S259-0813 - - - 14.0 114 40.5 2000R - - - - 14.0 114 40.6 70 24.0 7.99 34.9 36.1 13.8 114 40.5 50 17.1 7.89 35.0 7.3 14.1 114 40.6 440 14.4 7.83 35.0 7.3 14.1 114 40.5 550R	600R	-	-	-	-	14.0	113	40.9
1000 6.7 7.80 34.9 42.1 14.1 115 40.5 1200 - - - - 14.1 114 - 1200 4.7 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000 - - - 14.0 113 - SS259-0813 - - - 14.0 113 - SS259-0814 - - - 13.7 - 41.3 TOR - - - - 11.3 40.2 SS250 12.4 7.88 35.0 3.4 13.8 114 40.4 250 12.4 7.80 35.0 12.4 14.0 113 40.5 500 1.5.1	800	8.1	7.80	35.0	28.4	14.0	114	40.3
1200 5.6 7.81 34.9 60.0 14.0 114 39.8 1200R - - 14.1 114 - 1400 4.7 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - 14.0 113 - - 5 27.7 8.37 32.7 214.5 13.1 106 38.6 70R - - - 1.37 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.5 250R - - - - 1.4 113 40.4 250 9.5 7.81 35.0 7.3 14.1 114 40.7 550	1000	6.7	7.80	34.9	42.1	14.1	115	40.5
1200R - - - - 14.1 114 - 1400 4.7 7.81 34.9 75.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - 14.0 113 - SS259-0813 - - - 14.0 114 40.2 70 24.0 7.99 34.7 8.4 13.7 - 41.3 150 17.1 7.88 35.0 3.4 13.8 114 40.4 250 12.4 7.88 35.0 7.3 14.1 114 40.1 500 11.1 7.80 35.0 7.24 14.0 113 40.9 550R - - - - 14.0 113 40.7	1200	5.6	7.81	34.9	60.0	14.0	114	39.8
1400 4.7 7.81 34.9 7.5.9 14.0 113 - 1700 3.4 7.83 34.8 98.4 14.0 113 - 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - - 14.0 113 - SS259-0813 - - - 14.0 113 - SZ59-0813 - - - 13.7 - 41.3 70R - - - 13.7 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.4 250R - - - - - 115 - 350 11.1 7.82 35.0 7.3 14.1 114 40.5 550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 S5259-0815	1200R	-	-	-	-	14.1	114	-
1700 3.4 7.83 34.8 98.4 14.0 114 40.5 2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - 14.0 113 - SS259-0813 - - 14.0 113 - - SS259-0813 - - 13.7 - 41.3 70R - - - 13.7 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.4 250R - - - - 115 - - 350 11.1 7.82 35.0 7.3 14.1 114 40.6 440 10.4 7.80 35.0 7.3 14.1 114 40.5 550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 S2259-0816 - -	1400	4.7	7.81	34.9	75.9	14.0	113	-
2000 2.5 7.86 34.8 124.2 13.9 115 40.6 2000R - - - 14.0 113 - SS259-0813 - - - 14.0 113 - SV 24.0 7.99 34.7 8.4 13.7 114 40.2 70R - - - 13.7 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.4 250 12.4 7.88 35.0 3.4 13.8 114 40.4 250R - - - - 115 - - 350 11.1 7.82 35.0 7.3 14.1 14.0 40.4 2607 8.1 35.0 12.6 13.9 114 40.7 S5259-0816 - - - 13.8 13.0 102 37.3 S5259-0816 -	1700	3.4	7.83	34.8	98.4	14.0	114	40.5
2000R - - - 14.0 113 - SS259-0813 - - 14.0 113 - SS259-0813 - - 13.7 - 40.2 700 24.0 7.99 34.9 3.6 13.8 114 40.2 70R - - - - 13.7 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.4 250R - 14.0 114 40.40 40.4 40.5 5 50R - - - - 14.0 113 40.9 34.9 35.5 5 50R - - - - 14.0 13.4 40.7 5	2000	2.5	7.86	34.8	124.2	13.9	115	40.6
SS259-0813 5 7.7 8.37 3.2.7 214.5 1.3.1 1.06 3.8.6 70 24.0 7.99 34.7 8.4 1.3.7 1.14 40.2 70R - - 1.3.7 - 41.3 150 17.1 7.89 35.0 3.4 1.3.8 114 40.4 250R - - - 1.5 - 1.5 - 350 1.1.1 7.82 35.0 7.3 1.4.1 1.14 40.6 440 10.4 7.80 35.0 7.3 1.4.1 114 40.5 550R - - - - 1.4.0 113 40.5 550R - - - - 1.4.0 113 40.7 550R - 7.81 35.0 12.6 13.9 114 40.7 5259-0817 - - 12.6 13.0 102 35.1	2000R	-	-	-	-	14.0	113	-
5 27.7 8.37 32.7 214.5 13.1 106 38.6 70 24.0 7.99 34.7 8.4 13.7 114 40.2 70R - - - 13.7 - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.5 250 12.4 7.88 35.0 3.4 13.8 114 40.4 250 12.4 7.88 35.0 12.4 14.0 114 40.6 350 11.1 7.82 35.0 7.3 14.1 114 40.5 550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.0 102 37.3 5259-0816 - - - 12.6 101 - <	SS259-0813							
70 24.0 7.99 34.7 8.4 13.7 114 40.2 70R - - - - - - - 41.3 150 17.1 7.89 34.9 3.6 13.8 114 40.4 250 12.4 7.88 35.0 12.4 14.0 114 40.6 250R - - - - 115 - 350 11.1 7.80 35.0 7.3 14.1 114 40.6 440 10.4 7.80 35.0 7.3 14.0 113 40.9 640 8.9 7.81 35.0 8.6 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 Sz559-0817 - - - 12.3 97 34.9 30 28.3 8.41 31.5 207.1 12.5 101 35.5 Sz559-0817 - - 12.6 100 36.3 36.3	5	27.7	8.37	32.7	214.5	13.1	106	38.6
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550 9.5 7.81 35.0 8.6 14.0 115 40.5 550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 SS259-0814 - - 13.9 114 40.7 4 27.3 8.43 29.6 217.9 12.3 97 34.9 45 28.3 8.41 32.5 213.8 13.0 102 37.3 SS259-0815 - - - 11.5 207.1 12.5 101 35.5 SS259-0816 - - - 12.6 100 36.3 30 28.3 8.38 30.9 183.5 12.6 100 36.3 30R - - - 12.6 101 - - SS259-0817 - - - 12.6 101 - SS259-0818 - 26.7 8.42 29.1 211.0 12.4 99 34.3	440	10.4	7.80	35.0	7.3	14.1	114	41.1
550R - - - - 14.0 113 40.9 640 8.9 7.81 35.0 12.6 13.9 114 40.7 SS259-0814 4 27.3 8.43 29.6 217.9 12.3 97 34.9 45 28.3 8.41 32.5 213.8 13.0 102 37.3 SS259-0815 - - - 12.6 11.0 95 35.1 30 28.1 8.41 31.5 207.1 12.5 101 35.5 SS259-0816 - - - 12.6 100 36.3 30 28.3 8.38 30.9 183.5 12.6 100 36.3 30R - - - 12.6 101 - - SS259-0817 - - - 12.6 101 - SS259-0817 - - - 12.6 101 - SS259-0818 - - - 13.6 110 -	550	9.5	7.81	35.0	8.6	14.0	115	40.5
640 8.9 7.81 35.0 12.6 13.9 114 40.7 SS259-0814 27.3 8.43 29.6 217.9 12.3 97 34.9 45 28.3 8.41 32.5 213.8 13.0 102 37.3 SS259-0815 4 26.7 8.43 29.0 216.3 12.0 95 35.1 30 28.1 8.41 31.5 207.1 12.5 101 35.5 SS259-0816 - - - 12.6 100 36.3 30 28.3 8.38 30.9 183.5 12.6 100 36.3 30R - - - 12.6 101 - SS259-0817 - - 12.6 100 36.3 30R - - - 12.6 101 - SS259-0817 - - - 12.6 101 - SS259-0818 - - - 13.5 108 30.2 5 26.3	550R	-	-	-	-	14.0	113	40.9
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	\$\$259-0814							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4	27.3	8.43	29.6	217.9	12.3	97	34.9
SS259-0815	45	28.3	8.41	32.5	213.8	13.0	102	37.3
SS259-0815 4 26.7 8.43 29.0 216.3 12.0 95 35.1 30 28.1 8.41 31.5 207.1 12.5 101 35.5 SS259-0816 - - 101 35.5 35.1 4 26.5 8.51 24.5 254.2 11.0 82 29.7 30 28.3 8.38 30.9 183.5 12.6 100 36.3 30R - - - 12.6 101 - SS259-0817 - - 12.6 101 - 70 26.7 8.42 29.1 211.0 12.4 99 34.9 70 27.6 8.42 28.1 216.8 13.5 108 40.2 SS259-0818 - - - 13.6 110 - SS259-0819 - - - 13.6 102 37.2 110 20.9 7.97 <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>								
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SS259-0816 SS259-0816 SS2	30	28.1	8.41	31.5	207.1	12.5	101	35.5
SALE26.58.5124.5254.211.08229.73028.38.3830.9183.512.610036.330R12.6101-SS259-0817526.78.4229.1211.012.49934.97027.68.1933.7105.613.510840.2SS259-0818 $ -$ 13.510840.2SS259-0818 $ -$ 13.511039.160R- $ -$ 13.6110 $-$ SS259-0819 $ -$ 13.6110 $-$ SS259-0819 $ -$ 13.610237.211020.97.9734.83.513.811340.3SS259-0820 $ -$ 13.110437.05R $ -$ 13.210738.5SS259-08-51 $ -$ 13.310838.9SIR $ -$ 13.310839.7SS259-08-S2 $ -$ 13.410838.9	\$\$259-0816							
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GOR - - - 13.6 110 - SS259-0819 - - 13.6 110 - SS259-0819 - 20.9 7.97 34.8 3.5 13.0 102 37.2 110 20.9 7.97 34.8 3.5 13.8 113 40.3 SS259-0820 - - - 13.1 104 37.0 5R - - - 13.1 104 37.0 5R - - - 13.1 105 37.5 SS259-08-S1 - - - 13.2 107 38.5 SS259-08-S1 - - - 13.3 108 38.9 SIR - - - 13.3 108 39.7 SS259-08-S2 - - - 13.4 108 38.9	60	26.5	8.19	34.0	92.2	13.5	110	39.1
SS259-0819526.88.4230.7217.713.010237.211020.97.9734.83.513.811340.3SS259-0820527.78.4032.2214.613.110437.05R13.110537.5SS259-08-S113.210738.5SS259-08-S213.310838.9S1R13.310839.7SS259-08-S313.410838.9	60R	-	-	-	-	13.6	110	-
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SS259-08-S1 - - - 13.2 107 38.5 SS259-08- - - - 13.3 108 38.9 S1R - - - 13.3 108 39.7 SS259-08-S2 - - - 13.4 108 38.9	5R	-	-	-	-	13.1	105	37.5
SS259-08- - - - 13.3 108 38.9 SIR SS259-08-S2 - - - 13.3 108 39.7 SS259-08-S3 - - - 13.4 108 38.9	SS259-08-S1	-	-	-	-	13.2	107	38.5
S1R SS259-08-S2 - - - 13.3 108 39.7 SS259-08-S3 - - - 13.4 108 38.9	SS259-08-	-	-	-	-	13.3	108	38.9
SS259-08-S2 - - - 13.3 108 39.7 SS259-08-S3 - - - 13.4 108 38.9	S1R					40.0	100	
SSZS9-U8-S3 13.4 108 38.9	SS259-08-S2	-	-	-	-	13.3	108	39.7
	32259-08-53	-	-	-	-	13.4	108	38.9

Table	2	(continued)
Tubic	~	(commucu)

	Depth (m)	Temp (°C)	рН	Salinity	DO (µmol/l)	U (nmol/kg)	Mo (nmol/kg)	Re (pmol/kg)
	SS259-08-S4 SS259-0820	-	-	-	-	13.4	107	38.9
	SS259-08-S5	-	-	-	-	13.6	108	39.3
	SS259-08-	-	-	-	-	13.5	108	-
	S5R							
	SS259-08-S6	-	-	-	-	13.4	107	39.1
	SS259-08-S7	-	-	-	-	13.0	103	37.2
	SS259-08-	-	-	-	-	13.0	103	37.4
	S7R							
	SS259-08-S8	-	-	-	-	13.5	107	38.9
-:	not measured							

R: repeat analysis of the same sample.

D: Duplicate sampling from the same water depth.

The present study is on the distribution and behavior of U, Mo and Re in the water column of the Bay of Bengal. This investigation is motivated by two principle considerations, (1) the BoB is an oceanic region which receives a large quantity of fresh water and suspended matter, 1887 km³/year and 2.1×10^{12} kg/year, respectively, from various rivers, the Ganga-Brahmaputra, Godavari, Irrawadi-Salween, Krishna, Cauveri, and the Mahanadi (Bird et al., 2008; http://www. cciw.ca/atlas-gwq/table3-e.html). Sediment trap studies in the deep and shallow BoB have reported total particulate matter flux ranging from 29 to 63 g m⁻² y⁻¹ with lithogenic fraction varying from 15% at the distal southernmost site to 46% at the site near the continental margin (Ramaswamy and Gaye, 2006; Unger et al., 2003). The particulate matter flux shows significant seasonal and inter-annual variations. The bay, therefore serves as a natural laboratory to investigate the role of fresh water and suspended matter in governing the distribution of various elements and (2) the intermediate water of the bay is suboxic (Rao et al., 1994; Sardessai et al., 2007; Wyrtki, 1971). This provides an opportunity to investigate the role of suboxicity and high particulate input in determining the behavior of RSEs in the water column.

The fresh water discharge into the bay leads to the formation of a thick low salinity water lens over the denser saline water in the BoB causing salinity stratification and inhibiting wind driven vertical mixing in the surface layers. Nutrients supplied by riverine discharge enhance the primary productivity in the coastal region (Ramaswamy and Nair, 1994). The oxidation of sinking organic matter contributed by marine and terrigenous sources results in an oxygen minimum zone at intermediate depths of 200–800 m in the northern BoB (Rao et al., 1994; Sardessai et al., 2007; Wyrtki, 1971). The suboxic conditions in the BoB show seasonal variations, with models suggesting overall oxygen minimum conditions sustained throughout the year by the physical and biological pumps (Sarma, 2002). The abundance and distributions of the redox sensitive elements in oxic and suboxic waters experiencing high particulate fluxes provides a handle to learn about their behavior in these conditions.

2. Materials and methods

2.1. Sampling

Seawater samples from surface and various depths characterized by oxic and suboxic conditions in the water column were collected during November, 2008 onboard FORV Sagar Sampada, cruise SS-259 covering a large meridonal transect along 87°E from 5.8°N to 21.0°N in the northern Bay of Bengal (Fig.1). Several seawater samples were collected near the mouth of the Ganga–Brahmaputra river system (Fig.1). Details of the sampling locations along with the number of samples collected at each station are given in Table 1. The depth profiles of seawater samples were collected using 12 L Niskin bottles mounted on a 12-bottle rosette with a Seabird CTD. A few surface water samples were also collected using a plastic bucket while the

ship was moving. Samples for trace element and isotope (TEI) analysis were filtered through $0.45 \,\mu m$ Millipore filters and acidified to pH ~2 with quartz distilled 6 N HCl and stored in acid cleaned LDPE bottles.

2.2. Onboard analysis

Selected hydrographic and chemical properties of samples were measured onboard. The pH of the samples was measured using a pHmeter (Radiometer, PHM 84). Dissolved oxygen was measured by the Winkler's method (Knap et al., 1996; Strickland and Parsons, 1968) using an auto-titrator (Metrohm, Dosimat 655). These data are presented in Table 2 along with other measured properties. The precision of pH measurements based on repeat measurements is better than 0.02 pH units, whereas for dissolved oxygen the coefficient of variation over its wide range of concentration is 7.1%.

2.3. Measurement of dissolved U, Mo and Re

The concentration of dissolved U and Mo were measured using isotope dilution technique. A known weight of seawater samples were diluted precisely (typically 20-25 times) with 0.4 N HNO₃ to decrease the matrix level and spiked with ²³⁶U and ¹⁰⁰Mo tracers. After complete equilibration of the sample and spike, the intensities of ²³⁸U, ²³⁶U, ⁹⁸Mo and ¹⁰⁰Mo were measured using a guadruple ICP-MS (Thermo Xseries^{II}), the U and Mo concentrations in samples were calculated from the measured isotope ratios. For Re measurements, Re was extracted from a known weight of seawater (typically 30–60 g) following the protocol used in our laboratory (Rahaman and Singh, 2010). Samples were spiked with ¹⁸⁵Re tracer and allowed to equilibrate in oxidizing medium, dried and taken in 0.8 N HNO3. Re was separated from the sample by ion exchange using AG1X-8 (100-200 mesh) resin. Re was eluted from the resin with 8 N HNO₃, dried and the pure Re fraction was dissolved in 0.4 N HNO3. Re concentrations were determined by measuring $^{^{185}}\text{Re}/^{^{187}}\text{Re}$ of the solution using ICP-MS.

Complete procedural blanks for U and Mo were 1.0 ± 0.8 pg (n=2) and 170 ± 20 pg (n=3) respectively, whereas blank for Re was ~2 pg (Rahaman and Singh, 2010). The coefficients of variation (CV %) based on several repeat measurements of various samples are 1, 2 and 1% for U, Mo and Re, respectively.

Along with the samples, an international seawater reference, NASS-5 and estuarine water, SLEW-3 were also analyzed for uranium and molybdenum. The concentrations obtained in these reference samples are consistent within uncertainty with their reported values (Table 3a). Beside these reference materials, a few SAFe (Sampling and Analysis of Fe) seawater samples were also analyzed for U, Mo and Re (Table 3b). Concentrations of U, Mo and Re in these SAFe samples are not reported, however, salinity normalized ratios of these elements are similar to those reported for their open ocean ratios (Anbar et al., 1992; Chen et al., 1986; Collier, 1985; Ku et al., 1977) attesting to the accuracy of measurements.

3. Results

3.1. General observations

The surface water temperatures show a north–south gradient with the lowest temperature (26.3 °C) at the northernmost station, SS259-0818, while the equatorial station, SS259-0806, shows the maximum temperature (29.3 °C; Fig. 2a). Surface waters of shallow coastal stations have pH 8.3–8.4. Salinity (reported on Practical Salinity Scale) contours show a north–south gradient due to fresh water supply from the Ganga–Brahmaputra (G–B) river system (Fig. 2b); the surface water sample salinity ranges from 24.0 to 34.9, with lowest values in the northern station increasing southward (Table 2). Both dissolved oxygen and pH show lower values in intermediate waters (Fig. 2c

Table 3a

U and Mo in reference seawater and estuarine waters.

Standard	U (nmol/kg)		Mo (nmol/kg)		
	This study	Recommended	This study	Recommended	
NASS-5 SLEW-3	$\begin{array}{c} 11.8 \pm 0.1 \; (n\!=\!6) \\ 7.0 \pm 0.1 \; (n\!=\!5) \end{array}$	10.9 ^a 7.6 ^a	$\begin{array}{c} 97\!\pm\!2\;(n\!=\!8)\\ 58\!\pm\!3\;(n\!=\!3) \end{array}$	$\begin{array}{c} 100.1 \pm 10.4 \ (n \!=\! 8) \\ 53.2^{a} \end{array}$	

The errors are 2σ based on 'n' number of measurements.

^a Information value only.

and d, Table 2). In general, dissolved oxygen decreases drastically in the depth interval 200–800 m at all stations sampled in the Bay of Bengal. It becomes suboxic (DO<10 μ mol/l and as low as 3 μ mol/l) at stations north of 11 °N (Fig. 2d) consistent with that reported earlier during the fall-inter-monsoon. The OMZ in the BoB is due to remineralization of sinking organic particles and surface water stratification inhibiting vertical mixing (Gupta and Naqvi, 1984; Rao et al., 1994). The entire OMZ in BoB shows lower pH (Fig. 2c and 3) as a consequence of remineralization of sinking organic debris (Fig. 3).

3.2. The distribution of dissolved U, Mo and Re

The dissolved concentrations of U, Mo and Re measured in the water columns of the Bay of Bengal are given in Table 2. In the surface water (depth \leq 5 m), concentrations of U, Mo and Re increase steadily from a minimum of 11.0 nmol/kg, 82 nmol/kg and 29.7 pmol/kg at the northernmost station, SS259-0816, to 13.5 nmol/kg, 109 nmol/kg and 39.4 pmol/kg respectively at the southernmost station, SS259-0806 (Fig. 4 and Table 2). The increase parallels that of salinity, resulting from north-south decrease in the mixing proportion of river water and seawater. The concentrations of U, Mo and Re in the shallow and deep waters generally vary within a narrow range, 13.7-14.2 nmol/ kg, 112-116 nmol/kg and 39.6-43.5 pmol/kg for the salinity and dissolved oxygen ranges of 34.6-35.1 and 3.2-186.5 µmol/l, respectively (Table 2). The only exception to the trend is surface waters of station SS259-0811, which shows a slightly higher concentration of Re (~45 pmol/kg). The concentration ranges of U, Mo and Re in the BoB are similar to those reported for other oceanic basins (Anbar et al., 1992; Chen et al., 1986; Collier, 1985; Colodner et al., 1993; Ku et al., 1977; Morris, 1975; Nameroff et al., 2002; Rengarajan et al., 2003; Sarin et al., 1994).

4. Discussion

4.1. Dissolved U, Mo and Re in surface waters

Concentrations of dissolved U, Mo and Re in surface waters of the BoB show a north–south gradient mimicking that of salinity (Fig. 4). This trend can be attributed to dilution from supply of river water,

Га	ble	3b						
U,	Mo	and	Re i	n :	SAFe	water	samples	a

SAFe samples	Salinity ^b	U (nmol/kg)	Mo (nmol/kg)	Re (pmol/kg)
		This study	This study	This study
GD-31 S-107 GS-49 D1-242	34.98 34.9 36.65 34.4	$13.9 \pm 0.4 (n=3)$ $13.9 \pm 0.2 (n=3)$ $14.4 \pm 0.4 (n=3)$ 13.4 + 0.5 (n=3)	$110 \pm 3 (n=3)$ $111 \pm 4 (n=3)$ $118 \pm 5 (n=3)$ 111 + 3 (n=3)	41.4 (n=1) 40.9 (n=1) 43.4 (n=1) 39.6 (n=1)
D2-142	34.4	$13.6 \pm 0.4 (n=3)$	$111 \pm 4 (n=3)$	nm ^c

The concentrations of U, Mo and Re are not normalized with respect to salinity, errors are $\pm 2\sigma$ internal precision. ^a SAFe (sampling and analysis of Fe) samples are seawater provided by Prof. Ken

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

^b The salinities in the large volume tanks, from which these samples are taken, were not measured during sample collection. The salinity values given above are measured for profiles that were collected from close locations at the same time.

^c nm: not measured.





particularly from the G–B, with lower concentrations of these elements. The large influx of fresh water from several major and medium rivers into the BoB significantly influences its salinity and U, Mo and Re distributions in surface waters. The annual input of fresh water to the Bay of Bengal (area $\sim 2.2 \times 10^6$ km²; average depth ~ 3 km) is

 1.89×10^{15} l (Bird et al., 2008; http://www.cciw.ca/atlas-gwq/table3-e. html; Sarin et al., 1990), compared to the volume ~ 6.6×10^{18} l of the bay. Thus, the residence time of water in the bay relative to river input is only ~ 3.5×10^3 years compared to the global average value of ~ 3.8×10^4 years. This shorter residence time of water in the bay relative to fresh water



Fig. 3. Scatter plot of dissolved oxygen vs pH. Both decrease with water depth with a minimum in the range of 200–800 m (shown by red squares) due to remineralization of sinking organic particles. Arrow points along increasing depth.

input highlights the importance of riverine discharge on the properties and distributions of elements in the bay.

The concentrations of U, Mo and Re in the surface water samples covary with salinity (Fig. 5a). The strong positive correlations between the abundances of these elements and salinity, as mentioned earlier, suggest that their distributions are dominated by river-seawater mixing. The concentrations of U, Mo and Re in seawater end-member (salinity 35) calculated from the regression lines of concentration-salinity scatter plots for samples from depth ≤ 5 m (Fig. 5a) are 14.0 \pm 0.9 nmol/kg, 113 \pm 6 nmol/kg and 41.0 \pm 2.4 pmol/kg, respectively. These values are consistent with those reported for open ocean samples from other regions (Table 3c) and those measured in this study for deeper BoB waters with salinities close to 35. The concentrations in the

riverine end-member also deduced from these lines (Fig. 5a), are 3.85 ± 0.53 nmol/kg, 11.54 ± 4.04 nmol/kg and 4.90 ± 1.70 pmol/kg for U, Mo and Re respectively. These end-member values overlap within errors to those reported for the Meghna (combined Ganga–Brahmaputra, G–B) in Bangladesh, 3.15 nmol U/kg (Chabaux et al., 2001), and the Hooghly River in India, 13.8 nmol Mo/kg and 6.6 pmol Re/kg (Rahaman and Singh, 2010; Rahaman et al., 2010). The agreement between the riverine endmember estimated in this study with that reported in literature indicates that among the rivers the G–B system is the dominant contributor of these elements in the BoB.

Among the various stations sampled, the Re concentration in surface waters of station SS259-0811, is 45.0 pmol/kg (Table 2, Fig.4) about 13%, higher than that expected from the salinity of this water, 33.9 (Fig. 7b). Further the data seems to show a systematic decrease in Re concentration up to 300 m in contrast to concentrations observed in other stations from this region, but similar to the trend reported in the Pacific Ocean (Anbar et al., 1992). Although, the higher Re concentration in surface waters of this station and its distribution in the upper layer seems consistent with its supply via atmospheric deposition (Chappaz et al., 2008; Colodner et al., 1995; Colodner et al., 1993; Rauch et al., 2003), it seems unlikely as nearby stations do not show elevated Re in surface water. One likely source for this high [Re] in surface water can be the Godavari River that enters the BoB about 400 km west of this station. This river has Re concentration about 3 times higher than dissolved Re in seawater (Rahaman et al., Manuscript in Preparation). The Re, thus introduced by the Godavari has to be transported to the station SS259-0811, a mechanism for this could be clockwise gyres that develop in the surface waters of the BoB, offshore the Godavari River during early winter (Unger et al., 2003) when these samples were collected. Alternatively, strong eddies present in the BoB (Sasamal, 1990) could also transport water eastward from the Godavari to station SS259-0811. The role of the Godavari in determining the Re distribution in surface water of the BoB, can be



Fig. 4. Salinity and dissolved concentrations of U, Mo and Re in surface waters of the BoB along 87°E transect. The data shows a north-south gradient due to river water-seawater mixing, with dominant water supply from the G-B river system.

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Fig. 5. Scatter plots of U, Mo and Re dissolved concentrations with salinity (a) for surface waters (depth <5 m). The strong linear correlations indicate control of salinity on these concentrations. Note that the data point in the red circle is excluded from the regression analysis. (b) For samples from depths >5 m. Figures in insets are for higher salinity samples, that are enlarged for clarity. It is evident from these plots that oxygen concentrations in seawater do not affect the distributions of U, Mo and Re. In Fig. 5b, black, green and red symbols represent samples with DO concentration >10, 5–10, <5 μ mol/l, respectively.

better assessed through more systematic measurements of Re from the Godavari coast to mid BoB. If the results of this study and the hypothesis to interpret these are confirmed through more systematic studies of Re distribution in the BoB, then dissolved Re can be used to track the movement of Godavari River waters in the BoB, as the Re

Table 3c

Salinity normalized U, Mo and Re concentrations in various oceanic basins.

concentration of this particular river is significantly higher than seawater.

4.2. Depth profiles of U, Mo and Re in OMZ

The concentration-salinity plots of U, Mo and Re in all samples other than those collected near the surface are presented in Fig. 5b. The elemental concentrations show good linear correlations with salinity; however the correlation coefficients are lower compared to those for the surface samples (Fig. 5a). This seems to result from scatter in the concentration data in the high salinity samples, where both salinity and Re concentrations are within restricted range. The U, Mo and Re concentrations of the samples at all the stations with salinity 35 are in the range of 13.7 to 14.2 nmol/kg (av. 14.0 ± 0.1), 112 to 116 nmol/kg (av. 114 \pm 2) and 39.6 to 43.5 pmol/kg (av. 41.0 \pm 0.4), respectively. The ranges in U and Mo concentration at salinity 35 are ~4%, whereas Re has a wide range, ~10% (insets in Fig. 5b). The cause for the wider range in Re abundance is puzzling and needs to be investigated further. The mean U, Mo and Re concentrations at salinity 35 are consistent within errors with those reported for other oceanic regions (Table 3c).

It is borne out from the foregoing discussion that the dominant factor controlling dissolved U, Mo and Re concentrations in the BoB samples is salinity (Figs. 2b, 5b and 6). Considering that all the three elements are redox sensitive, attempts were also made to look for the impact of dissolved oxygen concentration on their distribution. Dissolved oxygen concentration decreases with depth in all the profiles sampled; with minimum DO concentration in the depth range of 200-800 m (Fig. 2d and 7). This decrease attains very low values, <10 µmol/l in stations north of 11°N. Comparison of dissolved oxygen concentration contours (Fig. 2d) with U, Mo and Re contours (Fig. 6) show that U, Mo and Re concentrations do not show any measurable change with DO, even within the OMZ prevalent north of 11°N (Fig. 7). The U, Mo and Re concentrations even in waters of extreme suboxicity $(DO <5 \mu mol/l; e.g. 175 m depth in station SS259-0808, salinity$ ~34.9), are 14.0 nmol/kg, 113 nmol/kg and 40.5 pmol/kg, respectively, indistinguishable from those in waters with significantly higher DO concentration.

Fig. 5b is a scatter plot of U, Mo and Re concentrations with salinity in samples of >5 m depth. The plot includes samples with a wide range of DO concentration, <5 μ mol/l to >250 μ mol/l. The plots show significant linear correlations with salinity and do not seem to be impacted by the DO levels in the samples. It is seen that even samples having oxygen content <5 μ mol/l have U, Mo and Re concentrations overlapping with those of others with much higher oxygen content. This leads to the conclusion that observed variations in the concentrations of U, Mo and

Oceanic Basin	U (nmol/kg)	Mo (nmol/kg)	Re (pmol/kg)	Reference
Antarctic Ocean	13.4 ± 0.2			(Ku et al., 1977)
Arabian Sea	13.5 ± 0.8			(Sarin et al., 1994)
	13.1 ± 0.8			(Rengarajan et al., 2003)
Arctic Ocean	14.1 ± 0.2			(Ku et al., 1977)
Atlantic Ocean	13.8 ± 0.4			(Ku et al., 1977)
	13.14 ± 0.03			(Chen et al., 1986)
		109.0 ± 8.7		(Morris, 1975)
			$40.1\pm0.4^{\rm a}$	(Colodner et al., 1995; 1993)
Bay of Bengal	14.0 ± 0.1	114 ± 2	41.0 ± 0.4	This study
East China Sea and Yellow Sea		104 ± 6		(Sohrin et al., 1999)
Pacific Ocean	13.8 ± 0.4			(Ku et al., 1977)
	13.7 ± 1.1			(Miyake et al., 1970)
	13.43 ± 0.03			(Chen et al., 1986)
	13.4 ± 0.3	103.4 ± 2.1	40.8 ± 0.8	(Nameroff et al., 2002)
		105 ± 5		(Collier, 1985)
			39.8 ± 0.2	(Anbar et al., 1992)
			39.5 ± 0.6^{a}	(Colodner et al., 1995; 1993)

^a The Re values published in Colodner et al., 1993 have been modified here by 10% as corrected in Colodner et al., 1995.
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Fig. 6. Distributions of U, Mo and Re in the water columns of BoB. The waters in BoB seem to have nearly uniform concentrations of these elements; the marginal variations being governed by salinity. For Re, there may be anomalous supply from the Godavari River.

Re in the Bay of Bengal is not dependent on dissolved oxygen (Fig. 5b and 7), and are mainly due to salinity variations.

The lack of dependence of U, Mo and Re concentrations on DO in the BoB waters inference is consistent with the earlier reports from other suboxic oceanic regions, e.g. the eastern tropical North Pacific (Nameroff et al., 2002). It must be added here that the distribution of uranium in H₂S rich waters of the Black Sea and the Cariaco basin (Anderson, 1987; Anderson et al., 1989a), show divergent behavior with former showing its significant removal, which in the latter basin is nearly conservative. These results suggest that even in addition to H₂S, there must be additional factors that control the removal of uranium. The BoB though has a large particulate flux, the absence of H₂S in its water column, inhibits the formation of more particle reactive Mo-complexes resulting in its removal.

The U, Mo and Re distributions in the BoB water column are conservative despite the presence of strong suboxic layer in the intermediate waters and large particulate flux. The dominant factor regulating the distributions of these three RSEs is salinity.

5. Conclusions

The dissolved concentrations of U, Mo, Re, and salinity exhibit a north–south gradient in surface waters of the Bay of Bengal due to mixing of seawater with fresh water supplied by various rivers, the dominant being the Ganga–Brahmaputra river system. The U, Mo and Re concentrations of both surface and deeper waters of BoB covary with salinity, displaying their conservative behavior in the entire Bay of Bengal. A few samples from the surface and upper water columns from the central Bay of Bengal seem to have Re concentration disproportionately higher than that expected from salinity. This higher concentration, if confirmed through more systematic measurements, may be a result of supply from the Godavari River, which has Re concentration three times higher than seawater.

Suboxic conditions $(DO < 10 \,\mu mol/l)$ in intermediate waters (200-800 m) were found north of $11^{\circ}N$ along meridian $87^{\circ}E$ in the Bay of Bengal. The distributions of U, Mo and Re in the BoB water column are independent of the suboxic conditions in the

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Fig. 7. Depth profiles of U, Mo, Re, dissolved oxygen (black line) and salinity (blue line). DO decreases in the depth range of 200–800 m at all stations, with pronounced low values (less than 10 µmol/l) at stations north of 11°. In general, salinity of surface waters is lower. Dark gray bands represent suboxic range. The distributions of U, Mo and Re in the water columns follow salinity variations and are independent of DO. Uncertainties on U, Mo and Re measurements are shown by horizontal bar for the station, SS259-0806.

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intermediate depth. Similarly, the high flux of suspended material including detrital organic matter does not seem to regulate the abundances and distributions of U, Mo and Re in the water column.

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Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: Role of particulate matter and mixing of water masses

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Abstract

The concentration and isotope composition of dissolved Nd have been measured in the water column along an 87°E transect (GIO1 section of International GEOTRACES Program) in the Bay of Bengal (BoB) to investigate the effect of water mass mixing and Nd release from particulate matter in determining these properties. The concentration of Nd in surface waters of the BoB shows a North–South decreasing non-linear trend (~46 to ~22 pmol/kg) with salinity, whereas its depth profiles typically show a high value in surface waters, a minimum (~15 to ~23 pmol/kg) in the shallow subsurface (~50–200 m), followed by a gradual increase with depth. The Nd concentration of BoB waters is generally higher than that in nearby oceanic basins. On the other hand, the ε_{Nd} values in the BoB are less radiogenic compared to those reported for other regions of the global oceans (except Baffin Bay, the North Atlantic Subpolar Gyre and the Niger delta margin), and show a greater variation in the upper water column. Surface waters of the southernmost profile (~6°N) show a more radiogenic ε_{Nd} value ~-8, which decreases to -15 in the northernmost profile (~20°N), close to the values for dissolved and particulate phases of the Ganga–Brahmaputra (G–B) Rivers. This latitudinal trend is most likely a result of variations in mixing proportion between the more radiogenic Indonesian Throughflow surface waters (IW) and unradiogenic BoB low salinity water; the former's signature being more clearly discernible in surface waters of the two southernmost profiles (~6°N and ~8.5°N).

Attempts to balance the Nd budget in the water column based on an inversion model, suggest that in addition to water masses other source(s) is required, the strength of which is estimated to vary from 1% to 65% of the measured Nd concentration. The calculations also show that the ε_{Nd} of this additional source(s) has to be in the range of $\sim -16 \pm 2$, typical of G–B river sediments. These observations, coupled with the North–South distribution of dissolved Nd and ε_{Nd} , indicate that this additional source is release from particulate phases supplied by the G–B river system. The calculations also bring out the presence of "hot-spots" of Nd release (excess Nd) near the sediment–water interface along the northern slope of the bay, indicating supply of Nd from continental margin sediments. This study underscores the significant role of dissolved/particulate Nd from the Ganga–Brahmaputra river system in contributing to the dissolved Nd budget of the global oceans. © 2012 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The distribution of dissolved Nd in seawater, along with its radiogenic isotope composition, serves as a water mass tracer on an ocean-wide scale. The oceanic residence time

* Corresponding author. *E-mail address:* satinder@prl.res.in (S.P. Singh). of neodymium, though not well established, is known to be of the order of the ocean mixing time (Broecker and Peng, 1982; Jeandel et al., 1995; Nozaki and Alibo, 2003; Tachikawa et al., 2003; Johannesson and Burdige, 2007). This leads to the dispersal of continental Nd in the global oceans through water circulation. The ε_{Nd} data of different oceanic regions reflect those of its sources, predominantly continental supply, and their subsequent modification by

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water mass mixing and boundary exchange (Frank, 2002; Goldstein and Hemming, 2003 and references therein; Piepgras and Wasserburg, 1987; Jeandel, 1993; Lacan and Jeandel, 2005).

There have been a number of studies that have utilized Nd isotopes to investigate water mass mixing in the Arctic, Atlantic and the Pacific Oceans (Piepgras and Wasserburg, 1987; Andersson et al., 2008; Amakawa et al., 2009; Porcelli et al., 2009; Rickli et al., 2009, 2010; Carter et al., 2012). Similar studies in the Indian Ocean, however, are sparse (Bertram and Elderfield, 1993; Jeandel et al., 1998; Amakawa et al., 2000; Tazoe et al., 2011). The limited available results show that ε_{Nd} values of the Indian Ocean are intermediate between the less radiogenic Atlantic and the more radiogenic Pacific Ocean values (Bertram and Elderfield, 1993; Jeandel et al., 1998; Frank, 2002). These findings are based primarily on the equatorial and southern Indian Ocean. There have been only a few studies on the northern Indian Ocean, particularly in the Bay of Bengal and the Arabian Sea, both of which receive significant input of fresh water and particulate matter from rivers draining the Himalaya. These rivers, the Ganga, Brahmaputra, Irrawaddy and the Indus all drain terrains in the Himalaya characterized by unradiogenic neodymium (Robinson et al., 2001; Singh and France-Lanord, 2002; Singh et al., 2008). This study focuses on the measurements of dissolved Nd concentration and its isotope composition in waters of the Bay of Bengal, which receives large quantities of fresh water and particulate matter through the Ganga-Brahmaputra (G-B) and the Irrawaddy river systems draining the Himalaya.

The Bay of Bengal (BoB) covers an area of 2.2×10^6 km² in the northern Indian Ocean, with an average depth of 3 km. The G-B river system contributes ${\sim}1000~{\rm km}^3$ of freshwater to the bay, corresponding to $\sim 25\%$ of the annual input of fresh water to the BoB (Sarin et al., 1989; Sengupta et al., 2006). The annual delivery of fresh water to the BoB accounts for about 0.06% of the total inventory of water in the bay. This large influx of fresh water is also responsible for the stratification of the upper water column commonly observed in the bay (Murty et al., 1992; Gopalakrishna et al., 2002). The water mass structure of the bay has been well characterized (Sastry et al., 1985; Dileep Kumar and Li, 1996; Rao et al., 1996; You, 1997, 2000) and circulation of the upper water column has been shown to be prone to monsoon-driven seasonal changes (Wyrtki, 1973; Colborn, 1975; Shetye et al., 1996; You, 1997; Shenoi et al., 1999; Schott and Mccreary, 2001; Shankar et al., 2002). In the present study, the concentration as well as isotope composition of dissolved Nd in the BoB water column have been measured to characterize the water masses, to learn about geochemical cycling of Nd in the region, particularly to assess the role of particulate Nd in modifying the abundance of dissolved Nd and its isotope signature in different water masses. The latter objective becomes significant in the BoB, as it is one of the oceanic regions receiving the world's largest flux of particulate matter, ~10¹² kg/year (Milliman and Mead, 1983; Galy and France-Lanord, 2001).

2. MATERIALS AND METHODS

2.1. Sampling

Seawater samples from the surface and various depths down to the sea floor were collected during November, 2008 the fall inter-monsoon season, onboard FORV Sagar Sampada, cruise SS259. The sampling was done along the $87^{\circ}E$ meridian in the Bay of Bengal, from $\sim 20^{\circ}N$ to \sim 6°N (Fig. 1). All samples were filtered through 0.45 µm Millipore filters onboard, soon after their recovery. The Nd concentration and its isotope composition determined in these filtered waters are treated as dissolved phase measurements. For the determination of Nd-isotope composition, REEs were pre-concentrated onboard from $\sim 10 \text{ L}$ of seawater using the Fe co-precipitation protocol (Amakawa et al., 2000) for stations 0807, 0809, 0810, 0812 and 0813 or from \sim 5 L of seawater following the C18 cartridge method (Jeandel et al., 1998) for stations 0806, 0808 and 0811. The REEs extracts from the Fe(OH)₃ or the cartridges were taken up in 50 ml 6 N HCl and stored in acid cleaned LDPE bottles until their analysis. In the laboratory, these stored extracts were dried and re-dissolved in 2 N HCl. The re-dissolved solution was loaded on a cation exchange resin, AG 50W-X8 (200-400 mesh) to separate REEs from other major ions. The REEs were eluted with 6 N HCl after removing the major ions with 2 N HCl. The solution containing REEs was evaporated to dryness, and re-dissolved in 0.16 N HCl. The Nd was separated from REEs by loading the solution onto a reverse phase chromatographic column (Ln Resin, LN-B50-S in a quartz column). The Nd was eluted using 0.25 N HCl from this resin. The purified Nd was dried and re-dissolved in 0.4 N HCl to measure its isotope composition using MC-ICPMS.

For the determination of dissolved Nd, one liter seawater samples, soon after their recovery, were filtered on deck through 0.45 μ m Millipore filters. The filtered seawater samples were acidified to pH ~2 with quartz distilled 6 N HCl and stored in acid cleaned LDPE bottles for further analysis. From this filtered and acidified seawater a precisely weighed aliquot (~500 g) was spiked with a known amount of ¹⁵⁰Nd tracer and the REEs were pre-concentrated and purified using Fe co-precipitation followed by cation exchange separation (Tachikawa et al., 1999; Amakawa et al., 2000). The Nd concentration in these extracts was measured by the isotope dilution technique using a quadrupole ICPMS.

2.2. Analysis

The Nd isotope composition of the purified Nd extracts was determined by MC–ICPMS (Neptune) using a PFA100 nebulizer with an *APEX* introduction system as Nd⁺ in static multi-collection mode by measuring the intensities at masses 143, 144 and 146 for 40 cycles. Sm correction, if any, was done by measuring the intensity at mass 147. Amplifiers connected to Faraday cups are rotated after every 10 cycles to eliminate amplifier efficiency variations. The signal intensity of Nd at mass 144 in the samples depended on their Nd concentration, and typical values were



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Fig. 1. Locations of sampling sites (red circles) in the BoB during the cruise SS259. The pink triangle represents the sampling location of PA-9 (Nozaki and Alibo, 2003), and the yellow squares are sediment trap locations (Unger et al., 2003). All the color contours (bathymetry) in this and subsequent figures are plotted with the help of ODV4 software (Schlitzer, 2010). The bathymetry data for the section contours are taken along the 87°E transect using GMRT grid (http://www.geomapapp.org; Ryan et al., 2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the range 0.2–0.6 V. Instrumental mass bias was corrected using an exponential law relative to ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219. To check the accuracy and precision of measurements, an international standard, JMC321 was repeatedly run during the period of analysis. The measured average ¹⁴³Nd/¹⁴⁴Nd of JMC321 was 0.511024 \pm 0.000016 (2σ , n = 9) against the reported value of 0.511123 \pm 0.000012 (Barrat and Nesbitt, 1996). The measured ¹⁴³Nd/¹⁴⁴Nd of JMC321 was lower compared to its reported value and hence the ¹⁴³Nd/¹⁴⁴Nd in samples was corrected by normalization to the reported ¹⁴³Nd/¹⁴⁴Nd of JMC321.

The concentration of Nd was determined on a quadrupole ICPMS (Thermo X-series-II) based on the isotope dilution technique. Samples were analyzed for the intensities of Nd–Sm isotopes and the Nd concentrations were calculated after Sm correction. The total procedural blank of Nd for concentration determination was 50 ± 2 pg (n = 2) and for Nd isotope determination it was 70 ± 2 pg (n = 2) based on the iron co-precipitation method and $\sim 600 \pm 50$ pg (n = 2) for Nd extraction using C18 cartridge similar to earlier reported blank levels (Lacan and Jeandel, 2004). The coefficient of variation (CV%) for dissolved Nd concentration based on repeat measurements of nine different samples was determined to be 2.5%.

The hydrographic data (temperature, pH, salinity and dissolved oxygen) of the profiles are reported elsewhere (Singh et al., 2011). However, for the sake of completeness

the potential temperature and salinity data used for interpretation in this study are given in Table 1.

3. RESULTS AND DISCUSSION

The Nd concentration in the water column along the 87°E transect of the BoB covers a wide range, from 14.8 to 46.4 pmol/kg (Table 1). For convenience of interpretation, the data are sub-grouped into the northern BoB (north of 17°N), central BoB (10°N-17°N) and the southern BoB (south of 10°N). The concentration of Nd in surface waters of the BoB decreases from north to south, while the subsurface value exhibits a minimum at a water depth of around 100 m (c.f. Sections 3.1 and 3.2). Nozaki and Alibo (2003) have reported Nd concentration-depth profile at a station (PA-9; 8.000°N, 88.995°E) near to station 0807 measured in this study. The Nd concentrationdepth profiles at these stations are similar, but the Nd concentrations measured in this study are systematically higher by $\sim 10\%$ than those reported for PA-9. The cause for this difference is unclear; it could be due to spatial variability and/or calibration uncertainties. A cursory look at the Nd concentration data in the northern and central BoB waters from the upper water column (~100 m to \sim 2000 m) also show that they are higher (about two fold) than those reported for similar depths from other oceanic basins (Stordal and Wasserburg, 1986; Bertram and Elderfield, 1993; Jeandel et al., 1998; Nozaki and Alibo, 2003;

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 Table 1

 Depth profiles of potential temperature, salinity, dissolved Nd and Nd isotope composition in the Bay of Bengal.

Station	Depth (m)	Pot. temp. (°C)	Salinity	Nd (pmol/kg)	$\epsilon_{ m Nd}{}^{ m a}$	$2\sigma_{\mu}^{b}$
0806	5	29.252	33.351	22.1	-8.0	1.2
(5.813°N, 86.997°E;	60	27.523	35.034	18.6	-8.7	0.7
max. depth \approx 3890 m)	130	18.541	34.807	16.8	nm	nm
-	200	13.818	35.027	18.1	-11.3	0.5
	290	11.766	35.061	19.7	-12.1	0.2
	380	11.038	35.082	17.0	nm	nm
	420	10.707	35.066	_	-10.8	0.2
	460	10.376	35.050	21.4	nm	nm
	600	9.454	35.030	21.1	-11.4	0.4
	800	8.035	34.989	21.2	-11.4	0.4
	1000	6.634	34.936	21.5	-10.0	0.3
	1200	5.738	34.903	24.3	nm	nm
	1400	4.893	34.871	25.4	-10.2	0.3
	1700	3.397	34.813	27.7	-10.5	0.2
	2000	2.577	34.777	29.2	-10.2	0.3
	2300	2.082	34.755	30.3	nm	nm
	2600	1.//2	34.742	30.9	-10.0	0.1
	2900	1.542	34.734	33.8	nm 0.7	nm 0.2
	3200	1.365	34.720	20.8	-9.7	0.2
	3800	1.211	34.725	39.0	0.1	0.2
	3800	1.097	34.719	36.2	-9.1	0.2
0807	5	29.211	33.305	24.2	-10.4	0.6
(8.494°N, 87.007°E;	70	27.284	34.878	17.8	-12.8	0.9
max. depth \approx 3630 m)	160	16.446	34.999	18.8	-13.6	0.6
	300	12.127	35.052	22.7	-13.1	0.6
	400	10.857	35.050	21.5	-12.8	0.5
	600	9.053	35.010	22.1	-12.5	0.8
	800	7.820	34.980	23.3	-19.1	0.1
	900	7.148	34.958	24.8	-11.2	0.2
	1000	6.628	34.938	23.5	-12.5	0.3
	1300	5.190	34.880	27.5	-11.3	0.3
	1500	4.296	34.849	33.2	nm	nm
	1800	3.097	34.800	nm 22.(-11.2	0.4
	2100	2.420	34.771	32.0	nm	nm o 2
	2400	1.989	34.732	25.2	-11.0	0.3
	2700	1.070	34.739	55.2 pm	10.6	0.2
	3300	1.305	34.732	40.5	-10.0	0.2 nm
	3550	1.174	34 721	36.4	-10.6	0.3
	5550	1.171	51.721	50.1	10.0	0.5
0808	5	28.796	33.313	34.5	-13.9	0.4
(11.270°N, 86.990°E;	70	25.648	34.947	24.8	-13.6	0.5
max. depth \approx 3314 m)	175	14.793	34.947	22.7	-12.3	0.4
	280	11.583	35.032	21.1	-11.5	0.4
	380	10.588	35.032	20.5	-10.5	0.5
	495	9.563	35.006	29.9	-12.8	0.4
	600 700	8.827	34.980	24.2	-11.0	0.4
	700	6.002	34.903	25.1	-12.1	0.4
	300	5 204	24.945	20.1	-12.5	0.3
	1200	3 306	34.830	29.0	-11.6	0.4
	2300	2.072	34 755	43.3	-11.0	0.3
	2900	1 549	34 727	38 5	-11.7	0.3
	3200	1.324	34 727	41.2	-11.0	0.2
	5200	1.521	51.727			0.2
0809	5	28.671	33.207	35.6	-14.8	0.2
(13.769°N, 87.004°E;	85	25.232	34.961	14.8	-14.0	0.3
max. depth ≈ 3028 m)	180	14.938	34.966	22.2	-16.3	0.2
	300	11.604	35.038	21.5	-13.9	0.3
	400	10.537	35.035	23.1	-13.4	0.2
	500	9.768	35.027	23.8	-14.5	0.4
	600	9.012	35.010	23.9	-13.9	0.4
	700	8.242	34.988	24.5	-14.8	0.2

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Table 1 (continued)

Station	Depth (m)	Pot. temp. (°C)	Salinity	Nd (pmol/kg)	$\epsilon_{ m Nd}{}^{ m a}$	$2\sigma_{\mu}{}^{b}$
	800	7.720	34.973	33.1	-14.3	0.4
	900	7.172	34.954	25.9	nm	nm
	1000	6.475	34.929	25.6	-10.9	0.3
	1400	4.764	34.864	27.8	-14.2	0.2
	2000	2.617	34.778	34.1	-10.6	0.5
	2600	1.793	34.743	36.8	-10.1	0.2
	2900	1.524	34.733	35.2	-10.5	0.2
0810	5	28.389	32.117	43.1	-13.7	0.2
(16.420°N, 90.498°E;	40	28.882	33.541	32.9	-13.3	0.3
max. depth \approx 2437 m)	140	20.670	34.650	21.0	-13.6	0.5
	200	14.306	34.959	22.6	-13.0	0.3
	300	11.445	35.031	23.0	-10.3	0.4
	400	10.549	35.030	23.7	-11.8	0.3
	500	9.917	35.024	23.3	-12.9	0.3
	600	9.222	35.012	23.4	-12.5	0.3
	700	8.511	34.992	24.2	-12.5	0.4
	800	7.791	34.971	25.8	-11.7	0.4
	1000	6.574	34.930	28.5	-16.4	0.4
	1200	5.594	34.894	29.0	-11.0	0.3
	1400	4.783	34.864	30.4	-11.0	0.3
	1700	3.493	34.814	31.4	-11.8	0.3
	2000	2.587	34.777	34.4	-11.6	0.2
	2200	2.246	34.762	34.8	-12.2	0.4
0811	5	28.327	33.856	34.0	-15.0	0.3
(16.759°N, 86.993°E;	70	23.162	34.747	26.5	-14.5	0.3
max. depth ≈ 2580 m)	110	19.491	34.874	23.1	-14.5	0.3
	180	14.670	34.960	23.7	-14.8	0.4
	300	11.475	35.032	23.7	-14.6	0.4
	400	10.550	35.033	24.7	-14.0	0.4
	500	9.776	35.024	26.8	-13.4	0.4
	600	9.049	35.009	26.8	-14.1	0.4
	/00	8.473	34.993	27.4	-13.3	0.5
	900	6 191	34.934	20.4	-12.1 nm	0.4
	1300	5 328	34.917	30.2	nm	nm
	1500	1.128	34.854	31.0	11.0	0.3
	1700	3 590	34.818	32.9	-11.0	0.5 nm
	1900	2 920	34 791	34.7	-11 7	0.4
	2100	2.920	34 770	38.5	nm	nm
	2300	2.169	34.759	35.8	-12.0	0.4
	2500	1.859	34.746	37.7	-11.9	0.3
0812	5	27.497	32.049	45.4	-14.5	0.3
(18.759°N, 86.997°E;	50	25.633	34.311	31.0	-13.9	0.3
max. depth ≈ 2128 m)	110	18.693	34.875	22.5	-13.4	0.3
1	200	13.249	34.991	25.8	-14.0	0.4
	300	11.472	35.028	26.3	-13.3	0.3
	400	10.564	35.030	30.0	-14.0	0.4
	500	9.885	35.024	25.7	-13.2	0.5
	600	9.232	35.012	28.3	-14.2	0.2
	800	7.986	34.979	28.0	-11.8	0.3
	1000	6.634	34.934	29.4	-13.1	0.3
	1200	5.506	34.892	31.1	-13.0	0.3
	1400	4.552	34.855	32.0	-12.7	0.2
	1700	3.225	34.803	37.2	-12.2	0.2
	2000	2.351	34.766	38.8	-11.7	0.2

(continued on next page)

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Table 1 (continued)
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Station	Depth (m)	Pot. temp. (°C)	Salinity	Nd (pmol/kg)	$\epsilon_{ m Nd}{}^{ m a}$	$2\sigma_{\mu}^{\ b}$
0813	5	27.652	32.668	46.4	-15.0	0.3
(20.047°N, 87.262°E;	70	23.952	34.661	24.4	-13.9	0.3
max. depth ≈688 m)	150	17.110	34.895	22.5	-16.0	0.3
	250	12.411	35.008	25.3	-13.1	0.2
	350	11.053	35.029	24.8	-13.3	0.3
	440	10.350	35.028	27.0	-12.6	0.3
	550	9.411	35.016	27.3	-13.5	0.3
	640	8.824	35.003	30.4	-11.7	0.3

nm: Not measured.

^a ε_{Nd} is calculated with respect to ¹⁴³Nd/¹⁴⁴Nd value 0.512638 of CHUR (Jacobsen and Wasserburg, 1980).

[°] Internal precision.

Amakawa et al., 2004, 2009; Porcelli et al., 2009; Rickli et al., 2009; Bayon et al., 2011; Carter et al., 2012).

 ε_{Nd} in the Bay of Bengal displays large variability, from -16.4 to -8 (n = 124; Table 1), with one sample from station 0807 (depth ~800 m) having a highly unradiogenic value of -19.1 possibly contributed by rivers draining peninsular India. Surface and intermediate waters of the northern and central bay have lower ε_{Nd} compared to waters from similar depths of the southern bay (c.f. Sections 3.1 and 3.2). ε_{Nd} in the southern BoB compares favorably with the available data for a few samples from this region (Amakawa et al., 2000). The ε_{Nd} of the northern and central BoB waters is less radiogenic compared to those reported from other regions of the Indian Ocean (Bertram and Elderfield, 1993; Jeandel et al., 1998; Amakawa et al., 2000; Tazoe et al., 2011), and also the rest of global oceans; the only exceptions being Baffin Bay, the North Atlantic Subpolar Gyre and the Niger delta margin (Stordal and Wasserburg, 1986; Amakawa et al., 2004, 2009; Porcelli et al., 2009; Rickli et al., 2009; Bayon et al., 2011; Carter et al., 2012). It is interesting to note that the ε_{Nd} values of bottom waters in the profiles 0806-09 south of 15°N (-9 to -11) and in profiles 0810-0813 north of 15°N (-11 to -13) overlap with reported ε_{Nd} values of Holocene sediments from the region (Colin et al., 1999). The close resemblance of $\epsilon_{\rm Nd}$ values of bottom waters and Holocene sediments is indicative of the role that sediments of the BoB play as sources or sinks of dissolved Nd to bottom waters. More recently, Piotrowski et al. (2009) have utilized the Nd isotope composition of sedimentary Fe-Mn oxyhydroxides to trace deep water circulation in the Indian Ocean. The composition of core top ε_{Nd} values of those Fe–Mn phases shows good agreement with $\epsilon_{\rm Nd}$ of bottom water measured in this study from similar depths at adjacent locations (depth ~3800 m at station 0806), which re-affirms the application of Nd isotope composition of Fe-Mn oxyhydroxides as a proxy of Nd isotope composition of deep waters.

3.1. Surface waters

Samples from depths ≤ 5 m are considered as surface samples. The salinity of surface waters in the northern Bay of Bengal is generally low due to a large influx of fresh water from the Ganga–Brahmaputra river system. Similarly the contribution of less saline Indonesian Throughflow water through an eastward Equatorial Jet (EJ), generally encountered during the fall inter-monsoon (Shenoi et al., 1999), decreases the salinity in southern BoB surface waters. In the central BoB, the salinity of surface waters at station 0811 is marginally higher compared to those of the northern and southern bay (Fig. 2a). This could be due to eddy pumping of more saline subsurface water from 50-100 m depth in the region (Murty et al., 1992). In contrast to salinity, the concentration of dissolved Nd in surface waters of the BoB shows a North-South decreasing trend (Fig. 2b), ranging from 46.4 to 22.1 pmol/kg, albeit with significant scatter. The plot of Nd concentration in surface waters with salinity (Fig. 3a) shows an overall decreasing trend, although the data points do not fall on the theoretical mixing line. This suggests that in addition to water mixing, other processes also influence the dissolved Nd abundance and distribution in these surface waters. Similar to dissolved Nd in surface waters of the bay, ε_{Nd} also shows a North–South trend (Fig. 2c), with less radiogenic values ($\varepsilon_{Nd} \approx -15$) at station 0813 in the northernmost surface waters, compared to that in surface waters of the southernmost station 0806 ($\varepsilon_{Nd} \approx -8$). The dissolved Nd in surface waters of the northern and central BoB has ε_{Nd} values in range of -14 ± 1 (Fig. 2c). The North–South trend in ε_{Nd} values can be explained in terms of source functions of Nd to the bay. The major contributors of dissolved Nd to the bay are the dissolved and particulate phases of the G-B and the Irrawaddy Rivers along with inputs from the peninsular rivers, the Godavari and the Krishna. Yet, there is no published data on dissolved ε_{Nd} of the G–B Rivers. Chatterjee et al. (personal communication) have measured dissolved ε_{Nd} values of -16 for the Ganga River, similar to or slightly more radiogenic compared to that of its particulate load (\sim -16 to -18; Goldstein et al., 1984; Goldstein and Jacobsen, 1987; Singh et al., 2008). The isotope composition of dissolved Nd of the Brahmaputra River is not available, but it supplies sediments with $\varepsilon_{Nd} \approx -14$ (Galy and France-Lanord, 2001; Singh and France-Lanord, 2002), more radiogenic than the Ganga River. The combined flow of the Ganga-Brahmaputra, therefore, is likely to supply dissolved Nd with $\varepsilon_{Nd} \approx -15 \pm 1$ to the BoB. Another potential source of low radiogenic Nd to surface waters of the northern BoB is its release from particulate matter supplied by the G-B Rivers and/or from the shelf sediments of the bay, which are also dominated by contributions from the G-B Rivers.



Fig. 2. The distribution of (a) salinity, (b) dissolved Nd concentration and (c) ε_{Nd} in surface waters along the 87°E transect. Salinity increases southward, except at station 0811 where it is higher compared to the rest of BoB surface waters. The Nd concentration shows a North–South decreasing trend, with more negative ε_{Nd} values in the northern BoB compared to that in the southern BoB. The high Nd concentration and lower ε_{Nd} in the northern and central BoB reflects dissolved Nd sourced from the G–B river system.

Such a release can also support the non-conservative behavior of dissolved Nd in BoB surface waters. Thus, the supply of Nd to the BoB from the G–B river system both as dissolved and particulate phases can account for the measured ε_{Nd} in the northern bay. On the other hand, the more radiogenic ε_{Nd} in surface waters of the southern BoB (Fig. 2c), could be a result of mixing of the Indonesian Throughflow Surface water (IW), having $\varepsilon_{Nd} \sim -4.1$ (Jean-del et al., 1998; Amakawa et al., 2000), with surface waters of the central bay ($\varepsilon_{Nd} \approx -14 \pm 1$), a proposition corroborated by the salinity data. Alternatively, if the peninsular



Fig. 3. Scatter plots of (a) salinity versus Nd concentration; (b) 1/Nd versus ε_{Nd} in surface waters of the BoB. The salinity versus Nd concentration plot shows a decreasing trend, albeit with significant scatter. 1/Nd versus ε_{Nd} also exhibits an overall linear trend, with data for the northern and central BoB scattering around the mixing line.

rivers, the Godavari and the Krishna supply significant amounts of low radiogenic Nd, then its mixing with more radiogenic ε_{Nd} water from the Irrawaddy system may also explain the Nd isotope composition of the southern BoB surface waters. Data on the dissolved Nd concentration and isotope composition in the peninsular and the Irrawaddy Rivers are unavailable to validate the above alternative. Given the likely similarity in ε_{Nd} values of particulates of the G-B and the peninsular rivers (Ahmad et al. 2005, 2009), and considering that water and particulate matter discharge of the peninsular rivers is orders of magnitude lower than that of the G-B river system, it seems unlikely that the contribution of the peninsular rivers to the budget of Nd and the $\epsilon_{\rm Nd}$ of the BoB would be significant. This inference however needs to be attested through direct measurements of dissolved Nd concentration and its ε_{Nd} in the peninsular rivers and their estuaries. Similarly, the dominance of the G-B river contribution over that of the Irrawaddy River is also indicated in the ε_{Nd} value of surface waters of station 0810 (Fig. 1). This station in the eastern BoB along the track of the Irrawaddy mouth has ε_{Nd} - ≈ -13.7 , significantly less radiogenic than the river value $(\varepsilon_{Nd} \approx -10;$ Allègre et al., 2010). Further, modeling the surface water circulation in this region (Shankar et al., 2002) using an Oceanic General Circulation Model (OGCM) has shown that the flow of the Irrawaddy river water to the southern BoB during the period of this study (November) is restricted. Thus the available data seem to indicate that the Ganga-Brahmaputra river system dominates over the Irrawaddy and the peninsular rivers in terms

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of their contribution to the dissolved Nd budget in the BoB surface waters along the 87°E transect.

Fig. 3b is a plot of 1/Nd vs ε_{Nd} in surface waters. The data show an overall mixing trend with data points from the northern and central BoB scattering around the mixing line. This overall trend, though indicative of two endmember mixing in surface waters of the BoB, also suggests that, analogous to dissolved Nd concentration, the behavior of ε_{Nd} in these waters is also not strictly conservative due to possible Nd release from particulate matter. The North–South features of dissolved Nd and its isotope composition in surface waters bring out the roles of dissolved and particulate phases of the G–B river system and the Indonesian Throughflow waters in determining their distribution (Fig. 3a and b).

3.2. Subsurface waters

The contours of dissolved Nd concentration in the Bay of Bengal are shown in Fig. 4a. A common feature of the Nd concentration-depth profiles (Table 1) is that it decreases from a high value at or near the sea surface to a minimum at about 100 m, followed by a gradual increase with depth (Fig. 5). The high concentration of Nd in surface waters is typical of many other elements that include Al, Pb, etc. observed in various oceanic regions (Bruland and Lohan, 2003 and references therein; Measures and Vink, 1999, 2000; Obata et al., 2004). These enhanced concentrations in surface waters, particularly in

open ocean regions, have been interpreted in terms of their release from eolian dust as it interacts with surface waters. The high surface concentration of Nd in the BoB, on the other hand, may have multiple sources: dissolved Nd from the G-B endmember, the Bay of Bengal Low Salinity water (GB-BBLS) at station 0812 and its release from particulate matter (Amakawa et al., 2000; Lacan and Jeandel, 2005; Jacobson and Holmden, 2006). The source of this particulate matter could be either that discharged by the G-B river system or eolian dust or both. Further, Amakawa et al. (2000) observed that dissolved Nd distribution in surface waters of the BoB follows the distribution of ²²⁸Ra sourced from the continental shelf. These results highlight the important role of particulate matter and shelf sediments in supplying Nd to surface waters of the bay.

The additional Nd (Nd_{Add}) in the BoB surface layer (top ~100 m) from these source(s) (equal to the difference in the area between the measured Nd concentration–depth profile and the extrapolated Nd profile from its minimum to the sea surface) is calculated to range from ~285 to ~1350 nmol/m² (Table 2). This addition represents the sum of *in situ* release of Nd from the particulate phases at the sampling sites and that transported as dissolved phase by estuarine and low salinity water following its release from G–B River particles. The *in situ* release could be from both eolian dust and river particles. The Nd_{Add} shows an overall North–South decreasing trend with significant scatter. This trend is similar to that reported for



Fig. 4. The distribution of dissolved Nd (a) concentration; (b) isotope composition in the water column of the Bay of Bengal along the 87°E transect.



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Fig. 5. Concentration-depth profiles of dissolved Nd in the water column of the northern, central and southern BoB along the 87° E transect. Note the increase in water column depth from north to south. The data show a North–South decreasing trend (shift in the grey band representing Nd concentration in the depth interval ~100 to ~2000 m). Nd concentrations in the bottom waters of the southern BoB show a marginal decrease similar to the trend reported for PA-9 (Nozaki and Alibo, 2003).

settling lithogenic particle flux (Table 2, Unger et al., 2003), suggestive of their inter-relation. The calculated Nd_{Add} allows us to constrain the leachable Nd from particulate phases, if data on Nd abundance in particles, their fluxes and residence time of dissolved Nd are available. The Nd concentration of the G–B particulate phases is assumed to be the same as that measured for Nd in suspended and bed sediments in the Ganga and Brahmaputra River basins (Singh and France-Lanord, 2002; Singh et al., 2008). These values are similar to the Nd abundance in Upper Continental Crust (UCC) and Holocene sediments of the bay (Colin et al., 1999; McLennan, 2001). The particulate lithogenic flux has been reported for different locations in the bay (Fig. 1, Unger et al., 2003). Using these lithogenic fluxes and assuming a residence time of

Table 2
The settling lithogenic flux, additional Nd (Nd_{Add}) and fractional
solubility of Nd in top 100 m.

Station	Lithogenic ^a flux (g/m²/year)	Nd _{Add} (nmol/m ²)	Fractional solubility ^b (%)
0806	4.3	285	15
0807	7.9 ^c	300	9
0808	11.2	780	16
0809	10.0 ^c	800	18
0810	11.6 ^c	1160	23
0811	11.6 ^c	600	12
0812	14.5	1180	18
0813	14.5	1350	21

^a From Unger et al., (2003).

[°] Fractional solubility (%) = $(Nd_{Add}/Lithogenic particulate Nd) \times 40$.

Calculated average flux.

2.5 years (Amakawa et al., 2000) for dissolved Nd in surface waters ($\sim 100 \text{ m}$), it can be estimated that the Nd_{Add} corresponds to a minimum Nd release of \sim 9–23% from sinking G–B particulate matter (Table 2). This is likely to be an upper limit, considering that a significant part of NdAdd may be released in estuaries (Sholkovitz, 1993; Sholkovitz and Szymczak, 2000 and references therein) and transported as dissolved Nd to the sampling locations. The dip in Nd concentration in the upper thermocline (~100-200 m, Table 1) is therefore an artifact of the surface addition of Nd, if there is no supply of Nd from estuaries and/or particulate matter then its profile would likely have been similar to those of nutrients, characterized by surface water removal and sub-surface water regeneration. The steady increase in the concentration of dissolved Nd with depth (Table 1) can result from its release from sinking particles as they transit through the water column. Alternatively, supply of Nd to the bottom waters from sediment pore waters (benthic flux) and its subsequent upward diffusion can also generate profiles similar to those observed. The importance of pore water as a source of dissolved Nd to bottom waters is debated. The results of Haley et al. (2004) and Bayon et al. (2011) from the California margin, off Peru and the Niger delta for the stations away from cold seeps support the hypothesis, whereas the data of Nozaki and Alibo (2003) for station PA-9 in the BoB and that of Carter et al. (2012) for two stations in the eastern Pacific Sector of the Southern Ocean, seem to indicate potential removal of Nd in the benthic boundary layer rather than its release. The relative significance of Nd release from the sinking particles vis-à-vis benthic supply can be assessed only when data on dissolved Nd concentration in sediment pore waters become available.

The distribution of $\varepsilon_{\rm Nd}$ in the upper water column (Fig. 4b; Table 1) shows a wide range, between -8 and -15, attributable to multiple sources of dissolved Nd with their distinct $\varepsilon_{\rm Nd}$ signatures. In the following section an effort has been made to estimate the particulate Nd release and its source signature using an inverse modeling approach.

3.3. Dissolved Nd supply from various water masses and from particulate phases in the Bay of Bengal

3.3.1. Inverse modeling

The lateral and vertical distributions of dissolved Nd concentration and its isotope composition in the BoB waters are the result of a complex mixture of Nd contributions from various water masses, sinking particulate matter and sediment–water interactions with their characteristic $\varepsilon_{\rm Nd}$ values. An inverse modeling (Tarantola, 2005; Tripathy and Singh, 2010) approach has been used to determine the contributions from these sources, particularly release from particulate matter. For an underdetermined system such as considered in this study, an inverse model provides the most probable estimates of the fraction of various water masses and the amount of excess dissolved Nd along with their uncertainties based on the mass balance equations of salinity, temperature, Nd concentration and its radiogenic isotope composition.

The inversion method used in this study relies on the following set of mass balance equations for the '*i*th' water mass and the '*j*th' water sample.

$$\sum_{i=1}^{9} f_{ij} = 1$$
 (1)

$$\sum_{i=1}^{9} f_{ij} x_i = x_j \tag{2}$$

$$\sum_{i=1}^{9} f_{ij} \mathrm{Nd}_i + \mathrm{Nd}_j^{\mathrm{excess}} = \mathrm{Nd}_j$$
(3)

$$\sum_{i=1}^{9} f_{ij} \mathrm{Nd}_i \varepsilon_{\mathrm{Nd}_i} + \mathrm{Nd}_j^{\mathrm{excess}} \varepsilon_{\mathrm{Nd}_j^{\mathrm{excess}}} = \mathrm{Nd}_j \varepsilon_{\mathrm{Nd}_j}$$
(4)

where, f_{ij} is the water mass fraction of the '*i*th' water mass in '*j*th' sample, x_i and x_j are either potential temperature or salinity of the '*i*th' water mass and '*j*th' sample, and Nd_i^{excess} is the fraction of dissolved Nd in '*i*th' sample in excess of the sum of contributions from different water masses. These equations are written in a matrix form i.e., d = g(v), where "d" and "v" form the measured and unknown parametric matrices associated by a transformation matrix "g". In this approach, it has been assumed that the variables (elements of matrix "v") follow the log normal probability distributions for the constraint of positivity and the data set (elements of matrix "d") is a linear (quasi-linear) combination of these variables. The quasi-Newton method (Tarantola, 2005) has been used to find the most probable set of variables (v) along with their uncertainties by minimizing the misfit between the matrices, "d" and "g(v)". Considering the underdetermination of the problem and lower sampling frequency at deeper depths, the entire data set is dealt with collectively to seek the most probable solution of the problem.

3.3.2. A priori information

The application of inverse modeling requires *a priori* knowledge of various water mass endmembers contributing Nd to a given sample, their Nd concentration and ε_{Nd}

values. The prominent water masses present in the surface and subsurface layers of the BoB have been discussed previously by several authors (Sastry et al., 1985; Dileep Kumar and Li, 1996; Rao et al., 1996; You, 1997, 2000). Among these, nine water masses are assumed to contribute dissolved Nd to the region of this study (Table 3). These are, (1) G-B dominated Bay of Bengal Low Salinity Water (GB-BBLS); (2) Bay of Bengal Subsurface Water (BBSS); (3) Arabian Sea High Salinity Water (ASHS); (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. These data for GB-BBLS and BBSS are taken to be the same as those measured in this study for surface waters of station 0812, and for the sample from a water depth of 70 m from the central BoB profile at 0811 since its occasional shoaling can measurably alter salinity, Nd and ε_{Nd} in the BoB surface waters. These parameters for ASHS, NIIW and NIDW, water masses forming in the Arabian Sea (Wyrtki, 1973; Dileep Kumar and Li, 1996) are based on unpublished results from station 0802 (14.419°N, 69.418°E; Goswami et al., in preparation) in the eastern Arabian Sea. The values of these properties for the IW and IIW are those reported from the Indonesian straits (Jeandel et al., 1998; Amakawa et al., 2000). The data for MNADW are taken to be the same as that measured at a depth of 3100 m in the profile CD-1504 (27.01°S, 56.97°E) in the Madagascar basin (Bertram and Elderfield, 1993). The potential temperature and salinity data for AABW are assumed to be the same as those reported for water from a depth of 4709 m at GEOSECS station 430 (Dileep Kumar and Li, 1996). The ε_{Nd} and dissolved Nd data for AABW are taken from Frank (2002), Jeandel (1993) and Zieringer et al. (2011).

3.3.3. A posteriori values

The best fit endmember values of potential temperature, salinity, Nd concentration and ε_{Nd} of different water masses calculated based on the inverse model are also given in Table 3. The model sensitivity is checked by varying Nd input of concentrations by ${\sim}20\%$ and ${\sim}2$ units of ϵ_{Nd} for GB– BBLS and AABW, which are the dominant contributors of dissolved Nd to BoB waters. The model results are found insensitive to these variations in a priori values. The uncertainty on water mass fractions estimated from model calculations for the dominant water masses like GB-BBLS, IW and AABW is less than 15%. The average uncertainties on various water mass fractions are $\sim 25\%$, which are lower for higher fractions and vice versa. The proportions of various water masses contributing to the Nd concentration and its isotope composition at different depths along 87°E transect are shown in Fig. 6. The model derived Nd contributions from various water masses to the measured Nd abundance at selected depths in stations 0806 and 0812 are presented in Fig. 7.

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Table 3					
A priori and a posteriori	values of	the water	mass	endmembers.	

Water mass	Pot. temp. (°C)	Salinity	Nd (pmol/kg)	€ _{Nd}
A priori values				
GB-BBLS	27.497 ± 0.001	32.049 ± 0.001	45.4 ± 1.1	-14.5 ± 0.3
BBSS	23.162 ± 0.001	34.747 ± 0.001	26.5 ± 0.7	-14.5 ± 0.3
ASHS	26.347 ± 0.001	36.514 ± 0.001	14.0 ± 0.4	-7.1 ± 0.3
NIIW	11.677 ± 0.001	35.506 ± 0.001	13.5 ± 0.3	-9.0 ± 0.3
NIDW	2.717 ± 0.001	34.813 ± 0.001	17.5 ± 0.4	-10.7 ± 0.3
IW	29.700 ± 0.001	33.970 ± 0.001	7.4 ± 0.2	-4.1 ± 0.3
IIW	4.470 ± 0.001	34.612 ± 0.001	17.6 ± 0.4	-3.6 ± 0.3
MNADW	1.774 ± 0.001	34.738 ± 0.001	24.9 ± 0.6	-8.5 ± 0.3
AABW	-0.615 ± 0.001	34.659 ± 0.001	$34.0\pm0.9^{\rm a}$	$-8.6\pm0.3^{\rm b}$
A posteriori values				
GB-BBLS	27.521 ± 0.001	32.020 ± 0.001	44.7 ± 1.0	-14.8 ± 0.2
BBSS	23.162 ± 0.001	34.747 ± 0.001	25.5 ± 0.7	-17.1 ± 0.3
ASHS	26.347 ± 0.001	36.514 ± 0.001	12.8 ± 0.4	-8.1 ± 0.3
NIIW	11.677 ± 0.001	35.506 ± 0.001	13.0 ± 0.3	-9.8 ± 0.3
NIDW	2.717 ± 0.001	34.814 ± 0.001	16.5 ± 0.4	-13.8 ± 0.3
IW	29.738 ± 0.001	33.912 ± 0.001	7.1 ± 0.2	-4.5 ± 0.3
IIW	4.470 ± 0.001	34.612 ± 0.001	17.2 ± 0.4	-3.9 ± 0.3
MNADW	1.774 ± 0.001	34.739 ± 0.001	24.0 ± 0.6	-9.2 ± 0.3
AABW	-0.615 ± 0.001	34.665 ± 0.001	32.3 ± 0.8	-8.7 ± 0.2

Data source:

GB–BBLS; this study; station 0812 (18.76°N, 87.00°E), depth ≈ 5 m.

BBSS; this study; station 0811 (16.76°N, 86.99°E), depth \approx 70 m.

ASHS; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth ≈ 65 m.

NIIW; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth ≈ 500 m.

NIDW; Goswami et al. (unpubl.); station 0802 (14.42°N, 69.42°E), depth \approx 2100 m.

IW; (Amakawa et al., 2000); station PA-7 (9.99°S, 101.98°E), depth ≈ 5 m.

IIW; (Jeandel et al., 1998); station 20 (11.50°S, 115.95°E), depth \approx 1099 m.

MNADW; (Bertram and Elderfield, 1993); station 1504 (27.01°S, 56.97°E), depth ≈ 3100 m.

AABW; (Dileep Kumar and Li, 1996); station GEOSECS 430 (59.98°S, 60.98°E), depth \approx 4709 m.

^a Zieringer et al. (2011).

^b Jeandel (1993) and Frank (2002).

3.3.3.1. Nd contribution from different water masses. In surface waters, as would be expected, GB-BBLS makes significant contribution to the water mass budget $(f_{GB-BBLS} > 5\%)$ along the entire 87°E transect (Fig. 6a) with its maximum value ($f_{GB-BBLS} > 80\%$) at station 0812 in the northern Bay of Bengal. The Nd contributed by the GB-BBLS decreases generally southward from >95% at the northern station 0812 to $\sim 10\%$ at the southernmost station 0806, and drastically below a depth of ${\sim}50\,\text{m}$ ($f_{\text{GB-BBLS}} \sim 10\%$ or less; Figs. 6a and 7). On the other hand, the Nd contribution of IW decreases from $\sim 30\%$ in surface waters at station 0806 to $\sim 10\%$ at ~ 50 m depth at station 0812 (Fig. 7). The depth of penetration of IW also decreases northward (Fig. 6b); it has Nd contribution of >5% at depths of $\sim 200 \text{ m}$ in the southernmost profile ($\sim 6^{\circ}\text{N}$). These two water masses, GB-BBLS and IW by and large account for almost 100% of salinity but only ~ 40 to \sim 95% of dissolved Nd in BoB surface waters, with lower values in the southern region. This suggests that the surface water salinity of the BoB in the latitude belt $\sim 20^{\circ}$ N–6°N is determined by the Ganga-Brahmaputra in the north (characterized by GB-BBLS) and the Indonesian Throughflow waters in the south. For dissolved Nd, in addition to these two water masses additional source(s) is required to balance the budget. This finding is consistent with earlier observations based on Nd–Salinity and ε_{Nd} –1/Nd relation (c.f. Section 3.1).

Below the surface layer, significant water mass fraction (~30%) of ASHS and BBSS waters are noticed south and north of 13°N respectively, without any discernible signature of their upwelling (Fig. 6c and d). The results indicate that the ASHS water mass enters the southern BoB at a depth interval of ~50–100 m and spreads northward consistent with the finding of Murty et al. (1992) and Sastry et al. (1985). The Nd contribution of ASHS is at a maximum (~30%) at 60 m depth at station 0806, and decreases both northward as well as with depth to values of ~5% at ~800 m depth (Fig. 7). On the other hand, Nd contribution of BBSS is ~15% at 200 m depth at station 0812, decreasing both above and below this depth.

IW is the dominant source of surface waters of the southern and central BoB. In contrast, intermediate water from the Indonesian straits (IIW) is only minor ($f_{\rm IIW} \sim 5\%$) along the 87°E transect (Fig. 6e). This fraction accounts for ~5–10% of Nd in the depth range of 200–1400 m at station 0806 (Fig. 7). The NIIW, a mixture of Persian Gulf Water (PGW) and Red Sea Water (RSW) with ASHS water, enters the southern Bay of Bengal

from the Arabian Sea, contributing a maximum of ~25% Nd at ~400 m depth at station 0806 (Figs. 6f and 7). The Nd contribution (>10%) of NIIW shows a South–North gradient in the depth range ~200–1400 m. This high salinity water mass (NIIW) is present throughout the BoB at an intermediate depth interval of 300–500 m (Wyrtki, 1973; Dileep Kumar and Li, 1996), and is responsible for the high salinity at these depths along the entire 87° E transect in the bay. Below this high saline water mass, NIDW, MNADW and AABW constitute the BoB deep waters (Fig. 6g, h and i). The average depth (NIDW ~900 m and MNADW ~1700 m) of appearance of both NIDW and MNADW (Fig. 6g and h) are shallower com-

pared to their depths of occurrence in the Arabian Sea (at station 0802) and the Madagascar Basin (at station 1504), respectively (Bertram and Elderfield, 1993). This result hints at shoaling of the waters sourced from the Atlantic Ocean due to mixing during their transport to the BoB. In contrast to NIDW and MNADW, AABW seems to be the major contribution of Nd in the BoB deeper waters with its Nd contribution varying from ~80% to the bottom waters (depth ~3800 m at station 0806) to ~20% at depths ~800 m (Fig. 7). Nd concentration at depths shallower than ~800 m is determined by roughly similar contributions from the NIIW, NIDW and MNADW (Fig. 7).



Fig. 6. Distribution of the prominent water masses at different depths along the 87°E transect, (a) GB–BBLS (G–B dominated Bay of Bengal Low Salinity Water); (b) IW (Indonesian Throughflow Surface Water); (c) ASHS (Arabian Sea High Salinity Water); (d) BBSS (Bay of Bengal Subsurface Water); (e) IIW (Indonesian Throughflow Intermediate Water); (f) NIIW (North Indian Intermediate Water); (g) NIDW (North Indian Deep Water); (h) MNADW (Modified North Atlantic Deep Water); (i) AABW (Antarctic Bottom Water). The contour lines indicate the water mass fractions in the water column of the bay.



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additional sources to balance the budget. The need for excess Nd persists even if the measured Nd concentrations of all samples are reduced by 10% to account for potential overestimation of Nd abundance due to measurement uncertainty if any (c.f. Section 3). The excess Nd (i.e., Nd_{measured} - Nd_{calculated}) contribution to the samples ranges from ~ 1 to $\sim 65\%$ of the measured Nd concentration (Fig. 8a), with \sim 85% of total number of samples requiring in excess of 10% of measured Nd to balance its budget. The ϵ_{Nd} values of excess Nd \sim -16.0 \pm 2.0 (Fig 8b) overlap with that of the G-B and peninsular river sediments, in contrast to eolian dust with $\epsilon_{Nd}\approx -13.8$ (Goldstein et al., 1984). Considering that the G-B fluvial sediment flux is orders of magnitude more than that from the peninsular rivers, it is tempting to attribute this excess Nd to its release from G-B sediments depositing on the margins of the northern bay.

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The sources of excess Nd in the BoB waters can be its release from *in situ* riverine particulate matter as well as from margin sediments. The distribution of dissolved Nd concentration with depth also shows a North–South decreasing trend, with systematically higher concentrations throughout the water column in the northern bay relative to the southern stations (Fig. 5). The parallel North–South feature of both dissolved Nd concentrations and settling lithogenic fluxes (Fig. 5; Table 2) is an indication of Nd release from settling particles, analogous to the observation of Nozaki and Alibo (2003) in the Bay of Bengal and the Andaman Sea. Assuming a one dimensional vertical advection–diffusion–scavenging model (Nozaki and Alibo, 2003), the total remineralization flux, J (pmol/kg/year) can be estimated from Eq. (5).

$$K_z \left(\frac{\partial^2 C_d}{\partial z^2}\right) + w \left(\frac{\partial C_d}{\partial z}\right) = R \tag{5}$$

where *R* is a function of *J* flux, the concentration of Nd in various particle classes and their aggregation–disaggregation coefficients, K_z is the eddy diffusion coefficient; *w* is the advection velocity; C_d is the Nd concentration in the dissolved phase and *z* is vertical depth below the sea surface. The solution of this equation with various parameters drawn from Nozaki and Alibo (2003) predicts a linearly increasing trend of dissolved Nd concentration with depth. The slope of this trend is a measure of the *J* flux. The *J* fluxes estimated from the slope of linear fit of C_d (anomalously high C_d at top ~100 m are excluded from the regression) and depth (*z*) of profiles and various S.P. Singh et al./Geochimica et Cosmochimica Acta 94 (2012) 38-56



Fig. 7. The Nd contribution from different water masses for the southernmost station, 0806 and one northern station, 0812. The sum of Nd contributed (ΣNd_{mixing} (%)) by the various water masses at various depths are also given. It seems that ΣNd_{mixing} (%) do not account for the measured dissolved Nd concentrations at several depths in the profiles suggesting the need for additional Nd source(s).

parameters used for profile PA-9 (Nozaki and Alibo, 2003) yield values of ~ 0.14 pmol/kg/year for the central and southern BoB (Table 4). The similarity in J fluxes of Nd in the central and southern BoB suggests that the collective behavior of particles and their properties in these two regions is similar. This is in contrast to the northern BoB where J fluxes a factor of two higher are most likely due to increased particle density. However, despite the similar settling particulate fluxes at the two

stations, 0812 and 0813 in the northern BoB, their J fluxes are significantly different (Table 4). High remineralization rate (J flux) at the latter shallow station is due to its close proximity to the continental slope sediment efflux. This observation further corroborates that in-situ particle dissolution is not the only cause of excess Nd in the BoB.

Furthermore, the observation that there are "hot-spots" of modeled excess Nd (orange patch, Fig. 8a) near the sediment-water interface of the continental margin hints at

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Fig. 8. The BoB water column distribution of (a) excess Nd concentration and (b) excess ε_{Nd} as calculated from the inverse model. The "hot-spots" of Nd release in the northern slope region are indicative of a source of this element from margin sediments (see text). The ε_{Nd} of $\sim -16.0 \pm 2.0$ for the excess Nd overlaps with that of G–B particles, suggesting that the excess Nd is most likely sourced from the G–B Rivers.

Table 4 The *J* flux based on a one dimensional vertical advection–diffusion– scavenging model.

Station	J ^a flux (pmol/kg/year)		
0806	0.13		
0807	0.14		
0808	0.15		
0809	0.14		
0810	0.14		
0811	0.13		
0812	0.17		
0813	0.32		

^a Based on Nozaki and Alibo (2003).

possibility of a sediment source in this region. The release of Nd from margin sediments can be facilitated by solution of Fe–Mn oxyhydroxide coatings on the grains but this requires suboxic redox conditions. Concurrent measurements of dissolved Fe, Mn, REEs and DO would help in testing this hypothesis. Higher remineralization rates in the northern BoB could be due to sediment efflux shown by the hot-spots. Thus, the release of Nd from margin sediments can be an important process (Boundary Exchange) controlling the dissolved Nd budget of the Bay of Bengal similar to earlier studies from other oceanic regions (Jean-del et al., 1998; Lacan and Jeandel, 2005; Arsouze et al., 2009).

The excess Nd from sinking particles and/or from margin sediments contributes significantly to the dissolved Nd budget of coastal and remote regions of this basin receiving a large sediment flux. Considering the average J flux ~ 0.14 pmol/kg/year, the average excess Nd content (~7.5 pmol/kg) in the water column of the BoB can be built up in \sim 50 years only, in comparison to the residence time of Nd ~200 years in the bay (Nozaki and Alibo, 2003). The ε_{Nd} of the water column resulting from the mixing of different water masses is altered due to the addition of this excess Nd and exhibits non-conservative behavior. Thus, it would be difficult to use ε_{Nd} of the water column to track water masses in the presence of the excess Nd derived from particulates. It is therefore important to know the geographical extent to which this process could be significant in a basin in order to use ε_{Nd} as a water mass tracer. In the case of the BoB, receiving a huge sediment influx from the Ganga-Brahmaputra river system, the only station that seems to be free from excess Nd is 0806. For the entire water column, except at the surface and at the bottom of station 0806, the excess Nd is negligible. Hence based on the example of BoB, it can be estimated that the impact of particulate Nd is diminished, and the conservative nature of ε_{Nd} in the water column could be retrieved, at about 1500 km away from the source of the particulates. However, this will vary from basin to basin and will depend on the source strength and flow direction in the basin.

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4. CONCLUSIONS AND IMPLICATION

The lateral and vertical distribution of dissolved Nd and ε_{Nd} in the water column of the Bay of Bengal along 87°E transect exhibits significant lateral and depth variations. The results show that GB-BBLS (Ganga Brahmaputra-Bay of Bengal Low Salinity Water) and AABW (Antarctic Bottom Water) are the dominant sources of dissolved Nd to the surface and deeper waters of the Bay of Bengal. On the other hand, NIIW (North Indian Intermediate Water), NIDW (North Indian Deep Water) and MNADW (Modified North Atlantic Deep Water) make significant Nd contributions to intermediate waters. However, the budget calculations show that the sums of Nd contributions from all the different water masses are inadequate to balance the measured Nd abundances, underscoring the need for an additional source. The source is inferred to be release of Nd from particulate matter delivered by the G-B river system bearing ε_{Nd} $\sim -16.0 \pm 2.0$. Calculations based on an inverse model bring out the existence of "hot-spots" of "Nd excess" along the northern margin sediment-water interface. This excess is most likely a result of Nd release from margin sediments, probably through dissolution of Fe-Mn oxyhydroxide coatings enriched in REEs (Nd) on the nascent settled particles. Consistent with other modeling studies, this study highlights the importance of particle-water interaction in estuaries and sediment-water interaction in margins in regulating the spatial distribution of dissolved Nd and its ε_{Nd} .

The dominant role of GB–BBLS and AABW in regulating Nd and $\varepsilon_{\rm Nd}$ distribution in the water column suggests that variations in their fluxes to the BoB would influence the Nd and $\varepsilon_{\rm Nd}$ in the bay and global oceans through water circulation. Further, significant variations in the supply of particulate matter from the G–B river system and/or sediment water exchange can modify the $\varepsilon_{\rm Nd}$ of surface and bottom waters of the bay. Investigations of these records can provide insight into these processes and their causative factors. The studies of Burton and Vance (2000), Gourlan et al. (2010), Piotrowski et al. (2009) and Stoll et al. (2007) attest to this application.

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