

**LATE QUATERNARY FLUCTUATIONS IN  
CARBONATE AND CARBONATE ION CONTENT  
IN THE NORTHERN INDIAN OCEAN**

Thesis submitted to

**GOA UNIVERSITY**

for the degree of

**DOCTOR OF PHILOSOPHY**

in

**Marine Sciences**

by

**SUSHANT SURESH NAIK**

**National Institute of Oceanography**

**Dona Paula – 403 004, Goa, India**

**2008**

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**2008**

**DEDICATED TO MY PARENTS**

## **DECLARATION**

*I hereby state that the present thesis entitled, "Late Quaternary Fluctuations in Carbonate and Carbonate Ion Content in the Northern Indian Ocean", is original contribution and the same has not been submitted on any previous occasions. To the best of my knowledge, the present study is first comprehensive work of its kind for the area mentioned. The literature related to the problem investigated has been cited. Due acknowledgements have been made wherever facilities and suggestions have been availed of.*

**Sushant Suresh Naik**

*Dr. P. Divakar Naidu*  
*Scientist 'F'*

*June 21<sup>st</sup>, 2008*

**CERTIFICATE**

*As required under the university ordinance OB-9.9, I certify that the thesis entitled "Late Quaternary Fluctuations in Carbonate and Carbonate Ion Content in the Northern Indian Ocean", submitted by Mr. Sushant Suresh Naik for the award of the Degree of Philosophy in Marine Sciences is based on original studies carried out by him under my supervision. The thesis or any part thereof has not been previously submitted for any other degree or diploma in any university or institution.*

**(P. Divakar Naidu)**

Research Guide

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2. **Naik, S.S.**, and Naidu P.D. (2008), Possible factors that control the calcite dissolution in the Western Tropical Indian Ocean, *Current Science*, 95(1), 22-23.

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## PREFACE

Carbon dioxide is one of the most important greenhouse gases responsible for global warming. The Oceans serve as major sinks and source of this gas through adjustments in its calcium carbonate reservoir. Investigation of this entity provides much of our knowledge of paleoclimatic change and is valuable in understanding the global carbon cycle (Farrell and Prell, 1989). The spatial and temporal accumulation patterns of calcium carbonate in the marine sediment records are thus a primary source of data about the carbonate chemistry, circulation of past oceans, global biogeochemical cycle of CO<sub>2</sub> (Peterson, 2001). Since the dissolution of calcium carbonates in the ocean sediments is primarily controlled by the degree of bottom water saturation with respect to the carbonate ion, the changes in carbonate ion concentrations during glacial and interglacials have attracted the attention of paleoceanographers (Broecker, 2004).

Three important paleocarbonate ion proxies find their application in understanding the depth of the calcite transition zone; the size index parameter (Broecker and Clark, 1999); shell weights of planktonic foraminifera (Lohmann, 1995) and; calcite crystallinity (Bassinot et al, 2004). Though these proxies have been largely applied to the Atlantic and Pacific, their application to the Indian Ocean is rare (Broecker and Clark, 1999; Broecker and Clark, 2001). The Indian Ocean remains to be a relatively lesser-studied region and more importantly so the northern Indian Ocean, with its unique monsoon circulation characteristics (Wyrтки, 1973) is a genuine platform to evaluate the glacial to interglacial changes in CO<sub>2</sub> sequestration.

In this context, the proposed research is aimed to understand the Late Quaternary fluctuations in carbonate and carbonate ion content in the northern Indian Ocean with the following specific objectives:

- To identify suitable paleocarbonate ion proxy/proxies for understanding calcite dissolution in the Indian Ocean.
- To compare these proxies within themselves and use of these proxy/proxies in identifying calcite dissolution events and understanding the dissolution mechanisms on the seafloor.
- To understand the dependency of planktonic foraminiferal shell weights on initial growth conditions i.e. carbonate ion and/or temperature from tropical waters.
- To reconstruct the carbonate ion content for the northern Indian Ocean during the Late Quaternary.

This thesis consists of five chapters; contents of each chapter are listed below:

## **Chapter I**

This chapter deals with general introduction to carbon dioxide, its importance as a greenhouse gas, dissolution in seawater and its control over sedimentary calcite, the formation of carbonate ion and its significance. Also discussed here the circulation patterns of the Northern Indian Ocean during the Southwest (SW) and Northeast (NE) monsoons and whether Indian Ocean is a source or sink for CO<sub>2</sub>. An overview of available literature concerning the tackled problem is also put forth.

## Chapter II

This chapter deals with materials and methods. To achieve the proposed objectives, detailed work has been carried out on sediment core top samples from the western and eastern tropical Indian Ocean; SK199C/6, 7, 8, 9, 10, 11, SK218/A and Ocean Drilling Program Site (ODP) 752. Four sediment cores have been used; 1) Arabian Sea core AAS9/21, 2) Bay of Bengal core SK218/A, 3) ODP Site 715 from northern equatorial Indian Ocean on the eastern margin of Maldives Ridge and 4) ODP Site 752 from the eastern Indian Ocean near the crest of Broken Ridge. Data set for 10 cores from Atlantic, Pacific and Indian oceans were obtained from National Geophysical Data Centre (NGDC) of NOAA.

Core tops as well as sectioned core samples were subjected to size fraction analysis and calcium carbonate analysis, of  $>63\mu\text{m}$  and bulk sediment. The size index parameter was calculated from the  $>63\mu\text{m}$   $\text{CaCO}_3$  and bulk sediment  $\text{CaCO}_3$  data. Additionally, Carbonate analysis were carried out from  $<63\mu\text{m}$  fraction of sediment from ODP Sites 715 and 752. The ODP Site 752 core site is situated towards the southern Indian Ocean on a topographic high and has been used for a comparison. Carbonate ion concentration for the respective core sites was estimated from GEOSECS (GEOchemical SECTIONS Study) data. Shell weights (*Globigerinoides sacculifer*, *Neogloboquadrina dutetrei* and *Pulleniatina obliquiloculata*) were determined on selective coretop samples. *Globigerinoides sacculifer* shell weights were determined for the AAS9/21 and SK218/A cores. Shell weights for *Globigerinoides ruber* were determined for the ODP Site 715. Calcite crystallinity was measured on the species *Globigerinoides sacculifer* for the coretops. Scanning Electron Micrographs of *Globigerinoides sacculifer* shell were taken for specific



samples to show the impact of dissolution. Mg/Ca data from *Globigerinoides sacculifer* from the cores AAS9/21 and SK218/A was used as a proxy for temperature. Accelerator Mass Spectrometer radiocarbon dates were used to establish the chronology in AAS9/21 and SK218/A whereas for the ODP Sites 715 and ODP 752 available age control from nannofossil datum's were used (Duncan, 1990; Rea, 1990).

### **Chapter III**

This chapter gives a detailed account of the results obtained from the measurements stated above. The CaCO<sub>3</sub> variations patterns for the Atlantic, Pacific and Indian Oceans have been presented covering a time span of last 600kyr. Various carbonate ion proxies i.e. size index, shell weight and calcite crystallinity are compared within themselves using the core top samples. In-situ carbonate ion calculated from GEOSECS stations data have been used wherever comparison was required with respect to carbonate ion. The comparison shows significant relationships and suggests that all the three proxies can prove useful in the northern Indian Ocean to understand calcite dissolution and underlying mechanisms. A comparison has been made using the ODP Sites 715 and 752 and the CaCO<sub>3</sub> content of finer (<63 μm) and coarser fraction (>63 μm) to understand the temporal significance of size index proxy. ODP Site 752 shows high carbonate content throughout the 400kyr period, which is attributed to winnowing at shallow depths. Results show that carbonate content of the finer size fraction controls the bulk CaCO<sub>3</sub> variations in core ODP Site 715 as opposed to ODP Site 752. Shell weights from cores AAS9/21 and SK218/A are compared with the Mg/Ca data to understand the

effects of sea surface temperatures on shell weights. The core SK218/A is seen to be composed largely of broken foram shells for the last 10kyr as compared to core AAS9/21 which displays a continuous well preserved record and heavier shells.

## **Chapter IV**

This chapter consists of discussions on four important issues; 1) An overview  $\text{CaCO}_3$  fluctuations during glacial and interglacials in equatorial regions of Pacific, Atlantic and Indian Oceans A positive correlation has been found between carbonate content and bottom water carbonate ion concentration at respective depths for all the three major oceans which suggests a carbonate ion control over dissolution in the equatorial regions; 2) Using core top sediment samples from a western tropical Indian Ocean transect,  $\text{CaCO}_3$  size index, shell weights and calcite crystallinity have been successfully utilized to understand the calcite dissolution and is found that calcite dissolution starts from as shallow as 2500m and becomes intense from 3900m onwards in the equatorial Indian Ocean. This is because of bottom water undersaturation with respect to carbonate ion and not due to acidification of pore waters. It has also been shown that shell weights are dependant on growth conditions i.e. surface water carbonate ion in the tropical Indian Ocean. (3) The contradictory variations between size index and  $<63 \mu\text{m}$   $\text{CaCO}_3$  content in ODP Site 715 as compared to ODP Site 752 suggest that at ODP Site 715, the finer fractions mainly composed of coccoliths, controls the  $\text{CaCO}_3$  content of the sediment. This presents a severe drawback for application of the size index to understand the temporal carbonate ion variations; 4) Absence of sufficient number of planktonic foraminifera shells during the Holocene from core SK218/A suggest the corrosive nature of Bay of Bengal waters at 3000m during the Late Holocene compared to the Last Glacial

Maximum (LGM) when the carbonate ion gradient was steeper. Results from AAS9/21 show that the 90ppmV change in atmospheric CO<sub>2</sub> from LGM to the present interglacial has produced a 45- $\mu$ mol/kg change in surface water carbonate ion causing CO<sub>2</sub> sequestration.

## **Chapter V**

Deals with summary and conclusions on the use of proxies in understanding the glacial-interglacial carbonate ion changes in the Northern Indian Ocean.

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Foremost, I am greatly indebted to **Dr. P. Divakar Naidu**, my thesis guide who has encouraged me throughout. At the time of my PhD registration I got an opportunity to be a part of the National Centre for Antarctic and Ocean Research, and had to juggle between two diverse research fields. My research guide has been very patient in this regard in seeing me complete my thesis work. Needless to say this thesis would not have been possible without his guidance.

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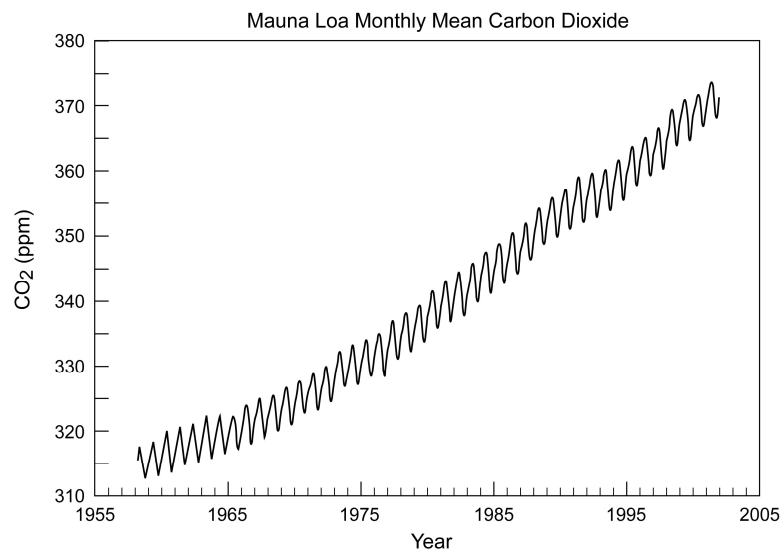
Finally, I thank my parents for their unending love and support throughout. I also thank little **Suhani**, my daughter who has helped me in shuffling and re-shuffling many of the reprints used in this thesis.

# CHAPTER I

## INTRODUCTION

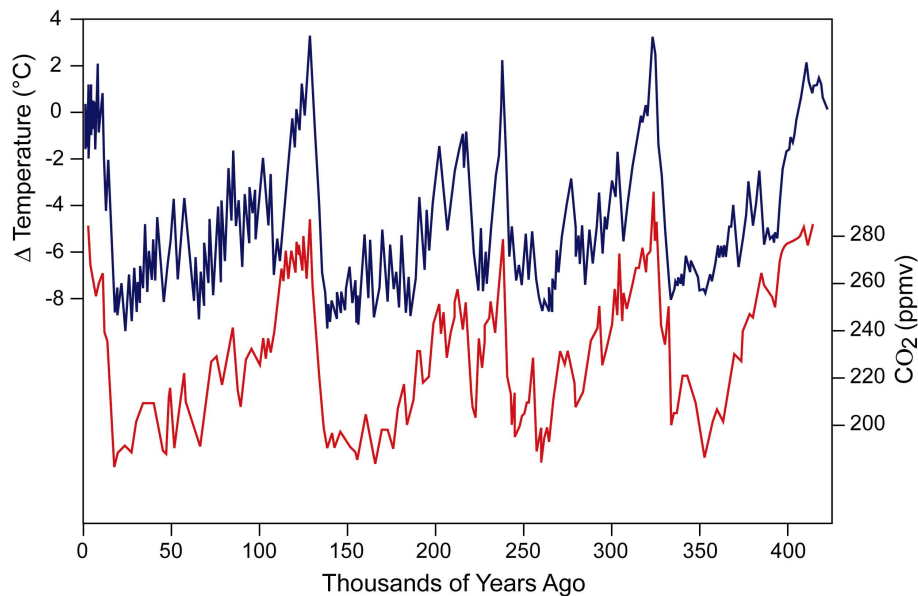
### 1.1 General Introduction:

The greenhouse effect is one of Earth's natural processes which helps to regulate the temperature of our planet and hence is essential for life on Earth. It is the result of heat absorption by certain gases in the atmosphere known as 'the greenhouse gases' because they effectively 'trap' heat in the lower atmosphere and re-radiate some of the heat downwards. Without a natural greenhouse effect, the temperature of the Earth would be about 0°F (-18°C) instead of its present 57°F (14°C). Water vapor is the most abundant greenhouse gas, followed by carbon dioxide and other trace gases. The foremost among these and of growing concern is carbon dioxide emitted from combustion of coal oil and gas. Human activity has been increasing the concentration of greenhouse gases in the atmosphere. The present values of this gas in the atmosphere have exceeded 380 ppmv (Fig. 1).



**Fig. 1. Mauna Loa Carbon Dioxide Record documents a 0.53% or two parts million per year increase in atmospheric carbon dioxide since 1958. This gas alone is responsible for 63% of the warming attributable to all greenhouse gases according to NOAA's Earth System Research Lab (source: National Oceanographic and Atmospheric Administration)**

The direct evidence for natural variations in atmospheric CO<sub>2</sub> comes from the air that is trapped in Antarctic glacial ice. Records from Antarctic ice cores indicate that the concentration of CO<sub>2</sub> in the atmosphere has varied in step with the waxing and waning of ice ages (Barnola *et al.*, 1987; Petit *et al.*, 1999) (Fig. 2). The concentration of CO<sub>2</sub> in our atmosphere today is the highest, not been exceeded in the last 420,000 years, and likely not in the last 20 million years (Petit *et al.*, 1999). At the end of the last ice age 18 thousand years ago (18ka), CO<sub>2</sub> rose from a glacial minimum of 189 ppm to 265 ppm at the beginning of the Holocene.

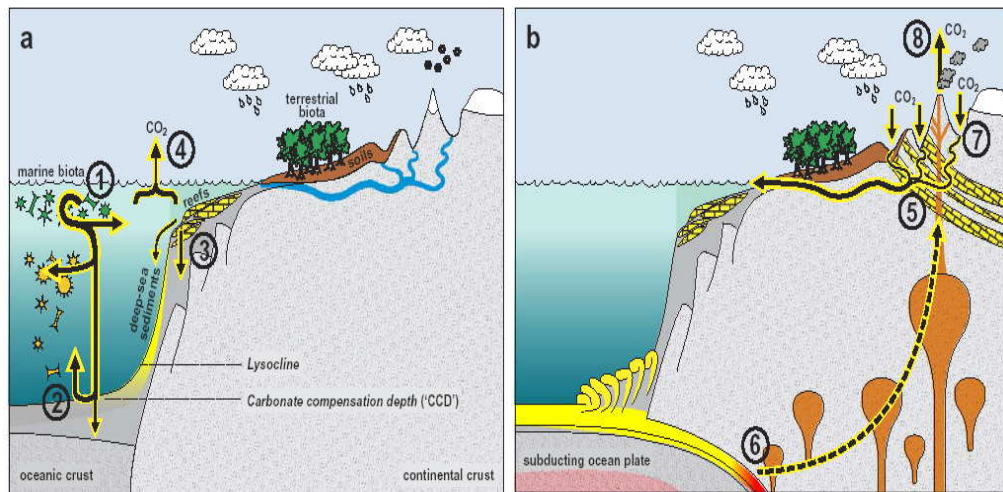


**Fig. 2. Temperature and CO<sub>2</sub> concentrations in atmosphere over the past 400,000 years (from Petit *et al.*, 1999).**

This concentration of CO<sub>2</sub> in the atmosphere is set by the separation of carbon between the various reservoirs of the ‘surficial’ system and ‘geological’ reservoirs (Berner and Caldeira, 1997). The former includes atmosphere, oceans, biosphere, soils and exchangeable sediments in the marine environment (Fig. 3a and b) while the



latter include crustal rocks and deeply buried sediments in addition to the underlying mantle.



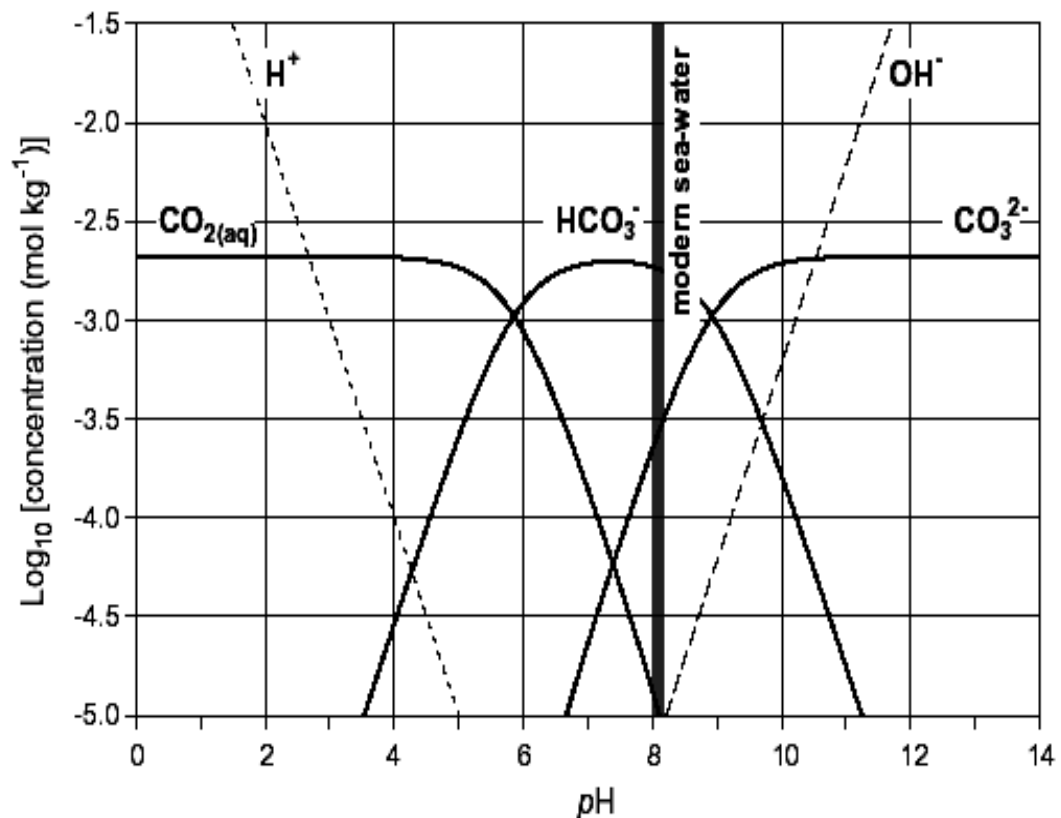
**Fig. 3. The global biogeochemical cycling of calcium carbonate. (a) Modes of CaCO<sub>3</sub> transformation and recycling within the surficial system and loss to the geological reservoir (labeled '1' through '4'). 1) Precipitation of calcite by coccolithophores and foraminifera in the open ocean, 2) Carbonate reaching deep-sea sediments and subsequent dissolution if the bottom water is under-saturated and/or the organic matter flux to the sediments is sufficiently high, 3) Precipitation of CaCO<sub>3</sub> by corals and shelly animals. Because modern surface waters are over-saturated relatively little of this carbonate dissolves *in-situ*, and instead contributes to the formation of reefal structures or is exported to the adjoining continental slopes, 4) Precipitation of CaCO<sub>3</sub> resulting in higher pCO<sub>2</sub> at the surface, driving a net transfer of CO<sub>2</sub> from the ocean to the atmosphere. (b) Modes of CaCO<sub>3</sub> transformation and recycling within the geologic reservoirs and return to the surficial system (labeled '5' through '8'). 5) CaCO<sub>3</sub> laid down in shallow seas as platform and reef carbonates and chalks can be uplifted and exposed to erosion through rifting and mountain-building episodes. CaCO<sub>3</sub> can then be directly recycled, 6) Thermal breakdown of carbonates subducted into the mantle, resulting in release of CO<sub>2</sub>, 7) Weathering of silicate rocks, 8) Emission to the atmosphere of CO<sub>2</sub> produced through decarbonation. This closes the carbon cycle on the very longest time-scales (from Ridgwell and Zeebe,2005)**

## 1.2 Seawater carbonate chemistry:

In seawater, carbon occurs as several species: CO<sub>2</sub> gas, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> as well as carbon combined in organic molecules. HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> are the most important of these. Precipitation of CaCO<sub>3</sub> from seawater may be described by the following reaction:



Under typical marine conditions, carbon dioxide will largely hydrate to form a proton ( $\text{H}^+$ ) and a bicarbonate ion ( $\text{HCO}_3^-$ );  $\text{H}_2\text{O} + \text{CO}_2(\text{aq}) \rightarrow \text{H}^+ + \text{HCO}_3^-$ , while true carbonic acid ( $\text{H}_2\text{CO}_3$ ) is only present in very small concentrations. A fraction of  $\text{HCO}_3^-$  dissociates to form a carbonate ion ( $\text{CO}_3^{2-}$ );  $\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-}$ . The sum total;  $\text{CO}_2(\text{aq}) + \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$  is collectively termed dissolved inorganic carbon (DIC) (Fig. 4).



**Fig. 4.** The concentrations of the dissolved carbonate species as a function of pH : Dissolved carbon dioxide ( $\text{CO}_{2(\text{aq})}$ ), bicarbonate ( $\text{HCO}_3^-$ ), carbonate ion ( $\text{CO}_3^{2-}$ ), hydrogen ion ( $\text{H}^+$ ), and hydroxyl ion ( $\text{OH}^-$ ). At modern seawater pH, most of the dissolved inorganic carbon is in the form of bicarbonate. Note that in seawater, the relative proportions of  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  control the pH and not vice versa. (from Ridgwell and Zeebe, 2005).

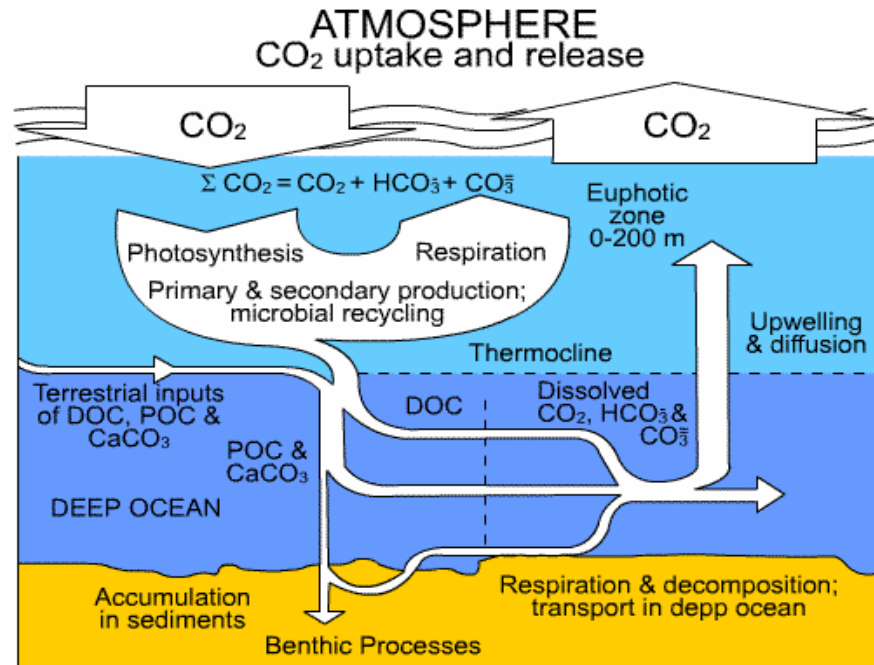
The climatic importance of the  $\text{CaCO}_3$  precipitation reaction arises because although the sum total of dissolved carbon species (DIC) is reduced, the remaining carbon is re-partitioned in favor of  $\text{CO}_2(\text{aq})$ , resulting in a higher partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) in the surface ocean. Precipitation of carbonate carbon drives an increase

in ocean  $p\text{CO}_2$ , and with it, an increase in atmospheric  $\text{CO}_2$  concentration. Conversely, dissolution of  $\text{CaCO}_3$  drives a  $p\text{CO}_2$  (and atmospheric  $\text{CO}_2$ ) decrease. Whether  $\text{CaCO}_3$  precipitates or dissolves depends on the relative stability of its crystal structure. This can be directly related to the ambient concentrations (strictly, activities) of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{=}$  by the saturation state (also known as the solubility ratio)  $\Omega$  of the solution, defined;  $\Omega = [\text{Ca}^{2+}] * [\text{CO}_3^{=}] / K_{\text{sp}}$ , where  $K_{\text{sp}}$  is a solubility constant (Zeebe and Gladrow, 2001). The precipitation of calcium carbonate from seawater is thermodynamically favorable when  $\Omega$  is greater than unity and occurs at a rate taking the form of a proportionality with  $(\Omega - 1)^n$  (Zhong and Mucci, 1993), where 'n' is a measure of how strongly the precipitation rate responds to a change in  $\text{CO}_3^{=}$ . Conversely,  $\text{CaCO}_3$  will tend to dissolve at  $\Omega < 1.0$ , and at a rate proportional to  $(1 - \Omega)^n$  (Walter and Morse, 1985). As well as the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{=}$ , depth in the ocean is also important because  $K_{\text{sp}}$  scales with increasing pressure. Since  $K_{\text{sp}}$  and  $\Omega$  are inversely related, the greater the depth in the ocean the more likely the ambient environment is to be under-saturated (i.e.,  $\Omega < 1.0$ ).

### 1.3 Carbonate production in the ocean:

Biological productivity in the ocean plays a central role in the sequestration of atmospheric carbon dioxide, which is referred to as the “biological pump” (Fig. 5). The biological pump extracts carbon from the “surface skin” of the ocean that interacts with the atmosphere, presenting a lower partial pressure of carbon dioxide to the atmosphere and thus lowering its  $\text{CO}_2$  content (Sigman and Haug, 2003). The ocean receives a continual input of calcium from riverine and groundwater sources and from the hydrothermal alteration of oceanic crust at mid-ocean ridge spreading centers. Balancing this input is the biological precipitation of calcium carbonate

(CaCO<sub>3</sub>) by shell and skeletal-building organisms in both shallow marine and open-ocean environments.



**Fig. 5. Schematic of the ocean carbon biological pump. Transfer of CO<sub>2</sub> from the surface oceans to the deep water is brought about by photosynthesis. Marine algae are responsible for nearly one third of the global gross photosynthetic production. The important fraction of this cycling is the amount of carbon that is lost from the surface layer to the deeper ocean (the export production) compared to the carbon that is simply recycled in, or near, the euphotic zone (up to the top 50 metres). The sequestration of carbon in the ocean interior by the growth of phytoplankton in the sunlit surface ocean, the downward rain of organic matter back to carbon dioxide (CO<sub>2</sub>). The nutrients and CO<sub>2</sub> are reintroduced to the surface ocean by mixing and upwelling. The biological pump lowers the CO<sub>2</sub> content of the atmosphere by extracting it from the surface ocean (which exchanges CO<sub>2</sub> with the atmosphere) and sequestering it in the isolated waters of the ocean interior. In most of the lower and mid-latitude ocean, the surface is isolated from the deep-sea by a temperature-driven density gradient, or “thermocline” (Houghton et al., 1996).**

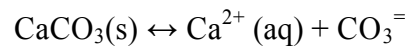
In the deep sea, the primary contributors to the carbonate budget of open-ocean sediments are the skeletal remains of calcareous plankton that have settled down from the surface after death. Calcareous skeletal material is made of either calcite or aragonite, both of which have the same chemical formula, CaCO<sub>3</sub>, but different crystalline structure. Foraminifera are amongst the important carbonate

producers in the open ocean along with coccolithophorids, unicellular phytoplankton and zooplankton. Foraminifera produce a calcareous shell or 'test', a few hundred microns in size that sinks after death or reproduction to the seafloor. They construct their skeletal elements out of mineral calcite, the more stable polymorph of  $\text{CaCO}_3$ . Seafloor sediments consisting of more than 30% by weight calcium carbonate are traditionally referred to as calcareous or carbonate ooze. Such oozes accumulate at the rate of 1-4cm per 1000yrs and cover roughly half of the ocean bottom. Carbonate oozes are the most widespread biogenous sediments in the ocean.

While the biological production of calcium carbonate in oversaturated surface waters determines the input of carbonate to the deep sea, it is the dissolution of carbonate in undersaturated deep waters that has the dominant control on calcium carbonate accumulation in the open ocean. Since carbonate production rates in the surface ocean today greatly exceed the rate of supply of calcium, this 'compensation' through dissolution must occur in order to keep the system in steady state. Increased dissolution at depth is largely a function of the effect of increasing hydrostatic pressure on the solubility of carbonate. However superimposed on this bathymetric effect are regional preservation patterns related to differences in carbonate input and the carbonate chemistry of deep water masses. Carbonate oozes in the deep-sea serve as a major reservoir of calcium and carbon dioxide on the earth's surface. Their spatial and temporal accumulation patterns in the marine stratigraphic record are thus a primary source of data about the carbonate chemistry and circulation of past oceans as well as of the global biogeochemical cycle of  $\text{CO}_2$ .

## 1.4 Lysocline and the CCD:

The distribution of carbonate sediments in the ocean basins is far from uniform. Although surface productivity and dilution by non-carbonate sediment sources can locally influence the concentration of carbonate in the deep-sea sediments, the clear-cut relationship between calcium carbonate content and water depth indicates that carbonate dissolution plays a major role in governing carbonate dissolution patterns (Peterson, 2001). To a first approximation, the dissolution of carbonate on the sea floor is a function of the corrosiveness or saturation state of the overlying bottom waters.



At equilibrium, the rate of carbonate dissolution is equal to the rate of its precipitation and the seawater is said to be saturated with respect to the carbonate phase. In the deep sea, the degree of calcium carbonate saturation (D) can be expressed as:

$$D = \frac{[\text{Ca}^{2+}]_{\text{seawater}} \times [\text{CO}_3^{2-}]_{\text{seawater}}}{[\text{Ca}^{2+}]_{\text{saturation}} \times [\text{CO}_3^{2-}]_{\text{saturation}}}$$

Where  $[\text{Ca}^{2+}]_{\text{seawater}}$  and  $[\text{CO}_3^{2-}]_{\text{seawater}}$  are the *in situ* concentrations in the water mass of interest and  $[\text{Ca}^{2+}]_{\text{saturation}}$  and  $[\text{CO}_3^{2-}]_{\text{saturation}}$  are the concentrations of these ions at equilibrium or saturation at the same conditions of pressure and temperature (Peterson, 2001). Since shell formation and dissolution cause the concentration of  $\text{Ca}^{2+}$  to vary less than 1% in the ocean, the degree of calcium carbonate saturation (D) can be simplified and expressed in terms of the concentration of the carbonate ions only:

$$D = \frac{[\text{CO}_3^{=}] \text{ seawater}}{[\text{CO}_3^{=}] \text{ saturation}}$$

D is thus a measure to the degree to which a seawater sample is saturated with respect to calcite. Values of  $D > 1$  indicates oversaturation while values of  $D < 1$  indicate undersaturation and a tendency for calcium carbonate to dissolve. Since the saturation carbonate ion concentration increases with increasing pressure and decreasing temperature, calcium carbonate is more soluble in deep sea than at the surface. At the depth in the water column where  $D = 1$ , the transition from oversaturated to undersaturated conditions is reached. This depth is known as the saturation horizon.

The carbonate used by many planktonic organisms to form their hard parts redissolves when the organisms die and sink into deep water, releasing calcium and carbonate ions back into solution. The depth at which the dissolution of calcareous skeletal material begins (i.e. the depth where the water has become significantly undersaturated) is called the **lysocline**. The depth at which all the carbonate has dissolved is called the Calcite Compensation Depth (**CCD**). The aragonite structure is thermodynamically less stable than that of calcite, so aragonite dissolves more readily than calcite. Therefore the lysocline and CCD are shallower for aragonite than for calcite, because skeletal material is much more commonly formed of calcite than aragonite. It is rare to find aragonite remains in sediments below 1-2km and sediments below 4km seldom contain significant amount of calcite debris.

Variations in depth of the lysocline are controlled by the chemistry of the water column (carbonate equilibria and pH). Variations in the CCD are controlled partly by chemistry and partly by the supply of calcareous material sinking from the

surface. Because it is not easy to determine how much material has been dissolved, both lysocline and CCD are depth zones rather than precisely defined levels. High biological production results in large populations of organisms and a high rate of supply of calcareous skeletal material to deep water when the organisms die. A heavy 'rain' of carbonate debris will reach greater depths before it all dissolves than would a meager supply of calcareous material sinking from a region of low biological production. So the CCD tends to be depressed beneath areas of high biological production. Cullen and Prell, (1984), made an extensive study using surface sediment samples from the northern Indian Ocean to determine how abundance of planktonic foraminifera species are affected by dissolution. Variations in abundance of dissolution resistant planktonic foraminifera species with water depth reveal the foraminiferal lysocline (FL) to be at 3800m in the equatorial Indian Ocean, 3300m in the Arabian Sea and 2600 to 2000m in the Bay of Bengal. Lower to these depths whole foraminiferal tests are absent, below 4600m in eastern equatorial region, below 5000m in western equatorial region and below 3000m in the Bay of Bengal (Cullen and Prell, 1984). This depth is the Foraminiferal Compensation Depth which is similar to the CCD.

### **1.5 Importance of $\text{CO}_3^{=}$ in the oceanic $\text{CO}_2$ cycle:**

In today's ocean, marine organisms secrete calcitic hard parts at a rate several times faster than  $\text{CO}_2$  is being added to the ocean-atmosphere system (via planetary outgassing and weathering of continental rocks) (Broecker, 2003). While the state of saturation in the ocean is set by the product of the  $\text{Ca}^{2+}$  and  $\text{CO}_3^{=}$  concentrations, calcium has such a long residence ( $10^6$  yr) that, at least on the timescale of a single glacial cycle ( $\sim 10^5$  yr), its concentration can be assumed to have remained unchanged



(Broecker, 2003). In contrast, the dissolved inorganic carbon in the ocean is replaced on a timescale roughly equal to that of the major glacial to interglacial cycle ( $10^5$  yr). But, since in the deep sea  $\text{CO}_3^{=}$  ion makes up only  $\sim 5\%$  of the total dissolved inorganic carbon, its adjustment time turns out to be only about one-twentieth that for dissolved inorganic carbon  $\sim 5,000$  yr (Broecker, 2003). Hence, the concentration of  $\text{CO}_3^{=}$  has gradients within the sea and likely has undergone climate-induced changes. These changes involve both the carbonate ion concentration averaged over the entire deep ocean and its distribution with respect to water depth and geographical location. It is the global average carbonate ion concentration in the deep sea that adjusts in order to assure the burial of  $\text{CaCO}_3$  in the sediments matches the input of  $\text{CO}_2$  to the ocean atmosphere system. As part of the Geochemical Section Studies (GEOSECS), Transient Tracers in the Ocean program (TTO), South Atlantic Ventilation Experiment (SAVE) and World Ocean Circulation Experiment (WOCE) ocean surveys,  $\Sigma \text{CO}_2$  and alkalinity measurements were made on water samples at various depths from the world oceans. Given the depth, temperature, salinity and phosphate it is possible to compute *in situ* carbonate ion concentrations. Taro Takahashi from Lamont Doherty Earth Observatory has played a key role in these measurements and conversion to *in situ* carbonate ion concentrations. A complete picture of the  $\text{CO}_3^{=}$  ion concentrations in the deep sea is now available. Below 1,500m in the world ocean, the distribution of carbonate ion concentration is remarkably simple. For the most part, waters in the Pacific, Indian and Southern Oceans have concentrations confined to the range  $83 \pm 8 \mu\text{mol kg}^{-1}$  (Takahashi, 2001). The exception is the northern Pacific, where the values drop to as low as  $60 \mu\text{mol kg}^{-1}$ . In contrast much of the deep water in the Atlantic has concentrations in the range  $112 \pm 5 \mu\text{mol kg}^{-1}$  (Takahashi, 2001).

Attention is therefore now focused on distribution of  $\text{CO}_3^{=}$  concentration in the deep sea for it alone sets the depth of the transition zone.

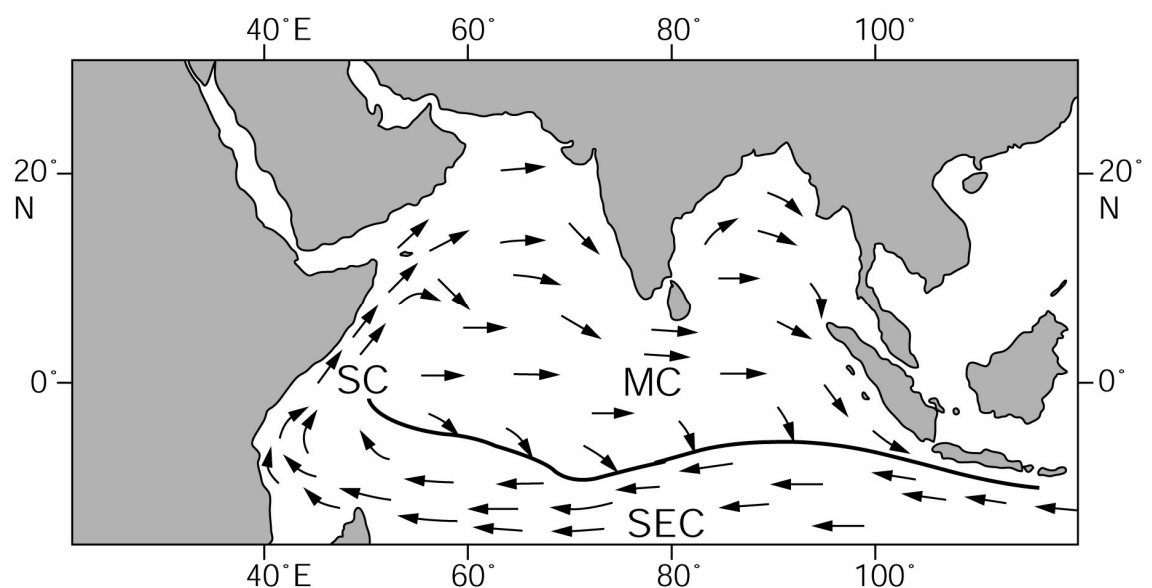
Dissolution of calcite proceeds probably by three different mechanisms: The first of these is termed water column dissolution. As foraminifera shells fall quite rapidly and as they encounter calcite-undersaturated water only at great depth, it might be concluded that dissolution during fall is unimportant. But it has been suggested that organisms feeding on falling debris ingest and partially dissolve calcite entities (Milliman *et al.*, 1999). The two other processes involve dissolution of calcite after it reaches the seafloor. A distinction is made between dissolution that occurs before burial (i.e. interface dissolution) and dissolution that take place after burial (i.e. pore water dissolution). The former presumably occurs only at water depth greater than that of the saturation horizon. But the later has been documented to occur above the calcite saturation horizon. It is driven by respiration  $\text{CO}_2$  released to the pore waters.

## **1.6 Study Area:**

### **1.6.1 Oceanographic settings:**

The Indian Ocean ranks third in size amongst the major oceans of the world. It covers an area of 73million square kilometers. It has a triangular and asymmetric shape with width exceeding 10,000kms between the Cape of Good Hope and Western Australia and decreases sharply on moving northwards to India. The Indian Ocean is unique in that it is limited in the north by the Asian continent and lies well below  $30^\circ\text{N}$ , cut off from the cold waters of polar origin.

The most unique characteristics of the northern Indian Ocean are the semi-annually reversing monsoon winds (Wyrтки, 1973). The influence of the monsoons on the Indian Ocean is seen in the reversal of the surface circulation and in the hydrographical conditions of the surface waters down to 10-20°S. During the South West (SW) monsoon (May through October) the surface low level of southeasterly trade winds of the Southern Hemisphere extend across the equator to become southerly or southwesterly in the Northern Hemisphere which drive the Somali Current (SC), South Equatorial Current (SEC) and the Monsoon Current (MC) (Fig. 6). The northward flowing Somali Current invokes intense upwelling along the coast of Somalia (Bruce, 1974; Schott, 1983). During the SW monsoon period the strong winds blow parallel to the Oman coast and develop another centre of intense upwelling. The volume and nutrient enrichment caused by the upwelling along the Oman Margin is stronger compared to the volume and enrichment resulting from upwelling along the Somali Margin (Wyrтки, 1973; Bruce, 1974; Shallow, 1984). Along the west coast of India weak upwelling centres develop under favourable conditions during this period (Wyrтки, 1973).

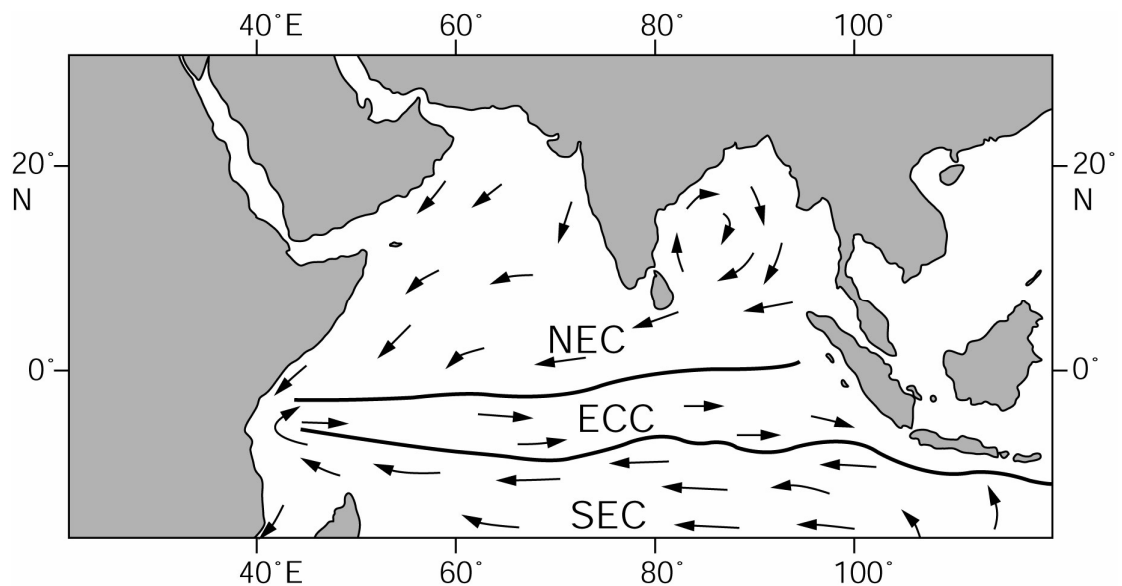


**Fig. 6. Surface circulation in the Indian Ocean during the peak period (August) of the SW monsoon (from Wyrтки, 1973)**

Oceanic circulation during the NE monsoon is relatively weak and characterized by the North Equatorial Current (NEC), an eastward flowing Equatorial Counter Current (EEC), and a moderately developed anticyclonic gyre (Fig.7).

Two surface-water masses form in the northern Indian Ocean (Wyrтки, 1973). A high-salinity water mass is formed in the Arabian Sea due to excess evaporation and the subsurface flow of Persian Gulf and Red Sea water. A low-salinity water mass is formed in the Bay of Bengal by excess precipitation and abundant river runoff. Thus a great salinity gradient exists in the northern Indian Ocean. The low-salinity water mass of the Bay of Bengal flows to the south of Ceylon; one branch continues westward along latitude of 5°N and another branch extends northwestwardly along the coast of India during the North East (NE) monsoon.

In contrast to the salinity patterns in the northern Indian Ocean, variation in sea-surface temperature (SST) is minor.



**Fig. 7. Surface circulation in the Indian Ocean during the peak period (February) of the NE monsoon (from Wyrтки, 1973)**

Much of the regional temperature variation is due to upwelling of cooler subsurface waters in the western Arabian Sea during the SW monsoon. This creates an east-west temperature gradient in the region. During the NE monsoon, equatorial surface waters remain between 28°C and 28.5°C. A weak north-south temperature gradient is observed in the Bay of Bengal, and a weak NW- SE gradient occurs in the Arabian Sea. However, equatorial upwelling does not occur in the Indian Ocean as in the Pacific and Atlantic, because in those oceans, upwelling occurs as a result of the southeast trade winds blowing across the equator and causing surface divergence, which are not present in the Indian Ocean. The Indian Ocean, north of the Hydrochemical Front (a strong discontinuity in hydrochemical structure at 10°S), has been believed to serve as a source of CO<sub>2</sub> to the atmosphere for quite some time (George *et al.*, 1994; Takahashi, 1989). Due to the very high partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in subsurface waters (>1000 l atm), upwelling and vertical mixing were expected to favor outgassing of CO<sub>2</sub> from the surface layer in the northwestern Indian Ocean (George *et al.*, 1994). This effect would be aided by the biological precipitation of CaCO<sub>3</sub> (calcification), which raises pCO<sub>2</sub> of surface waters (pCO<sub>2</sub><sup>sw</sup>), but opposed by the high rate of photosynthetic production, which lowers pCO<sub>2</sub><sup>sw</sup>, sustained by copious nutrients in the mixed-layer. The results of the Joint Global Ocean Flux Study (JGOFS) undertaken between 1993 and 1997 have conclusively established that the Arabian Sea serves as a source of CO<sub>2</sub> for the atmosphere at almost all places and during all seasons (Naqvi *et al.*, 2005). An earlier study by George *et al.* (1994), had led to an estimate of 79 Tg C for the annual CO<sub>2</sub> emission from the Arabian Sea (area 6.2 x 10<sup>6</sup> km<sup>2</sup>). Thus, while the unique physical forcing results in extremely pronounced changes in the flux of CO<sub>2</sub> both in space and time with the SW Monsoon accounting for the bulk of the emissions, the overall contribution of the Arabian Sea

to the global air–sea CO<sub>2</sub> exchange is not very significant due to its small area. The northwestern Indian Ocean, which receives outflows from the Persian Gulf and the Red Sea, appears to hold more anthropogenic CO<sub>2</sub> than the equatorial Indian Ocean. The total inventory of anthropogenic CO<sub>2</sub> in the Indian Ocean north of 35°S has been estimated to be 13.6 Pg C (1 Pg = 10<sup>15</sup> g). Also, unlike the Pacific and the Atlantic Oceans the equatorial Indian Ocean appears to be a relatively small source of atmospheric CO<sub>2</sub> (Sabine *et al.*, 2000). The net annual flux of CO<sub>2</sub> for the region lying north of 36°S was 150 Tg C, and it was directed from the atmosphere to the ocean. The Indian Ocean as a whole (north of 36°S) oscillates between a weak net source (22 Tg) during January– March to a net sink (87 Tg) during July–September (Sabine *et al.*, 2000). Interestingly the period of maximal net absorption is the same as that of maximal SW Monsoon-forced emissions from the Arabian Sea, reflecting the dominance of removal by CO<sub>2</sub> -undersaturated waters in determining the CO<sub>2</sub> uptake/emission balance in the region.

Comparison for the three major world oceans shows that the Atlantic Ocean is the largest net sink for atmospheric CO<sub>2</sub> (39%) followed by Southern Ocean (26%), the Indian Ocean (24%) and the Pacific Ocean (11%) (Takahashi *et al.*, 1997; Takahashi, 2001). The behavior of the Atlantic Ocean as a strong sink of CO<sub>2</sub> is due to the fact that the North Atlantic contain low CO<sub>2</sub> concentrations, which are in turn caused primarily by the short residence time (~80y) of the North Atlantic Deep Waters (Takahashi, 2001). The Pacific Ocean behaves as a weak sink due to its balance as a CO<sub>2</sub> source during El Niño and non sink during El Niño periods whereas cold temperatures and moderate photosynthesis is responsible for the large CO<sub>2</sub> uptake by the Southern Ocean (Takahashi, 2001).

## 1.7 Previous Studies:

### 1.7.1 Calcium carbonate fluctuations:

The existence of interglacial/glacial  $\text{CaCO}_3$  cycles in the equatorial Pacific Ocean was first observed during the Swedish Deep Sea Expedition (1947-1948) (Arrhenius, 1952). Since then many studies have been devoted to unraveling  $\text{CaCO}_3$  cyclicity in the Pacific and Atlantic oceans and a few in the Indian Ocean. There has been a debate whether productivity of  $\text{CaCO}_3$  secreting organisms or dissolution of  $\text{CaCO}_3$  essentially control the  $\text{CaCO}_3$  cycles. Arrhenius (1952, 1988) Olausson (1965, 1985), Emerson and Bender (1981) and Archer (1991) argued that productivity has the most important influence on  $\text{CaCO}_3$  content in the deep-sea sediments, whereas Gardner (1975), Berger (1973,1992), Farrell and Prell (1989) were of the opinion that it is mainly controlled by dissolution.

In the Pacific Ocean, it is widely accepted that  $\text{CaCO}_3$  content is higher during glacials and lower during interglacials (Volat *et al.*, 1980). This pattern has been termed as the 'Pacific pattern'. In contrast, in the Atlantic Ocean,  $\text{CaCO}_3$  content is generally higher during interglacials and lower during glacials (Volat *et al.*, 1980), which is termed as the 'Atlantic pattern'. However, the typical Pacific pattern of  $\text{CaCO}_3$  variation has only a limited geographical extent in the Pacific (Snoeckx and Rea, 1994), and thus the entire Pacific Ocean is not marked by the same pattern of  $\text{CaCO}_3$  changes in the Quaternary. The Quaternary  $\text{CaCO}_3$  patterns in the Indian Ocean have not been analyzed in such detail as in the Pacific and Atlantic Oceans. In the Indian Ocean some sites exhibit a Pacific pattern (Olausson, 1967, 1969, 1971; Oba, 1969; Naidu, 1991, 1994; Berger, 1992), whereas others show both Pacific and Atlantic patterns (Peterson and Prell, 1985; Naidu *et al.*, 1993).

A few studies with regard to calcium carbonate fluctuations have been carried out in the Indian Ocean. Peterson and Prell (1985b) have used a foraminifera-based Composite Dissolution Index (CDI) to identify the present level of the lysocline to be at a water depth of 3800m. Cores from the Ninetyeast Ridge at 6°S from the same study, suggest that the dissolution of carbonate is out of phase with glacial-interglacial  $\delta^{18}\text{O}$  cycles.

Naidu (1991), have shown using two cores from the western continental margin in the Arabian Sea that  $\text{CaCO}_3$  variations depend on the productivity of the overlying waters and that the productivity was higher during the glacials and vice versa. Also the riverine material from the Indus River in the eastern Arabian Sea influences the glacial-interglacial  $\text{CaCO}_3$  variations. Such terrigenous dilution, caused by variations in the terrigenous lithogenic flux derived from the Arabian and Somalian Peninsulas has been studied by Murray and Prell (1992). By using the Berger Dissolution Index (BDI) on three cores (SDSE 144, 147 and 154) from the western equatorial Indian Ocean, Naidu *et al.*, (1994), have demonstrated that there is a good agreement between carbonate maxima and less dissolution as well as carbonate minima and more dissolution. This suggests that the dissolution of  $\text{CaCO}_3$  controls the Quaternary  $\text{CaCO}_3$  cycles in the equatorial Indian Ocean. Dissolution indices data show that the CCD depth has shown cyclic variations in the Late Pleistocene. Another study by Naidu and Malmgren (1999) shows that in the western equatorial Indian Ocean, productivity changes are very significant for the last 1370kyr.



### 1.7.2 Paleocarbonate ion Proxies:

Calcite dissolution in marine sediments is driven by saturation state of the overlying waters and/or responds to sedimentary organic matter respiration and the acidification of pore waters that results from that (Emerson and Bender, 1981; Archer and Maier-Reimer, 1994). Specifically, differences in the carbonate ion concentrations of bottom water are believed to be responsible for the first-order variations in the depth of the lysocline between and within oceans (Peterson and Prell, 1985).

Attempts to reconstruct the carbonate ion history from sediments of the world oceans amongst others have yielded two important proxies; the size index (Broecker and Clark, 1999) and the shell weight method (Lohmann, 1995). Both these proxies have been applied largely to the Atlantic Ocean (Broecker and Clark, 1999; Broecker *et al.*, 1999; Broecker and Sutherland, 2000; Broecker and Clark, 2001a; Broecker and Clark, 2001b; Broecker and Clark, 2001c; Broecker and Clark, 2001d; Broecker *et al.*, 2001b; Broecker and Clark, 2002a; Broecker and Clark, 2003a; Broecker and Clark, 2003b; Broecker and Clark, 2003c; Broecker and Clark, 2003d) the Pacific Ocean (Broecker and Clark, 1999; Broecker and Sutherland, 2000; Broecker *et al.*, 2001a; Broecker *et al.*, 2001b; Broecker and Clark, 2001a; Broecker and Clark, 2001c; Broecker and Clark, 2001d; Broecker and Clark, 2003a; Broecker and Clark, 2003b; Broecker and Clark, 2003c; Broecker and Clark, 2003d) the Indian Ocean (Broecker and Clark, 1999; Broecker and Clark, 2001a) and the Caribbean Sea (Broecker and Clark, 2002b, Broecker *et al.*, 2003). Largely, in the above studies the shell weights of selected planktonic foraminifer species has been successfully utilized

in understanding the carbonate ion variations during the Holocene and the Last glacial maxima (LGM).

The size index and planktonic foraminifera shell weight have also been employed to discuss calcite dissolution above the lysocline in the Atlantic, Pacific and Indian oceans (de Villiers, 2005; Schulte and Bard, 2003). Though these studies could quantify the  $\text{CO}_3^{=}$  concentrations to some extent, they could certainly identify the calcite dissolution and preservation events (Broecker *et al.*, 2003). Another parameter, calcite crystallinity, was also used as a proxy of carbonate ion in the Atlantic and Pacific Oceans (Bassinot *et al.*, 2004; Gehlen *et al.*, 2005). Recently, shell weights have been used to understand the CCD variations and hence carbonate ion over the course of the Cenozoic (Broecker, 2008). However, the paleocarbonate ion studies in the Indian Ocean are very sparse compared to more rigorously studied Atlantic and Pacific oceans.

## **1.8 Objectives:**

The primary objectives of this study are:

1. To identify suitable paleocarbonate ion proxy/proxies for understanding calcite dissolution in the Indian Ocean.
2. To compare these proxies within themselves and use of these proxy/proxies in identifying calcite dissolution events and understanding the dissolution mechanisms on the seafloor.
3. To understand the dependency of planktonic foraminiferal shell weights on initial growth conditions i.e. carbonate ion and/or temperature from tropical waters.

4. To reconstruct the carbonate ion content for the northern Indian Ocean during the Late Quaternary.