CHAPTER I

INTRODUCTION

It is well established that the Earth's climate has changed in the past, both on short and on long time scales. Reconstruction of past climates provides not only snap shots of conditions that prevailed during that time but also a tool to test climate models. Availability of instrumental records of climate are limited to the past several decades at isolated sites. Hence for a better understanding of natural climate variability it is necessary to extend the available limited instrumental climatic records both in space and time, using different natural archives as proxy indicators of climate. Long lived hermatypic corals preserve in them high quality, high resolution records of "ocean climate" for the past few centuries. The study of isotopic and chemical tracers in the annual bands of corals has been shown to provide accurate records of seasonal and interannual variability of meteorological and oceanographic parameters such as the sea surface temperature (SST), salinity, upwelling, rainfall and air-sea gas exchange (Fairbanks & Dodge 1979; Dunbar & Wellington 1981; Druffel & Suess 1983, Druffel 1985, 1987; Pätzold 1984; Cember 1989; McConnaughey 1989; Shen *et al.* 1987, 1992; Cole & Fairbanks 1990). Recognizing the importance of corals in providing high resolution proxy climate records for the past several centuries, their study has been brought under the umbrella of the International Geosphere Biosphere Programme (IGBP). One of IGBP's core project is Past Global Changes (PAGES) which aims to reconstruct high resolution (≤1yr) palaeoclimatic information for the last 2000 years from corals and a few other repositories, *e.g.* tree rings, varved and coastal sediments.

The present work focuses on the study of corals from the northern Indian Ocean region to explore their potential as a source of high resolution climatic and environmental records.

I.1 CORALS : A SOURCE OF PAST ENVIRONMENTAL RECORDS

Corals are marine organisms that grow in shallow sea water in tropical regions. They deposit aragonitic calcium carbonate, and are mainly classified as hermatypic and ahermatypic corals. The hermatypic corals form reefs and host endosymbiotic algae called zooxanthellae (*e.g. Gymnodinium microadriaticum).* These corals generally grow at rates of a few mm to a few cm per year with alternate high and low density growth bands. In many coral species, a high density and low density band together constitute a year's growth (Dodge & Thompson 1974). The mechanism of band formation is not fully understood. Wellington and Glynn (1983) proposed that banding in corals is a complex phenomenon governed by endogenous processes (*e.g.* reallocation of energy from growth to reproduction) mediated by exogenous factors (*e.g.* light intensity and productivity). Highsmith (1979) suggested that variable density banding is a result of differential calcification rates mediated by the effect of light and temperature on zooxanthellar activity and by the effect of temperature on extracellular $CaCO_3$ precipitation rate. Despite the complexity in understanding the density band formation, they provide a means of accurately determining the chronology of coral growth. These density bandings can be revealed by X-radiography (Knutson *et al.* 1972; Buddemeier *et al.* 1974; Macintyre & Smith 1974; Barnes & Lough 1989; Lough & Barnes 1990) and their annual nature ascertained through stable isotope systematics (Fairbanks & Dodge 1979). Many corals, thus are easily datable and can provide high resolution (~months) records of climate and environmental history of the region where they grow.

I.2 PROXY CLIMATIC RECORDS IN CORALS

During the past 1-2 decades, several studies have demonstrated that corals contain in them several isotopic and chemical tracers which can serve as proxy climatic indicators. Table I.1 lists some of these well established and promising tracers in corals for the retrieval of past environmental parameters.

Table I.1 Proxy environmental indicators in corals

Tracer	Index of	Reference
Oxygen isotopes	SST, salinity, rainfall	Fairbanks & Dodge 1979; Dunbar & Wellington 1981; Pätzold 1984; Druffel 1985; McConnaughey 1989; Cole & Fairbanks 1990
Carbon isotopes	insolation, nutrient dynamics, CO_2 air-sea exchange	Nozaki *et al.* 1978; Druffel & Suess 1983; Aharon 1985; Cember 1989
Sr/Ca	SST	Smith *et al.* 1979; Beck *et al.* 1992; de Villiers *et al.* 1993
Ba/Ca	nutrient dynamics, runoff	Shen *et al.* 1992
Cd/Ca	upwelling, nutrient dynamics	Shen *et al.* 1987; Lea *et al.* 1989; Shen & Sanford 1990; Cole *et al.* 1992; Shen *et al.* 1992

Of the tracers listed in Table I.1, oxygen isotopes are the most well established and commonly used tracers for climatic reconstruction.

Different environmental parameters influence the coral calcification, their isotopic ratios and abundances of trace elements. Among them are temperature, light intensity, nutrient supply, isotopic and chemical composition of sea water, turbidity, ocean mixing and runoff. The calcification can be expressed by the reaction:

$$Ca^{++}+2HCO_3^- \rightleftharpoons CaCO_3+H_2O+CO_2 \qquad (1.1)$$

The symbiotic algae (zooxanthellae) which reside in hermatypic corals consume CO_2 for photosynthesis thus favouring the forward reaction *i.e.* calcification (Swart 1983). During the calcification process the corals incorporate in them different chemical and isotopic tracers of climatic and environmental importance.

I.2.a Stable oxygen isotopes

The oxygen isotopic ratio in the coral $CaCO_3$ is a function of two parameters, the SST and the oxygen isotopic ratio of the ambient sea-water. During $CaCO_3$ precipitation there is an exchange reaction of oxygen isotopes between $CaCO_3$ and H_2O:

$$1/3\ CaCO_3 + H_2{}^{18}O = 1/3\ CaC^{18}O_3 + H_2{}^{16}O \qquad (1.2)$$

The equilibrium constant for this reaction is given by

$$K = [CaC^{18}O_3]^{1/3}[H_2{}^{16}O]/[CaCO_3]^{1/3}[H_2{}^{18}O] \qquad (1.3)$$

Since the equilibrium constant (K) depends on temperature (T), calcium carbonate precipitated from water of a constant oxygen isotopic composition but at different temperatures, will have different $^{18}O/^{16}O$ ratios. This is the basis underlying the quantitative determination of palaeotemperatures of ocean water from oxygen isotopes studies of $CaCO_3$ (Urey 1947).

The isotopic fractionation that occurs during various physico-chemical processes is described in terms of fractionation factor α, which is defined as:

$$\alpha_{a-b} = R_a/R_b \qquad (1.4)$$

where R is the ratio of the abundance of the heavy to that of the light isotope. The subscripts a and b refer to two phases, A and B. The ratio R, in the different phases is reported in terms of the deviation of the isotopic ratio of the sample relative to that of a standard. This deviation, δ, is expressed in parts per thousand (or permil) as given below:

$$\delta(‰) = [(R_s/R_r) - 1]\ 10^3 \qquad (1.5)$$

where R_s and R_r are the $^{18}O/^{16}O$ (or $^{13}C/^{12}C$) in the sample and the standard respectively. The empirical relationship between $\delta^{18}O$ of the inorganically precipitated $CaCO_3$ and temperature was initially established by Epstein *et al.* (1953), and was later modified by Craig(1965). This has the following form:

$$T = a + b(\delta_c - \delta_w) + c(\delta_c - \delta_w)^2 \qquad (1.6)$$

where T is the temp of the water in °C, in which the precipitation of $CaCO_3$ occurs. δ_c is the $\delta^{18}O$ of CO_2 obtained from the carbonate by reacting it with 100% phosphoric acid at 25°C. δ_w is the $\delta^{18}O$ of CO_2 equilibriated isotopically at 25°C with water from which the carbonate was precipitated; both δ's measured relative to the same laboratory standard CO_2.

This equation was applied successfully for the determination of the palaeotemperature of ocean water based on oxygen isotopic studies in foraminiferal shells in ocean sediments. Though the equation was derived originally for calcite-water-bicarbonate system, it was shown to be equally valid for aragonite-water-bicarbonate system *i.e.* corals and bivalves (Grossman & Ku 1986).

The biologically precipitated $CaCO_3$ in equilibrium with sea water has a temperature coefficient of -0.22‰ per °C, *i.e.* $\delta^{18}O$ of the $CaCO_3$ decreases by 0.22‰ for every degree rise in water temperature (Epstein *et al.* 1953). In corals the biological processes mediated by endosymbiotic activity also control the isotope fractionation. These processes deplete the oxygen isotopic ratio in the coral skeleton with respect to that expected from the isotopic equilibrium. This depletion or offset is shown to be generally constant within a coral genus. The pioneering work of Weber & Woodhead (1972) established the $\delta^{18}O$-SST relationship for 44 genera of corals of Indo-Pacific origin. Subsequently various investigators (Fairbanks & Dodge 1979; Dunbar & Wellington 1981; Pätzold 1984; McConnaughey 1989) showed that the coral $\delta^{18}O$ can be used for the accurate reconstruction of past SST variations. It was also used to investigate climatic features like the El Niño and the Southern Oscillation (Druffel 1985).

As mentioned earlier, in addition to temperature, the $\delta^{18}O$ of ambient sea water also controls the coralline $\delta^{18}O$. Therefore in principle it should be possible to determine the sea water $\delta^{18}O$ variations based on coral $\delta^{18}O$ if independent estimates of SST variations are available. However in general this is not a major application of oxygen isotope studies in corals as most of the tropical oceanic regions show minimal changes in surface water $\delta^{18}O$. Therefore, such studies are restricted to oceanic regions having significant $\delta^{18}O$ variability resulting from evaporation, precipitation and runoff. Recently, Cole & Fairbanks (1990) showed that in the Tarawa Atoll coral $\delta^{18}O$ was controlled mainly by the sea-water isotopic composition. Intense precipitation in this region changes the sea water isotopic composition which is recorded in the coral $\delta^{18}O$. There is a significant negative correlation between $\delta^{18}O$ and rainfall, making it a useful index of rainfall variability in this region.

Summarizing, the coral $\delta^{18}O$ is a powerful tool for quantitatively assessing historical variations in SST, salinity, rainfall and thus provides a measure of "ocean climate" of the recent past.

I.2.b Stable carbon isotopes

The use of $\delta^{13}C$ signal in coral skeletons as an environmental indicator often poses difficulties due to the complicated interaction of physiological processes within the coral-algae system, which produces large and variable disequilibrium-isotopic-fractionation of carbon isotopes. The parameters controlling carbon isotopic systematics in coral $CaCO_3$ are: (i) the isotopic composition of seawater ΣCO_2 (Nozaki *et al.* 1978; Aharon 1985) (ii) the coral geometry and growth rate (Land *et al.* 1975; McConnaughey 1989) and (iii) the endosymbiotic photosynthesis (Weber & Woodhead 1972; Goreau 1977; Fairbanks & Dodge 1979). The $\delta^{13}C$ of sea water (from which corals precipitate $CaCO_3$) is controlled by photosynthesis and respiration, air-sea CO_2 exchange and varying contribution of upwelled waters. The endosymbiotic photosynthesis and respiration are critical factors in controlling the $\delta^{13}C$ of coral $CaCO_3$. Photosynthesis preferentially removes light isotopes from sea water thereby enriching the residual inorganic carbon pool in ^{13}C causing an increase in the skeletal $\delta^{13}C$. On the other hand respired CO_2 which is depleted in $\delta^{13}C$ relative to dissolved inorganic carbonate (DIC) makes the carbon pool lighter and hence also the coral skeleton lighter in ^{13}C. Summarizing, one can say that the isotopic composition of coral skeleton results from the mixing of two carbon components. One of these components consists of DIC, whereas the other is the metabolic CO_2. However the extent of the contribution of the metabolic CO_2 is not known, but could be significant, and probably varies with species.

Endosymbiotic photosynthesis which depends largely on the light intensity provides qualitative information on cloudiness and hence insolation. The $\delta^{13}C$ in coral $CaCO_3$ is in someway controlled by endosymbiotic photosynthesis and hence may provide information on cloudiness and insolation. Indeed in many places coralline $\delta^{13}C$ shows a covariation with the seasonal insolation variation (Pätzold 1984; McConnaughey 1989). Fairbanks & Dodge (1979) observe that the $\delta^{13}C$ of the *Montastrea annularis* of Bermuda covaries with insolation.

Though the application of coralline $\delta^{13}C$ to retrieve climatic parameters is not straightforward, it appears to be a useful tracer for obtaining qualitative information on insolation and surface ocean productivity.

I.2.c Radiocarbon in annual bands of coral

The radiocarbon content of surface ocean water at any location is a dynamic balance between its supply and removal processes such as the air-sea exchange, lateral transport and upwelling. Corals contain in them a chronological record of ^{14}C variations of surface sea water, analogous to $\delta^{13}C$. These records provide details of air-sea exchange of CO_2. Information on the rate of air-sea CO_2 exchange is critical to determine the fate of fossil fuel CO_2, and hence models related to the greenhouse warming. The air-sea CO_2 exchange rate (ASCER) is influenced by physical, chemical and biological processes occurring in the oceans.

The natural distribution of radiocarbon in the environment was perturbed considerably by the injection of large quantities of ^{14}C in the atmosphere through nuclear (bomb) tests conducted primarily during the late 50's and early 60's. The abundance of bomb carbon in the atmosphere has been decreasing since ~1963, resulting from its exchange with ocean. From a knowledge of the rate of change of bomb ^{14}C activity in the atmosphere and in surface sea water it is possible to determine ASCER (Stuiver 1980; Druffel & Suess 1983; Cember 1989). The temporal evolution of surface water bomb-radiocarbon activity can be obtained from dated coral bands and that of the atmospheric bomb radiocarbon variation can be retrieved from tree rings. Following this approach Druffel & Suess (1983) made detailed studies of ASCER in the west Atlantic and the equatorial Pacific region and Cember (1989) in the Red Sea. In addition to determining the air-sea exchange of CO_2, radiocarbon in corals can also provide information on water mass renewal and ventilation rates (Druffel 1989). All these studies have demonstrated that the measurement of radiocarbon activity in coral bands is useful for monitoring surface water radiocarbon activity, which helps in understanding the ocean mixing processes and the determination of air-sea CO_2 exchange rate.

I.2.d Trace elements

Corals incorporate in their skeleton various minor and trace elements such as Mg, Sr, Ba and Cd during calcification process. All these elements are cations with charge +2, and can substitute for Ca in the $CaCO_3$. The ratio of the (metal/Ca) incorporated in the $CaCO_3$ by and large depends on their abundance ratio in the ambient water and the SST. Elements like Cd and Ba, have nutrient like distribution in sea water (*i.e.* concentration increases from surface to deep waters mimicking nutrient (phosphates and nitrate) profiles (Bruland 1983)) and their concentrations in surface water is influenced by upwelling and biological activities. Therefore, through a high resolution (~ 2-3 months) studies of Ba/Ca and Cd/Ca in corals it is possible to obtain information on upwelling characteristics in the region of coral growth (Cole *et al.* 1992). The Sr/Ca ratio, on the other hand, has been shown to be a sensitive index of SST, analogous to oxygen isotopes (Smith *et al.* 1979; Beck *et al.* 1992; de-Villiers *et al.* 1993). The Sr/Ca in coral (*P. clavus*) has a temperature coefficient of $-6.245X10^{-5}$ $°C^{-1}$ (Beck *et al.* 1992). High precision measurement of Sr/Ca ratios is required for its use as a monitor of SST.

I.2.d(i) *Cadmium*

Chemical analysis of lattice bound cadmium in scleractinian corals has been shown to be a sensitive tracer of oceanic upwelling. Cadmium is a nutrient-like element, depleted in the surface ocean relative to deeper waters. (Boyle *et al.* 1976, Shen *et al.* 1987).

The lattice bound Cd in corals from the eastern equatorial Pacific has been shown to be correlated with sea surface temperature changes associated with interannual ENSO variability (Shen *et al.* 1992). Similarly various investigators have reported the use of Cd as an upwelling indicator and its usefulness in understanding nutrient dynamics (Shen *et al.* 1987; Cole *et al.* 1992).

I.3 SCOPE OF THE PRESENT WORK

As mentioned earlier, the aim of this thesis is to explore the potential of corals in the northern Indian Ocean for extracting high resolution palaeoclimatic data.

Moore & Krishnaswami (1974) first reported isotopic studies on a coral from this region. They used environmental radionuclides (^{228}Ra, ^{210}Pb, ^{90}Sr, and ^{14}C) to determine coral growth rate (Moore *et al.* 1973) and compared the results with the band thickness measurements based on X-radiography. Taxonomic analysis of corals and their demographic distributions in the seas around India are available (Wafar 1986; Pillai & Patel 1988). There is, however no earlier work from this region on the use of corals as a source of proxy climate indicators. It was, therefore thought worthwhile to make a detailed study of corals from this region to assess their utility as a source of palaeoclimatic and environmental records. This was prompted by the results from other oceanic regions mentioned in the earlier sections. The following paragraphs summarize some of the scientific problems in the Arabian Sea region which are amenable to examination using coral isotopic data.

One of the characteristic climatic features over the Arabian Sea is the occurrence of monsoon. The south west monsoon (SWM) occurs during summer, Jun-Sep and the north east or winter monsoon prevails during Nov-Feb. The SWM is associated with intense winds which results in large scale surface circulation in the Arabian Sea and the monsoon rainfall in the Indian subcontinent. One of the consequences of the SWM is the upwelling of cool, nutrient rich water in several areas of the Arabian Sea, notably in the Somali basin, off the coast of Arabia and to some degree along the westcoast of India. Thus the SWM causes high biological productivity in the Arabian Sea. The high productivity and the strong winds also produce intense air-sea exchange of CO_2.

This unique climatic characteristic of the Arabian Sea makes it an interesting oceanic region for studying the behaviour of the monsoon over interannual to century time scales. Compared to the mid-latitude weather systems, the prediction of the tropical monsoon system is extremely difficult. This difficulty is accentuated by the absence of adequate spatial and temporal coverage of climatological data set including SST.

Some of these problems can be addressed through detailed high resolution studies of isotopic and chemical tracers in corals as they have been proven to be sources of climatic indices in other oceanic regions. Corals, as discussed earlier, are known to incorporate various physical and chemical signatures of "ocean climate" (SST, salinity, rainfall etc.) on different time scales. The corals having high growth rates (>10 mm/yr) are ideally suited for monitoring seasonal features with a resolution as high as about a month. The proxy records obtained from their growth bands can extend "ocean climate" data to several centuries in the past, much longer than those available from the instrumental records.

Corals occur in several regions in the northern Indian ocean (Wafar 1986; Pillai & Patel 1988); two regions were selected for the present study, The Lakshadweep (LDP) sea and the Gulf of Kutch (GKh). The climate of these two regions are influenced by different processes. The SST variations in LDP are influenced by the monsoon induced cooling in summer, whereas those in the GKh are mainly controlled by summer heating and winter cooling. Different species of corals grow around these coastlines. In the adjoining seas and lagoons of LDP they form huge reefs and colonies, in the GKh they grow in isolated patches. We collected coral samples of different genera and species from these two regions. In addition, we also analyzed one coral sample from the Stanley Reef of the Great Barrier Reef of Australia. The main goals are:

1) to identify corals from LDP and GKh areas that can provide high resolution record of climate and environmental parameters. Towards this, growth rates of corals were determined by X-radiography and oxygen isotope cyclicities. In addition to the growth rate an important constraint in retrieving high resolution records is the sampling thickness and the sampling interval (for mass spectrometric measurements). A model simulation study was made to determine the effects of sampling on the retrieval of climatic signal from the coral $\delta^{18}O$ record.

2) to determine the extent of isotopic disequilibrium in $\delta^{18}O$ in *Porites*, the most abundant coral genus in the LDP region, to establish an empirical relation between SST and $\delta^{18}O$ of this coral species and assess the usefulness of this relation in the reconstruction of SST (LDP sea) on seasonal time scales by comparing this with available instrumental

data.

3) to examine the influence of monsoon rainfall on coral $\delta^{18}O$ and its possible implications.

4) to determine the air-sea CO_2 exchange and water mass mixing rates in the GKh region from the radiocarbon time series data from coral bands and tree rings. Such data find application in modelling the oceanic uptake of fossil fuel CO_2, and

5) to determine Cd concentrations with sub-seasonal resolution in one of the LDP corals and to explore its use as a tracer to investigate upwelling phenomena in this region.

In addition to the above studies of corals from the Indian coast, stable oxygen and carbon isotope analyses of a coral from the Stanley Reef of the Great Barrier Reef was carried out to assess the intraband-isotopic-variability, and the factors influencing the density band formation.

During the course of this investigation the author participated in the setting up of a new radiocarbon laboratory. He also established the capability for measuring nanogram levels of Cd in corals. Such a comprehensive analysis of corals has been done for the first time in the country.

The following chapters describe the measurements made to address the above goals and their interpretations.