CHAPTER 1

The foraminiferal paleoclimatic proxies: A brief insight

1.1 Introduction

Climate is one of the important factors that affect the fate of mankind on earth. Changes in the climate can lead to significant cultural changes, large-scale migration or even demise of civilizations (Polyak and Asmerom, 2001; Haug et al., 2003; Gupta, 2004). Therefore precise information of imminent climatic variations is necessary to secure the fate of mankind on earth and for long and short-term policy planning. Continuous efforts are made to develop models to predict future climatic variations. Training and validation of climate prediction models requires knowledge of inter-relationship among various climatic parameters, as well as short and long-term changes in the climate. In view of absence of written records of climate variations prior to the last ~100-150 yr, indirect techniques called proxies are used to infer past climate changes. An index sensitive to changes in the physico-chemical characteristics of the ambient environment and having good preservation potential (resistant to any pre or post depositional change, especially the changes that can alter the signatures of environmental conditions) can be used to infer past climatic conditions.

The aquatic bodies, with continuous accumulation of sediments are among the ideal places to retrieve paleoclimatic proxies and records. The sediments accumulating at the bottom of aquatic bodies contain various indices that incorporate signatures of environmental conditions. In the aquatic bodies, the indices containing climatic signatures are immediately buried below subsequent sediments, to be preserved for long time. Though various characteristics of sediments, including physical and chemical properties of the sediments, retrieved from the sea floor have been used to infer paleoclimatic variations (Bassinot, 1993; Weber et al., 1997), the variations in the characteristics of the biological component of the sediments have been used most extensively. The preferred application of biological components arises due to the high sensitivity and enhanced response of biological components to the changes in ambient environment. Since marine sediments contain plenty of remains of marine microorganisms like coccolithophores, radiolarians, pteropods, ostracodes, foraminifera, etc., such remains serve as potential proxy to infer past climatic conditions. Out of these remains of various marine microorganisms, the hard
outer skeletal remains of foraminifera, termed as tests, are among the most widely used paleoclimatic proxy.

Foraminifera are unicellular, preferentially marine microorganisms with the single cell protected by a hard outer covering, called test. The foraminiferal test is made up of either calcium carbonate secreted by the cell, or various size sediments cemented together with calcitic cement. The foraminifera inhabit both the upper few hundred meters of the seawater column (planktic foraminifera) as well as the sediments on the sea floor (benthic foraminifera). The near coastal waters are almost exclusively inhabited by benthic foraminifera while both benthic and planktic foraminifera are found in oceanic regions deeper than ~75-100 m but above carbonate compensation depth (CCD). Though the planktic foraminifera still inhabit the surface water column in even deeper oceanic regions but their test almost completely dissolve before reaching the seafloor due to over saturation of deeper oceanic waters by carbon dioxide (Berger, 1967).

While the benthic foraminifera show vast diversity with thousands of species reported from different parts of the world oceans, there are only ~40 species of planktic foraminifera found in modern world oceans. The tests of foraminifera, especially benthic foraminifera, show wide variations in size and shape, from being single chambered (unilocular) to chambers arranged in one, two or many linear rows (uniserial, biserial and multiserial, respectively) as well as chambers arranged in circular fashion (spiral forms). The planktic foraminiferal tests in general have globular and highly perforated chambers and also comparatively large aperture.

1.2 Foraminiferal Proxies

The variation in the morphology and composition of the foraminiferal tests is adaptive response of the foraminifera to the changes in environment inhabited by foraminifera. Thus the changes in the foraminiferal tests in response to climatic changes, makes it possible to apply various foraminiferal characteristics to infer past environmental conditions. Various characteristics of the foraminiferal tests that have been used to infer past climatic variations include:

1.2.1. Total Foraminiferal Number
1.2.2. Benthic:Planktic Ratio
1.2.3. Foraminiferal Fraction index
1.2.4. Foraminiferal Size Fraction
1.2.5. Species Assemblages
1.2.6. Species Abundance
1.2.7. Test Size/Diameter
1.2.8. Coiling Direction
1.2.9. Average Number of Chambers
1.2.10. Proloculus Size
1.2.11. Test Abnormalities
1.2.12. Test Weight
1.2.13. Isotopic Composition of the Tests
1.2.14. Elemental Composition of the Test

Since a few of these foraminiferal proxies have been discussed by Boltovskoy and Wright (1976), and SenGupta (1991), only the recent developments in their application are discussed here. However, significant advances have been made in the application of chemistry (elemental and isotopic composition of the tests) of the foraminiferal tests for paleoclimatic reconstruction and these are discussed in much detail.

1.2.1. Total Foraminiferal Number

The total foraminiferal number (TFN) is defined as the number of foraminifera in one gram dry sediment. The foraminiferal population has definite environmental control, depending upon the water depth, food availability, sediment characteristics, energy conditions of the region and other physico-chemical characteristics (Boltovskoy and Wright, 1976; Murray, 1991a; 1991b; Lee and Anderson, 1991; Naidu, 1993). Dissolution, during the sinking of planktic foraminiferal tests from the surface to the sea bottom as well as the post-depositional dissolution at the sea bottom, plays a significant role in controlling the foraminiferal population (Berger, 1967; 1968; Peterson and Prell, 1985; de Villiers, 2005). Since the planktic and benthic foraminifera represent the top several hundred meters of the water column, and bottom water as well as sediment characteristics, respectively, separate estimates of changes in population of benthic and planktic foraminifera are more efficient proxy than the combined population, i.e. total foraminiferal number. The variations in planktic, benthic or total foraminiferal population have been used for stratigraphic correlation (Berggren and Boersma, 1969; Reiss et al., 1980), changes in the concentration of pollutants (see Nigam et al., 2006 for review), bathymetric
changes (Bandy, 1956; Sharma and Takayanagi, 1982; Nigam and Henriques, 1992), 
lysocline changes (Cullen and Prell, 1984), etc.

1.2.2. Benthic: Planktic Ratio

The abundance of planktic foraminifera in general increases with depth till 
foraminiferal lysocline. Below the foraminiferal lysocline, significant dissolution of the 
foraminiferal tests leads to decreased foraminiferal abundance. Therefore, the changes in 
the relative abundance of benthic and planktic foraminifera indicate, changes in the 
bathymetry (Stehli and Creath, 1964; Wright, 1977), changes in the position of 
foraminiferal lysocline as well as carbonate compensation depth (Pinxian et al., 1995; 
Chen et al., 1997), and productivity changes (Berger and Haass 1988).

1.2.3. Foraminiferal Fraction Index

The foraminiferal fraction index is defined as the number of fragments of 
foraminiferal tests per gram dry sediment. The fragmentation of the foraminiferal tests 
increases under high-energy conditions (increased turbidity). The variation in the amount 
of dissolved carbon-dioxide and carbonate ions also affects the rate of fragmentation of 
foraminiferal tests. Thus the foraminiferal fragmentation index provides information about 
turbidity currents as well as changes in the concentration of dissolved CO2 and carbonate 
ions (Peterson and Prell, 1985; Pinxian et al., 1995; Chen et al., 1997; Govil et al., 2004). 
Dittert and Henrich (2000) proposed, ultrastructure breakdown in Globigerina bulloides as 
proxy to infer the position of lysocline and carbonate compensation depth. Similarly, the 
degree of attrition of tests of planktic foraminiferal species Globorotalia menardii and 
Globorotalia tumida has been applied to estimate amount of calcium carbonate dissolved 
from the sediments (Ku and Oba, 1978).

1.2.4. Foraminiferal Size Fraction

The foraminiferal tests, especially the planktic foraminiferal tests of different 
species fall within a particular size range. Thus the sediments of different size fractions are 
dominated by different species (Bé and Hutson, 1977; Peeters et al., 2000). Therefore, the 
variation in weight of different sized foraminiferal tests in the sediments where sand 
fraction (>63 µm) consists almost entirely of foraminiferal tests can be applied to
document past variation in relative abundance of different species and to infer past climatic variations. However, in such studies, the temporal variation in size of certain foraminiferal tests must also be considered.

### 1.2.5. Species Assemblages

Certain foraminiferal species prefer similar restricted environmental conditions, while a few others occur over a wide range of seawater conditions. The group of species that inhabit similar and restricted environment is referred to as species assemblage. Such species assemblages are thus representative of specific environmental conditions (Murray, 1973; SenGupta, 1977; Lutze and Coulbourn, 1984; SenGupta et al., 1993; Gooday, 1994; Mackensen et al., 1995; Jorissen et al., 1998; Loubere and Fariduddin, 1999; Gooday, 2003). Therefore, temporal variation in such species assemblages is applied to infer variation in environmental conditions and is one of the most extensively used foraminiferal proxies to infer paleoclimatic variations (Nigam et al., 1992; Mackensen et al., 1994; Gupta et al., 2001a; Gupta and Thomas, 2003). Application of species assemblages is preferred over that of the relative abundance of individual species due to usually statistically significant number of individuals representing a species assemblage than individual species.

### 1.2.6. Species Abundance

The foraminiferal studies from the surface sediments and sediment traps show significant changes in the abundance of foraminiferal species with changing ambient environmental conditions (Bé and Tolderlund, 1971; Boltovskoy and Wright, 1976; Bé and Hutson, 1977; Corliss, 1985; Thunnel and Honjo, 1987; Murray, 1973; 1991a; 1991b; Lee and Anderson, 1991; Naidu, 1993; Guptha et al., 1997; Kawahata et al., 2002; Mohiuddin et al., 2005). The changes in the abundance of certain planktic as well as benthic foraminiferal species under specific physico-chemical conditions are applied to infer paleoclimatic changes. Among the planktic foraminifera, the temporal variation in the abundance of *Globigerina bulloides* has very often been used to infer past upwelling changes from the Indian Ocean (Prell and Curry, 1981; Naidu et al., 1999; Anderson et al., 2002). The abundance and diameter of planktic foraminiferal species *Orbulina universa* have been shown to be influenced by the ambient seawater temperature and salinity and thus, has been used to infer past temperature and salinity from the Indian Ocean (Colombo
and Cita, 1980; Haenel, 1987; Nigam, 1990). The variation in the abundance of benthic foraminiferal species *Epistominella exigua* has been applied to infer past changes in organic matter production (Gupta and Melice, 2003; Saraswat *et al.*, 2005). The disappearance of pink variety of *Globigerinoides ruber* from the Indian and Pacific Ocean at 120,000 yr B.P. has been used as a biostratigraphic datum (Thompson *et al.*, 1979).

### 1.2.7. Test Size/Diameter

The morphological changes, especially the variation in size, in response to the changes in the physico-chemical conditions like temperature, salinity, upwelling intensity, have long been recorded from both field as well as laboratory culture studies of foraminifera (Bé *et al.* 1973; Hecht, 1976; Caron *et al.*, 1987a; 1987b; Bijma, 1990; Naidu and Malmgren, 1995; Schmidt *et al.*, 2004). Bé *et al.* (1973) showed that the test diameter of *Orbulina universa* from tropical and subtropical Indian Ocean shows a latitudinal variation and that the mean diameter of the test of *O. universa* in surface sediments and surface waters is strongly associated with the distribution of water masses in the southern Indian Ocean and northern Atlantic Ocean. Except physico-chemical control on the size of foraminifera, evolutionary changes have also been reported to result in an increase in the size of planktic foraminifera (Arnold *et al.*, 1995). Thus, the temporal changes in foraminiferal test dimensions have been applied to infer past variations in physico-chemical parameters as well as in evolutionary studies (Naidu and Malmgren, 1995; Arnold *et al.*, 1995).

### 1.2.8. Coiling Direction

The foraminiferal tests, especially that of benthic foraminifera, show a wide variation in the number and arrangement of chambers. The chambers are arranged trochospirally in a few foraminiferal species, out of several thousand species of foraminifera. In the species belonging to this group, the chambers may be arranged either in dextral (clockwise) or sinistral (anticlockwise) manner. Various studies have shown that the ambient environmental conditions influence the direction in which the chambers are arranged in certain species of foraminifera (Bolli, 1950; Ericson, 1959; Nigam and Khare, 1992; Naidu and Malmgren, 1996). This preferred coiling pattern of both benthic and planktic foraminiferal species has been applied to infer past climatic conditions (Ericson *et al.*, 1954; Bé, 1960; Thiede, 1971; Keany and Kennett, 1972; Williams, 1976; Nigam and
However, of late, with the application of molecular biology techniques, it has been established that the differently coiled specimens, formerly considered to belong to the same species, are in fact different species (Darling et al., 2000; Bauch et al., 2003).

1.2.9. Average Number of Chambers

Many species of foraminifera have bimodal reproduction with morphologically distinct sexual and asexual phases. The tests belonging to offsprings of sexual and asexual mode of reproduction have several differences, including different number of chambers. The environmental conditions influence the mode of reproduction in foraminifera (Boltovskoy and Wright, 1976; Nigam and Rao, 1987; Nigam and Caron, 2000) and thus the number of chambers in the individuals belonging to the same foraminiferal species. This characteristic of variation in average number of chambers, in certain foraminiferal species as a result of changing mode of reproduction under different environmental conditions, has been proposed as tool to infer paleoclimatic variations (Saraswat and Nigam, in preparation).

1.2.10. Proloculus Size

The proloculus is the first formed chamber of the foraminiferal test. The changing mode of reproduction as discussed in the previous section, also influences the size of the proloculus with megalospheric specimens having larger proloculus as compared to microspheric specimens (Boltovskoy and Wright, 1976). As noted above, that the mode of reproduction in foraminifera is environmentally controlled, the mean proloculus size of selected foraminiferal species have been applied to infer past climatic variations (Nigam and Rao, 1987; Nigam and Sarkar, 1993; Nigam and Khare, 1995; Saraswat et al., 2005).

1.2.11. Test Abnormalities

Abnormal foraminiferal tests have been reported in surface sediments collected from ecologically stressed (both naturally as well as anthropogenically) environments as well as in laboratory culture experiments (Boltovskoy et al. 1991; Yanko et al., 1994; 1998; Alve, 1995; Stouff et al., 1999; Scott et al., 2001; Saraswat et al., 2004; Nigam et al., 2006). The abnormalities in foraminiferal tests from ecologically stressed
environments include stunted tests, comparatively smaller or bigger chambers, chambers oriented away from the normal plane of addition of chambers, tests with regressed or completely absent ornamentation. Thus the unusual presence of abnormal foraminiferal tests is applied as a proxy to infer ecologically-stressed environmental conditions (Nagy and Alve, 1987; Schafer et al., 1991; Scott et al., 1995; Nigam et al., 2002; Panchang et al., 2005). However, the application of test abnormalities to infer 'specific' ecologically-stressed environment is hampered due to the report of nearly similar test abnormalities from differently stressed environments.

1.2.12. Test Weight

A majority of the foraminiferal tests are calcareous. This shell calcite is a mixture of primary calcite and secondary calcite. Most planktic foraminifera grow larger by adding chambers formed from primary calcite to their shells. In contrast, secondary calcification thickens existing chamber walls, which can double a shell's mass without significantly affecting its size (Lohmann, 1995). The different effects that primary and secondary calcification have on shell size allow their relative proportions to be estimated. The secondary calcite is added to the shell when there is excess CO$_3^{-2}$ available, i.e., the more the CO$_3^{-2}$ concentration, more the secondary calcification will occur (Broecker and Clark, 1999). Hence, if we can determine the secondary calcite amount then we can infer the CO$_3^{-2}$ concentration of the seawater. Therefore, species in which secondary calcification changes only shell mass (e.g. Pulemetaina obliquiloculata and Globoquadrina dutertrei) and not the size, the amount of secondary calcite added to a shell reflects the change in the CO$_3^{-2}$ concentration of the seawater.

1.2.13. Isotopic Composition of the Tests

Most of the foraminiferal proxies for paleoclimatic reconstruction discussed so far provide qualitative estimates of the past climatic variations. Though this knowledge is helpful to understand a broad trend of climatic variations, precise quantitative estimates of variation in climatic parameters is required for developing and testing the climate prediction models. Variation in chemistry (isotopic and elemental composition) of foraminiferal tests is commonly applied to generate quantitative estimates of variation in climatic parameters, over the geologic past. Commonly used proxies that are based on the
isotopic composition of the elements, comprising the foraminiferal tests, are discussed in the following section.

A. Oxygen Isotopes

Oxygen, an essential component of both the seawater and foraminiferal calcite, has three stable isotopes, viz. $^{16}\text{O}$, $^{17}\text{O}$, and $^{18}\text{O}$. However, out of these three stable isotopes of oxygen, due to the scarcity of $^{17}\text{O}$ and comparatively high biophysico-chemically controlled fractionation between $^{16}\text{O}$ and $^{18}\text{O}$, than between $^{16}\text{O}$ and $^{17}\text{O}$ or $^{17}\text{O}$ and $^{18}\text{O}$, the changes in the ratio of $^{18}\text{O}$ to $^{16}\text{O}$ are applied for paleoclimatic studies. Since the relative change in $^{18}\text{O}/^{16}\text{O}$, than the absolute concentration of $^{18}\text{O}/^{16}\text{O}$, is required to infer paleoclimatic changes, the $^{18}\text{O}/^{16}\text{O}$ ratio of a sample is expressed as change with respect to a standard.

$$\delta^{18}\text{O}_{(\text{foraminifer})} = \left(\frac{^{18}\text{O}^{16}\text{O}_{(\text{foraminifer})}}{^{18}\text{O}^{16}\text{O}_{(\text{standard})}}\right) - 1 \times 10^3$$

The temperature dependent preferential removal of $^{18}\text{O}$ from liquid (water) to the solid (calcite) phase and of $^{16}\text{O}$ from liquid to gaseous (vapour) phase (owing to the high vapour pressure of $^{16}\text{O}$ as compared to $^{18}\text{O}$, leads to distinct differences in the isotopic composition of the foraminiferal tests formed from seawater of varying isotopic composition and warmth. Thus, the isotopic composition of the foraminiferal tests is a measure of the seawater oxygen isotopic composition, the temperature of the seawater at the time of formation of the test, and a few species-specific vital effects. Thus the changes in the oxygen isotopic composition of a foraminiferal species can be resolved as

$$\Delta\delta^{18}\text{O}_{(\text{foraminifer})} = \Delta\delta^{18}\text{O}_{(\text{seawater})} + \Delta T_{(\text{seawater})}$$

Out of these, the oxygen isotopic composition of the seawater reflects a change due to variation in the global ice volume (it accounts for ~70% of the change in the oxygen isotopic composition of the foraminiferal calcite over glacial-interglacial transitions) and local precipitation-evaporation changes.

$$\Delta\delta^{18}\text{O}_{(\text{foraminifer})} = \Delta\delta^{18}\text{O}_{(\text{ice volume})} + \Delta\delta^{18}\text{O}_{(\text{local})} + \Delta T_{(\text{seawater})}$$

The change in the oxygen isotopic composition of the foraminiferal calcite due to changing ice volume on earth is global in nature. These ice volume changes have been quantified (Shackleton, 1987; 2000; Waelbroeck et al., 2002) and can be
subtracted from the total change in the foraminiferal calcite recorded from any location. The resultant oxygen isotopic changes thus reflect the local precipitation-evaporation and seawater temperature changes. However, in case of benthic foraminifera, oxygen isotopic records also include a change in the oxygen isotopic composition of the source water. The planktic foraminiferal oxygen isotopic records from the cores retrieved from the locations far away from the influence of precipitation-evaporation changes provide local sea surface temperature changes. The relationship between foraminiferal calcite and temperature is expressed as

\[ T (°C) = a + b (\delta^{18}O_{\text{foraminifer}} - \delta^{18}O_{\text{seawater}}) + c (\delta^{18}O_{\text{foraminifer}} - \delta^{18}O_{\text{seawater}})^2 \]

Where, a, b and c are species-specific constants. Based on field studies and laboratory culture experiments, various paleotemperature equations have been proposed (Epstein et al., 1953; Emiliani, 1955; Duplessy et al., 1981; Bouvier-Soumagnac and Duplessy, 1985; Bemis et al., 1998).

The planktic foraminiferal oxygen isotopic records from locations under the influence of local precipitation-evaporation changes can be resolved into sea-surface temperature and changes due to local evaporation-precipitation, if independent estimates of sea-surface temperature variations are available.

#### B. Carbon Isotopes

Carbon like oxygen is also a component of calcite and is present in different forms in the seawater, including dissolved carbon-dioxide, bicarbonate (HCO$_3^-$) and constituent of various forms of organic matter. Carbon has three naturally occurring isotopes out of which two are stable (\(^{12}\)C and \(^{13}\)C) and one (\(^{14}\)C) is a radioactive isotope. However, unlike significant physico-chemical control on the fractionation of oxygen isotopes during precipitation of calcite from seawater resulting in change in the oxygen isotopic composition of the calcite from that of the seawater, the carbon isotopic composition of the inorganically precipitated calcite is nearly equal to the carbon isotopic composition of the seawater.

The formation of the organic matter, that involves fixation of huge amount of carbon through photosynthesis, results in significant negative fractionation of carbon isotopes (depletion of organic matter in \(^{13}\)C with respect to the seawater or
atmosphere). Since photosynthesis is the primary mechanism of the incorporation of the carbon and is at the base of the food chain that supports complete life on earth, all the organic carbon compounds on earth have depleted $\delta^{13}C$ ratio. Therefore, increased production of organic matter will result in increased removal of $^{12}C$ from the seawater or enrichment of seawater in $^{13}C$. The planktic foraminiferal tests formed under such conditions will therefore be enriched in $^{13}C$. However, dissolution of more organic matter in the near bottom waters will lead to increased abundance of $^{12}C$ in the bottom waters which will be reflected in the carbon isotopic composition of the benthic foraminifera. The fractionation of carbon during organic matter production through photosynthesis also varies as per the amount of dissolved carbon dioxide [$CO_2(gas)$] in the seawater (the organisms being less 'choosy' when less $CO_2(gas)$ is available in the seawater), which in turn is dependent on the temperature of the seawater (lower the temperature, higher is the amount of $CO_2(gas)$ dissolved in the seawater). Thus, a change in the organic matter production is reflected in the isotopic composition of the foraminifera.

But, this simple fractionation of carbon during organic matter production is further complicated by the continuous exchange of carbon-dioxide between surface seawater and atmosphere leading to a change in the carbon isotopic composition of the seawater in tandem with the changes in the atmospheric carbon isotopic composition. Any change in the carbon isotopic composition of the terrestrial carbon reservoir, due to an increase or decrease in the forest cover, will subsequently lead to a change in the carbon isotopic composition of the surface seawater and thus the planktic foraminifera.

During the glacial periods lowered sea level exposes huge continental shelves. The rivers then erode the organic matter trapped along the continental shelves and bring it to the sea. This organic matter eroded from the continental shelves comprise of isotopically lighter carbon, which in turn affects the carbon isotopic signatures of the foraminifera, thus further complicating the carbon isotopic variations over glacial-interglacial time scales. The carbon isotopic composition of the benthic foraminifera also includes changes in the source water carbon isotopic ratio, change in the circulation rate of bottom water (slower the circulation rate, more incorporation of carbon through flux of organic matter from surface and respiration of benthic organisms). Therefore, the temporal changes in
the carbon isotopic composition of the foraminifera from any location indicates changes in the

- Organic matter production (productivity) at that location
- Isotopic composition of the dissolved carbonates
- Deep-water circulation changes (in case of benthic foraminifera)

C. Calcium Isotopes

Calcium has six stable isotopes ($^{40}\text{Ca}$-96.98%, $^{42}\text{Ca}$-0.64%, $^{43}\text{Ca}$-0.13%, $^{44}\text{Ca}$-2.06%, $^{46}\text{Ca}$-0.003%, $^{48}\text{Ca}$-0.18%), out of which $^{40}\text{Ca}$ is most abundant (Russell et al., 1978). In view of long residence time of calcium in seawater (Zhu and Macdougall, 1998) and imperceptible diagenetic effects (Nagler et al., 2000), attempts have been made to apply the $^{44}\text{Ca}/^{40}\text{Ca}$ ratio to infer past temperatures. The Ca isotopic composition of various compounds has been reported to vary as per both the isotopic fractionation during biological (Skulan et al., 1997) and physical-chemical processes, and the production of $^{40}\text{Ca}$ from $\beta$ decay of $^{40}\text{K}$. But, contrasting results and limited fractionation have hampered application of calcium isotopes as an efficient paleotemperature proxy (Russell et al., 1978; Skulan et al., 1997; Zhu and Macdougall, 1998; Nagler et al., 2000; Sime et al., 2005).

D. Neodymium Isotopes

Oceanic thermohaline circulation is an important component of earth’s climate system. The thermohaline circulation redistributes energy and material between different ocean basins. Because of redistribution of energy between different ocean basins by thermohaline circulation, climatic variations over glacial-interglacial time-scales have often been recognized as implications of changes in thermohaline circulation (Broecker, 1997). Climate induced changes in the terrestrial input to the thermohaline circulation are reflected in the change in the concentration of various elements and isotopes, which are incorporated by the biological components of the ocean. Thus the selected isotopic and elemental composition of marine organisms is helpful to infer past climatic and thermohaline circulation changes. In order to infer past thermohaline circulation changes, elements or isotopes with a residence time of the order of turnover time of thermohaline circulation are applied.
Neodymium (Nd) occurs in trace amount in various rocks. Climate dependent weathering and erosion of terrestrial rocks results in transfer of Nd from land to the oceans, wherein Nd becomes part of the ocean thermohaline circulation. The residence time of Nd in the oceans has been estimated to be a few thousand years (Tachikawa et al., 1999), which is comparable to the oceanic mixing time. Thus Nd isotopic composition of past oceans, if reconstructed, can provide an idea about the changing oceanic circulation and climate. The Nd isotopic ratio is represented as $\varepsilon_{\text{Nd}}$, and is expressed as the deviation of $^{143}\text{Nd}/^{144}\text{Nd}$ of the sample from the present-day chondritic reservoir value (0.512638) in parts per $10^4$ (Vance and Burton, 1999). It has been demonstrated that the Nd isotopic composition of foraminifera represents the Nd isotopic composition of contemporary seawater, and thus the climate induced changes in weathering and erosional patterns and rate of ocean circulation (Vance and Burton, 1999). But, Pomies et al. (2002) based on Nd isotopic analysis of planktic foraminifera from different depths and seawater in the Indian Ocean, emphasized for further studies to rule out the alteration of Nd isotopic signature of foraminifera by secondary diagenetic processes. However, Burton and Vance (2000) showed that the secondary Nd contamination can be effectively removed and generated the planktic foraminifera based glacial-interglacial Nd isotopic variation record for the Bay of Bengal.

E. Boron Isotopes

Out of two dominant aqueous species of boron in seawater [$\text{B(OH}_3$ and $\text{B(OH)}_4$] (Hershey et al., 1986), only tetrahedral, isotopically lighter $\text{B(OH)}_4^-$ enters in marine carbonates with insignificant boron isotopic fractionation between seawater and carbonate, during its incorporation (Hemming and Hanson, 1992). Since the availability of $\text{B(OH)}_4^-$ in seawater depends on the pH of the seawater (Hemming and Hanson, 1992), boron isotopic composition of the foraminifera indicates the pH of the seawater. Spivack et al. (1993) showed the potential application of foraminiferal boron isotopes to infer past seawater pH. This possibility was further strengthened by laboratory culture experiments of foraminifera and inorganic precipitation of calcite at different pH (Sanyal et al., 1996, 2000). The boron isotopic composition of planktic foraminifera has been used to infer past seawater pH from different oceanic basins (Spivack et al., 1993;
Sanyal et al., 1997; Palmer et al., 1998). The boron isotopic composition of foraminifera is represented as $\delta^{11}B$ and is expressed as

$$\delta^{11}B (\%) = \left(\frac{^{11}B/^{10}B_{\text{sample}}}{^{11}B/^{10}B_{\text{standard}}} - 1\right) \times 1000$$

Except these, Hoefs and Sywall (1997) attempted to infer past seawater lithium isotopic composition, while Dasch and Biscaye (1971) and Henderson et al., (1994) inferred past strontium isotopic composition of seawater based on the strontium isotopic composition of the foraminifera. However, Hoefs and Sywall (1997) noted that the diagenetic processes possibly affect the glacial-interglacial variation in lithium isotopic composition of the foraminifera.

1.2.14. Elemental Composition of the Test

The foraminiferal tests also have minor amount of various elements that replace the major elements constituting the tests. The replacement of the major constituent elements of the test by other elements mainly depends on the chemical feasibility (size, valency, and electronic configuration of the elements). Though possible physico-chemical control on the replacement of certain elements was suggested, complete understanding of the factors influencing the replacement of elements in the tests remained obscure for long due to inefficient cleaning procedures and non-availability of instruments to measure that low concentration of the elements. With the development of refined cleaning procedures (Boyle, 1981; Boyle and Keigwin, 1985; Nurnberg et al., 1996; Martin and Lea, 2002; Barker et al., 2003) and measurement techniques (Lea and Boyle, 1993; Rosenthal et al., 1999; de Villiers et al., 2002) the application of elemental ratios in foraminiferal tests became a routine and foraminiferal elemental composition has been shown to be an efficient recorder for concentration of these elements in seawater (Haley et al., 2005). The elemental ratios commonly applied in palaeoceanography are discussed below.

A. Magnesium/Calcium

The incorporation of Mg into the calcite is suggested to be temperature dependent (Chave, 1954; Katz, 1973; Oomori et al., 1987) with a sensitivity of 3% increase in the Mg uptake for every 1°C rise in temperature, in case of inorganically precipitated calcite (Rosenthal et al., 1997; Lea et al., 1999). The temperature sensitivity of Mg uptake in foraminiferal calcite is reported to be of the order of 10% increase per 1°C increase of temperature (Lea et al., 1999; Barker...
et al., 2005). The advantage of Mg/Ca palaeothermometry lies in the long residence time of both Mg and Ca ($10^7$ and $10^6$ years, respectively) and thus an almost constant Mg/Ca ratio of seawater over glacial-interglacial periods. However, the Mg-Ca content of foraminiferal tests is altered by post-depositional dissolution of the foraminiferal tests (Brown and Elderfield, 1996) for which measures have been suggested to estimate temperature, after correcting for dissolution-induced changes (Rosenthal and Lohmann, 2002). The pH and salinity of the seawater have also been shown to affect the Mg/Ca ratio of the foraminiferal shells, but the changes are relatively very small (-6% change in Mg/Ca for 0.1 pH unit increase and +4% per salinity unit increase) (Lea et al., 1999). Based on various calibrations (Lea et al., 1999; Dekens et al., 2002; Anand et al., 2003) the seawater temperature can be calculated from the Mg/Ca ratio in foraminiferal calcite by using an equation of the following order

$$\text{Mg/Ca} = B \exp (A \times T)$$

Where, $A$ and $B$ are species specific constants and $T$ is temperature in °C.

B. Cadmium/Calcium

Productivity is a measure of the nutrient utilization in any area. Among various nutrients required to sustain productivity, nitrates, phosphates and silicates are biolimiting and thus an estimate of availability of these nutrients can be used as a measure of the amount of surface productivity. Out of these phosphorous is incorporated in the organic part and gets remineralized as soon as the organic matter decays after the death of the organisms, thus making it difficult to directly estimate past productivity variations. However, cadmium (Cd) behaves in a manner similar to that of phosphorous, and changes in the concentration of cadmium and phosphorus have been shown to be linearly related in the global oceans (Boyle, 1986). Cadmium is readily incorporated in the foraminiferal calcite as a replacement for calcium. Therefore, planktic foraminiferal Cd/Ca ratio is used as proxy for past phosphate utilization or surface nutrient availability (Elderfield and Rickaby, 2000). However, foraminiferal Cd/Ca ratio have to be corrected for reported influence of temperature on the incorporation of the cadmium in the planktic foraminiferal tests (Rickaby and Elderfield, 1999) and preferential
incorporation of cadmium than phosphorous (Elderfield and Rickaby, 2000), before being applied as a measure of past phosphate utilization. Further the Cd uptake in calcitic foraminifera has been found to be depth dependent. However, Boyle et al. (1995) showed that the Cd uptake in the aragonitic benthic foraminifera *Hoeglundina elegans* is not depth dependent.

**C. Barium/Calcium**

Modern day profiles of barium in oceanic waters are remarkably similar to that of silica (a biolimiting nutrient), radium (decay product of thorium and a potential time tracer) and alkalinity (Chan et al., 1976; 1977). The similarity between nutrients and Ba arises because of precipitation of BaSO₄ in the decaying organic matter and thus removal of Ba from surface waters in proportion to the organic matter (Chow and Goldberg, 1960). Thus estimates of Ba content of past oceans can be applied to infer nutrient availability and alkalinity in the past. Ba replaces Ca in marine carbonates (Kitano et al., 1971). Laboratory culture experiments have established a proportional uptake of Ba in foraminiferal shells (Lea and Boyle, 1991) and negligible influence of significant variation in temperature and salinity on Ba uptake in foraminifera (Lea and Spero, 1994). The development of an efficient cleaning (Boyle, 1981; Boyle and Keigwin 1985) and measurement techniques (Lea and Boyle, 1993; Lea and Martin, 1996) for foraminiferal shell Ba, has lead to the application of Ba/Ca as a proxy for past nutrient and alkalinity estimates (Lea and Boyle, 1990; Lea, 1993; Martin and Lea, 1998).

Except these, a few other elements (lithium, strontium) were analysed in foraminiferal tests in order to evaluate the potential application of the composition of these elements in foraminiferal calcite to reconstruct concentration of these elements in the seawater during the geologic past. But contrasting results restrict application of such elemental ratios of foraminiferal tests, on a regular basis (Graham et al., 1982; Delaney et al., 1985; Hall and Chan, 2004).

Since the foraminiferal proxies discussed above were developed based on the studies from specific regions, an efficient application of any of the above mentioned
foraminiferal paleoclimatic proxies to infer climatic variations from other regions require an evaluation of the proxy for that region. In order to find out which of the above-mentioned proxies have been applied to infer paleoclimatic information from the northern Indian Ocean region, a detailed literature review of the paleoclimatic studies based on foraminiferal proxies, was carried out and the same is discussed in the next chapter.