

## CHAPTER III

### RESULTS

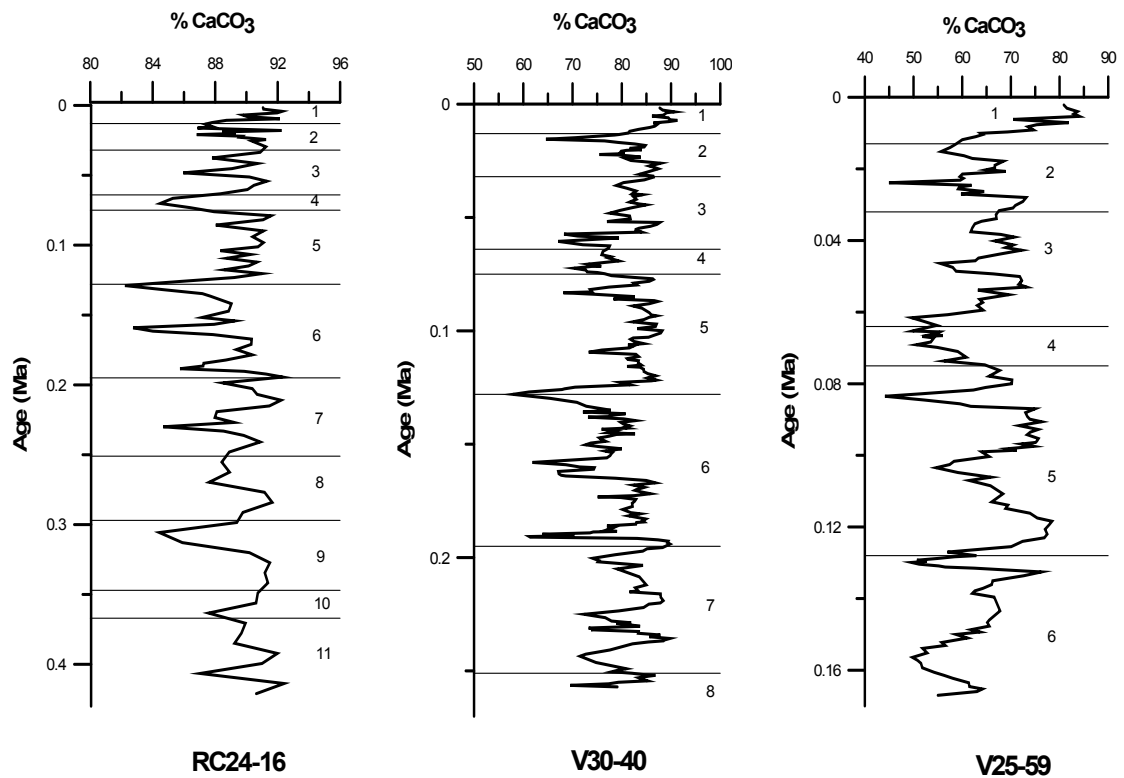
#### **3.1 CaCO<sub>3</sub> fluctuations in the equatorial region of the major world oceans:**

CaCO<sub>3</sub> content data of ten cores collected from the equatorial region over the world oceans are used to reconstruct bathymetric patterns of CaCO<sub>3</sub> preservation spanning the past 0.6 Ma (Table 1, Fig. 8), which clearly cover the major glacial/interglacial intervals of the Late Quaternary period. The exceptions to these are cores from the Atlantic Ocean, which cover a maximum time span of 0.42 Ma. CaCO<sub>3</sub> fluctuations from the equatorial regions of Atlantic, Pacific and Indian Ocean are discussed individually.

##### **3.1.1 The Atlantic Ocean:**

Three cores have been selected to discuss the CaCO<sub>3</sub> fluctuations in the Atlantic Ocean (Fig. 11). All the cores are from above the lysocline depth. The total length of the Core RC24-16 spans back to 0.42 Ma, Core V30-40 covers the past 0.26 Ma and Core V25-59 covers 0.17 Ma. The CaCO<sub>3</sub> content ranges from 82 to 92% in Core RC24-16, 58 to 91% in Core V30-40 and 44 to 84% in V25-59. In general, interglacials show high CaCO<sub>3</sub> content whereas glacials show low CaCO<sub>3</sub> content (Fig. 11). Marine Isotopic Stage (MIS) 1 which is the interglacial shows a calcium carbonate peak in all the three cores. The %CaCO<sub>3</sub> maximum of MIS 1 is very prominent in Core V25-59. CaCO<sub>3</sub> content in MIS 2, representing the late Wisconsin glacial maximum shows a dissolution pattern for the three cores whereas in MIS 3,

preservation is noticed. The transition from interglacial to glacial maximum shows a sharp depletion. In Core V25-59 this depletion in  $\text{CaCO}_3$  is from 84 to 56% and in Core V30-40 it ranges from 91 to 65%. Core RC24-16 does not show a very distinguished peak in this respect. MIS 4 shows %  $\text{CaCO}_3$  minima in all the three



**Fig. 11.  $\text{CaCO}_3$  fluctuations during the Late Quaternary in the Atlantic Ocean cores. Marine Isotope Stages boundaries are marked with horizontal lines and MIS stage numbers are labeled.**

cores, whereas MIS 5 i.e. last interglacial coincides with a preservation event and is a common feature in all the cores. MIS 6, which is the glacial maxima, shows relative depletion in all the three cores. Core V25-59 that is retrieved from the mid-Atlantic ridge shows high fluctuations in % $\text{CaCO}_3$  content unlike other 2 cores.

In general the observed pattern shows maximum values during interglacials and minimum values during glacials, which has already been termed as the ‘Atlantic

pattern'. The maxima and minima values for  $\text{CaCO}_3$  may not be the same for any of the cores as they lie in different sedimentary regimes. Therefore, there will be diverse contributions from each factor controlling total carbonate (dilution, dissolution and productivity). But, the factors vary in such a way that their combined nature and timing produces the observed classic patterns.

### **3.1.2 The Pacific Ocean:**

Five cores covering a time span of 0.6Ma were chosen from the equatorial Pacific region (Fig. 12). The cores were collected from a water depth range of 3900 to 4500m. All these cores are from below the lysocline but lie above the present day CCD (Farell and Prell, 1989).  $\text{CaCO}_3$  content ranges from 59 to 91% in DSDP Site 572, from 38 to 90% in Core SDSE 59, from 47 to 95% in Core RC11-210, from 26 to 84% in Core V28-179 and 24 to 91% in Core SDSE 60. All peaks and troughs in  $\text{CaCO}_3$  content are correlative from core to core. Interglacials show low  $\text{CaCO}_3$  values and glacials show high  $\text{CaCO}_3$  values in all these cores (Fig. 12). Such a  $\text{CaCO}_3$  fluctuation pattern has been termed the 'Pacific pattern' showing better preservation during glacials. As seen in Fig. 12, most of the preservation maximas lie towards the latter half of the glacial stages. A gradual increase in the amplitude of  $\text{CaCO}_3$  variations is noticed with increase in water depth. Core SDSE 60 shows the greatest variations in % $\text{CaCO}_3$  and Core DSDP-572 the least variation. Both these cores demonstrate the effect of carbonate dissolution with increasing water depth.

### **3.1.3 The Indian Ocean:**

The ODP Site 709A and core SDSE 154 were chosen to document the  $\text{CaCO}_3$  fluctuations in the Indian Ocean (Fig. 13). ODP Site 709A was drilled at a water

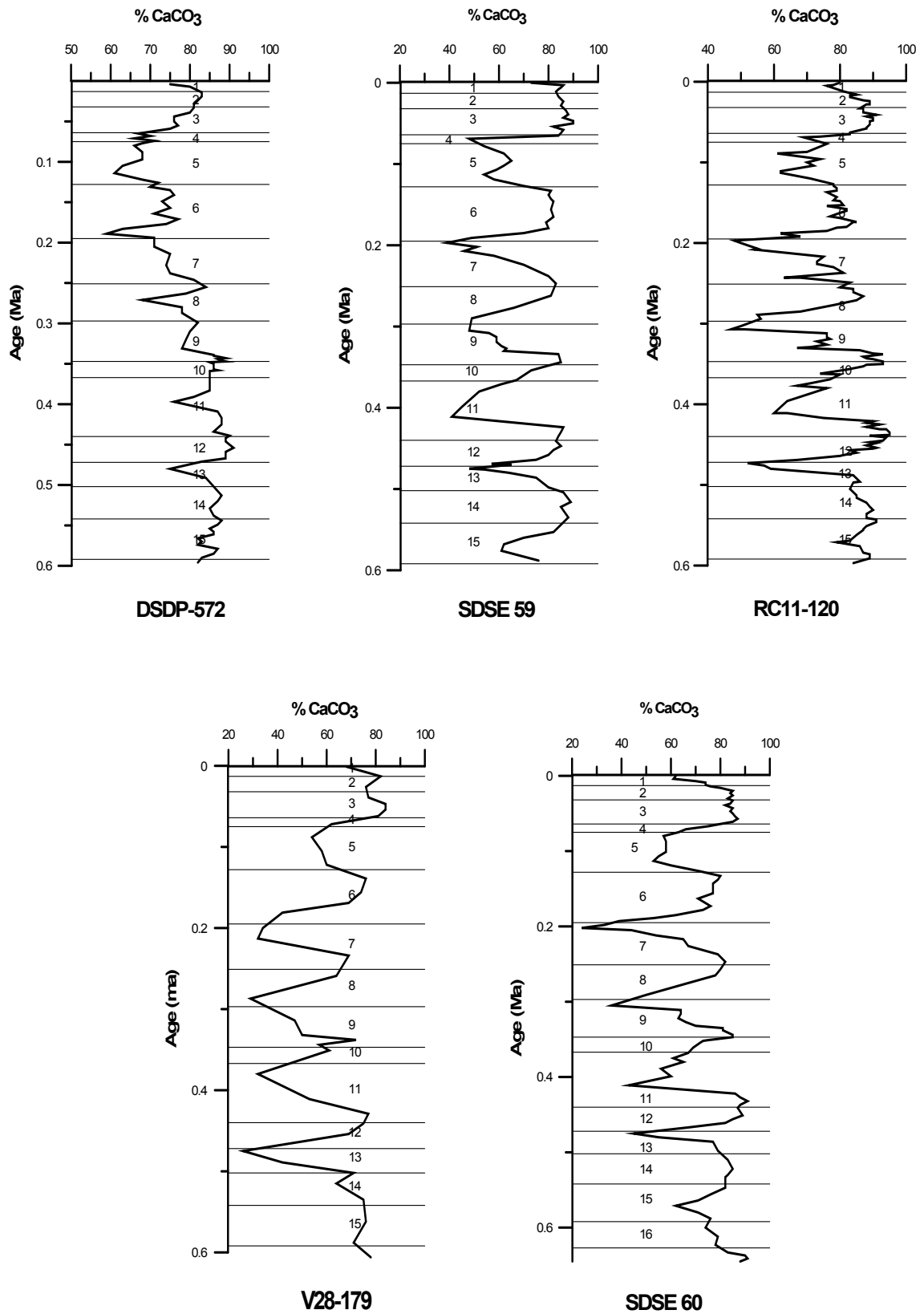
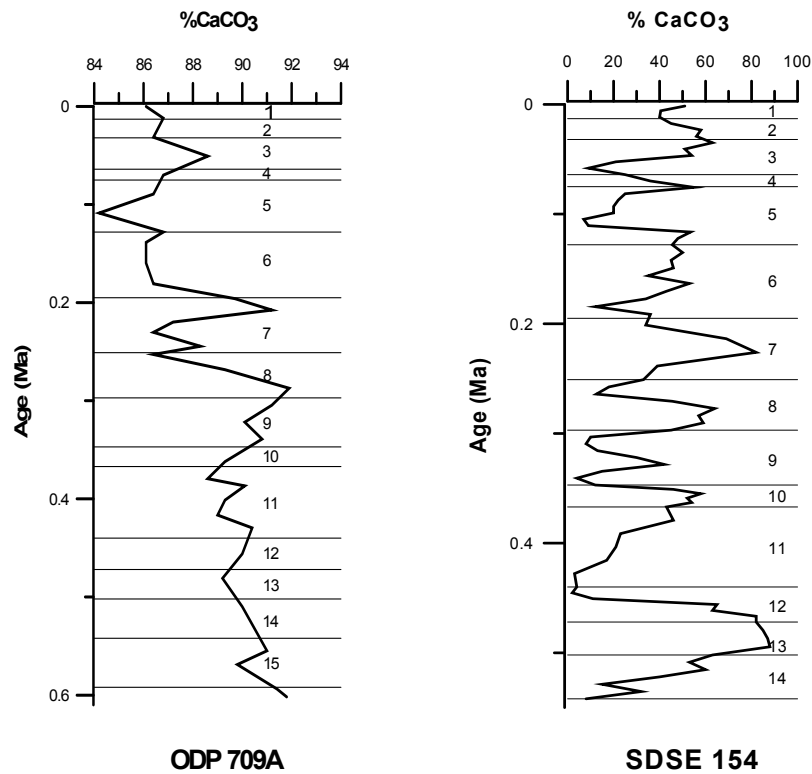


Fig. 12. CaCO<sub>3</sub> fluctuations during the Late Quaternary in the Pacific Ocean.

depth of 3800m which lies above the regional calcite lysocline depth. The  $\text{CaCO}_3$  content in this core varies from 84.2% to around 92% for the last 0.6Ma.  $\text{CaCO}_3$  variations do not exhibit any specific type of variations throughout the glacial-interglacial stages, which indicates that the  $\text{CaCO}_3$  content in the total sediment is



**Fig. 13.  $\text{CaCO}_3$  fluctuations for the past 0.6Ma in the Indian Ocean.**

apparently not related to the glacial and interglacial  $\delta^{18}\text{O}$  cycles (Naidu and Malmgren, 1999). The high concentrations of  $\text{CaCO}_3$  at the ODP Site 709A probably rules out a significant influence from dilution by non-carbonate and terrigenous material. Therefore  $\text{CaCO}_3$  fluctuations could reflect either the surface water carbonate productivity or dissolution effects.

Core SDSE 154 was collected from the western equatorial Indian Ocean (Somali basin) at a water depth of 4860m, which lies below the regional lysocline and covers a time period of 0.55Ma. Higher percentages of  $\text{CaCO}_3$  occur during glacial and lower during interglacial isotope stages. Interglacial MIS 7 and 13 display exceptionally high percentages of  $\text{CaCO}_3$ . This core shows a ‘Pacific type’ dissolution pattern caused owing to dissolution due to organic matter degradation (Naidu *et al.*, 1993).

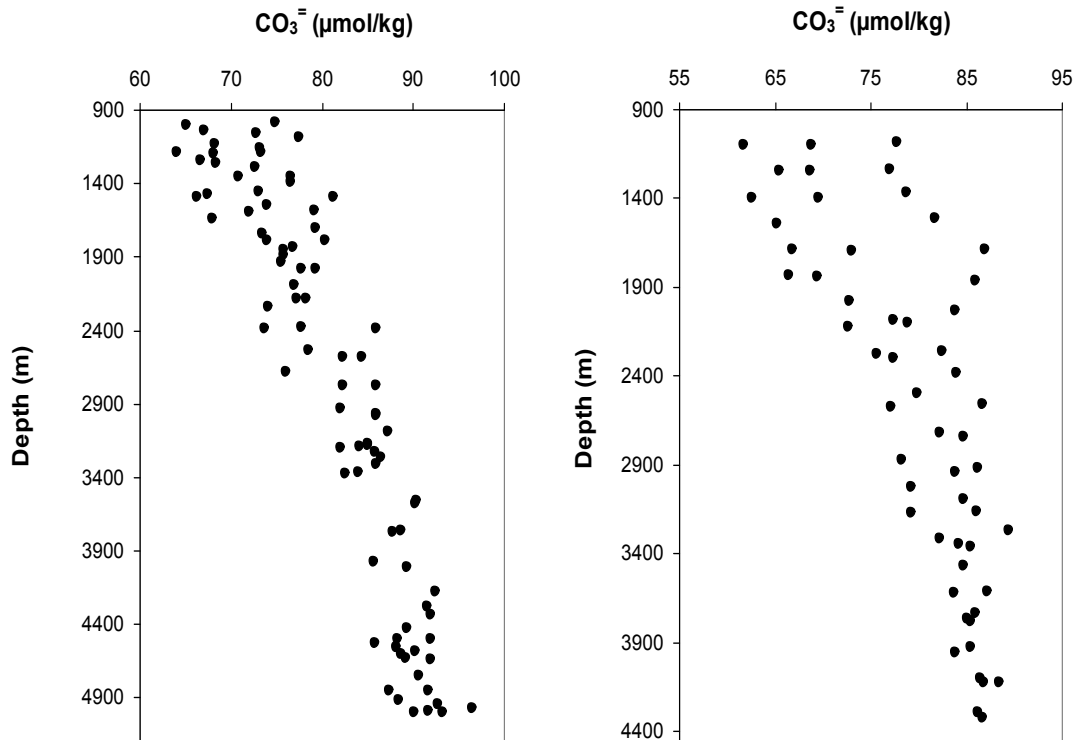
Comparison of  $\text{CaCO}_3$  fluctuations during Late Quaternary from the three major oceans reveal that the Indian and Pacific Ocean show higher  $\text{CaCO}_3$  content in the glacial and/or at glacial/interglacial transitions. By contrast in the Atlantic Ocean, higher  $\text{CaCO}_3$  content during interglacials and lower  $\text{CaCO}_3$  content during glacial were noticed. The  $\text{CaCO}_3$  cycles observed in the Atlantic and Indo-Pacific Oceans show a correspondence with the  $\text{CO}_2$  variations and ice volume observed in the Vostok ice cores with an increase in the  $\text{CO}_2$  concentrations during the interglacials and a decrease during glacial (Petit *et al.*, 1999).

## **3.2 Changes of Carbonate ion concentrations in the Indian Ocean:**

### **3.2.1 Core top sediment samples:**

The *in-situ* carbonate ion concentrations [ $\text{CO}_3^{=}$ ] of the water bathing the core tops, were computed from different GEOSECS stations for the Western and Eastern Indian Ocean separately (Table 2,3 & 4, Fig. 9 &14). GEOSECS Station Nos. 417,420 and 425 which lie along a transect in the western Indian Ocean and in proximity to the coretop locations were selected. For the western Indian Ocean GEOSECS stations 446, 448, 451 and 437 were selected for similar reasons. The  $\text{CO}_3^{=}$  concentration with respect to water depth show good similarity for the western

and eastern Indian Ocean. Below a depth of 1000m the concentrations are known to be remarkably similar in the Atlantic, Pacific and Indian Oceans (Broecker, 2003). Therefore, these concentrations can be confidently extrapolated to our core top

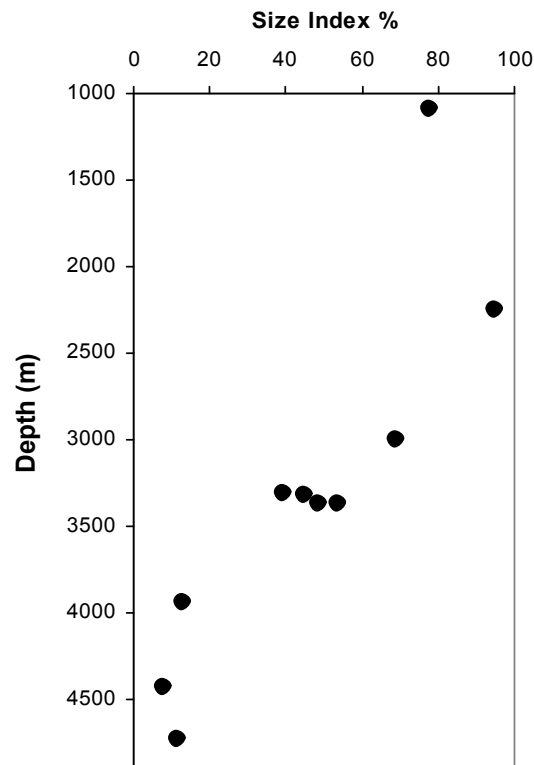


**Fig. 14. In-situ  $\text{CO}_3^{=}$  concentrations ( $\mu\text{mol/kg}$ ) calculated from GEOSECS stations with respect to depth(m) at (a) stations 417, 420, and 425 for the western tropical Indian Ocean and (b) station 446, 448, 451, and 437 for the eastern tropical Indian Ocean.**

locations. Plots show that  $\text{CO}_3^{=}$  concentrations decrease from a range of 60 to 80  $\mu\text{mol/kg}$  at 900m to a much tighter range of 85 to 90  $\mu\text{mol/kg}$  at the deeper depths. The reason for computing  $\text{CO}_3^{=}$  concentrations for depths below 900m is that the core tops have been recovered from lower water depths.

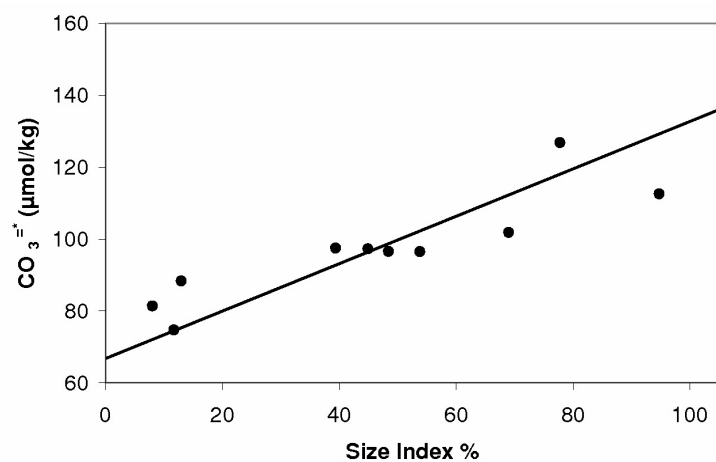
Size index of coarse calcite to total calcite shows high values for core tops from above 3307m water depths (Table 2 and Fig. 15). Values for depths above 3307m are as high as 95%. Strikingly, a significant change of size index varying from

8 to 95% is noticed in the water depth range of 1000 to 4700m. A gradual decrease in size index values is noticed from 2250m water depth onwards. In the present study



**Fig. 15.** Size index values plotted as a function of depth in the tropical Indian Ocean. A gradual decrease in the size index values from 2250 m onward and a drastic decrease from 3900 m water depth are noticed.

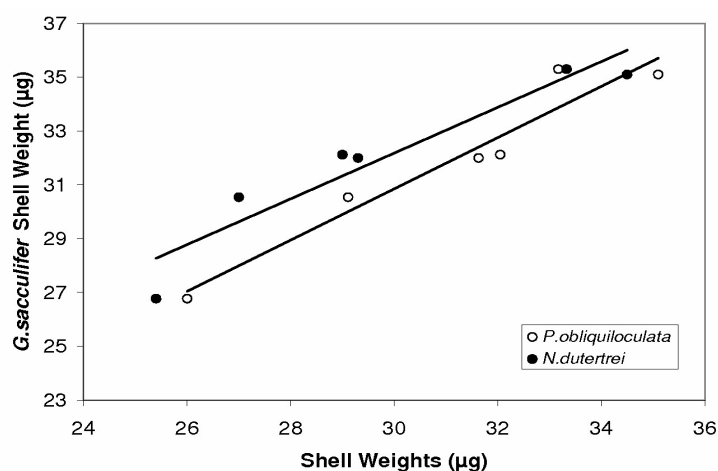
a linear decline in the ratio of  $\text{CaCO}_3$  in the  $>63\mu\text{m}$  fraction to the total  $\text{CaCO}_3$  in bulk sample occurs in the  $\text{CO}_3^{=}$  concentration range of 126 to  $70\mu\text{mol/kg}$ , (Fig. 16).



**Fig. 16.** Size index versus  $\text{CO}_3^{=}$  concentration ( $\mu\text{mol/kg}$ ) plotted on a reference line (Broecker and Clark, 1999) for the three major world's oceans.



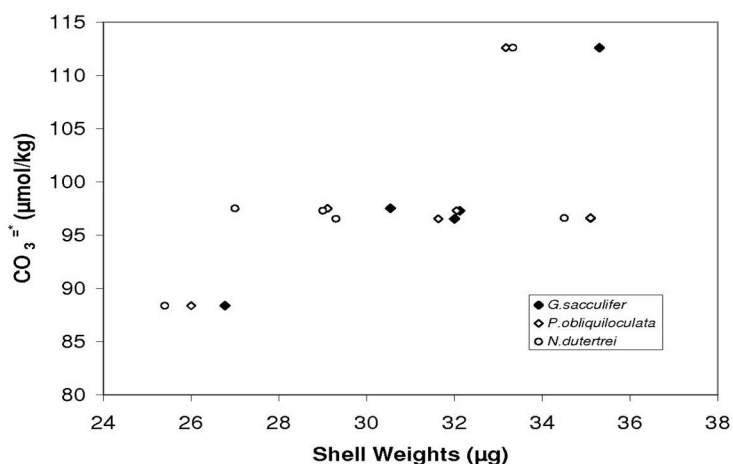
Shell weight measurements were performed on planktonic foraminifera, *G. sacculifer*, which is a species sensitive to dissolution and eventually on two other species *N. dutertrei* and *P. obliquiloculata*. Shell weights of *G. sacculifer* range from 26.77 to 35.3 $\mu\text{g}$ , *P. obliquiloculata* shell weights range from 26 to 35.1 $\mu\text{g}$  whereas that for *N. dutertrei* ranges from 27 to 34.5 $\mu\text{g}$ . All the three foraminifera species exhibit more or less similar shell weights. A good correlation is seen between *G. sacculifer* shell weights and *N. dutertrei* and *P. obliquiloculata* shell weights, which confirm that there is no measurement error or shell fill (Fig. 17).



**Fig. 17.** *Globigerinoides sacculifer* shell weights versus *Pulleniatina obliquiloculata* and *Neogloboquadrina dutertrei* shell weights show a linear trend, suggesting no measurement error or shell fill.

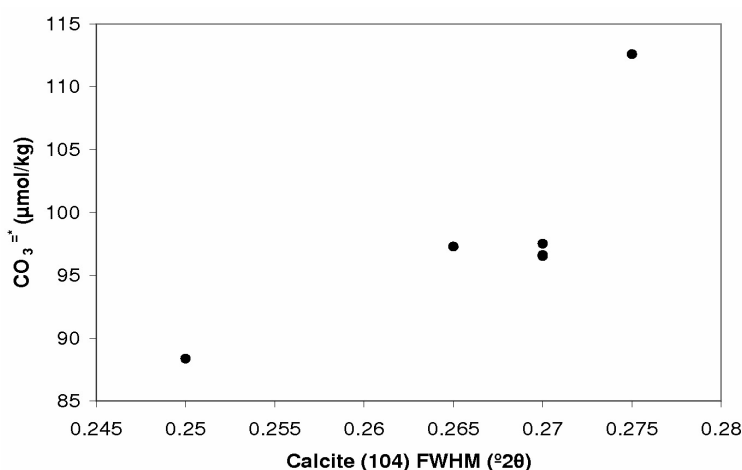
A linear decrease in shell weight is observed in the pressure-normalized carbonate ion ( $\text{CO}_3^{=}$ ) range from 90 to 125 $\mu\text{mol kg}^{-1}$  in the tropical region of the world oceans with a weight loss of  $0.30 \pm 0.05\mu\text{g } \mu\text{mol}^{-1}\text{kg}^{-1}$  (Broecker and Clark, 2001d). Bottom water  $\text{CO}_3^{=}$  concentration bathing the core tops are in the range of 88 to 113  $\mu\text{molkg}^{-1}$ , lying in the shell weight decrease zone documented by Broecker and Clark (2001d). It is found that in the present study foraminifera shell weights show marginally higher values than those in the eastern Indian Ocean documented by Broecker and Clark, (2001d). A large variability in shell weights corresponding to

$\text{CO}_3^{=}$  concentration of around  $97 \mu\text{mol kg}^{-1}$  is found, which lie at a depth of 3300 to 3400m ( Fig. 18).



**Fig. 18.** Shell weights of *Globigerinoides sacculifer*, *Pulleniatina obliquiloculata*, and *Neogloboquadrina dutertrei* versus bottom water  $\text{CO}_3^{=}$  concentrations. A large variability is seen at pressure-normalized carbonate ion concentrations of  $97 \mu\text{mol/kg}$ .

Calcite crystallinity measurements have been carried out on *G. sacculifer*, which is a dissolution sensitive species. Sites SK199C/6, 9, 10, 11 and 14 show similar crystallinity ranging from 0.275 to 0.265 $^{\circ}2\theta$  values over a range of bottom water [ $\text{CO}_3^{=}$ ] (Fig. 19) which indicate that dissolution affects more or less evenly in the water depths ranging from 3300 to 3400m.



**Fig. 19.** Calcite (104) FWHM ( $^{\circ}2\theta$ ) values plotted against pressure-normalized  $\text{CO}_3^{=}$  concentrations ( $\mu\text{mol/kg}$ ). The lowest value of calcite (104) FWHM is seen at a  $\text{CO}_3^{=}$  concentration of  $88 \mu\text{mol kg}^{-1}$ .

Comparatively, Site SK199C/7 shows lower calcite (104) FWHM (Full Width at Half Maximum) value of 0.25 suggesting intense dissolution at this water depth (3900m). All the three proxies, size index, shell weights and calcite crystallinity, applied to a set of core top samples in the western Indian Ocean show a linear regression which varies from 0.7 to 0.75 between them (Fig. 20).

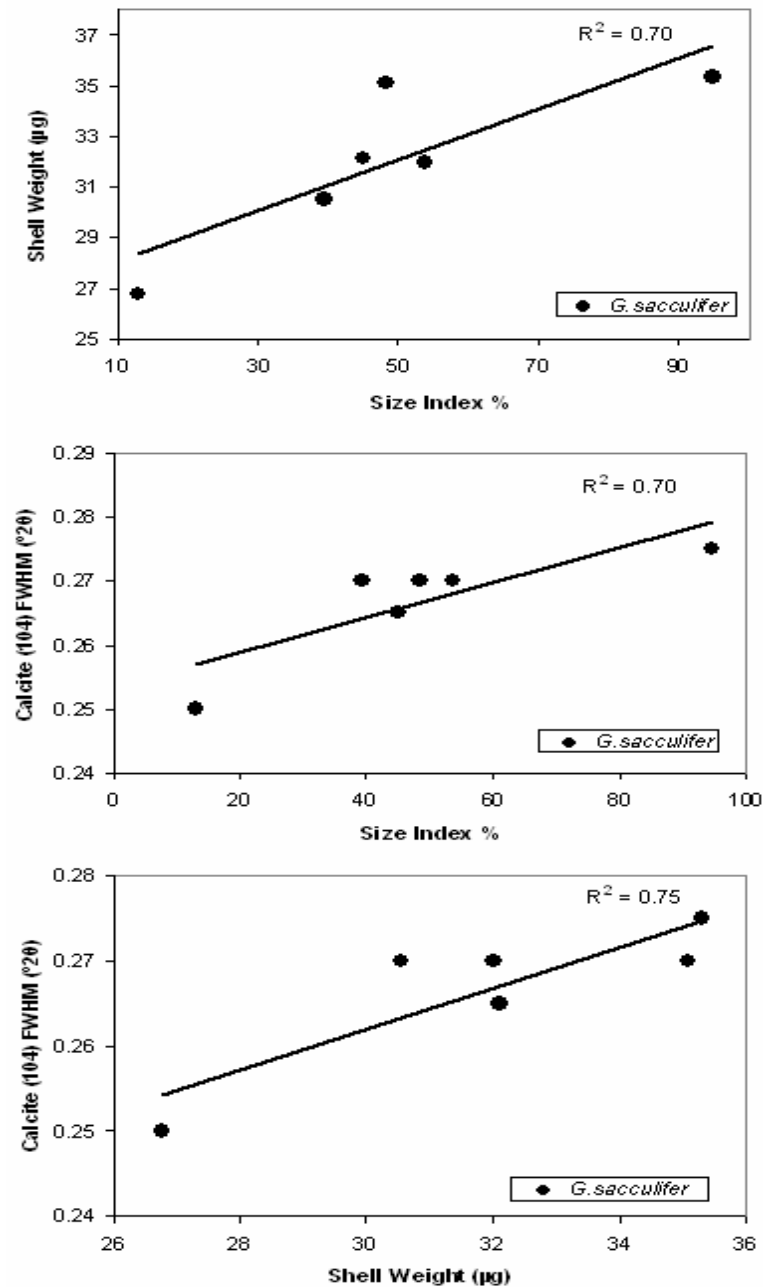
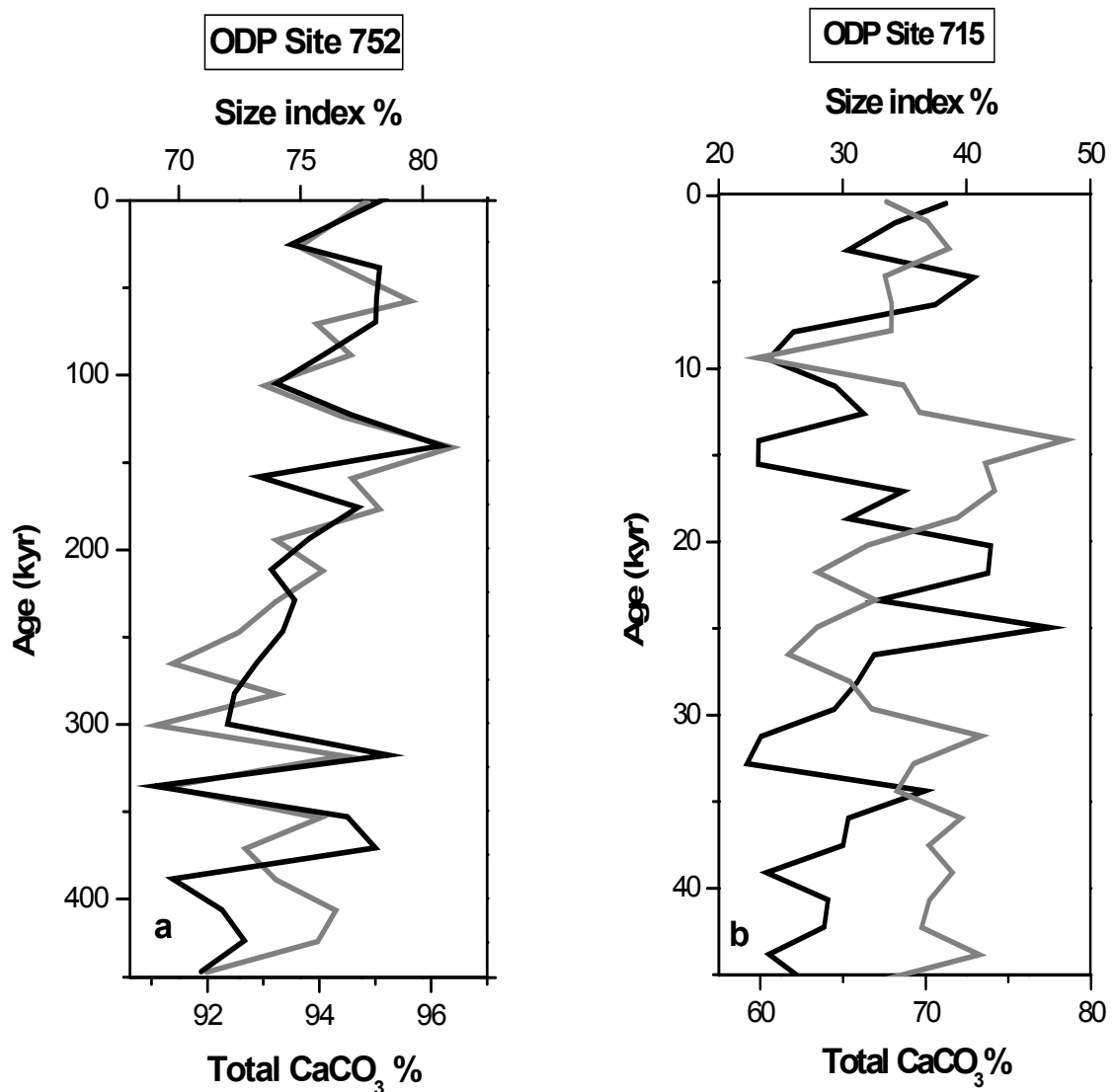


Fig. 20. Comparison between the three proxies shows good linear regression. (a) Shell weight ( $\mu\text{g}$ ) versus size index % ( $R^2 = 0.7$ ), (b) calcite (104) FWHM ( $^{\circ}2\theta$ ) versus size index % ( $R^2 = 0.7$ ), and (c) calcite (104) FWHM ( $^{\circ}2\theta$ ) versus shell weight ( $\mu\text{g}$ ) ( $R^2 = 0.75$ ).

### 3.2.2 ODP Site 752 and 715:

Two cores, ODP Sites 752 and 715 were drilled at shallow water depths from the (Table 3, Fig. 9). Top 1m of ODP Site 752, which covers a time span of 442kyr was analyzed for  $\text{CaCO}_3$ . Since this core has been recovered from a very shallow depth of 1086m, from a topographic high, it is used in the present study to make a comparison with another deep core as well as to understand supralysoclineal dissolution if any. At this site, total  $\text{CaCO}_3$  content varies from 91 to 96% over the last 442 kyr (Fig. 21a). There is no specific variation pattern in carbonate content noticed throughout the core. Very high  $\text{CaCO}_3$  content and minor changes of  $\text{CaCO}_3$  variation at Site 752 suggests that dilution plays a very insignificant role here. Furthermore, this site is situated relatively far away from landmass and therefore, dilution by terrigenous material is not significant. Since this site lies very much above the lysocline, dissolution does not seem to affect this core. Basically the minor variations observed in the carbonate content at ODP Site 752 may be due to changes in productivity of the overlying waters. At ODP Site 715, total  $\text{CaCO}_3$  content varies from 59 to 77% over last 45kyr (Fig. 21b). During the Holocene  $\text{CaCO}_3$  content is comparatively lower than during 13 to 24kyr, which corresponds to MIS 2 and documents high  $\text{CaCO}_3$  content. Thereafter,  $\text{CaCO}_3$  content remains low. Overall, this core does not seem to be display any specific pattern of  $\text{CaCO}_3$  fluctuations. Larger variations in  $\text{CaCO}_3$  content at Site 715 are possibly attributed to its proximity to the Indian sub-continent and hence influence by terrigenous material derived from the landmass.

The size index shows variation from 69 to 81% with a core top value of 78% at Site 752 (Fig. 21a). There has been a significant variation in the size index for this



**Fig. 21.** Fluctuations of total CaCO<sub>3</sub> and size index values at a) ODP Site 752 and b) ODP Site 715.

core. The high size index values obtained for ODP Site 752 confirms the finding that dissolution does not affect the sediments from this region. The size index values for ODP Site 715 vary from 23 to 41% with core top value of 34% (Fig. 21b). Again there is a large variation in size index for this core. Lower size index values obtained from ODP Site 715 cannot be attributed only to dissolution and further reasons need to be determined. Further, the CaCO<sub>3</sub> content of the finer fraction has been determined for both the cores. The <63 $\mu$ m fraction CaCO<sub>3</sub> for Site 752 remains high throughout

and varies from 82 to 96% (Fig. 22a). For Site 715 the  $<63\mu\text{m}$  fraction  $\text{CaCO}_3$  shows large variations ranging from 50 to 77% (Fig. 22b). There is a striking resemblance of  $<63\mu\text{m}$  fraction  $\text{CaCO}_3$  with the total  $\text{CaCO}_3$  content for Site 715. This feature is not seen for the  $<63\mu\text{m}$  fraction  $\text{CaCO}_3$  of Site 752.

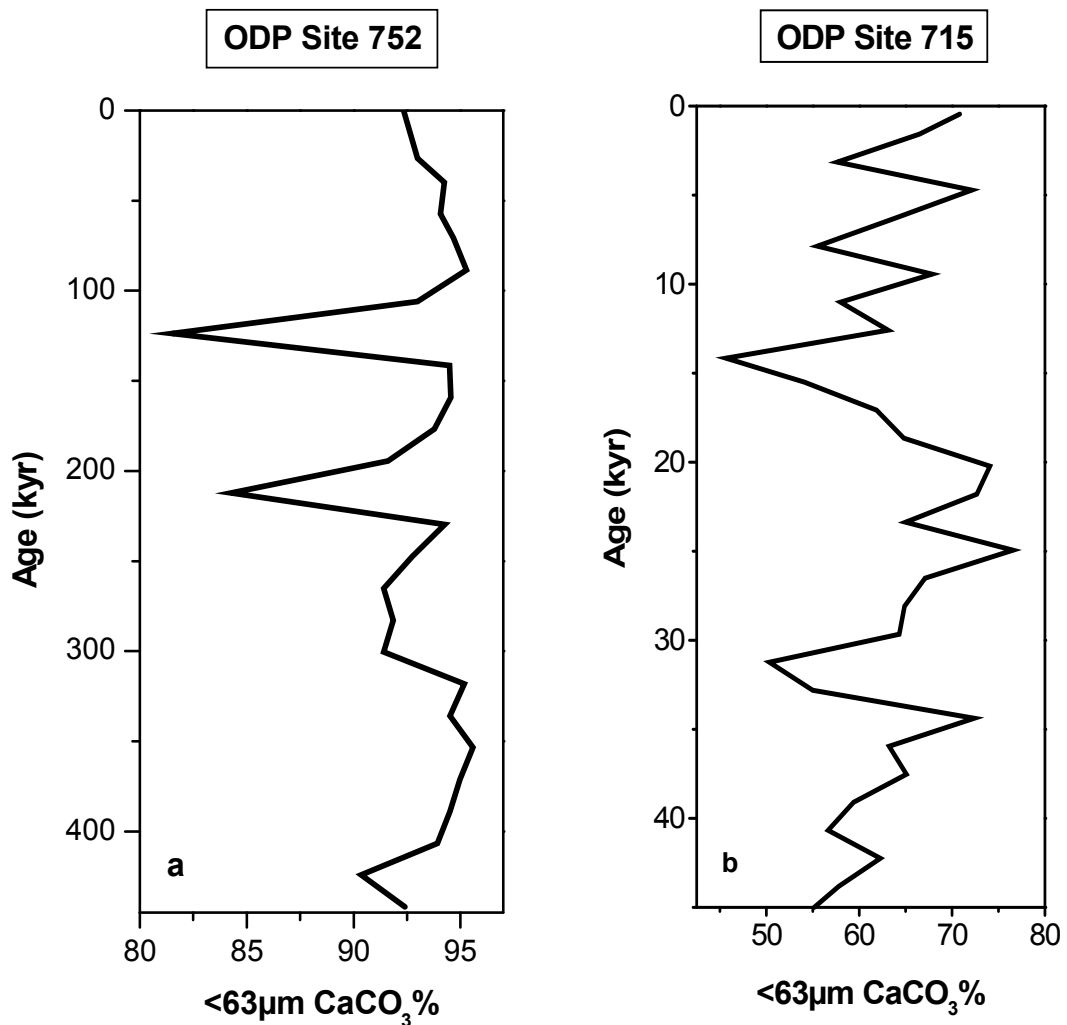


Fig. 22. Fluctuations of  $\text{CaCO}_3$  in  $<63\mu\text{m}$  fraction at a) ODP Site 752 and b) ODP Site 715.

Another, paleocarbonate ion proxy, planktonic foraminifera shell weight has been applied to the ODP Site 715. In order to get a better picture of the processes controlling the  $\text{CaCO}_3$  variations in this core, shell weight measurements were performed on *G. ruber* for the entire core. Shell weights show variability from 16 to

20.26 $\mu\text{g}$  throughout the core (Fig. 23). *G. ruber* shells do not show a typically expected glacial-interglacial difference in weight. Overall the shell weight trend is anomalous throughout the core thus obscuring the topic of concern.

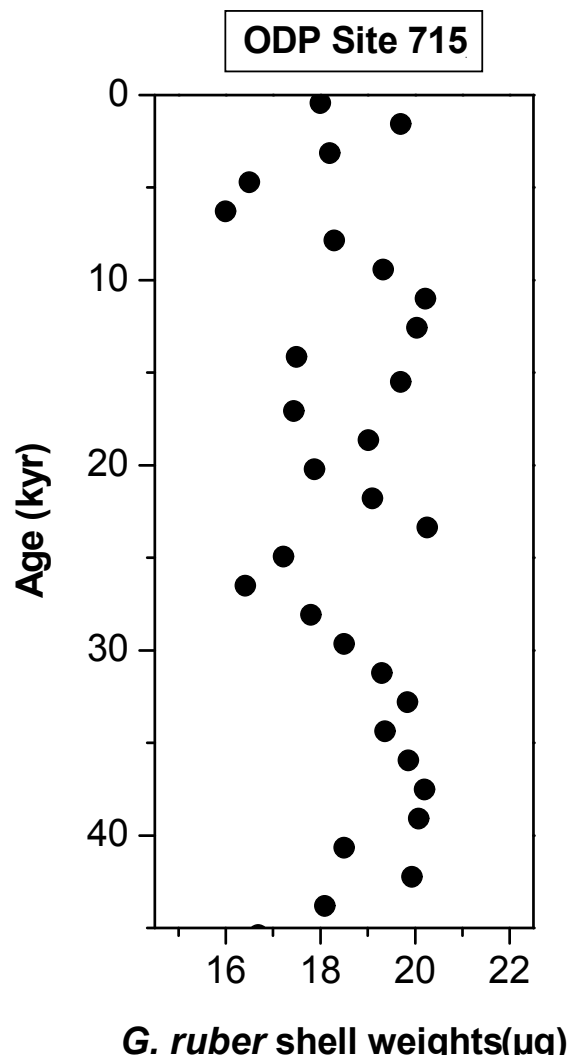


Fig. 23. Fluctuations in *G. ruber* shell weights at ODP Site 715.

### 3.2.3 Cores AAS9/21 and SK218/A:

Core AAS9/21 was recovered from the Arabian Sea, and core SK218/A, was recovered from the Bay of Bengal (Table 3, Fig. 9). Both cores lie in two unique environments but along a similar latitudinal transect. Both cores cover a time span of 25kyr, which covers the Last Glacial Maximum (LGM). Core AAS9/21 from the

Arabian Sea lies at a depth of 1807m.  $\text{CaCO}_3$  content in this core ranges from 18 to 45% (Fig. 24a). Low  $\text{CaCO}_3$  values were noticed from 0 to 10kyr and relatively high  $\text{CaCO}_3$  values were noticed from 10 to 20kyr. At around 18kyr highest  $\text{CaCO}_3$  values are recorded. In core SK218/A,  $\text{CaCO}_3$  values ranges from 1 to 12.5 % throughout the core (Fig. 24b). The  $\text{CaCO}_3$  content remains comparatively lower up to 10kyr i.e.

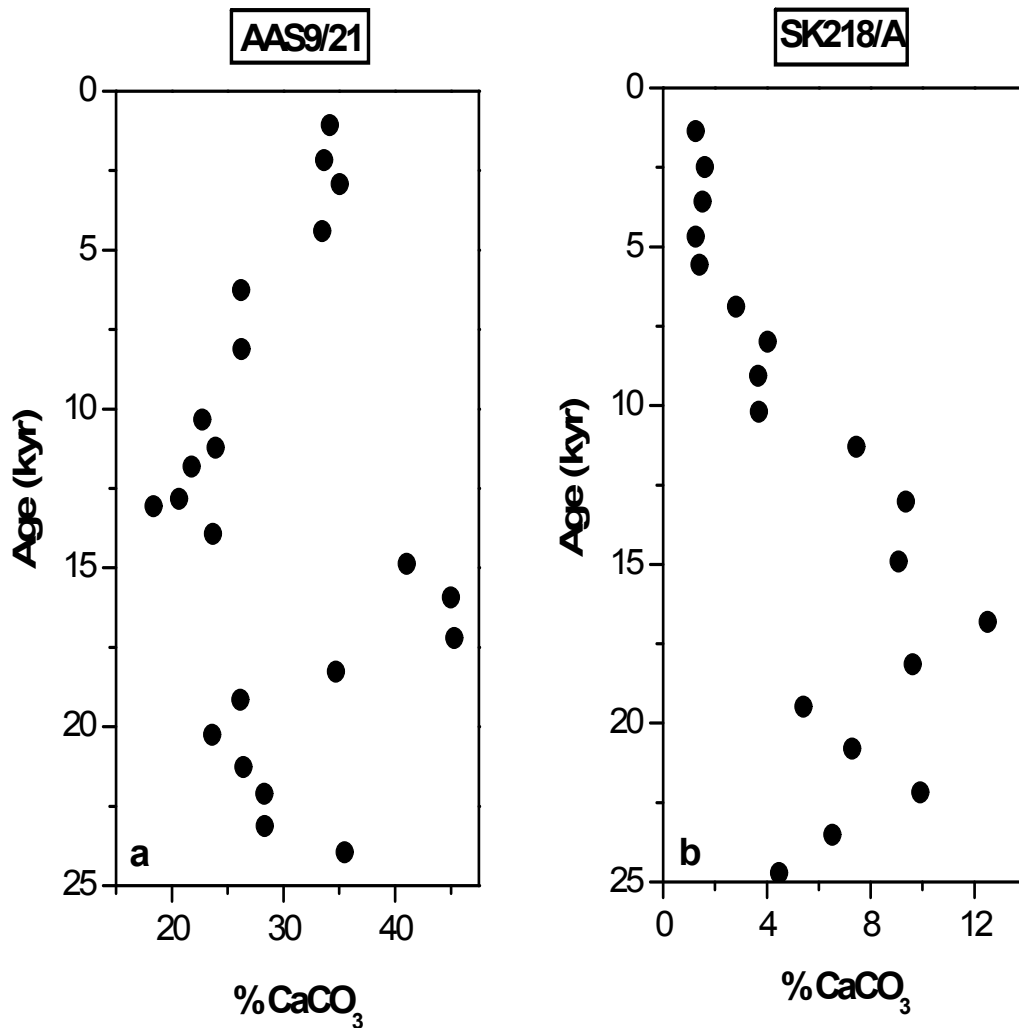


Fig. 24. Fluctuations in  $\text{CaCO}_3$  for the two cores a) AAS9/21 and b) SK218/A.

during the Holocene. During this period the  $\text{CaCO}_3$  content ranges from 1 to 4% below which a steep increase is noticed. The peak point in  $\text{CaCO}_3\%$  occurs at around 17kyr, which is of 12.5%. This corresponds to Late Glacial Maximum (LGM). Such a



CaCO<sub>3</sub> variation is indicative of the ‘Pacific pattern’. Size index values in core AAS9/21 show a gradual increase from glacial to the Holocene and then a marginal increase during the course of the Holocene. The range of size index values is from 10 to 40% (Fig. 25a). Holocene values range from 10% to 24%. A maximum in size index value of 40% is noted at around 19kyr. Size index in core SK218/A ranges from 10 to 46%. Size index remains comparatively lower during the Holocene, with values ranging from 10% to 20% (Fig. 25b). From 10kyr downwards there is a increase in

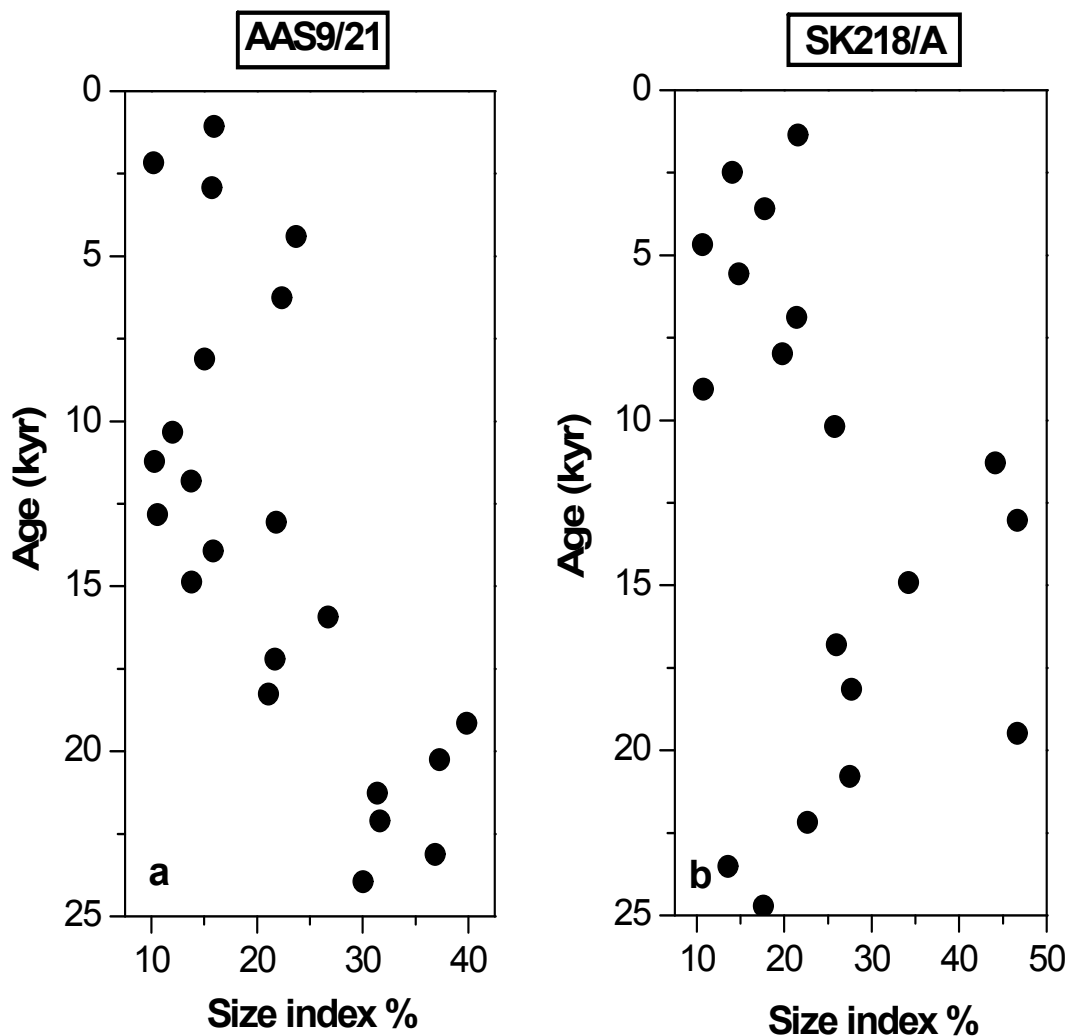


Fig. 25. Fluctuations in size index for the two cores a) AAS9/21 and b) SK218/A .

size index values with maximum value of 46% at around 19kyr, which corresponds to the LGM. The coretop size index value observed is 21%, which shoots up to 44% during the last glacial period. The size index values are indicative of dissolution, but reasons cannot be ascertained based on this lone indicator. In general the  $\text{CaCO}_3$  content and size index for both the cores, AAS9/21 and SK218/A show lower values during the interglacial and higher values during the glacial, indicative of a Pacific pattern of carbonate content fluctuation.

*G. sacculifer* shell weights from AAS9/21 show an increase from 31 to 41  $\mu\text{g}$  for the entire core (Fig. 26a). The steep increase in shell weights is encountered only

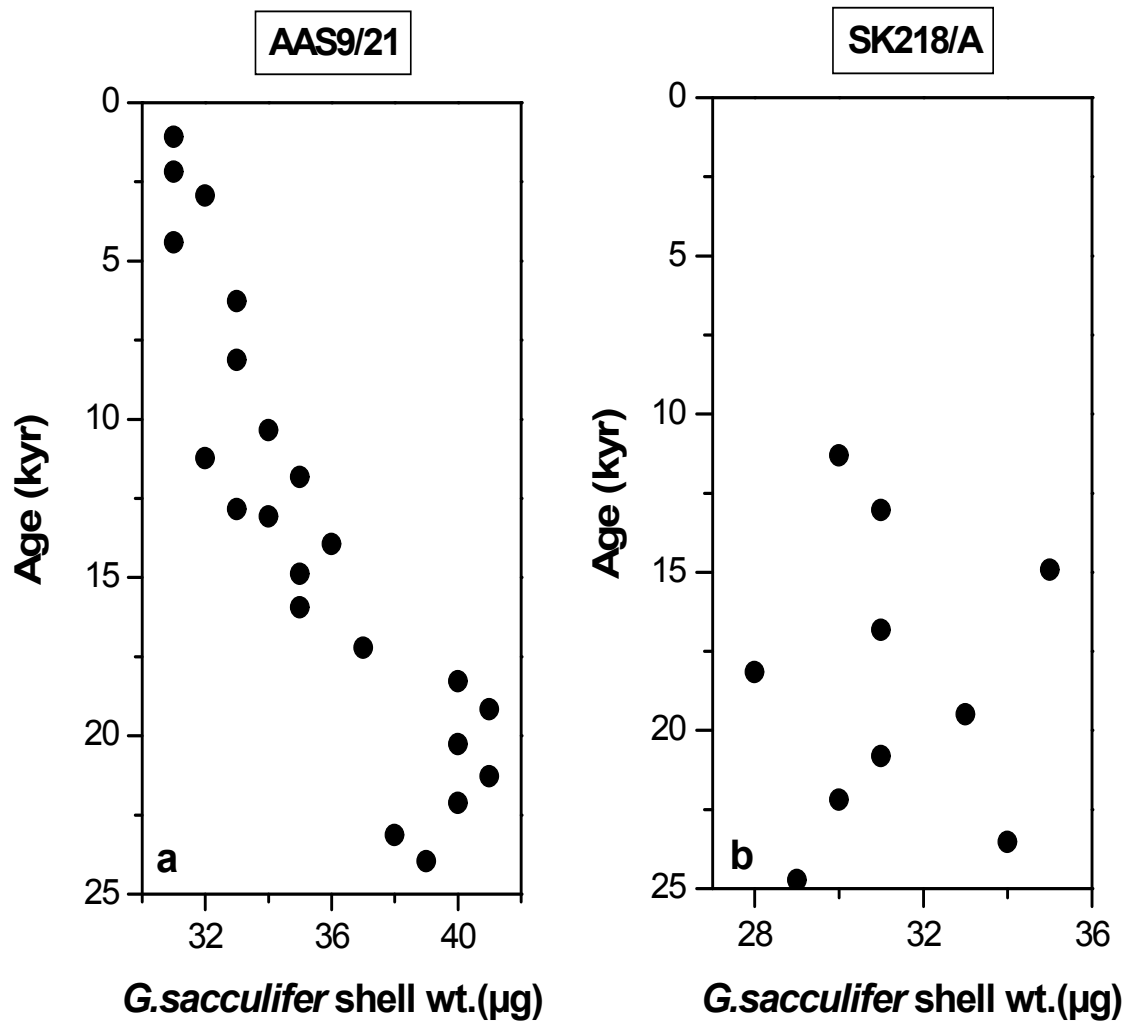


Fig. 26. Fluctuations in *G. sacculifer* shell weights for the two cores a) AAS9/21 and b) SK218/A.

after the Holocene as observed in  $\text{CaCO}_3$  content and size index. Maximum shell weight of  $41\mu\text{g}$  is observed at 19kyr. In the Core SK218/A, shell weights of *G. sacculifer* range from 28 to  $35\mu\text{g}$  (Fig. 26b). For the Holocene period broken *G. sacculifer* shells are encountered and therefore no shell weights can be derived for this interval. Below 10kyr, shell weights do not show any noticeable increase during the LGM as encountered in  $\text{CaCO}_3$  content and size index.

Mg/Ca ratios of foraminifera have been determined for the two cores AAS9/21 and SK218/A (Fig. 27a and b). Mg/Ca ratios of foraminifera are a well

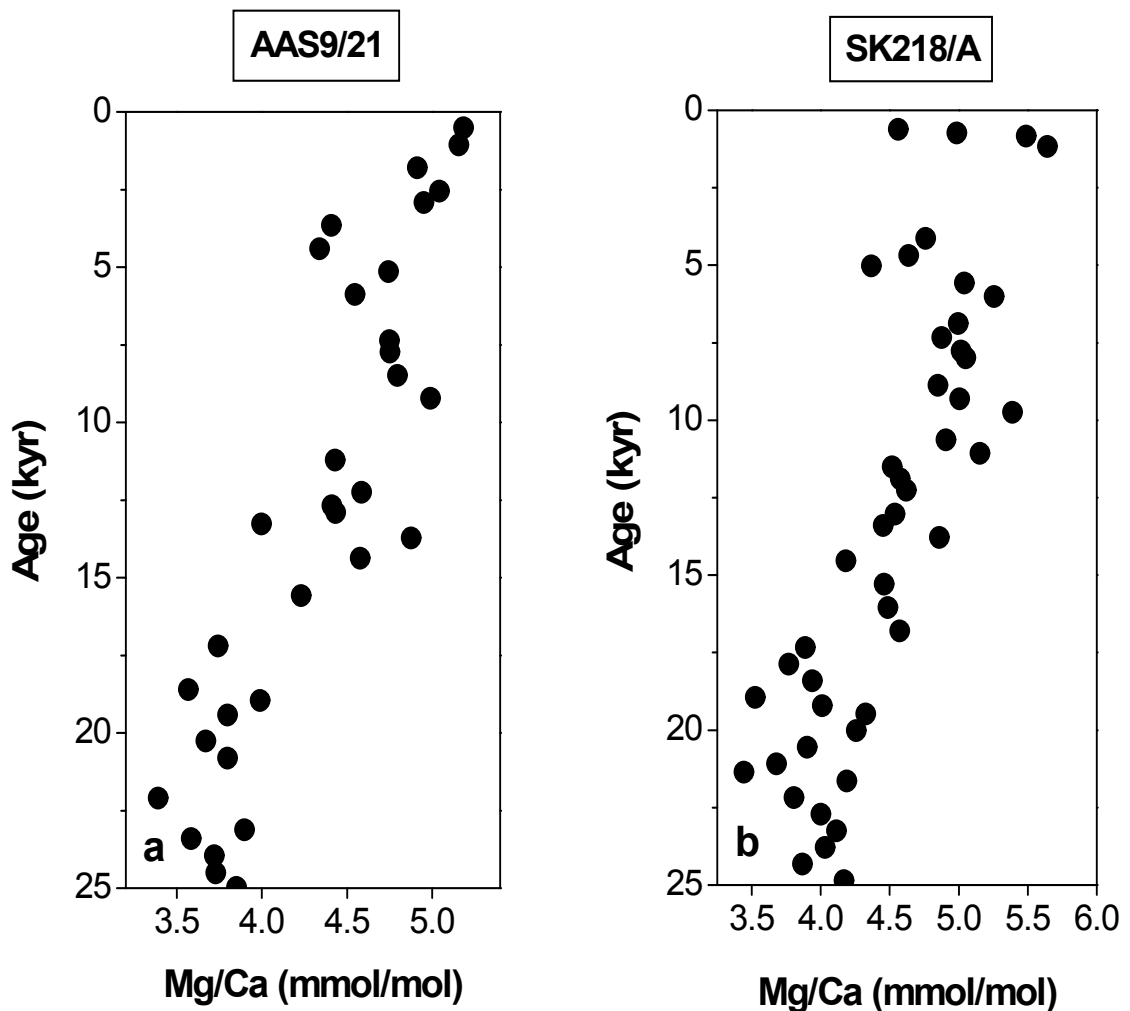


Fig. 27. Fluctuations in Mg/Ca for the two cores a) AAS9/21 and b) SK218/A.

established proxy for Sea Surface Temperature (Nürnberg *et al.*, 1996).  $Mg^{2+}$  is one of several divalent cations which may substitute for  $Ca^{2+}$  during the formation of biogenic calcium carbonate. Its incorporation into foraminiferal calcite is influenced by the temperature of the surrounding seawater during growth such that foraminiferal Mg/Ca ratios increase with increasing temperature (Barker *et al.*, 2005). Mg/Ca results from both the cores AAS9/21 and SK218/A show a downcore decrease which is an indicator of the temperature increase since the past 25kyr. In AAS9/21, Mg/Ca values range from 3.4 to 5.2mmol/mol (Fig. 27a). During the Holocene, Mg/Ca values show a decreasing trend with values in the range of 5.2 to 4.3mmol/mol. Thereafter, a steep decrease is seen from 4.9 to 3.4 mmol/mol during the last glacial. The lowest value is encountered at ~22kyr which is around the LGM. Mg/Ca values in Core SK218/A range from 3.4 to 5.6mmol/mol (Fig. 27b). Holocene values in this core also show a decreasing trend in the range of 5.6 to 4.4mmol/mol. Mg/Ca values started to decline from 13kyr onwards and minimum values were noticed during the LGM.

## CHAPTER IV

### DISCUSSIONS

#### 4.1 Calcium Carbonate fluctuations from the world oceans:

The  $\text{CaCO}_3$  patterns over the equatorial sector of the Atlantic, Pacific and Indian oceans, covering a time span of last 0.6Ma are assessed to address the basic differences amongst the three oceans.  $\text{CaCO}_3$  fluctuations over the last 0.6Ma covers the major glacial/interglacial intervals of the Late Quaternary Period and thus provides an overview about the relationships between climate and  $\text{CaCO}_3$ . This exercise shall give a synoptic view of the world's ocean  $\text{CaCO}_3$  cycle and a better understanding of the past  $\text{CO}_2$  variations.

The total carbonate content at any given location may fluctuate due to three major factors: 1) productivity of carbonate secreting organisms, 2) dilution by non-calcareous material and; 3) dissolution of calcareous tests during and after deposition (Damuth, 1975). In the Pacific Ocean, it is widely accepted that  $\text{CaCO}_3$  content was higher during glacials and lower during interglacials. 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, which is termed as the 'Atlantic pattern'. 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 are known to exhibit a Pacific pattern (Olausson, 1965; Oba, 1969; Naidu, 1991; Naidu et al., 1993), whereas other cores show both Pacific and Atlantic patterns (Peterson and Prell, 1985). Swedish Deep Sea Expedition core 154 (Volat *et al.*, 1980), generally exhibits a Pacific type of dissolution pattern in major portion of the records whereas

studies from above the lysocline depth eg., core ODP709A, do not show either a Pacific or an Atlantic type pattern (Naidu and Malmgren, 1999).

It has been discussed here, which factor is the most important in shaping the calcium carbonate patterns from the equatorial region of the world oceans.

#### **4.1.1 Dilution by non-calcareous material:**

The principal source of dilution by non-calcareous material is terrigenous input, the other source being siliceous productivity. Olausson (1969) states that the continental surface drained to the Atlantic Ocean is almost twice that drained to both the Pacific and Indian oceans. This is due to the major rivers, which drain into the Atlantic (Amazon, Mississippi, Niger, Congo etc). Therefore dilution could be an important factor controlling the  $\text{CaCO}_3$  variations in the Atlantic Ocean. But the scenario in the Indian and Pacific oceans is different. A detailed study of the  $\text{CaCO}_3$  distribution in surficial sediments indicate that the dilution effects are very insignificant in the equatorial Indian Ocean (Kolla *et al.*, 1976), whereas the central Pacific Ocean is relatively unaffected by dilution from terrestrial sediment sources (Adelseck and Anderson, 1978).

#### **4.1.2 Productivity:**

High surface productivity leads to high accumulation of  $\text{CaCO}_3$  due to enhanced supply of biogenic material. Olausson (1985) suggested that accumulation of  $\text{CaCO}_3$  increased during glacials in the Indo-Pacific Ocean due to intensified sink water formation in the northernmost Atlantic Ocean and intensified upwelling in the Indo-Pacific Ocean. This hypothesis would explain the difference in dissolution patterns between Atlantic and Pacific oceans (Olausson, 1985). One would expect a

Pacific type of carbonate pattern in Indian Ocean cores raised from above the lysocline depth if simultaneous upwelling takes place in Indo-Pacific oceans. Instead as seen in Site 709A (Fig. 13), where variations in  $\text{CaCO}_3$  are suggested to be due to productivity changes, does not show either a clear Pacific pattern of  $\text{CaCO}_3$  fluctuation or any relationship with glacial/interglacial cycles. This points to a lack of coeval upwelling in the equatorial Pacific and Indian Oceans (Naidu and Malmgren, 1999). Therefore, the  $\text{CaCO}_3$  patterns differ between the Indian and Pacific Oceans at shallow depth sites.

Surface water productivity changes are of secondary importance in the central Pacific Ocean (Adelseck and Anderson, 1978). Arrhenius (1952) and other workers in the Atlantic are of the opinion that productivity increased during glacials. Wiseman (1956), (1965); Kellog (1975), (1976); Ruddiman and McIntyre (1976) agree with the correspondence between high productivity and interglacials in the Atlantic. Berger (1992) states that productivity increased during glacials in the Indian Ocean. Increased plankton productivity leads to a high vertical flux of organic carbon to the sea floor, and consequently more carbon dioxide is released into the bottom water by decay of organic matter, lowering the pH and increasing carbonate dissolution. On a larger scale high productivity means stronger extraction of carbonate from water, which then becomes under saturated (Berger, 1977). The rain rates of calcite and organic carbon to the sediments depend on the surface water productivity (Olausson, 1971, 1985; Arrhenius 1952, 1988; Archer, 1991). Thus, low productivity may induce good general preservation of tests. The core SDSE 154, is an example of enhanced dissolution of  $\text{CaCO}_3$  during interglacials due to high productivity (Naidu *et al.*, 1993).

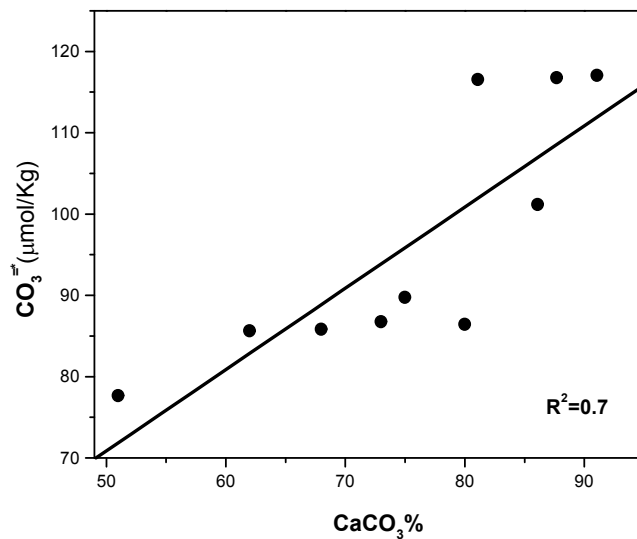
### 4.1.3 Dissolution:

Dissolution of  $\text{CaCO}_3$  in marine sediments is controlled by two factors, the understauration of calcite or aragonite in bottom waters and the undersaturation in pore waters due to production of  $\text{CO}_2$  by oxic respiration. Kuenen (1950), states that by far the greatest amount of dissolution takes place on the sea floor and not during settling. The  $\text{CO}_2$  content increases progressively in bottom water when flowing, owing to benthic organism's respiration and oxidation process, so that bottom water and dissolution are not directly correlated; "old" bottom water enhances dissolution much more than recently produced water (Volat *et al.*, 1980). Berger, (1977) stated that carbonate cycles during glacial and interglacial periods in the Pacific Ocean are largely a function of dissolution cycles. Broecker and Takahashi (1978) showed that the state of preservation does correspond to saturation on a global scale, at least in the vicinity of the lysocline and away from continental margins. A comparison of calcium carbonate preservation records of the Indian Ocean (Peterson and Prell, 1985a) with the calculated carbonate ion saturation in the water (Gröstch *et al.*, 1991) indicated that the preservation state is tied to saturation levels with respect to carbonate ion. The Indian and Pacific Oceans correspond in a similar way to changing deep-water circulation.

To better document the effect of  $\text{CO}_3^{=}$  undersaturation on the calcite preservation patterns from the three major world oceans, the dependency of  $\text{CaCO}_3$  content on  $\text{CO}_3^{=}$  was considered. For this purpose, GEOSECS stations were chosen from Atlantic, Pacific and Indian Ocean. The  $\text{CO}_3^{=}$  concentration profiles were calculated from Station Nos. 109, 334 and 420 from the Atlantic, Pacific and Indian oceans respectively. The selection of single stations for the three oceans is justified, as mentioned earlier, below 1500m  $\text{CO}_3^{=}$  concentrations are nearly constant. The



pressure-normalized carbonate ion concentration was then computed for respective depths and plotted versus the coretop  $\text{CaCO}_3$  content for all the ten cores. A linear fit is observed with significant correlation between the two ( $R^2=0.7$ ) (Fig. 28). This suggests that the  $\text{CaCO}_3$  patterns over the world oceans are closely tied to bottom water saturation with respect to carbonate ion and hence amongst other factors affecting regionally, calcite dissolution is the most important factor in shaping the



**Fig. 28. The  $\text{CaCO}_3$  % from core tops of the Atlantic, Pacific and Indian Ocean showing a linear variation with respect to pressure-normalised  $\text{CO}_3^{2-}$  calculated from GEOSECS stations ( $R^2=0.7$ ).**

$\text{CaCO}_3$  patterns.

Considering dissolution as the most important criteria in shaping the  $\text{CaCO}_3$  profiles, Van Andel (1975) suggested the criteria that the CCD is the depth wherein the  $\text{CaCO}_3$  content decreases to 20%. Ever since, various workers have made an attempt to calculate the depth of the CCD in different oceans. Peterson and Backman (1990) provide a CCD history for the western equatorial Indian Ocean, which suggests that from 22 to 2 million years it ranged from 3.8 to 4.5km. Then, during the last 2 million years, it deepened to 5km. Broecker and Peng (1982) include a summary of core top  $\text{CaCO}_3$  content versus water-depth plots for eight areas of the

ocean. On the basis of the 20% criteria, these plots suggest that in the Indian and Pacific oceans, the CCD currently resides at  $4.6 \pm 0.2$  km depth and in the northern Atlantic it resides at  $5.1 \pm 0.4$  km. Peterson and Prell (1985a) made a detailed study of the state of  $\text{CaCO}_3$  preservation on Ewing core tops from the  $90^\circ\text{E}$  Ridge in the Indian Ocean. They found a steady increase in the extent of fragmentation of whole foraminifera shells between 2.0 and 4.5 km. However, below this depth, the abundance of fragile shells (i.e., *G. ruber* and *G. sacculifer*) dropped precipitously while that of robust shells (i.e., *G. menardii*) decreased far more slowly.

Since, the importance of bottom water carbonate ion has been revealed; the criteria of Van Andel, (1975) can be applied to the cores in the present study. It was found that all the cores from the Atlantic Ocean are from above the CCD; those from the Pacific are immediately at or above the CCD; while those from the Indian Ocean include one from above the CCD and another, Core SDSE 154 from below the CCD. All the ten cores form classical examples of  $\text{CaCO}_3$  patterns from different oceans and illustrate the changing bottom water circulation and hence carbonate ion changes amongst oceans.

De Menocal *et al.* (1997) proposed that glacial-interglacial changes in deep Atlantic circulation were primarily responsible for the observed timing and spatial distributions of Pliocene–Pleistocene global carbonate burial cycles. Glacial reductions in NADW production allowed corrosive (low  $[\text{CO}_3^{=}]$ ) AABW to advance into the carbonate-rich sediments of the tropical and North Atlantic. Extensive and instantaneous Atlantic carbonate dissolution resulted from the associated rise in Atlantic calcite lysocline levels. Glacial mean ocean alkalinity levels increased in response to this dissolution, and the global ocean net carbonate burial (the amount of calcite which must be buried to balance the continental weathering supply of

alkalinity to the ocean) must have increased in the Pacific and Indian Oceans to balance decreases in Atlantic burial fluxes. This was achieved by a deepening of the calcite lysocline in the Pacific and Indian basins in response to increased mean ocean alkalinity levels, which thereby increase oceanic  $[\text{CO}_3^{=}]$  levels (using  $[\text{CO}_3^{=}] = [\text{Alk}] - [\Sigma\text{CO}_2]$ ; Broecker and Peng, 1982). However, this process of restoring the equilibrium global calcite burial is not instantaneous, but rather, is constrained by the mean response time of the oceans. Today, well ventilated (and hence high  $\text{CO}_3^{=}$ ) NADW water the Atlantic ocean is more preserving to calcite than the rest of the world's oceans. NADW accumulates  $\text{CO}_2$  oxidized from falling debris on its "grand journey" to the Pacific and Indian oceans and becomes more corrosive to carbonate than the NADW (Broecker and Peng, 1982). During the last glacial NADW either formed more slowly or was less ventilated than it is today (Boyle and Keigwin, 1982; Shackleton *et al.*, 1983; Curry and Lohmann, 1983; Mix and Fairbanks, 1985). The production of NADW was diminished therefore less  $\text{CO}_2$  was pushed into deep Pacific by NADW (Boyle and Keigwin, 1985). Thus the distribution pattern was reversed. It is still an open discussion as to whether the good glacial Pacific carbonate preservation can be attributed to a source of well-ventilated deep water in the Pacific (Moore *et al.*, 1978; Keigwin, 1987; Curry *et al.*, 1988).

$\text{CaCO}_3$  in marine sediments as a function of water depth in today's ocean or at any specific time in the past is a useful index of the extent of dissolution (Broecker, 2003). This relationship is highly non-linear. Deep water formed in the northern Atlantic has a higher  $\text{CO}_3^{=}$  concentration than that produced in Southern Ocean. The difference in  $\text{CO}_3^{=}$  concentration between NADW and the rest of the deep ocean is related to the difference in  $\text{PO}_4$  concentration. NADW has half the concentration of  $\text{PO}_4$  than the other water. The high phosphate content waters upwelling in the

southern ocean lose part of their excess  $\text{CO}_2$  to the atmosphere. This results in an increase in their  $\text{CO}_3^{=}$  ion content. In contrast low  $\text{PO}_4$  content water reaching in the northern Atlantic has  $\text{CO}_2$  partial pressures well below that in the atmosphere and hence they absorb  $\text{CO}_2$ . This reduces their  $\text{CO}_3^{=}$  concentration. In Pacific and Indian Oceans much of the floor lies below the transition zone. Hence most of the  $\text{CaCO}_3$  falling into the Deep Pacific and Indian Ocean dissolves. In the South Pacific Ocean and South Indian Ocean the  $\text{CO}_3^{=}$  ion concentration remains largely unchanged. Only in the northern reaches of these oceans does the release of metabolic  $\text{CO}_2$  overwhelm the supply of  $\text{CaCO}_3$  allowing the  $\text{CO}_3^{=}$  concentration to drop (Broecker, 2003).

Again, certain preservation and dissolution events of the Indo-Pacific and Atlantic Oceans are known to be in phase (Crowley, 1983). From the results put forth here it is interpreted that the Indian Ocean carbonate records do not exhibit a straightforward relationship with glacial-interglacial cycles. However, additional high-resolution studies are necessary from different physiographic regions of the Indian Ocean to enhance our understanding of the carbonate fluctuations during the Quaternary Period. To understand the glacial-interglacial changes in  $\text{CaCO}_3$  and hence  $\text{CO}_2$  better, it is necessary to be aware of the  $\text{CO}_3^{=}$  fluctuations during the glacial-interglacial changes in ocean operation. Three important paleocarbonate proxies are used in this attempt. But prior to any direct application of these proxies to the Indian Ocean sediments, they require to be validated.

## **4.2 Validation and application of paleocarbonate ion proxies in the Indian Ocean:**

Ten core top samples, providing a good spatial coverage in the tropical Indian Ocean, have been used in order to validate three important paleocarbonate ion proxies

for the northern Indian Ocean (Fig. 9). The chosen GEOSECS locations are expected to provide a complete picture of the  $\text{CO}_3^{=}$  concentration for required locations and water depth. In the Indian Ocean high values of size index have been reported above the lysocline depth (Peterson, 1984; Broecker and Clark, 1999). Peterson (1984) has reported size index values of 60 to 80% for water depth ranging from 2000 to 3000m in the tropical Indian Ocean, whereas above 4000m water depth the index is found to be nearly constant at a value of  $52 \pm 2\%$  (Broecker and Clark, 1999). In the present study size index value of 95% at a water depth of 1000m is noticed which seems to be very high as compared to the earlier reports from the Indian Ocean (Fig. 15). This could be due to winnowing at these shallow depths, which enriches the sediments in the larger entities. The values of size index in the Indian Ocean also are quite contrary to those obtained by Broecker and Clark, (1999) for the Atlantic and Pacific Oceans. From 2250m water depth onwards a gradual decrease in size index values is observed. The linear decline suggests that dissolution could be affecting shallowest samples from the depth of 1000m onwards. In the present study pressure-normalized carbonate ion concentrations [ $\text{CO}_3^{=*}$ ] have been computed for the coretop samples. Broecker and Clark (1999) have shown that for pressure-normalized carbonate ion concentrations below  $105\mu\text{mol/kg}$ , a linear decline in size index occurs for samples from all the three major oceans. Finally the index results were plotted against  $\text{CO}_3^{=*}$  and the offset was assessed between regions and scatter of results within a given region. To do this a best fit reference line for the Pacific and Indian Oceans was established. The slope of this line estimated by them was  $6.6\mu\text{mol/kg}$  per 10% change in the index.

Size index values were superimposed on the reference line of Broecker and Clark, (1999), show a considerable close fit with an average offset of  $-0.33$  from the

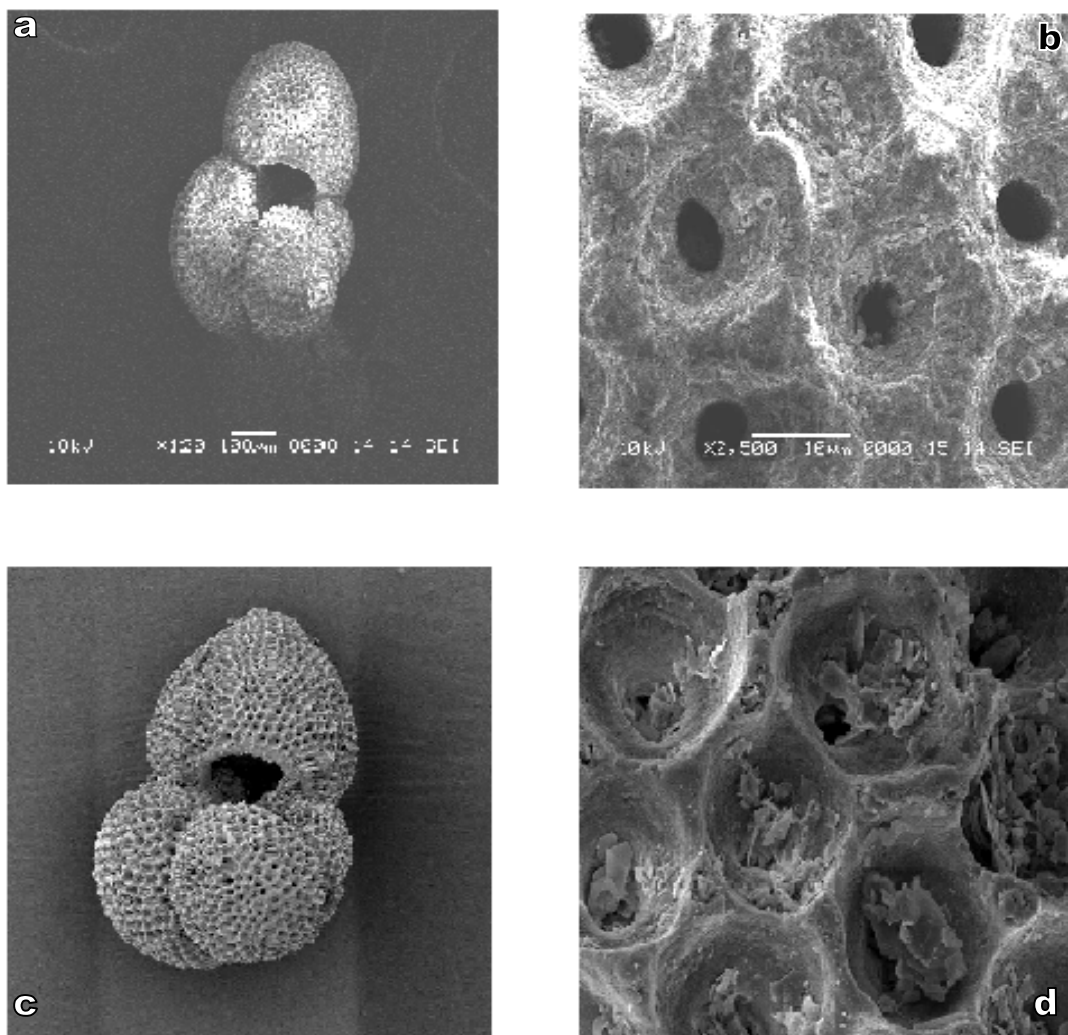
reference line (Fig. 16). This translates to a very negligible shift of 150m in saturation horizon of  $\text{CO}_3^{=}$  in the Indian Ocean. Large variation size index values (14%) within a change of  $1\mu\text{mol/kg}$  in  $\text{CO}_3^{=*}$  concentration (from 96 to  $97\mu\text{mol/kg}$ ) within a water depth range of 100m (3300 to 3400m) is noticed, which is significant in the Indian Ocean (Fig. 16). To better document the dissolution processes at these depth, the shell weight method of Lohmann (1995) was applied to selected core tops.

The shell weight method is also known to give a better picture of the dissolution intensity as it specifically targets at cleaned shells that are from a narrow size range nullifying the ill-effects caused by finer entities (Broecker and Clark, 2001c). *P. obliquiloculata* shells from the Indian Ocean weigh on the average  $\sim 10\mu\text{g}$  less than those from the Pacific Ocean and *N. dutertrei* shells from the Atlantic Ocean appear to be heavier than their Indian and Pacific Ocean counterparts (Broecker and Clark, 2001d). In the present study, it is found that *G. sacculifer* shell weights show marginally high values than those in the eastern Indian Ocean as documented by Broecker and Clark, (2001d). The large variability documented in the size index in the water depth range of 3300 to 3400m is manifested in the shell weights also (Fig. 18). To further shed light on the problem, calcite crystallinity was measured on the respective samples.

Shells that show a narrow (104) calcite peak on XRD powder diagrams are interpreted as being better crystallized than those showing a broader diffraction peak and dissolution improves shell crystallinity (Bassinot *et al.*, 2004). Therefore the calcite crystallinity could be used as a dissolution index that could be tied to a carbonate ion change in the deep sea (Bassinot *et al.*, 2004). Crystallinity measurements on *G. sacculifer* show similar crystallinity values over a range of bottom water [ $\text{CO}_3^{=*}$ ] (Fig. 19), which indicate that dissolution affects more or less

evenly in the water depths ranging from 3300 to 3400m whereas Site SK199C/7 shows lower values suggesting intense dissolution at this water depth (3900m).

In addition, we have compared the SEM micrographs of *G. sacculifer* from deeper depth (3944m) Site SK199C/7 and shallower depth (2250m) Site SK199C/6. Apparently, *G. sacculifer* from deeper depth site show dissolution features (Fig. 29 a and b), whereas, shallow depth site show well preserved *G. sacculifer* shells (Fig. 29 c and d). This observation as well as less abundance of *G. sacculifer* and *G. ruber*



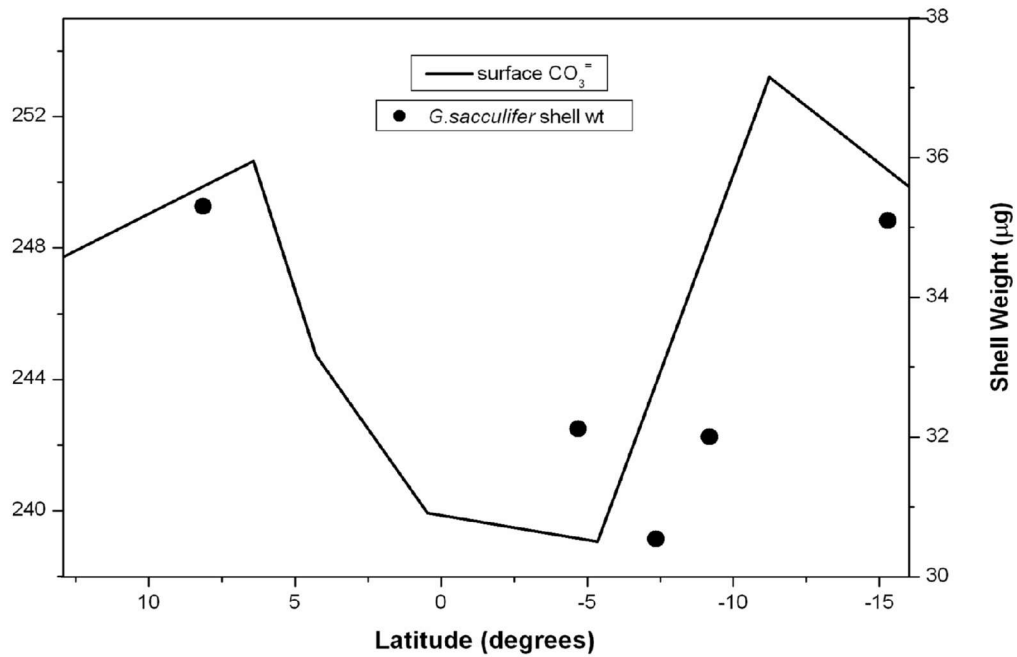
**Fig. 29. (a and b) SEM micrographs of *Globigerinoides sacculifer* from 3944 m water depth (SK199C/7) showing dissolution features. (c and d) Well-preserved tests of *Globigerinoides sacculifer* from 2250m water depth (SK199C/6).**

(P.D. Naidu unpublished data) from the sediments beyond 3900m water depth endorses that intense calcite dissolution occurs from 3900m depth in the Indian Ocean.

All three proxies reveal that dissolution affects planktonic foraminifera from 2250m and that intense dissolution occurs from 3900m onwards. However, a large variation in size index, shell weight and calcite crystallinity is noticed within a narrow range of 100m (3300 to 3400m) water depth. Foraminiferal shell weights from surface sediments not only depend on bottom water  $\text{CO}_3^{=}$ \* concentrations but also by the carbonate ion concentrations in the waters wherein they calcify (Barker and Elderfield, 2002). Thus, shell weight of several species of planktonic foraminifera from core top sediments vary systematically as a function of latitude in the North Atlantic Ocean (Barker and Elderfield, 2002). *G. sacculifer* is a surface dwelling species and calcifies at shallower depths as compared to *N. dutertrei* and *P. obliquiloculata* (Fairbanks et al, 1982) and therefore *G. sacculifer* shell weight should be affected by the carbonate ion concentrations of the surface waters. To understand relationship between shell weights and surface water carbonate ion concentration, shell weights variability of *G. sacculifer* from sites SK199C/6, 7, 9, 10, 11 and 14 has been compared to surface water carbonate ion concentrations for these sites in the western Indian Ocean (Fig. 30). Though there could possibly be marginal difference in the present surface carbonate ion concentrations and those at which the shells must have calcified, shell weights at sites SK199C/6, 9, 10, 11 and 14 shows a reasonably good correspondence with surface water  $\text{CO}_3^{=}$  concentrations. Surface waters are supersaturated with respect to  $\text{CO}_3^{=}$  concentrations, therefore, higher calcification rates in surface waters produce thicker shells without any change in shell size which is



reflected in the shell weights of planktonic foraminifera (Barker and Elderfield, 2002). It is observed here that foraminiferal calcite from sediment bathed by similar  $\text{CO}_3^{=}$  concentration from depths shallower than 3900, trace the surface ocean  $\text{CO}_3^{=}$  concentrations.



**Fig. 30.** Surface ocean  $\text{CO}_3^{=}$  concentrations (calculated from GEOSECS stations 417, 418, 419, 420, 421, 424, and 425) and *Globigerinoides sacculifer* shell weights plotted as a function of latitude. Shell weights correspond well with the surface  $\text{CO}_3^{=}$

#### 4.2.1 Understanding calcite dissolution mechanisms in the Indian Ocean:

The calcite dissolution mechanism proposed by Lohman (1995) has some drawbacks. It suffers from an inability to distinguish changes in bottom-water carbonate ion concentration from changes in bottom-water to pore-water concentration offset (Broecker, 2003). It becomes seemingly important to understand whether the shell weight change is caused due to bottom water or pore water undersaturation, in order to use it as a reliable paleocarbonate ion proxy. As seen

above, by applying three paleocarbonateion proxies, calcium carbonate size index, planktonic foraminifera shell weights and calcite crystallinity to a set of core top samples it has been documented that calcite dissolution commences from 2250m onwards and intensifies at around 3900m water depth in the Western Tropical Indian Ocean. Two processes involve dissolution of calcite on the seafloor; 1) Interface dissolution and 2) pore-water dissolution. The former occurs only at water depths greater than that of saturation horizon, but the later occurs above calcite saturation horizon. It is driven by respiration CO<sub>2</sub> released to pore waters (Emerson and Bender, 1981). It is required to understand whether the dissolution occurring at the 3900m water depth in the western Tropical Indian Ocean is due to saturation state of the overlying bottom waters or due to acidification of pore waters during organic matter remineralization. In this quest, the shell weights have been used following a method by de Villiers, (2005).

As mentioned earlier, calcite dissolution in sediments above lysocline depths could take place in acidified pore waters. The core top foraminifera are also initially exposed to the benthic fluff layer at the sediment-water interface (de Villiers, 2005). Therefore, this interface is perhaps a better description of the initial exposure environment of coretop foraminifera. Therefore the term  $\Delta\text{CO}_3^{\text{=}}_{\text{interface}}$  is used instead of  $\Delta\text{CO}_3^{\text{=}}_{\text{pore-waters}}$ .

To understand whether dissolution taking place at site SK199C/7 is due to this corrosive benthic fluff layer the  $\Delta\text{CO}_3^{\text{=}}_{\text{interface}} - \Delta\text{CO}_3^{\text{=}}_{\text{bottom water}}$  gradient was calculated. For doing this the relationship from the core top data of Broecker and Clark, (2001a) for *P.obliquiloculata* shell weight and bottom water  $\Delta\text{CO}_3^{\text{=}}$  from the Indian Ocean given below was used:

$$\Delta\text{CO}_3^{\text{=}} = [P.obliquiloculata \text{ shell weight } (\mu\text{g}) - 24.53] / 0.2759.$$

Using the above relation and shell weights of *P.obliquiloculata*,  $\Delta\text{CO}_3^{=}$  interface was calculated. The gradient ( $\Delta\text{CO}_3^{=}$  interface -  $\Delta\text{CO}_3^{=}$  bottom water) was then calculated using  $\Delta\text{CO}_3^{=}$  bottom water values. Thus, a value of +5 $\mu\text{M}$  is obtained at 3900m water depth. de Villiers (2005) has determined the  $\Delta\text{CO}_3^{=}$  interface to be within  $\pm 10\mu\text{M}$  of bottom water. The value of +5 $\mu\text{M}$  falls within the range of  $\pm 10\mu\text{M}$  suggesting that dissolution at 3900m water depth is due to undersaturation in  $\text{CO}_3^{=}$  concentration of bottom waters.

In an attempt to understand the factors which control calcite dissolution along a transect of tropical Indian Ocean, for the first time, the shell weights were employed as a paleocarbonate ion proxy to a set of core tops from depth ranges 2250 to 3900 m in the tropical Indian Ocean. Using the relationship between *P.obliquiloculata* shell weight and bottom water  $\Delta\text{CO}_3^{=}$  from the core top data of Broecker and Clark, (2001d) from the Indian Ocean and the data from the present study,  $\Delta\text{CO}_3^{=}$  interface -  $\Delta\text{CO}_3^{=}$  bottom water is calculated to be +5 $\mu\text{M}$ . Shell weight measurements of planktonic foraminifera species *G. sacculifer* and *N. dutertrei* also reveal the gradient;  $\Delta\text{CO}_3^{=}$  interface to be within  $\pm 10\mu\text{M}$  of bottom water values. This suggest that there is no gradient in  $\Delta\text{CO}_3^{=}$  across the sediment-bottom water interface below a depth of 1000m. The planktonic foraminifera shell weights in this sector of the tropical Indian Ocean clearly display that the dissolution of foraminifera shells is not due to corrosiveness of bottom waters caused due to pore water acidification. Rather, the corrosive effect of the bottom waters is due to the  $\text{CO}_3^{=}$  undersaturation of the bottom water. This is an important findings in terms of understanding the paleocarbonate ion concentration in this sector of the Indian Ocean and eliminates an important drawback of the shell weight as a carbonate ion proxy as stated earlier.

#### **4.2.2 Constraints in using size index and shell weights to determine carbonate ion concentrations:**

As seen above, the size index, planktonic foraminifera shell weights and calcite crystallinity have proven to be valid paleocarbonate ion proxies at least when applied to spatially distributed core top samples. In order to apply the size index and planktonic foraminifera shell weights as paleocarbonate ion proxies so as to reconstruct the past changes in carbonate ion and hence understand the carbon dioxide sequestration in the northern Indian Ocean both these proxies need to be validated for temporal sediments. Therefore both these proxies have been applied to the cores from ODP Site 752 and ODP Site 715.

The Site 752 is characterized by very high values of  $\text{CaCO}_3$  throughout the core. This is due to the location of this core on a topographic high where winnowing of sediments is an important factor and this enriches the sediments in larger entities. As stated earlier, the core from Site 752 has been recovered from a very shallow depth of 1086m it was felt that it could be very useful in understanding supralysocline carbonate behavior. The high values and minor range in  $\text{CaCO}_3$  variation rules out two important factors controlling the  $\text{CaCO}_3$  content, dilution and dissolution at this site. Therefore the minor variations observed in the carbonate content at site 752 may be due to changes in productivity of the overlying waters. The much lower  $\text{CaCO}_3$  values from Site 715 are due to terrigenous dilution probably from the Indus River discharge due to its proximity to the Indian sub-continent. The  $\text{CaCO}_3$  records from the eastern Arabian Sea are mostly influenced by terrigenous dilution caused by variations in the terrigenous lithogenic flux derived from the Indus River (Naidu, 1991). The  $\text{CaCO}_3$  fluctuations in Site 715 could be caused due to dilution or dissolution, but the major controlling factor is productivity.

Both the Sites 752 and 715 are situated above lysocline depths. It has been estimated that about 25% of  $\text{CaCO}_3$  produced above the lysocline undergoes dissolution (Milliman, 1993). Consequently, dissolution could possibly play an important role here. Therefore the size index has been employed to possibly figure out the role of dissolution at both the sites. Size index values for both the cores show a large disparity. The size index values for ODP Site 752 are high and can be attributed again to winnowing which enriches the sediment in the  $>63\mu\text{m}$  fraction. On the contrary the size index values from the ODP Site 715 are much lower though the core is from above the lysocline. Broecker and Clark (1999), showed that in the pressure-normalized  $\text{CO}_3^{=}$  ion concentration range of 105-70 $\mu\text{mol/kg}$ , a linear decline in the ratio of  $\text{CaCO}_3$  in the  $>63\mu\text{m}$  fraction to the total  $\text{CaCO}_3$  in the bulk sample occurs. This size index change was observed to be from a value of 55% to 0. These results suggested that the size index could be used as a paleocarbonate ion proxy. The results implied that the initial size composition of the  $\text{CaCO}_3$  deposited throughout the tropical region of the Atlantic, Pacific and the Indian Ocean is quite uniform and that influence of variations in the flux ratio of organic carbon to that of  $\text{CaCO}_3$  must be small. Depth transect of shallower cores on the Ceara Rise suggest that for  $\text{CO}_3^{=*}$  values higher than 105 $\mu\text{mol kg}^{-1}$  the index values stand no longer valid. For water depths above 4000 m the index is nearly constant at a value of  $52 \pm 2\%$ . Broecker *et al.*, (1999), suggested that the size index validated for the water depths below 4000 m does not continue for water depths above. It has been observed that higher values of the index are to be found in tropical Indian Ocean cores from between 2000m and 3000m depth (Peterson, 1984). By contrast, results from Sites 752 and 715 in the present study are at odds with the findings by Broecker *et al.* (1999) and Peterson (1984). Also the size fraction index at the core top for the ODP site 715 of 34% is not

consistent with the values obtained by Peterson (1984), for the Indian Ocean cores from depths ranging from 2000 to 3000m. Therefore there is a need to verify the reasons for the observed values in size index.

The size index and total CaCO<sub>3</sub> percentage versus age for Site 752 and 715 show contrasting results (Fig. 21 a and b). At Site 752 the variations in size index and total CaCO<sub>3</sub> percentage show a similar trend and hence it can be inferred that the observed high values in both size index and CaCO<sub>3</sub> content are a result of supersaturation with respect to CO<sub>3</sub><sup>=</sup> ion concentrations of waters bathing the sediment. But, the values are substantially higher as compared to values reported by Broecker and Clark (1999), in pressure-normalized CO<sub>3</sub><sup>=</sup> ion concentration range of 105-70µmol/kg, ruling out any dissolution at this Site. This endorses the fact that the minor variations observed in the carbonate content at site 752 could be only due to changes in productivity of the overlying waters. As stated earlier both the cores lies above the lysocline. At shallow depths the CO<sub>3</sub><sup>=</sup> is nearly constant through time. The coretop variations observed between the cores used in the present study and other cores from the Indian Ocean may be attributed to rain rates of non-calcareous material and/or calcite and organic carbon to the sediments, which depend on the surface-water productivity.

The Site 715 shows an exactly opposite variation pattern for CaCO<sub>3</sub>% and size index (Fig. 21b). The size index in this case may not reflect the dissolution pattern. Two possible explanations are offered for the observed variations. i) Breakup in foraminifer's shells can continue for thousands of years after burial. This Organic matter respiration is a likely driving mechanism for dissolution in sediments overlain by supersaturated bottom waters (Adler *et al.*, 1989; Cai *et al.*, 1995; Hales and Emerson, 1997). Significant dissolution occurs as a result of metabolic CO<sub>2</sub> release

from decaying organic matter into sediment pore waters (Emerson and Bender, 1981; Jahnke *et al.*, 1997). It has been proposed that an ocean-wide change in the ratio of organic to inorganic carbon in the sinking biological material could decouple the preservation history of  $\text{CaCO}_3$  from seawater  $\text{CO}_3^{=}$  (Archer and Maier-Reimer, 1994). The  $>63\mu\text{m}$  size fraction is related to the percentage of whole foraminifera. During dissolution whole foraminifera break into fragments, coarse fragments break into finer fragments, and fine fragments then become completely dissolved (Le and Shackleton, 1992). In this case the size index will underestimate the  $\text{CO}_3^{=}$  concentration of the waters bathing the sea floor.

de Villiers, (2005) suggests that in addition the respiratory dissolution flux in shallower sediments is not necessarily the pore waters but rather the benthic fluff layer. This layer can be centimeters thick in shallower sediments (Beaulieu, 2002). It has been reported that sedimentary organic carbon respiration is most rapid when a fluff layer is present (Martin and Sayles, 1999). The  $\text{CaCO}_3$  must pass through this layer before burial. The exposure time of foraminifera to under saturation in the fluff layer will be a function of sedimentation rate as well as the frequency of phytodetrital input (de Villiers., 2005). ii) As stated earlier, there is a striking resemblance of  $<63\mu\text{m}$  fraction  $\text{CaCO}_3$  with the total  $\text{CaCO}_3$  content (Fig. 22 b). Hence it can be interpreted as  $<63\mu\text{m}$  fraction controls the total  $\text{CaCO}_3$  content of sediment at this site. McCave *et al.*, (1995) using a more sophisticated method of sediment characterization has shown that the sediment ( $<10\mu\text{m}$ ) is dominantly coccoliths and the  $10\text{-}63\mu\text{m}$  fraction contains mainly foraminiferal fragments. In the present scenario the size index expresses predominantly the ratio of whole adult foraminifera to coccoliths and foraminiferal fragments and juveniles, respectively. If one considers

that no breakup takes place after deposition, this index directly reflects the variations in calcareous nannofossils productivity.

*G. ruber* is a dissolution sensitive species and smaller size fractions of *G. ruber* are better preserved than the larger ones (de Villiers, 2005). *G. ruber* shell weights from the core ODP Site 715 show an anomalous trend throughout the core (Fig. 23). Such difference has been attributed to different morphological differences in *G. ruber* shells from the glacial and Holocene (Broecker *et al.*, 2003 and reference therein). Overall trend of shell weights show a resemblance to the size index and total CaCO<sub>3</sub> only during the last 10kyr. This actually means that as predicted by Broecker and Clark (2001a), the influence of coccoliths is seen throughout the glacial period which is a major drawback in applying the size index to glacial as a paleocarbonate ion proxy. Secondly, the shell weights of *G. ruber* are also not very robust in determining the glacial-interglacial carbonate ion content.

Broecker and Clark (1999) envisioned their size index to be a measure of the extent of fragmentation of foraminifera shells. However, in support of findings in the present study, a recent study conclusively shows similar results (Chiu and Broecker, 2008). Rather, the size index is a measure of the ratio of foraminifera CaCO<sub>3</sub> to coccoliths CaCO<sub>3</sub>. This ratio decreases with the extent of dissolution because foraminifera dissolve far more rapidly than coccolithophores.

### **4.3 Reconstruction of paleocarbonate ion in the northern Indian Ocean:**

Cores AAS9/21 and SK218/A from Arabian Sea and Bay of Bengal respectively recovered from two different oceanic regimes. Both show a gradient in CaCO<sub>3</sub> content from LGM to Holocene and then within the Holocene (Fig. 24 a and



b). Core AAS9/21 shows a smooth transition from high  $\text{CaCO}_3$  content from LGM to recent. Whereas, Core SK218/A shows a decrease in  $\text{CaCO}_3$  content from LGM to around 12kyr and then an increase. The  $\text{CaCO}_3$  values from Core SK218/A located in the Bay of Bengal are a result of terrigenous dilution. This core is fed by sediments from the Ganges-Bhramaputra river system. Terrigenous dilution also affects cores from the Arabian Sea through sediment supply from the Indus River. From the  $\text{CaCO}_3$  content it is evident that dilution must be effecting both the core locations to different levels.

It is hereby aimed to understand the  $\text{CO}_3^{=}$  concentration changes during the glacial-interglacial which in turn gives an idea of the extent of dissolution. The simplest method of understanding dissolution of carbonates is to determine the  $\text{CaCO}_3$  content of sediment. But the  $\text{CaCO}_3$  content as a function of water depth in today's ocean or at any specific time in the past is highly non-linear (Broecker, 2003). Therefore, it is sought to obtain aid from specific proxies targeting at dissolution effects.

In the present study, the paleocarbonate ion reconstruction task is taken up through the application of two important proxies, namely the size index and planktonic foraminifera shell weights. The size index in particular has been applied extensively and has some important drawbacks. Size index when applied to glacial age sediments, the core top calibration relationship did not apply (Broecker and Clark, 2001a). This was attributed to ratio of fine to coarse  $\text{CaCO}_3$  grains in initial material which was higher during glacial than during Holocene. Despite its drawback this method has led to some important findings. First is that during glacial times the mean depth of transition zone did not differ greatly from today's. This finding eliminates the hypothesis, which has been put forward to explain the lower glacial atmospheric

CO<sub>2</sub> content, namely the 'coral reef hypothesis' (Berger, 1982). According to this idea, shallow-water carbonates (corals and coralline algae) formed during high-sea stands of period of interglaciation would be eroded and subsequently dissolved during the low-sea stands of periods of glaciations, alternately reducing and increasing the seas CO<sub>3</sub><sup>=</sup> concentration. For this hypothesis to be viable the transition zone would have to have been displaced downwards by several kilometers during glacial times. It was suggested that this displacement was not more than a few hundred meters (Broecker and Clark, 2001). Two other findings stand out, first as shown by Farrell and Prell (1989), at water depths in 4km range in the eastern equatorial Pacific, the impact of dissolution was greater during interglacials than during glacials (i.e. the transition zone was deeper during glacial time). Secondly, it was demonstrated that there was better preservation during the glacials than in the interglacials (Imbrie, 1992). These findings gave rise to the conclusion that the difference between the depths of the transition zone in the Atlantic from that in the Pacific was somewhat smaller than now during glacial time. In addition, the existence of a pronounced dissolution event in the Atlantic Ocean at the onset of the last glacial cycle has also been documented (Curry and Lohmann, 1986).

Such major findings provide credibility to the size index proxy and hence it has been used further on the cores AAS9/21 and SK218/A. To comprehend these results, the planktonic foraminifera shell weights are also used. Both the proxies applied collectively ought to give a better picture of dissolution process in this region. This justifies the idea of having a multiproxy approach to the problem. As seen earlier from the application of three proxies to the coretop samples distributed throughout the tropical Indian Ocean, it was concluded that more than one proxy is required to elucidate the carbonate ion concentration history. Such an idea is also supported by

recent studies emphasizing the use of a multiproxy approach (Mekik and Raterink, 2008; Ni *et al.*, 2007).

For the application of size index proxy one important assumption need to be tested, that whether the initial size distribution of the carbonates remained constant with time. As a test of this assumption measurements have been made on a core, AAS9/21 collected from shallow water depths in the Arabian Sea, much above the lysocline. The planktonic foraminifera shell weights also need to be tested for similar reasons.

Size index values in AAS9/21 range from 10 to 40% which are marginally lower compared to the core SK218/A which range from 10 to 46% (Fig. 25a and b). Moreover, size index results show a change from the LGM to Holocene. These results imply that the initial size distribution of the  $\text{CaCO}_3$  deposited throughout the tropics is not uniform during the Holocene and LGM. The size index change in AAS9/21 which is clearly lying much above the lysocline could be due to a change in size distribution during glacial-interglacial or due to abundance of coccoliths as encountered in Site 715. Size index values from SK218/A show a decreasing trend possibly because of manifestation of dissolution due to change in saturation state of bottom water  $\text{CO}_3^{=}$  during the Holocene. The second important proxy namely, the foraminifera shell weights from AAS9/21 show an increase from 31 to 41  $\mu\text{g}$  and those from SK218/A range from 29 to 35 $\mu\text{g}$  (Fig. 26a and b). It has been shown in the present study that the initial shell weights depend on surface water carbonate ion in the tropics. This relation needs to be evaluated for the glacial-interglacial period.

### 4.3.1 Role of temperature and/or carbonate ion in determining initial shell weights:

High concentrations of carbon dioxide in the atmosphere cause surface seawater to become more acidic and lower the calcium carbonate saturation state through the consequent decrease in  $[\text{CO}_3^{=}]$  (Broecker and Peng, 1982). If marine calcification is sensitive to the concentration of atmospheric carbon dioxide, its effect should be reflected in the paleoceanographic record as a response to glacial-interglacial fluctuations in  $p\text{CO}_2$  (Barker and Elderfield, 2002).

Earlier it was pointed out that thickness and weight of foraminifera shells vary with growth conditions which is caused due to carbonate ion concentrations (Barker and Elderfield, 2002). The unanswered question is whether or not the dependence of shell weight on surface water carbonate ion concentration established for the temperate species apply to tropical species (Broecker, 2003). The present study demonstrates that this dependence does apply to the tropical species as well.

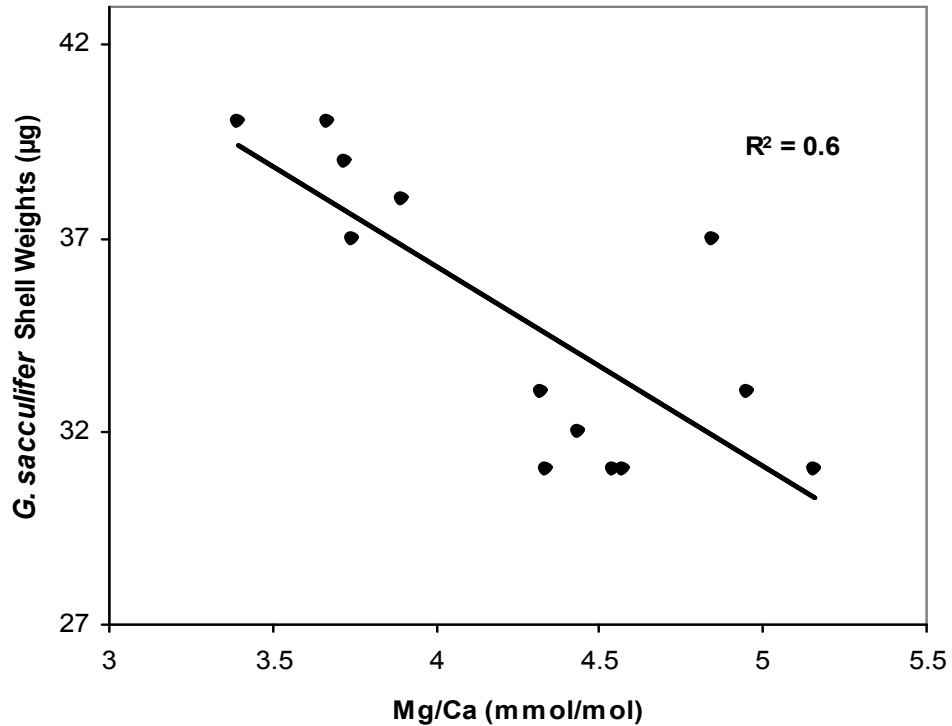
Broecker and Clark, (2002b), point out that in today's ocean a very tight correlation exists between surface water  $\text{CO}_3^{=}$  and temperature, and therefore coretop shell weights cannot be used to distinguish between a temperature or a  $\text{CO}_3^{=}$  dependence. Shell weights of several planktonic foraminiferal species from narrow size fractions from the North Atlantic were found to vary systematically as a function of latitude (Barker and Elderfield, 2002). They combined these findings with a record of shell weight across glacial-interglacial Termination-I to demonstrate that the changes are a result of ambient  $[\text{CO}_3^{=}]$  changes rather than calcification temperature and are consistent with known changes in atmospheric  $p\text{CO}_2$ . However  $\text{CO}_3^{=}$

concentration and temperature relationship are not constant from basin to basin (Broecker, 2003).

Atmospheric  $p\text{CO}_2$  at the LGM was  $\sim 90\text{ppmv}$  lower than preindustrial (Holocene) (surface  $[\text{CO}_3^-]$  was higher) and temperature was lower as well. Therefore temperature control would be indicated by lower shell weights before Termination I whereas a carbonate ion control would be indicated by higher shell weights (Barker and Elderfield, 2002).

It is important at present to see whether the dependence of shell weights on surface water  $\text{CO}_3^-$  concentrations applies for temporal samples or not. Results in the present study were combined with Mg/Ca thermometry, a proxy for paleotemperature. The Mg/Ca data was not available for all the sections where the shell weights have been determined. Only sections where this data was available have been plotted. There seems to be a linear relationship between *G. sacculifer* shell weights and Mg/Ca ratios, with higher shell weights corresponding to lower Mg/Ca ratios; indicative of lower temperatures ( $R^2=0.6$ ) (Fig. 31). Due to strong temperature dependence of  $\text{CO}_2$  solubility in seawater and the subsequent dissolution of  $\text{CO}_2(\text{aq})$  into  $\text{HCO}_3^-$  and  $\text{CO}_3^-$ , modern open ocean surface water  $[\text{CO}_3^-]$  varies as a function of temperature. Thus, the observed trend in shell weight would fit with a  $[\text{CO}_3^-]$  control as well as a temperature control. In the present study shell weights are highest during the LGM and show a large decrease in the early Holocene. Due to the fact that shell weights are heavier during glacial time suggests that the control on shell weight is carbonate ion and not calcification temperature. This places new constraints on the coral reef hypothesis and could possibly explain the survival of reef corals on Bermuda. Therefore, this study suggest that, glacial-interglacial changes in foraminifera shell

weight are related to changes in ambient carbonate ion concentration through time in response to changing atmospheric CO<sub>2</sub>.



**Fig. 31.** *G. sacculifer* shell weights from both the cores AAS9/21 and SK218/A at selective sections show a linear relation to Mg/Ca ratio at corresponding depths ( $R^2=0.6$ ).

Attempts to reconstruct past CO<sub>3</sub><sup>=</sup> distributions suffer from the common drawback that much of the dissolution occurs in sediment pore waters rather than on the seafloor. This dissolution is driven by respiration CO<sub>2</sub> which lowers the pore-water CO<sub>3</sub><sup>=</sup> concentration below that in bottom water. It has already been shown using the shell weight technique that in today's waters of the western tropical Indian Ocean, there is no offset between bottom water and pore-waters. Therefore the statement that the dissolution occurring at the depths in the western tropical Indian Ocean is due to bottom water undersaturation can be confidently put forward. But, in order to convert shell weights to bottom-water carbonate ion concentrations there is one important postulate which need to be satisfied (Broecker *et al.*, 2003); whether the magnitude of

pore water dissolution was same or different during Holocene and glacial period. This is dealt with in subsequent discussions.

#### 4.3.2 Carbonate ion change from Last Glacial Maximum to Holocene:

Size index application to the cores AAS9/21 and SK218/A shows a change of 25% between LGM and Holocene. This amount when translated using the best fit line between size index and pressure-normalized carbonate ion concentration, as determined by Broecker and Clark, (1999), yields a value of  $16\mu\text{mol/kg}$  in terms of  $\text{CO}_3^{=}$  concentration which is an underestimation. Overall the size index values during the Holocene are quite low (10 to 25%) for these shallow depth cores as compared to the coretop studies discussed earlier (Broecker and Clark, 1999). This could be probably due to the terrigenous material affecting these cores. Since the size index gives an underestimation of the  $\text{CO}_3^{=}$  concentration it proves inefficient here in predicting the  $\text{CO}_3^{=}$  change, the second alternative, i.e. shell weight is used.

The core AAS9/21 lays much above the lysocline and therefore it is very interesting to notice the change in *G. sacculifer* shell weights from the LGM to present. Barker and Elderfield (2002) established the initial shell weight dependency on carbonate ion concentration in surface water for temperate planktonic foraminifera species. The application to tropical species was hitherto unknown before the present study. Since during the peak glacial time the atmosphere's  $\text{pCO}_2$  was 90ppmv lower than until the pre-industrial era, the carbonate ion concentration in tropical surface waters must have been  $40\text{-}50\mu\text{mol/kg}$  higher at that time. Based on the Barker and Elderfield (2002) trend of  $\sim 1\mu\text{g}$  increase in shell weight per  $9\mu\text{mol/kg}$  increase in carbonate ion concentration, this translates to an  $8\mu\text{g}$  heavier initial shell weights during glacial times. While this correction does not change the depth dependence or

interocean concentration difference, it does greatly alter the magnitude of the change. The indistinctness of the shell weight variations in the glacial-interglacials need to be made explicable for getting a comprehensive design of the glacial-age deep-sea carbonate ion concentrations (Broecker, 2003).

To convert shell weights into  $\text{CO}_3^{=}$  this study has adopted a  $0.3\mu\text{g}$  drop in shell weight per  $\mu\text{mol/kg}$  drop in pressure-normalized  $\text{CO}_3^{=}$  concentrations (Broecker and Clark, 2001d). Carbonate ion concentrations were calculated from shell weights of both the cores AAS9/21 and SK218/A. The  $\text{CO}_3^{=}$  concentrations calculated from core AAS9/21 do not give an estimation of the bottom water concentrations but is a manifestation of  $\text{CO}_2$  dissolution in the surface seawaters and gives a carbonate ion change in surface waters during the glacial-interglacial.

During the Holocene the atmospheric partial pressure of  $\text{CO}_2$  ( $\text{pCO}_2$ ) is typically close to 280 parts per million by volume (p.p.m.v.). During peak glacial times, such as the LGM about 18kyr ago, atmospheric  $\text{pCO}_2$  is 180 to 200 ppmv or roughly 80 to 100 ppmv lower (Petit *et al.*, 1999). The core AAS9/21 exhibits a shell weight variation which when translated to glacial-interglacial carbonate ion concentration translates to a  $45\mu\text{mol/kg}$  change. In terms of shell weight this change is from  $41\mu\text{g}$  to  $31\mu\text{g}$  i.e. a change of  $10 \pm 2\mu\text{g}$  during the glacial-interglacial transition against the change of  $8\mu\text{g}$  suggested by Barker and Elderfield (2002) (Fig. 32). This glacial-interglacial carbonate ion concentration when overlaid on the  $\text{CO}_2$  record of an ice core from Taylor Dome, Antarctica (Smith *et al.*, 1999) shows that corresponding to a 90ppmv change in atmospheric  $\text{CO}_2$  a change of  $45\mu\text{mol/kg}$  in  $\text{CO}_3^{=}$  occurred (Fig. 32). The record from the present study is in excellent agreement with the ice core records and is suggestive of the extent of  $\text{CO}_2$  sequestration occurring in the Arabian Sea. The 180 to 280ppmv glacial-interglacial  $\text{CO}_2$  change



has occurred constantly for at least eight 100kyr cycles known at present (EPICA community members, 2004).

Several mechanisms have been put forth which elucidate the glacial-interglacial carbonate ion and hence CO<sub>2</sub> changes. Shackleton (1977) suggested mass of carbon stored in the terrestrial biomass was smaller during glacial than during the interglacial periods which was later confirmed by Curry *et al.*, (1988) based on benthic foraminifera <sup>13</sup>C records. Broecker (1982) suggested a glacial increase in the strength of the biological pump as the driver of lower glacial CO<sub>2</sub> levels. McElroy (1983) described possible mechanisms by which the reservoirs of phosphate and nitrate might increase during glacial times, which would allow enhanced low-latitude biological production to lower atmospheric CO<sub>2</sub>. Later several workers have suggested increased nutrient utilization in the high-latitude surface ocean to cause lower atmospheric pCO<sub>2</sub> of glacial times (Sarmiento and Toggweiler, 1984; Broecker and Peng, 1989; Martin, 1990). Toggweiler (1999) hypothesizes reduced deep-water ventilation of the glacial Southern Ocean to cause lowering of glacial atmospheric CO<sub>2</sub> whereas, that increased nutrient utilization and reduced deep-water ventilation of the glacial Southern Ocean caused lowering of glacial atmospheric CO<sub>2</sub> is demonstrated by Sigman and Boyle (2000).

Another possible mechanism was put forth by Archer and Maier-Reimer (1994) who explained the lower CO<sub>2</sub> content of the glacial atmosphere. An increase in the organic carbon/calcite ratio of material reaching the sediments was postulated for the last glacial (rain ratio). In a scenario with the effects of porewater chemistry on carbonate preservation, a higher relative rate of organic carbon rain decreases the porewater saturation with respect to calcite and would lead to a proportionally greater dissolution in the sediment driven by respiratory carbon dioxide (Emerson and

Bender, 1981; Berelson *et al.*, 1990; Archer, 1991; Jahnke *et al.*, 1997). This would lead to an increase of the carbonate ion in the bottom water and, through the mechanism of  $\text{CaCO}_3$  compensation would decrease the atmospheric carbon dioxide content. While Jahnke *et al.*, (1994) found no evidence for dissolution driven by metabolic carbon dioxide above the saturation horizon, Hales *et al.*, (1994) observed dissolution. Another proposed explanation for a higher carbonate ion concentration in the ocean, and hence, lower atmospheric  $\text{CO}_2$  content during glacials, is the “coral reef hypothesis” (Berger, 1982; Opdyke and Walker, 1992). According to this hypothesis, the coral growth rates were lower during glacials when the sea level had dropped and the continental shelves were exposed. This would imply a shift of  $\text{CaCO}_3$  deposition to the deep sea and therefore would have led to a deepening of the oceans saturation horizon and better carbonate preservation. However, this hypothesis calls for a global ocean increase in the saturation state (Opdyke and Walker, 1992; Archer and Maier-Reimer, 1994), and cannot be invoked to explain the observed preservation difference between the Atlantic and the Indo-Pacific, respectively.

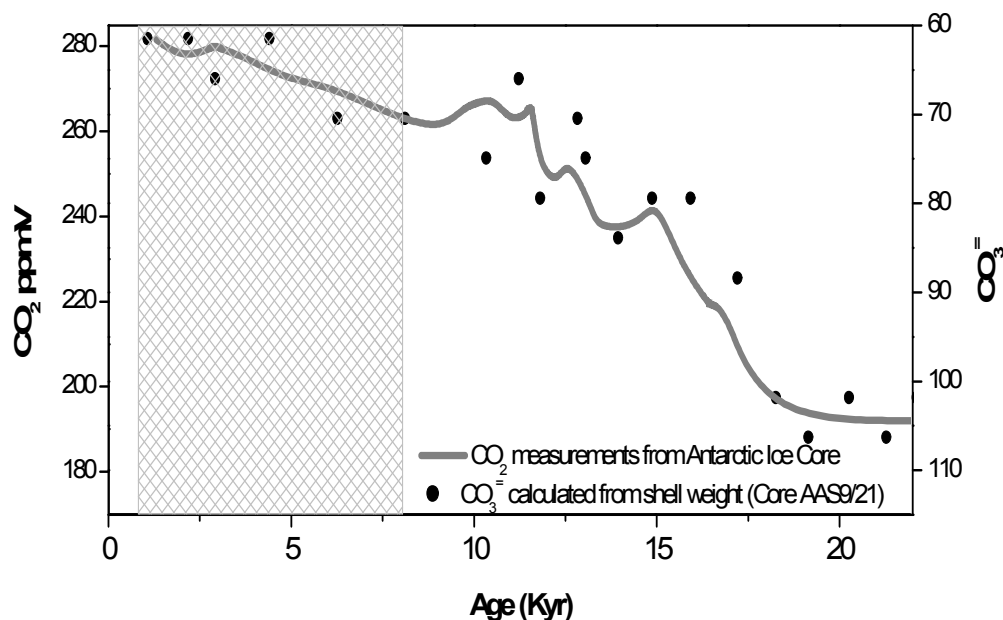
The observed late Pleistocene preservation cycles are also consistent with estimated glacial–interglacial pH changes in the Atlantic and Pacific (Sanyal *et al.*, 1995) wherein the deep water of both oceans had a higher pH during the last glacial period. Accordingly, both the Atlantic and Pacific Oceans had a higher glacial deep-sea carbonate ion concentration. However, it is very likely that the boron isotope-based carbonate ion change will not be equivalent to the amount of change in preservation, as the boron-based paleo-pH estimates need to be coupled with dissolution driven by metabolic  $\text{CO}_2$  so as not to have an unrealistic change in lysocline depth of several kilometers. Better deep-sea carbonate preservation implies a high deep-sea carbonate-ion concentration, which in turn would lead to lowered

glacial atmospheric carbon dioxide content. Yet another recent mechanism is the ‘glacial burial hypothesis’ (Zeng, 2003) in which vegetation and soil carbon is buried and preserved under ice sheets during glaciations, and released back into the atmosphere during deglaciation.

#### 4.3.3 Carbonate ion change during the Holocene:

As stated in earlier discussions, the size index from both the cores does not give a good estimation of the in-situ carbonate ion concentration for the glacial-interglacial. This is probably due to the effect of terrigenous dilution at both the core sites. The situation for the Holocene seems to be even more complicated. Therefore the size index has been avoided in discussing the carbonate ion change.

In the Holocene period the change in carbonate ion calculated from the shell weight data from core AAS9/21 (change of  $2\mu\text{g}$ ) is  $9\mu\text{mol/kg}$  (Fig. 32). In terms of



**Fig. 32.**  $\text{CO}_3^{2-}$  concentrations calculated from *G. sacculifer* shell weights from the core AAS9/21 show a close relation to  $\text{CO}_2$  measurements from an ice core (Taylor Dome, Antarctica. \* see text) Shaded portion shows the Holocene period.

CO<sub>2</sub> rise this change is of 20ppmv (Indermülhe, 1999). Indermülhe (1999) presented a high-resolution record of CO<sub>2</sub> concentrations as measured in air bubbles trapped in an ice core from Taylor Dome, Antarctica, covering the entire Holocene. The record shows a decrease of the CO<sub>2</sub> concentration from 268 ppmv at 10.5 kyr BP (the end of the transition from the last glacial to the Holocene) to 260 ppmv at 8.2 kyr BP. During the recent 7kyr, the CO<sub>2</sub> concentration increased almost linearly to 285 ppmv (Indermülhe, 1999). The results from core AAS9/21 are in agreement with the changes discussed from ice cores as well as the results from Broecker and Clark, (2007), who suggest that this change during the Holocene is from 6 to 13  $\mu\text{mol/kg}$ .

In the Bay of Bengal core SK218/A, size fraction of 355 to 420 $\mu\text{m}$ , most of the *G. sacculifer* shells are broken for the last 10kyr. This signifies the corrosiveness of this region at 3307m depth during the Holocene period. This could also mean that the transition zone of carbonate ion is situated quite shallow compared to the rest of this region, which needs further studies before confirmation. Shell weights of *G. sacculifer* do not show a gradual decrease from the LGM to Holocene as expected. The situation seems to be that the organic matter respiration or pore water dissolution was pronounced in this region during the LGM with the effect increasing in magnitude during the Holocene period. In practice, since the planktonic foraminifera shells trace the surface water carbonate ion concentrations a correction of around 8 $\mu\text{g}$  would be required to be applied to the glacial shells. However, as in the present core SK218/A the shell weight trend seems to be indicating pore water dissolution. Since the extent of this pore water dissolution is not known hence correction is not applied here. Rather this pore water dissolution could be contributing to lighter shells during the glacials.

Broecker *et al.*, (1999) proposed that the rise in the atmosphere's CO<sub>2</sub> content during the last 8 kyr was driven by the compensation for the 500 gigatons of carbon withdrawn from the ocean-atmosphere system to regenerate the forest wood and soil humus destroyed during the last glacial period. Ridgwell *et al.*, (2003) reasoned this on the growth of coral reefs, whereas Ruddiman (2005) calls on deforestation conducted by humans. The results presented here suggest that the drop in abyssal ocean carbonate ion concentration over the past 8 kyr may have been larger than that required matching the 20 ppmv increase in atmospheric CO<sub>2</sub> content. If so, it would require that the carbonate ion decrease in the abyssal ocean was larger than that in the surface ocean. To generate such a difference would require either a change in the pattern of large-scale thermohaline circulation or a change in the power of the biologic pump, or both (Broecker and Stocker, 2006). Another possibility is that a shift in either circulation pattern or biological pumping has been taking place over the last 8 kyr. One possible explanation is that the production of deep water in the northern Atlantic has weakened relative to that in the Southern Ocean (Broecker and Clark, 2007)

Ruddiman, (2003) claims that the rise in atmospheric carbon dioxide (CO<sub>2</sub>) over the last 8000 years is anthropogenic rather than natural in origin. His case was based on the fact that following each of the three preceding glacial terminations; the CO<sub>2</sub> content of the atmosphere peaked early on and then underwent a steady decline. Without interaction with sedimentary CaCO<sub>3</sub>, Ruddiman's scenario requires a release of about 570 gigatons of terrestrial carbon (GtC). Model simulations that include interaction with sedimentary CaCO<sub>3</sub> increase this requirement to 700 GtC (Joos *et al.*, 2004). The release of 700 GtC from the terrestrial biosphere would lower the <sup>13</sup>C to <sup>12</sup>C ratio in the entire inventory of ocean-atmosphere carbon by about 0.45 per mil.

Indermühle *et al.*, (1999) interpreted carbon isotope measurements made on eight samples of CO<sub>2</sub> recovered from Antarctic ice to suggest a 0.2 per mil <sup>13</sup>C decline over the last 8000 years.

However, Broecker *et al.*, (2001b) challenged the validity of this <sup>13</sup>C decline. They pointed to a Holocene record of <sup>13</sup>C to <sup>12</sup>C ratio in planktonic foraminifera from the equatorial Pacific that showed no downward trend over the last 8000 years. Broecker *et al.*, (1993) proposed that the post-8000-year CO<sub>2</sub> rise was the result of CaCO<sub>3</sub> compensation triggered by the extraction of CO<sub>2</sub> from the ocean to create the early Holocene increase in forest biomass. With the onset of warm conditions, the forests and bogs destroyed during glacial time reformed. On the basis of the <sup>13</sup>C record kept by the benthic foraminifera, this re-growth sequestered about 500 GtC (Curry *et al.*, 1988). The removal of this amount of CO<sub>2</sub> from the ocean-atmosphere reservoir lowered the atmosphere's CO<sub>2</sub> content and increased the carbonate ion content of ocean water. Thus, the drop in atmospheric CO<sub>2</sub> caused by the re-growth of forests would have been followed by a recovery related to a readjustment of the ocean carbonate chemistry. As CaCO<sub>3</sub> has nearly the same carbon isotope composition as seawater, compensation would not produce any <sup>13</sup>C change. Such a rise in atmospheric CO<sub>2</sub> content as a result of calcium carbonate compensation was not seen during the last interglacials. The explanation likely lies in the current smaller eccentricity with associated decline in Northern Hemisphere summer insolation associated with the 20,000- year cycle (Broecker, 2006). The explanation for the absence of a CO<sub>2</sub> plunge during the present interglacial is that the 20,000-year cycle is too weak to initiate a rapid decline toward glacial conditions and thus to produce a 'short' interglacial period. Hence, while in three previous interglacials the CO<sub>2</sub> decrease driven by the 20,000-year precession cycle overwhelmed the upward trend

due to calcium carbonate compensation, during the present one this has not happened. A test of the orbital explanation was provided recently by the stage 11 CO<sub>2</sub> record from the Dome Concordia (Antarctica) (EPICA Community Members, 2004) with that from Vostok (Siegenthaler *et al.*, 2005). New CO<sub>2</sub> measurements on the EPICA ice core now cover all of stage 11. This spliced record shows that atmospheric CO<sub>2</sub> stayed above 270 ppm for about 28,000 years, from about 420 thousand years before present (kyr B.P.) to 392 kyr B.P. The early part of MIS 11 is similar to that for the Holocene. Hence, the cause for the CO<sub>2</sub> rise during the last 8000 years was ‘natural’ and not ‘anthropogenic’ (Broecker, 2006).

Though several mechanisms are now available which inform us regarding the mechanisms of glacial/interglacial CO<sub>2</sub> changes, much work remains to be done before an agreement can materialize on the specific driver. The results from the present study suggest that the carbonate ion change brought about by a change in atmospheric CO<sub>2</sub> in the northern Indian Ocean is at par with that of the rest of the world oceans in general. Yet, this study is not aimed at unraveling the exact mechanism to bring about the said change. More intense studies will be required in pinning down a specific driver of glacial/interglacial CO<sub>2</sub> change. The mystery of glacial/interglacial CO<sub>2</sub> change has certainly provided a focus for study of the interaction among the diverse processes operating in the natural environment, resulting in real progress toward a science of the Earth (Sigman and Boyle, 2000).

#### **4.4 The Indian Ocean CCD change:**

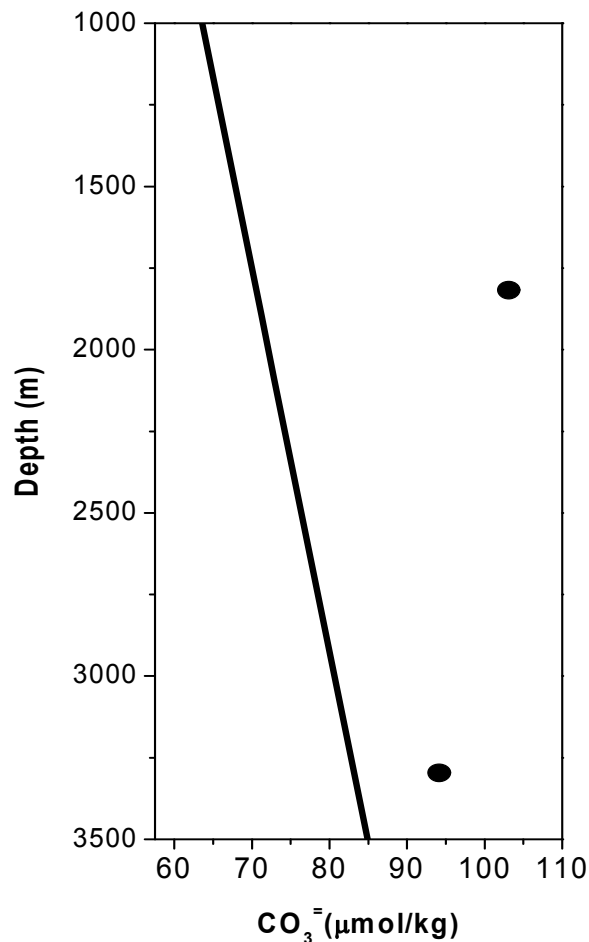
Various workers have attempted to estimate the depths of the lysocline and the CCD in the Indian Ocean. Present day CCD in the 10°N-0° region is estimated to be at 4500 m in the Bengal Fan region, at 4800 m in the Arabian Sea and in excess of

5100m in the Somali Basin and at the equatorial zone where it is the deepest (Kolla *et al.*, 1976). Cullen and Prell, (1984), based on variations in abundance of dissolution resistant foraminifera with water depth reveal that 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. The Foraminiferal Compensation Depth, which is similar to the CCD is below 4600m in eastern equatorial region, below 5000m in western equatorial region and below 3307m in the Bay of Bengal (Cullen and Prell, 1984). Sabine *et al.*, (2002) suggest that the calcite saturation depths in the Indian Ocean range from 2900–3900 m with the deepest saturation depth in the central Indian Ocean. This is necessarily the lysocline and as shown in earlier discussions of the present study, intense dissolution has been encountered at a depth of 3900m water depth. Banakar *et al.*, (1998), place the lysocline at 4400m and the CCD at 4700m water depth at the equator in the central Indian Ocean.

In the present study  $\text{CO}_3^{=}$  concentration has been calculated for the glacial Indian Ocean using *G. sacculifer* shell weights from cores AAS9/21 and SK218/A. The LGM value has been determined averaging the shell weights from 18 to 20kyr for both the cores. At a depth of 1807m the glacial  $\text{CO}_3^{=}$  calculated from *G. sacculifer* shell weights is  $103\mu\text{mol/kg}$ . The present  $\text{CO}_3^{=}$  at the water depth of 1807m calculated from GEOSECS station 417 is  $70\mu\text{mol/kg}$ . This means there is a large difference of  $\sim 33\mu\text{mol/kg}$  between present and glacial  $\text{CO}_3^{=}$  concentrations (Fig. 33). As stated earlier, shell weights from core AAS9/21 are a manifestation of  $\text{CO}_2$  dissolution in the surface seawaters and give a carbonate ion change in surface waters during the glacial in the present case. Since the core is from a very shallow depth, there are no noticeable effects of dissolution. Therefore the carbonate ion concentrations calculated from shell weights do not give the actual picture of bottom water  $\text{CO}_3^{=}$



concentrations at this depth. If the shell weight correction of  $8\mu\text{g}$  as stated earlier be applied to the shell weights from core AAS9/21 and based on the Barker and Elderfield (2002) trend of  $\sim 1\mu\text{g}$  increase in shell weight per  $9\mu\text{mol/kg}$  increase in  $\text{CO}_3^{=}$  concentration and taking into consideration the uncertainty in shell weight measurements of  $\pm 2\mu\text{g}$ , the  $\text{CO}_3^{=}$  concentration during the glacial will work out to be equivalent to the present. Such a lack of difference in the  $\text{CO}_3^{=}$  concentrations during the glacial and today has been observed for the Pacific Ocean also, at depth of 2.3km (Broecker and Clark, 2001c).



**Fig. 33.**  $\text{CO}_3^{=}$  versus water depth (m) for today's Indian Ocean (shown by smooth line). The black dots are the glacial  $\text{CO}_3^{=}$  concentrations calculated from *G. sacculifer* shell weights from the cores AAS9/21 and SK218/A.

Using the extent of calcium carbonate dissolution observed in foraminifer faunal assemblages from the CLIMAP data set, a decrease in carbonate ion concentration was observed in glacial Atlantic Ocean, by roughly 20  $\mu\text{mol/kg}$ , while a little change of 5  $\mu\text{mol/kg}$  occurred in the Indian and Pacific relative to today (Anderson and Archer, 2002). Today's in-situ carbonate ion concentration at the depth of 3307m is  $\sim 83 \mu\text{mol/kg}$  as calculated from GEOSECS stations (Fig. 9). At 3307m water depth, the LGM calculated  $\text{CO}_3^{=}$  is 93  $\mu\text{mol/kg}$ . So a difference of 10  $\mu\text{mol/kg}$  is observed from LGM to present. Therefore it is seen that the  $\text{CO}_3^{=}$  gradient was steeper during the glacial, increasing from almost no difference between glacial and today at 1807m to 10  $\mu\text{mol/kg}$  at 3307m and should be even more at greater water depths. Broecker and Clark, (2001c) also point out to increasing gradients in  $\text{CO}_3^{=}$  concentrations with water depth during glacials. Considering the change in  $\text{CO}_3^{=}$  of 15  $\mu\text{mol/kg}$  per km increase in water depth (Broecker, 2008), the difference of 10  $\mu\text{mol/kg}$  in the present case for the Indian Ocean implies at least a  $\sim 600\text{m}$  difference in the saturation horizon. From the fact that the *G. sacculifer* shells are absent and/or broken during the Holocene at a depth of 3307m (Core SK218/A) it is evident that the present day CCD is very shallow and lies at  $\sim 3300\text{m}$  or shallower in the Bay of Bengal. This estimation is also supported by the study of Cullen and Prell (1984). The difference of  $\sim 600\text{m}$  stated above would mean that during glacial the CCD was at around 3900m water depth.

Since the pore water dissolution during the glacial is unknown the exact variation in the CCD from glacial to present cannot be exactly estimated. Also, this result is fraught with potential biases as it is averaged from shell weights from a single core i.e., SK218/A. Broecker, (2008), propose that the CCD must have been 0.4 km deeper in the tropical Indian Ocean during glacial. The results in the present study,

stating a difference of ~600m (0.6km) are somewhat in agreement with this. More significantly the  $\text{CO}_3^{=}$  gradient observed during the LGM is greater relative to present. Such large gradients in  $\text{CO}_3^{=}$  concentration in the glacial ocean have important implications because such gradients are absent in today's ocean (Broecker et al., 2001c). The implications of such a gradient are that the waters supplying the deep sea had a greater range in density, thereby permitting stratification to persist.