

CHAPTER II

MATERIALS AND METHODS

2.1 Materials:

2.1.1 Cores from Atlantic, Pacific and Indian Ocean:

Ten cores were chosen from the equatorial regions of Atlantic, Pacific and Indian Ocean. Core locations and water depths of these cores are shown in Table 1, Fig. 8.

Table 1. Cores recovered from the Atlantic, Pacific and Indian oceans at various locations and water depths.

OCEAN	Core	Latitude	Longitude	Water Depth (m)
Atlantic	RC24-16	05.04°S	10.19°W	3559
	V30-40	00.20°S	23.15°W	3706
	V25-59	01.37°N	33.48°W	3824
Pacific	DSDP-572	01.43°N	113.85°W	3903
	SDSE 59	03.05°N	133.10°W	4370
	RC11-210	01.82°N	140.05°W	4420
	V28-179	04.62°N	139.60°W	4509
	SDSE 60	01.58°N	134.95°W	4540
Indian	ODP 709A	03.91°S	60.56°E	3038
	SDSE 154	01.00°S	54.00°E	4860

The equatorial region of the world ocean is known to be a strong CO₂ source to the atmosphere (Takahashi *et al.*, 1997). The core locations are chosen such that they are situated far off from the continental landmass so that the effect of terrigenous dilution is minimal. Such a selection is used to focus attention on carbonate variations

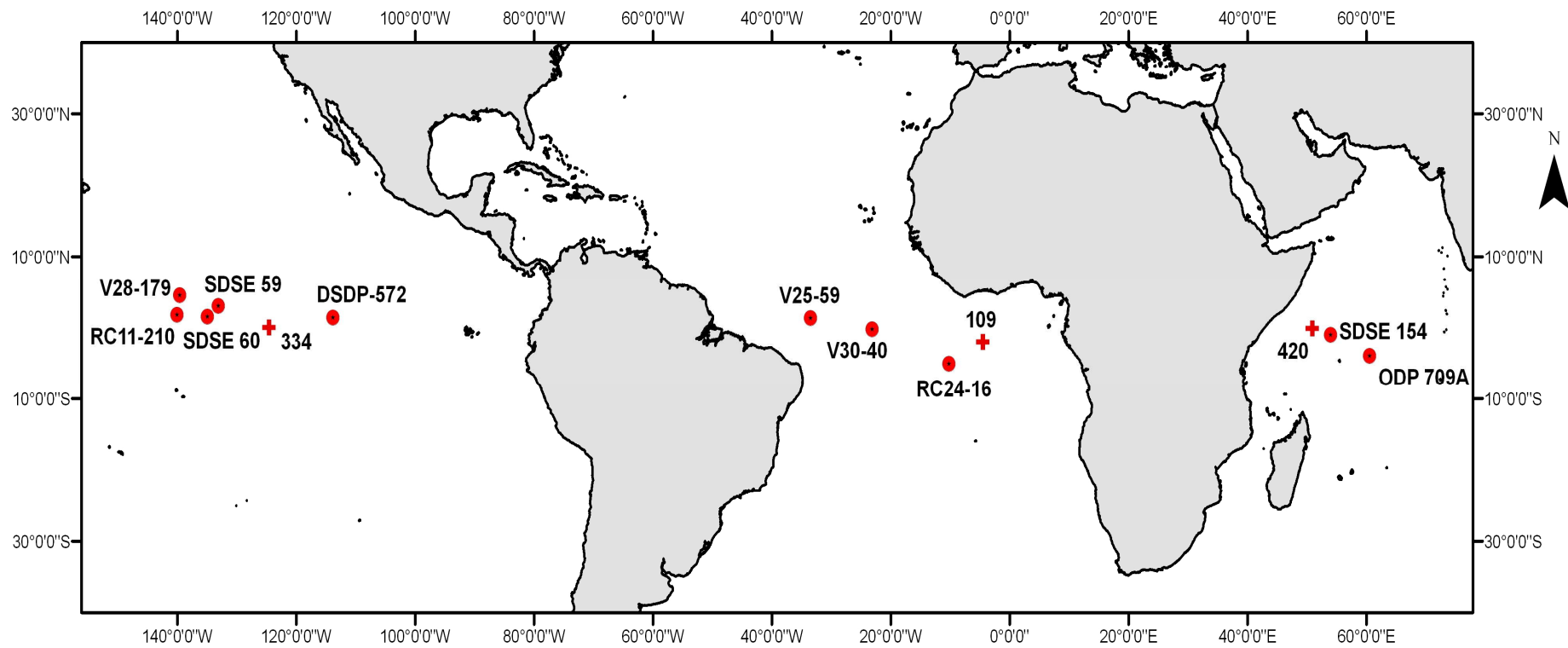


Fig. 8. Map showing location of deep-sea cores in the equatorial Pacific, Atlantic and Indian Ocean, shown by dots. Plus signs indicate the GEOSECS stations.

due to dissolution. The cores having a continuous sediment record have been preferred. The CaCO₃ data set for the ten cores used is obtained from National Geophysical Data Centre (NGDC) of NOAA. This data set was contributed by Dr. William Ruddiman of the Lamont-Doherty Geological Observatory, and by Dr. John Farrell of Brown University. J. Imbrie and A. Duffy of Brown University compiled ages for the cores for the SPECMAP project. The cores cover a time span of 0.6Ma, which clearly covers six major glacial-interglacial cycles.

2.1.2 Core tops from the Indian Ocean:

The paleocarbonate ion proxies have been tested using several core top samples from the western and eastern tropical Indian Ocean. These core tops were collected during the SK199 cruise in December 2003 and core tops of ODP Sites 711, 718 and 752 were obtained from the Ocean Drilling Programme repository (Table 2, Fig. 9).

Table 2. Core tops from the Indian Ocean at various locations and water depths.

Station.	Water Depth (m)	Latitude	Longitude
SK199C/6	2250	08.13°N	73.56°E
SK199C/10	3305	07.36°S	67.17°E
SK199C/9	3320	04.86°S	67.09°E
SK199C/14	3368	15.27°S	66.01°E
SK199C/11	3373	09.17°S	65.95°E
SK199C/7	3944	05.51°N	69.34°E
ODP 711	4430	02.74°S	61.16°E
ODP 718	4730	00.92°S	81.39°E

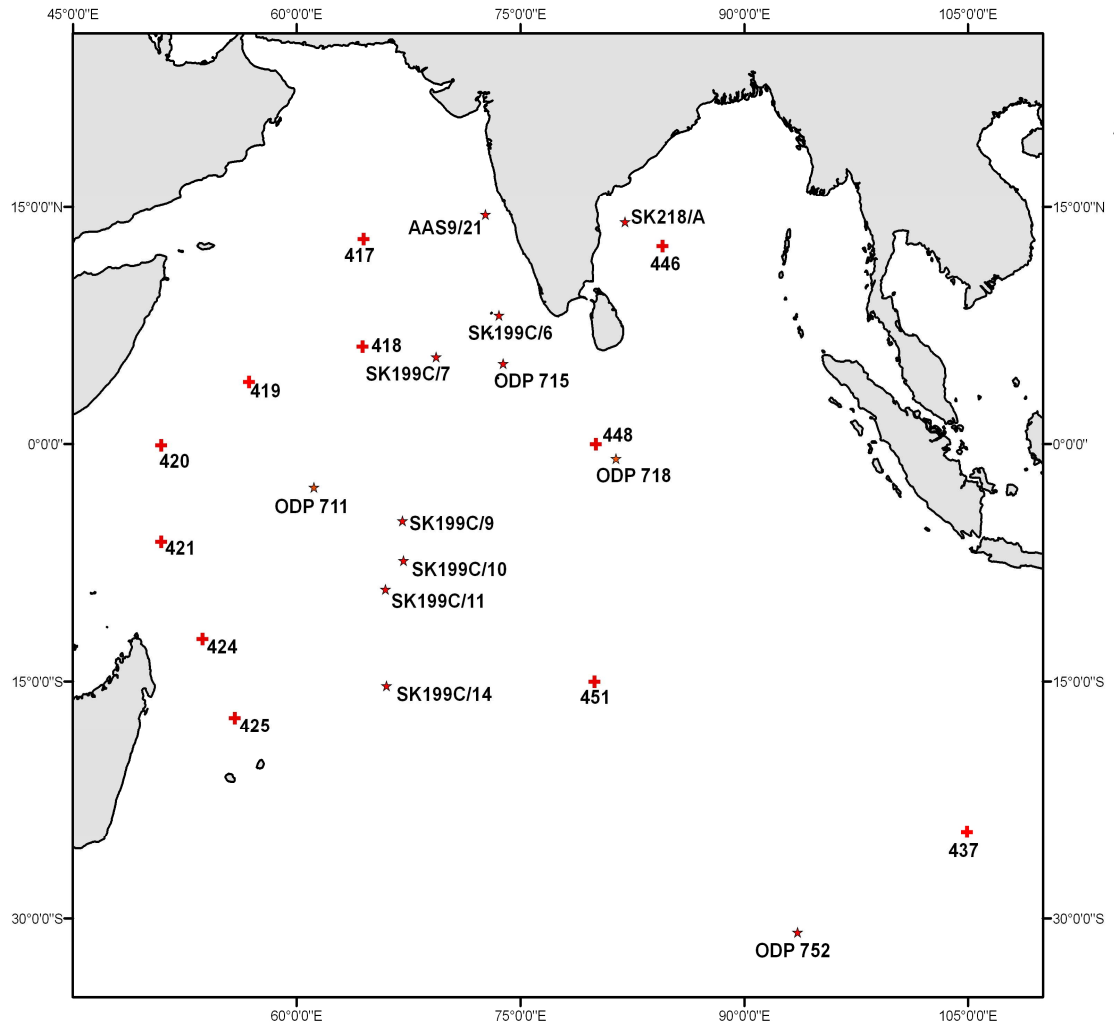


Fig. 9. Core tops and cores from the northern Indian Ocean indicated by stars, and GEOSECS stations indicated by crosses.

2.1.3 Cores from the Indian Ocean:

Four sediment cores have been selected from the Indian Ocean (Table 3, Fig. 9), ODP Site 752 was recovered from the eastern Indian Ocean near the crest of Broken Ridge which lies on a topographic high, whereas ODP Site 715 was recovered from the northern equatorial Indian Ocean on the eastern margin of Maldives Ridge. ODP Sites

752 and 715 are used to examine the suitability of size index and planktonic foraminifera shell weights applied to understand temporal carbonate ion variations. Cores AAS9/21 and SK218/A were recovered from the Arabian Sea and Bay of Bengal (Fig. 9).

Table 3. Cores from the Indian Ocean from various locations water depths. Also shown is the length of core recovered and used in the present study.

Station.	Water Depth (m)	Latitude	Longitude	Core length (m)	Length of core used (m)
ODP 752	1086	30.89°S	93.58°E	217.3	1.01
ODP 715	2266	05.08°N	73.83°E	137.6	1.89
AAS 9/21	1807	14.51°N	72.65°E	4.4	2.16
SK 218/A	3307	14.04°N	82.00°E	8.26	4.40

These cores were chosen to study the relationship between carbonate ion concentration and temperature.

2.2 Methods:

2.2.1 Size fraction analysis:

All the samples were oven dried at 50°C; a portion of the sample was weighed and disaggregated by soaking in distilled water to remove the lumps of clay and organic matter, 10ml of 10% Sodium Hexa-Meta-Phosphate and 5ml of Hydrogen Peroxide was added, respectively and kept overnight. The samples were then wet sieved through a 63µm sieve, taking care to see that no shells were broken or material lost. Both the size fractions, >63µm and <63µm were collected carefully. The >63µm fraction was dried again in an oven at 50°C. The <63µm fraction, which contained a copious amount of washing water was left for settling. Later it was decanted by discarding the supernatant

clear solution and the residue was then dried in an oven at 50°C. The material, coarse and fine fractions were then weighed separately following the procedure described by Broecker and Clark, (1999). The content of CaCO₃ in the sediment sample as a whole, < 63µm and in the >63µm fractions were determined using coulometric titration method as described hereafter.

2.2.2 Calcium carbonate analysis of sediment:

An automated carbon dioxide coulometric titrator was used in this work. Carbon dioxide was evolved from the sample by addition of 4ml 2M-Hydrochloric acid. A small portion of the acid was added initially with mixing to ensure complete wetting of the sample. Carrier gas of Potassium Hydroxide-scrubbed air was passed through the heated sample slurry at a flow rate of 100 cm/min. The CO₂ laden carrier gas was passed through two gas scrubbers, which contained 3% H₂O₂ and saturated with AgSO₄ at pH 3 for removal of chlorine and sulphur. After removal of interferences the CO₂ was adsorbed in the coulometric titration cell. The cell contained a platinum cathode, silver anode and a proprietary solution containing monoethanolamine and thymolphthalein indicator (Coulometrics®). Carbon dioxide was converted to hydroxyethylcarbamic acid, which was automatically titrated with a coulometrically generated base to a coulometric endpoint by means of a photometric detector set at 612 nm (Engleman *et al.*, 1985). A normal sample analysis required seven to ten minutes. The coulometer was calibrated with synthetic (commercially available CaCO₃) as well as geological standard contained from U.S. Geological Survey (MAG-1). The precision obtained is ± 0.7% (n=10).

2.2.3. Calculation of Size Index parameter:

The CaCO₃ content of all the three fractions, < 63µm, >63µm and total sediment were converted to weights in 'g'. The size index is calculated as the ratio of coarse calcite to total calcite [$(>63\mu\text{m CaCO}_3/\text{Total CaCO}_3) \times 100$]. It has been shown by Broecker and Clark (1999) that in today's tropical ocean the percentage of CaCO₃ contained in grains >63µm in size is closely tied to the pressure-normalized carbonate ion of water bathing the sea floor. The idea being that, since the >63µm fraction is dominated by foraminifera shells and the lesser fraction contains coccoliths, juvenile foraminifera and foraminiferal fragments, this size index actually is the ratio of CaCO₃ contained in whole foraminifera shells to CaCO₃ contained in total sediments.

2.2.4 Calculation of in-situ and pressure-normalized carbonate ion concentration:

Carbonate ion concentrations were calculated using a programme in visual basic designed by Dr. Taro Takahashi of Lamont Doherty Earth Observatory. The following parameters were the inputs for the programme: Depth (dB), Temperature (°C), Salinity (‰), Alkalinity (µEq/kg), Total CO₂ (µmol/kg), Silicate (µmol/kg) and Phosphate (µmol/kg). Data from the GEOSECS stations in the Indian, Atlantic and Pacific Oceans was used for this purpose (Table 4, Fig. 8 & 9). It is necessary to take into account the increase in calcite solubility with pressure and hence water depth. Following the method of Broecker and Clark, (1999), The CO₃⁼ concentrations were normalized to a depth of 4km as follows:

$$\text{CO}_3^{=*} = \text{CO}_3^{=} + 20(4-h) \mu\text{mol/kg}$$

Where h is the water depth in km at the core site and $20\mu\text{mol/kg}$ is the increase with water depth of the solubility of calcite. $\text{CO}_3^{=}$ is used to avoid the necessity of selecting a value for the solubility of calcite.

Table 4. Various GEOSECS locations used in the present study from the Atlantic, Pacific and Indian Oceans.

Station	Latitude	Longitude
ATLANTIC OCEAN		
109	04.50°W	02.00°S
PACIFIC OCEAN		
334	124.57°W	00.06°N
INDIAN OCEAN		
419	03.95°N	56.80°E
420	00.05°S	50.93°E
421	06.15°S	50.91°E
424	12.30°S	53.69°E
425	17.30°S	55.85°E
446	12.52°N	84.51°E
448	00.02°N	80.05°E
451	14.98°S	79.96°E
437	104.93°E	24.48°S

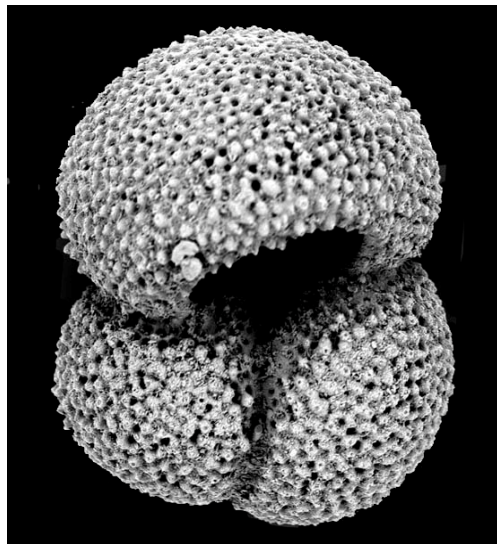
2.2.5 Shell weights:

Shell weight measurements were done following the procedure of Lohman (1995). A portion of the coarse fraction ($>63\mu\text{m}$) separated previously was cleaned and sonicated in methanol at 40hz for 8secs in order to remove fines that could fill the last chambers. The material was then dried in an oven at 50°C and then passed through sieves in order to isolate the $300\text{-}350\mu\text{m}$ and $350\text{-}420\mu\text{m}$ size fractions. About 50 whole shells of

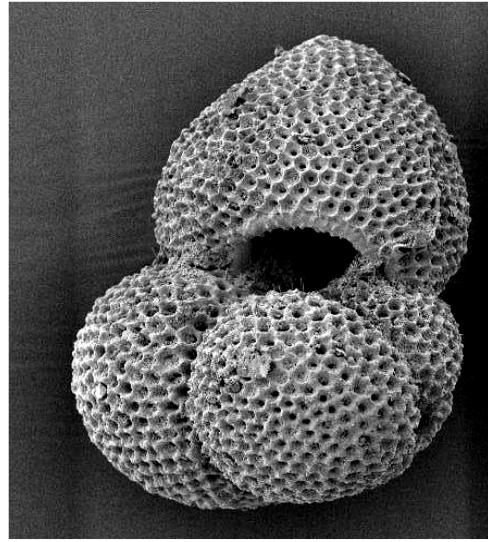
Globigerinoides ruber from the 300-350 μ m fraction and *Globigerinoides sacculifer*, *Pulleniatina obliquiloculata* and *Neogloboquadrina dutertrei* from the 350-420 μ m size fractions were picked by using Sterio Binocular Microscope and weighed on a microbalance, which has the least count of 1 μ g (Fig. 10). Precision obtained is \pm 2 μ g. Planktonic foraminifera species were identified by following the taxonomy of Bé (1967) and Hemleben *et al.*, (1983).

2.2.6 Calcite Crystallinity:

The crystallinity, measured by X-Ray Diffraction (XRD), is related to the degree of perfection of a given crystal lattice [e.g., Lipson and Steeple, 1970]. The full width at half maximum (FWHM) of the (104) calcite X-ray diffraction peak (given in $^{\circ}2\theta$) was used which is as an indication of the degree of crystallinity of foraminifera shells (Bassinot *et al.*, 2004). Shells showing a narrow (104) calcite peak on XRD powder diagrams are interpreted as being better crystallized than those showing a broader diffraction peak. Ultimately, XRD peak broadening depends on two main parameters at the lattice level: (1) it can be related to strain within the crystal structure, or (2) it can reflect the granulometry of the perfectly crystallized subdomains (hereafter referred to as “crystallites”) that constitute the whole crystal. In the later case, peak broadening results from the slight misalignment of crystallites with respect to each other (“mosaic” structure of the crystal lattice); the smaller the average size of these crystallites, the broader the diffraction peaks (e.g., Lipson and Steeple, 1970). *Globigerinoides sacculifer* which was hand picked from the 350– 420 μ m size fraction was soaked in methanol and ultrasonically cleaned in order to remove fines that could fill the chambers. The purpose



a



b



c



d

Fig. 10. SEM images of a) *G. ruber* b) *G. sacculifer* c) *P. obliquiloculata* and d) *N. dutertrei*.

of such a cleaning procedure is to reduce the contribution of coccolith calcite to the XRD crystallinity results. Because the broadening of foraminiferal calcite X-ray diffraction peak is likely related to the size of the perfectly crystallized sub domains that constitute the calcite, it is crucial that the sample preparation does not introduce a granulometry bias. Shells were gently crushed with a glass slide, directly in the sample holder following the method from Barthelemy-Bonneau (1978). This is too coarse a granulometry to introduce a bias in the width of calcite XRD peak since apparent grain size of crystallite affecting XRD peak broadening is smaller than a few tenth of micrometers. Thus, this sample preparation technique ensures that no peak-broadening bias is introduced and that data genuinely reflect calcite crystallinity from the foraminifera shells. Each sample was run three times. Average value of calcite (104) FWHM and the related standard deviation were calculated from those three. The internal standard deviation thus obtained is $\pm 0.003^{\circ}2\theta$ (1σ). The system is a Philips PW1840-XRD (Cu-K α , 40 KV, 20mA). The following manual adjustments were possible within the instrument: Counting aperture; 0.2mm and goniometer rotation speed; 1.2 $^{\circ}2\theta/\text{min}$.

2.2.7 Scanning Electron Micrographs:

Scanning Electron Micrographs were obtained in order to visually examine any changes in shell structure as an evidence of dissolution following the procedure of Dittert and Henrich, (2000). Individual foraminifera shells were placed on a sticky SEM stub and gold-palladium coated for 30–40 s in a JEOL JFC-100 auto fine sputter coater. The stubs were then imaged using a JEOL instrument. The SEM was tuned to get a resolution

of 150X and then a higher resolution for observing the dissolution feature at 2500X. The JEOL JSM –6360LV microscope was used with a voltage setting at 10 kV.

2.2.8 Chronology of the sediment cores:

The chronology of the cores from Atlantic, Pacific and the Indian Ocean was based on oxygen isotope stage boundaries, compiled by J. Imbrie and A. Duffy at Brown University for the SPECMAP project. Chronology of the Sites 715 and 752 was based on calcareous nanofossil datum's (Duncan *et al.*, 1990; Rea, 1990). Carbon-14 dates obtained by Accelerator Mass Spectrometer (AMS) at Kiel University, Germany were used to establish the chronology of AAS9/21 and SK218/A. About 10 mg of planktonic foraminifera, consisting of diverse species in the size range of 250-350 μ m, were used for AMS carbon dates. ^{14}C dates were calculated to calendar years by using the calibration program online CalPal version quickcal 2005 ver 1.4 (Weninger *et al.*, 2006).

2.2.9 Mg/Ca:

Mg/Ca analyses were carried out at Bremen University, Germany. In calcareous skeletons of foraminifera made up of CaCO_3 ; some of the Ca atoms are replaced by other bivalent cations such as Mg atoms. As incorporating atoms of abnormal size in a crystal lattice requires additional energy, this occurs in warm environments due to sufficient availability of thermal energy. Therefore, ratio of Mg to Ca in a calcite shell serves as a measure of past sea water temperature. For determination of Mg/Ca, for each sample 30 to 40 individuals of *Globigerinoides ruber* (white variety) from a size range of 250 to 350 μ m were picked. The picked specimens were then cleaned using the elemental analysis technique (Barker *et al.*, 2003). Splits of the cleaned sample were then analyzed

for 'Mg' and 'Ca' by inductively coupled plasma atomic mass spectrometry (ICP-MS) by the method described by Barker *et al.*, (2003). Study shows that the reproducibility of the method, for *G. ruber* in a core-top sample from the Arabian Sea was $\pm 1.8\%$ for Mg/Ca (Barker, 2003). During the present study 40 replicate *G. ruber* samples were measured from site SK218/A. However, the repeatability for Mg/Ca was routinely better than 0.1mmol/mol. The analytical error for the Mg and Ca concentrations was better than 0.7% relative standard deviation (RSD).