Chapter 2
Chapter 2

MATERIALS AND METHODS

Sediment Cores

Sediment gravity cores collected during different cruises of *O.R.V. Sagar Kanya* (SK) and *MV A.A. Siderenko* (AAS) - a Russian research vessel chartered by the Department of Ocean Development (DOD), New Delhi, were used for the present study. Table 2.1 gives the details of cruise number, location, and water depth at which the cores were collected and length of the core recovered.

Table 2.1. Details of sediment cores used for the present study.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Cruise No.</th>
<th>Core No</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>Core length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bay of Bengal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SK148</td>
<td>2</td>
<td>10°00'00&quot; N</td>
<td>84°00'00&quot; E</td>
<td>3600</td>
<td>3.46</td>
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<tr>
<td>2</td>
<td>AAS37</td>
<td>2</td>
<td>2°25'12&quot; S</td>
<td>81°02'36&quot; E</td>
<td>4000</td>
<td>1.14</td>
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<tr>
<td>Arabian Sea</td>
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<td></td>
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<tr>
<td>3</td>
<td>SK148</td>
<td>22</td>
<td>24°27'36&quot; N</td>
<td>68°09'00&quot; E</td>
<td>56</td>
<td>7.02</td>
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<tr>
<td>4</td>
<td>SK148</td>
<td>21</td>
<td>21°28'58&quot; N</td>
<td>67°00'57&quot; E</td>
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<td>SK148</td>
<td>32</td>
<td>20°24'57&quot; N</td>
<td>69°25'48&quot; E</td>
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<td>4.37</td>
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<td>6</td>
<td>SK148</td>
<td>38</td>
<td>19°58'58&quot; N</td>
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<td>55</td>
<td>17°45'00&quot; N</td>
<td>70°51'36&quot; E</td>
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<td>9</td>
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<td>50</td>
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<td>70°51'36&quot; E</td>
<td>2650</td>
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<td>10</td>
<td>AAS 6</td>
<td>GC3</td>
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<td>72°54'00&quot; E</td>
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<td>39</td>
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<td>GC5</td>
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In Chapter 3, two cores, SK148/2 and AAS37/2 from the Bay of Bengal are discussed. For Chapter 4, sediment samples were selected from 12 gravity cores recovered along the western margin of India at different water depths (Sr. No. 3-14; Table 2.1). In chapter 5 results from three cores, SK-126/16 (core 16), SK-126/39 (core 39) and SK126/50 (core 50) from the SW Arabian Sea are discussed.

Colour and lithology of the sediment were noted onboard immediately after collecting the cores. The cores from the Bay of Bengal were sub-sampled at 2 cm interval. The cores 16, 39 and 50 from the southwestern continental margin of India were sub-sampled onboard at 2 cm interval for the top 20 cm and 5 cm interval up to 100 cm and 10 cm for the rest of the core. Representative sediment samples were oven-dried at 55°C temperature and utilized for all further studies.

Grain size of the sediments

(a) Pipette analysis

The textural analysis of the sediments was carried out on 33 to 35 representative sediment sample intervals in each core (cores 16, 39 and 50). For this, 10-13 g of dried representative samples were weighed and transferred into 1000 ml beakers. The samples were made salt free by repeated washings using distilled water. The salt free samples were dispersed using 25 ml of 10% sodium hexa-metaphosphate solution for 4 hours. The total amount of sample was transferred to a 63 μm sieve and wet sieved using distilled water and content passing through the sieve was collected in 1000 ml measuring cylinder. The sand fraction (> 63 μm) retained in the sieve was dried and weighed, while the mud fraction collected in the cylinder was made up to the mark and subjected to the pipette analysis following (Folk, 1968). The aliquant from the cylinder was stirred vigorously for 45 seconds. Using stokes settling velocity principle, exactly after 1 hour 40 min 13 sec using a 25 ml pipette connected with a tube was lowered to 10 cm down the water level.
and 25 ml of aliquant containing clay was pipetted out and transferred to 50 ml beaker, dried and weighed. Weight of clay in the sample is determined as

\[
\text{Clay weight} = (\text{clay weight} - 0.0625) \times \left(\frac{1000}{25}\right),
\]

0.0625 is the weight of the sodium hexa-metaphosphate in 25 ml of aliquant. Based on initial weight of the sample and clay weight the weight percent of sand silt and clay fraction was calculated on each sample and texture of the sediment was noted.

(b) Using Laser diffraction particle size analyser

The Laser-diffraction-size analysis is based on the principle that particles of a given size diffract light through a given angle, the angle increasing with decreasing size. A narrow beam of Helium-Nicon laser is passed through a suspension and the diffracted light is focused on to a detector. This senses the angular distribution of scattered light energy.

Particle size analyses were carried out on the mud fraction (<63 µm) of the sediments that was separated from the total sample after wet sieving. A total of 116 representative samples were selected from SK148/2 (67) and AAS37/2 (49) cores. The mud fraction was made free of CaCO₃ and organic matter, by treating with 1N HCl and hydrogen peroxide, respectively. About 10 ml of sodium hexametaphosphate was added to disperse the sediment particles and to remove the iron oxide coating (if present) of the particles. The sample was washed with distilled water to remove acid. Different size fractions of the mud between 0.01 µm and 63 µm were determined using MALVERN MASTERSIZER 2000. A Helium-Nicon laser beam of monochromatic light was used to conduct the experiment. The sample was dispersed in distilled water and kept in suspension by a cell system comprising of an ultrasonic tank with stirring facility while a pump circulates the sample to the measurement. The sizer was attached to a computer, with a database. Based on the scattering signal received from the instrument computer calculates volume size distribution.
Organic carbon, Total Nitrogen

(a) Organic carbon using titration method

The organic carbon (OC) content of the sediment samples was determined on 108 samples from the three cores (cores 16, 39 and 50) by the wet oxidation method (El Wakeel and Riley, 1957). This works on principle based on the oxidation of organic carbon with chromic acid and titrimetric determination of the oxidant consumed. The method is widely used and reported to produce reliable results when the availability of organic carbon is ≥ 1%.

About 0.1-0.3 g of the finely powdered sample was weighed and transferred into a test tube and 10 ml of chromic acid was added and covered with aluminium foil. The test tube was heated in water bath for 15 minutes. Contents were allowed to cool and were transferred into a 250 ml conical flask containing 200 ml distilled water. About 2-3 drops of ferrous-phenanthroline indicator was added and titrated with 0.2 N ferrous ammonium sulphate solution until a pink colour just persists. A blank determination was also carried out in the same manner. Then, the concentration of the organic carbon available in the sediment was estimated as: 1 ml of 0.2 N ferrous ammonium sulfate consumed = 1.15 x 0.6 mg of carbon. The percentage of organic carbon in the sample = 0.6 x ((Blank reading-Sample reading) / (Weight of the sample in mg)) x 1.15 x 100. Reproducibility of the results was checked by running replicates of sediment samples and it was found to be better than ± 5%.

(b) Organic carbon and total nitrogen using CNS analyser

Organic carbon and total nitrogen in core SK148/2 (67 samples) and total nitrogen in cores 16, 39 and 50 (50 samples) was determined using CNS elemental analyser. The principle of operation is founded on sequential steps: - the sample, held in a light weight tin capsule, is energetically oxidized yielding a gas mixture. This gas mixture is swept into a chromatographic
column from which any eluted pure combustion gas passes through thermoconductivity detector. The thermoconductivity detector generates an electrical output signal proportional to the amount of eluted gas. Such signal feeds an integrator or an automatic workstation, which provides the sample element composition report.

About 5 g of the bulk sample was taken and treated with 1N HCl, to remove CaCO$_3$ and washed with distilled water to remove excess acid. The sample was dried and weight of the CaCO$_3$ free sample was noted. About 5 mg of CaCO$_3$ free sample was weighed in a tin capsule and placed into autosampler drum where it is de-aerated (to remove any atmospheric nitrogen) and introduced into a vertical quartz tube heated at 1000°C with a constant flow of helium (carrier gas) stream. A few seconds before the sample drops into the combustion tube, the helium stream is enriched with a measured amount of high purity oxygen to achieve a strong oxidizing environment which guarantees almost complete combustion / oxidation even of thermally resistant substances. To achieve quantitative oxidation the combustion gas mixture is driven through an oxidation catalyst tungsten zone, then through a subsequent one of copper which reduces nitrogen oxides and sulphuric anhydride, eventually formed during combustion or catalyst oxidation, to elemental nitrogen and sulphurous anhydride and retains the oxygen excess. At the outlet of the reaction tube the gas mixture (N$_2$, CO$_2$, H$_2$O, SO$_2$) meet trap containing anhydrone that absorbs water. The resulting three components of the combustion mixture are eluted and separated by Porapack PQSW column and subsequent detected by a thermoconductive detector in the sequence N$_2$, CO$_2$, SO$_2$ and gives report of elemental composition, total carbon (TC) and total nitrogen. Organic carbon (OC) and total nitrogen (TN) were calculated as \([X - \text{weight of CaCO}_3 \text{ free sample}) / \text{bulk weight of the sample}].\) Where X is total carbon and total nitrogen measured on the instrument. Running standards after every 10 samples checked the reproducibility of the organic carbon measurements and it was found to be better than ± 1%.
Calcium carbonate

(a) Titration Method

The CaCO$_3$ content of the sediment was determined using titration method (Herrin et al., 1958). About 1 gm of powered sample was weighed in 250 ml beaker, 50 ml of 0.5 N HCl was added to the sample and heated to about 90°C for 20 minutes. The pH was tested using indicator paper, and if pH was found to be greater than 2, another 50 ml of HCl was added and heated for 20 minutes. When pH remained < 2, distilled water was added till the beaker becomes half-full and phenolphthalein indicator was added (2 to 3 drops) and stirred constantly and back titrated with 0.25 N of NaOH to phenolphthalein endpoint. The CaCO$_3$ percent was calculated for total of 50 samples from the cores 16, 39 and 50 using CaCO$_3$% = 100 x 0.05 x (ml of HCl x normality of HCl) —(ml of NaOH x normality of NaOH).

(b) Weight loss Method

The CaCO$_3$ content of representative samples from the cores SK148/2 and AAS37/2 for the total of 94 samples was determined using weight loss method (Black et al., 1965). About 2 g of sample was weighed in 250 ml beaker. About 10 ml of distilled water and 5 ml of 1 N HCl were added and stirred to promote reaction. After initial reaction had ceased additional 2 ml of 0.1 N HCl was added each time until no further reaction was observed. Excess acid was decanted and carefully washed in distilled water to remove CaCl$_2$. The sample was evaporated to dryness and heated to 110°C and transferred to desiccators to cool. The sample was reweighed. The CaCO$_3$ percentage was calculated using

\[ \text{CaCO}_3\% = \left(100 \times \text{weight loss}\right) / \text{Initial dry weight of the sample}. \]

Reproducibility of the CaCO$_3$ was checked by running replicates of sediment samples and it was found to be better than ± 8%.
Coarse fraction studies

The sand fraction (>63 µm) obtained by wet sieving was further split into >250 µm and 125-250 µm fraction. The 125-250 µm fractions were examined under a binocular microscope for the relative abundance of the components (such as planktic and benthic foraminifers, keels (rims of foraminifers remained after undergoing dissolution), pyritized grains and terrigenous particles. A total of 117 samples were analysed from four cores.

Clay mineralogy

Clay mineral studies were carried out on 72 samples for the chapter 4, and on 21 samples for chapter 5. About 12-15 g of sample was made CaCO$_3$ free using 1N HCl and organic matter free using hydrogen peroxide. About 10 ml of sodium hexametaphosphate was used for the dispersal of the clays. The sample was then repeatedly washed for removing the acid used. The samples were wet sieved using 63 µm sieve content and the material passing through the sieve were collected in 1000 ml cylinder, made up to the mark and stirred vigorously for 45 seconds. After 6 hours 42 minutes whole aliquant from top 10 cm (containing < 2 µm clay) was transferred to the 500 ml beaker. Oriented slides were then prepared by pipetting 1 ml of the concentrated clay suspensions on glass slides and allowing them to dry in air. Remaining clay was dried and preserved for the Sr and Nd isotope study.

X-ray diffraction studies were carried out on the clay slides by scanning them from 3° to 22° 2θ at 1.2° 2θ min$^{-1}$ on a Philips X ray diffractometer (1840 model) using nickel-filtered Cu Kα radiation, operated on 20 mA and 40 kV. The samples were then glycolated by exposing the slides to ethylene glycol vapours at 100°C for 1 hour and rescanned the slides under the same instrumental settings. The areas of the principal peaks of the clay minerals kaolinite and chlorite (7 Å), illite (10 Å) and smectite (17 Å) were measured above the background response using glycolated sample X-ray diffractograms. The principal peak areas of the clay minerals kaolinite and chlorite, illite and
smectite were multiplied by the weighting factors 2, 4 and 1, respectively and weighted peak area percentage of each clay mineral were calculated following the semi-quantitative method of Biscaye (1965). All the samples were scanned from 24 to 26° 20 at ½° 20 min⁻¹ for the resolution of kaolinite and chlorite (Biscaye, 1964). The area under each peak was estimated and the ratios of kaolinite to chlorite (K/Ch) and smectite to illite (S/I) were also calculated. The ratios are less affected by the sample treatments and ambiguity of relative abundance.

Sr - Nd isotope analysis

The $^{87}$Sr/$^{86}$Sr and Nd ($\varepsilon_{Nd}$) isotopes were determined on 16 and 11 samples, respectively for the samples reported in chapter 4. For chapter 5 the Sr isotopes were determined on 24 samples (including a repetition) and $\varepsilon_{Nd}$ on 20 samples.

The powdered <2 μm fraction of the clay samples were digested with HF-HNO₃ acid mixture. The Sr and REE were then separated using columns packed with Cation Exchange Resin (DOWEX 50WX8). Nd was separated from the REE fraction with columns packed with HDEHP-coated teflon. The Sr and Nd isotope ratio measurements were carried out on VG 354 Thermal Ionization Mass Spectrometer (TIMS) in the dynamic triple collector mode at NGRI, Hyderabad. The $^{87}$Sr/$^{86}$Sr ratios were corrected for fractionation with $^{87}$Sr/$^{86}$Sr = 0.1194 and normalized to SRM 987 standard value of 0.710220 ± 0.000024 (2 sigma S.D.; n=10). $^{143}$Nd/$^{144}$Nd ratios were corrected for fractionation with $^{146}$Nd/$^{144}$Nd =0.7219 and normalized to La Jolla standard value of 0.511850 ± 0.000010 (2 sigma S.D.; n=8). Blank contributions in the Nd isotopic measurements were negligible (<25 pg). The $\varepsilon_{Nd}$ was determined using $\varepsilon_{Nd} =[(^{143}\text{Nd}/^{144}\text{Nd} / 0.512638)-1] \times 10000$. $^{87}$Sr/$^{86}$Sr isotope determinations were repeated for some samples. The errors for the samples are given in respective tables in the chapters.
Rock-magnetic properties

Magnetic susceptibility (MS) for cores SK148/2 (170 samples) and AAS37/2 (50 samples) was determined on dried samples using a Barrington MS-2 magnetic susceptibility meter (with an AC magnetic field amplitude of 80 A/m) linked to a MS2B dual frequency sensor (470 Hz and 4700 Hz) at the Indian Institute of Geomagnetism, Alibagh, India. Representative samples were air-dried and packed into 8 cm³ styren cubic pots and the following magnetic parameters were measured. (a) Magnetic susceptibility (χ) is the ratio of induced magnetization acquired by a sample in the presence of earth’s magnetic field, to the applied field. Low frequency, χlf, (0.47 kHz) and high frequency χhf, (4.7 kHz) magnetic susceptibilities were measured on these samples and mass specific values are presented in 10⁻⁸ m³/kg SI units. All remanences were measured using a Molspin fluxgate spinner magnetometer. (b) Anhysteretic Remanent Magnetization (ARM) was imparted on the samples by superposing a DC biasing field of 0.05 mT on a smoothly decreasing alternating field with a peak of 100 mT. It is customary to express ARM as an anhysteretic susceptibility χARM (mass specific ARM / strength of the biasing field). (c) Isothermal Remanent Magnetizations (IRM) acquisition were carried out by using the Molspin Pulse magnetizer. Saturation Isothermal Remanent Magnetization (SIRM) was imparted using a maximum field of 1T. SIRM responds primarily to the ferromagnetic material concentration, but unlike low field susceptibility (χlf) it is not affected by diamagnetic and paramagnetic minerals. After acquisition of SIRM, the samples were subjected to reverse DC fields of 0.3T and the remanence was measured by using the Molspin magnetometer. To investigate the magnetic mineral composition, (d) HIRM (hard IRM) and (e) S-ratio (S₀/₀.₃T) were calculated by using the definitions of Robinson (1986) and Bloemendal et al. (1992). HIRM = (IRM₁T+IRM₀.₃T)/2; S-ratio% = ((1-IRM₀.₃T/IRM₁T)/2)*100. The ratios of (f) χARM/SIRM and χARM/χlf were calculated to identify the stable single domain magnetic grain sizes (0.03 to 0.06 μm) unambiguously in the sediment cores.
Parameters of Rock-Eval Pyrolysis

A total of 46 representative samples were analysed for Rock-Eval pyrolysis from cores 16, 39 and 50 of the southwestern margin of India at the Oil India Limited, Duliajan, Assam, using a Rock Eval III apparatus, following the procedures of Espitalié et al., (1985). Rock-Eval pyrolysis is commonly used method to assess terrigenous organic matter in marine sediments. Originally, this method was used to evaluate the petroleum-generated potential and thermal maturity of rocks (Espitalié et al., 1977; Peters, 1986). It consists of progressive heating of sediment samples and measurement of the amount of hydrocarbon that escape from the sediment at different temperatures. During heating from ~200°C to 600°C three main signals \( S_0 \), \( S_1 \), \( S_2 \) are generated. The \( S_0 \) corresponds to gaseous hydrocarbon; \( S_1 \) to volatile hydrocarbons and \( S_2 \) to hydrocarbon component produced due to thermal cracking of kerogen and \( T_{\text{max}} \) is temperature at which maximum hydrocarbons are produced. The Hydrogen Index (HI) represents hydrocarbon potential of total organic matter in mg HC/g OC, and represent H/C ratios (Espitalié et al., 1977). The HI is calculated based on \( \text{HI} = \frac{(S_2 *100)}{OC} \) and can provide information about the geochemical quality and origin of the bulk organic matter (Tissot and Welte, 1984). The HI values used to reconstruct the modified “van Kervelen” diagram (Peters, 1986; Delveaux et al., 1990) enables to determine kerogen type I to IV. Kerogens are substances that are residues of once living matter and have resisted destruction by chemical and biological forces during geological time. The kerogen types I to IV can differentiate mixture of biodegraded, marine, terrestrial and oxidized organic matter.

The nitrogen isotopic analysis

The nitrogen isotopic analysis in sediments was carried out at the Hydrospheric-Atmospheric Research Center (Institute for Hydrospheric-Atmospheric Science), Nagoya University, Nagoya, Japan. A total of 39 representative samples at different levels in cores 16 and 39 (up to LGM) were decalcified (treated with 1N HCl for the removal of CaCO\(_3\)) and washed with
distilled water to remove the acid and oven dried. The decalcified sediment samples (~20 mg) were weighed and directly loaded into tin foil boats for combustion. The high temperature (1000°C) flash combustion was carried out in a Carlo Erba NA2500NC elemental analyser that was coupled to a Finnigan MAT 252 isotope ratio mass spectrometer. The system was used in the automated, continuous-flow mode using helium as the carrier. Solid alanine was used as the organic standard and replicate measurements were found to be reproducible to ± 0.2‰. The δ¹⁵N values are expressed relative to the atmospheric N₂.

\[ \delta^{15}N (\text{‰}) = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{air}}} - 1 \right) \times 1000 \]

Radiocarbon dating

A few species of planktic foraminifer *Globigerinoides ruber* were handpicked (8-10 mg) ultrasonically cleaned and age was determined using Accelerator mass spectrometer (AMS). The CO₂ liberated from the samples was treated with 100% phosphoric acid at 90°C; resulting carbon/iron mixture was pressed in the target holder. The ¹⁴C measurements were carried out at the Leibniz-Labor of University of Kiel, Germany. Chronostratigraphy for the cores 16 and 39 is based on three AMS dates measured on *G. ruber* and two bulk sample dates obtained by the conventional radiocarbon method at the Birbal Sahni Institute of Paleobotany (BSIP), Lucknow. The measured ages were corrected for surface global ocean reservoir age (400 years) and local ΔR correction (100 years ± 30 Dutta et al., 2001) and calibrated using CALIB 4.3 program, following (Stuiver et al., 1998).