CHAPTER-2

Materials and Methods

Two sediment cores (Figure 2.1) were studied from Arabian Sea to achieve the objectives of the present study. The sediment cores were collected by Physical Research Laboratory research team during the oceanographic cruise expedition ORV Sagar Sampada cruise no. SS-164. Nutrient profile and other parameters at the sample locations have been presented in Bhushan et al. (2003). A sediment core (4018) from western Arabian Sea was selected to reconstruct the palaeo-upwelling and its impact on SWM rainfall, aeolian flux and its influence on CEF. The location of 4018 sediment core is 13° 12.8’ N latitude and 53° 15.4’ E longitude (Figure 2.1). Core length is 130 cm and the water depth at core location is 2830 m. The core is located in the Somali upwelling region where intense upwelling takes place during SWM season. Therefore the 4018 core would help in understanding the past changes in Somali upwelling and associated palaeoceanography. The other core (4016) is located on the middle Indus submarine fan in Northern Arabian Sea (19.765^0 N, 64.61^0 E; Figure 2.1) at a water depth of 3242 m. The 4016 sediment core is 147 cm long and subsampled onboard at 2 cm interval. The location of 4016 sediment core is best suited to study the open ocean conditions and Indus sediment flux during the past.

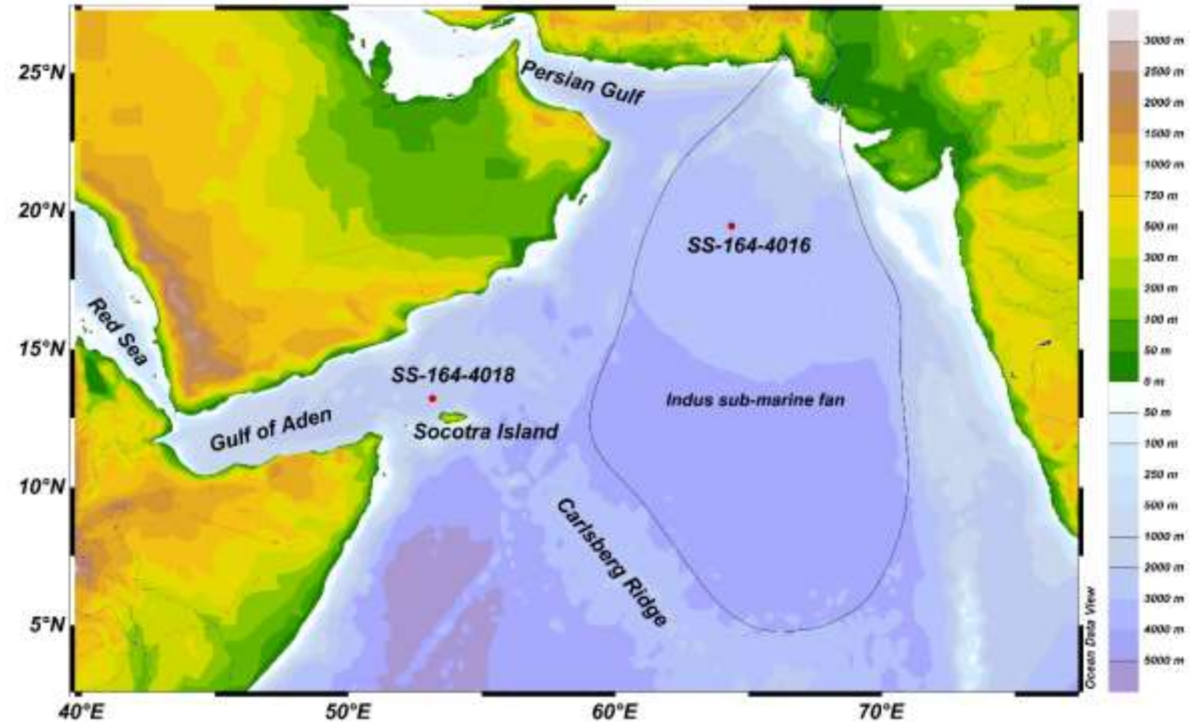

Figure 2.1: Location of sediment cores 4018 and 4016 are marked with red dots in the bathymetry map of Arabian Sea. Map has been plotted using licensed copy of Ocean Data View (https://odv.awi.de/).

2.1 Analytical methodology

2.1.1 Radiocarbon dating

Chronology is an important part of any palaeoclimate and palaeoceanographic study. Radiocarbon dating is the best method used to study the recent sediments spanning the last 50000 years. This method can be used in various organic and inorganic matter present in the sample. Selection of particular component from the sample is solely based on the users need and availability. Planktonic foraminifera shells are the most preferred material used to date the recent marine sediments (Broecker et al., 1984). Foraminifera shells are made up of inorganic calcium carbonate ($CaCO_3$). The carbon in the $CaCO_3$ is the time clock which tells us about the time of death of organism, in other words the age of deposition. However the age obtained using radiocarbon dating of foraminifera shell may not represent the calendar age (Reimer et al., 2013). There are two reasons for the deviation in calendar age and the age of foraminifera shell. First reason is associated with the age of the water in which the foraminifera was living (Broecker et al., 1984). This aspect is important because the foraminifera incorporate the bicarbonate ion from the water. The average difference between a radiocarbon date of living organism in terrestrial environment (tree) and marine (Planktonic foraminifera shell) would be around 400 years (Stuiver and Braziunas, 1993). The age of oceanic water is controlled by the exchange rate between atmospheric CO_2 and ocean bicarbonate as well as by the mixing of upwelled deep water (old) with surface waters (Mangerud, 1972). This is the reason that the age obtained from ^{14}C dating of foraminifera shell is called Apparent age. Reservoir age (ΔR) correction is the method to convert the apparent age into radiocarbon age. The ΔR is the deviation between the regional marine ^{14}C age and the global model marine ^{14}C age at any given time (Stuiver and Braziunas, 1993; Dutta et al., 2001). Therefore ΔR has to be incorporated with the global mean reservoir age (400 years) to achieve the age correction needed for any local region. Apart from reservoir correction the radiocarbon age need to be corrected for the atmospheric ^{14}C concentration at any given time, because it varies through production rate, caused by changes in cosmic-ray flux and carbon cycle (Reimer et al., 2013). This correction is made using calibration curves which is prepared from precisely dated record that has incorporated carbon directly from the atmosphere at the time of formation. Calibration curves are prepared by radiocarbon research community from time to time (IntCal 98-Stuvier et al., 1998; Marine 04-Hughen et al., 2004; Marine 09-Reimer et al., 2009; Marine 13-Reimer et al., 2013).

The age depth model for 4018 sediment core was developed by Tiwari et al. (2010) based on 14 radiocarbon ages (Figure 2.2) obtained on selected species of planktic foraminifera (*G. ruber, G. sacculifer, O. universa and N. dutertrei*) of 250–500 μm in size from the NSF accelerator mass spectrometer (AMS) facility, University of Arizona, USA. Calibration of AMS radiocarbon ages have been made using Calib 4.1 (INTCAL 98; Stuiver et al., 1998) with a ΔR of 163 ± 30 a (Dutta et al., 2001; Southon et al., 2002). The bottom of 4018 sediment core yield the calibrated age of 19000 years. The time resolution based on the age depth model is 300 y i.e. each subsample represent 300 years. For determining the age of the 4016 sediment core, 8 samples were selected at uniform depth interval. Sediments were then wet sieved using 125 micron mesh and dried in oven at 80°C. Dried sample has been examined under reflected light microscope for the physical separation of foraminifera shells. Sufficient amount (>10 mg) of complete shells (non-broken) of surface dwelling foraminifera species (*G.ruber*, *G.sacculifer* and *G.minardi*) were picked from sediment. The foraminifera shell samples were then sent to the NSF accelerator mass spectrometer (AMS) facility, University of Arizona, USA in collaboration with Professor A.J.T. Jull. The processing of foraminifera shells and subsequent AMS ^{14}C dating were carried out at USA. AMS radiocarbon ages have been calibrated to calendar ages using Marine13 calibration curve in Calib 7.1.0 online tool (Stuiver and Reimer, 1993; Reimer et al., 2013) with a ΔR of 129±35 a (Dutta et al., 2001). The bottom unit of the 4016 core gave the age of 34.6 ka B.P., whereas the top unit yielded an age of 2.83 ka B.P. (Table 2.1). The age-depth model (Figure 2.12) of the 4016 core based on the slope between the eight calibrated age points suggests that the sedimentation rate varied between 1.3 to 7.4 cm/ka with an average temporal resolution of ~235 years/sample.

Sample Id	Lab code	Depth interval (cm)	Carbon yield (mg)	Radiocarbon age (yr B.P.)	Calibrated age range (cal yr B.P.)	Calibrated age (cal yr B.P.)
PRL-AS-11	AA104069	3-4.5	1.21	3192 +/- 32	2761 – 2877	2830
PRL-AS-12	AA104070	20-22	1.24	10392 +/- 44	11177 – 11314	11255
PRL-AS-13	AA104071	42-44	0.93	14555 +/- 56	16910 – 17165	17035
PRL-AS-14	AA104072	62-64	1.07	17255 +/- 68	20051 – 20288	20175
PRL-AS-15	AA104073	82-84	1.04	19542 +/- 91	22725 – 23028	22880
PRL-AS-16	AA104074	102-104	1.03	22380 +/-130	25922 – 26180	26065
PRL-AS-17	AA104075	122-124	1.01	25960 +/- 200	29212 – 29786	29520
PRL-AS-18	AA104076	138-140	1.01	29930 +/- 330	33254 – 33909	33560

Table 2.1: AMS ^{14}C dates of 4016 sediment core based on planktonic foraminifera shells with diameter >125 µm.

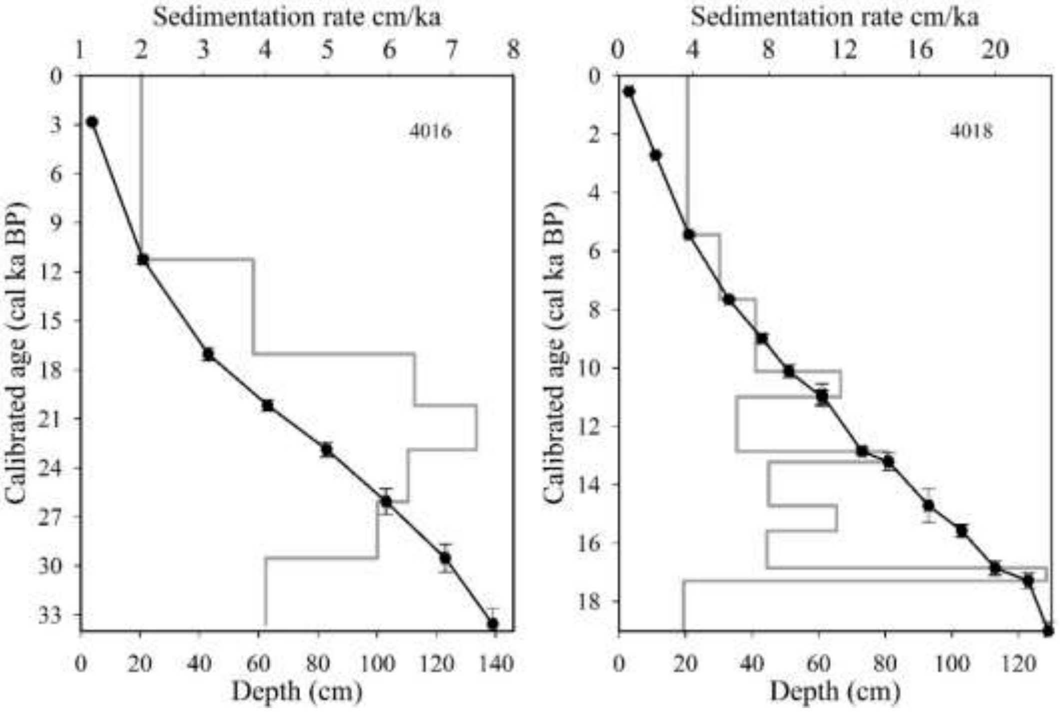

Figure 2.2: Age-depth model of 4016 and 4018 sediment cores. Age model for 4018 is based on Tiwari et al., 2010. Grey line indicates the sedimentation rate.

2.1.2 Geochemical analysis

2.1.2.1 Measurement of TOC, TN and $CaCO_3$

Organic matter present in marine sediments may have been produced in the surface water (export flux) or derived from terrestrial source. However the terrestrial organic matter is confined to the continental margins and river mouths. Therefore the organic matter present in the open marine sediments and locations surrounded by arid land regions, are probably of marine origin (Emerson and Hedges, 1988). The ratio between carbon and nitrogen of organic matter and carbon isotopic composition would help in identifying the source of organic matter. The organic matter concentration in these marine settings would tell us about the changes in overhead productivity, provided that it is diagenitically unaltered/well preserved. Preservation of organic matter is controlled by the water depth and sedimentation rate. Regions with high sedimentation rate are supposed to preserve the original signal of export flux due to the fact that there is not enough time for degradation before burial (Muller and Suess, 1979; Henrichs and Reeburg, 1987). Regions with strong oxygen minimum zone (OMZ) at intermediate depth may have higher preservation efficiency than the regions with no OMZ. Arabian Sea is known to have a perennial OMZ in the intermediate depth (200-1000 m) due to the seasonal high productivity and perennial denitrification (Naqvi et al., 1998). Overall it appears that the organic matter present in the 4018 and 4016 sediment cores can be used as proxy for overhead productivity due to high sedimentation rate and the presence of mid-depth OMZ in Arabian Sea.

On the other hand the $CaCO_3$ content in marine sediments is mainly used to understand the calcareous productivity at the surface. The $CaCO_3$ in marine sediments were derived from the surface production of calcareous phytoplankton (coccolithophore), pteropods and foraminifera shells (Naidu et al., 2014). Therefore it may represent the collective flux and can vary with the change in their partial contribution. The shells of coccolithophore and foraminifer are made of calcite, however, the pteropods shells are made up of aragonite, an unstable form of $CaCO_3$, more soluble in seawater than the calcite. In general pteropods shells get dissolved in water column leading to their absence in deep sea sediments. The aragonites compensation depth (ACD) below which aragonite completely dissolves, lies at the depth of 250 to 700 m (Berger, 1978; von Rad et al., 1999). The water depth at both core (4018 and 4016) locations is more than 2000 m, therefore the $CaCO_3$ in these sediments only represents the export flux of coccolithophore and foraminifer shells. Calcite also gets dissolved in seawater as depth increases due to the reduction in seawater pH caused by the respiration of organic matter (Emerson and Bender, 1981). The amount of dissolved CO_2 present in the water also affects the preservation of $CaCO_3$. Lysocline is a depth in the water column below which the dissolution of Calcite increases enormously. At present the depth of lysocline in Arabian Sea is ~3800 m (Peterson and Prell, 1985), which is well below the depth of sediment cores studied here. Naik et al. (2013) noted the absence of dissolution effect on foraminifera shells collected at the depth of 4020m in Arabian Sea. Hence we understand that the $CaCO_3$ flux in both the sediment cores were controlled by surface productivity alone.

In order to measure the total organic carbon (TOC) and nitrogen in sediment core samples, ~200 mg of subsamples were processed with 0.1N HCl to remove the inorganic carbon. Around 10-20 mg of decarbonated sample was packed in tin capsules and loaded to the auto sampler attached to NC Elemental Analyzer (Flash 2000). Auto-sampler drops the sample into a combustion chamber heated at 1020^oC. High purity oxygen is used to aid the combustion of organic matter. CO_2 and NO_x were produced by the combustion of organic matter in oxic condition. Helium was used as a carrier gas to carry the CO_2 and NO_x from combustion chamber into a reduction chamber heated at 650^oC and filled with pure copper wires which reduces the NO_x into N_2. The gases were purified for water vapor and Sulphur. The purified gases were passed through gas chromatograph where N_2 and CO_2 were separated by the difference in retention time. After separation the gases enter the Thermal Conductivity Detector (TCD), one after another. TCD produces electric signal equivalent to the concentration of gas in the helium flow. Signal peak height and peak area of both gases were extracted from the signal graph. Low Organic Soil Sample (LOSS), Batch number 647582814, was used to calibrate the instrument. The concentration of C and N were estimated from the peak area using the calibration curve. The precision associated with the organic carbon and nitrogen measurement is less than 5%.

The concentration of $CaCO_3$ in all sub-samples of 4018 and 4016 sediment core was measured using UIC Coulometer, Model 5012. This instrument has two units, first one is for acidification and subsequent release of CO_2 from $CaCO_3$ and the other for the measurement of CO_2. Carbon dioxide free air, generated by passing natural air through 50% KOH solution, is used as carrier gas in coulometer. ~20 mg of bulk sediment was taken in the sample tube and treated with 5 ml of 40% Ortho Phosphoric acid (H_3PO_4). The evolved CO_2 along with carrier gas pass through activated silica gel and $MgClO_4$, before entering the second unit. The dried CO_2 was then bubbled into the coulometer titration cell which contains monoethanol amine as electrolyte with

Pt cathode and Ag anode. Coulometer produces electric signal equivalent to the volume of CO_2 mixed in the titration cell. Pure sodium carbonate was used for obtaining calibration curve between signal and amount of CO_2. Sample's signal were then converted to CO_2 concentration and subsequently to $CaCO_3$. Sodium carbonate was used as check standard to verify the precision and sample repeats were used to check the reproducibility of measurement.

2.1.2.2 Measurement of Biogenic silica

Biogenic silica in marine sediments were derived by the downward flux of diatom frustules and other siliceous microfossils. Biogenic silica has been a good proxy for diatom abundance (Conley, 1988) and for other siliceous microfossils like sponges (Conley & Schelske, 1993) and phytoliths (Schwandes, 1998). The biogenic silica is a recorder of diatom productivity in most marine settings (Ragueneau et al., 1996). The biogenic silica concentration was measured in each sub-sample of 4018 core using the method described by Carter and Colman (1994). Dried homogenized samples weighing 50 mg were placed in centrifuge tubes. Five milliliters of 10 % H_2O_2 was added to each sample at room temperature, and the samples were stored for 2 hours to remove organic matter. Five milliliters of 1N HCl was added to each tube. After acid treatment, 20 ml of distilled water was added, and the samples were centrifuged for 15 minutes. Sample tubes were kept in an oven after removal of the supernatant. Thirty milliliters of 2 M Na_2CO_3 was added to each sample tube, and the tubes were kept in a shaker bath at 95^0 C for 5 hours. After 5 hours, the samples were centrifuged for 5 minutes, and 3 ml of hot supernatant was pipetted out of each sample and added to exactly 30 ml of distilled water in pre-cleaned sample tubes. These solutions were acidified by adding 0.9 ml of concentrated HNO_3. Sample tubes were sealed after effervescence. Silicon and aluminum concentrations were measured in these samples using ICP-AES (Jobin-Yuvon, Model 38S at Physical Research Laboratory, Ahmedabad). The silicon concentrations were then corrected for clay mineral dissolution by using the formula given by Carter and Colman (1994) (Eqn. 2.1):

$$\Delta Si = Si - (Al * 1.93) \qquad (2.1)$$

Where, ΔSi is the corrected silicon concentration, Si and Al are the measured concentrations of silicon and aluminium in the sample, and 1.93 is the Si to Al ratio in smectite. Smectite is an abundant clay mineral in the northern Arabian Sea (Sirocko and Lange, 1991). Biogenic silica concentrations were calculated using the formula given below (Eqn. 2.2):

$$Biogenic\ silica = \Delta Si * \mathcal{K} \tag{2.2}$$

Where, K is a constant that equals 2.4, which accounts for the ~10 % water content in biogenic silica (Mortlock and Frolich, 1989). Overall, the error associated with the biogenic silica measurement is less than 5 % based on repeat measurements. The biogenic silica flux is calculated by multiplying the biogenic silica fraction by the sedimentation rate (SR) and the dry bulk density (DBD) (Eqn. 2.3),

$$B.Si.flux(g.m^{-2}.y^{-1}) = B.Si * SR(m.y^{-1}) * DBD(g.m^{-3}) \tag{2.3}$$

The uncertainties associated with the biogenic silica concentration (B.Si) is estimated from the error in Aluminium and Silicon concentration based on measurements of repeat and standard material. The maximum error in biogenic silica concentration is within 5%. Dry bulk density (DBD) is calculated from CaCO3 concentration using an empirical equation suggested by Clemens et al. (1987). The standard uncertainty in DBD calculation is 0.091 g/cm^3. The uncertainty in average sedimentation rate (SR) is 0.12 cm/ka. Finally the uncertainty associated with biogenic silica flux (B.Si flux) is propagated using the below equation,

$$\sigma B.Si\ flux = B.Si\ flux * \surd\{({}^{\sigma B.Si}/_{B.Si})^2 + ({}^{\sigma DBD}/_{DBD})^2 + ({}^{\sigma SR}/_{SR})^2\} \tag{2.4}$$

Where, prefix “σ” stands for uncertainty. Uncertainty in biogenic silica concentration is below 5%. But the uncertainty in flux are up to 15%. This increase in uncertainty is due to the high standard error associated with empirical derivation of Dry bulk density.

2.1.2.3 Major and trace element analysis

Inorganic geochemistry of marine sediment can be used to understand several oceanographic processes. In general these processes can be divided into two categories, allochthonous and autochthonous. For example, Al, Ti and Mg content in marine sediment is used as an indicator for the terrigenous supply of sediments (Sirocko et al., 2000). While Ca, Sr, Ba, Zn and Cd flux in marine sediment may record the signature of overhead productivity. In order to understand the palaeoceanographic processes at the core sites, the major (Al, Fe, Ca and Mg) and trace elements (Ti, V, Cr, Mn, Zn, Sr, Ba, Co, Ni, Cu, Mo and Cd) were measured in all sub-samples of both the sediment cores (4018 and 4016). Bulk (un-processed) sediment were used for the elemental geochemistry analysis. Samples were dried and finely powdered. About 0.3-0.5g of sediment was taken in taflon vial and 3ml HNO_3 was added to it. Sediment and HNO_3 mixture was kept open in a fume hood for an hour to enable the gases, evolved by the decomposition of easily oxidised organic matter and carbonate, to escape before commencing the closed digestion procedure. This procedure is useful to prevent the excess pressure during microwave digestion (Lamble and Hill, 1998). 3 ml HCl, 3 ml HF and 1 ml de-ionised water were added to the mixture in the taflon vial. After adding all the acids the vial was tightly closed and kept inside microwave digestion instrument (Milestone start D). Digestion procedure was done as per the standard protocol preset in the system, temperature was raised to 150°C for 25 minutes. After system temperature fell down to room temperature, the vials were taken outside and opened to check the digestion efficiency. If the solution is not clean then the digestion procedure repeated again otherwise the solution was poured in Teflon beakers and kept in hotplate to dry. The dried sample was dissolved in 50ml of 0.4N HNO_3 using standard flask. The samples were suitably diluted for the major element measurements using ICP-AES (Jobin-Yuvon, Model 38S) and trace element measurement in Q-ICP-MS (Thermo-X series2). An internal laboratory standard NOVA (Amin et al, 1975) and USGS standard MAG-1 (Govindaraju, 1994) were prepared and measured along with the sediment samples to assess the precision of the measurement, which has different value for different element.

2.1.2.4 Measurement of REE’s

Rare Earth Elements (REE’s) concentration in ocean water shows nutrient like profile, low at surface and high concentrations in deep water (German and Elderfield, 1990). The adsorption/desorption variations also can fractionate the concentration of REE’s. Therefore the REE concentration in marine sediments may give some ideas about the biology and water mixing at the core site (Sirocko et al., 2000). REE’s pattern also can be used to understand the sediment provenance. REE concentration were measured in all sub-samples of both the sediment cores. The digested fraction, which was prepared for major and trace element analysis, of samples were suitably diluted for the REE measurement in Q-ICP-MS (Thermo-X series2). Light rare earth element (LREE- La, Ce, Pr, Nd and Sm) and Heavy rare earth element (HREE- Eu, Gd, Dy, Er and YB) concentrations were measured. The USGS standard MAG-1 (Govindaraju, 1994) was prepared and measured along with the sediment samples to assess the precision of the measurement.

Element	**Standard value**	**Measured**
Al (%)	8.21	8.06±0.15
Fe	5.82	5.77±0.14
Mg	2.33	2.52±0.17
Ba (μg/g)	1648	1631±69
Co	101	100±4
Cr	84	74±9
Cu	403	416±44
Mn	7125	6926±147
Mo	23.8	21.5±1.9
Ni	224	206±8
Sr	182	180±9
Ti	4076	3881±173
V	144	133±9
Zn	146	169±4

Table 2.2. Measured concentration of major and trace elements in NOVA sediment alongwith standard values.

Element	Standard value	Measured
Al (%)	8.67±0.16	8.43±0.08
Ca	0.98±0.07	1.19±0.08
Fe	4.75±0.42	5.22±0.09
Mg	1.81±0.06	1.83±0.06
B (μg/g)	140±6	141±11
Ba	480±41	482±40
Cd	0.2±0.03	0.34±0.02
Ce	88±9	86±6
Co	20±1.6	19±1
Cr	97±8	94±9
Cu	30±3	28.8±2.8
Dy	5.2±0.3	5.4±0.8
Er	3	3.0±0.1
Eu	1.6±0.14	1.33±0.09
Ga	20±1.5	22±2
Gd	5.8±0.7	5.4±0.3
La	43±4	45±3
Mn	759±69	708±46
Mo	1.6	1.3±0.2
Nd	38±5	38±6
Ni	53±8	45.2±3.5
Pb	24±3	23±2
Pr	10	12±1
Sm	7.5±0.6	6±0.4
Sr	150±15	142±8
Ti	4496±419	4304±288
V	140±6	136±10
Yb	2.6±0.3	2.6±0.3
Zn	130±6	141±10

Table 2.3. Measured concentration of major, trace and rare earth elements in MAG-1 sediment along with standard values.

2.1.3 Isotopic analysis

Isotopic analysis marine organic matter is an important tool to understand the productivity and nutrient dynamics. The most preferred stable isotope measurements in marine organic matter are carbon and nitrogen. The isotopic composition (ratio between less abundant to more abundant isotopes) of unknown sample is measured along with the standard material. Vienna Peedee Belemnite (VPDB), a marine fossil, is the standard material for carbon isotopic measurement. The atmospheric nitrogen is the standard for nitrogen isotopic measurement. Final value is expressed using "δ" notation which shows the comparison between the isotopic ratio of sample and standard. In other words, δ values are negative for samples with depleted heavy isotope as compared to standard and positive for samples with enriched heavy isotopes. This can be useful to delineate the process responsible for enrichment or depletion in the sample. The "δ" value is estimated using the following equation,

$$\delta = \{\left(\frac{Rx}{Rs}\right) - 1\} \times 1000 \tag{2.5}$$

Where, δ represents $\delta^{13}C$ or $\delta^{15}N$, Rx and Rs are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratio of sample and standard respectively. Final value is presented with per mil (‰) unit.

2.1.3.1 Measurement of δ^{13}C in organic matter

In order to measure the carbon isotopic composition of organic matter the inorganic carbon should be removed before the analysis of sediment samples. About 100 mg of bulk sediment was treated with 0.1N HCl to remove the carbonate fraction. After the effervescence stopped the supernatant was removed and the sample was washed with de-ionised water to remove the excess acid. All these process are done using centrifugation technique to minimize the lass of sample and processing time. The decarbonated sample was dried in the oven before packing for analysis. About 10-15mg of decarbonated sample was packed in tin capsules. Packed samples were analysed for carbon isotopic composition in an Elemental analyzer (Flash EA 2000) interface with continuous flow mass spectrometer (Delta V Plus) facility at the Physical Research Laboratory, Ahmedabad.

2.1.3.2 Measurement of δ^{15}N in organic matter

Nitrogen isotopic composition of marine organic matter is an important recorder of nitrogen cycling and biogeochemistry (Altabet et al., 1999). The $\delta^{15}N$ of organic matter is controlled by the $\delta^{15}N$ of surface NO_3^-, productivity, nitrogen fixation, internal mixing and denitrificaton. Isotopic composition of organic nitrogen was measured in bulk sample. About 20 mg of bulk sediment sample was packed in tin capsule and analyzed in an Elemental analyzer (Flash EA 2000) interface with continuous flow mass spectrometer (Delta V Plus) facility at the Physical Research Laboratory, Ahmedabad. The precision for the $\delta^{15}N$ determination has been observed to be better than ±0.2‰.

2.1.4 Magnetic susceptibility measurements

Magnetic mineralogy of sediment depends on the source region, transporting medium and depositional environment. Magnetic susceptibility measurements in marine sediments were mainly used to understand the terrestrial contribution (Larrasoaña et al., 2008). For this purpose 10 cm^3 sediment samples were packed in clean plastic container for which the magnetic property is known. Magnetic susceptibility of sediment samples were carried out using Bartington MS2 system available at Indian Institute of Geomagnetism (IIG), Mumbai. Magnetic susceptibility at high (4.7 kHz) and low (0.47 kHz) frequency were measured using a dual frequency Bartington MS2 susceptibility meter. Frequency dependent susceptibility (χ_{fd}%) was calculated using the formula $(\chi_{LF}-\chi_{HF})/\chi_{LF}*100$ where χ_{LF} is magnetic susceptibility at low frequency and χ_{HF} is susceptibility at high frequency (Dearing et al., 1996).