Chapter 3

MATERIALS AND METHODOLOGY

The present work is a systematic attempt to understand the overall geological evolution of the Great Rann of Kachchh (GRK) basin using comprehensive field studies and multiproxy studies on two deep cores obtained from the difficult terrain of the Great Rann for the first time. Sediment coring-drilling was performed in 2010 from the central and south marginal part of the GRK basin. The central Dhordo core is ~60 long and the south marginal Berada core is ~50 m long (Maurya et al. 2013). After the collection of the cores, X-radiographs were generated on every core pipe in the field prior to shipping at the M. S. University of Baroda. The cores were spitted and sampled at every 2 cm and half part of every pipe is preserved in the low-temperature environment at Baroda. Depending on the physical observations both the cores were divided into several zones and several samples from each zone were subjected to grain size analysis (Maurya et al. 2013). The samples selected from the two cores for obtaining the radiocarbon dates were thoroughly examined from the x-ray images to spot broken shells and an abundance of foraminifera shells. Some samples from both the cores were selected strategically keeping the coarse grain size of the sediments.

An integrated approach of field and various laboratory analyses was applied to achieve the objectives of this study by using several scientific methods. The field survey and geomorphic mapping are used as a primary component to study the present geomorphic set-up of the rann basin. The surface and exposed sediments were subjected to sedimentological, environmental magnetism and palynological studies to decipher the modern and past environmental conditions. The present chapter describes the approach and methodological aspects of the field as well as laboratory exercises included in the study.

The study is based on multiproxy studies carried out in various laboratories to fulfil the objective. The sample collection was done at an advanced sedimentology laboratory, Department of Geology, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara. The sample was collected and subjected to the particle size analysis at the advanced sedimentology laboratory, Department of Geology, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara. The analysis related to environmental magnetism and palynology was carried out at BSIP, Lucknow. Figure 3.1 demonstrates the schematic diagram/flowchart of various analyses carried out for this study.

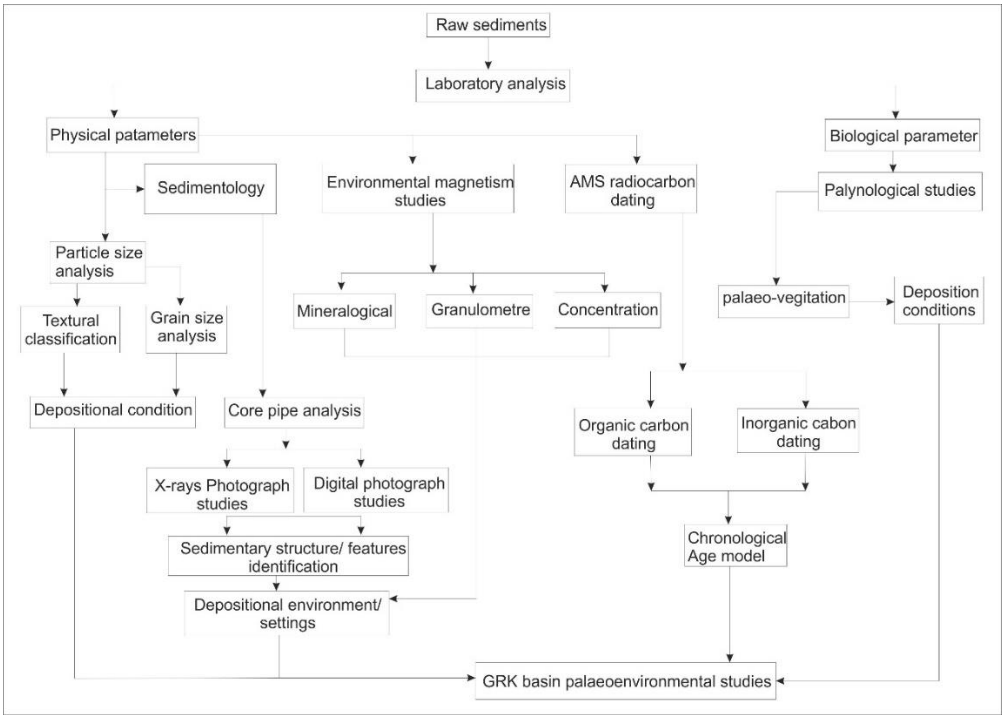

Figure 3.1 Schematic view of the multi-proxy studies carried out during the study.

PARTICLE SIZE ANALYSIS

The physical character has proved vital in understanding the change in the sediment source and revealing key climatic conditions during the depositions (Pethick., 2000; Beierle et al., 2002). Moreover, the grain size variations reveal the depositional conditions are related to the environmental variations (Beierle et al., 2002). The fluctuations in the silt, clay and sand are indicative of changes in depositional energy conditions. The link between the environmental change and depositional change can be inferred through grain size variations (Chen et al., 2004; Conroy et al., 2008). The depositional condition is majorly reflected/carried by the change in the percentage of silt/clay whereas the relatively higher percentage of fine sand in both cores, is conclusive of higher energy depositional condition (Maurya et al., 2013; Rajganapathi et al., 2013).

Particle size analysis on the selected 181 samples at regular intervals of ~60 cm was carried out on both the cores raised from GRK using Laser Diffraction Particle Size Analyser (Beckman Coulter) at Birbal Sahni Institute of Palaeosciences (BSIP), Lucknow, India. The samples were measured from the range of coarse sand to clay. All the samples were air-dried and mildly crushed before treating them for carbonate and organic matter removal using a mild 30% concentration of HCL (Hydrochloric Acid) and Hydrogen Peroxide following standard procedure (Folk, 1966). After removal of organics and carbonates, samples were treated with Sodium hexametaphosphate $(NaPO_3)6$ for dispersion before measurements and mixed well-using a shaker/sonicator. All the processed samples were then run on the particle size analyser and the data was processed and compiled using the Gradistat program in Microsoft Excel (Blott and Pye, 2001).

SEDIMENTOLOGY

The sedimentary features produced by the physical and chemical activities during the sedimentation were considered. The sedimentary facies, structures (ripple mark, cross lamination, falser bedding, and mud ball), scours, laminations, bio-turbidation and scattered organic layers are the few features which can be used for the sedimentological interpretations. The cores raised from the study area were processed under x-ray to produce the image without disturbing the insitu sedimentary features intact in the PVC core pipes. The raised cores' x-ray images (Figure 3.2 and Figure 3.3) were thoroughly studied to mark these features to depict the changes accrued during the deposition of the sediments in the context of palaeoenvironmental implications.

ENVIRONMENTAL MAGNETICS

Environmental magnetism (EM), also known as mineral magnetism measures the inherent magnetic properties such as concentration of magnetic minerals, mineralogy and granulometry in natural samples (Figure 3.4, Figure 3.5 and Figure 3.6) (Thompson and Oldfield, 1986; Maher and Thompson, 1999; Evan and Heller, 2003). The EM methods are inexpensive, fast proxies that require relatively less preparation time and also allow measurement of a large number of samples in lesser time (Peters and Dekkers, 2003; Phartiyal et al., 2003; Warrier et al., 2011 Walden et al., 1999; Dearing, 1999).

Magnetic susceptibility (χlf) is one of the widely used parameters for paleoclimate/paleoenvironmental studies from a variety of archives ranging from terrestrial to marine, and lacustrine environments on broader scales (Banerjee et al., 1981; Maher and Thompson, 1992; Nawrocki et al., 1996; Geiss and Banerjee, 1997; Langereis et al., 1997; Chlachula et al., 1998; Evans and Heller, 2001; Anderson et al., 2002; Zhnag and Yu, 2003; Demory et al., 2005; Maher, 2011; Zhnag et al., 2012) (Table 3.1). Rock magnetic/EM properties of deep-sea sediments from world oceans are also found to correlate with the major climatic variability on shorter and longer time scales (Colin et al., 1998; Lean and McCave, 1998; Bloemendal, 1989). Similarly, changes in aeolian fluxes, fluvial inputs, and shifts in ocean currents have also been tracked successfully using mineral magnetic studies (Bloemendal et al., 1992, Oldfield, 1977; Thouveny et al., 1994; Robinson and McCave, 1994; Robinson et al., 1995). The loess sediments from the Chinese Plateau, during the late Quaternary, showed a good correlation of low field magnetic susceptibility with the paleoclimatic variability (Chen et al., 1997) which further correlates with the δ18O record from the Arabian Sea (Kukla et al., 1988). The mineral magnetic measurements can also be used for determining sediment provenance, transport pathways as a supportive proxy along with geochemical proxies and particle size data (Oldfield and Yu, 1994; Lepland and Stevens, 1996; Bonnett et al., 1988; Oldfield et al., 1993; Hutchinson and Prandle, 1994; Clifton et al., 1997, 1999; Xie et al., 1999, 2000; Zhang et al., 2001; Booth et al., 2005). In addition to the magnetic properties of natural sediments, the grain size parameters provide one of the basic and equally important datasets about the depositional environments and their variability through time (Joshep et al., 1998). The correlation between these two helps to reconstruct the palaeoenvironmental conditions through time, for e.g. mineral magnetic parameters have been widely used to infer climatic signals in marine and deltaic sediments (Basavaiah and Khadkikar, 2004; Sangode et al., 2007).

Attempts have been made for paleoenvironmental reconstructions and even to assess the sea-level fluctuations using magnetic parameters from variety of archives (Ouyang et al. 2014; Basavaiah et al., 2015). A study from arid region of Thar desert interpreted paleoclimate based on mineral magnetic studies done on sediments from Bap Malad and Kanod playas (Deotare et al., 2004). Magnetic susceptibility (χlf) of the sediment gives concentration of magnetic minerals in particular sample. Similarly, ARM, IRM and SIRM also reflect the magnetic mineral concentrations (Thompson and Oldfield, 1986). The sediment magnetic properties found to co-vary with the particle size of the magnetic mineral grains (Thompson and Morton, 1979; Thompson and Oldfield, 1986, Gale and Hoare, 1991; Yim et al., 2004; Maher, 1988; Boar and Harper, 2002). The magnetic susceptibility and grain-size of the sediments are generally related to the depositional environments and may be linked with the climatic variability (Bloemendal et al., 1992; Oldfield and Robinson, 1985, David et al., 2001). Many studies evaluated the magnetic susceptibility as a rainfall proxy and advocate its usage in paleomonsoonal reconstructions (Sandeep et al., 2017; Basavaiah and Kadhkikar, 2004; Prasad et al., 2014: Heller et al., 1993; Maher et al., 1994). The magnetic grain size analysis along with median grain size and sorting of sediments was carried out to delineate the environmental deposition conditions (Joseph et al., 1998). Basically, the response acquired through magnetic measurements under varied environmental conditions can help to reconstruct the paleomoonsoon/paleoenvironmental conditions of an area (Shankar et al., 2006; Jelinowska et al., 1995).

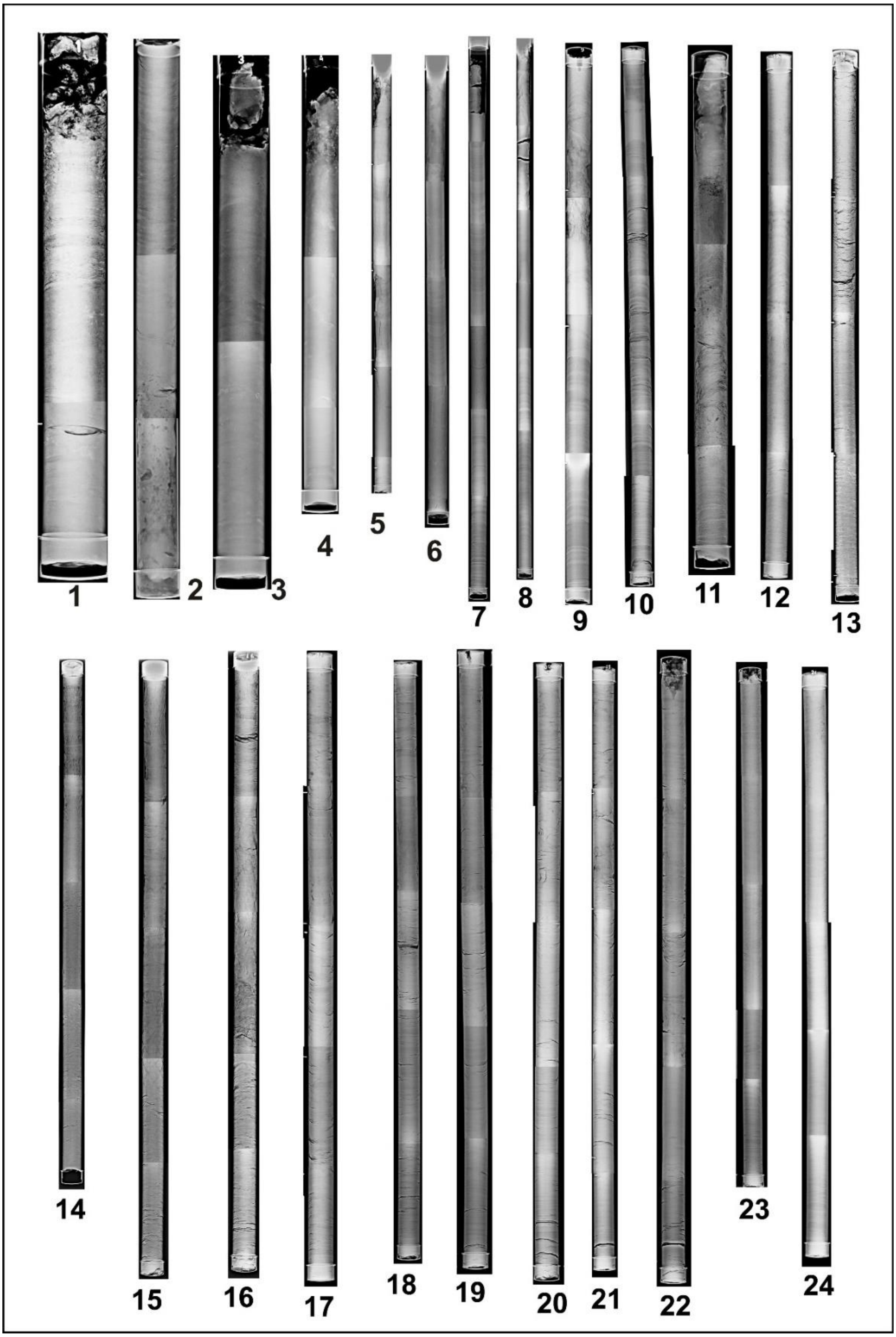

Figure 3.2 X-Ray radiographs of all core pipes from the Dhordo Core site. Note the excellent core recovery and fine-scale laminations in the core pipes.

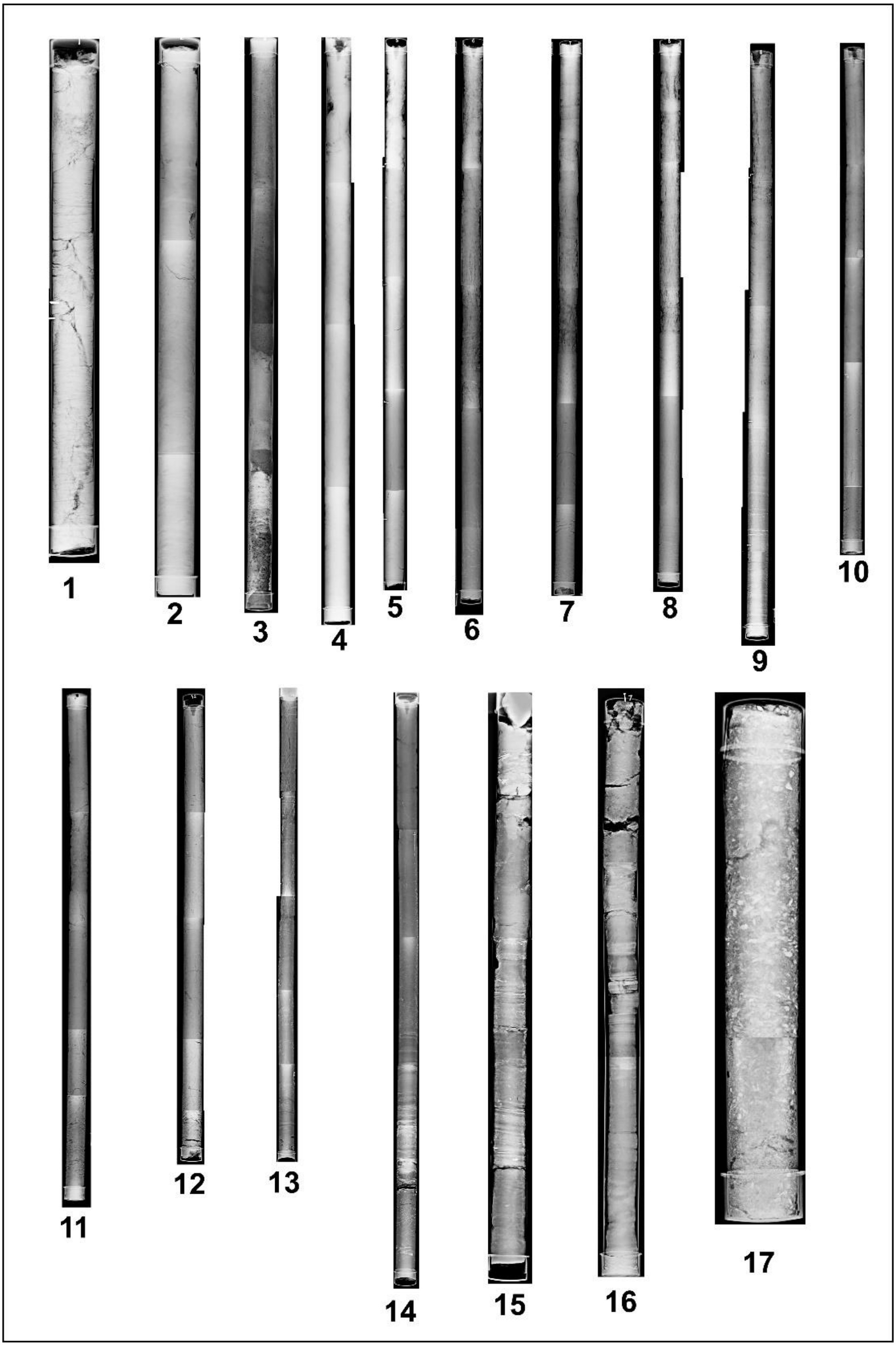

Figure 3.3 X-Ray radiographs of all core pipes from the Berada core location. Note the excellent core recovery and fine-scale laminations in the core pipes.

Table 3.1 Table showing temporal scale variability in the environmental magnetic parameters calculated for concentration, granulometry and mineralogical parameter in Dhordo and Berada core.

χlf	Increase in the reading shows an increase of ferrimagnetic minerals in the sample. Decrease shows less concentration of the magnetic minerals
ARM	Increase means high concentration of finer grain sizes of ferrimagnetic minerals. Decrease shows the dominance of coarser sediments.
S-ratio	SIRM increase shows increase of ferrimagnetic minerals, whereas decrease shows decrease in ferrimagnetic minerals and increase in anti-ferromagnetic minerals
ARM/ χlf	Higher value shows an increase in grain size around stable single domain (SSD) of ferrimagnetic minerals in a sample
SIRM/ χLF	Increase shows increase in the dominant magnetic grain size of SD (single domain). Decrease shows increase in grain size SP grain size of magnetite grains
χARM/SIRM	Indicative of magnetic grain size of, ferrimagnetic minerals the ratio shows with the lower value there is a presence of MD grains higher value indicates SD grain size.

Environmental magnetic analysis was carried out at Paleomagnetic laboratory in BSIP (Birbal Shani Institute of Paleoscience), Lucknow, India. The general characteristics of the magnetic parameters are mentioned in Table 2. ~10 g of air-dried sample was filled in non-magnetic sample holders for analysis. Magnetic susceptibility (χlf) at low frequency (0.47 kHz) was determined on Bartington Susceptibility Meter (Model MS2) (noise level ~3x10x-9m3 kg-1 for a 10 g sample). Anhysteric remanent magnetization (ARM) was induced in the samples using a Molspin AF demagnetizer (with an ARM attachment) in a constant biasing field of 0.1 mT superimposed on a decaying alternating field (a.f.) with a peak of 100mT at the decay rate of 0.001 mT per cycle. The susceptibility of ARM (χARM) was calculated by dividing the mass specific ARM by size of the biasing field (0.1mT= 79.6A/m; Walden, 1999b). Isothermal remnant magnetization (IRM) was induced in the samples at different field strengths of 20, 50, 70, 100, 200, 300 up to 800 mT and back fields up to -300 mT using ASC Scientific IM 10-30 Impulse Magnetizer. The remenance were measured in a Minispin magnetometer of Molspin Ltd. (sensitivity ~10x -7Am2 kg-1 for a 10 g sample). The interparametric ratios that were used are S-ratio, SIRM/χlf and χARM

/SIRM, ARM/ χlf, Soft IRM and Hard IRM. The isothermal remenance induced at 800mT was considered as the saturation isothermal remanent magnetization (SIRM). S-ratio was calculated by the expression (-IRM-300mT/SIRM2500mT). χARM/SIRM, SIRM/χlf were calculated to determine magnetic grain size. For magnetic mineralogy, the IRM acquisition was performed on all samples (Maher et al., 1999; Walden, 1999; Evans and Heller, 2003).

Figure 3.4 Bartington MS2WFP Susceptibility Meter (noise level ~$3x10x^{-9}m^3\,kg^{-1}$ for a 10 g sample). The instrument is used to calculate concentration of magnetic mineral.

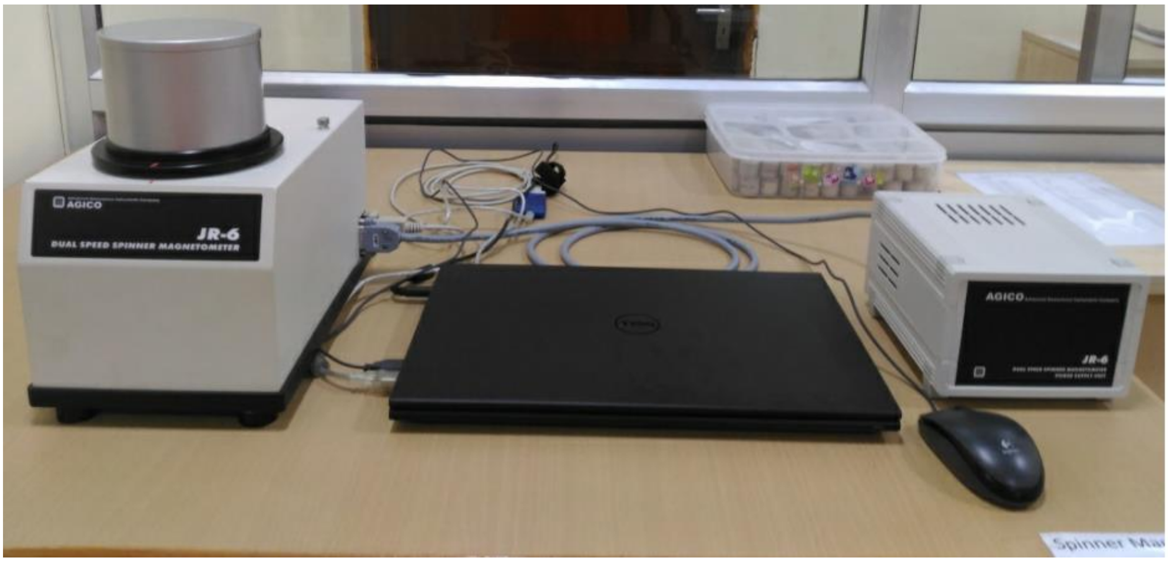

Figure 3.5 AGICO JR-6 Spinner Magnetometer (JR-6 Dual Speed Spinner Magnetometer) Measurement over 11 magnitudes (10^6 - 10^4 A/m).

Figure 3.6 ASC Scientific D2000 Alternating Field Demagnetizer.

PALYNOLOGY

Vegetation plays a critical role in the Earth's climate through its effects on surface albedo (Mykleby et al., 2017), atmospheric aerosol (Jin and Wang 2018) and greenhouse gas composition and global carbon cycle (Piao et al., 2009). As a result, vegetation and ecosystems are extremely sensitive to climate change. Pollen grains and spores, abundantly produced by the plants, get preserved in the sedimentary environments and serve as important proxy evidence for palaeovegetation and palaeoclimate reconstructions (Faegri and Iversen, 1964; Sun and Wu, 1987; Gasse et al., 1991; Gunnell, 1997; Bonnefille et al., 1999; Chen et al., 2006; Quamar, 2019; Quamar et al., 2017; Quamar and Bera, 2017; Kar and Quamar, 2019 and references cited therein).

Extraction of the palynomorphs, especially pollen and spores, from the sediment samples followed the conventional method proposed by Erdtman (1943). Chemical treatments comprise treatment of about 10 g of each sediment sample with 10% KOH solution to remove the hummus and also to deflocculated the pollen and spores and thereafter with 40% HF solution to dissolve the silica. Subsequently, the samples were processed with an acetolysis mixture, comprising the acetic anhydride ($C_4H_6O_3$) and concentrated sulphuric acid (H_2SO_4) in the ratio of 9: 1, respectively, to remove pollen kit, protoplasm and other cellulosic materials. Five ml of 50% glycerine solution was added to the treated substrate residues, and kept in vials, for microscopic examination and further storage. In addition, two ml of phenol was also added to avoid any post-maceration microbial contamination.

Counting of pollen and spores was carried out under a transmitted light microscope (Olympus BX50) with attached DP 26 software for photography, using an X40 objective lens at the Quaternary Palynology Laboratory of the Birbal Sahni Institute of Palaeosciences, Lucknow. The published reference materials (Mao et al., 2012, Pandey et al., 2014; Quamar and Chauhan, 2012; Quamar and Bera, 2017; Quamar and Kar, 2020, Rao et al., 2020 and references cited therein) were utilized for the identification of the recovered palynomorphs under the microscope (Pollen plates 1 and 2).

RADIOCARBON DATING/ CHRONOLOGY

Carbon dating is an extremely important tool to work out the palaeoclimate and palaeoenvironmental events. The carbon-14 dating could be a method to work out the estimated age of carbon-based materials derived from the living organism. There are mainly two sorts of carbon which are used for dating i.e., organic and inorganic $CaCO_3$ (Calcium Carbonate). It will be measured by calculating the quantity of carbon-14 in a sample. the fundamental concept behind the radiocarbon is so far the carbon isotope (Carbon- 14). Radiocarbon is extremely unstable and weakly radioactive whereas Carbon 12 and Carbon 13 are stable isotopes. The formation of C could be a continuous process within the upper atmosphere by the effect of ionizing radiation neutron on Nitrogen 14 atom which rapidly oxidised to greenhouse gas which successively becomes a part of the global carbon cycle. The plant and animal respirate dioxide after they die the carbon exchange stops and the radioactive carbon starts disintegrating. The measurement of this radioactive carbon is decided by law of decay. carbon dating is basically a way designed to live residual radioactivity (Figure 3.7).

Accelerator mass spectrometry (AMS) may be a modern dating method that's considered to be the more efficient thanks to measuring the radiocarbon content of a sample. During this method, the radiocarbon content is directly measured relative to the carbon 12 and carbon 13 present. The strategy doesn't count beta particles, but the number of carbon atoms present within the sample and therefore the proportion of the isotopes. Not all materials are radiocarbon dated. Mostly all the chemical compound is dateable and inorganic carbon involves the shell which is carbonate. The shell aragonite is additionally dateable as long as it is in equilibrium with the atmospheric radiocarbon.

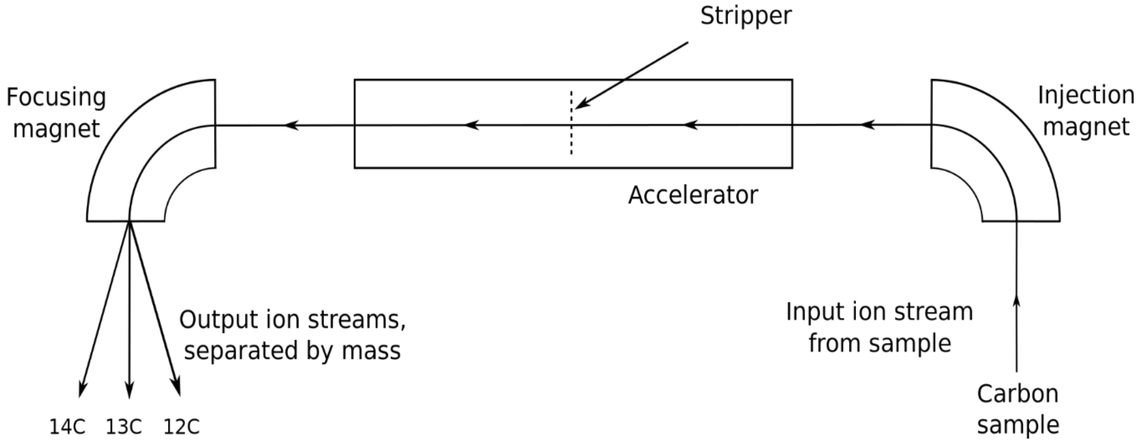

Figure 3.7 Demonstration of a complete working model of Accelerator mass spectroscopy used for radiocarbon dating.

The fabric is converted into graphite and is created to emit C- ions (carbon atoms with one negative charge) then it's loaded into the accelerator. The accelerated ions are made to pass through the stripper which removes the electron which carries an electric charge and therefore leaves ions with an electric charge (Figure 3.7). The ions, which can have from 1 to 4 positive charges (C+ to C4+), betting on the accelerator design, are then seasoned with a magnet that curves their path; the heavier ions are curved but the lighter ones, that the different isotopes emerge as separate streams of ions. A particle detector which records the number of ions is recorded in the C14 stream and counts are determined by measuring the electrical current created by the Faraday cup.

The calculations to be performed on the measurements taken rely upon the technology used since beta counters measure the sample's radioactivity whereas AMS determines the ratio of the three different carbon isotopes within the sample. to work out the age of a sample whose activity has been measured by beta counting, the ratio of its activity to the activity of the quality must be found. To work out this, a blank sample (of old, or dead, carbon) is measured, and a sample of known activity is measured.