Chapter - 2

Methodologies

To achieve the goals of this study several field and laboratory methods were employed. Field studies and collection of appropriate samples for various experimental studies were a key component of this work. Field studies were also aimed at establishing accurate stratigraphy of the sampled horizons. Experimental studies included geochronology, trace element geochemistry and isotope geochemistry. Since each chapter hereafter contains some details of the experimental data and these analytical methods are established techniques, only brief descriptions of each of the methods are given here with appropriate referencing.

2.1 Field studies

Strategic sampling was integral part of this work. The collection of the Quaternary sediment samples is tricky as the older sediment horizons are buried below the present day alluvium in most of the cases. For the current study, we have made our sampling strategy at the initial stages, based on the existing reports and satellite imageries which delineate the palaeo-drainages. During the course of the work we further explored the terrains with several field works and sampled new sediment horizons. The sampling was done during the period of 2013-2016 in several field works. The field areas included the Ghaggar floodplain, the Luni alluvium, the Thar desert, the Great Rann of Kachchh and the Aravalli mountain ranges. Sampling was mainly done from exposed cliff sections/terraces, pits, trenches made at field, bore holes, wells and dune fields. The detailed sampling locations and lithologs are presented in the subsequent chapters.

Before venturing into the provenance studies establishment of a proper stratigraphy is of utmost importance. The problem with the Late Quaternary sediment deposits especially those associated with fluvial systems is that they are spatially not continuous. Due to the highly dynamic character of the fluvial and aeolian environments and discontinuities in depositions, the events happening in a particular time period are not preserved in every location of these terrains. The events are preserved in pieces, all along the alluvium. Things become more complex in cases of buried paleo-fluvial systems (eg. the Ghaggar alluvium) where the present day surficial deposits cover the older horizons. Therefore, during the present work we have covered larger areas and several locations in particular alluviums for sampling. While doing so, we have emphasised on establishing the field relation between various sedimentary facies based on stratigraphic principles. The depths of occurrence of different sedimentary facies are noted properly for preparing the lithologs. The details of the field co-relations and lithologs are discussed in subsequent chapters. The stratigraphy was further established with the help of C-14 and Optically Stimulated Luminescence (OSL) dating of different sediment horizons. For sampling the Thar desert sand we have taken several traverses across the desert.

2.2 Pre-treatment of samples before analysis

Various methodologies were used to generate analytical data for chronology and geochemistry, for achieving the objectives of the current work. Care was taken to avoid any type of contamination during the analyses. Prior to analysis all the collected samples have gone through several cleaning/pre-treatment procedures as follows:

- First the samples were grinded to very fine powder for homogenization and further processing.
- Samples were then washed with MILLI-Q water multiple times to remove salt and then dried at 110°C. The samples were then re-homogenized using agate mortar.
- Powdered samples were then heated at 650°C for 2 h to remove organic matter and leached in dilute HCl to remove carbonates.
- For all the geochemical and isotopic analyses we have used the silicate fractions only.
- For separation of various grains sizes we have passed the non-powdered samples through different sieves of required diameters. To separate the clay and silt sized fractions from the rest we used gravity separation technique. Once the desired grain size fraction is separated, it is treated following the above mentioned procedure before further chemical analysis.
- The decarbonated, homogenized powdered samples were then dissolved using standard HF-HNO_3 silicate dissolution procedure. The details are discussed in the subsequent sections of this chapter.

2.3 Geochronology

2.3.1 C-14 dating

In the arid to semi-arid climate of the western India, preservation of organic carbon within the sandy sediments is rare. We have focussed on collecting mollusc shells (bivalves and gastropods) buried along with the sediments for C-14 dating which can give a constrain to the sediment depositional ages. The mollusc samples collected for the C-14 dating were pre-cleaned with Milli-Q. Then the shells were soaked in H_2O_2 to remove any organic matter. Followed by it the shells were soaked in 0.1N HCl for a very short period to remove the outermost altered layer. For the AMS dating samples were drilled from the umbo region of the shells (generally least altered) using a micro-drill. Also, bulk sediments containing abundant foraminifera shells from the Great Ran of Kachchh, have been analysed for dating using conventional C-14 dating.

Radiocarbon dating was carried out on bivalve samples from Anupgarh region and inorganic carbonates of bulk sediments from Khadir island, to determine their ages by the conventional β-counting method at the PRL, Ahmedabad. 10 gm of powdered fresh bivalve sample was taken in an evacuated flask and reacted with Orthophosphoric acid. For the bulk sediments larger amount of sample was taken and then reacted with Orthophosphoric acid. The emitting carbon dioxide generated by the reaction was then converted to benzene. Then, its C-14 activity was measured using a liquid scintillation counter (Quantulus 1220). Radiocarbon dating was carried out by liquid scintillation spectrometry method at the PRL following procedures described in Yadava and Ramesh (1999). The half-life used for the conventional C-14 dating is 5730 years. Average $\delta^{13}C$ value used for fractionation correction for the foram bearing bulk sediments was 1.0 $^{0}/_{00}$ with respect to V-PDB. For the bivalve samples collected from the fluvial sands of the Ghaggar alluvium $\delta^{13}C_{PDB}$ was considered to be -10 $^{0}/_{00.}$

Further, for more precise dating of the bivalve samples, AMS C-14 dating was carried out at Centro Nacional de Aceleradores (CNA), Spain. The C-14 dates have been calibrated using INTCAL 13 curve of Reimer et al., (2013).

2.3.2 Optically Stimulated Luminescence (OSL) dating

Optically stimulated luminescence dating is a method to determine the depositional age of buried sediment horizons. It is considered that the geological luminescence reduces to a zero or near zero value due to sunlight exposure during the sediment transport (Aitken, 1998; Singhvi et al., 2001). Post burial the luminescence signal starts accumulating due to the ambient radioactivity and continues until the sediment is excavated. The luminescence level in a sample is proportional to the burial time and the concentration of the radioactivity in the sample environment, with a presumption that the rate of irradiation is generally constant. The sediment samples were collected from freshly cleaned up sections using specially designed aluminium pipes (Chandel et al., 2006). At the laboratory, all samples were processed in subdued red light conditions. The 90 – 125μm grain-size fraction was used for dating, after treatment with hydrochloric acid and hydrogen peroxide to remove carbonates and organic matter, respectively. Magnetic separation was carried out to isolate the quartz grains, and the resulting material was etched using hydrofluoric acid to remove the alpha-irradiated outer surface of the quartz grains and remove any non-quartz minerals still present. Using the Single Aliquot Regeneration (SAR) protocol proposed by Murray and Wintle (2000) the OSL dating of the separated quartz grains was done. The paleodose (De) measurements for age calculations were based on a weighted mean of values in the region defined by the minimum value and the minimum value + (2σ) (Juyal et al., 2006).

2.3.3 Ar-Ar dating of Detrital Muscovite

About 200 mg of muscovites are separated by handpicking from pre-cleaned sediments (grain size > 250 mm) was packed in aluminium capsules and irradiated in the DHRUVA reactor at BARC, Mumbai, for ~120 h. The Minnesota hornblende reference material (MMhb-1) of age 523.1 ± 2.6 Ma (Renne et al., 1998) was used as the flux monitor and high-purity CaF_2 and K_2SO_4 salts for interference corrections arising from the production of Ar from Ca and K isotopes (Pande et al., 2017). Argon was extracted by incremental heating between 750°C and 1400°C at steps of 50°C and isotopic ratios were measured in a Thermo Fisher ARGUS-VI multi-collector mass spectrometer at the National Facility in the Department of Earth Sciences, IIT Bombay, India (Ray et al., 2005). Plateau and isochron ages were calculated and plotted using the software ISOPLOT 2.49 (Ludwig, 2000). The Fisc

Canyan Sanidine (26.27-28.29 Ma) standard was used as an unknown sample and it gave an age of 28.24 Ma.

2.4 Trace element analysis

All the trace element concentrations including Rare Earth Elements (REEs) were measured on silicate fractions of bulk sediments using Thermo X-Series 2 Q-ICPMS facility, at Geosciences Division, of Physical Research Laboratory (PRL), India. The set-up, installation and calibration for routine measurement of rock samples were carried out during research activity (Ray et al., 2008). 50-60 mg of decarbonated samples were then dissolved using a combination of ultrapure HF and HNO_3 (2:1) acid mixture (Acids were from Seastar Chemicals®) in a Savillex Teflon vial. The sample was further treated with 8N HNO_3. Finally, a stock sample solution (~50 ml) was prepared using 2% HNO_3 with ~1000 dilution factor. An international rock standard from USGS, BHVO-2 was used to check the accuracy and precision of analyses. Several aliquots of BHVO-2 were digested and analysed as unknowns. Blank solutions and various dilutions of BHVO-2 were used to generate Calibration curves. Reproducibility of trace element contents, based on repeated analyses of the standard, was ≤3% for REEs and ≤6% for all other trace elements at 2σ level. Table 2.1 represents the BHVO-2 values from this study and the recommended values.

Table 2.1 Trace element data for BHVO-2 Standard. Concentrations are in ppm. Reproducibility (2σ): REE ≤ 3%; others ≤ 6%. Reported values for BHVO-2 are from Jochum et al. (2005).

Sample	BHVO-2 (Reported)	2σ	BHVO-2 (Measured)
Cs	0.1	0.1	0.12
Rb	9.11	0.04	10.3
Ba	131	1	130
Th	1.22	0.06	1.1
U	0.403	0.001	0.42
Nb	18.1	1	17
Ta	1.14	0.006	0.95
La	15.2	0.1	15
Ce	37.5	0.2	39
Pb	1.6	0.3	1.2
Pr	5.35	0.17	5.2

Sr	396	1	388
Nd	24.5	0.1	24
Zr	172	11	163
Hf	4.36	0.14	3.9
Sm	6.07	0.01	5.9
Eu	2.07	0.02	2
Gd	6.24	0.03	6.1
Tb	0.92	0.03	0.84
Dy	5.31	0.02	5.2
Y	26	2	23.4
Ho	0.98	0.04	0.89
Er	2.54	0.01	2.5
Tm	0.33	0.01	0.3
Yb	2	0.01	1.9
Lu	0.274	0.005	0.26

2.5 Analysis of Radiogenic Isotopes

The chemical procedures for the separation of Sr and Nd from samples and associated mass spectrometric analyses on Thermal Ionisation Mass Spectrometer (TIMS) and Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) are mentioned only briefly in this section as they were based on already established routine procedures of our laboratory.

In Sr-Nd isotope analyses, decarbonated sediment samples were dissolved using the standard HF-HNO_3-HCl dissolution procedure for silicate rocks, as discussed in the earlier section. Separation of Sr was done by conventional cation exchange column chemistry (Resin AG® 50W-X8, 200-400 mesh size) and Nd was separated from other REEs using Ln-specific resin from Eichrom® with dilute HCl (0.18N) as elutant (Awasthi et al., 2014; Dickin, 2000). In case of Sr isotopic measurements of the mollusc shells, ~50mg of sample was dissolved using HCl and then was passed through Eichrom Sr-specific resin. The Sr was collected with Milli-Q elutant. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ were measured in static multicollection mode on an Isoprobe-T thermal ionization mass spectrometer (TIMS) and Thermo Neptune Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) respectively, at the PRL, Ahmedabad (Awasthi et al., 2014). Sr samples were loaded with 0.1 M phosphoric acid on pre-degassed, oxidized single Ta filaments while Nd samples were loaded on the outer Ta filaments of triple (Ta-Re-Ta) filament arrangements for the TIMS measurements.

The measured isotopic ratios were corrected for fractionation using $^{86}Sr/^{88}Sr$ = 0.1194 and $^{146}Nd/^{144}Nd$ = 0.7219, respectively. The average values for NBS987 and JNdi measured on TIMS over a period of 5 years are $^{87}Sr/^{86}Sr$ = 0.71023 ± 0.00001 (n = 70) and $^{143}Nd/^{144}Nd$ = 0.512104 ± 0.000004 (n = 60; ±0.1 in εNd units) at 2σ level of uncertainty. The value of $^{143}Nd/^{144}Nd$ = 0.512104 for JNdi corresponds to a value of 0.511847 for the widely used La Jolla Nd standard (Tanaka et al., 2000). USGS standard BHVO-2 was analysed for $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ during the course of the analyses regularly with each set of samples. $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ for BHVO-2 measured gave values of 0.70346 ± 0.00004 and 0.512967 ± 0.000008 (n = 10; ±0.2 in εNd units at 2σ) respectively, which are same as the reported values of 0.70344 ± 0.00003 and 0.51296 ± 0.00004 within 2σ (Raczek et al., 2001). To compare our data with that from literature, all the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were normalized to 0.71025 for NBS987 and 0.511858 for La Jolla, respectively. The average $^{143}Nd/^{144}Nd$ of the in-house lab standard, Merck Nd solution, was 0.511705±27 (2σ, n=56) for the MC-ICPMS measurements. The sample data were normalized using its reported $^{143}Nd/^{144}Nd$ ratio of 0.511734, which is equivalent to La Jolla $^{143}Nd/^{144}Nd$ ratio of 0.511858 (Yang et al., 2011). BHVO-2 yielded $^{143}Nd/^{144}Nd$ ratio of 0.512971±18 (2σ, n=19), which is within the reported $^{143}Nd/^{144}Nd$ ratio of 0.512979±28 (2σ), (Jochum et al., 2005). All plots and discussion in this work are based on the normalized ratios. $^{143}Nd/^{144}Nd$ ratios in this work are presented as ε_{Nd}. It is defined as, $\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd)_{sample}/ (^{143}Nd/^{144}Nd)_{Chondrite} - 1] \times 10^4$. The present day $(^{143}Nd/^{144}Nd)_{Chondrite}$ value is considered to be 0.512638.