Chapter – II

Methodologies

This chapter gives a brief account of the sample preparation methods and various analytical techniques used in the present work. The experimental techniques described below are well established protocols, and are carried out routinely in our laboratory. Details of the field works, sampling locations, and descriptions of the samples used in this study from both the Marwar and Chhattisgarh basins are given in chapters 3 and 4, respectively. All geochemical analyses were carried out at Physical Research Laboratory, Ahmedabad.

2.1 Field studies

Extensive field studies and sampling covering the entire basins were vital part of this work. Multiple traverses across the basins were taken to sample most of the formations. Samples from Marwar basin were collected on field trips carried out during January and March 2014, November 2015, and March 2017. The carbonate sampling was carried out in various limestone mines. High resolution sampling was done in vertical profiles from top to the bottom of the formations at 5-10 cm intervals. Siliciclastics were sampled in and around Jodhpur, Nagaur, and Dulmera localities in Rajasthan. The probable source rocks for fingerprinting the provenance were samples along the Aravalli Mountain range during July 2015. Similar strategy was followed for the sampling of Chhattisgarh basin too in an extensive field trip during February 2015.

2.2 Preparation of samples

In order to sample the unaltered/least altered components of the limestone/dolostone samples, both petrographic and geochemical techniques were employed. Rectangular slabs of selected samples were cut, and a thin section and a polished thick section were prepared from each slab so that one mirrored the other. Thin sections were stained using freshly prepared mixture of Potassium Ferricyanide and Alizarine Red S as prescribed by Dickson, (1965) for identification of various carbonate minerals. Micrite/microsparite components were identified under plane polarized light in thin sections and samples for geochemical analyses were micro-drilled from the mirror image polished thick sections using carbide dental drill bits. Carbonate samples that lacked multiple components were micro-drilled directly from the hand specimens.

Fresh chips of the siliciclastic samples were cleaned using distilled water, and were finely powdered in a tungsten carbide vibratory disc mill. The powdered siliciclastics were decarbonated using dilute HCl and washed multiple times using MilliQ to remove any leftover acid. They were dried at 110 ^{o}C, homogenized in an agate mortar and were further heated at 650 ^{o}C for two hours in silica crucibles to remove organic matter before geochemical analyses. Same procedure was followed to separate the silicate fraction from the siliceous limestone samples. The calcareous volcaniclastics were decarbonated using dilute HCl and only the silicate fraction was analysed. Igneous and metamorphic rocks studied for geochronology and/or source compositions were powdered in large quantities for thorough homogenization so as to avoid mineralogical bias.

2.3 Stable carbon and oxygen isotope analyses

Stable C and O isotopic ratio analyses of the carbonate samples were carried out in a Thermo MAT 253 isotope ratio mass spectrometer. CO_2 was extracted using Kiel IV Carbonate Device, after reaction with 100% orthophosphoric acid at 72^{0}C. The CO_2 masses 44, 45 and 46 were measured with respect to a laboratory reference CO_2 in dual inlet mode. A lab standard of known isotopic composition (MAKMARB- Makrana marble standard) was measured after every ten samples to calibrate the reference CO_2. $\delta^{13}C$ and $\delta^{18}O$ were calculated from the $\delta^{46}CO_2$ and $\delta^{45}CO_2$ using Craig correction (Brand et al., 2010; Craig, 1957). The mean value based on repeated analyses of the international standard NBS-19 and the internal standard MAKMARB carried out over a period of three years are given in Table 2.1.

Table 2.1: Comparison between the measured and recommended values of carbonate standards

	$\delta^{13}C_{VPDB}$‰	1σ	$\delta^{18}O_{VPDB}$‰	1σ
MAKMARB (Lab Standard)				
Measured Value (n=13)	3.96	0.07	-10.58	0.15
Recommended Value	3.9	0.1	-10.7	0.2
NBS-19 (International Standard)				
Measured Value (n=13)	2.02	0.10	-2.20	0.12
Recommended Value	1.95		-2.20	

2.4 Major and trace element analyses

Ca, Mn, Mg and Sr contents of the carbonate samples and trace element contents of the siliciclastics were analysed using a Thermo Element X Series 2 Quadrupole-ICPMS. About 6 mg of micro-drilled limestone/dolostone samples were dissolved and further diluted using 2% HNO_3. The measurements were carried out using COQ-1, a carbonatite standard from USGS, as a calibration standard. COQ-1 was also run as an unknown for accuracy and precision checks. The details of the COQ-1 are given in Table 2.2. External reproducibility was better than 5% at 2σ level based on repeated analyses of COQ-1.

Table 2.2: Comparison between measured and recommended values of COQ-1

	Measured Value (n=9)	1σ	Recommended Value
Ca	340756	6043	345200
Mg	7366	294	7237
Mn	3305	58	3330
Sr	11696	257	12000

Note: Concentrations are in ppm. Recommended values are from USGS.

About 50 mg of a decarbonated siliciclastic samples was dissolved using conventional HF-HNO_3 acid dissolution protocol and diluted using 2% HNO_3 for trace element analyses. Concentrations of trace elements (including REEs) were measured using BHVO-2 rock standard (from USGS) as a calibration standard. BHVO-2 was also used as an unknown for accuracy and precision checks. The data for BHVO-2 are given in Table 2.3. The external reproducibility, based on repeated runs of BHVO-2, was better than 3% for REE and 8% for other trace elements at 2σ level. Machine drift was corrected using 10 ppb solution of Ga, In and Bi as internal standards.

Table 2.3: Comparison between the measured and recommended values of BHVO-2

	Measured Value (n=8)	1σ	Recommended Value	1σ
Sc	32	1	32	1
V	314	8	317	11
Cr	275	5	280	19
Co	45	1	45	3
Ni	118	2	119	7
Rb	9.23	0.47	9.11	0.04

Sr	391	9	396	1
Y	26	1	26	2
Zr	170	5	172	11
Nb	17.7	1	18.1	1
Cs	0.10	0.01	0.1	0.01
Ba	130	2	131	1
La	15.1	0.2	15.2	0.1
Ce	37.2	0.6	37.5	0.2
Pr	5.32	0.07	5.35	0.17
Nd	24.4	0.4	24.5	0.1
Sm	6.06	0.11	6.07	0.01
Eu	2.05	0.034	2.07	0.002
Gd	6.24	0.15	6.24	0.03
Tb	0.91	0.01	0.92	0.03
Dy	5.30	0.11	5.31	0.02
Ho	0.97	0.01	0.98	0.04
Er	2.53	0.07	2.54	0.01
Tm	0.32	0.01	0.33	0.01
Yb	2.0	0.03	2	0.01
Lu	0.270	0.009	0.274	0.005
Hf	4.29	0.11	4.36	0.14
Ta	1.08	0.08	1.14	0.06
Pb	1.6	0.1	1.6	0.3
Th	1.19	0.04	1.22	0.06
U	0.400	0.021	0.403	0.001

Note: Concentrations are in ppm. Recommended values are from Jochum et al., (2005)

2.5 Analyses of Sr and Nd isotopic ratios

The micro-drilled limestone/dolostone samples were pre-leached using dilute CH_3COOH and the leachates were discarded to avoid the contribution of radiogenic Sr from exchangeable sites and secondary carbonate overgrowths. They were leached further using 10% CH_3COOH. Care was taken to avoid the complete dissolution of the samples to ensure no contribution of Sr from the silicate impurities. Sr was separated by means of column chromatography using Sr-specific resin from Eichrom with H_2O as elutant. The details of the procedure are given in Ray et al. (2003).

About 50 mg of a decarbonated siliciclastic samples was dissolved using conventional HF-HNO_3-HCl protocol for Sr and Nd isotope ratio analyses. Sr was separated from other elements by means of conventional cation exchange column chromatography using AG 50W-

X8 resin (200-400 mesh) with 2N HCl as elutant and Nd was separated from other REE's by column chemistry using Ln-specific resin from Eichrom with 0.18N HCl as elutant.

^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd were measured on an Isoprobe-T TIMS and a Thermo Neptune MC-ICPMS, respectively, in static multi-collection modes. Sr was loaded on degassed and oxidized single Ta filament over 0.1M H_3PO_4 for TIMS. Isotopic ratios were corrected for mass fractionation using ^{86}Sr/^{88}Sr ratio of 0.1194 and ^{146}Nd/^{144}Nd ratio of 0.7219. The average ^{87}Sr/^{86}Sr ratio of international standard NBS 987 measured on TIMS over a period of 4 years is 0.71023±0.00001 (2σ, n=50). The average ^{143}Nd/^{144}Nd of the in-house lab standard, Merck Nd solution, was 0.511705±0.000027 (2σ, n=56). 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). International standard BHVO-2 yielded ^{87}Sr/^{86}Sr value 0.703471±0.000039 (2σ, n=3) and ^{143}Nd/^{144}Nd of 0.512971±0.000018 (2σ, n=19), which is within the recommended ^{87}Sr/^{86}Sr value 0.703478±0.000068 (2σ) and ^{143}Nd/^{144}Nd of 0.512979±0.000028 (2σ), (Jochum et al., 2005). The total procedural blank for Sr was <200 pg and that for Nd was <500 pg.