CARBON 13 AND OXYGEN 18 ISOTOPE RECORD OF THE EARLY EOCENE NAMMAL FORMATION, SALT RANGE, PAKISTAN

S. Ghazi, T. Hanif and Z. Sajid

Institute of Geology, Punjab University, Quaid-e-Azam Campus, Lahore-54590, Pakistan.
Corresponding Author E-mail ghazigeo6@gmail.com

ABSTRACT: The Nammal Formation is the lowermost unit of the Early Eocene succession in the Salt Range, Pakistan. It is well exposed throughout the Salt Range. The Nammal Formation having 30 to 35 meters thickness is predominantly composed of nodular limestone interbedded with marl and shale. The present study was focussed on stable carbon 13 and oxygen 18 isotopic analysis based on data from two stratigraphically importantsections. The samples from the Nilawahan section provided with the $\delta^{13}C$ values varied between 1.34 to -1.56‰ (VPDB) and values of $\delta^{18}O$ fluctuated between -4.47 to -6.59‰ (VPDB). Likewise the sample analysis of BadshahPur section exhibited that the $\delta^{13}C$ values changes from1.09 to -1.65‰ (VPDB) and $\delta^{18}O$ values rangefrom -4.17 to -6.85‰ (VPDB). The isotopic records of carbon 13 and oxygen 18 indicated the shallow marine deposition of the Nammal Formation under tropical conditions. It highlighted the palaeoclimatic and diagenetic conditions of the Nammal Formation at the time of deposition in the Salt Range region.

Key words: Early Eocene, Nammal Formation, Carbon13 and Oxygen18isotopes, Salt Range.

INTRODUCTION

Isotopic analysis of stable oxygen and carbon is of a particular importance in various geochemical techniques for the interpretation of sedimentary and diagenetic conditions and environments (Hudson, 1977; Anderson and Arthur, 1983; Marshall, 1992 and Corfield, 1995). Naturally abundant stable isotopes of oxygen (^{18}O and ^{16}O) and carbon (^{13}C and ^{12}C) are mostly used by means of their ratios, between samples the variations of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios are measured by high-precision mass spectrometry (Fairchild *et al*., 1988). The abundance of ^{18}O and ^{13}C in a sample is conventionally reported as the per mil (=mg/g or ‰) difference in delta (δ) notation ($\delta^{18}O$ and $\delta^{13}C$) between isotope ratios in the sample and those in the international Pee Dee Belemnite (PDB) standard which has $\delta^{18}O$ and $\delta^{13}C$ values of 0‰ (Hudson, 1977). Increasingly negative, or more depleted, δ values with respect to PDB imply a relative increase in the lighter isotopes (^{16}O, ^{12}C) while more positive, or enriched, values indicate a relative increase in the heavier isotopes (^{18}O, ^{13}C) (Nelson and Smith, 1996).

The δ ^{18}O values of a carbonate precipitated from water depends mainly on the δ ^{18}O salinity and temperature of the water (Nagarajan *et al*., 2008;Strasser*et al*., 2012). More negative values of the $\delta^{18}O$ are indicative of decreasing salinity and increasing temperature (Hudson, 1977). The $\delta^{13}C$ of a carbonate precipitated from water primarily reflects the source of biocarbonate dissolved in the waters (Hudson, 1977; lrwin *et al*., 1977; Coleman, 1993 and Mozley and Burns, 1993). Thus, in natural waters the carbonate precipitation at or near isotopic equilibrium tend to reflect characteristic range of $\delta^{18}O$ and $\delta^{13}C$ isotope values that shows, reasonably closely, their genetic environment (Nelson and Smith, 1996).

Stable carbon 13 and oxygen 18 isotopic analysis of the Nammal Formation has been carried out for the very first time from Nilawahan and Badshahpur sections in the Salt Range (Fig. 1). The aim of this study is to interpret the palaeoclimate of depositional environment and diagenetic conditionsof the Nammal Formation in the Tethys Sea and impact of global Palaeocene-Eocene thermal maxima on deposition of Early Eocene in Eastern Tethys.

The Nammal Formation is predominantly composed of well-bedded nodular limestone, shale, and marl. The limestone and marl have light-grey to bluish colour, while the shale is grey to olive-green in colour. The nodules of limestone are 10-12 cm in diameter and at places 16-20 cm. The lithological variations in the Nammal Formation divided it into four well defined unitsas follows; i) Alternate marl and limestone, ii) Well-bedded limestone with chert nodules iii) Limestone interbedded with shale iv) Dolomitic limestone.

The Nammal Formation has its lower contact with the Patala Formation which is recorded in coal mines (Fig. 2a). It has sharp and wavy upper contact with the Sakesar Limestone (Fig. 2b).A detailed lithological log of the Nammal Formation exposed in the Nilawahan and BadshahPur sections along with its chemostratigraphy is presented in Figures 3 and 4.

METHODOLOGY

Eighteen carbonate samples were collected from the Nilawahan and BadshahPur stratigraphic sections (Fig. 1)from Palaeocene-Eocene boundary (Nammal Formation lower contact with Patala Formation) to upper contact of the Nammal Formation with the Sakesar Limestone in the Salt Range for analysis of their ^{18}O and ^{13}C abundance.

The samples were processed at the Cornel University (New York, USA) Isotope Laboratory at Thermo Delta V isotope ratio mass-spectrometer (IRMS) interfaced with a Temperature Conversion Element Analyzer (TC/EA). Isotope results for ^{13}C are reported in delta (δ) notation as per mil (‰), with an accuracy of 0.31‰, deviations from the Vienna Pee Dee Belemnite (VPDB) reference standard and ^{18}O delta values are corrected for primary reference Vienna Standard Mean Oceanic Water (VSMOW). Summary statistics of the isotope data for the analyzed samples, from bottom to top in both sections, are given in Table 1.

RESULTS AND DISCUSSION

At Nilawahan section, in the lower part of the Nammal Formation (sample NN-1 to NN-3) the δ ^{13}C isotope ratios varies from -1.56‰ (VPDB) to -1.06‰ (VPDB) and δ ^{18}O isotope ratios fluctuates from -6.59‰ (VPDB) or 24.13‰ (SMOW) to -5.93‰ (VPDB) or 24.75‰ (SMOW) while from sample NN-4, the δ ^{13}C values suddenly changed from negative to positive values. Sample numbers NN-4 to NN-5 the δ ^{13}C showed variation in isotope ratios from 1.00‰ (VPDB) to higher positive values of 1.34‰ (VPDB) and δ ^{18}O isotope ratios decreased in negative values from -5.85‰ (VPDB) to -4.65‰ (VPDB) or 24.89‰ (SMOW) to 26.12‰ (SMOW). In the middle parts of the formation (from NN-6 to NN-8) the δ ^{13}C isotope ratios decreased in positive values from 1.02‰ (VPDB) to 0.99‰ (VPDB) and δ ^{18}O isotope ratios increases in negative values from -4.91‰ (VPDB) or 25.86‰ (SMOW) to -5.11‰ (VPDB) or 25.60‰ (SMOW).Towards the top of the formation(from NN-9 to NN-10), the δ ^{13}C isotope ratios followed the same positive trend and decreased in positive values from 0.73‰ (VPDB) to 0.23‰ (VPDB) and δ ^{13}C isotope ratios also decreased from -5.36‰ (VPDB) or 25.39‰ (SMOW) to -4.47‰ (VPDB) or 26.31‰ (SMOW).

At BadshahPur section, sample BN-1 to BN-2the δ ^{13}C isotope ratios variedfrom negative value of -1.46‰ (VPDB) to -1.65‰ (VPDB) and δ ^{18}O isotope ratios varied from -6.49‰ (VPDB) or 24.23‰ (SMOW) to -6.85‰ (VPDB) or 23.85‰ (SMOW), upward in sample BN-3 decreased in negative value of -1.32‰ (VPDB) ofδ ^{13}C isotope ratios and also in δ ^{18}O isotope decreased to -5.62‰ (VPDB) or 25.13‰ (SMOW). In the middle part of the formation, like wise in Nilawahan section, the δ ^{13}C isotope ratios (sample BN-4 and BN-5) followed the same trend of positivevalues ranges between1.09‰ (VPDB) to 0.87‰ (VPDB) and δ ^{18}O isotope ratios varied from -4.55‰ (VPDB) to -5.10‰ (VPDB) or 26.23‰ (SMOW) to 25.66‰ (SMOW). Towards the top from sample BN-6 to BN-7 δ ^{13}C isotope ratios decreased from 0.21‰ (VPDB) to 0.00‰ (VPDB) and δ ^{18}O isotope ratios fluctuated from -4.34‰ (VPDB) or 26.42‰ (SMOW) to -4.17‰ (VPDB) or 26.62‰ (SMOW). After zero δ ^{13}C isotope ratios there is an increase in value to 0.43‰ (VPDB) and δ ^{18}O isotope ratios also increased in negative value of -5.01‰ (VPDB) or 25.75‰ (SMOW).

The negative or more depleted δ values with respect to PDB at the base of the Nammal Formation indicated a relative increase in the lighter isotopes (^{16}O, ^{12}C) (cf. Nelson and smith, 1996). Increase of δ ^{13}C values upward in the Nammal Formation could be related to reduced recycling of ^{12}C into the environment and accumulation in the Nammal marls with high organic content (Patterson and Walter, 1994; Immenhauser *et al*., 2003; Colombie *et al*., 2010;Strasser *et al*., 2012), marking the transgression phase. High and gradually increasing organic activity assimilated the inorganic carbon decreasing the overall concentration of CO_2 and hence raising the values of ^{13}C from lower boundary to upper boundary of Nammal Formation that was confirmed with increased concentrations of foraminifers fauna upwards in the Nammal Formation. The higher values showed high photosynthetic productivity that relatively depicted moderately warm conditions supporting life (Patterson and Walter, 1994; Immenhauser *et al*., 2003; Colombie*et al*., 2010; Strasser *et al*., 2012). In warm temperatures the solubility of CO_2 decreased resulting in higher values of ^{13}C. Relatively lower δ ^{13}C and more negative δ ^{18}O values in the start of Early Eocene was due to the short term effects of the PETM (Palaeocene-Eocene Thermal Maximum) and consistently increasing values showed a gradual increase in temperature in a warm climate. However experiments have shown that there was no linear relationship between temperature and δ ^{13}C values (Rau *et al*., 1989), but^{18}O values influenced the temperature. More the negative values of the ^{18}O, higher will be the temperature. Although greenhouse conditions prevailed during the Eocene (Zachos*et al*., 2001;Gingerich, 2006; Jahren, 2007; Hollis *et al*., 2009) and substantial faunal and floral changes occurred which were caused by the almost continuous global cooling that followed the Early Eocene Climatic Optimum (Zachos *et al*.,2001; Francis and Poole, 2002; Dupont *et al*., 2007). Most information about Eocene climate dynamics is still derived from the marine realm (Zachos *et al*., 2001). The results of this study have been plotted in a δ ^{13}C versusδ ^{18}O (Fig. 5) cross plot diagram (Hudson, 1977), in which plot of the Nammal Formation samples was in the fields of marine limestones. Lighter values of δ ^{18}O with its most negative value of -6.85‰ PDB indicated a temperature of about 50^{o}C inferred tropical environments at time of deposition of the Nammal Formation. Likewise in many tropical carbonate deposits, in this study the range of δ ^{18}O values in all samples was supportive of cementationunder shallow to moderate burial conditionsof shallow marine environments (Nagarajan*et al*., 2008;Swei and Tucker, 2012).

Table-1.Summary of statistics for ^{18}O and ^{13}C isotopes. Here sample ID denotes to the name of the sample, where N-N is for Nilawahan-Nammal samples and same as B-N for BadshahPur- Nammal samples. δ^{18}O vs. VSMOW is the corrected isotope delta value for ^{18}O measured against the primary reference Vienna Standard Mean Oceanic Water. δ^{13}C vs. VPDB is the corrected isotope delta value for ^{13}C measured against the reference standard Vienna Pee Dee Belemnite (VPDB).

Sections	Sample ID	δ^{13}C vs. VPDB	δ^{18}O VPDB	δ^{18}O VSMOW
Nilawahan	N-N-1	-1.56	-6.59	24.13
	N-N-2	-1.23	-6.27	24.45
	N-N-3	-1.06	-5.93	24.75
	N-N-4	1.00	-5.85	24.89
	N-N-5	1.34	-4.65	26.12
	N-N-6	1.02	-4.91	25.86
	N-N-7	0.56	-5.24	25.52
	N-N-8	0.99	-5.11	25.60
	N-N-9	0.73	-5.36	25.39
	N-N-10	0.23	-4.47	26.31
BashahPur	B-N-1	-1.46	-6.49	24.23
	B-N-2	-1.65	-6.85	23.85
	B-N-3	-1.32	-5.62	25.13
	B-N-4	1.09	-4.55	26.23
	B-N-5	0.87	-5.10	25.66
	B-N-6	0.21	-4.34	26.45
	B-N-7	0.00	-4.17	26.62
	B-N-8	0.43	-5.01	25.75

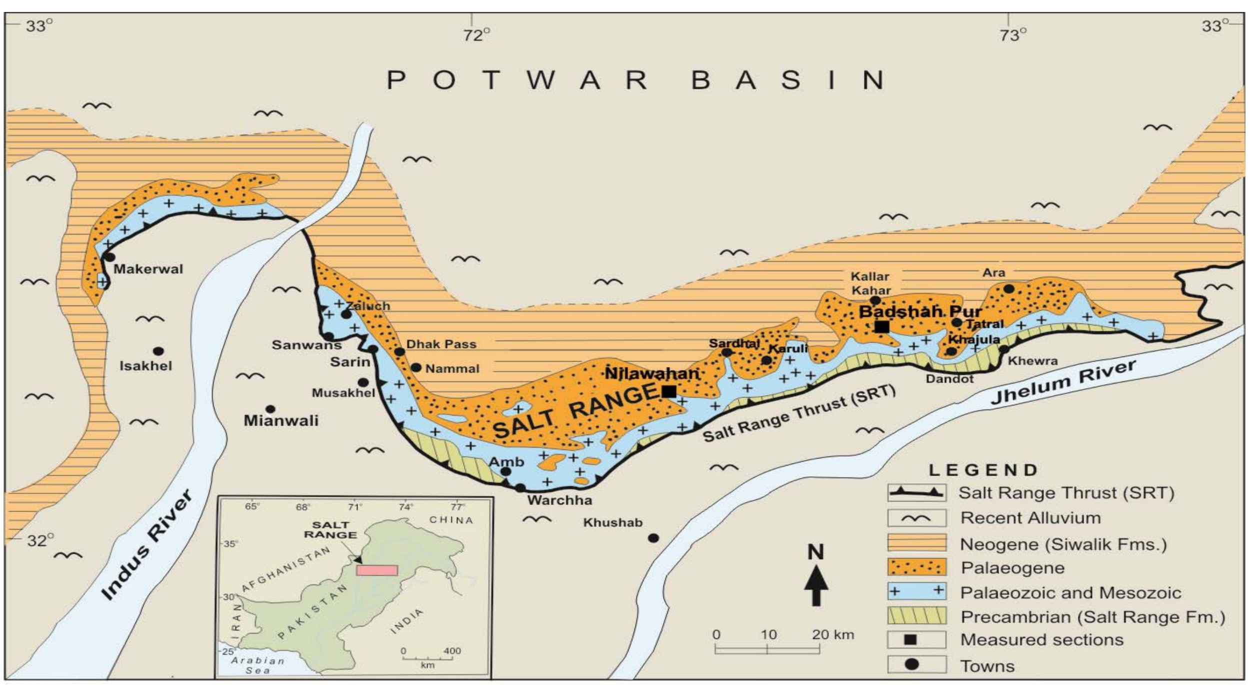

Fig-1. Location map of the study area, showing measured sections of the Nammal Formation, Salt Range, Pakistan.

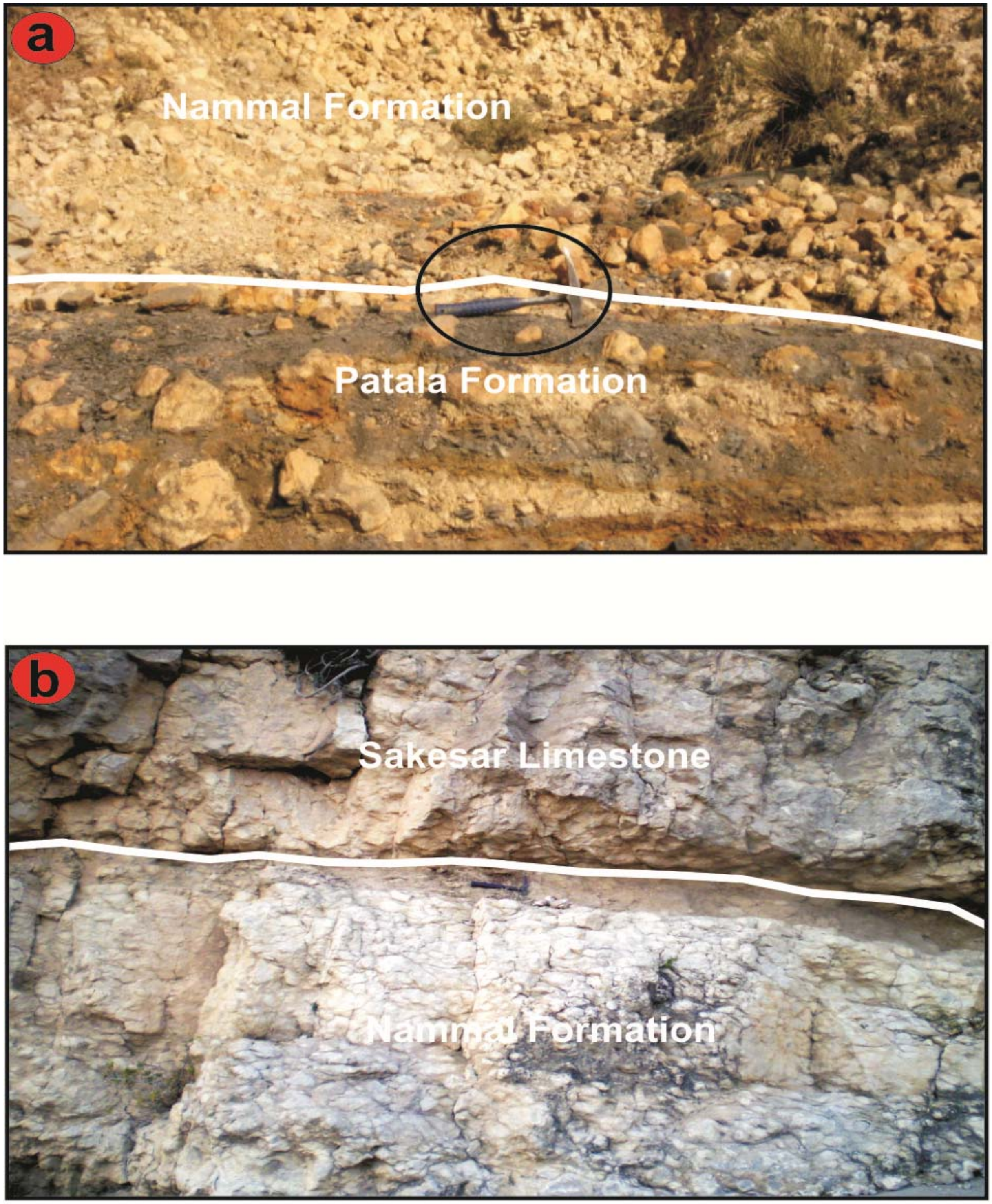

Fig-2. a) Outcrop exposure of the Nammal Formation showing its lower contact with the Patala Formation, Salt Range, Pakistan. b) Outcrop exposure of the Nammal Formation showing its upper contact with the Sakesar Limestone, Salt Range, Pakistan.

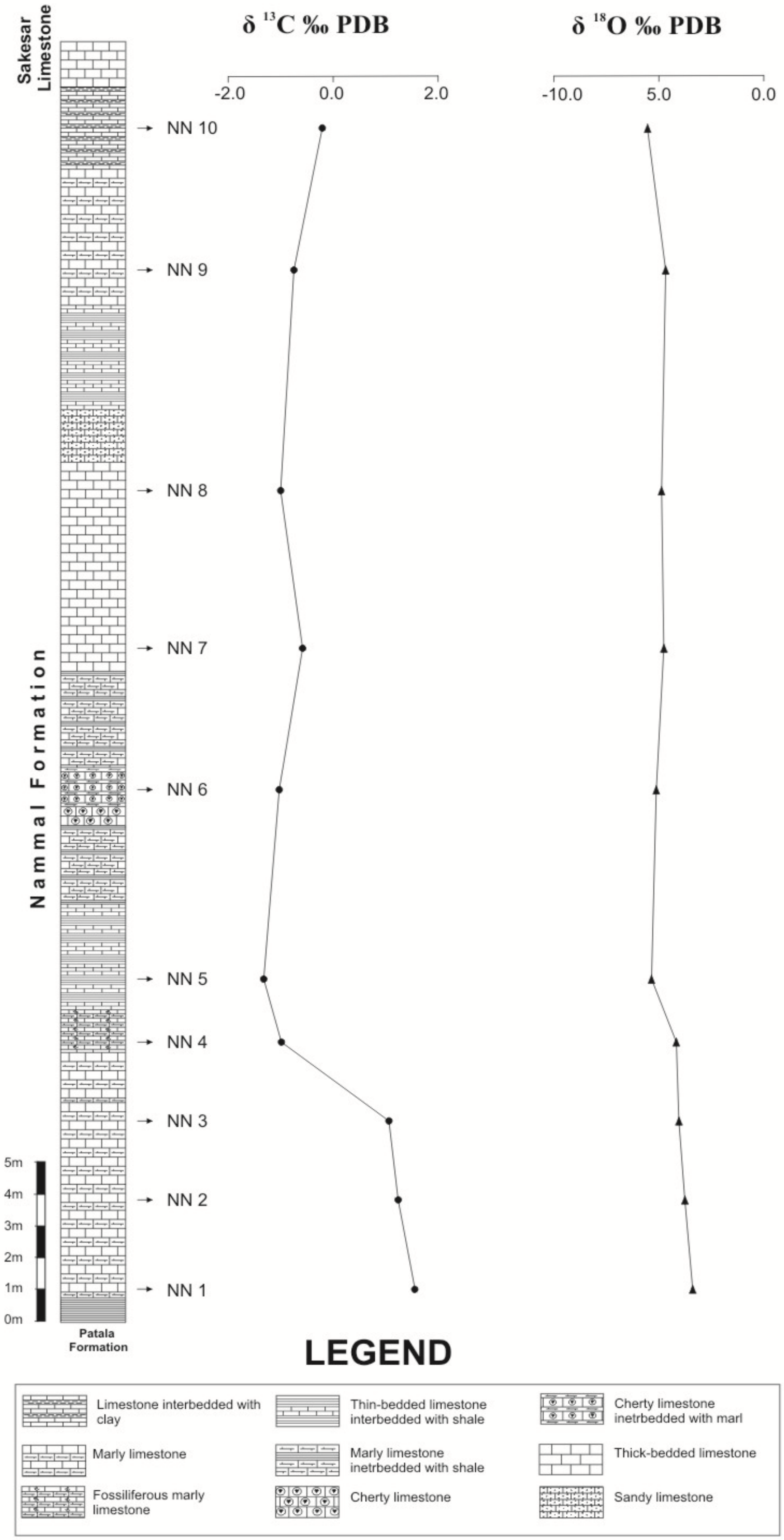

Fig-3.Carbon and oxygen isotope chemostratigraphy of the Nammal Formation from the Nilawahan section, Salt Range, Pakistan.

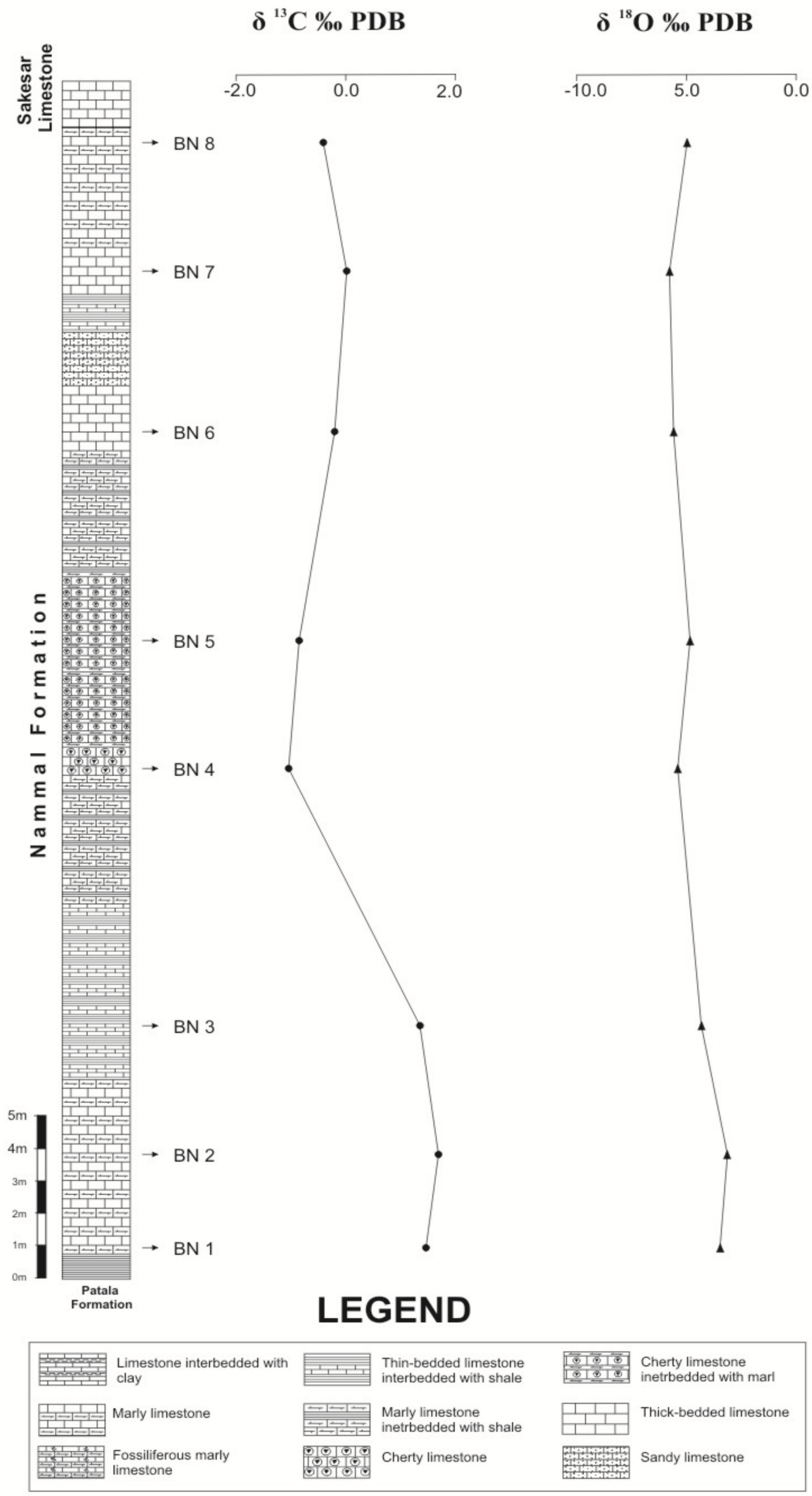

Fig-4.Carbon and oxygen isotope chemostratigraphy of the Nammal Formation from the BadshahPur section, Salt Range, Pakistan.

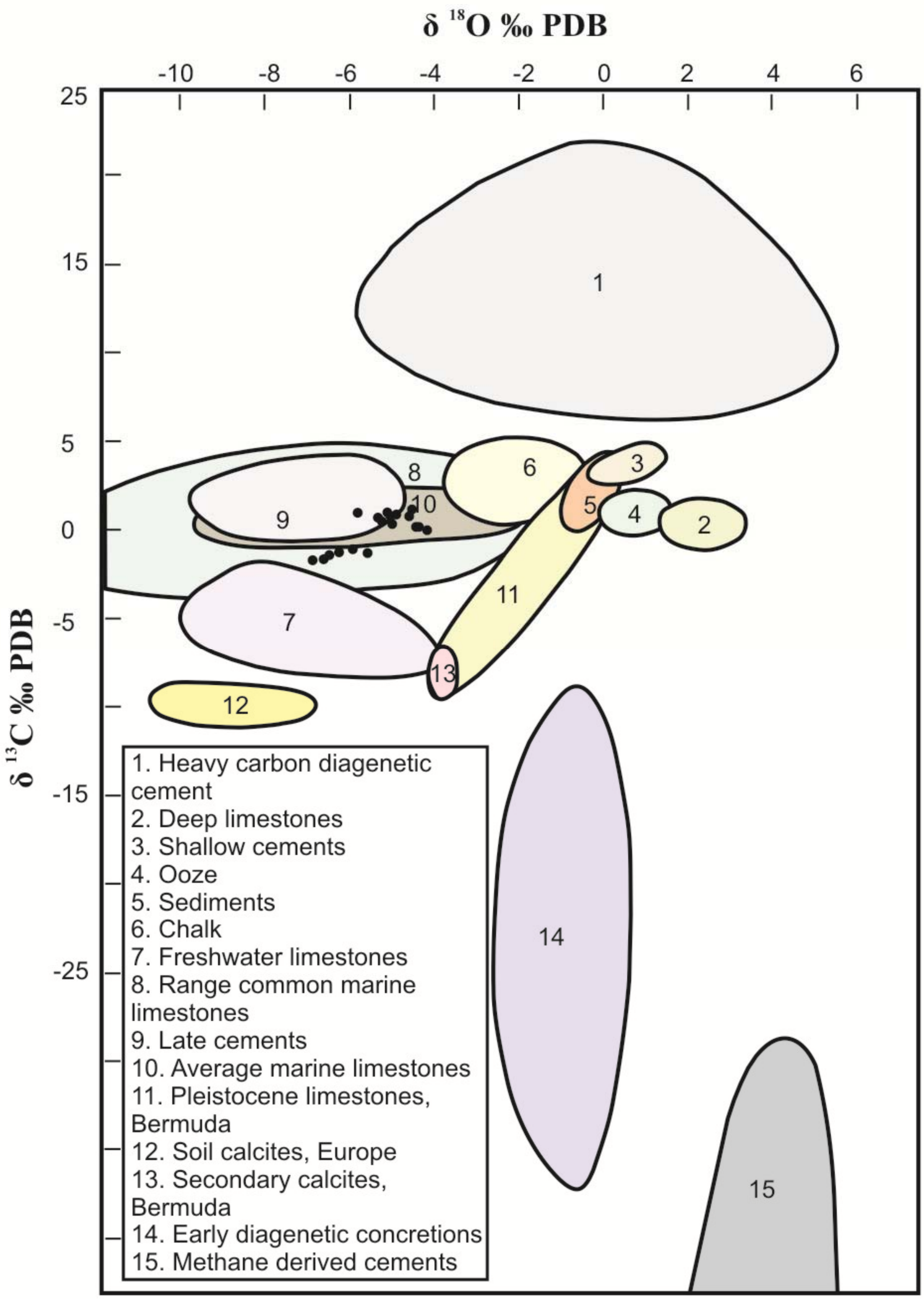

Fig-5.Plot of δ ^{13}C versus δ ^{18}O for the Nammal Formation along the different carbonate rocks proposed by Hudson (1977).

Conclusions: The oxygen and carbon isotope analysis from measured Nilawahan and BadshahPur stratigraphic sections revealed the carbonate sedimentation of the Nammal Formation under tropical conditions of shallow marine environments.

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