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Carbon Isotopic Profile Across the Bilara Group Rocks of Trans-Aravalli Marwar Supergroup in Western India: Implications for Neoproterozoic – Cambrian Transition

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Abstract

The rocks of Marwar Supergroup in the trans-Aravalli sector in western India are presumed to span the time interval between Neoproterozoic and early Cambrian. This, predominantly unfossiliferous, marine sedimentary sequence is characterized by a lower arenaceous facies (Jodhpur Group), middle carbonate facies (Bilara Group) and upper argillaceous– arenaceous facies (Nagaur Group) rocks. The sedimentation has been essentially in a shallow basin, described either as the fore-land slope of the rising Aravalli mountains or a sag-basin which developed and evolved due to subsidence of the updomed crust during Neoproterozoic Malani magmatism that failed to open rifts. The carbon isotopic profile for the Bilara Group carbonate rocks in the lower part shows marked oscillations and broadly negative $\delta^{13}C$ character with negative anomalies as low as $<-4.3‰_{PDB}$, observed near the base of Dhanapa Formation (lower unit) and $<-6.5‰_{PDB}$ in the overlying Gotan Formation (middle unit). The upper part of the profile shows a gradual positive shift. The carbon isotopic signatures of the Bilara Group rocks can be correlated with the end-Neoproterozoic - early Cambrian (Vendian – Tommotian) carbon isotopic evolution curve. Extremely low $\delta^{13}C$ values indicate the glaciation related cold climatic postulates of the end-Neoproterozoic, followed by the warmer climatic conditions as indicated by the positive shift. The carbon isotopic data for Gotan Formation carbonates, at variance with the globally observed $\delta^{13}C$ trends for early Tertiary, do not support the recently proposed Tertiary age for the Bilara Group.

Key words: Neoproterozoic/Cambrian, carbon isotopes, carbonates, Bilara Group, western India.

Introduction

The interval from late Neoproterozoic to the emergence of animal life was the time of extreme climatic oscillations from severe cold conditions (glacial to inter-glacial) to the warmer climate during the Cambrian. The period has been associated with significant physico-chemical changes like enhanced availability of atmospheric oxygen (conducive for animal life) and rapid burial of organic carbon (Karhu and Holland, 1996). Four negative $\delta^{13}C$ excursions between 723 and 543 Ma have been identified, two of which definitely related to the global glaciation events (Brasier et al., 2000). The period also coincides with the final redistribution of continental fragments and consequent increase in their latitudinal velocities, following the initial break-up of the supercontinent Rodinia during 750 –725 Ma (Torsvik et al., 1996).

The Precambrian/Cambrian boundary, initially kept close to the first appearance of shelly fossils (Cowie, 1985), was redefined later at the emergence of the trace fossil Rhycodes pedium (Brasier et al., 1994a). However, purely biologic constraints to document the Neoproterozoic/Cambrian transition have proved to be redundant by the evidence of skeletal biomineralization in the Precambrian (Shields, 1999). The imperfection of the Neoproterozoic/Cambrian correlation through palaeontological criteria has necessitated the search for more precise and reliable technique where carbon chemostratigraphic studies have proved to be significantly relevant. In comparison to the oxygen isotopes, the carbon system is less subjected to exchange during diagenesis and burial metamorphism (Megaritz et al., 1991). Well-preserved carbon isotopic record of sedimentary sequences provides an independent chronometer to monitor the changes in the geological past as the readable $\delta^{13}C$ variations. The $\delta^{13}C$ variations are also capable of providing fine-scale stratigraphic resolution (high precision of analytical measurements), far exceeding the precision obtainable through purely biostratigraphic criteria. Extreme fluctuations in the $\delta^{13}C$ trend have been successfully correlated with the major global events like stratigraphic boundaries, palaeo-climatic changes and tectonic activity.

As a consequence of the focussed attention during last one and a half decades, and the advancements made in the application of carbon chemostratigraphy to resolve major boundary problems, the Neoproterozoic/Cambrian transition is now better understood on the basis of vital isotopic information having made available for the critical sections from all over the world, like China (Hsü et al., 1985), Siberia (Brasier et al., 1994b; Kaufman et al., 1996; Bartley et al., 1998), Australia (Tucker, 1986; McIlroy, 1997), U.S. and Canada (Brasier et al., 1992; Smith et al., 1994; Kaufman et al., 1992), East European platform (Felitsyn et al., 1998), Oman (Brasier et al., 2000) and Morocco (Renner, 1994). The Neoproterozoic/Cambrian transition in India has been studied from the lesser Himalayan region (Aharon et al., 1987), however, the vast tracts of peninsular India still await such attention. Recently, Banerjee and Majumdar (1999) have attempted a regional correlation of $\delta^{13}C$ fluctuations from various continental blocks of the East Gondwana assembly including NW Indian craton, and positive $\delta^{13}C$ excursion has been reported from the Paleoproterozoic Aravalli rocks of Udaipur region (Sreenivas et al., 1996; Maheshwari et al., 1999). This communication presents carbon isotopic data from the carbonate facies rocks (Bilara Group) of predominantly unfossiliferous sedimentary sequence of Marwar Supergroup in NW Indian craton, believed to mark the Neoproterozoic/Cambrian transition in this region (Pareek, 1984). Besides documenting the interval between Neoproterozoic and Cambrian, the data also make a contribution to the data-base on global carbon isotopic evolution record, hitherto unavailable from this terrane. Our findings also assume wider implications in view of the recent controversy regarding the 'age' of these rocks, following the discovery of Tertiary fossils by Raghav (2000).

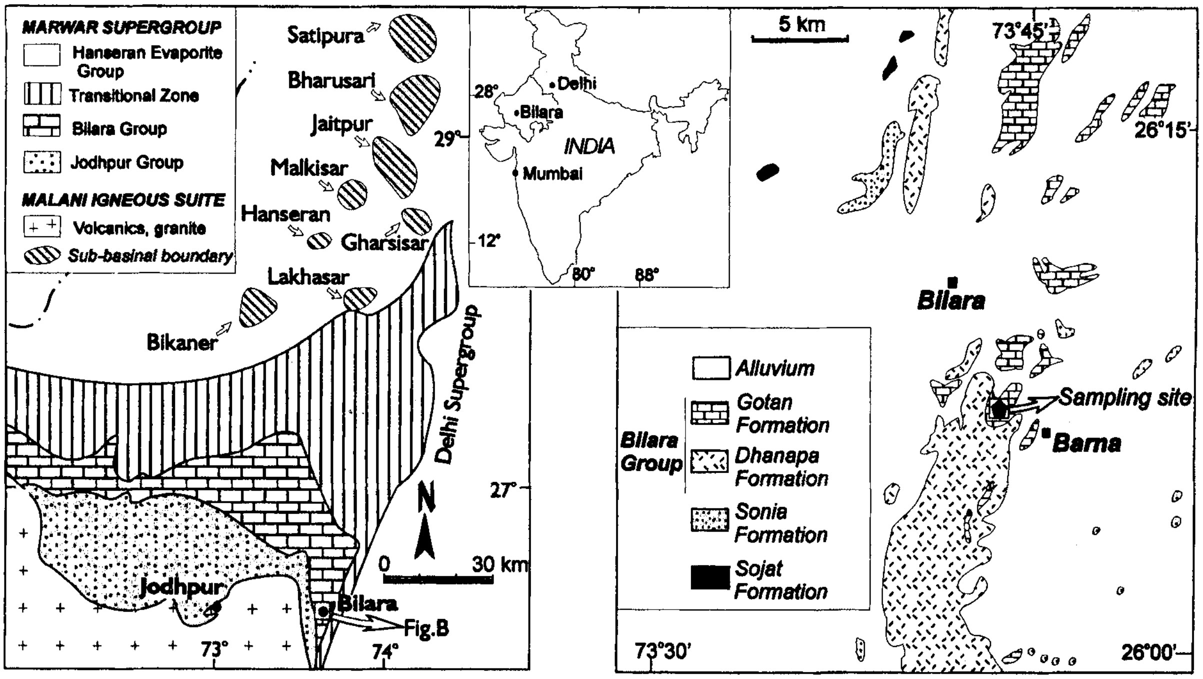
Background Geology

Erstwhile 'Trans-Aravalli Vindhyans' of Heron (1953), correlated with the upper Vindhyan (Crawford and Compston, 1970), were subsequently identified as an independent stratigraphic entity and renamed as Marwar Supergroup (GSI, 1977), comprising essentially of unfossiliferous marine sedimentary sequence that unconformably overlies the Delhi metamorphites or Neoproterozoic Malani igneous suite (Pareek, 1984; Chauhan, 1999; Sinha-Roy et al., 1998). The basin of sedimentation, popularly known as 'Nagaur Basin' is a large NNE-SSW trending, westerly tilted asymmetric basin, described as 'fore-land slope' of the rising Aravalli mountains (Das Gupta et al., 1987). Chauhan (1999) considered this to be an intra-cratonic sag-basin, as an outcome of the Malani magmatism that failed to open rifts but resulted in up-doming of the crust that gradually cooled and subsided. This also explains the predominantly 'shallow' nature of the basin. The Marwar Supergroup, having a cumulative thickness of over 2000 m (Pareek, 1981, 1984), has been subdivided into Jodhpur, Bilara and Nagaur Groups, representing arenaceous, calcareous and argillaceous-arenaceous facies sedimentation, respectively. The distribution of Marwar Supergroup rocks in western India is shown in figure 1A.

We have studied and sampled the calcareous facies rocks of the Bilara Group which forms the middle part of the Marwar Supergroup and shows general thinning both towards east and west (Fig. 1A). Having an estimated thickness of 100 to 300 m (Pareek, 1984), the Bilara Group is further subdivided into three main rock formations. The rock exposures are, however, scanty. Dhanapa Formation (approximately 100 m), the lowest unit of Bilara Group, comprises of a basal chert unit, followed up by dolostone, siliceous dolostone with chert and stromatolitic limestone interbeds. Gotan Formation (middle unit) comprises of industrial grade limestone with interbands of clay and chert. Its thickness is approximately 30 m, however, the thickness of the Hanseran Group (considered equivalent to Gotan Formation) has been reported to be more than 130 m (Sinha Roy et al., 1998). Pondlu Formation (50 to 80 m), the top-most unit of Bilara Group, includes dolostone, cherty dolostone, claystone, siltstone and sandstone. Top 1.5 m section of the Pondlu Formation, immediately underlying the Nagaur Group (Nagaur Sandstone) is stromatolitic. Bilara Group rocks are considered to be generally unfossiliferous, however, Raghav (2000) has recently reported Tertiary foraminifers from the Gotan Formation near Barna. Broad geological features of the Bilara Group in the Bilara – Barna area and location of the sampling site are presented in figure 1B.

Carbon Isotopes

We have analyzed 27 representative samples of Bilara Group carbonate rocks for C and O isotopes, collected from well-exposed quarry sections. Samples for Gotan



(A) (B)

Fig. 1. (A) Geological map showing disposition of Marwar Supergroup in the 'Nagaur basin' in northwestern India. Other sub-basins, occurring to the north of Nagaur basin have also been indicated. Map adapted and modified from Das Gupta et al. (1987) as reproduced in Sinha Roy et al. (1998). (B) Schematic geological map of Bilara – Barna region showing distribution of rocks of Bilara group. Map compiled from Geological Survey of India publications and Raghav (2000). Sojat Formation: phyllite, slate, sandstone with quartzite; Sonia Formation: sandstone with shale and cherty dolomite bands; Dhanapa Formation: cherty limestone, claystone and dolomitic limestone; Gotan Formation: limestone, dolomitic limestone with interbedded chert and claystone bands.

Formation were collected from two quarry sections, west of Barna (Fig. 1B). The samples from Dhanapa Formation were collected from a section approximately 50 km north of Bilara. The litho-section is, however, analogous to the Dhanapa rocks exposed west of the Barna quarry (Fig. 1B). The 18 m thick section exposed in the Barna quarry can thus be considered to represent the lower part of the Gotan Formation. Detailed geological sections of Dhanapa and Gotan Formations (Barna Phase I and Phase II quarry sections) are provided in figure 2A. The Pondlu Formation (sampled from 5 km north of Dhanapa section) is, however, poorly exposed.

Powdered samples were treated with 85% H_3PO_4 at 25° C for 3 days to release the CO_2 (McCrea, 1950). The $\delta^{13}C$ and $\delta^{18}O$ values were measured on cryogenically cleaned CO_2 (Craig, 1957) in a triple collector SIRA II mass spectrometer at NEG LABISE, University of Pernambuco, Brazil. The C and O isotopic data for the carbonate rocks are presented (as standard ‰ deviation with reference to PDB) in table 1. Borborema Skarn Calcite (BSC), calibrated against international standards, was used as the reference gas and reproducibility of the measurements was better than ± 0.1‰, in general. The values obtained for NBS-20 (as unknown) in a separate run against BSC yielded $\delta^{13}C$ = –1.05‰$_{PDB}$, and $\delta^{18}O$ = –4.22‰$_{PDB}$. These are in close agreement with the values reported by the US Bureau of Standards (-1.06‰$_{PDB}$, and –4.14 ‰$_{PDB}$, respectively).

The C isotopic profile of Bilara Group carbonate rocks shows negative $\delta^{13}C$ values with prominent oscillations and negative $\delta^{13}C$ excursions in the middle part (Fig. 2B). Lower part of the profile, represented by Dhanapa Formation rocks, shows rather consistent up-section increase in $\delta^{13}C$, beginning with the lowest value of –4.3‰$_{PDB}$, recorded near the base of the section, to –2.3‰$_{PDB}$, close to the top of the section, maintaining the broadly negative character. This is followed up by a slight positive shift noticed at the base of the Gotan Formation with moderate $\delta^{13}C$ values of –0.02 and –1.5‰$_{PDB}$ observed in Barna Phase I and Phase II, respectively. The middle part of the Gotan Formation shows significant fluctuations and low $\delta^{13}C$ values (up to < –6.5‰$_{PDB}$). The top of the section shows a significant positive shift and the values remain either positive or close to 0‰$_{PDB}$ through the upper part of the section. The carbonate rocks are not wide-spread in the Pondlu Formation, however,

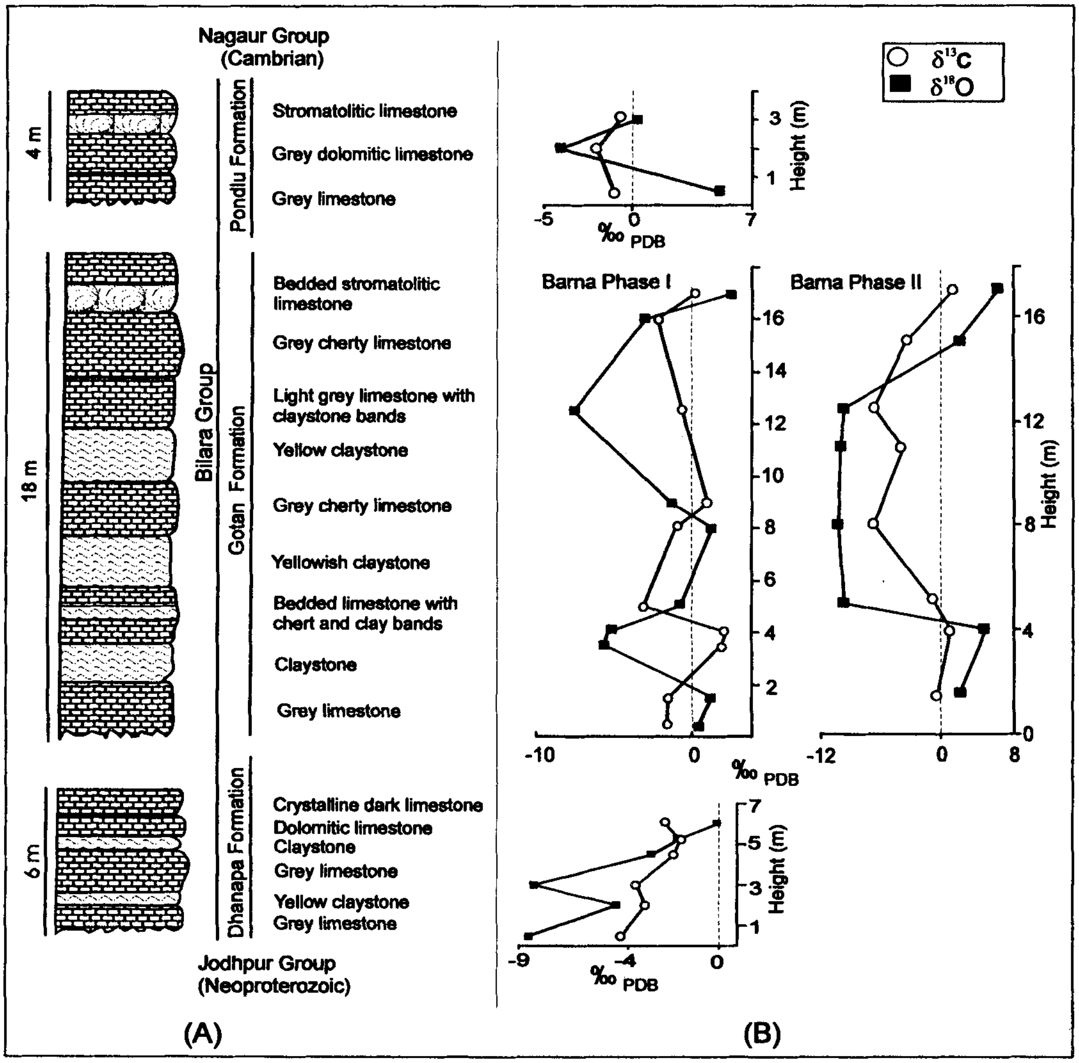


Fig. 2. Composite C and O isotopic profile for Bilara Group carbonate rocks corresponding with the sampled sections. (A) Detailed stratigraphy of the Dhanapa, Gotan and Pondlu Formations as exposed in sampled sections. (B) Corresponding C and O isotopic profiles of sampled sections showing oscillations in the isotopic trends and negative $\delta^{13}C$ anomalies. Height (in meters) indicates approximate height with reference to the base of the sampled section.

limited samples demonstrate near zero $\delta^{13}C$ values postulating warmer climatic conditions. Slight variation in the absolute isotopic values between two different sections of Gotan Formation is discernible. The $\delta^{18}O_{PDB}$ trends show generally matching behaviour and correspondence with the C isotopic profile (Barna Phase II) which can be attributed to the post-depositional modifications brought out by prolonged interaction with circulating waters (Fig. 2B). The oxygen isotope values in case of Barna Phase II section appear to have been homogenized by circulating fluids but the carbon isotopes, fluctuating more widely, have apparently been unaffected or insignificantly affected. The $\delta^{13}C$ values for Barna Phase II section are marginally lower as compared to Barna Phase I (Table. 1). Such lack of uniqueness in C isotopic behaviour is not uncommon (Shields, 1999). The decoupling between C and O isotopic trends in the lower part of the Barna Phase I section indicates the O isotopic ratios to be the unmodified primary values and the fluctuations in O-isotopic trends can be correlated with the climatic oscillations within a short time span.

The carbon isotopic profile for Bilara Group carbonates is characterized by negative $\delta^{13}C$ excursions that begin with the lower part of the Dhanapa Formation ($\delta^{13}C$ = –4.3‰$_{PDB}$) and become more pronounced in the middle part of the Gotan Formation ($\delta^{13}C$ = -6.5‰$_{PDB}$), beyond which the trends show positive shift with minor fluctuations and gradual enrichment in the heavier C isotope. Negative $\delta^{13}C$ excursions with minor positive fluctuations can be attributed to the glacial and interglacial

Table 1. C and O isotopic ratios (presented as standard ‰ notation with reference to PDB) of the carbonate rocks of Bilara Group, western India. (1 to 3 – Pondlu Formation; 4 to 13 – Gotan Formation (Barna Phase I), 14 to 21 - Gotan Formation (Barna Phase II) and 22 to 27 – Dhanapa Formation).

Sl. No.	Sample No.	$\delta^{13}C_{PDB}$	$\delta^{18}O_{PDB}$	Height*
1	PNDL/1	-0.56	0.39	3
2	PNDL/2	-1.91	-4.12	2
3	HRDN/1	-0.93	4.81	0.5
4	B/1	0.2	2.53	17
5	B/3	-2.13	-2.98	16
6	B/4	-0.6	-7.58	12.5
7	B/5	1.14	-1.29	9
8	B/6	-1.04	1.39	8
9	B/7	-3.07	-0.73	5
10	B/8A	2.37	-5.32	4
11	B/8B	2.07	-5.64	3.5
12	B/9	-1.49	1.45	1.5
13	B/10	-1.55	0.57	0.5
14	B2/1	1.73	6.27	17
15	B2/2	-3.14	2.07	15
16	B2/3	-6.42	-9.61	12.5
17	B2/4	-3.43	-10.01	11
18	B2/5	-6.51	-10.17	8
19	B2/6	-0.22	-9.65	5
20	B2/7	1.37	5.15	4
21	B2/8	0	2.38	1.5
22	DHP/1	-2.34	0.11	6
23	DHP/1A	-1.6	-1.7	5.25
24	DHP/3	-1.93	-2.89	4.5
25	DHP/5	-3.62	-8.26	3
26	DHP/5A	-3.22	-4.55	2
27	DHP/6	-4.32	-8.5	0.5

* approximate height from the base of section (in meters)

conditions, respectively, a common feature of the end-Neoproterozoic period. However, the top of the Bilara Group indicates relatively warmer climatic conditions (near zero $\delta^{13}C$ values).

Discussion

The C isotope stratigraphy is based on the primary assumption that the C isotopic ratios of the sea-water carbonate species fluctuate through time, largely in response to the changes in the net rate of organic burial (Shields, 1999). Dolomitization is considered to be the potential agent for C isotopic alteration but in case of Proterozoic successions it is widely accepted that most of the dolomites are isotopically indistinguishable from the associated limestones because during the Proterozoic the dolomitization was syn-depositional in the presence of fluids isotopically similar to the sea-water (Narbonne et al., 1994; Tucker 1983; Fairchild et al., 1991). Thus, we consider the isotopic signatures of the Bilara Group carbonates to be pristine and representative. A common feature of the Neoproterozoic – early Cambrian isotopic behaviour of the carbonate rocks is the positive $\delta^{13}C$ values during Neoproterozoic and oscillations and prominent negative $\delta^{13}C$ excursions during the transition, followed by a positive shift and near zero values in the early Cambrian (Brasier et al., 1992, 1996, 2000; Bartley et al., 1998; Magaritz et al., 1991; Strauss et al., 1997). The time interval marking the Neoproterozoic/Cambrian transition was a period of extreme climatic changes related to intense glaciation (end-Neoproterozoic) and subsequent warming (early Cambrian). Rapid negative $\delta^{13}C$ excursions coincident with the end-Neoproterozoic can be attributed to the mixing of ^{13}C depleted deep water with the shallow water on carbonate platforms during glacially enhanced circulation (Kaufman et al., 1992). Extreme negative $\delta^{13}C$ excursions, close to the boundary are a wide-spread, if not ubiquitous, feature of this time-interval (Brasier et al., 2000; Shields, 1999; Aharon et al., 1987; Kaufman and Knoll, 1995; Kimura et al., 1997). The post-glacial period is represented by globally observed enrichment of ^{13}C during early Cambrian (590 – 550 Ma). However, the absolute values for the isotopic composition as well as the magnitude of the isotopic fluctuations varies considerably from one section to the other. The global character of the observed secular variations has also been established through both organic and inorganic parameters as well as by independent Sr isotope chronometer.

Unfossiliferous and undeformed sedimentary sequence of the Marwar Supergroup is considered to span through the interval between Neoproterozoic and lower Cambrian (Pareek, 1981, 1984; Sinha-Roy et al., 1998; Chauhan, 1999), however, in the absence of any reliable age constraints, the boundary remains to be speculative. Recent report of the Tertiary fossils (Raghav, 2000) has made the issue all the more contentious and debatable. We now have the precise age constraints on the Malani volcanics, based on U-Pb geochronology of zircons that yield 770 to 750 Ma age for the felsic volcanics and intrusive granites (Tucker et al., 1999; Torsvik et al., 2001). Well-documented unconformable relationship between marine Jodhpur sandstone and subaerially erupted Malani felsic volcanics clearly makes the Marwar Supergroup to be significantly younger than 750 Ma. The closure of the Malani magmatism was followed by the development of a sag-basin where sedimentation was probably initiated near the close of Neoproterozoic and continued into the lower Cambrian (Chauhan 1999; Sinha Roy et al., 1998; Pareek, 1984). As the studied Marwar Group rocks lack direct geochronological constraints, it would be desirable to compare the results with well-established Vendian - Tommotian sections having well-constrained ages (geochronological and/or palaeontological). In the Huqf

Supergroup in Oman, the negative $\delta^{13}C$ excursion ($<-5‰_{PDB}$) with strong oscillations has been correlated with the Neoproterozoic - Cambrian transition and the values for Cambrian succession are reported to be generally positive with minimum shifts (Brasier et al., 2000). The $\delta^{13}C$ values for a 300 m section in Siberian platform (identified as key reference section for Proterozoic - Phanerozoic transition) show pronounced negative excursion ($< -6‰_{PDB}$) followed by a steady rise to near zero values, higher in the section (Bartley et al., 1998). The Neoproterozoic - Proterozoic transition in Mongolia is also marked by frequent negative $\delta^{13}C$ excursions ($< -5‰_{PDB}$) and a shift to near zero values with minor fluctuations, latter correlated with the Cambrian (Brasier et al., 1996). The Vendian - Tommotian interval, evaluated in six different sections in Siberia and Morocco, indicates positive $\delta^{13}C$ values during Vendian with a drop to significant negative values (Vendian - Cambrian transition) and near zero values in the early Cambrian (Magaritz et al., 1991). Our carbon isotopic data, showing significant oscillations and negative $\delta^{13}C$ excursions ($\sim -5‰_{PDB}$) appears to be consistent with the globally observed trends associated with the Neoproterozoic - Cambrian transition. Negative $\delta^{13}C$ values, approaching as low as $< -6.5‰_{PDB}$, and prominent oscillations correspond to the globally recorded glaciation during the end-Neoproterozoic. The positive shift in the $\delta^{13}C$, as observed in the upper part of the Gotan Formation and Pondlu Formation, corresponds to the beginning of the warmer conditions, coinciding with the end of the Proterozoic. The carbon isotopic profile of the Bilara Group carbonate rocks also shows a close correspondence with the global carbon isotopic evolution curve (Shields, 1999; Brasier et al., 2000; Hoffman et al., 1998) for the terminal Neoproterozoic (Fig. 3). Higher $^{87}Sr/^{86}Sr$ values, recorded for this time-interval, indicate enhanced continental input into the marine sediments due to increased rate of continental erosion consequent to the Pan-African uplift (Asmeron et al., 1991).

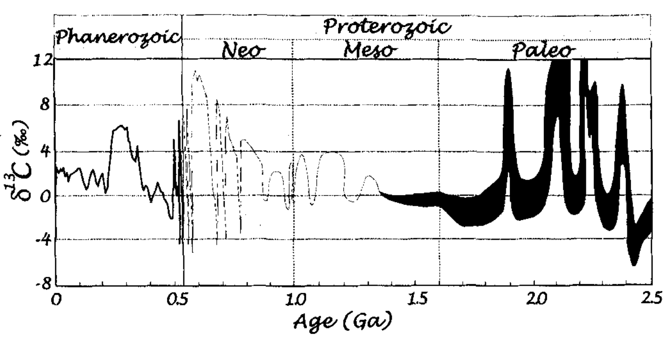


Fig. 3. Curve showing secular $\delta^{13}C$ variations in the geologic past; compiled from Hoffman et al. (1998) and Kha et al. (1999). The thin line corresponds to well-constrained carbon isotopic curve while the thick line represents a compilation of preliminary carbon isotopic ratios.

The $\delta^{13}C$ fluctuations can be interpreted to conclude that the Bilara Group rocks probably mark the interval between Neoproterozoic and Cambrian in this region. The Jodhpur Group represents the Neoproterozoic sedimentation and Nagaur Group can be correlated with the lower Cambrian in this region. The global carbon isotopic evolution curve (Fig. 3) does not indicate any significant fluctuations during the Phanerozoic and the carbon isotopic evolution for the Tertiary has been associated with generally positive $\delta^{13}C$ values, with minor fluctuations, that usually do not transgress into the negative values. The values reported here for the Barna section show oscillations and a significantly negative character, in contrast to the carbon isotopic behaviour for the Tertiary (Hoffman et al., 1998). Our data, thus, do not support the Tertiary age of the Gotan Formation, as suggested by Raghav (2000) and the issue needs to be resolved by comparing the fossil record from correlative units.

Although the C isotopic system has been presumed to be unaffected by diagenetic changes, making the $\delta^{13}C$ trends of particular use (Holser, 1997), it is desirable to have room for healthy skepticism where the $\delta^{13}C$ values are the sole means of correlation (Jensen, 1996). Studies are under way to substantiate the findings through independent Sr isotopic constraints.

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