# Stable isotopic study of late Neoproterozoic-early Cambrian (?) sediments from Nagaur-Ganganagar basin, western India: Possible signatures of global and regional C-isotopic events

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Carbonate rocks of late Neoproterozoic-early Cambrian (?) age occur in two extremities of the Nagaur-Ganganagar basin in western India: in east as part of Bilara hills (type locality) and in west as part of Baghewala oil field. These rocks have close stratigraphic correlation with the Ara Formation (Huqf Group, south Oman salt basin) which transgresses the late Neoproterozoic-early Cambrian boundary. Sedimentological and stable isotopic studies of these rocks show prevalence of arid and evaporitic conditions during their depostion. Close resemblance of C-isotopic profiles of Hanseran evaporites and Bilara carbonates allows intra-basinal correlation and suggests that they are coeval facies variants. There are several characteristic carbon isotopic excursions one of which can be tentatively correlated with the globally recorded excursion close to the late Neoproterozoic-early Cambrian boundary. In contrast other peaks are possibly of regional significance and can be attributed to fluctuations in bioproductivity, correlatable with variation in nutrient supply on a basinal scale. Highly depleted carbon isotopic composition of the organic matter in subsurface organic-rich carbonates (Upper carbonate Formation, Baghewala-II core) has been ascribed to incorporation of biomass synthesized by chemoautotrophic bacteria under anoxic or eutrophic basinal condition caused by salinity stratification.

Keywords: carbon isotope, Neoproterozoic, Cambirian, limestone, dolomite

## INTRODUCTION

The late Neoproterozoic-early Cambrian transition was a time of remarkable changes in the history of earth. It is characterized by tectonic readjustments (McKerrow *et al.*, 1992; Powell *et al.*, 1993; Unrug, 1997), paleo-oceanographic (Aharon and Lieu, 1992; Brasier, 1992; Kaufman and Knoll, 1995) and paleoclimatic changes (Hoffman *et al.*, 1998), major biological changes like advent and diversification of metazoans (Glaesner, 1984) and appearance of small shelly fauna (Brasier, 1990, 1991). Paleoclimatic and oceanographic changes caused perturbations in isotopic ratios of carbon (Aharon *et al.*, 1987; Kaufman and Knoll, 1995), strontium (Derry *et al.*, 1992; Jacobsen and Kaufman, 1999) and sulfur (Strauss, 1997; Strauss *et al.*, 2001; Walter *et al.*, 2000) in the marine realm. This transitional period also witnessed widespread deposition of phosphorites, black shales and cherts in parts of Gondwanaland (Cook and Shergold, 1986;

Donnelly *et al.*, 1990; Brasier, 1990, 1992; Aharon and Lieu, 1992; Banerjee *et al.*, 1997; Banerjee and Mazumdar, 1999). In addition, several fault basins were formed due to rifting/wrenching in the parts of Gondwanaland stretching from India and Pakistan across the Arabian Shield to the central Iran where great volumes of carbonate (dolomite/limestone) and evaporite deposited (Husseini and Husseini, 1990). Late Proterozoic plate tectonic reconstructions by Gorin *et al.* (1982), Husseini and Husseini (1990), McKerrow *et al.* (1992) and Mattes and Conway Morris (1990) show that restricted marine-evaporite deposits in northwestern India (Nagaur-Ganganagar basin), Pakistan (Salt Range), Oman (south Oman salt basin), Iran (Kerman Basin) and Saudi Arabia formed in rift grabens that were in close proximity to each other within a broad carbonate shelf along the western margin of east Gondwanaland.

Late Neoproterozoic-early Cambrian transitional age has been suggested for the Bilara carbonates of Nagaur-Ganganagar Basin (western Rajasthan, India) by Pandit *et al.* (2001). These authors proposed late Neoproterozoic glaciation event as the causative factor for the observed C-isotopic perturbations which needs to be substantiated through sedimentological studies. In view of the significance of the Bilara carbonates in deciphering the late Neoproterozoic-early Cambrian ocean chemistry a fur-

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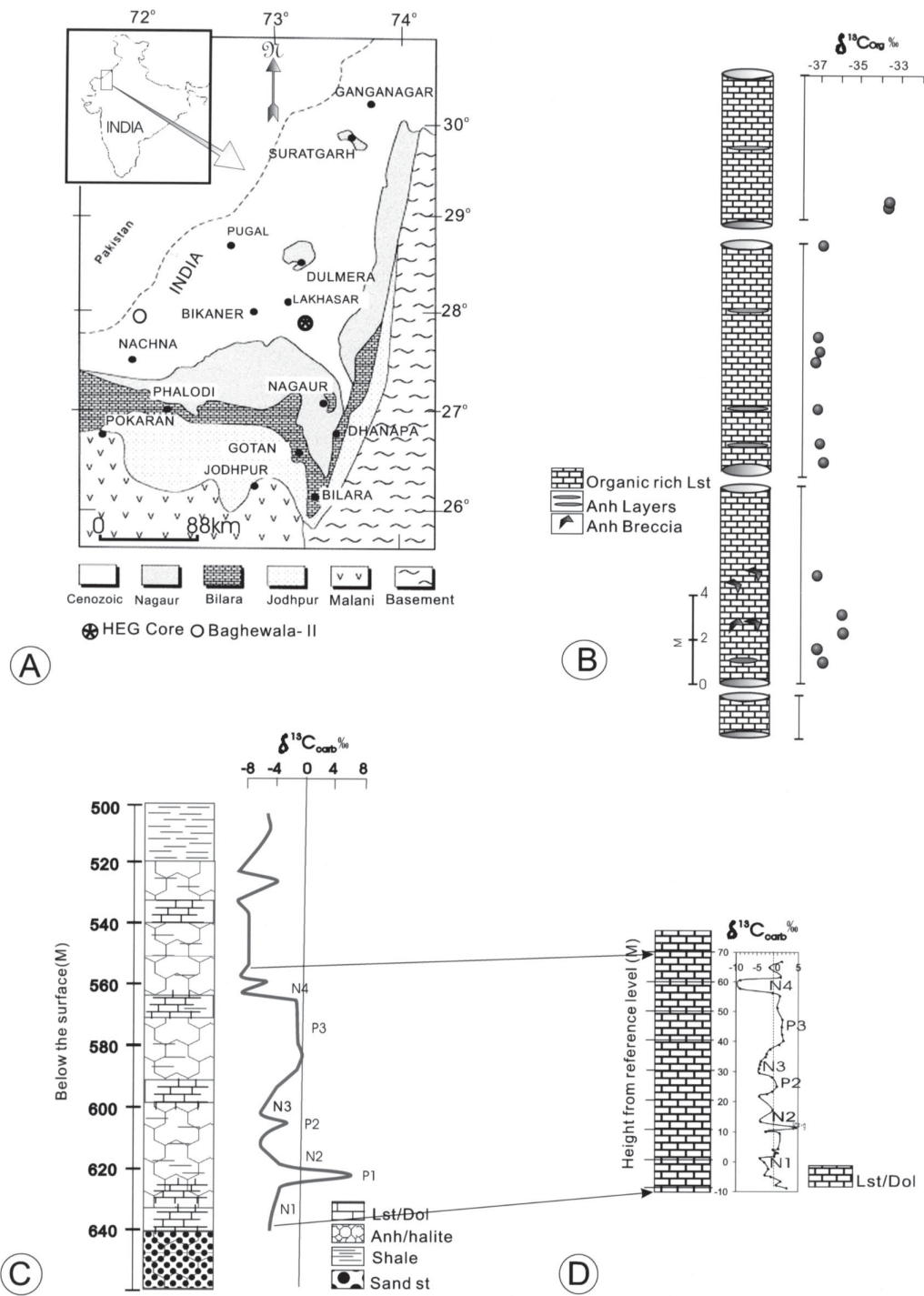
Fig. 1. A. Geological map of Nagaur-Ganganagar basin (modified after Strauss et al., 2001). B. Carbon isotopic composition of organic matter in Baghewala-II core. C. Carbon isotopic profile through Hanseran evaporite (Core P/47, Banerjee and Mazumdar, 1999). D. Carbon isotope stratigraphy of Bilara carbonates, Bilara Hills. Carbon isotopic values are in permil (‰) relative to PDB.

ther detailed study was undertaken by us and the results are presented here. In addition we have made an attempt to constrain and contrast the depositional environment of the subsurface carbonate sequence from the western extremity of the basin, presumably close to the same time window as the Bilara Group.

### GEOLOGY AND STRATIGRAPHIC SETTING

The Nagaur-Ganganagar Basin (Fig. 1A) in western Rajasthan, India, is an elongated asymmetrical sedimentary basin trending NNE-SSW and covering an area of over 100,000 km$^2$. It is bounded by the Aravalli Mountain Range in the east, Delhi-Lahore subsurface ridge in the northeast and north and Devikot-Nachna subsurface high in the southwest. The Marwar Supergroup (Pareek, 1981) suspected to be the late Neoproterozoic-early Cambrian succession in the Nagaur-Ganganagar basin, rests on the Precambrian gneisses, granites and rhyolites belonging to the Malani Group (Fig. 2). Malani Group represents a polyphase igneous activity which ranges in age from 780 to 680 Ma (Rathore *et al.*, 1999) and puts a basal limit for the Marwar Supergroup. The Marwar Supergroup consists of (i) Jodhpur Group, (ii) Bilara Group and (iii) Nagaur Group in ascending order. Jodhpur Group is comprised of cross-bedded, reddish sandstone with maroon clay beds. The beds dip gently 2–5° towards

N and NW. Lenses of conglomerate derived from Malani Rhyolite locally underlie the Jodhpur Group. Bilara Group is comprised of limestone and dolomite with occasional clay beds and conformably overlies the Jodhpur Group. The presence of abundant stromatolites (Figs. 3A and B),







*Fig. 3. Stromatolites (A, B) and crenulated algal mat (C) from Bilara hill. Scale: Big division = 1 inch and small division = 1 cm.*
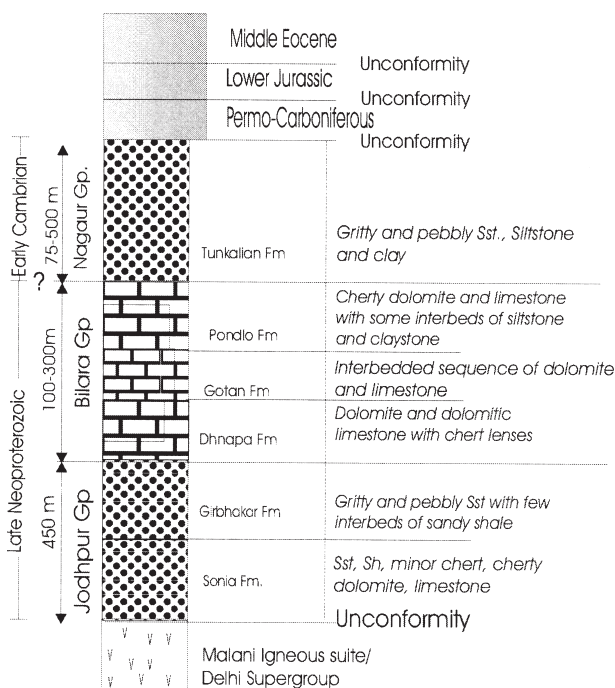


*Fig. 2. Generalized stratigraphy of Marwar Supergroup. ? = uncertainty in placing the late Neoproterozoic-early Cambrian boundary (modified after Pareek, 1981).*
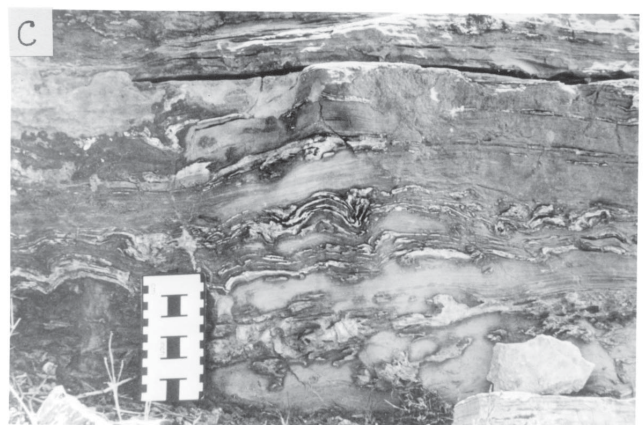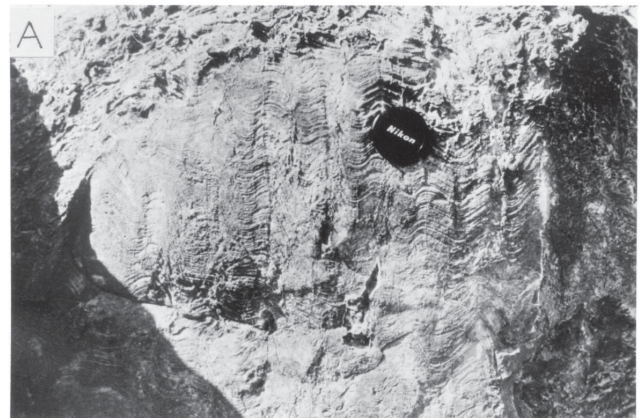
microbial laminites (Fig. 3C), ripple laminites and mudchip conglomerates indicate shallow marine depositional environment. The Bilara Group shows extensive development of biohermal stromatolites (Collenia, Colloniella, Cryptozoon and Irregularia; Burman, 1980, 1987). This unit is overlain by a sequence of medium to coarse grained, cross-bedded, reddish brown, sandstone belonging to Nagaur Group. Hanseran Evaporite Group (HEG) represents the time equivalent facies variant of the Bilara Group and is underlain and overlain by Jodhpur and Nagaur Groups respectively (Dasgupta *et al.*, 1988; Kumar, 1999). HEG has been encountered in subsurface boreholes and is well developed in the central and northern parts of the Nagaur basin. A total of seven evaporite cycles have been identified from HEG. Each cycle is comprised of dolomite, anhydrite and halite with clay bands in ascending order. Exploration for hydrocarbon by Oil India Limited in the western flank (Baghewala) of the Nagaur-Ganganagar basin resulted in the discovery of heavy crude oil in multiple zones (Dasgupta and Balaguda, 1994). Based on geochemical characterization of the crude oil in Jodhpur sandstone (zone III), underlying the Bilara carbonates in Baghewala-I core, Peters *et al*. (1995) proposed that the Cambrian-Infracambrian marine carbonates deposited under anoxic, sulfate reducing conditions as the source rocks for the crude oils. Two other crude oil zones overlying zone-III have been reported from Hanseran evaporites and Upper carbonates. Peters *et al*. (1995) correlated these oils with the late Neoproterozoic-early Cambrian Huqf oil of southern Oman and Karampur-I oil of East Pakistan. We obtained a core (Baghewala-II) representing the Upper carbonate sequence overlying the Nagaur sandstone having a length of 28.56 m (Fig. 1B) from the Oil India Limited, Jodhpur for the present work.

*Age constrain of Bilara Group through correlation with Ara Formation*

We have attempted to correlate the Bilara Group and Hanseran Evaporite Group with the Ara Formation of south Oman salt basin for a better age constraint. Ara Formation (late Neoproterozoic to early Cambrian) is the uppermost unit of the Huqf Group which consists of Khufai, Shuram and Buah Formations (in ascending order) underlying the Ara Formation (Gorin *et al*., 1982). Ara Formation is markedly similar to the Bilara and Hanseran evaporite Groups of Nagaur-Ganganagar basin in many respects. The Ara Formation consists of a thick sequence of evaporite (sulfates, halite and potash salts) and carbonate. Six carbonate/evaporite cycles have been recorded in the basin and on the surrounding platforms comparable with similar cycles recorded in HEG. Age of Ara Formation is well constrained by the record of Cloudina spp. (Conway Morris *et al*., 1990) and calcified

alga Angulocellularia spp. (Mattes and Conway Morris, 1990) suggesting late Neoproterozoic-early Cambrian (?) age. Although no index fossil demarcating Precambrian-Cambrian boundary has been recorded from HEG/Bilara Group, several lines of evidences *viz*., synchronous basin forming event (Husseini and Husseini, 1990), age of the basement of Marwar Supergroup, similarity of sulfur isotopic composition (+27 to +39‰: Strauss *et al*., 2001) to that recorded from Ara evaporites (+36.6‰: Mattes and Conway Morris, 1990), record of late Proterozoic-early Cambrian oil from Ara Formation (Edgell, 1991; Terken *et al*., 2001) and Bilara carbonate and Upper carbonate (Baghewala-I: Dasgupta and Balaguda, 1994) and similar carbon isotopic composition of the organic matter from Ara source rocks and Baghewala cores (Peters *et al*., 1995 and this work) suggest that the Ara evaporite and HEG/Bilara Group belong to the same age brackets.

*Mineralogy and petrography*

The carbonate rocks have been sampled along a profile in the Tigada mine located in Bilara Hill (numberd as BLH in Table 1) near the Bilara Township and along the Baghewala-II core drilled near Baghewala, western Rajasthan. Sampling locations are marked on the Map in Fig. 1A. Semi-quantitative estimation of relative percentages of dolomite and calcite in carbonate phase was made following Tennant and Berger (1957). Bilara hill samples range in composition from pure dolomite to pure calcite and intermediate types with variable percentages of dolomite and calcite. Although anhydrite was recorded in few samples in petrography, it could not be detected in XRD owing to its minor amount. Quartz, illite, chlorite and mixed layer illite-smectite are present as acid insoluble residues. Quartz is mostly present as early diagenetic chert or detrital grains. Authigenic chert is common and often pervasively replaces the carbonate mineralogy. Early silicification has nicely preserved the algal laminites and filaments. Bilara hill carbonates are characterized by microbialites, thinly bedded micritic limestone, dolostone, microsparites, coarse sparite and micropelletal limestone. Petrographic observations show presence of early diagenetic recrystallization features like isopachous layers and blocky crystals and micro-dolomite rhombs associated with post depositional mineralogical stabilization involving transformation of high Mg-calcite and aragonite to low Mg-calcite or early diagenetic dolomite. Micropelletal grains surrounded by clear blocky cement indicate early meteoric water diagenesis. There is no evidence of burial diagenesis or thermal effect. The Baghewala-II core samples (Table 2) studied here are primarily dolomicrite with Quartz, illite, chlorite, corrensite, mixed layer illite-smectite and kerogen present as acid

*Table 1. Carbonate mineralogy and $\delta^{13}C_{org}$ data for Bilara hill carbonates*

| Sample name | Relative height (m) | Carbonate mineralogy | $\delta^{13}C_{carb}$ | $\delta^{18}O_{carb}$ | $\delta^{13}C_{org}$ | $\Delta\delta$ |
|---|---|---|---|---|---|---|
| BLH-1 | 66.9 | >90% Dol | 1.0 | 6.3 | | |
| BLH-2 | 64.9 | NA | −2.0 | −0.02 | | |
| BLH-3 | 61.6 | >90% Dol | 0.7 | 4.6 | −31.1 | 31.7 |
| BLH-4 | 60.6 | >90% Dol | −8.8 | 4.8 | −30.8 | 22.0 |
| BLH-5 | 57.8 | >90% Dol | −9.5 | 7.8 | −29.5 | 20.0 |
| BLH-6 | 56.3 | >90% Dol | −1.3 | 6.9 | −27.7 | 26.4 |
| BLH-7 | 55.3 | >90% Dol | 0.5 | 4.6 | | |
| BLH-8 | 51.3 | >90% Dol | −0.1 | 6.7 | −28.9 | 28.8 |
| BLH-9 | 47.3 | >90% Dol | 1.2 | 7.7 | −28.0 | 29.2 |
| BLH-10 | 44.9 | 60% Cal | −1.3 | −1.3 | | |
| BLH-11 | 42.4 | >90% Dol | 1.1 | 6.6 | −27.3 | 28.4 |
| BLH-12 | 40.4 | >90% Dol | 1.4 | 6.9 | −26.5 | 27.9 |
| BLH-13 | 39 | >90% Dol | 0.3 | 5.6 | −27.2 | 27.6 |
| BLH-14 | 37.5 | 60% Cal | −1.8 | −2.1 | −27.1 | 25.3 |
| BLH-15 | 35.9 | 80% Cal | −2.6 | −4.5 | | |
| BLH-16 | 34.9 | >90% Cal | −2.9 | −4.3 | −28.2 | 25.3 |
| BLH-17 | 33.5 | >90% Cal | −4.0 | −1.2 | −29.0 | 25.0 |
| BLH-18 | 32.4 | 60% Cal | −3.3 | −0.6 | −28.5 | 25.2 |
| BLH-19 | 31.05 | 65% Cal | 1.7 | −0.9 | | |
| BLH-20 | 29.6 | 60% Cal | −4.5 | −3.2 | −30.3 | 25.8 |
| BLH-21 | 28.2 | 70% Cal | −1.4 | −1.7 | | |
| BLH-22 | 25.2 | 70% Cal | −0.2 | −0.6 | | |
| BLH-23 | 23.4 | >90% Cal | −1.3 | 0.9 | −26.9 | 25.6 |
| BLH-24 | 22.6 | >90% Cal | −2.6 | −3.9 | −27.4 | 24.8 |
| BLH-25 | 21.8 | 60% Cal | −4.4 | 0.8 | −28.0 | 23.6 |
| BLH-26 | 17.3 | 70% Cal | −1.2 | 1.7 | | |
| BLH-27 | 13.5 | >90% Cal | −4.1 | −0.5 | −29.1 | 25.0 |
| BLH-28 | 11.5 | >90% Cal | 4.5 | −0.1 | −28.2 | 32.7 |
| BLH-29 | 10.5 | >90% Cal | −1.8 | 0.1 | −27.6 | 25.8 |
| BLH-30 | 10.15 | >90% Cal | −2.9 | −5.9 | −28.1 | 25.2 |
| BLH-31 | 9.6 | >90% Cal | 0.5 | −5.5 | −27.6 | 28.1 |
| BLH-32 | 4.4 | >90% Cal | 0.1 | −1.5 | | |
| BLH-33 | 4.1 | >90% Cal | −1.1 | −5.6 | −28.1 | 27.0 |
| BLH-34 | 3 | >90% Cal | 0.1 | −1.9 | | |
| BLH-35 | 2.95 | >90% Cal | −0.6 | −2.9 | | |
| BLH-36 | 1.9 | >90% Cal | −0.8 | −3.7 | −28.2 | 27 |
| BLH-37 | 1.3 | >90% Cal | −4.3 | −2.1 | −27.5 | 23 |
| BLH-38 | 0 | >90% Cal | −3.2 | 0.7 | −29.4 | 26 |
| BLH-39 | −2.2 | 60% Cal | −2.2 | 1.5 | −28.7 | 26 |
| BLH-40 | −4.4 | 55% Dol | −3.1 | −2.7 | −27.6 | 24 |
| BLH-41 | −4.9 | 70% Cal | −1.6 | 1.1 | | |
| BLH-42 | −6.5 | >90% Cal | 0.7 | 0.3 | −30.3 | 31.0 |
| BLH-43 | −7.7 | 80% Cal | −0.3 | −0.7 | | |
| BLH-44 | −8.7 | >90% Dol | 2.2 | 3.6 | −28.8 | 31.0 |
| BLH-45 | 12 | >90% Cal | −4.3 | −1.7 | | |
| BLH-46 | 11 | 60% Dol | −2.2 | 1.5 | | |
| BLH-47 | 10 | >90% Cal | −1.2 | −1.7 | | |
| BLH-48 | 9 | >90% Cal | −1.3 | −6.7 | | |
| BLH-49 | 8 | 60% Dol | −0.6 | 2.3 | | |
| BLH-50 | 7 | >90% Cal | −2.4 | −1.7 | | |
| BLH-51 | 6 | 60% Dol | −2.5 | 2.8 | | |
| BLH-52 | 5 | >90% Cal | −4.3 | −7.0 | | |
| BLH-53 | 4 | 70% Dol | −0.0 | 2.6 | | |
| BLH-54 | 3 | NA | 1.9 | 0.7 | | |
| BLH-55 | 2 | >90% Cal | 1.0 | −4.9 | | |
| BLH-56 | 1 | NA | 1.6 | 0.8 | | |

*Note: BLH-45 to 56 is for Fig. 4B.*

*Table 2. Carbonate mineralogy and $\delta^{13}C_{org}$ data for Baghewala-II core*

| Depth (m) | Carbonate mineralogy | $\delta^{13}C_{org}$ |
|---|---|---|
| 484.42 | Dolomite > 90 | −33.0 |
| 484.63 | do | −33.6 |
| 513.49 | do | −36.9 |
| 517.45 | do | −37.1 |
| 518.27 | do | −37.0 |
| 519.31 | do | −37.1 |
| 521.8 | do | −36.5 |
| 522.08 | do | −37.1 |
| 523.35 | do | −36.9 |
| 548.8 | do | −37.1 |
| 550.5 | do | −35.8 |
| 551.705 | do | −35.5 |
| 552.375 | do | −37.1 |
| 553.26 | do | −36.7 |

insoluble fractions. Quartz is primarily detrital with occasional authigenic chert fragments. Organic matter is present as disseminated particles, thin bitumen layers or as pockets.

*Analytical method*

Prior to the isotopic investigations all the samples were examined in petrographic thin sections and corresponding halves of the sections were used for micro-sampling. Micro-sampling of homogeneous micritic or microsparitic portions free of late diagenetic veins was carried out using a dentist's drill. Carbonate powders were treated with 100% phosphoric acid ($\rho = 1.89$ g/ml) at 25°C for 72 hours in evacuated reaction tubes to produce $CO_2$ (McCrea, 1950). Experiments involving stepwise $CO_2$ extraction during reaction of calcite-dolomite mixtures by Clayton *et al.* (1968), Magaritz and Kafri (1981) and Ray and Ramesh (1998) showed that 85 to 95% dissolution of dolomite is achieved during 72 hours reaction time. In contrast almost complete dissolution of calcite is possible in less than 1 to 2 hours (Walters *et al.*, 1972; Magaritz and Kafri, 1981). Several repeat analyses were carried out to ascertain that the $CO_2$ produced after 72 hours of equilibriation at 25°C is a representative sample gas in terms of carbon and oxygen isotopic composition of the sample powder. For determination of C-isotopic composition of organic matter, sample powders were treated with 2N HCl repeatedly in order to remove the carbonates. XRD of representative samples was carried out to ascertain complete decalcification. The decarbonated fraction was mixed with CuO and sealed in evacuated quartz tubes for combustion at 850°C for 6 hours. The evolved $CO_2$ gas in both the cases (carbonate and organic carbon) was cryogenically purified and the isotopic compositions were determined by Europa Geo 20-20 mass spectrometer.

Carbon and oxygen isotope ratios are reported in the standard delta ($\delta$) notation as permil (‰) relative to Pedee belemnite (PDB) standard. Reproducibility as determined by replicate analyses of the in-house laboratory standard was generally better than 0.03‰ for carbonate carbon, 0.2‰ for organic carbon and 0.05‰ for oxygen. The in-house standards used are Z-Carrara marble ($\delta^{13}C_{PDB} = 2.24$‰, $\delta^{18}O_{PDB} = -1.33$‰) and UCSD glucose ($\delta^{13}C_{PDB} = -9.9$‰). A total of 56 carbonate samples were analyzed for carbonate carbon and oxygen isotopic compositions and 30 samples for carbon isotopic composition of organic matter from the Bilara hill. Carbon isotopic compositions of organic matter in 14 samples from the Baghewala-II core are reported here. Total organic carbon content has not been measured in any of the samples.

## RESULTS

Mineralogical and stable isotopic compositions of Bilara carbonates from Bilara hill (Tigada mine) and Baghewala-II core are presented in Tables 1 and 2 respectively. The variations in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ along the Tigada mine profile with reference to stratigraphy are shown in Figs. 4A and B. Barring two samples with extremely negative carbon isotopic compositions (−8.8 and −9.5‰), $\delta^{13}C_{carb}$ of Bilara Hill carbonates show relatively less spread (−4‰ to +4‰) compared to that of $\delta^{18}O_{carb}$ (−7‰ to +8‰). We have recorded four negative (N1, N2, N3, N4) and three positive (P1, P2, P3) excursions along the carbonate carbon isotope profile. In order to check the reproducibility of the nature of isotopic profile, peak P1 was verified from another nearby location in the mine having the same lithology and stratigraphic level (BLH-45 to 56; Fig. 4B). However, the peak P1 at the two profiles differs in magnitude. The plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ for Bilara Hill samples does not show any covariance for dolomite, calcite or dolomite-calcite mixed samples (Fig. 5A). Figure 5B is a plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ against percentage of dolomite in carbonate. Oxygen isotopic enrichment with increasing dolomite content is evident whereas carbon isotopic composition does not show any significant shift with dolomitization. The isotopic compositions of the organic carbon ($\delta^{13}C_{org}$) separated from the Bilara Hill samples vary from −31 to −27‰. Whereas $\delta^{13}C_{org}$ of Baghewala-II core samples range from −33 to −37‰.

## DISCUSSION

*Diagenesis*

Bilara Hill carbonates are characterized by dolostones, limestones and intermediate lithologies with variable percentages of calcite and dolomite. The upper part of our
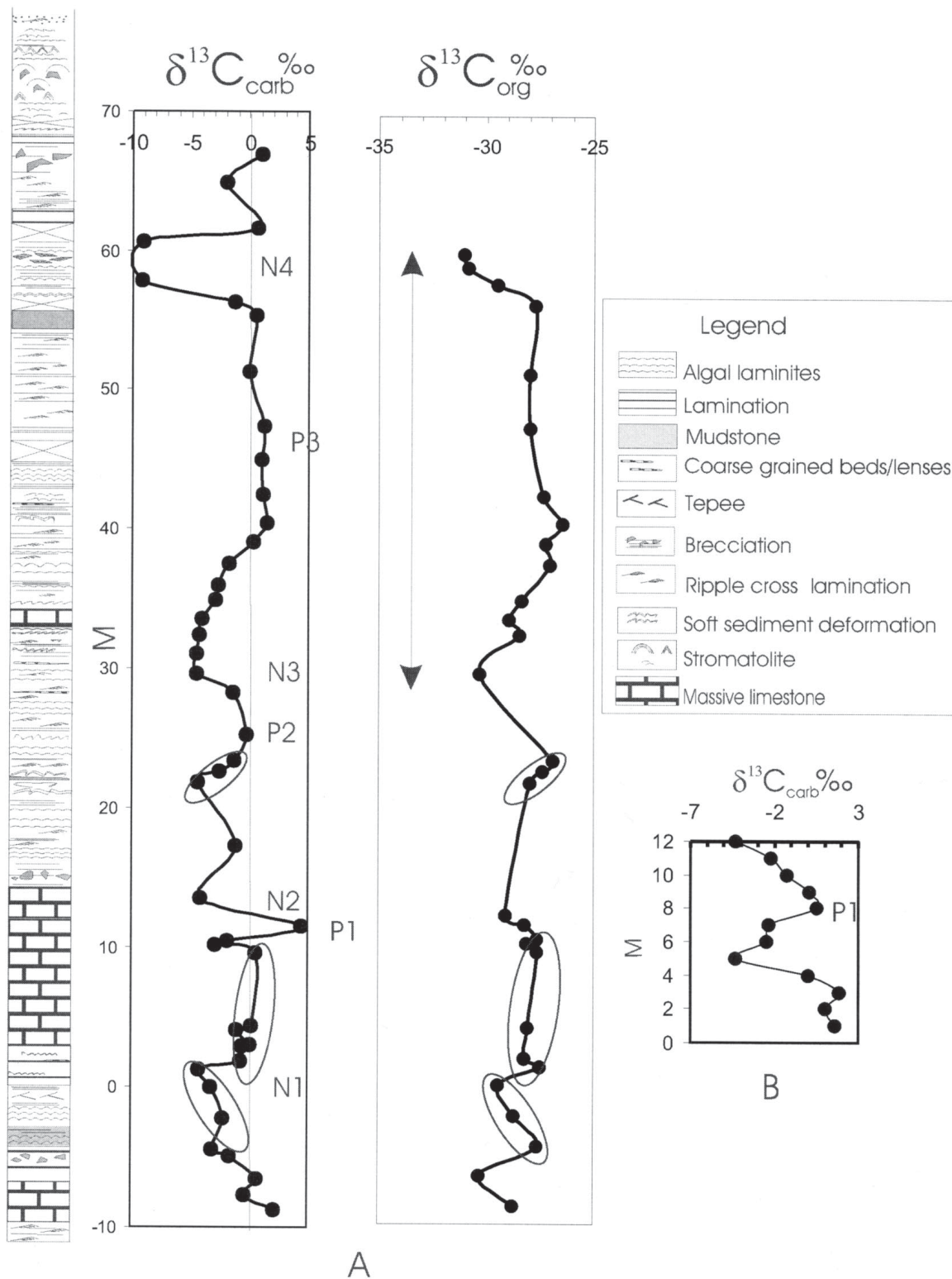
*Fig. 4. A. Carbonate carbon and organic carbon isotope stratigraphy of Bilara carbonates, (Tigada Mine) Bilara Hills. B. Carbon isotope profile near to the Tigada Mine section to check the reproducibility of peak P1. Carbon isotopic values are in permil (‰) relative to PDB. Negative height indicates below the reference point of zero meters.*
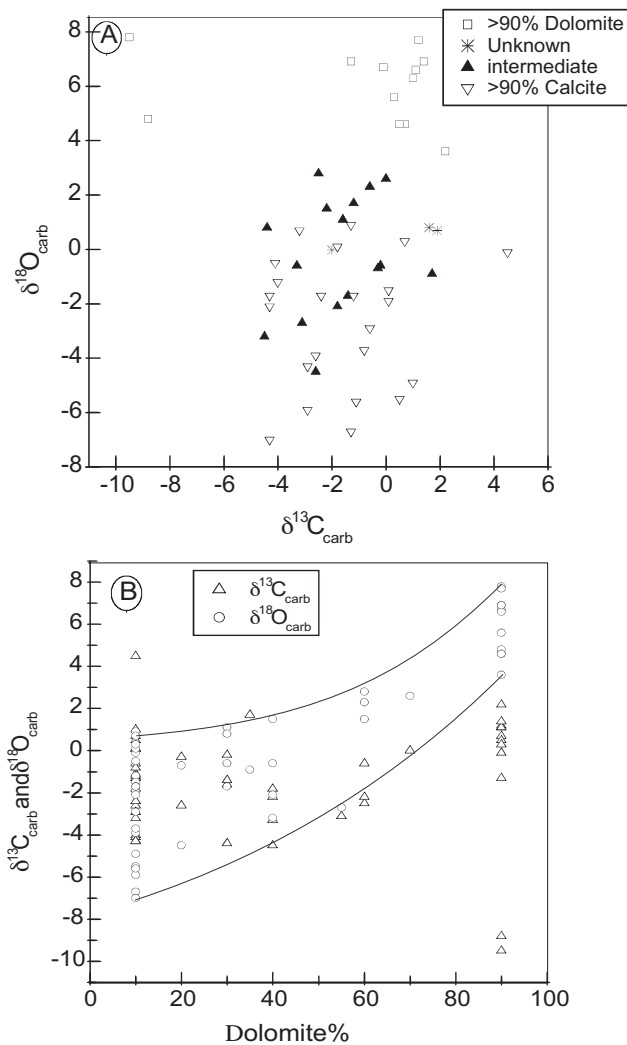
*Fig. 5. A. Cross-plot of carbon and oxygen isotope data of Bilara carbonates (Bilara Hill). B. Variation of $\delta^{13}C$ and $\delta^{18}O$ against percentage of dolomite in the carbonate phase of Bilara carbonate. Isotopic compositions are in permil (‰) relative to PDB.*

studied section is composed predominantly of dolomite and is characterized by significant oxygen isotopic enrichment (Table 1). Such isotopic enrichment represents strongly evaporitic milieu. Good preservation of depositional features *viz.*, algal mat fabric and fine laminations at microscopic scale support an early diagenetic dolomitization through reflux of dense, hypersaline, Mg rich brine (Pierre *et al.*, 1984; Peryt and Scholle, 1996) and absence of burial or thermal overprints. Presence of anhydrite in Bilara carbonates and existence of coeval facies variant Hanseran evaporites, support existence of arid and warm environmental condition. Compared to the dolomites, limestones display depleted oxygen isotopic ratios (Fig. 5B) suggesting that diagenetic stabilization

of these sediments took place in the meteoric water regime. The spread in the oxygen isotopic composition may be attributed to variable extent of meteoric water cementation during dissolution/reprecipitation processes. On the other hand intermediate lithologies with variable amounts of calcite and dolomite indicate a transitional zone between meteoric water and hypersaline brine which is further confirmed by a large variation in oxygen isotopic ratios. It is evident from Fig. 5B that in contrast to oxygen, the carbon isotopic compositions show no significant variation with mineralogy. Although, carbon isotopic enrichment during dolomitization in an evaporitic milieu has been suggested by Budd (1997) and Pierre *et al.* (1984), such a process could not be envisaged in the present case as the carbon isotopic excursions (Fig. 4) are not restricted to zones of dolomitization or $^{18}O$ enrichment.

A cross plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ have been used by many workers in order to verify the response of carbon isotopic composition to meteoric water alteration (Brand and Veizer, 1981; Veizer, 1983; Fairchild *et al.*, 1990; Marshall, 1992). A negative trend in $\delta^{13}C_{carb}$ with progressive decrease in $\delta^{18}O_{carb}$ indicates alteration of primary carbon isotopic ratios through depleted meteoric water during diagenesis. No covariance exists between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ in case of Bilara Hill carbonates (Fig. 5A); this indicates that the circulating meteoric fluid volume was insufficient to re-equilibrate and alter the carbon isotopic composition to any significant extent owing to the fact that the carbon system is rock buffered whereas the oxygen system is water-dominated. Studies on Proterozoic limestone/dolomites by Tucker (1983), Knoll *et al.* (1986), Narbonne *et al.* (1994) and Kaufman and Knoll (1995) rely on similar argument in selecting least-altered samples.

The difference $\delta^{13}C_{carb} - \delta^{13}C_{org}$ ($=\Delta\delta$) expresses the net isotopic fractionation between the inorganic and organic carbon pools. Hays *et al.* (1999) estimated a range of 28 to 32‰ for $\Delta\delta$, resulting from photosynthetic carbon fixation during Neoproterozoic and early Cambrian. $\Delta\delta$ higher than 32‰ has been attributed to incorporation of chemoautotrophic bacterial biomass in the total organic carbon (Hays *et al.*, 1999). Many of the $\Delta\delta$ values reported in this study for Bilara Hill carbonates (Table 1) are considerably below the range for Neoproterozoic and early Cambrian. The low $\Delta\delta$ values may be attributed to incorporation of biogenic bicarbonate in calcite/dolomite lattice during early diagenesis.

*Intrabasinal correlation*

Resemblance of $\delta^{13}C_{carb}$ profile along the Bilara Hill and the Hanseran Evaporite core (Banerjee and Mazumdar, 1999) allows intrabasinal correlation and verifies our contention that Bilara and Hanseran Groups rep-
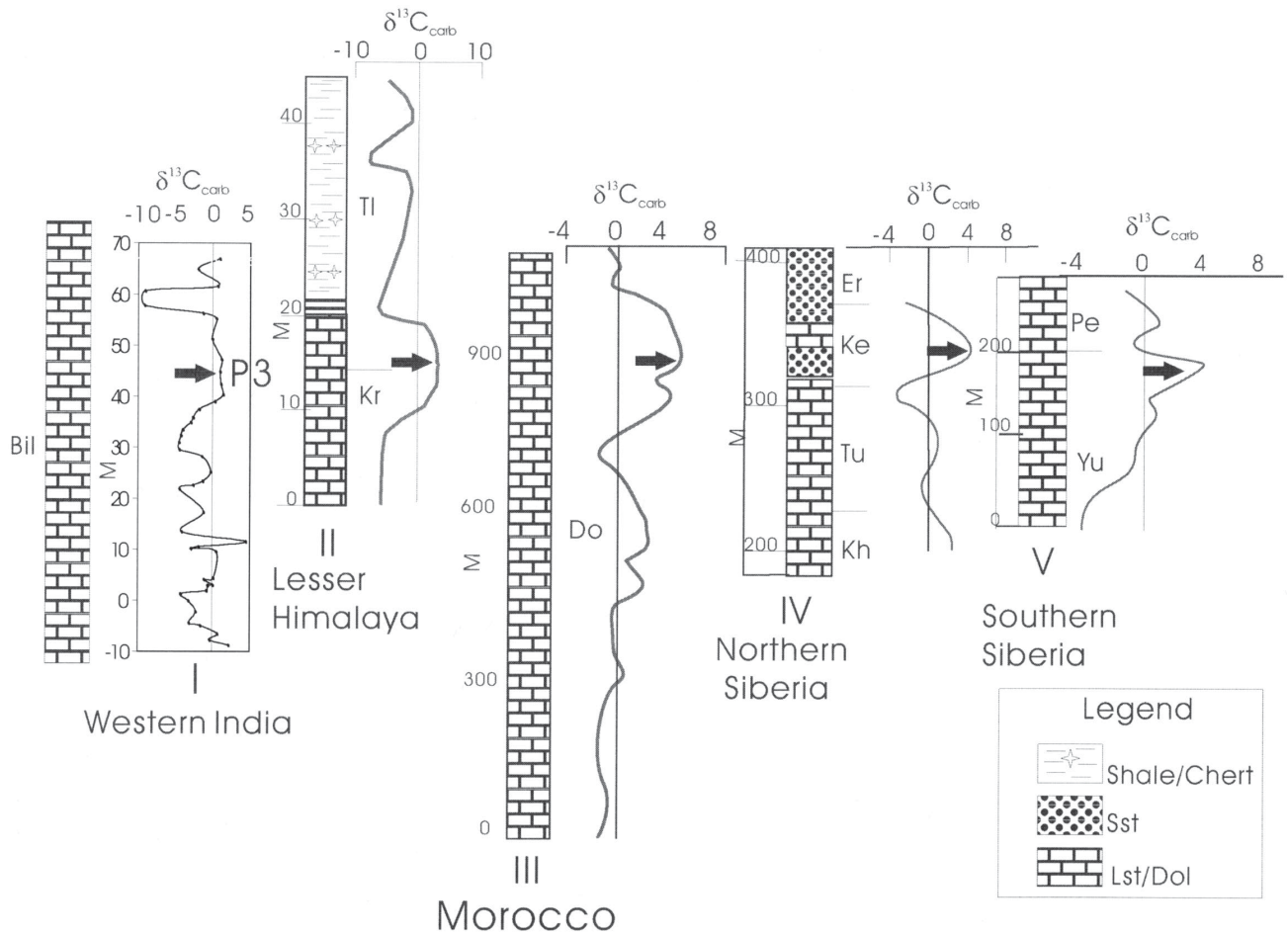
*Fig. 6. Graphical correlation of carbon isotopic excursions across late Neoproterozoic-early Cambrian sections. I = Bilara Group, India; II = Lesser Himalaya, India (Banerjee et al., 1997); III = Oued Sdas, Morocco (Magaritz et al., 1991); IV = Olenek Uplift, N. Siberia (Knoll et al., 1995); V = Aldan River, S. Siberia (Magaritz et al., 1986). Bil = Bilara Group, Yu = Yudoma Fm., Pe = Pestrotsvet Fm., Do = Dolomite Inferieur Fm., Kh = Khatyspyt Fm., Tu = Turkut Fm., Ke = Kessyusa Fm., Er = Erkeket Fm., Kr = Krol Fm., Tl = Tal Fm. Vertical scale heights in meter, carbonate carbon isotopic composition in parts per mil (‰) relative to PDB, Lst = Limestone, Dol = Dolomite, Sst = Sandstone. Arrow represents the isotopic excursions spanning the late Proterozoic-early Cambrian transitions.*

resent coeval facies variants. All the positive and negative excursions on the Bilara Hill profile (Fig. 1D) can be identified on the Hanseran Evaporite core profile (Fig. 1C). Carbon isotopic composition records partitioning of carbon between organic (reduced) and inorganic (oxidized) reservoirs during specific time interval and serves as a proxy for changes in paleo-oceanography and bioproductivity as well as rate of organic burial. The magnitude of carbon isotopic excursion indicates the extent of carbon isotopic partitioning between the reduced and oxidized carbon reservoir. It is apparent that P1, P2, N2 and N4 represent relatively rapid isotopic excursions compared to N1, N3 and P3. P1 shows maximum excursion of 12‰ (in evaporite core P/47) and 10‰ (in Bilara hill). Although the carbon isotopic profiles show similarity

between the Bilara Hill and Hanseran Evaporite core, the total isotopic excursions for individual peaks differ. The cause for the difference may be due to local differences in depositional/diagenetic milieu.

*Isotopic covariance*

$\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ (Fig. 4A) display covariance through N3, P3 and N4 but otherwise the covariance is less well defined. The zones of covariance below N3 are encircled (see Fig. 4A). Such covariance in the isotopic compositions through time reflects secular changes in the $^{13}C/^{12}C$ ratio of aquatic carbon reservoir and can not be an artifact of secondary processes (Knoll *et al.*, 1986; Narbonne *et al.*, 1994; Kimura *et al.*, 1997). The positive excursion of $\delta^{13}C_{carb}$ may be linked to preferential bio-

logical fixation of $^{12}$C into organic material and its enhanced rate of burial, which leads to enrichment of $^{13}$C in contemporary carbonate sediment. Increase in organic burial flux causes decrease in dissolved carbon dioxide from surface water [$CO_{2(aq)}$]. Lowering of [$CO_{2(aq)}$] in surface waters enriches the carbon isotopic composition of organic matter owing to reverse relationship between [$CO_{2(aq)}$] and $\delta^{13}$C of phytoplanktonic organic carbon (Popp *et al.*, 1989; Rau *et al.*, 1989, 1992; Jasper and Hayes, 1990; Hollander and McKenzie, 1991). On the other hand, depletion in $^{13}C_{carb}$ indicates a significant reduction in organic carbon burial, caused by reduced overall productivity as a result of lower nutrient supply. Enhanced supply of isotopically light, organically derived carbon into the carbon cycle through upwelling can also lead to $^{13}$C depletion in organic matter.

*Possible global and regional C isotopic signatures*

Based on the geological comparison with Ara Evaporite Formation (south Oman basin), the HEG/Bilara rocks may tentatively be assigned a late Neoproterozoic-early Cambrian age. It is well known that carbon isotopic fluctuations through late Neoproterozoic-early Cambrian are global in nature. However, owing to lack of accurate faunal or radiogenic ages, variable lithology and depositional rates, global correlation of all the isotopic profiles is problematic. Possibly the most well recognized late Neoproterozoic isotopic perturbation is the one through terminal Neoproterozoic-Nemakit-Daldynian-Tommotian. $\delta^{13}C_{carb}$ excursion through this time window has been recorded from Aldan river section (southern Siberia, Magaritz *et al.*, 1986), Anti Atlas mountain in Morocco (Tucker, 1986), Krol Belt in lesser Himalaya (Aharon *et al.*, 1987; Banerjee *et al.*, 1997), Oued Sdas in Morocco (Magaritz *et al.*, 1991), Olenek Uplift in northern Siberia (Knoll *et al.*, 1995), McKenzie Mountain in north western Canada (Narbonne *et al.*, 1994), Elburz mountain, Iran (Kimura *et al.*, 1997), Meischucun, China (Brasier *et al.*, 1990) and Death Valley in United states (Corsetti and Hagadorn, 2000). Figure 6 is a graphical correlation of the C-isotopic perturbation through N3-P3-N4 from the Bilara Hill section with the C isotopic excursion through late Neoproterozoic-early Cambrian transitional successions in lesser Himalaya (India), southern Siberia, northern Siberia and Morocco. However, we believe that this correlation is tentative and detailed biostratigraphic data is required to ascertain the global significance.

In contrast to the $\delta^{13}C_{carb}$ perturbation though N3-P3-N4, peaks P1, P2, N1 and N2 along the Bilara hill profile possibly represent local or basinal changes, which has been used in this work for regional correlation and to understand the geochemical processes of the evaporite basin which could affect the intrabasinal carbon isotopic

budget. Phosphorous and nitrogen are the primary nutrients responsible for bioproduction. Owing to restricted basinal conditions, evaporite basins are deprived of nutrient supply *via* upwelling from open ocean. It results in nutrient depleted condition in the surface waters due to lack of sustained replenishments. However, evaporation of marine water brought in to the closed basin through transgressions can increase the nutrient concentrations significantly (Kirkland and Evans, 1981; Eugster, 1985). Under evaporitic conditions the nutrient (phosphate and nitrate) concentrations in the water increases in general in direct proportion to the increase in salinity. In the mesohaline condition (12% salinity), the brine may contain compounds of phosphorous and nitrogen in optimum amounts to support the phytoplankton bloom (Kirkland and Evans, 1981) which eventually affects the carbon isotopic balance in the aquatic realm. We propose that the carbon isotopic fluctuations in Bilara and Hanseran sediments may be attributed to the fluctuation in nutrient concentrations (NEW or NDW) in the contemporary basin (Brasier, 1992).

*Contrasting $\delta^{13}C_{org}$ composition*

The contrasting $\delta^{13}C_{org}$ of Bilara hill and Baghewala-II core samples needs critical scrutiny. Samples of Bilara Hill section from the eastern part of the basin ranges from −31 to −27‰ and represents average late Neoproterozoic organic carbon isotopic value. Relatively shallow oxic basinal condition is suggested for this part of the basin. In contrast, Bilara carbonates encountered in the Baghewala-I core (Peters *et al.*, 1995) and Upper carbonates in Baghewala-II on the western extremity of the Nagaur-Ganganagar basin are significantly enriched in organic matter and has highly depleted organic carbon isotopic ratios (−33 to −37‰, avg. −36.2‰). $\delta^{13}C_{org}$ in Baghewala-II core samples are remarkably similar to those reported from the contemporary sedimentary sequence in eastern Pakistan (Karampur-1 well, avg. −37‰, Grantham *et al.*, 1987, 1990) and southern Oman (Ara Formation, −34.7 to −37.2‰, Peters *et al.*, 1995). Presence of sulfur rich organic matter (Peters *et al.*, 1995), dark laminated nature of the sediment and highly depleted C-isotopic composition of Baghewala-II samples suggests existence of relatively deep anoxic sulfate reducing depositional milieu in contrast to the largely oxic environment of Bilara hill carbonates. Recently, Hollander and Smith (2001) has demonstrated that the incorporation of biomass synthesized by chemoautotrophic or methanotrophic bacteria under anoxic or eutrophic basinal condition results in strong depletion of organic carbon isotopic composition of total organic matter in the sediment. Studies on $C_{31}$ to $C_{35}$ homohopane distribution (Peters *et al.*, 1995) in the Baghewala-I oil shows elevated $C_{35}$ homohopanes indicating anoxic depositional condi-

tion. In addition, the presence of anhydrite layers in Baghewala-II core implies deposition from brine solution. Therefore, the anoxia may be attributed to salinity stratification and formation of stable halocline (Mattes and Conway Morris, 1990), since persistent density stratification as a result of brine formation causes cessation of oxygen circulation below the chemocline.

Bottom-water anoxia has commonly been regarded as the primary control responsible for accumulation and preservation of organic matter (Demaison and Moore, 1980; Tyson, 1987; Tyson and Pearson, 1991). Such conditions are conducive to the accumulation and preservation of organic matter in fine-grained sediments. However, based on recent oceanographic studies, elevated primary productivity in surface waters has been proposed as an alternative to bottom-water anoxia as the primary control on organic matter accumulation (Parrish, 1982; Pederson and Calvert, 1990). Increased phytoplanktonic productivity can be triggered by a number of factors including upwelling currents that carry nutrients up into the photic zone, elevated salinity, and influx of terrestrial nutrients. Enhanced productivity results in increased flux of organic matter, and deplete oxygen levels in the surrounding water creating an oxygen minimum zone. In the present case the high productivity (lipid rich organic flux) was brought about by evaporative concentration of nutrient elements in the surface water where as the bottom water anoxia was the result of salinity stratification.

## CONCLUSION

In this paper we have presented carbon and oxygen isotopic compositions of carbonate phase as well as organic matter from the Bilara hill and Baghewala-II core of the Nagaur-Ganganagar basin. Existing carbon isotope profile (Banerjee and Mazumdar, 1999) through the Hanseran evaporite sequence (core P/47 near Lakhasar, Fig. 1C) in the central part of the basin has been compared with the Bilara Hill isotope profile. We have made an attempt to identify possible global and local/basinal carbon isotopic excursions preserved in this section. The isotopic perturbations have been used for global and regional correlation and to understand the geochemical processes which affected the carbon isotopic budget in the contemporary depositional basin. In particular, the following inferences are drawn:

1. We have tentatively identified the isotopic excursion through N3-P3-N4 as a global signature characterizing the late Neoproterozoic-early Cambrian transitional phase.

2. Resemblance of isotopic profiles through Bilara and Hanseran evaporites suggests correlated intrabasinal events with the two members representing coeval facies variants.

3. In contrast to organic-poor Bilara and Hanseran rocks, the organic-rich subsurface carbonate facies of Baghewala-II core samples suggests deposition under anoxic bottom water condition. The presence of sulfur rich organic matter indicates prevalence of sulfate reducing condition. Highly depleted C isotopic composition of the organic matter suggests potential presence of chemoautotrophic bacterial biomass in the sediment synthesized in an anaerobic and highly productive environment.

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