# CARBON AND OXYGEN ISOTOPE STRATIGRAPHY OF THE DEOBAN GROUP (MESOPROTEROZOIC) GARHWAL LESSER HIMALAYA, INDIA

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### ABSTRACT

The Carbon and Oxygen isotope stratigraphy from the Mesoproterozoic (Riphean) stromatolitic carbonate strata of Deoban Group, Garhwal Lesser Himalaya, India is interpreted in terms of the biosedimentological and palaeoen-vironmental changes of the sequence.

### INTRODUCTION

Palaeobiological activities on earth had started around 3800 million years ago and carbon is the main element in organic matter (Schidlowski et al., 1975; Eichmnn and Schidlowski, 1975). The ratio of stable carbon isotopes reflects the effect of biological activity in the carbon cycle. Isotopic fractionation of about 25% between the two carbon species (terrestrial or carbonate carbon and organic or reduced carbon) has been recorded from the rocks about 3500 million years old (Eichmann and Schidlowski, 1975; Schidlowski et al., 1975; Schidlowski et al., 1989). Carbon isotope stratigraphies of Proterozoic and Early Cambrian sequences have been established in recent years from different parts of the world. For example, Siberian platform (Magaritz et al., 1986; Knoll et al., 1995), Morocco (Tucker, 1986), Greenland-Spitsbergan (Fairchild and Spiro, 1987), China (Hsu et al., 1985; Lambert et al., 1987; Brasier et al., 1990), Krol-Tal sequence of the Lesser Himalaya (Aharon et al., 1987; Tewari, 1991; Kumar and Tewari, 1995; Aharon and Liew, 1992; Brasier et al., 1990), Iran (Brasier et al., 1990), Namibia (Kaufman et al., 1991). Analysis of global Proterozoic and Cambrian boundary sequences by Ripperdan (1994) suggest that all these localities preserve the secular variations in the carbon isotope composition of the global ocean system. The carbon isotope excur-

sions across the Precambrian and Cambrian boundary has been interpreted to explain evolutionary diversification and extinction events, palaeoenvironmental and palaeooceanic conditions, changes in sea water chemistry, extraterrestrial impacts and to establish chemostratigraphy (see reviews of Brasier et al., 1990; Brasier, 1992; Ripperdan, 1994). Tucker (1996) also made an attempt to explain the formation of rifted basins and passive continental margins in the Late Precambrian-Cambrian transition affecting the isotopic composition of seawater. Most of the isotope data for Proterozoic successions has been published from Late Riphean and Vendian (1000 to 545 Ma) or Neoproterozoic basins (Schidlowski et al., 1983; Knoll et al., 1995). Detailed carbon and oxygen isotopic analysis of Precambrian sedimentary carbonates between 1600 to 850 Ma done by Schidlowski, Eichmann and Junge (1975) and Schidlowski, Hays and Kaplan (1983) have  $\delta^{13}$ C values of 0 ± 2 permil. The  $\delta^{13}$ C variation within narrow limits from 1600 Ma to 850 Ma ago is guite interesting in palaeobiological and biogeochemical changes. A high resolution carbon isotope stratigraphy and depositional environment can be established for Mesoproterozoic (Lower to Middle Riphean) carbonates. A carbon isotope relationship between



Fig. 1. Location map and depositional model of the Deoban Group, type area, Lesser Himalaya.

stromatolites, phytoplankton and sea water (photosynthetic process) may also be studied for Mesoproterozoic carbonates. In this paper C and O isotopic data from an important Mesoproterozoic sequence of Deoban Group, Garhwal Lesser Himalaya, India generated at Max Planck Institute for Chemistry at Mainz in Germany is given. Present study also provide us C and O isotopic signatures below the Neoproterozoic Krol basin of the Lesser Himalaya.

### BIOSEDIMENTOLOGY

The Deoban type area near Chakrata (Fig. 1) was systematically sampled for carbon and oxygen isotope analysis on stromatolitic, oolitic and cherty dolomite facies of Deoban Group. Deoban Group comprises an approximately 1000 m thick succession of carbonate rocks (stromatolitic dolomites, cherty dolomite rich in microbiota and oolites) with thin beds of grey and black shales, slates and thinly laminated calcareous silty layers in the upper part (Fig. 2). Detailed litholog showing the lithology, types of microbial buildups and sample locations was prepared in the field (Figs. 1,2). The description of samples selected for carbon and oxygen isotope analysis is given Table 2. Deoban Group in (Mesoproterozoic/Lower to Middle

Riphean) in age in the type area (Tewari, 1993, 1996) is overlying the Damta Group (Chakrata

## TABLE 1

System	Period	Stage	Lesser Himalaya (Group)
Lower Cambrian	Lenian	Toyonian	
		Botomian	
	Aldanian	Atdabanian	Tal ( <i>Talian</i> )
2		Tommotian	
Terminal Proterozoic	Vendian	Ediacaran	Krol (Krolian)
	Cryogenian	Varanger	Blaini ( <i>Blainian</i> )
	UNCONFOF		
Neoproterozoic			Jaunsar ( <i>Jaunsarian</i> )
Mesoproterozoic	Riphean		Deoban ( <i>Deobanian</i> )
•			Damta



Fig. 2. Litholog of 1000 m thick Deoban Group showing various lithologies, microbial buildups and variations in carbon and oxygen isotopes.

Slates) of Lower Riphean age and followed by a shallow marine sequence of argillo- siliciclastic deposit known as Jaunsar Group (= Simla Group) of Upper Riphean age which in turn is unconformably overlain by Blaini Group of early Vendian (Cryogenian) age (Table 1, Tewari, 1996).

Fine grained carbonates, oolites and shales containing acritarch *Chuaria circularis* were analysed for present study. Whole rock samples were analysed but petrographically the carbonates and oolites are not much altered diagenetically and good preservation of original fabric and texture was found in thin section study. Tewari and Joshi (1993) have done detailed study of microstructures of stromatolites Deoban Group and from well preserved recorded microfabric representing original microbial texture. Petrographically controlled samples were analysed in the present study and care taken for selection of samples while avoiding coarse grained carbonates, recrystallisation veins and other diagenetic features. The ooids show primary fabric and no later calcite/dolomite cement has been observed. Thus, the  $\delta$  <sup>13</sup>C values of the carbonates represent pristine signatures and isotopic composition of the Deoban sea during Mesoproterozoic time. The carbon and oxygen isotope values obtained for 25 samples of the Deoban carbonates are shown in Fig. 2 and Table 2. Very light to quite heavy (-20 to + 10%) $\delta^{13}$ C values may result due to presence of organic matter and diagenesis in the carbonate

rocks, however in the present

isotopic analysis  $\delta^{13}$ C range from -3.7 to 6.6‰ (PDB) and mostly between 0 to 2‰ PDB. Thus, the  $\delta^{13}$ C values of the dolomites analysed are considered to be very close to the Proterozoic  $\delta^{13}$ C values recorded by Schidlowski *et al.* (1975, 1983) and represent original marine values.

The Deoban carbonates are tidal flat (shallow marine) deposits (Tewari, 1994, 1996) and the facies analysis of the Deoban Group (subtidal to

## 98 TEWARI

## TABLE 2

NO.	DESCRIPTION OF SAMPLE	(δ <sup>13</sup> c ‰PDB)	(δ <sup>18</sup> 0% oSMOW)
1 D1	Grey dolomite, lowermost Deoban Chakrata-Deoban road section 1 km near the contanct with Chakrata slates (Damta Group)	1.4	19.2
2 D2	Dark bluish dolomite with chert lenses and layers (microbiota), Chakrata-Deoban road, 1.2 km.	1.8	17.3
3 D3	Dark bluish (organic) cherty laminated dolomite (microbiota bearing), Chakrata-Deoban road, 1.3 km.	3.2	25.4
4 D4	Oolitic-intraclastic, coated carbonate grains near bifurcation to Deoban Forest Rest House (DFRH) mule path, Deoban 3 km.	4.6	19.9
5 D5	Light grey dolomite with large <i>Kussiella kussiensis</i> biostrome and small <i>Conophyton</i> sp. biostrome, DFRH road, 100 m from bifurcation.	2.9	24.5
6 D6	Light grey dolomite with Stratifera sp. 1 km form biofurcation.	3.0	22.7
7 D7	Dark bluish dolomite with <i>Baicalia nova</i> biostrome, 500 m west of DFRH (altitude 9232 feet)	1.7	17.8
8 D8	Greyish black shale with <i>Chuaria circularis</i> megascopic acritarch between stromatolitic buildups, 500 m west of DFRH. Locality as D7	6.6	27.2
9 D9	Dark black (organic) silty shale (similar to D8)	0.3	18.9
10 D10	Dark bluish grey dolomite with <i>Jurusania</i> sp. and <i>Minjaria</i> sp. biostrome, 100 m below DFRH.	-3.7	21.5
11 D <b>11</b>	Dark bluish grey dolomite with <i>Jurusania</i> sp. and <i>Minjaria</i> sp. biostrome, 100 m below DFRH.	2.0	22.6
12 D12	Dark bluish grey dolomite with <i>Tungussia</i> sp.	1.4	20.4
13 D13	Dark bluish grey-dolomite with elongated conical <i>Georginia</i> sp. and <i>Conophyton</i> sp.) structures.	1.4	18.5
14 D14	Light grey dolomite foot path to Deoban summit.	2.0	21.1
15 D15	Light grey dolomite after 100 feet interval	2.1	21.9
16 D16	Light grey dolomite after 100 feet interval	1.5	19.6
17 D17	Light grey dolomite after 100 feet interval	0.9	16.8
18 D18	Light grey dolomite after 100 feet interval	1.2	21.0
19 D19	Light grey dolomite after 100 feet interval	1.3	21.1
20 D20	Light grey dolomite after 100 feet interval	0.9	16.8
21 D <b>21</b>	Alternating thin dolomite and silty layers	4.8	27.3
22 D22	Finely laminated calcareous silty layers	4.3	29.4
23 D23	Light grey dolomite (altitude 9000 feet).	1.1	20.9
24 D24	Light grey laminated dolomite (altitude 10,000 feet).	1.4	20.6
25 D25	Light grey laminated dolomite (altitude 10,000 feet).	1.1	19.1

ooid shoals, protected intertidal flats, (Fig. 1) is similar to the modern tidal flat (Sabkha) deposits which have near marine  $\delta^{13}C$  values.

## ANALYTICAL PROCEDURE

Finely powdered sample (10 mg) of carbonates and shales (n = 25) were treated with anhydrous (100%) phosphoric acid at 25 °C for two days according to the method described by Craig (1957). The resulting carbon dioxide gas was subjected to mass spectrometric analysis. VG Isogas PRISM isotope ratio mass spectrometer of the Max Planck Institute of Chemistry (Biogeochemistry Department) Mainz, Germany was used for the determination of C and O isotopic compositions. Results are reported as  $\delta^{13}$ C values relative to the PDB standard with

$$δ13C = \frac{\binom{13}{2}C/\binom{12}{2}sample - \binom{13}{2}C/\binom{12}{2}standard}{\binom{13}{2}C/\binom{12}{2}standard} \times 1000(\%) PDB$$

All values are corrected for Craig correction (Craig, 1957). For determination of organic (reduced) carbon 0.5 gm powder of organic rich material, 1.0 gm of medium organic rich and 2.0 gm of low organic material was used. Carbonate carbon was removed with diluted (1:4) phosphoric acid at 50°C. The material was then reacted with CaO as oxidising agent at 900° under vacuum.

## CARBON AND OXYGEN ISOTOPE STRATIG-RAPHY

The results of C and O isotope measurements on Deoban carbonate and shales are shown in Table 2. The carbon and oxygen isotope stratigraphy of the Deoban Group is presented in Fig. 2. The number of samples analysed (25) from 1000 m thick Deoban Group is certainly too small to definitely establish a high resolution isotope stratigraphy. However, the important microbial build ups, organic rich shales and light grey dolomite (bulk lithology of the Deoban Group) has been investigated which covers the important facies of Deoban Group from base to top in the type area. As a whole, the isotopic composition of the dolomites seems to be fairly uniform throughout the Deoban Group except (D 9 in black organic) shales and the dolomite immediately overlying the shales (Sample No. D 10) where isotopically lighter (0.2 to -3.7) values have been recorded due to organic matter (?). The heaviest carbon ( $\delta^{13}C$  = + 6.6‰) has been recorded in grevish black shale with acritarch Chuaria circularis between the stromatolitic buildups, 500 m west of the DFRH.

Following major carbon isotopic trends have been recorded from the Deoban Group.

- (i) low positive values (+ 1.4 to + 1.8‰) for the first 100 meters of grey dolomite at the lower part of the Deoban Group.
- (ii) high positive values (+ 3.2 to +4.6‰) for next 100 metres of dark bluish black (organic) dolomite and oolitic dolomite.
- (iii) a gradual low positive values (+ 2.9 to 3.0%) for next 100 metres for microbial buildups of *Kussiella kussiensis*, small *Conophyton* sp. and *Stratifera* sp.
- (iv) low positive value (+ 1.7%) for *Baicalia nova* microbial buildups for next 25 metres.
- (v) highest positive value (+ 6.6‰) for greyish black shale with acritarch *Chuaria circularis* for next 25 metres.
- (vi) drastic drop in the positive value from + 6.6 to 0.28‰ for dark black silty shales for next 50 metres.
- (vii) a shift from positive value to moderately negative value (- 3.7‰) for dark bluish grey dolomite with *Jurusania* sp. which become again positive within 100 metres thickness (+ 2‰).
- (viii) low positive values +0.9 to 2.1‰) persist for about next 300 metres for light grey dolomites.
- (ix) high positive values (+ 4.3 to + 4.8‰) for next 100 metres for light grey laminated dolomite with silty layers.
- (x) low positive values (+ 1.1 to 1.4‰) for the last 100 metres (uppermost part) of the Deoban Group.

The  $\delta^{18}$ O (SMOW) values of the Deoban Group varies from + 16.8 to + 29.4‰ (Figure 2). Since  $\delta^{18}$ O signature of a marine carbonates precipitate is a reflection of the isotopic composition of seawater and the temperature and the values may change for biogenic carbonates (Tucker, 1986).  $\delta^{18}$ O of Deoban Group is mostly in the range of + 17.3 to + 25.4‰ in the lower 400 metres. The increase in  $\delta^{18}$ O (+ 27.2‰) has been

### 100 TEWARI

recorded in the greyish black shales with *Chuaria circularis* acritarchs.  $\delta^{18}$ O of bluish grey dolomite and light grey dolomite varies in a narrow range of + 6.8 to 22.6‰ in next 400 metres. This steady value shift to a more positive (maximum) value of 29.4‰ in finely laminated calcareous silty layers for 100 metres.  $\delta^{18}$ O value of light grey laminated dolomite in the upper part of Deoban Group (100 metres) varies from 19.1 to 20.9‰.  $\delta^{18}$ O (PDB) values of the Deoban Group are very negative (mostly -1.3 to 12.6‰ PDB). The negative  $\delta^{18}$ O signatures may be interpreted as a result of diagenetic overprint and these values are diagenetic.

### DISCUSSION AND CONCLUSIONS

Carbon and Oxygen isotope data of whole rock carbonates from Mesoproterozoic Deoban Group, Lesser Himalaya has been investigated.  $\delta^{13}$ C values vary from -3.7 to + 6.6% (PDB) depicting one main distinct signatures of <sup>13</sup>C maxima minima.  $\delta^{18}$ O values vary from + 16.8 to 29.4‰ (SMOW) and -1.3 to 12.6‰ (PDB). Two distinct signatures of  $\delta^{18}$ O maxima-minima have been recorded. The recorded isotope data represent pristine isotopic signature. The Deoban Group carbonates are mostly stromatolitic and microbial in nature and the deposition of these carbonates indicate increased productivity of stromatolitic microbial communities which preferentially fixes <sup>12</sup>C in the form of organic carbon (C org.) resulting <sup>13</sup>C enrichment in carbonate carbon. The  $\delta^{13}$ C maxima (6.6‰) recorded in Deoban organic shales, thus relate to overall increase in sedimentary carbon (C carb. + Corg.) budget, increased availability of carbon dioxide in the environment and possibly warmer climates and alkaline pH conditions. The  $\delta^{13}$ C values of the Deoban carbonates showing mostly positive trend of excursion could be the result of increased rate of organic matter burial in a shallow carbonate platform. The Deoban carbonates are quite rich in microbiota (organic rich) and a negative ( $\delta^{13}$ C - 3.7<sup>\omega</sup> PDB) to positive  $\delta^{13}$ C trend (+ 2<sup>\omega</sup> to

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The present attempt to establish a tentative carbon isotope stratigraphy of Deoban Group is useful in refining the Mesoproterozoic palaeobiological evolutionary events and high resolution chemostratigraphy with additional close sampling along this profile of the Deoban Group.

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