

Isotopic and sedimentological clues to productivity change in Late Riphean Sea: A case study from two intracratonic basins of India

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Enriched $^{13}\text{C}/^{12}\text{C}$ ratios with $\delta^{13}\text{C} \sim 3\%$ (w.r.t PDB) of two Late Riphean ($\sim 700\text{--}610$ Ma) intracratonic carbonate successions viz., Bhandar Limestone of Vindhyan Basin and Raipur Limestone of Chattisgarh Basin suggest higher organic productivity during this period. This view is supported by sedimentological evidence of higher biohermal growth and consequent increase in depositional relief in the low gradient ramp settings inferred for these basins. Oxygen isotope analysis of these carbonates show distinct segregation between enriched deeper water carbonate mudstone and depleted shallow water stromatolite facies that received fresh water influx. This shows that facies-specific analyses can be useful in understanding the depositional setting of these sediments.

1. Introduction

The Neoproterozoic period ($\sim 1000\text{--}545$ Ma) is characterised by highly positive carbon isotope ratios with average $\delta^{13}\text{C} \sim 4\text{--}5\%$ and intermittent negative excursions (Kaufman and Knoll 1995 and references therein). The enriched $\delta^{13}\text{C}$ pattern is explained in terms of high rate of organic matter burial, but the opinions vary regarding the causative mechanism for this increased burial. Enriched $\delta^{13}\text{C}$ values during the Vendian ($\sim 590\text{--}550$ Ma, associated with the Precambrian/Cambrian (Pc/C) boundary) are explained by increased burial due to higher sedimentation caused by enhanced continental erosion (Knoll *et al* 1986; Burns and Matter 1993; Corsetti and Hagadorn 2000; Santos *et al* 2000) whereas the enriched values during the upper Riphean ($\sim 730\text{--}620$ Ma) are related to large scale anoxia through volcanic/hydrothermal input (Kaufman and Knoll 1995). $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of marine carbonates in the sediments of the corresponding periods are ≥ 0.709 and ≈ 0.706 respectively

corroborating the above views (Kaufman *et al* 1992). Knoll (1991) suggested increased oceanic productivity (extracting relatively more ^{12}C compared to ^{13}C from the oceanic reservoir), for the enriched $\delta^{13}\text{C}$ values associated with Pc/C boundary. It is not known whether this mechanism applies to the enriched values of older Riphean time as well. Although sedimentological evidences are useful to test higher productivity, most of the studies used stable isotope tracers as stratigraphic markers and to study changes in carbon reservoir during the Meso- and Neoproterozoic interval. Only a few studies have addressed the sedimentary environment-isotope connectivity (Misi and Veizer 1998).

Here we report combined isotopic and sedimentological evidences of higher Neoproterozoic oceanic productivity for two upper Riphean carbonate successions of Chattisgarh (Raipur Limestone) and Vindhyan (Bhandar Limestone) Supergroups of central India. Detail facies analysis of the Bhandar Limestone (Sarkar *et al* 1996) provided the basis for facies-specific isotope studies.

Keywords. $\delta^{13}\text{C}$; Late Riphean; intracratonic; organic productivity.

Facies and isotope analyses for the Raipur Limestone Formation are the outcome of the present study.

2. Geology

Vindhyan and Chattisgarh are two extensive Purana basins in peninsular India containing the Meso and Neoproterozoic sediments (Radhakrishna 1987; Banerjee and Majumder 1999; figure 1). The basins are similar in their mixed siliciclastic-carbonate lithology, absence of metamorphic overprinting and very low tectonic disturbance. Intracratonic sag model has been favoured for both (Das *et al* 1992; Bhattacharya 1996). Palaeocurrent and facies distribution data of the Vindhyan suggest a restricted connection with open sea towards NW (Chanda and Bhattacharya 1982) but no conclusive evidence is available for the opening of Chattisgarh Basin. Instead, a bull's-eye lacustrine model was proposed for Chattisgarh sedimentation (Das *et al* 1992). These basins do not contain signatures of Varanger glaciation, which is common in most of the Neoproterozoic successions elsewhere. Two carbonate formations viz., Raipur Limestone (RL) and Bhandar Limestone (BL), which form parts of upper sedimentary successions of Chattisgarh Basin and Vindhyan Basin respectively (figure 1) constitute the materials for the present study.

Both Raipur Limestone and Bhandar Limestone suffer from lack of radiometric age data specific to these formations. Age connotations of these carbonate units are based on stromatolite biostratigraphy or dates available for the adjacent geological formations. A lower bound for the age of Raipur Limestone can be estimated from K-Ar date (~ 700 – 750 Ma; Kreuzer *et al* 1977) of authigenic glauconite minerals of an older stratigraphic horizon namely, sandstones of Chandarpur Group. Deb and Chaudhuri (2002) also regarded this age as the minimum age of sedimentation in Chattisgarh Basin. From studies of algal stromatolite assemblages in different formations of Chattisgarh Supergroup Chatterjee *et al* (1990) suggested middle to upper Riphean age. Observation of *Linella-Gymnosolen-Baicalia* stromatolite assemblage within Raipur Limestone prompted Moitra (1995) to suggest uppermost Proterozoic age.

Similarly, in Vindhyan succession most of the radiometric dates available are from Semri and Kaimur Formation, which are at lower stratigraphic level than Bhandar Limestone. Soni *et al* (1987) summarised these dates provided by earlier workers (Vinogradov *et al* 1964; Crawford and Compston 1970 and many others) and suggested a depositional age between 1400 Ma and

900 Ma for Semri and Kaimur Formation. Paul *et al* (1975) provided radiometric age of 974 ± 30 Ma to 1120 ± 45 Ma (K-Ar method) for kimberlite pipes of Majhgaoon area, which crosscut Rewa sediments. These data suggest a depositional age for Bhandar Limestone less than 900 Ma. Venkatachala *et al* (1996) from stromatolite biostratigraphy and microbial evidence derived Riphean age for Bhandar Limestone. Based on oxygen, carbon and strontium isotope studies Kumar *et al* (2002) put a 700–540 Ma age bracket for the entire Bhandar Group.

Various workers (Friedman and Chakraborty 1997; Banerjee and Majumder 1999) speculated continuation of both Raipur and Bhandar Limestone across the Pc/C boundary. Absence of tillites of Varanger glaciation (610–590 Ma) and metazoan assemblage of Cambrian affinity in these basins, however, rule out that these formations transgressed the Pc/C boundary. Within this broad age framework provided by available radiometric age data, consideration of stromatolite biostratigraphy and Sr isotope results together with relative stratigraphic positions of these units (for example Bhandar Limestone occurring towards lower part of the Bhandar Group, figure 1) prompted us to assign upper Riphean age lying within 700 to 610 Ma for both of these carbonate formations.

In general, omnipresent wave signature, consistent palaeoslope direction and parallel facies belts indicate homoclinal ramp geometry for deposition of these carbonate successions (Prasad and Varma 1991; Moitra 1995). Bhandar Limestone of Vindhyan Basin is considered to be of marginal marine origin (Banerjee 1974; Chanda and Bhattacharya 1982; Prasad and Varma 1991). Sarkar *et al* (1996) identified five distinctive facies of wide palaeogeographic significance, ranging between beach shore face to distal shelf. These include Stromatolite (SM), Plane laminated mudstone (PLM), Planar and cross-stratified calc-arenite (PCS), Heterolithic limestone-shale (HL) and shale (SH; table 1). In the absence of any laterally traceable marker horizon in Bhandar Limestone, a number of short sections exposed along roads and nala cuttings all along the belt reveal broad tabular geometry for most of these facies except for the SM and PCS facies. Reconstruction of lateral facies relationships revealed significant variation in the relief of SM facies (Sarkar *et al* 1996). The wedge shaped PCS facies that erosionally overlies deep-water stromatolite facies was interpreted as a product of lower sea level setting (Chakraborty 1996). A broad marine subtidal to intertidal palaeogeography has long been invoked for the dominantly stromatolitic succession of Raipur Limestone (Murti 1987; Moitra 1995). Detailed facies analysis also recognizes oscillation of this carbonate platform

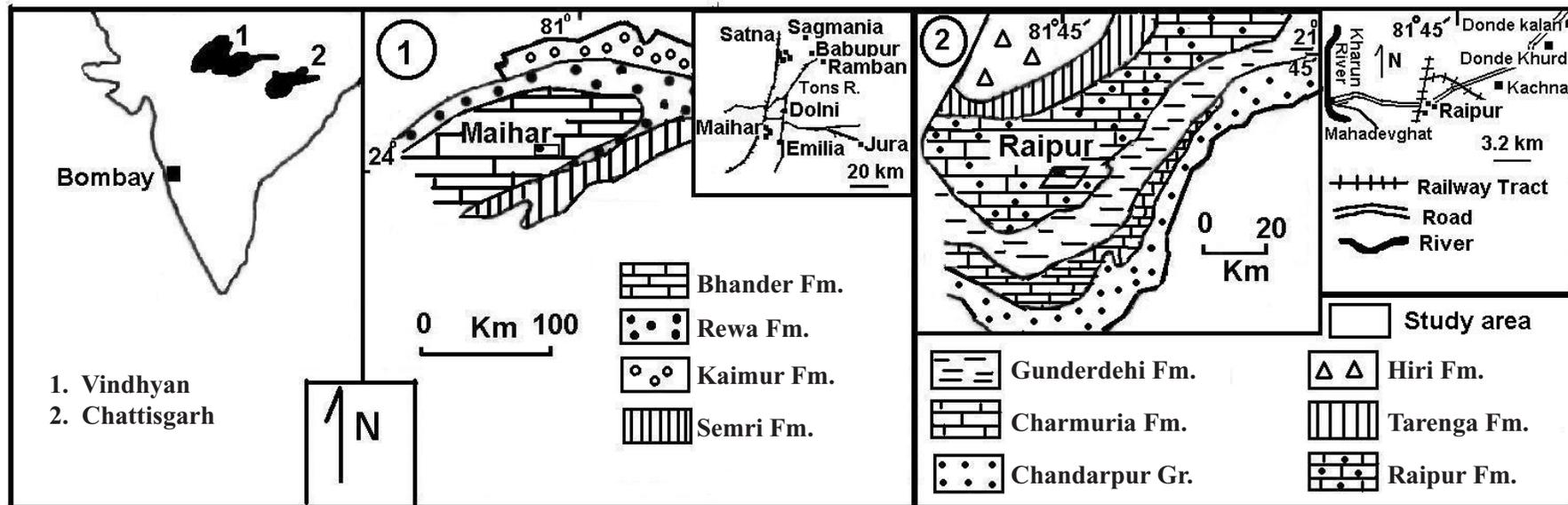


Figure 1. Geological map of Vindhyan (1) and Chattisgarh (2) Basin. Samples were taken from Bhander Formation in Vindhyan and from Raipur Formation in Chattisgarh, shown in frame (1) and (2) respectively.

Table 1. *Facies types, characters, inferred depositional environment and respective stable isotope data of Bhandar and Raipur Limestone. Facies data for BL are taken from Sarkar et al (1996).*

Bhandar Limestone				
BL facies code	Descriptions**	Environment	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Stromatolite (SM)	Dark coloured stromatolites, biohermal and stratiform; domal, composite and microdigitate form; common association with PCS and HIL	Shallow agitated subtidal (digitate form) to inner shelf (composite domal forms)	4.29	-6.49
			4.59	-8.08
			3.9	-9.92
			4.08	-8.85
			3.71	-8.19
			3.27	-7.59
			2.81	-9.66
			2.56	-5.34
			1.22	-3.98
			0.5	-5.21
			1.45	-7.6
			0.85	-6
			4.95	-8.4
			2.7	-7.52
2.75	-8.75			
Plane laminated mudstone (PLM)	Calcareous laminae with thick-thin alternation, interrupted occasionally by graded or ungraded storm generated beds	Offshore, below storm wave base	2.93	-6.66
			3.54	-3.51
			4.42	-6.11
			3.54	-4.73
			3.51	-2.61
			4.03	-3.2
			2.42	-4.22
			4.3	-5.21
			3.54	-5.82
			4.53	-4.32
			3.14	-3.2
			3.16	-4.66
3.91	-2.28			
Planar and cross stratified (PCS)	Light coloured calc arenite in sharp erosional contact with underlying facies, tabular bed geometry, herringbone with subordinate chevron cross stratification, polymodal current pattern	Wave and tide affected shore face	-1.73	-5.09
			-1.63	-5.32
			-0.91	-7.37
			-0.62	-4.14
			-1.43	-5.64
			0.29	-5.22
			0.75	-5.22
			-0.38	-4.70
			0.30	-3.72
			-0.75	-5.67
			-0.90	-4.16
			0.28	-6.4
			-0.26	-6.62
-0.26	-6.62			
-1.1	-5.20			

Heterolithic (HL)	Alternating couplets or mechanical laminites of basal coarse grained deposits grading upward in laminated fines; extensively dolomitised; wave ripple and hummocky cross stratified, gutter cast at the sole	Storm dominated inner shelf	nm	nm
Shale (SH)	Greenish gray silty shale, plane laminated with starved siltstone ripples; at places thin limestone layers; upward grading into reddish colour with isolated scours	Distal offshore close to storm wave base	nm	nm
Raipur Limestone				
RL facies code	Description	Environment	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Stromatolite (SM)	(i) Dark coloured stromatolites with domal hemispheroids, individual radiating columns.	Shallow subtidal	2.79	-10.32
			3.57	-9.03
			3.42	-8.97
			2.67	-9.58
			3.24	-9.19
			2.27	-10.88
			2.67	-9.61
		2.52	-10.52	
	(ii) Laminated, non-linked, vertically stacked columns of cylindrical or club shape; occasional desiccation cracks and fenestrae.	Agitated to protected intertidal	3.73	-7.54
			3.71	-8.08
Plane laminated mudstone (PLM; figure 3b)	Alternating cm. scale limestone and muddy siliciclastic layers; calcareous laminae at places show internal grading; no current or wave signature.	Offshore below storm wave base	3.79	-4.76
			3.66	-5.07
			2.42	-7.18
			3.89	-4.07
Conglomerate (CGL)	Calcirudite, essentially of fragmented stromatolite columns; tabular or channelised bed geometry, erosional with underlying PLM facies, occasionally amalgamated; clast to matrix ratio variable.	Autoclastic related to local slope generation; mass flows independent of any specific environment; shallow inner shelf to distal offshore.	nm	nm

nm: Not measured. **From Sarkar *et al* 1996.

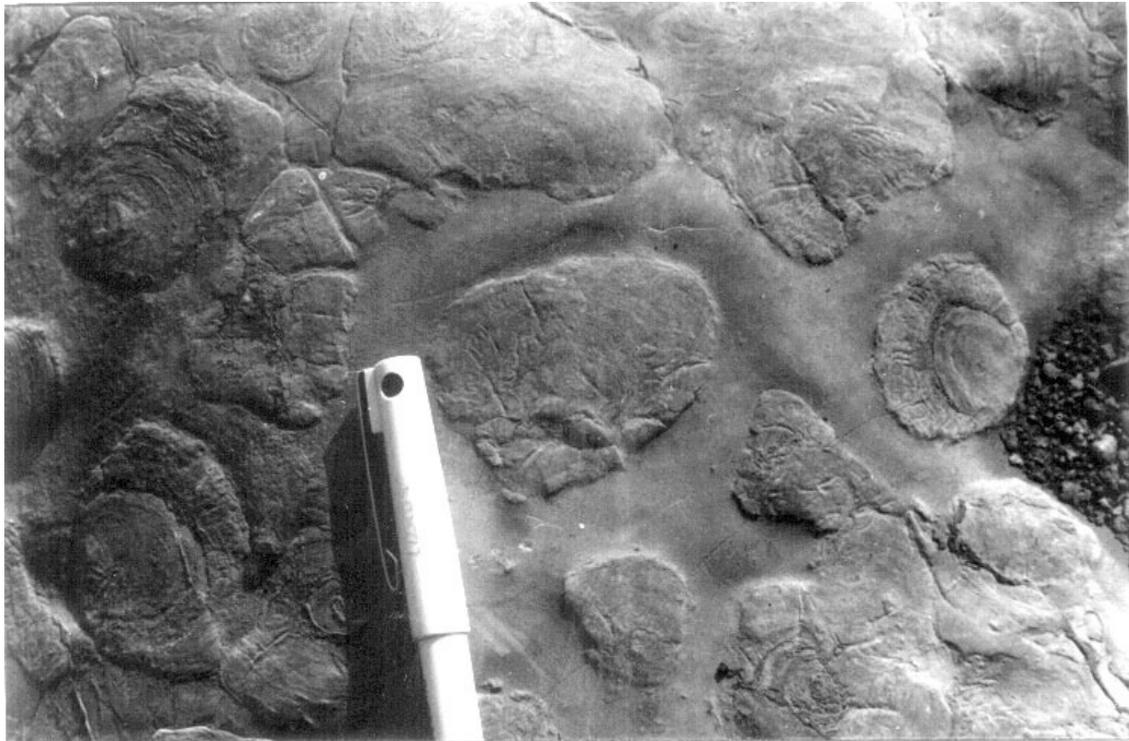


Figure 2. Bedding plane exposure showing concentric tapering (desiccation) cracks on isolated stromatolite columns, Pikridih, Raipur Limestone, Chattisgarh; note high amount of inter columnar material.

between high and low depositional energy (discussed below).

3. Results

Detailed facies analyses of BL have been presented earlier by Sarkar *et al* (1996); here we report some relevant sedimentological aspects of RL. Stromatolites in the Raipur Limestone show columnar, domal and stratiform morphology. Character and volume of inter-columnar material, disposition of columns with respect to bedding plane and influx of siliciclastic detritus vary from place to place. Emergent features like desiccation cracks on solitary columns with high granular intercolumnar material (figure 2) at some discrete levels of stromatolite succession and plane laminated lime mudstone (figure 3) without any signature of wave or current action are also identified. A thick (~ 35 m) intrabasinal autoclastic conglomerate within the RL is exclusively composed of stromatolite clasts (figure 4). Although dominantly of bedded geometry, these conglomerates, at places, preserve a channelised form that erosionally overlies the plane laminated lime mudstone.

Carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotope analyses have been carried out on facies-specific carbonate samples (15 and 13 number of samples from SM and PLM facies of BL; 10 and 4 number of samples from SM and PLM facies of RL; table 1) follow-

ing the procedure of Sarkar *et al* (1996). Analytical results are given in *d*-notation expressed w.r.t PDB with reproducibility of $\pm 0.1\text{‰}$ and $\pm 0.2\text{‰}$ for carbon and oxygen isotope ratios respectively. Alteration of original isotopic signatures due to diagenesis is minimum because none of these carbonate successions suffered deep burial diagenesis (Chanda *et al* 1977; Banerjee and Majumder 1999). Dominant micritic character of limestones, well preserved primary features including stromatolite laminae, pelloidal and intraclastic texture in lime mudstone (Burns and Matter 1993), poor correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (figure 5) and persistent facies independent $\delta^{13}\text{C}$ values (excepting the PCS facies; see later discussion) throughout the succession in both the formations supply additional evidence regarding absence of any deep burial diagenesis.

Mean $\delta^{13}\text{C}$ values of samples from stromatolite (SM) and plane-laminated mudstone (PLM) facies of Bhandar and Raipur Limestone are shown in figure 6. The $\delta^{13}\text{C}$ values are all positive for both RL (2.27‰ to 3.89‰; mean 3.19‰ $\pm 0.6\text{‰}$, $n = 14$) and BL (0.5‰ to 4.95‰; mean 3.32‰ $\pm 1\text{‰}$, $n = 28$). These values are similar to earlier reported values of $\delta^{13}\text{C}$ for BL (2.6 to 5.7‰; Friedman and Chakraborty 1997; Kumar *et al* 2002) and for RL (2.5 to 5‰; Schidlowski *et al* 1975). The mean δ -values of samples from both the formations are within the range of $\delta^{13}\text{C}$ values of marine carbon-

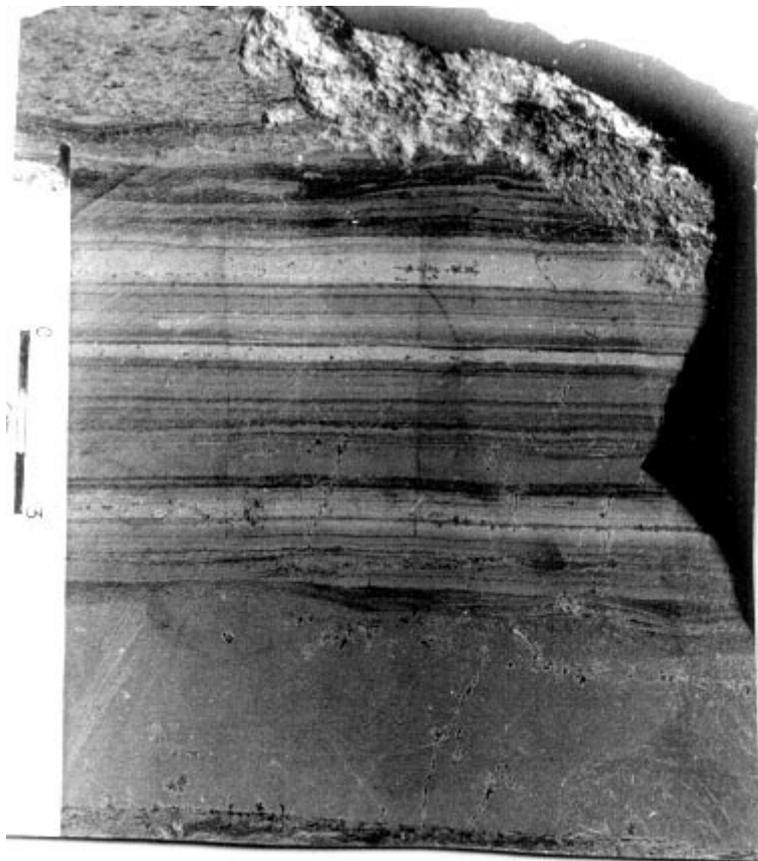


Figure 3. Plane laminated lime mudstone in Raipur Limestone, Kharun river, Raipur (see text).



Figure 4. Bedding perpendicular section showing autoclastic conglomerate (with random stromatolitic clasts), Raipur Limestone, Kharun river section, Raipur.

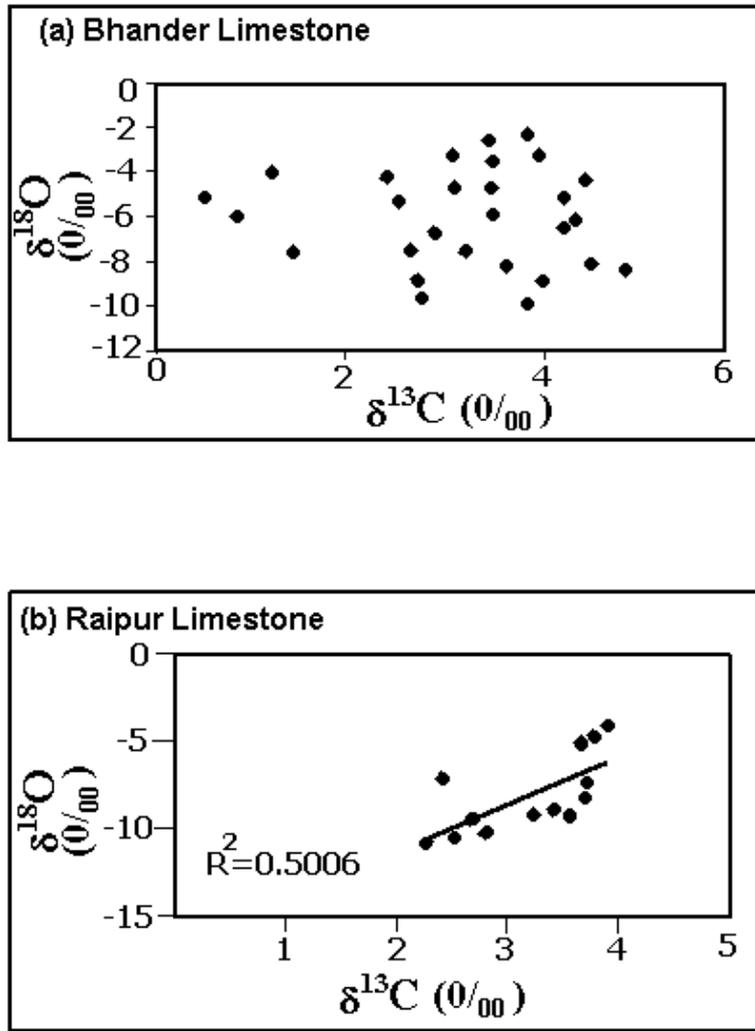


Figure 5. Plot of $\delta^{13}\text{C}$ values against $\delta^{18}\text{O}$ values for Bhander Limestone (a) and Raipur Limestone (b). Note poor correlation between the two in case of Bhander Limestone.

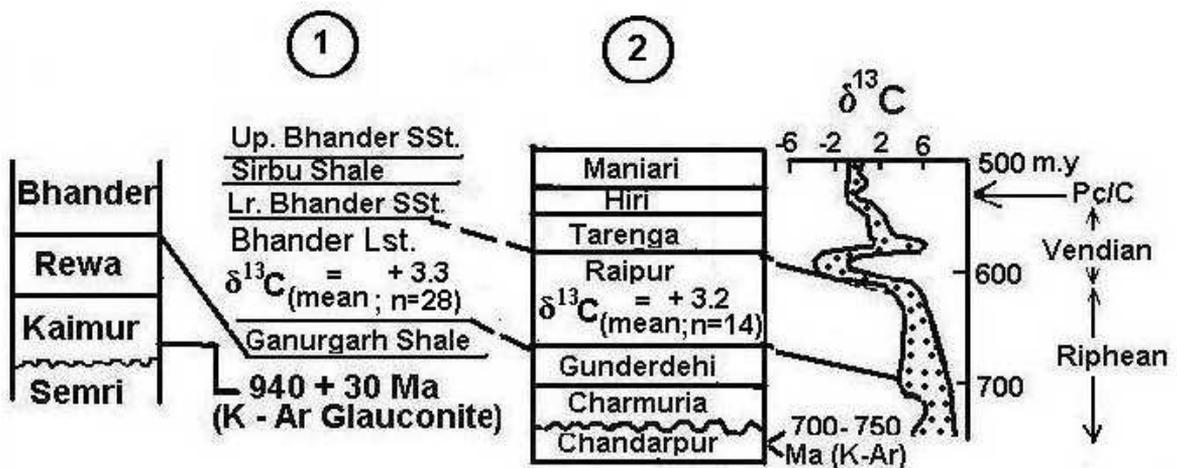


Figure 6. General stratigraphy for Vindhyan (1) and Chattisgarh (2) basin, inter-basinal correlation and average global $\delta^{13}\text{C}$ curve for late Proterozoic time (after Kaufman *et al* 1992).

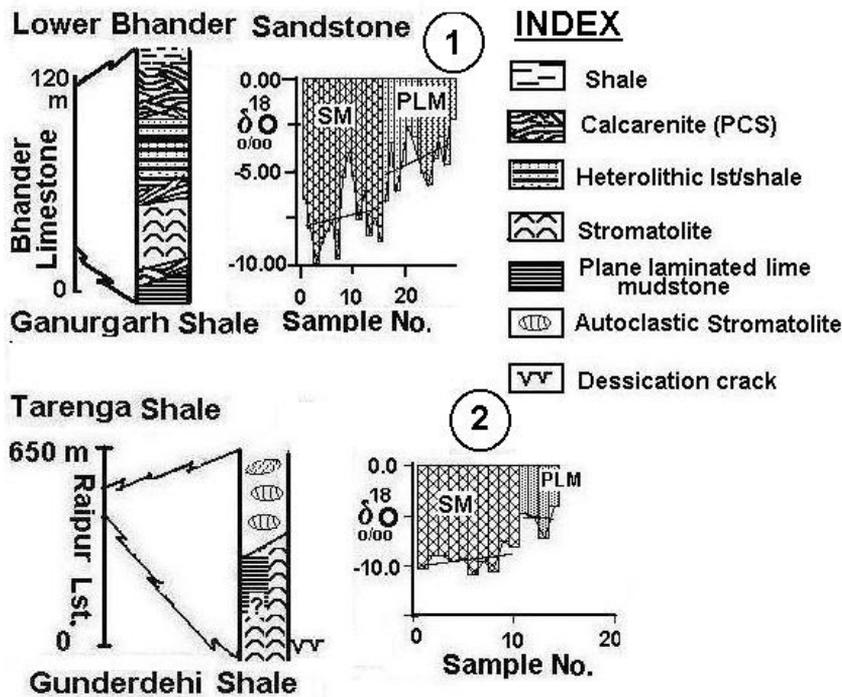


Figure 7. Representative lithologies for Vindhyan and Chattisgarh Basin. Difference in $\delta^{18}\text{O}$ values between stromatolite and plane laminated mudstone facies in both the sections are shown by histograms alongside. Note distinct break in trendline between the two facies.

ates reported for the late Riphean period (3 to 6‰; Kaufman *et al* 1992; Kaufman and Knoll 1995; figure 6). Such enriched $\delta^{13}\text{C}$ values from two widely separated basins (one land-locked and the other with restricted open ocean connection) may indicate a common forcing mechanism. In contrast to these general positive values of SM and PLM facies, $\delta^{13}\text{C}$ value for 14 number of samples analysed from PCS facies of BL varies from -1.73‰ to $+0.28\text{‰}$.

$\delta^{18}\text{O}$ values of plane laminated lime mudstone and stromatolite facies vary significantly (figure 7). The plane laminated distal carbonate facies is enriched by $\sim 3\text{--}4\text{‰}$ compared to the shallower (shoreface) stromatolite facies. Stromatolitic limestone of RL, showing desiccation cracks, is enriched by $\sim 2\text{‰}$ ($\delta^{18}\text{O}$ value ~ -7.5 to -8‰ ; table 1) compared to the subtidal biohermal stromatolite colony ($\sim -9.8\text{‰}$). $\delta^{18}\text{O}$ values from PCS facies of Bhandar Limestone show a random variation from -7.37‰ to -3.72‰ without clustering in a restricted range.

4. Discussions

Stromatolite morphology is a useful tool for deciphering palaeo-water depth (cf. Glumac and Walker 2000). Variation of stromatolite morphology and the variation in character (sandy/muddy) and volume of inter-columnar material, column disposition etc. in Raipur Limestone suggest that this

carbonate platform oscillated between high and low energy conditions. Emergent features like desiccation cracks with high granular intercolumnar material (figure 2) to distal plane laminated lime-mudstone (figure 3) suggest palaeogeographic variation from inner ramp (i.e., above fair weather wave base) to outer ramp (below storm wave base; cf. Burchette and Wright 1992). Occurrence of thick autoclastic conglomerate (figure 4) in this limestone sequence and the reported low-stand wedge of calc-arenite composition, encased within distal facies in BL (Chakraborty 1996) indicate generation of high accommodation space that is unlikely for an intracratonic platformal setting (Allen and Allen 1993). Bounding formations of Bhandar Limestone (Ganurgarh shale and Lower Bhandar sandstone) and Raipur Limestone (Gunderdehi shale and Tarenga shale; figure 1 and 6) contain dominant muddy lithology, indicative of general sediment starved depositional settings. Based on available age data and thickness of the units, Venkatachala *et al* (1996) estimated a low sedimentation rate ($\sim 70\text{ cm}/1000\text{ years}$) for the Vindhyan succession. This estimate does not consider the episodic nature of sedimentation history. Although no such estimate is available for the Chattisgarh Basin, the overall argillite-carbonate association of Raipur Group indicates a lower sedimentation rate. In the absence of signatures for syn-sedimentary tectonics (Chanda and Bhattacharya 1982; Murti 1987) or lack of any sig-

nal for abrupt rise in relative sea level generation of such accommodation space in homoclinal ramp settings (lacking shelf-slope break) with slow rate of sedimentation can be accounted through rapid organic build-up and biohermal growth (Chakraborty 1996). Evidences for such biohermal growth both within Bhandar Limestone and Raipur Limestone suggest high organic productivity in late Riphean time, irrespective of whether the depositional basin had open ocean connection (Vindhyan Basin) or not (Chattisgarh Basin). High $\delta^{13}\text{C}$ signature of these carbonates is in conformity with this suggestion. Such high $\delta^{13}\text{C}$ values (~ 1.5 to 3.5‰) are also recorded throughout the 200 m sequence of late Riphean carbonates from Bhima basin (Gopendra Kumar *et al* 1997).

In the absence of evaporitic condition, which may cause heavy carbon isotope enrichment (Knoll *et al* 1986) or increased reductant influx (and consequent anoxia; *op. cit.*; Kaufman and Knoll 1995) through coeval volcanic/hydrothermal activity, the uniformly enriched $\delta^{13}\text{C}$ values in Bhandar and Raipur Limestone Formations may indicate increased water column productivity since increased photosynthesis by rapid growth of algal community leads to enhanced $\delta^{13}\text{C}$ of the ΣCO_2 of the ambient oceanic reservoir. Lower $\delta^{13}\text{C}$ values in some of the samples from SM facies of BL (in comparison to the earlier reported values) and in the PCS facies of BL, in general, could be due to precipitation in shallow coastal zone where both stromatolites and clastic carbonate particles form under the influence of continent derived ΣCO_2 in the ambient water (Sarkar *et al* 1996).

Global average values of $\delta^{18}\text{O}$ for late Precambrian carbonates range from -10‰ (for limestones) to -6‰ (for dolostones; Veizer and Hoefs 1976). High depositional temperature, isotopically depleted seawater or continuous isotopic exchange can explain such low values. Considering the $d\delta^{18}\text{O}/dt \sim -0.25\text{‰}/^\circ\text{C}$ (*op. cit.*), the $\delta^{18}\text{O}$ difference of $\sim 3\text{--}4\text{‰}$ between the plane laminated facies (mean $\sim -5.7\text{‰}$) and stromatolite facies (mean -9.7‰) of Bhandar and Raipur Limestone Formations require a spatial temperature variation of $\sim 16^\circ\text{C}$. Such large intrabasinal ocean water temperature gradient between coeval supra- and subtidal zones is unlikely. The difference in δ -values cannot be explained by any diagenetic process either since there is no marked mineralogical contrast between the above-mentioned facies or proof of variable burial suffered by them. The $\delta^{18}\text{O}$ difference between these two facies thus probably reflects difference in $\delta^{18}\text{O}$ composition of the ambient water within the same basin. Such a situation has been envisaged earlier for the Kutch basin, where mixing of ocean water with ^{18}O -depleted freshwater

in marginal environments like tidal flats, lagoons etc. are suggested for the observed shift of $\delta^{18}\text{O}$ towards more negative values in the Kutch basin (Sarkar A *et al* 1996). The relatively enriched $\delta^{18}\text{O}$ values of distal plane laminated facies of both the basins might indicate deep-water isotopic composition (Fairchild and Spiro 1987). Depleted $\delta^{18}\text{O}$ values in the shallower stromatolite carbonates, on the other hand, suggest considerable influence of freshwater riverine influx. However, the $\delta^{18}\text{O}$ of intertidal stromatolites with desiccation cracks are enriched ($\sim 2\text{‰}$; table 1) compared to the deeper subtidal ones. As dolomitisation in both these facies is insignificant, the enriched $\delta^{18}\text{O}$ values may have resulted due to carbonate precipitation in an evaporative condition of protected (local sabkha?) intertidal nature. The $\delta^{18}\text{O}$ values in the PCS facies of BL exhibit a large range (-7.37 to -3.72‰) that is common for the cross-stratified clastic facies where carbonate particles are derived from various provenances. More $\delta^{18}\text{O}$ analyses of facies-specific samples are useful to decipher the depositional environment of the Proterozoic carbonate successions.

5. Conclusions

Stable isotope and sedimentological studies of late Riphean carbonate successions from the Proterozoic intracratonic Chattisgarh (Raipur Limestone) and Vindhyan (Bhandar Limestone) basins of India indicate the following:

- Stromatolite and plane laminated lime mudstone facies of Raipur and Bhandar Limestones show persistently enriched $\delta^{13}\text{C}$ values ($\sim 3\text{‰}$). These data are interpreted in terms of high organic productivity during this period. The $\delta^{13}\text{C}$ signature is independent of whether the basin had open ocean connection or not.
- Facies controlled $\delta^{18}\text{O}$ analyses indicate that the deep-water carbonate facies are enriched by about $\sim 3\text{--}4\text{‰}$ compared to the shallow stromatolite facies. The latter one is probably more influenced by freshwater influx from the continent. Thus facies-specific oxygen isotope analysis may be useful in deciphering the environment of deposition of marine carbonates.

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