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Stable isotopic studies of microbial carbonates from Talchir sediments of east-central India

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Laminated microbial carbonate (LMC) bodies with micro-morphological features resembling algal stromatolites were found in two Talchir basins of east-central India. Samples of these bodies along with carbonate nodules obtained from the Talchir sediments were analysed geochemically. $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate phase in the LMC range from 8.8 to 14.3‰ (w.r.t. SMOW) and –8.2 to –14.3‰ (w.r.t. PDB) respectively, indicating precipitation in freshwater environment. The carbon isotopic composition of carbonate free residual matter in the LMC ranges between –20.6 and –25.5‰. These values are similar to those of bacterial mats of modern lakes and confirm the biogenic origin of the LMC. The carbon to nitrogen ratio also matches with the composition of modern cyanobacterial matter. Presence of microbial mat on top of glacial debris suggests climatic amelioration subsequent to sterile environment of Talchir glaciation.

UNUSUAL occurrence of calcareous body fossils resembling stromatolites or oncolites from Talchir sediments near Angul town in Orissa was first described by Pandya[1]. Subsequently, Mohanti and Das[2] inferred the presence of bacterial colony and fungal strands in a few of these objects based on SEM photographs. No further attempt has been made to characterize these bodies geochemically and confirm these earlier findings. Since the presence of stromatolite-type objects in Talchir sediments would be of great significance in the context of its environmental implications, we carried out isotopic characterization of these objects in the present work.

Talchir formation comprises terrigenous sequence of glacial boulders, varve sediments (siltstones) and shales deposited during the melting of Gondwana glaciers at the end of Permo-Carboniferous Glaciation. In peninsular India, these sediments were deposited in a few isolated basins along three major river valleys: Mahanadi, Damodar and Narmada. However, there has been some debate regarding the environment of deposition of Talchir sediments. Various sedimentary features like ripple mark, hummocky cross-stratification, etc. suggest that the sedimentation took place in a vast water body, but it was not clear if the glacial debris was deposited in a glacier-fed lake or a near-shore marine setting[3–5]. To resolve this controversy we carried out geochemical analysis of authigenically precipitated carbonate nodules which are frequently present in the siltstone bed of the Talchir Formation. The stable isotopic analyses of these nodular carbonates show that these deposits are formed in freshwater environment[6], possibly in lakes formed by melt-water from glaciers where waves and currents could operate[5]. During the course of these investigations we came across objects similar to those described by Pandya[1] in two Talchir exposures: Rai village (latitude: 23°23', longitude: 85°23') in Damodar Valley Basin and Nandirjhor Nala section (latitude: 20°48', longitude: 85°01') of Bedasar village near Angul town in Mahanadi Valley Basin (Figure 1). The present work is an attempt in deciphering the origin of these objects. The morphology of these objects is described below.

These laminated microbial carbonate (LMC) objects are botroidal in appearance and range in size from 30 to

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50 cm. The top view resembles a cabbage-like growth with concentric laminations (Figure 2 *a* and *b*). The vertical stacking of discrete hemispherical laminae could have been initiated by draping of microbial mat over irregularities of the substrata as described by Logan *et al.*[7]. Examination of polished section shows that laminations are of uniform thickness (2–3 mm), being parallel to each other (Figure 2 *c*) and occasionally incorporating sand-size detrital grains in patches. The laminae are separated from one another by a thin film of clay and organic matter as seen by dark lines (Figure 2 *g*). These features suggest that the laminations were formed due to periodically (seasonal?) varying rate of carbonate precipitation in the presence of organic and detrital matter. Objects of similar nature have been found in Antarctic lakes where ice cover during winter favours growth of bacterial mat, while ice-free summers are conducive for deposition of silty and clayey layer[8]. Thin-section study shows that radially-grown fibrous microsparites are abundant in most of the samples. These crystal assemblages are organized into inverted cone-shaped units which, at places, show undulatory extinctions (Figure 2 *e* and *f*). Monty[9] described similar features in oncolites from Cretaceous blue-green algal deposits of the Province of Valencia, eastern Spain. Microscopic examination of thin sections also revealed a mosaic of dark lines, hemispherical to irregular in shape, appearing as growth discontinuity (Figure 2 *d*). This type of feature has also been seen in the Proterozoic sediments of South Africa by Bertrand-Sarfati and Pentecost[10], who have described them as Tussocky structure and compared them with a modern stromatolite builder rivularia. Thus, morphologically the Talchir LMC resembles microbial stromatolite.

Figure 1. Map showing the Gondwana Basins (shaded) of peninsular India. Arrows denote two locations of stromatolite occurrence.

A total of nine LMC samples from Nandirjhor Nala section and one sample from Rai village (Figure 1) were collected. As mentioned before, the LMC-containing bed is underlain by siltstone bed with lensoidal carbonates and nodules of various shapes and sizes and is overlain by sandstone containing mud cracks. Nodule samples were also collected from the lower strata at Nandirjhor Nala.

Samples were cleaned from surface contamination and thin sections were examined to select samples, which have not undergone significant alteration. Many of the samples are friable and have obvious features of alteration like vein deposition, sparitization and dolomitization. The altered samples usually have high Mn (222 to 2800 ppm) and were rejected for geochemical work. Powder samples were taken (using a micro-drill) from hand-picked slices after thorough cleaning with de-ionized water in an ultrasonic bath. Secondary growth of calcite and dolomite was identified in the thin sections after staining with Alizarin red S solution[11]. XRD analysis of fine powder was done to confirm the mineralogical composition derived from thin section study. A few milligrams of powder was reacted at 50°C with 100% orthophosphoric acid in vacuum using an on-line extraction system[12]. The evolved CO_2 was purified from water vapour and other gases before isotopic analysis in a VG 903 mass spectrometer. Samples were analysed along with NBS-19 (international standard) and internal laboratory standard Z-Carrara for calibration and routine check-up. The non-carbonate phase was separated from the sample powder after dissolving the carbonate phase with 20% HCl for 24 h. Residual matter was washed with water till neutral pH, dried and subsequently loaded with high purity CuO in quartz break-seal tube. Loaded tubes were evacuated and sealed followed by combustion at 700°C for 6 h. Evolved CO_2 was purified and analysed for carbon isotopic ratio using a GEO 20-20 mass spectrometer. To check the reproducibility of measurements, UCLA glucose standard was analysed along with each set of samples and some samples were re-analysed to check reproducibility. Isotopic ratios of carbon and oxygen are presented in the usual δ notation (defined as relative deviation of the sample isotopic ratio from that of a standard) and expressed in units of per mill (‰) w.r.t. international standard V-PDB and V-SMOW, respectively, with reproducibility of ± 0.1‰.

Carbon and oxygen isotopic ratios in the calcite phase and carbon isotopic ratio in the non-carbonate phase form the basis of the present work. The isotopic data ($\delta^{13}C$ and $\delta^{18}O$) are given in Table 1 and are shown as a correlation plot in Figure 3. The $\delta^{13}C$ values of the LMC samples range from −8.2 to −12.1‰ with average value of −10.3‰. In contrast, $\delta^{13}C$ values of the nodule samples are relatively enriched, lying between −3.5 and + 2.2‰. This difference is of significance in under-
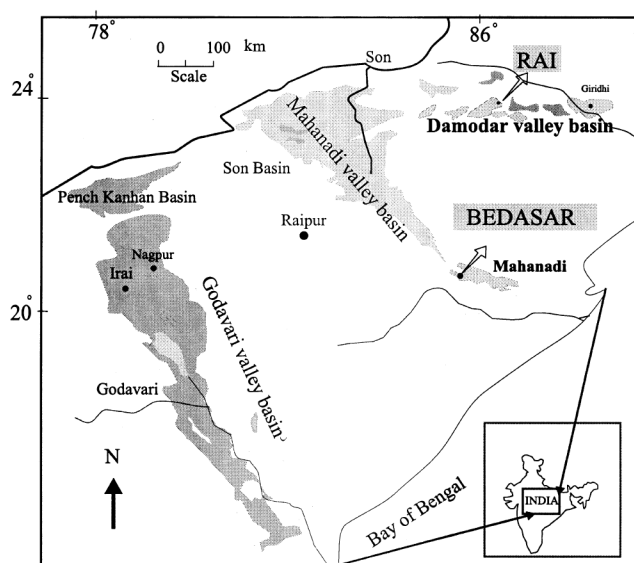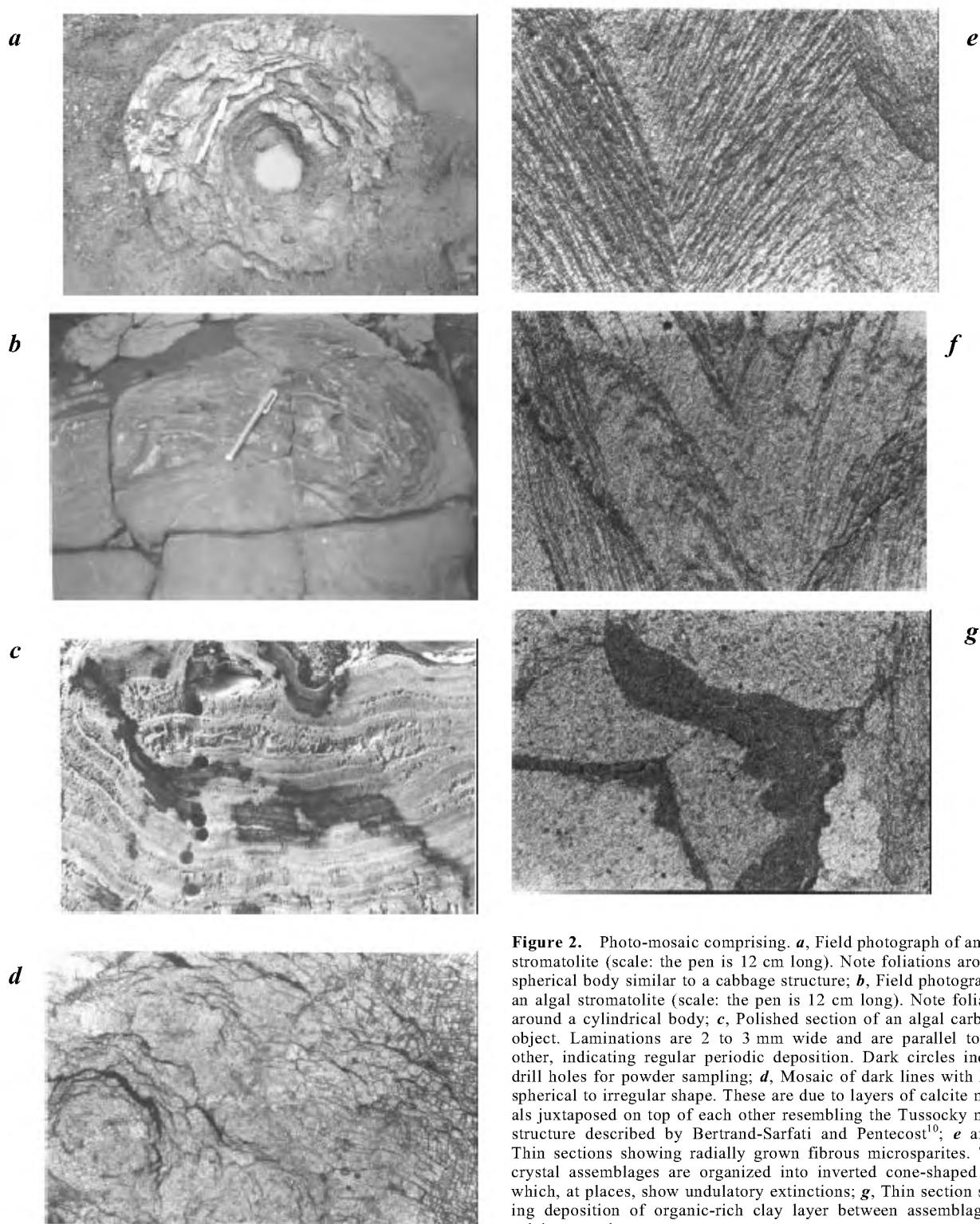
Figure 2. Photo-mosaic comprising. *a*, Field photograph of an algal stromatolite (scale: the pen is 12 cm long). Note foliations around a spherical body similar to a cabbage structure; *b*, Field photograph of an algal stromatolite (scale: the pen is 12 cm long). Note foliations around a cylindrical body; *c*, Polished section of an algal carbonate object. Laminations are 2 to 3 mm wide and are parallel to each other, indicating regular periodic deposition. Dark circles indicate drill holes for powder sampling; *d*, Mosaic of dark lines with hemispherical to irregular shape. These are due to layers of calcite minerals juxtaposed on top of each other resembling the Tussocky microstructure described by Bertrand-Sarfati and Pentecost[10]; *e* and *f*, Thin sections showing radially grown fibrous microsparites. These crystal assemblages are organized into inverted cone-shaped units which, at places, show undulatory extinctions; *g*, Thin section showing deposition of organic-rich clay layer between assemblages of calcite crystals.

standing the formation of the LMC. In our earlier work[6] it was proved that Talchir carbonates represent *in situ* precipitation in a big lake fed by melt-water from glacier. The $\delta^{13}C$ values of the carbonates, therefore, depend on the isotopic composition of the dissolved carbon in this lake, which can come from both biogenic and abiogenic sources. Since biogenically-derived carbon is extremely depleted in ^{13}C (about $-25‰$), its con-

Table 1. Carbon and oxygen isotopic compositions of carbonate phase of LMC and nodule samples from Talchir Formation. Carbon isotopic composition of non-carbonate phase of these along with C (org) and C/N ratio are also given

Stromatolites

Sample	Locality	Description	$\delta^{13}C$ (‰)*	$\delta^{18}O$ (‰)**	$\delta^{18}O$ (‰)*	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
NDJ-S1	Nandirjhor Nala, Bedasar village	Convolute lamination of carbonate and clay bands	−11.1	15.3	−15.1	1.24		12.1
NDJ-S2	Angul town, Orissa (Figure 1)	Cabbage-shaped structure, foliated outer layer	−10.2	13.2	−17.1			
NDJ-S3	Samples occur above the	Cabbage-shaped structure, foliated outer layer	−9.3	13.9	−16.5	1.01	−22.1	
NDJ-S4	calcareous siltstone layer and	Tufa and Travertine in shape	−9.9	13.1	−17.2			
NDJ-S5	varve belonging to Talchir	Cabbage-shaped structure, foliated outer layer	−9.9	13.1	−17.2			
NDJ-S6	Formation	Oncoids in stream bed	−10.1	13.3	−17.0			
NDJ-S7		Tufa or Travertine in appearance	−12.1	8.8	−21.4	1.29	−24.4	
NDJ-S8		Cabbage-shaped structure, foliated outer layer	−8.2	14.3	−16.1	1.07	−24.5	
NDJ-S9			−14.3	15.2	−15.2	1.02	−22.1	
RAI-S1	Rai village, Damodar valley Basin (about 140 km west of Giridih, Bihar)	Cabbage-shaped structure, foliated outer layer	−11.8	13.5	−16.8			

Nodules

Sample	Locality	Description	$\delta^{13}C$ (‰)*	$\delta^{18}O$ (‰)**	$\delta^{18}O$ (‰)*	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
NDJ-N1	Nandirjhor Nala, Bedasar village,	Cobble-size nodule, highly calcareous in composition	−3.5	5.2	−24.9			
NDJ-N2	Angul town, Orissa (Figure 1).	Calcareous body, irregular in shape, grey colour	−3.4	14.5	−15.9	0.45	−22.8	8.5
NDJ-N3	Nodules occur in the calcareous	Compound nodular bed, lensoidal in shape	−1.7	13.4	−16.9			
NDJ-N4	siltstone bed.	Cobble-size nodule, calcareous in composition	−2.7	13.5	−16.8			
NDJ-N5		Pebble-size nodule, calcareous core and detrital-rich rim	−3.2	14.7	−15.7			
NDJ-N6		Limestone rock forming a lensoidal bed	−2.8	13.2	−17.1	0.04	−20.6	10.4
NDJ-N7		Pebbles and stylolite growth observed in thin section	−2.1	13.4	−16.9	0.04	−21.1	9.3
NDJ-N8		Cobble-size nodule, calcareous in composon	−0.5	9.7	−20.5	0.09	−22.2	
NDJ-N9		Cobble-size nodule, calcareous in composition	2.2	12.5	−17.8	0.05	−21.1	

*w.r.t. PDB; **w.r.t. SMOW.
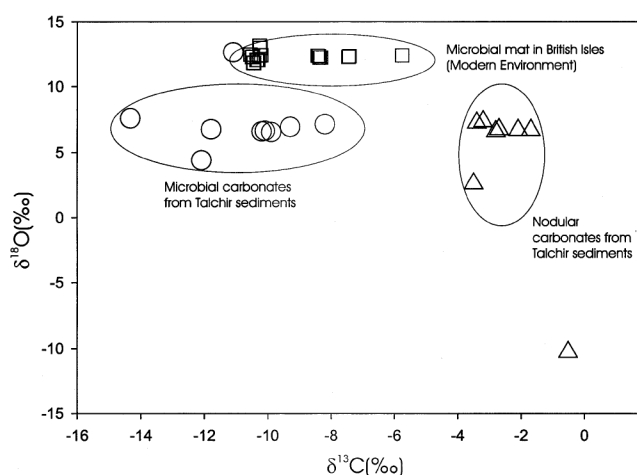
Figure 3. Correlation plot of oxygen and carbon isotopic ratios in calcite from laminated microbial carbonates (open circles) and underlying nodules (open triangles) with their respective fields of variation. Isotopic compositions of a number of carbonates from microbial mats present in modern-day freshwater environment from British Isles (from Andrews et al.[13]) are also shown (open squares) for comparison.

tribution to the dissolved carbon pool tends to reduce the $\delta^{13}C$ of the carbonate. The LMC objects were therefore formed in an environment with significantly more contribution from biogenic CO_2 relative to the underlying nodules. Such would be the case if the LMC precipitation occurred in shallow water in close association with microbial mat, where respiration and decomposition of microbes provided ^{13}C-depleted CO_2 to the local carbon pool. A modern analogue of such a situation is provided by the cyanobacterial carbonate associated with algal mats in British Isles (Figure 3) whose carbon isotopic ratios are similar to those of the Talchir LMC[13]. Development of large-scale cyanobacterial mats in late Talchir time indicates climatic amelioration (glacial retreat) subsequent to the sterile and cold glacier environment.

Additional evidence of microbial mat is provided by the $\delta^{13}C$ value of the non-carbonate phase. Four such samples were analysed and the values range from − 22.1 to − 24.5‰, similar to the values of algae and cyanobacteria found in modern Antarctic lakes[14]. It can be surmised that the non-carbonate phase represents trapped organic matter in carbonate minerals growing in an algae-rich environment. It is to be noted that the nodules also contain minor amounts of organic matter (less than 0.5% of organic carbon compared to more than 1% for LMC) whose carbon isotopic composition ranges from − 20.6 to − 22.8‰ and could be due to small amounts of lake biota trapped in the nodules.

The depleted carbon isotopic composition in the carbonate phase proves that carbonate precipitation took place in freshwater environment as marine carbonates are invariably characterized by $\delta^{13}C$ values lying close to zero[15], within a range of − 2 to + 2‰.

Oxygen isotope ratios in both the carbonates lie in a narrow range from 12.5 to 15.2‰ (w.r.t. SMOW) or − 17.8 to − 15.2‰ (w.r.t. PDB), not considering three samples which show large deviation from mean value of 13.2‰ (8.8 for stromatolite; 5.2 and 9.7 for nodules). Studies on ancient carbonates have shown that in sedimentary environment oxygen isotope ratio is more susceptible to change by alteration compared to carbon isotopic ratio[16]. Therefore, minor alteration could have changed the $\delta^{18}O$ of these three samples, leaving $\delta^{13}C$ unchanged. It is also noted that the nodules and the LMCs have overlapping oxygen isotopic composition, indicating similar environment of formation. Since $\delta^{18}O$ of a carbonate is determined by composition of the water medium and its temperature[17], one can use the $\delta^{18}O$ values to get information about the medium if the temperature can be inferred independently. The water temperature of the Talchir lake can be constrained by noting that the position of India at that time (Permo-Carboniferous) was in high southern latitude, possibly within 50 to 60°S (ref. 18). Modern surface air temperature in this belt is in the range of 10 to 20°C (ref. 19) and can be used as the water temperature to a first approximation. Using this range of temperature in the Friedman–O'Neil equation[20] of fractionation for carbonate precipitation:

$$1000 \ln \alpha = \frac{(2.78 \times 10^6)}{T^2} - 2.89,$$

and the mean $\delta^{18}O$ value of carbonate $\delta^{18}O$ (13.8‰), one gets a range of $\delta^{18}O$ values: − 15 to − 18‰ (w.r.t. SMOW) for the Talchir lake water. This range of $\delta^{18}O$ values again proves that Talchir basin contained freshwater whose probable source was the glacier melt.

Carbon to nitrogen ratio in one sample of LMC containing residual organic matter was also measured in order to determine the source of organic matter. The C/N ratio is 12.1, which is similar to the composition of modern-day macroalgae[21].

The results obtained from the isotopic study along with field and petrographic observations confirm the presence of microbial stromatolites in the late Talchir sediments of east-central India. Isotopic composition of carbonates indicates freshwater environment for deposition. Together with observed sedimentary structures like hummocky and herringbone cross-stratification described earlier in the Talchir sediment[5], isotopic data strongly suggest existence of a huge lake fed by glacier-melt water. Occurrence of microbial remnants in beds above the Talchir strata provides evidence of climatic warming soon after the period of Talchir glaciation.

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