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Carbonates and related facies with vestiges of biomarkers: clues to redox conditions in the Mesoproterozoic ocean

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Abstract

The Raipur Group of the Chattisgarh Basin preserves two major Late Mesoproterozoic carbonate platforms. The lower platform is about 490-m thick, separated from the upper platform (~670 m thick) by a 500-m thick calcareous shale. Carbonate strata cover almost 40% of the Chattisgarh Basin outcrop and represent two major platform types: a) a non-stromatolitic ramp (the Charmuria/Sarangarh Limestone); and b) a platform developed chiefly in the intertidal to shallow subtidal environment with prolific growth of stromatolites (the Chandi/Saradih Limestone). The first platform consists primarily of the black Timarlagal limestone that is locally replaced by early diagenetic dolomite. This carbonate platform experienced strong storm waves and was subsequently drowned by a major transgression, during which extensive black limestone-marl rhythmite was deposited, followed by deposition of the Gunderdehi Shale. The carbonate factory was later re-established with development of an extensive stromatolite-dominated Charmuria/Sarangarh platform that ranged from restricted embayment to open-marine conditions. Sea-level change played a major role in controlling the broad facies pattern and platform evolution. The δ¹³C signatures of the Chattisgarh limestones, falling within a relatively narrow range (0 to +4 ‰) are typical for Upper Mesoproterozoic carbonate rocks. δ¹⁸O values, however, have a greater range (-5.7 to -13.3 ‰) indicating significant diagenetic alteration of some samples. Likely dysoxic or anoxic conditions prevailed during deposition of the black Timarlagal limestone and well-
oxygenated conditions during deposition of the Gunderdehi Shale and Saradighi/Chandi stromatolite. The lack of 17β,21α (moretanes) and high T$_{\text{max}}$ values suggest mature organic matter in the non-stromatolitic ramp. A paucity of diagnostic eukaryotic steroids indicates that algae were rare in the Chattisgarh Basin. A high content of hopanes supports a generally bacterially-dominated Proterozoic ocean in which various stromatolites flourished.

**Keywords:** redox, Mesoproterozoic, biomarkers, Chattisgarh Basin, India

1. **Introduction**

   During the Great Oxidation Event (2500-2200 Ma) sustained oxygenation of Earth’s surface environments began and although the shallow oceans became mildly oxygenated, the deep oceans continued to be anoxic at least until 1850 Ma (Holland, 2006). The following Mesoproterozoic (1600-1000 Ma) has been regarded as a relatively quiet time in Earth history (Buick et al., 1995; Isley and Abbott, 1999; Holland, 2006; Bekker et al., 2010). However, even though distal shelf and basinal settings of the Mesoproterozoic appear to have been anoxic and eucinic (Shen et al., 2002, 2003; Poulton et al., 2004) or ferruginous (Poulton et al., 2010; Planavsky et al., 2011; Scott et al., 2012), there is a moderate increase in biospheric oxygen variability in the late Mesoproterozoic evidenced from increased carbon isotopic variability (Frank et al., 1997, 2003; Kah et al., 1999), an increase in marine sulphate concentration (Kah et al., 2004) from low sulphate concentrations in early Mesoproterozoic (Luo et al., 2015), the widespread appearance of marine gypsum (Kah et al., 2001, 2012), and increased oxidative sulphur cycling in marine and terrestrial environments (Johnston et al., 2005; Parnell et al., 2010). From a sedimentological point of view, the Mesoproterozoic was a time of extensive epeiric and epicratonic seas and a relative highstand of sea level, wherein thick successions of shallow-water carbonate strata were deposited in broad intracratonic basins, as in China (Guo et al., 2013; Mei and Tucker, 2013), Siberia (Bartley et al., 2001), West Africa (Kah et al., 2012; Gilleaudeau and Kah, 2013a,b; 2015), and the Canadian Arctic (Kah et al., 2001). Biologically, cyanobacteria were well established in the Mesoproterozoic but heterogeneity of redox conditions in the shallow oceans may have had fundamental implications for the evolution of unicellular and multicellular eukaryotes, which were evolving at a modest rate towards the end of the Mesoproterozoic – early Ediacaran (Butterfield, 2001; Knoll et al., 2006; Javaux, 2007; Pafrey et al., 2011). Moreover, despite evidence that early eukaryotes were abundant in some nearshore settings (Butterfield, 2000; Javaux et al., 2001; Knoll et al., 2006), similar environments from other basins but with
euxinic conditions record a distinct absence of eukaryotic biomarkers (Brocks et al., 2005; Blumenberg et al., 2012). This could have limited the zone of habitability for early eukaryotes, providing an explanation for the fragmentary nature of their early evolution and diversification. Anbar and Knoll (2002) have suggested that oxygenation of the mid-Proterozoic surface environment may have resulted in increased delivery of essential nutrients to the marine system thereby fostering eukaryotic diversification in nearshore settings. It also seems that spatial heterogeneity of redox-sensitive trace metals in the Mesoproterozoic ocean resulted in offshore micronutrient limitation which would have prevented eukaryotes from being widespread (Gilleaudeau and Kah, 2013b, Stüeken, 2013).

In this project, we explore two carbonate platforms of the Raipur Group, central India, with the aim of evaluating the controls on the development of two distinctly different platforms through time, one dominated by stromatolites, the other not. Thick carbonate successions are reported from all the Proterozoic cratonic basins of the Indian subcontinent (Das et al., 1992, Jiang et al., 2002, Mukhopadhyay et al., 1996, Patranabis-Deb 2001, Chakraborty et al., 2002, Saha and Patranabis-Deb, 2014). Combined sedimentological, isotope and organic geochemical data are used to assess the source and character of preserved organic matter. Redox conditions within the Chattisgarh Basin are evaluated in the context of the palaeogeographical position of the basin and its contribution to the understanding of redox heterogeneity in Mesoproterozoic oceans.

2. Regional geological setting

The Chattisgarh Basin developed within the Bastar craton, an Archean crystalline block. The Bastar craton is bounded by the Godavari and Mahanadi rifts to the southwest and northeast respectively, and bordered by the Central Indian Tectonic Zone (CITZ) to the northwest and the Eastern Ghats Mobile Belt to the southeast (Fig. 1). The Chattisgarh Basin covers an area of ~33,000 km², which unconformably overlies the Archean crystalline basement, the Neoarchean to Paleoproterozoic Sonakhan granite-greenstone belt and Dongargarh-Kotri volcanics (Fig. 1). Detailed geological mapping suggests that the Chattisgarh succession, which exceeds 2300 m in thickness, represents two unconformity-bound sequences. The lower unit is designated the Chandarpur-Raipur Sequence (CR sequence) and the upper unit is the Kharsiya Sequence (Patranabis-Deb and Chaudhuri, 2008) (Fig. 2). Radiometric dating indicates a Mesoproterozoic age for the Chandarpur Raipur Group, with the upper Kharsiya Group representing deposition in the early Neoproterozoic.
The CR sequence, the focus of this study, is characterized by a lower thick wedge of an immature assemblage of conglomerate, coarse feldspathic sandstone and shale, deposited in a fan delta-prodelta setting (Patranabis-Deb and Chaudhuri, 2007; Chakraborty et al., 2009), and a more stable upper assemblage of quartzose sandstone deposited in a shallow-marine shelf bar to intertidal location (Patranabis-Deb, 2005; Chakraborty and Paul, 2008). Intense storms and tides played an important role in sculpturing the sediments in the wide open shelf of the Chandarpur Group. A mixed carbonate-siliciclastic (limestone-shale) assemblage deposited in a cyclic fashion constitutes the overlying Raipur Group (Dutt, 1964, Murti, 1987, 1996; Moitra, 1995; Patranabis-Deb, 2004, 2008), with its two carbonate platforms. The basin-filling succession is characterised by remarkable facies variation in space and time, and a regionally variable lithostratigraphy resulting from uneven rates of subsidence and creation of accommodation space in different parts of the basin.

3. Age of the Chattisgarh Basin

Radiometric dates (EPMA) from monazite from a tuff horizon near the base of the Chattisgarh succession yielded an age c. 1500 Ma (Das et al., 2009). Bickford et al. (2011a) obtained a U-Pb zircon SHRIMP age of c. 1400 Ma for a welded tuff from the same horizon. These data suggest that Chattisgarh sedimentation was initiated during the early-to-mid Mesoproterozoic. Patranabis-Deb et al. (2007) published a U–Pb zircon SHRIMP age of c. 1000 Ma for the Sukhda welded tuffs from the uppermost part of the CR sequence from the eastern part of the basin. Bickford et al. (2011b) described the Dhamda tuff beds as waterlain, intrabasinal tuffs whose SHRIMP U-Pb zircon ages yielded 993±8 Ma. Thus, currently available geochronological data clearly establish that sedimentation in the Chattisgarh Basin occurred mostly in the later Mesoproterozoic with an extension into Neoproterozoic time.

4. Raipur Group stratigraphic framework

The Raipur Group has been divided into five formations, comprising three successions of shale alternating with two carbonate platforms (Fig. 2). The lower carbonate succession, the Charmuria/Sarangarh Limestone, developed on a homoclinal non-stromatolitic ramp (Read, 1985) and is capped by an extensive unit of black limestone. The upper carbonate succession, the Chandi/Saradih Limestone, is noteworthy for the abundant presence of stromatolites on a ramp with barrier-bank complexes.
4.1. Charmuria-Sarangarh Limestone

The Charmuria Limestone, with a maximum preserved thickness of about 490 m overlies shelf sandstone of the Kansapathar Formation with a sharp contact. The Sarangarh Limestone (~200 m), the lateral equivalent of the Charmuria in the eastern part of the basin, overlies the Kansapathar Sandstone with a thin unit of shale between, the Bijepur Shale (Fig. 2). The Sarangarh Limestone contains colour-defined stratigraphic units, i.e., brown, grey, black and mauve in ascending order. The lower brown and grey units, designated as the Gadhabhata Member, contain abundant intercalations of sandstone (Fig. 3a,b). In the eastern part of the basin there is a large-scale (several km across) lenticular conglomeratic unit cutting down into the Gadhabhata Member and several sheet sandstone bodies near the top of the Gadhabhata Member. Black limestone (the Timarlaga Member) overlies the Gadhabhata Member with a sharp contact; it is characterized by laterally persistent, limestone-marl rhythmites (Fig. 3c). The black limestone grades upward into a mauve limestone, and then into the brown shale of the Gunderdehi Formation.

4.2. Gunderdehi Shale

The Gunderdehi Formation is ~450 m thick and consists of brown splintery calcareous shale-siltstone with subordinate (<10%) green shale, dolomite and fine sandstone. The shale is characterized by 2-10 cm thick beds with millimetre-thick plane parallel laminae. Beds are plane-parallel and they make sets which are laterally persistent for many 10s of metres across the outcrop (Fig. 4a). Several 10-25 cm thick muddy-siltstone units contain mud-intraclasts, commonly with a normal grading and scoured base. Barite nodules have formed locally within calcareous shale (Das et al., 1992; Mukherjee et al., 2014) and millimetre thick laminae pass through and around the nodules indicating a diagenetic origin (Fig. 4b). Fine-grained dolomitic grainstone occurs as shoaling-up bars which coalesce to form a sheet-like body. The lows of the bars are filled with thin planar beds of dolomite and shale as an interbar facies, forming packages up to 5 m thick.

Stromatolites first appear as isolated bioherms enclosed within brown calcareous shale in the upper part of the Gunderdehi Formation, described in section 6.2 (Fig. 4c,d). The occurrence of the bioherms distinguishes the Gunderdehi Shale from two other brown shale-dominated beds within the Raipur Group.

4.3. Chandi-Saradih Limestone
The Chandi Limestone overlies the Gunderdehi Shale with a gradational contact and in turn this grades up into the Tarenga Shale. This limestone attains a maximum thickness of about 670 m in the central and western part of the Chattisgarh Basin and becomes relatively thin (~150 m) in the eastern part, where it is known as the Saradih Limestone (Das et al., 1992; Patranabis-Deb and Chaudhuri, 2008). The Chandi Formation mainly consists of brown and steel-grey limestone where stromatolites are common (Moitra, 1999); minor shale and a few intercalated tidal sandstone bodies (Deodongar Member) occur in the western and central part. By contrast, the Saradih section, exhibits rapid variations between major facies which include micritic dolomite, limestone-marl rhythmite, lime-clast conglomerate units, and a small number of stromatolite bioherms. The dolomite unit occurs mostly in the lower part of the succession, interbedded with red shale, whereas the upper part is dominated by alternating grey limestone-marl rhythmite.

4.4. Tarenga Shale

The Chandi Limestone grades upward into the Tarenga Shale, which is about 200 m thick, and comprises a heterogeneous succession of green shale, volcaniclastic sandstone, thick ignimbrite horizons, and small isolated bodies of dolomite and fractured chert (Fig. 5). The formation is laterally correlatable with the Churtela Shale, exposed in the eastern Chattisgarh Basin (Patranabis-Deb et al., 2007; Patranabis-Deb and Chaudhuri, 2008; Bickford et al., 2011b).

5. Methodology

The Raipur Group succession has been mapped and logged at many locations across the eastern Chattisgarh basin (Patranabis-Deb, 2001, 2004; Patranabis-Deb and Chaudhuri, 2008). Facies types and geometries have been determined and many thin-sections examined for their microfacies and diagenesis (Tables 1, 2). Twelve samples, eight from the black Timarlaga limestone (Sarangarh/Charmuria Formation), one sample from the Gunderdehi Shale (calcareous red shale), and two from brown stromatolitic limestone and one from grey stromatolitic limestone (Saradih/Chandi Formation) were collected for TOC analysis (Table 3). Forty-five samples covering different stratigraphic levels were analysed for bulk carbon and oxygen isotope analysis (Table 4). To assess the character of organic matter, black limestone and red shale samples were analysed by Rock-Eval pyrolysis, and the biomarker distributions and elemental compositions were determined (Table 5).
5.1 Carbon and oxygen stable isotopes

The bulk carbon and oxygen isotopic analyses of limestones and calcareous shales were performed using the following procedure: 100-200 µg of powdered carbonate were placed into 4 ml glass vials, and then sealed by a lid and pierceable septum. The vials were placed in a heated sample rack (90°C) where the vial headspace was replaced by pure helium via an automated needle system as part of an Isoprime Multiflow preparation system. Samples were then manually injected with approximately 200 µl of phosphoric acid and left to react for at least 1.5 hrs before the headspace gas was sampled by automated needle and introduced into a continuous-flow Isoprime mass-spectrometer. Duplicate samples were extracted from each vial, and a mean value obtained for both δ¹³C and δ¹⁸O. Samples were calibrated using IAEA standards NBS-18 and NBS-19, and reported as ‰ on the VPDB scale. Reproducibility within runs was 0.09 ‰ δ¹⁸O and 0.05 δ¹³C.

5.2 Rock-Eval pyrolysis

The measurements for the Rock-Eval II pyrolysis were conducted following the workflow described by Espitalié et al. (1985). The Rock-Eval analysis provides information about the amount, quality, type, and maturity of organic carbon in a sample. Measured parameters include free oil content (S₁ in kg HC/tonne rock), source potential (S₂ in kg HC/tonne rock), and thermal maturity (Tₘₐₓ in °C). In addition, total sulphur (TS) analysis was carried out on a Carlo Erba NC2500 Elemental Analyser. The results of the Rock-Eval and sulphur analyses are summarized in Table 3.

5.3 Biomarker analyses

Six powdered (40-70 g) rock samples, two from the black limestone, two from the red calcareous shale and two from Chandi stromatolites were extracted using a Soxhlet apparatus with 200 ml dichloromethane:methanol (9:1, v/v) for 24 h; copper was added to the round-bottom flask to remove elemental sulphur. Aliquots of total lipid extract were separated into apolar, aromatic and polar fractions using a column with activated silica gel (230-400 mesh, 4 cm bottom). Elution proceeded with 3 ml hexane (apolar fraction), hexane:dichloromethane (3:1, v/v; aromatic fraction), and 5 ml methanol (polar fraction). Among the lipids extracted from the analysed samples only aliphatic hydrocarbons were investigated because aromatic and polar compounds were not detected.
1 µl aliquots of each fraction were analysed by gas chromatography (GC) using a Hewlett Packard Series II 5890 instrument, fitted with an on-column injector and a capillary column with a CP Sil5-CB stationary phase (60 m x 0.32 mm, df = 0.10 µm). Detection was achieved with flame ionisation (FID) with helium as the carrier gas. The temperature program consisted of three stages: 70-130°C at 20°C per min; 130-300°C at 4°C per min; and 300°C at which the temperature was held for 10 min. Gas chromatography-mass spectrometry (GC-MS) analyses were performed using a Thermo Quest Finnigan Trace GC-MS fitted with an on-column injector and using the same column and temperature program as for GC analyses. The detection was based on electron ionization (source at 70 eV and scanning range 50-580 Daltons), and compounds were identified by comparison of retention times and mass spectra to the literature.

6. Facies associations of the Raipur carbonate platforms

6.1 Charmuria – Sarangarh Limestone Platform (Table 4)

The lower carbonate platform of the Raipur Group (Charmuria-Sarangarh Limestone, Fig. 2) comprises a thick succession of micritic limestone with the local presence of storm-deposited sands as thin streaks or beds. Unlike many other reported Proterozoic platforms the limestone unit is marked by a conspicuous absence of stromatolites and any coarse carbonate grains. The limestone can be divided into three assemblages with distinctly different modes of deposition in terms of platform evolution.

Assemblage I, the Gadhabhata Member, is ~200 m thick and comprises brown and grey limestone in ascending order with some intercalation in places. The coarser constituents are represented by siliciclastic sands which occur as stringers, thin layers, beds and lenticular bodies at different stratigraphic levels, and by intraformational limestone clasts in small lenses or thin sheet conglomerate. The sandstone beds, with sharp bases, are dominated by planar stratification, cross-stratification, hummocky cross-stratification and combined-flow ripples. High-energy storm-generated combined-flows episodically transported sands from the coastal area to the storm-tide dominated, carbonate-depositing shelf. The high-intensity storm surges also eroded semi-lithified carbonate beds, entrained rip-up clasts and redeposited them with sands and micrite in mixed graded beds and as edge-wise conglomerates. The Gadhabhata Member developed as an aggradational-progradational succession within an overall moderate depth (FWWB-SWB) platform.

Assemblage II comprises a succession filling a submarine channel incised within the grey limestone of Assemblage I. It comprises slump sheets with intensely folded and
contorted clasts of thin-bedded grey limestone, and debris-flow conglomerate with autochthonous lime-clasts floating within a matrix of micrite and coarse sands. There are a few boulder-sized clasts of black chert within a coarse-grained sandy matrix. The facies points to a lowering of relative sea level (FSST, falling stage systems tract, Catuneanu et al., 2011), the cutting of an incised channel into a gentle slope generated by the earlier aggrading-prograding platform, and transport of coarse sands during a sea-level lowstand (LST).

Assemblages I and II are overlain along a sharp contact by an extensive black limestone, reaching 40 m in thickness, the Timarlaga Limestone Member of the Sarangarh Limestone (i.e. Assemblage III). The limestone bed thickness occurs in two distinct clusters, one mostly 2 to 5 cm and the other 6 to 15 cm and they alternate with 0.5 to 2 cm thick marl layers to form limestone-marl rhythmites (Fig. 3c). This Timarlaga Member is marked by a remarkable facies consistency and conspicuous absence of sand-sized grains or clasts in black and mauve limestone. Pyrite occurs profusely in this unit as clusters and small cubes, generally less than 10 µm in size (Fig. 3d). Larger pyrite cubes are present in particular layers (Fig. 3e). With their scattered distribution through the limestone, the small pyrite is interpreted as early diagenetic in origin, whereas the larger cubes may well be a burial precipitate.

The basal surface of the black limestone marks a progressive unconformity; the black limestone successively oversteps grey and brown limestone (Gadhabhata Member), and finally onlaps medium- to coarse-grained tidal-bar sandstones of the Kansapathar Formation towards the western part of the Chhattisgarh Basin. Development of the black limestone points to a major drowning event through a relatively rapid sea-level rise. The black limestone formed as a relatively deep-water (below normal wave base to below storm wave base and with dysoxic or anoxic facies – as deduced from the biomarkers, later section – within a transgressive systems tract (TST)). Although actual water depth is notoriously difficult to deduce (Immenhauser, 2009), storm wave-base within an intracratonic basin is likely to have been at a depth of tens of m to 100 m, depending on the size of the storm and fetch. The uppermost part of the black limestone and the overlying mauve limestone represent the TST and HST of a sequence. The brown shale of the Gunderdehi Shale overlying the mauve limestone with the first appearance of stromatolite mounds in its upper part, indicates a sea-level fall (FSST-LST) to intertidal conditions.

6.2. Chandi-Saradih Limestone Platform (Table 5)
The Chandi platform is ~670 m thick and laterally correlative with the Saradih Limestone (~100 m) of the eastern Chattisgarh Basin. The studied sequence is composed of several distinct facies assemblages depicting an upward transition from shallow intertidal, back-reef assemblages to subtidal assemblages. The platform development can be classified into three distinct stages according to the external morphologies and internal structures of the stromatolites, and input of siliciclastic sand to the system.

Assemblage I consists of laterally discontinuous stromatolite mounds, the bioherms, which occur as isolated bodies at the transition between the Gunderdehi Shale and Chandi Limestone. The bioherms range in size from 15 to 50 cm, and the shape varies from sub-rounded to elliptical in planar section and mushroom shaped in cross section. The elongation directions of the mounds are towards the N-NE, which is subnormal to the palaeocoast-line, interpreted from the paralic succession of the Chandarpur Group. Within a few metres up the section, the stromatolite bioherms change from discontinuous mounds to laterally continuous planar tabular bodies, up to 2 m thick, with prominent surfaces developed on the top of the stromatolite biostromes (Fig. 6a). These could be discontinuity surfaces, representing a break or pause in deposition of the microbialites, perhaps when a mud parting or thin muddy bed was deposited across the bioherms. The mud layers were then compacted and affected by pressure dissolution on burial. Stromatolites within the bioherms are 5-15 cm high, characterized by parallel or divergent branching or non-branching columns (Fig. 6b). The columns are sub-parallel to an inverted cone shape, with convex-up crinkled internal laminae, commonly showing truncations. Small narrow pockets of edge-wise conglomerate, 20-30 cm wide, with intraformational platy clasts, 0.5 to 2 cm long, in a clastic sand matrix occur between stromatolite mounds.

The gradational contact between the Gunderdehi Shale and Chandi limestone points to gradual changes in sediment input/production, where clastic input diminished and the carbonate factory took over. This siliciclastic depositional change to carbonate signals a long-term shift in palaeo-oceanographic conditions within the basin. The initiation of carbonate deposition points to trapping of fine detrital material during initial transgression, which might have cleared the water to allow the growth of stromatolites, as isolated patches and finally as extensive biostromes. The elongation of mounds, erosion of stromatolite walls, and accumulation of fragments as edgewise conglomerates, point to storms and tides in a shallow epeiric sea. Sea-level fluctuations, and other associated environmental factors, controlled the changes in shape of the stromatolite bodies.
Assemblage II: The Chandi limestone unit conformably grades up to a sand-dominated unit, the Deodongar Member, whose maximum thickness is 60 m and lateral extent reaches 300 km to the east. The two major facies are: well-sorted, medium-grained, subarkosic to quartzose, glauconitic sandstone forming small lenticular shoaling-up bodies, and poorly-sorted fine-grained sandstone and siltstone occurring in the lows between the lenticular bodies. The sandstone beds preserve profusely developed symmetric to slightly asymmetric, sinuous to straight crested 3D dunes on a metre-scale (cf. Ashley, 1990). Stringers of well-rounded, very coarse sand and granules mantle the bedding-plane surfaces in places. The inferred palaeocurrents point to a strong bipolar, bimodal current with dominant northerly flow and subdued southerly flow.

High-energy tidal currents effectively transported the sands from the southern coast and deposited them as laterally discontinuous lenticular sand-bodies in the lower part of the Chandi succession in the western Chattisgarh. The input of sands within the carbonate depositing environment stopped production of carbonate. However, in the eastern and central parts of the basin, carbonate platform development continued. This was in response to a progressive change in environmental conditions mostly related to the changes in water depth during platform evolution.

Assemblage III: Thick sequences (~400 m) of large stromatolite mounds, elliptical in cross-section with a long axis about 1-2 m coalesce to form a major barrier-reef complex. Stumpy, branched stromatolites with numerous successive laminae, stacked on top of each other, form the columnar structures (Fig. 6c). Partly-linked columnar stromatolites within ridges also form part of the barrier-reef complex, along with stromatolite mounds. They are 10-15 cm wide and 10-35 cm high with up to 5 cm of synoptic relief. Column height increases stratigraphically up the section; the shape of the stromatolites in plan also changes from a circular to elongate form (Fig. 6d). These features suggest a direct relationship of change in morphology as a function of facies and are probably mostly related to changes in water depth during platform evolution. Laterally continuous beds probably formed in water depths shallower than the stromatolite mounds. Bioherms of partly linked columns probably formed in water depths comparable to the stromatolite mounds. In general, sediment production, sediment transport, tectonic subsidence, antecedent topography, and relative sea-level oscillation interacted to shape the Chandi platform.

7. Geochemical record of the Sarangarh Limestone

7.1. Carbon and oxygen stable isotopes
Stable isotopes of carbon and oxygen can be useful for understanding the deposition and diagenesis of carbonate sediments. They can also be used for chemostratigraphic correlation between sections and this can lead to insight into changes in the ocean-atmosphere system. For this project, $\delta^{13}C$ and $\delta^{18}O$ isotope analyses were measured on 45 samples from the Sarangarh and Chandi limestones (data shown in Table 4 and as a cross-plot in Fig. 7a).

The $\delta^{13}C$ values are in a relatively narrow range of 0 to +4.3‰. Separating the analyses into black, brown and stromatolitic limestones, they all show similar averages for $\delta^{13}C$: 2.98 (n = 12), 2.86 (n = 8) and 2.98 (n = 4) respectively. The oxygen data as a whole show more variability, with values for limestones ranging from -5.7 to -13.3‰ (Fig. 7a). Within these data, grey limestone generally has much more negative $\delta^{18}O$ values (average -11.1‰) than the black limestone (average -8.5‰); stromatolitic limestone is quite similar to the black limestone with $\delta^{18}O$ values averaging -7.9‰. Dolomite is a minor occurrence in the succession and only two samples were analysed; they do have the least negative $\delta^{18}O$ values of -4.3‰ and -3.9‰, compared to the limestones, but the $\delta^{13}C$ values (3.6 and 3.9‰) are within the same range as the limestones (Fig. 7a).

When plotted stratigraphically, the scatter of both C and O is apparent, although a general trend up-section towards more positive $\delta^{13}C$ values, from ~2 ‰ to ~4 ‰, can be discerned through the black Timarlaga Limestone Member (40 m) (Fig. 7b). The oxygen isotope values are much more scattered and do not reveal any clear pattern through the section (Fig. 7b).

The $\delta^{13}C$ data of all the samples fall within the range of modern marine carbonates (Tucker and Wright, 1990) and within the range of Mesoproterozoic carbonates (Shields and Veizer, 2002; Kah et al., 2012; Gilleaudeau and Kah, 2013a). Indeed, the low positive $\delta^{13}C$ values of 0 to +4‰ recorded for the Sarangarh Limestone are typical of upper Mesoproterozoic carbonate strata (age 1200/1300 to 1000 Ma), and contrast with the earlier Mesoproterozoic where values are generally close to and below 0‰ (Bartley et al., 2001; Kah et al., 2001; Kah et al., 2012; Guo et al., 2013). Early Neoproterozoic carbonate strata tend to have variable $\delta^{13}C$ and are followed by much higher values in the late Neoproterozoic, up to +5‰ (Kah et al., 2001). The quite stable and low to moderate positive $\delta^{13}C$ values for the late Mesoproterozoic are taken to reflect long periods of sea-level highstand in extensive epeiric seas, with relatively high organic productivity leading to the preferential extraction of $^{12}C$, and enhanced burial of organic matter (Bartley and Kah, 2004; Kah et al., 2012). By extension, in the Timarlaga Limestone the upward trend from +2 to +4‰ $\delta^{13}C$ (Fig. 7b) could
reflect increasing organic matter production and burial within the Chattisgarh Basin. The longer timescale change from near 0 to +4‰ δ¹³C through the Mesoproterozoic as a whole, is likely related to increased organic productivity, and this could have been responsible for the postulated global-scale increasing ocean oxygenation at this time (Kah et al., 2001; Guo et al., 2013).

Oxygen isotope data in carbonates are well known as being more likely to be altered post-deposition compared to carbon isotopes (Tucker and Wright, 1990). Hence in general there is much more scatter oxygen data from limestones/dolomites through time (Shields and Veizer, 2002). The oxygen isotopic composition of the Sarangarh Limestone is generally moderately negative (-6‰) to very negative (-13‰). Values as low as this would not be regarded as marine signatures in Phanerozoic carbonates; indeed here we suggest that they also reflect a combination of processes of cementation, recrystallization and neomorphism during burial (Tucker and Wright, 1990). The more negative δ¹⁸O values of the grey versus the black Sarangarh limestone most likely indicate that the former experienced more extensive recrystallization during burial, perhaps related to the difference in organic carbon content. Negative δ¹⁸O values in the Sarangarh Limestone could indicate meteoric diagenesis, but there is no evidence for this from the facies or petrography, and the δ¹³C values do not indicate this either. Meteoric exposure and karstification in the early Neoproterozoic Beck Spring Dolomite, California (1000-800 Ma) and late Mesoproterozoic Mescal Limestone (New Mexico, ~1100 Ma) have altered δ¹³C to as low as -6‰ (Kenny and Knauth, 2001). It has been suggested, however, that for mid-Mesoproterozoic (1400-1200 Ma) carbonates from China with good fabric preservation, δ¹⁸O values between -6 and -9‰ may well reflect little-altered marine isotopic compositions (Kah, 2000; Kah et al., 2012; Guo et al., 2013), and that samples with less negative oxygen isotopic compositions may reflect moderately evaporitic depositional conditions. This might imply that the less negative values from the Sarangarh Limestone are original marine signatures, meaning that Mesoproterozoic seawater was rather depleted in ¹⁸O compared to modern seawater. However, it is pertinent to note here that in the Beck Spring Dolomite with its extremely well-preserved textures (Harwood and Sumner, 2012), grains have δ¹⁸O values of -0.5 to -3.7‰, marine cements have values of -2 to -6‰, and burial cements have values of -6 to -13‰ (Tucker, 1982), so that whole rocks usually have a δ¹⁸O in the range -6 to -9‰. The δ¹⁸O signature for Lower Neoproterozoic marine carbonate rocks would thus appear to have been close to -2‰, which is not dissimilar from the modern value for Recent marine carbonate sediments.
7.2. Rock-Eval pyrolysis

Total organic carbon (TOC) contents obtained from the black Timarlaga limestone and Gunderdehi red shale are 0.04-0.07 % and 0.06 % respectively, whereas the organic carbon content in the grey and brown stromatolites of the Chandri Limestone varies from 0 to 0.1 % (Table 3). Rock-Eval S₁ values of 0-0.1 mg HC/g rock and S₂ values of 0.02-0.1 mg HC/g rock obtained from black limestone suggest no hydrocarbon generation potential. This is also confirmed by generally low hydrogen indices, ranging from 53-160 mg HC/g TOC, and very high oxygen index values (400-1290 mg CO₂/g TOC) (Table 1).

Most T_max values from Rock-Eval analysis of the black limestone and red shale are between 437-450°C and 476-514°C, respectively (Table 1). The T_max values in this range are equivalent to vitrinite reflectance of 0.7-0.9 % Rₒ and 1.4-2.3 % Rₒ, respectively, according to the formula published by Jarvie et al. (2001). Such values are consistent with the biomarker distributions, discussed below.

7.4. Biomarker characterization

Biomarkers become incorporated into sediments, either freely as bitumen or bound into macromolecular organic matter (kerogen), where they may be preserved for billions of years (Eglinton et al., 1964; Waldbauer et al., 2009). Where these compounds occur intact and uncontaminated, they represent direct evidence for ancient organisms which left indefinable traces of themselves in the fossil record. Biomarkers were not detected in the Chandi stromatolites but were recovered from the black limestone and red shale. Of concern is whether those biomarkers reflect contamination from migrating petroleum (like in some Archean rocks, Rasmussen et al., 2008), human activity and even low-level contamination (Sherman et al., 2007; Rasmussen et al., 2008), or are indigenous overmature hydrocarbons (French et al., 2015), and therefore, they are unsuitable for further analysis. As no petroleum staining or migration was observed in the black limestone and red shale samples collected from the outcrops, the extracted biomarkers appear to be indigenous. Nonetheless, we note that our findings should be treated cautiously until independently verified.

The aliphatic hydrocarbons are mainly composed of n-alkanes and subordinately of alkylbenzenes and hopanes. Acyclic isoprenoid alkanes, namely pristane and phytane, hopanes and very low amount of steranes were also detected. The n-alkanes show a unimodal distribution, dominated by either n-C₂₀ or n-C₂₁ in both the black limestone and red shale facies. The relative abundance of acyclic isoprenoids is low, with carbon numbers ranging
from C\textsubscript{18} to C\textsubscript{20}. The ratio of \textit{n}-C\textsubscript{17} to pristane (Pr) in the black limestone is 0.18-0.63 and in the red shale it is 1.35, whereas the \textit{n}-C\textsubscript{18} to phytane (Ph) ratio is 0.19-0.5 and 0.71, respectively (Table 5). Pr/Ph ratios in the black limestone range from 0.3 to 0.8, whereas in the red shale they are around 0.5, respectively (Table 5).

Pristane and phytane are typically ascribed an origin from the diagenesis of the phytol side-chain of chlorophylls (Brooks et al., 1969; but note alternative origins shown by ten Haven et al., 1988). A Pr/Ph value <1 is typically interpreted as indicative of deposition under typically marine anoxic conditions and a value >3 is indicative of oxic deposition (Didyk et al., 1978; Brocks et al., 2003). Peters et al. (2005) also argued that Pr/Ph ratios <0.8 can indicate saline to hypersaline conditions associated with evaporite and carbonate deposition. However, Brooks et al. (1969), Didyk et al. (1978) and ten Haven et al. (1988) showed that the Pr/Ph ratio can also be affected by additional inputs of precursors of either pristane or phytane. Crucially, they also showed that the ratio has a tendency to increase with increasing thermal maturity. Given the rather high thermal maturity of these samples, it is possible that the low Pr/Ph values observed here suggest a marine environment with reducing conditions during organic matter deposition.

7.4.3. Hopanes and steranes

The hopanes identified in the samples include the C\textsubscript{27} to C\textsubscript{31} 17\alpha,21(\beta)-hopanes; higher molecular weight components were not detected (Fig. 8). The 17\beta,21\alpha(H)-moretanes were not detected, consistent with a high thermal maturity, although this could also reflect post-depositional diagenetic changes and/or an oxic depositional environment (Peters et al., 2005). The ratios of C\textsubscript{27} 17\alpha-trisnorhopane (Tm) and C\textsubscript{27} 18\alpha-trisnorhopane (Ts) expressed as the Ts/(Ts+Tm) ratio are also consistent with a mature character of organic matter, although that parameter is also governed by lithology and depositional environment (Peters et al., 2005).

C\textsubscript{27}, C\textsubscript{28} and C\textsubscript{29} steranes were also detected but due to their very low abundance identification is only tentative. Steroids have been found in extremely low concentrations in Mesoproterozoic carbonate strata of the Barney Creek Formation (Brocks et al., 2005), but were not found in a Mesoproterozoic marine black shale of Mauritania (Blumenberg et al., 2012), and were not reported from central Russia Mesoproterozoic Arlan calcareous shale (Sperling et al., 2014).
8. Discussion: palaeogeography and palaeoceanographic conditions

The stratigraphic architecture of the Raipur Group indicates that a wide shelf and slope were generated during the expansion of the Chattisgarh Basin. Storms of different intensities, and tides, generally of macrotidal range, helped the development of an open-marine circulation system on the wide, gently sloping shelves of the Chattisgarh Basin (Fig. 9a,b). The significant lateral persistence of individual units, and strong palaeobathymetric fluctuations from close to mean sea level to fairly deep shelf, beyond the reach of coarse sand deposition, strongly support the notion of very wide shelves. Such extensive gently-sloping shelves with uniform marine circulation apparently were relatively common in Mesoproterozoic time when outer-shelf storms were perhaps more frequent than in younger basins (Chaudhuri and Howard, 1985; Eriksson et al., 1998). The expansion of the basin, creation of accommodation space and the basin-fill succession were generated through a number of alternating transgressions and progradations that operated on different scales. The mudstone-dominated sequences developed during transgressions when the input of terrigenous sand decreased substantially, or when the bulk of the coarser clastics were trapped in fluvial systems or in coastal areas (Catuneanu et al., 2011). Episodic development of shoaling-up sandstone bodies, on the other hand, was related to periods of sea-level stillstand or minor fall and shoreline progradation, as well as with uplift and emergence of the hinterland. The growth of the basin and its basin-fill succession was thus created by superposition of a number of discrete cycles of episodic character.

The Charmuria-Sarangarh Limestone and Chandi-Saradih Limestone are quite different from each other, and also from many other carbonate platforms of the Mesoproterozoic. The first platform (Charmuria-Sarangarh), dominated by well-bedded, relatively fine-grained limestone, without stromatolites, but with evidence of storm-influenced deposition, contrasts with the second platform (Chandi-Saradih) with its well-developed and diverse arrangement of stromatolites, formed in an inter- to sub-tidal setting. The contrast could be related to the degree of restriction of the broad, intracratonic Chattisgarh Basin, with the first platform more open, deeper and affected by storm-tidal effects, and the second with more restricted access to the open ocean permitting the development of microbialites in the overall shallower-water setting during its first stage of platform development. With time, these bioherms grew and formed a barrier whose seaward side was open. In addition, by way of contrast, many other Mesoproterozoic carbonate platforms are dominated by cyclic peritidal microbialite facies with much evidence of periodic exposure and locally evaporite precipitation. Examples occur in China (notably the
Jixian Group, Guo et al., 2013), Mauritania (Gilleaudeau et al., 2013a), and Arctic Canada (Baffin Bay and Bylot Island, Kah et al., 1999).

Another feature of the Chattisgarh carbonate rocks is that it is, for the most part, dominated by micritic calcite; many of the other Mesoproterozoic platform carbonate strata (in China, Mauritania and Canada, see above) are composed of dolomite, many with excellent fabric preservation from very early replacement of CaCO$_3$ or even ‘primary’ dolomite (e.g. Guo et al., 2013). The topic of Precambrian dolomites has been extensively discussed, especially for the Neoproterozoic (recently by Tewari and Tucker 2011; Hood et al., 2012), and changes in seawater Mg/Ca ratio have commonly been invoked, following Hardie (2003) and others, as well as the effects of microbial processes. There may well have been fluctuations in ocean Mg/Ca through the Proterozoic to explain changes in primary marine mineralogy and limestone versus dolomite formations, but precise dating of Proterozoic carbonate rocks is not yet possible. Alternatively, intracratonic basins with limited connection to the open ocean may have had a different Mg/Ca ratio, so that limestone could form locally, rather than dolomite which appears to be the dominant mineralogy of Proterozoic carbonate strata.

Our sedimentological and geochemical data indicate a low TOC setting with a lack of evidence for sulphidic (euoxic) conditions during formation of the black limestone, red shale, and the brown and grey stromatolite horizons. Aryl isoprenoid and other isorenierene derivatives derived from green sulphur bacteria (GSB) and indicative of euoxic conditions in the photic zone (Summons and Powell, 1986) were not detected. However, given the high thermal maturity and low biomarker contents, this is only tentative evidence for the absence of GSB from the Chattisgarh Basin. In particular, euoxic conditions during the deposition of the Timarlagar Limestone, which is characterised by low (<1) Pr/Ph ratios, cannot be excluded.

Kah and Bartley (2011) reviewed the cycling of sulphur through the Proterozoic and noted that although most Mesoproterozoic environments show evidence of euxinia, the nature and extent of these environments appear to have been quite variable. In fact, they argued that heterogeneity could have been the overarching characteristic for the Mesoproterozoic oceans. Ocean redox chemistry can also be evaluated by Mo isotopes (Scott et al., 2008), and Gilleaudeau and Kah (2013b) showed that Mo isotopic and marine redox variability could represent a hallmark of the relatively high sea levels and extensive shallow-marine platforms of the Mesoproterozoic. In addition, Lyons et al. (2012, 2014) stressed that euxinia definitely
was part of the Mesoprotерozoic oceans but that the environments of euxinia may have been limited to marginal marine settings. Sperling et al. (2014) provided evidence for the presence of free oxygen in the Mesoprotерozoic Arlan Member basinal calcareous shale in Russia, further supporting Protérozoic redox heterogeneity.

The development of the conspicuous black Timarlaga limestone is related here to a major flooding event / sea-level rise, and in that sense is analogous to many ‘oceanic anoxic events’ (OAEs) of the Phanerozoic (Jenkyns, 2010), which are prominent in the Cretaceous, but also in the Lower Jurassic and Upper Devonian. OAEs are related to enhanced organic matter production and burial, leading to positive δ13C excursions; the Timarlaga Limestone also shows a positive δ13C shift. However, the TOC contents of the Timarlaga Limestone are generally very low. These low TOC contents (especially in combination with low Pr/Ph ratios and the presence of black shales during highstands) could be an artefact, arising from either degradation or high maturity, although we note that low grade metamorphism did not occur in the Chattisgarh Basin (Chakraborty et al., 2012). It is also possible that organic carbon sequestration via anoxic deposition has occurred elsewhere in the deeper Chattisgarh Basin.

Despite these caveats, in the absence of evidence for elevated organic burial in the Chattisgarh Basin, we suggest that these high δ13C values likely reflect wider basin or even global processes rather than an active biological pump on the platform itself. The very low organic carbon content in the Chattisgarh Basin, therefore, could be indicative of relatively low productivity and/or oxidising conditions in this particular setting. For example, low nutrient supply (oligotrophic conditions) could have precluded high organic productivity within the basin, as also invoked by Sperling et al. (2014) for the Arlan shale. This could reflect macronutrient limitation, but it also could have been caused by limitation of trace metals, likely scavenged due to high seawater sulphide concentrations (Stüeken, 2013).

Desmethyl steranes (C27-29) were detected in the black Timarlaga limestone, but in very low concentrations. In Phanerozoic environments, C26 to C29 steranes are regarded as diagnostic markers for eukaryotes, particularly algae. The extremely low concentration of steranes in the studied rocks suggests that eukaryotic organisms were present in relatively insignificant abundances, at least relative to bacteria, in the Mesoprotérozoic Chattisgarh Basin. The lack of extensive eukaryotes provides additional evidence for this being a low productivity setting, although the relatively more abundant hopanes could be evidence for bacterially dominated production.
9. Conclusions

The Mesoproterozoic Raipur Group of the Chattisgarh Basin preserves two extensive carbonate platforms separated by calcareous shale. The lower platform is non-stromatolitic, with well-preserved lime-mud rhythmite facies pointing towards a passive-margin depositional setting. The upper platform developed in the intertidal to shallow subtidal environment with prolific growth of stromatolites forming a barrier. The platforms maintain the same trend in the disposition of the facies belt parallel to the palaeo-coast line. Distinct changes in morphologies of the stromatolites are probably related to changes in water depth during platform evolution. The basin history with repeated events of opening, sedimentation and closure continued for more than 400 my.

Sedimentological and geochemical data indicate a low TOC setting with little evidence for euxinic conditions in the Mesoproterozoic Chattisgarh Basin. Low TOC values possibly result from degradation, high thermal maturity, poor preservation of organic matter and/or low productivity due to poor nutrient supply. Dysoxic or anoxic conditions could have existed below storm wave base during the deposition of the Timarlaga Limestone, whereas red shale, brown and grey stromatolite facies were deposited in more oxic seawaters, all consistent with previously proposed redox heterogeneity in the Proterozoic oceans.

Acknowledgements

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Summons, R.E., Powell, T.G., 1986. *Chlorobiaceae* in Paleozoic seas revealed by biological


Figure 1. Generalized geological map of part of the peninsular India showing mobile belts and major tectonic lineaments. Inset map shows distribution of cratons, mobile belts and the Proterozoic cratonic basins on the Indian craton, Chattisgarh (Ch); Khariar (Kh); Indravati (I); Pranhita-Godavari Basin (PGB); Cuddapah (C); Vindhyan (V); Kaladgi (K); Bhima (B), Aravalli Fold Belt (AFB); Central Indian Shear Zone (CIS); Godavari Graben (GG); Mahanadi Graben (MG); Son-Narmada North Fault (SNNF) and Son-Narmada South Fault (SNSF). Modified after Ramachandra et al. (2001) and Chakraborty and Paul (2008).

Figure 2. Chattisgarh stratigraphy with existing interpreted tuff crystallization age constraints (modified after Saha and Patranabis-Deb, 2014). The red rectangle area marks the area of interest presented in Figure 7b.

Figure 3. Representative photographs of the sedimentary structures showing the mixed siliciclastic-carbonate facies of the Gadhabhata Member, Sarangarh Limestone: (a)
Thin stringers and mm thin discrete layers of glauconitic sandstone within grey limestone. (b) Debris-flow conglomerate comprising clast of grey limestone floating in a matrix of micrite (lst) and very well rounded coarse grained sandstone (sst) within Gadhabhata Member. Note the slumped beds of limestone in the lower part of the photograph. Width of the photograph is 50 cm. (c) Limestone-marl rhythmites in thin-bedded (2-8 cm) black lithographic limestone. Scale: length of pen is 12 cm (d) Black limestone bed (10 cm) with clusters of early diagenetic pyrites (note the arrow heads). (e) Pyrite cubes within black limestone.

Figure 4. (a) Thin-bedded splintery brown shale, Gunderdehi Formation. Note the lateral persistency of the bed sets. Hammer length 28 cm. (b) Authigenic barite nodule within brown shale. Note the swerving of the laminae, round the nodule. (c) Isolated bodies of stromatolite bioherms, enclosed within the Gunderdehi shales. (d) Close-up view of the bioherms within shale with sharp basal contact. Inter area is filled up with lime mud. Hammer length 25 cm.

Figure 5. Photomicrograph of the hydrofractured chert. Note the fracture-fill character of the chert pointing towards their secondary origin.

Figure 6. Chandi Limestone: (a) Stromatolite biostromes with well-developed pause planes (arrow heads). The area marked with black rectangle is highlighted in figure b. (b) Section perpendicular to bedding plane view the inclined non-branching stromatolites showing the configuration of laminae. (c) Bifurcate or trifurcate branching of subparallel stromatolite columns on bedding perpendicular view. Column height 20-35 cm, width 2-5 cm. (d) Plan view of stromatolites showing different shapes and rugged margins.

Figure 7. (a) Carbon and oxygen isotopic data ($\delta^{13}C$ vs $\delta^{18}O$) from the Chattisgarh limestones (black circles) and calcareous shales (red circles). (b) A close-up view of the marked area of Figure 2 showing carbon and oxygen isotopic data from the Chattisgarh limestones of different stratigraphic levels.
Figure 8. A partial GC-MS mass chromatogram of m/z 191 from a saturated hydrocarbon fraction, Chandri Formation, black limestone. Ts - C_{27} 18α-trisnorhopane; Tm - C_{27} 17α-trisnorhopane.

Figure 9. Palaeoenvironmental reconstruction of the (a) Charmuria/Sarangarh platform, and (b) Chandi/Saradih platform.

### Table 1. Major facies of the Sarangarh platform

<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Lithology</th>
<th>Sedimentary structures</th>
<th>Depositional environment interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shale-limestone heterolithic</strong></td>
<td>Interlayered brown calcareous shale and micritic limestone, 2-5 cm thick beds</td>
<td>Graded beds, planar parallel lamination, erosive base</td>
<td>Outer ramp, distal turbidites</td>
</tr>
<tr>
<td><strong>Brown micritic limestone</strong></td>
<td>Brown micritic limestone, 10-20 cm thick beds, intermixed fine sands</td>
<td>Planar tabular beds, massive graded or with mm thin planar lamination</td>
<td>Outer ramp, below normal wave base, distal storms</td>
</tr>
<tr>
<td><strong>Mixed carbonate-siliciclastic</strong></td>
<td>Micritic grey limestone and interstratified 1-2 cm streaks and single grain thick stringers of well sorted sandstone, 10-30 cm thick beds</td>
<td>Planar tabular beds, sharp bases, gradational top, normally graded, planar, parallel, stratified, or with HCS.</td>
<td>Mid ramp, within storm wave base, high-energy storm-flows, episodic transportation sands</td>
</tr>
<tr>
<td><strong>Flat pebble, lime clast conglomerate</strong></td>
<td>Conglomerate with flat 2-10 cm size intraformational limestone clast, medium to coarse grained siliciclastic sand and micrite matrix, 10-20 cm thick beds and 5-30 cm thick lenses</td>
<td>Clast imbrication and locally coarse tail reverse grading in bedded type, fan shaped orientation in lenses with deep erosive scours</td>
<td>Mid ramp storm deposit</td>
</tr>
<tr>
<td><strong>Rhythmite facies above storm wave base</strong></td>
<td>Alternation of 5-15 cm thick brown or black micritic limestone beds, with peloids, and 1-2 cm thick marl layers</td>
<td>Limestone beds wavy planar, or tabular, laterally very persistent, internally plane parallel or wavy parallel laminated, commonly with HCS, rhythmicity maintained throughout the section, bed-set</td>
<td>Outer ramp, with fluctuating sea level in cyclic pattern below and above storm wave base</td>
</tr>
</tbody>
</table>
Rhythmite facies below storm wave base

<table>
<thead>
<tr>
<th>Lithofacies</th>
<th>Lithology</th>
<th>Sedimentary structures</th>
<th>Depositional environment interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown calcareous shale with siltstone</td>
<td>Interlayered brown calcareous shale and siltstone, intermixed fine sands, pockets of mudclast conglomerates</td>
<td>2-10 cm thick, planar parallel lamination, graded beds, commonly with HCS, erosive base at places, low angle truncation between strata sets common, low amplitude ripples and soft sediment deformation common</td>
<td>Outer shelf mud, with occasional storm generated turbidites</td>
</tr>
<tr>
<td>Stromatolite mounds within brown calcareous shale</td>
<td>Brown calcareous shale with stromatolite mounds</td>
<td>Isolated small (10 cm to 100 cm) wide stromatolite mounds, elliptical in cross-section, stromatolites are small, columnar branching and non-branching type, rounded or elongate in planar section, occur at the transition between shale and limestone</td>
<td>Intertidal zone, shallow wide muddy shelf</td>
</tr>
<tr>
<td>Microbial laminite</td>
<td>5 cm to 1 cm thick couplets of fine silt and carbonate mud; locally argillaceous</td>
<td>Layering thins and fines up; passes up to crinkly layers; scours and erosion between strata sets common; locally mudcracks present</td>
<td>Intertidal microbial mats</td>
</tr>
<tr>
<td>Edgewise</td>
<td>Grey or brown micritic</td>
<td>5-7 cm thick tabular</td>
<td>Storm dominated</td>
</tr>
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</table>

Pattern show thickening and thinning of beds

Outer ramp, below storm wave base
<table>
<thead>
<tr>
<th>Conglomerate</th>
<th>Limestone with intermixed siliciclastic sands</th>
<th>Beds, 0.5 to 2 cm long platy clasts, haphazardly oriented locally vertical clasts embedded within mixed siliciclastic-carbonate matrix</th>
<th>Intertidal shelf</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Brown or grey micritic, peloidal stromatolitic limestone</strong></td>
<td>Brown micritic limestone, with biostromes (bedded stromatolite).</td>
<td>Bedded biostrome, bed thickness 15-30 cm. Stromatolites with branching and non-branching columns, 2-6 branches either parallel or divergent. Column height 5-15 cm width 1-3 cm, convex-up laminae with slight crinkling, narrow base and wide top</td>
<td>Subtidal – Intertidal</td>
</tr>
<tr>
<td><strong>Mauve or grey stromatolitic bioherm</strong></td>
<td>Mauve to grey micritic limestone, with stromatolite bioherm</td>
<td>5 to 2 m thick convex upward stromatolitic bioherms, coalesce to form continuous succession, more than 100 m thick. Stromatolites with branching columns, branches are parallel or diverging, digitate. Column height from 5 to 50 cm, convex up laminae, lamina sets truncated.</td>
<td></td>
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Table 3. Bulk geochemical results of Rock-Eval/TOC of the samples studied. N.a. – not analysed.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Colour &amp; Mineralogy</th>
<th>TOC (wt.%)^a</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)^b</th>
<th>S&lt;sub&gt;1&lt;/sub&gt; (mg/g)^c</th>
<th>S&lt;sub&gt;2&lt;/sub&gt; (mg/g)^d</th>
<th>HI^e</th>
<th>OI^f</th>
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</thead>
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<td>53</td>
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<td>786</td>
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<td></td>
<td>0.02</td>
<td>433</td>
<td>0</td>
<td>0.03</td>
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<td>861</td>
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<tr>
<td></td>
<td></td>
<td>0.04</td>
<td>436</td>
<td>0</td>
<td>0.06</td>
<td>155</td>
<td>570</td>
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<td></td>
<td></td>
<td>0.03</td>
<td>450</td>
<td>0</td>
<td>0.04</td>
<td>158</td>
<td>1292</td>
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<td>Gunderdehi Formation</td>
<td>Red calcareous shale</td>
<td>0-0.1</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Chandi Formation</td>
<td>Brown stromatolitic limestone</td>
<td>0-0.1</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Chandi Formation</td>
<td>Grey stromatolitic</td>
<td>0-0.1</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>
Table 4. Carbon and oxygen stable isotopic analyses of the carbonate samples studied.

<table>
<thead>
<tr>
<th>Limestone Type</th>
<th>δ¹³C</th>
<th>δ¹⁸O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brown calcareous shale (above fair-weather wave base, but at the transition zone).</td>
<td>4.2</td>
<td>-11.3</td>
</tr>
<tr>
<td>Brown limestone (below fair-weather wave base but above storm wave base).</td>
<td>3.9</td>
<td>-11.4</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>-10.4</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>-12.3</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>-12.3</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>-12.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-10.9</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>-8.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-10.9</td>
</tr>
<tr>
<td>Grey-brown mixed (below fair-weather wave base but above storm wave).</td>
<td>2.2</td>
<td>-8.9</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>-8.5</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>-8.2</td>
</tr>
<tr>
<td>Grey limestone (below fair-weather wave base but above storm wave).</td>
<td>2.4</td>
<td>-7.8</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>-13.3</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>-5.7</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>-9.5</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>-12</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>-9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-7.9</td>
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<tr>
<td></td>
<td>2.1</td>
<td>-8</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>-8.3</td>
</tr>
<tr>
<td>Black limestone (just above the storm wave base to below storm wave base).</td>
<td>2.4</td>
<td>-8.5</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>-9.6</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>-9.1</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>-6.3</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>-7.1</td>
</tr>
<tr>
<td></td>
<td>1.8</td>
<td>-8.9</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>-8</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>-8.2</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>-8.4</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>-9.9</td>
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<tr>
<td></td>
<td>3.8</td>
<td>-9.1</td>
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<tr>
<td></td>
<td>2.1</td>
<td>-8.2</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>-9.1</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>-7.24</td>
</tr>
<tr>
<td>Mauve limestone (below fair-weather wave base but above storm wave).</td>
<td>3.2</td>
<td>-11.1</td>
</tr>
<tr>
<td></td>
<td>2.2</td>
<td>-9.4</td>
</tr>
<tr>
<td>Limestones &amp; dolomites within shale.</td>
<td>2.2</td>
<td>-9.4</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>-11.1</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>-4.7</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>-3.9</td>
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<td></td>
<td>1.6</td>
<td>-11.9</td>
</tr>
<tr>
<td></td>
<td>2.23</td>
<td>-9.74</td>
</tr>
<tr>
<td>Brown stromatolitic limestone (above fairweather wave base).</td>
<td>4</td>
<td>-10.8</td>
</tr>
<tr>
<td></td>
<td>2.99</td>
<td>-8.71</td>
</tr>
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</table>
Table 5. General biomarker characteristics of the studied samples.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Mineralogy</th>
<th>Pr/Ph&lt;sup&gt;a&lt;/sup&gt;</th>
<th>n-C&lt;sub&gt;17&lt;/sub&gt;/Pr</th>
<th>n-C&lt;sub&gt;18&lt;/sub&gt;/Ph</th>
<th>Ts/Tm&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charmuria/</td>
<td>Limestone</td>
<td>0.3-0.8</td>
<td>0.18-0.63</td>
<td>0.19-0.5</td>
<td>0.46</td>
</tr>
<tr>
<td>Sarangarh</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gunderdehi</td>
<td>Calcareous shale</td>
<td>0.5</td>
<td>1.35</td>
<td>0.71</td>
<td>0.47</td>
</tr>
</tbody>
</table>

<sup>a</sup> Pr/Ph: pristane / phytane ratio

<sup>b</sup> Ts/Tm: C<sub>27</sub> 17<sup>α</sup>-trisnorhopane (Tm) / C<sub>27</sub> 18<sup>α</sup>-trisnorhopane ratio expressed as Ts/(Ts+Tm)