Chuaria circularis from the early Mesoproterozoic Suket Shale, Vindhyan Supergroup, India: Insights from light and electron microscopy and pyrolysis–gas chromatography

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Chuaria circularis (Walcott 1899) from the Suket Shale of the Vindhyan Supergroup (central India) has been reinvestigated for its morphology and chemical composition using biostatistics, electron microscopy and pyrolysis–gas chromatography. Morphology and microscopic investigations provide little clues on the specific biological affinity of *Chuaria* as numerous preservational artifacts seem to be incorporated. On the contrary, the predominance of *n*-aliphatic pyrolysates of presently studied *Chuaria* from India rather supports an algal affinity. Moreover, the reflectance of *C. circularis* can be used to obtain a comparative maturity parameter of the Precambrian sediments. The review of the age and geographical distribution of *C. circularis* constrains that this species cannot be considered as an index fossil for the Proterozoic time.

1. Introduction

The origin and nature of *Chuaria circularis* has long been a topic of debate in Precambrian paleobiology since its first recognition by Walcott (1899). *Chuaria* had been related to hyolithids, gastropods, brachiopod, chitinous foraminifera, medusoids, trilobite eggs or was even regarded as inorganic remains in various studies (see Hofmann 1992). Ford and Breed (1973) concluded that *Chuaria* was a plant, most probably being a large leiospherid acritarch. White (1928) first concluded that *C. circularis* might represent an alga. Later, this view was supported by many authors, e.g., Vidal (1974, 1976); Hofmann (1971, 1977), and Jux (1977). Due to its large size, *C. circularis* was placed into the Megasphaeromorphida of the Acritarcha Evitt 1963. More recent interpretation

was made by Sun (1987) considering *Chuaria* as probable colonies of filamentous cyanobacteria comparable to the modern colonial cyanobacteria *Nostoc*. Steiner (1997) accepted Sun's opinion, but also proposed that the widely distributed and simply constructed morphospecies *C. circularis* may have various biological affinities, i.e., mainly prokaryotic colonies of eubacteria and chroococcal or filamentous cyanobacteria, but partly even eukaryotic algae.

In India, Jones (1909) reported carbonaceous discs from the Suket Shale of Rampura area, Neemuch district, Madhya Pradesh (figure 1) and related them to either *Obolella* or *C. circularis*. Chapman (1935) assigned the specimens to the two new genera and four new species *Protobolella jonesi*, *Fermoria minima*, *F. granulosa* and *F. capsella*. Sahni (1936) placed all of them in the

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Figure 1. Geological map of the Rampura area, Neemuch district, Madhya Pradesh (after Kumar 2001) showing location of the study area (map of India within inset).

synonymy of *F. minima*, but erected the new name *Vindhyanella* for one of the specimens figured as *Protobolella jonesi* by Chapman (1935, plate 2). Maithy and Shukla (1977) suggested that the disc-like bodies are either imprints of acritarchs or algal colonies. Sahni (1977) considered the placement of *Fermoria* under *Chuararia* made by Ford and Breed (1973) an erroneous assignment. Maithy and Shukla (1984) agreed that morphologically these forms belong to *Chuararia* Walcott and compared them with the cryptarch genus *Orygmatozphaeridium*. Recently, Kumar (2001) studied the morphology of different carbonaceous fossils from the Suket Shale and considered *Chuararia* as a reproductive stage of a possibly cyst-like body of a Chlorophycean or Xanthophycean alga.

Molecular characterization of any Precambrian organic matter is difficult to carry out, because of its high thermal maturity. However, any structural investigation of organic matter of this age is essential in understanding evolution of Earth and life (Li et al 2004). Pyrolysis–gas chromatographic study is herein reported for the first time on well-defined organic material from the Proterozoic Vindhyan sediments of India. The pyrolytic degradation has been carried out in order to obtain information on the molecular composition of the organic matter, and its potential biological origin. Accordingly, this paper presents a comprehensive study including morphology, biostatistics, SEM and TEM images and molecular composition of *Chuararia* from the Suket Shale of the Lower Vindhyan, Semri Group.

2. Samples

The Vindhyan Supergroup represents a thick (up to 4500 m) succession of undeformed and slightly metamorphosed, Paleoproterozoic to Neoproterozoic sediments exposed in Rajasthan and Son valley regions. The study area is situated in the less-studied northwestern region of the Vindhyan basin.

The Vindhyan Supergroup is two-tiered and consists of the Lower Vindhyan Group (or the Semri Group) and the Upper Vindhyan Group. Vindhyan sedimentation took place largely in a shallow marine environment (Chanda and Bhattacharyya 1982), but the depositional environment fluctuated between offshore, deltaic, lagoonal, fluvial and even eolian settings (Bose et al 2001).

The Suket Shale occupies the low lying plains around Rampura (figure 1). The rocks are exposed in the Tilsoi River section, Nala cuttings and along the Rampura–Neemuch road section. The main lithologies of the Suket Shale are green shales, greyish yellow shales with subordinate occurrences of greyish black carbonaceous shales, siltstones and light brownish grey sandstones. The contact between Suket Shale and Kaimur Group is gradational. The Suket Shale is commonly correlated with the Rampur Shale in the Son valley (Sarkar et al 2002) where it consists of greyish and carbonaceous shales intervened by siltstones/fine grained sandstones. The Suket Shale of the Rampura area has not been dated so far,

however, its stratigraphical position can be inferred from a correlation with strata in the Son valley area. Absolute ages for Vindhyan strata from the Son valley are given by Rasmussen *et al* (2002) who dated the tuff bands occurring at the base of the Rampur Shale and fixed an age of 1599 ± 8 Ma by the U/Pb method. Sarangi *et al* (2004) recently obtained an age of 1599 ± 48 Ma for the overlying Rohtas Formation containing carbonaceous fossils (*Grypania*) by the Pb/Pb dating technique. On this basis the age of the Suket Shale can be estimated at roughly 1600 Ma. Samples for the present study have been collected from comparably fresh well cuttings near the Tilsoi River section and are preserved at the China Research Center (Sekt. ACK 14) of Technical University, Berlin.

3. Methods

For reflected light, scanning electron microscope (SEM) and transmission electron microscope (TEM) analyses, specimens of *Chuarina* were extracted from the rock matrix using 40% HF acid (for three days). After treatment with HF the samples were neutralized using a 10 μ m mesh filter. Well preserved individuals of *Chuarina* were picked from the organic residue by a pipette. Both, isolated specimens, and those preserved *in situ* on the rock surfaces were studied in reflected light under a Leitz-Wild-M3Z binocular microscope.

Specimens selected for SEM were mounted on a preparation stub and coated with a 20 nm layer of gold and investigated by a Hitachi S520 at TU Berlin. The wall thickness of specimens of *Chuarina circularis* was determined by measurement of transversal fractures under SEM or by measurement of embedded and sectioned individuals using light microscopy under high magnification. Extracted specimens for the TEM analysis were dehydrated using ethanol and embedded in Araldite CY 212 resin. The ultra-thin sections (thickness 70 nm) were cut perpendicular to the compressed surface of the specimens in an ULTRACUTE and placed on copper grids for study in a JEOL 200B TEM at TU Berlin.

For reflectance studies, whole rock fragments containing *Chuarina* as well as individuals of *Chuarina* isolated from the Suket Shale of India, the Visingsö Formation of Sweden and from the LiulaoBei Formation of China were embedded in Araldite resin and polished by a standard coal petrographic technique (Mackowsky 1982). The percentage of random reflectance was measured in oil immersion ($n_{oil} = 1.518$) at a 546 nm wave length at 23°C.

For pyrolysis, specimens of *Chuarina* were scratched off from the bedding planes of rock samples using a sharp scalpel and subsequently only the organic remains of *Chuarina* were handpicked under a stereomicroscope. Prior to chemical investigations, these organic walled fossils were cleaned several times with dichloromethane to remove free hydrocarbons.

Molecular characterisation of *Chuarina* was performed by open-system off-line pyrolysis method and pyrolysis products released during thermal degradation were first collected and studied at a later stage. Up to 1.0 mg of sample was heated in a flow of helium. Pyrolysis products released over a temperature range $< 300^\circ\text{C}$ (300°C held for 5 minutes) were vented. Products released over a temperature range from 300 to 600°C ($50^\circ\text{C}/\text{min}$) were collected in a cryogenic trap (liquid nitrogen cooling) from which they were then liberated by ballistic heating. Gas chromatographic analysis was carried out using a 50 m $\times$ 0.31 mm fused silica column (HP-1; 0.5 μ m film thickness) programmed from 40°C to 300°C with a heating rate of 5°C per minute. The relative abundance of compounds was determined using Multichrom chromatography data system (VG DATA SYSTEMS).

4. Systematic Description

Genus: *Chuarina* Walcott

Species: *Chuarina circularis* Walcott
(plate 1 and plate 2)

Lectotype: Ford and Breed 1973, p. 540, figure 1, USNM 33800

Synonymy: For synonymy, see Maithy and Shukla (1984), Steiner (1994), Talyzina (2000)

Type locality: Kwagunt Valley, Grand Canyon, Arizona, USA

Investigated locality: Rampura, Neemuch District, Madhya Pradesh, India

Lithology: Black shales, greyish black shales, yellow shales

Description: Circular to elliptical discs ranging in size from 0.25 mm to 4.75 mm are either preserved in the form of carbonised compressions on black/grey shale or imprints on weathered, yellow shale (plate 1a, 1b, 1c). Discs may contain concentric and irregular wrinkles resulting from the compression of originally spherical bodies (plate 1a). Rare three-dimensional specimens are occurring, probably due to infilling (plate 1d). Few specimens

Plate 1. (a) *C. circularis* with wrinkles at the boundary (sample number R₂/10/1); (b) *C. circularis* with thick carbonaceous matter and imprints of sediment on top of it (sample number R₂/4/2); (c) *C. circularis* showing elliptical shape, carbonaceous matter partially weathered out (sample number R₂/4/3); (d) Three dimensionally preserved *C. circularis* (sample number R₂/2/3); (e) *C. circularis* with strongly folded thick carbonaceous matter (sample number R₂/5/2); (f) Attached individuals of *C. circularis* of different size and different thickness of preserved organic matter (sample number R₂/3/2); (g) *C. circularis* after separation from rock matrix by HF. Note that the specimen shows a compactional crack structure (referred to as ‘opening structure’ by other authors) and opaque, thick organic matter with sediment grain imprints. Opacity is correlated with a mostly large maximum diameter (ca. 200–4000 μm) and great wall thickness (> 1000 nm); (h) *C. circularis* after separation from rock matrix by HF. Note circular and irregular folds, resulting from compaction of relatively thin organic matter. Medium brown colour is correlated with medium maximum diameter (ca. 200–2000 μm) and a relatively thin wall thickness (ca. 350 nm). All samples are derived from the Suket Shale, Vindhyan Supergroup, Rampura, Madhya Pradesh, India. Specimens are deposited at the China Research Center (Sekt. ACK 14) of TU Berlin.

Plate 2. (a) Scanning electron micrograph of *C. circularis*. Note that concentric wrinkles are not well developed, but sediment grain imprints are prominent; (b) Scanning electron micrograph of transversal fracture of a specimen of *C. circularis*, indicating massive single layer without a median split; (c) Scanning electron micrograph of transversal section of a specimen of *C. circularis* with folded layer; (d) Scanning electron micrograph of transversal section of a specimen of *C. circularis*, showing an irregular cavity within the wall, but no median line as it should be expected from the compaction of a central cavity of a vesicle; (e) Transmission electron micrograph of *C. circularis*, showing lamellar structure (magnification 30000 $\times$); (f) Transmission electron micrograph of *C. circularis*, showing cavity within the wall (magnification 25000 $\times$). All samples are derived from the Suket Shale, Vindhyan Supergroup, Rampura, Madhya Pradesh, India. Specimens are deposited at the China Research Center (Sekt. ACK 14) of TU Berlin.

occur as intergrown groups (plate 1f). The surfaces of most compression have been deformed to a varying degree by sediment grains from the surrounding rock matrix during compaction (plate 1b, 1e, 1g). Circular and irregular folds are also preserved in the specimen, isolated from rock matrix (plate 1h). Isolated specimens show yellow to dark brown colouration in transmitted light or are opaque.

4.1 Discussion

Difficulties in interpreting the original primary morphology and biological assignment of *Chuararia circularis* are derived from the fact that numerous preservational artifacts and taphonomic alterations are incorporated within this simple fossil. The species *Chuararia circularis* is herein regarded as a form-taxon of very simple morphology, which may embrace similar remains of different biospecies. The characters of *Chuararia circularis* are partly overlapping with those of several species of large leiospherid acritarchs. Species differentiation based on the presence of such characters of acids resistance, opacity and compressional fold arrangement may be practical, but are arbitrary. Therefore, acid resistance, opacity and fold arrangement are not used in taxonomical sense herein. Walcott (1899) in his original report described this species as a brachiopod showing regular ring-like wrinkles. *Chuararia* was later considered as spheroidal or a hollow spheroid with a narrow flange (Ford and Breed 1973). Duan (1982) believed that such concentric wrinkles are of inherent morphological features and may be diagnostic criterion and argued that the marginal flange described by Ford and Breed (1973) was originally a part of the ring-like wrinkles. Butterfield *et al* (1994) used the presence of concentric wrinkles as diagnostic character. Specimens of *Chuararia circularis* from the Suket Shale occur with marginal wrinkles (plate 1a), while others do not (plate 1g). However, similarities in their size range, composition and other characteristics seem to indicate that the concentric wrinkles are only preservational alterations caused by slightly differing modes of compaction. Variable preservation with partial lack of the often typical concentric wrinkles is also reported from an early diagenetically mineralized (pyritized) assemblage of chuarids (Yuan *et al* 2001). The specimens of the present study also show irregular microfolds (plate 1e) probably resulting from dewatering after deposition. Hofmann (1985a) also suggested that the folds and marks on carbonaceous megafossils are compactional artifacts. Overlapping of specimens is not common, even in dense accumulations. Therefore, Duan (1982) concluded that *Chuararia* was spherical in shape. Compactional cracks have been postulated as excystment structures of eukaryotic

megacysts (Yuan *et al* 2001) or 'opening-structure' for the release of spores on maturation of *Chuararia* (Kumar 2001; figure 6j). However, similar cracks were produced by compaction experiments on modern spherical colonies of cyanobacteria (Steiner 1994; plate 1, figure 3). Similar structures found in the present study (plate 1g) suggest a compressional origin, which is supported by the observation of Eisenack (1966) that cracks commonly occur in the younger stages rather than in mature specimens.

5. Colour

Butterfield *et al* (1994) discussed opacity as an inherent character of *Chuararia* and postulated that opacity of these fossils from the Svanbergfjellet Formation is not a direct function of wall thickness, but rather dependent on histological characteristics. Therefore, translucency, wall thickness and colour of *C. circularis* are herein systematically studied. Specimens of the present study show colour variation from yellow via brown to black (opaque). Three major characters may be considered to determine the colour of any fossilised organic substance:

- thermal maturity,
- wall thickness and
- type of the material.

Specimens of the present study are collected from the same stratigraphic horizon and at the same locality but show a wide range of colours implying that thermal alteration could have played a small role only. Wall thickness of this fossil may be the reason for colour variation. To study the relationship between colour, wall thickness and size of *Chuararia circularis*, a number of specimens were classified according to a subjective colour scale and their size and wall thickness were recorded (figure 2). Numerous specimens of each size class and colour group were measured. A systematic trend of increasing translucency and a presence of lighter colours with smaller maximum diameters of individuals of *C. circularis* was recognized. However, dark or opaque individuals occurred also in smaller size classes, although they were less abundant than individuals larger than 500 μm in diameter. Opacity occurred in Indian material from the Suket Shale at a total 'wall' thickness of about 1 μm or more, while translucent individuals with brown colouration ranged from ca. 350 to 750 nm in total thickness (figure 2). The recorded range of total 'wall' thickness from 0.3 to 23.85 μm , is quite large and contradicts an interpretation as vesicle or even cell walls of only one biological species. It is obvious that with increasing

Figure 2. Variation of colour with total 'wall' thickness of *Chuar circularis*, Suket Shale, Vindhyan Supergroup, India.

Figure 3. Size histogram of *Chuar circularis*, Suket Shale, Vindhyan Supergroup, India.

'wall' thickness, the colour of *Chuar* changes from yellow to brown to black (opaque). It has also been observed that large black (opaque) individuals of *Chuar* became translucent (brown) in areas of corrosion. Similar conclusions were also drawn by Steiner (1994) after detailed study of *C. circularis* from the Liulaobei Formation, north China. It can be concluded that opacity is a direct function of wall thickness and thus may not be an inherent property of *Chuar*. Regional differences in opacity of organic matter of *Chuar* may result from differing thermal history.

6. Biostatistics

Size statistic of *Chuar circularis* from the Suket Shale reveals a variation from 0.25 mm to 4.75 mm and a unimodal size distribution with a mode in

Figure 4. Scatter diagram for longer dimension plotted against shorter dimension for *Chuar circularis*, Suket Shale, Vindhyan Supergroup, India.

the size range of 2.25 mm to 2.75 mm (figure 3). In the scatter diagram (figure 4) the ratio between the longer and shorter diameter varies between 1 and 1.5. Both, smaller and larger forms exhibit almost identical morphological features. Gahre and Badve (1978) and Maithy and Shukla (1984) showed a size frequency distribution of *C. circularis* from the Suket Shale and concluded that large size specimens dominate in black shales whereas the smaller size are common in yellow shales. The present study, however, reveals equal occurrences of both, larger and smaller *Chuar* specimens, within the black shales (plate 1f).

The wall thickness ranges from 0.3 μm –23.85 μm for examined specimens from the Suket Shale (plate 2b–d). The original description of the type-species *Chuar* Walcott from the Chuar Group (Walcott 1899) does not provide any data on the total 'wall' thickness. However, Jux (1977) mentioned that 'wall' thickness of *C. circularis* varies from 2–2.5 μm . Ford and Breed (1973) mentioned a 'wall' thickness of 50–70 μm of *Chuar* from the Visingsö Formation, but Amard (1992) argued that the original wall thickness ranges from 15–30 μm in these same samples. The wide range in thickness may be the result of either biodegradation or differential compaction. Recently, Javaux *et al* (2004) suggested that variations in wall thickness of the Proterozoic organic walled microfossils could be due to compaction.

There is not much agreement on a potential size limitation as a diagnostic feature of *Chuar*. Ford and Breed (1973) mentioned *C. circularis* as flattened carbonaceous spheroids with wrinkles and cracks, but within a size limit of 500 to 5000 μm .

Vidal (1974, 1976) did not agree with Ford and Breed (1973) in applying size limits and reported that the size range of most of his specimens remain in the range of 0.09–0.2 mm and few up to 3 mm. Sun (1987) strongly recommended that *Chuar* is typically characterized as macroscopic in size and mentioned that the size range should be taken as a practical, convenient criterion to distinguish *Chuar* from various acritarch forms. But Steiner (1997) rejected that size limits are artificial in defining *C. circularis*. Kumar (2001) showed a bimodal distribution of *Chuar* and on this basis he erected the new species as *C. vindhyansis* which is distinguished from *Chuar circularis* by a smaller size. We do not agree with this interpretation, since both smaller and larger forms exhibit identical morphological features. In contrast to a biological interpretation, bimodality in size may indicate a sorting effect due to reworking if other characters do not differ.

7. Ultrastructure

SEM investigations reveal no special ornamentation on the surface of the specimens of *Chuar circularis* except a few pits interpreted as impressions of sediment grains or resulting from biodegradation (plate 2a). The ‘wall’ of the compressed carbonaceous spheres of *Chuar* is represented by a massive layer (plate 2b). At places small folds are randomly distributed on the wall surface (plate 2c). Irregular cavities are found in particular regions of the massive layer (‘wall’) in some specimens (plate 2d). Amard (1992) found that the wall exhibits a stepped row of horizontal dark and light lamellae and in some cases a column-like structure with perforations communicates between the lamellae and concluded that a number of lamellae are variable from one specimen to another depending on biological factors like juvenile or mature stage. Such structures have not yet been identified in the SEM images of *Chuar* from the Suket Shale of Rampura; and these structures have not been found in the specimens from the Chuar Group (Jux 1977), Liulaobei Formation (Steiner 1994) or the Visingsö Group (Steiner 1994; Talyzina 2000). According to SEM studies, the internal wall construction of *Chuar* from the Suket Shale seems to be single layered (plate 2b). The cavities within the solid organic body are observed in some specimens (plate 2d). These cavities were either formed by dissolution of sediment, which had been incorporated within the wall before fossilization or by biodegradation.

The ‘zonal dark lamellae’ of the topotype *C. circularis* reported by Jux (1977) using TEM and compared to those of Devonian *Tasmanites* and

Tapajonites (Jux 1977), are not comparable to the structures in *Chuar* of the Suket Shales. Microtome sections in the present study show lamellar structures (plate 2e and 2f). However, it is likely that these lamellar structures have formed during the sectioning process. Similar sectioning artifacts have also recently been described from organic microfossils of the Mesoproterozoic Roper Group of Australia (Javaux et al 2004; figures 3j, k). Jux (1977) observed in TEM ultrasections of *Chuar* a “fine network of trabecular ultrastructure of the wall” at very high magnification. This ultrafine structure (the mesh of which is of the order of 0.001 μm) is regarded by him as a fundamental feature of the topotype *C. circularis*. Amard (1992) also reported radial canals comparable to those reported by Jux (1977), but such ultrastructure has not been recorded in TEM ultrasections of *Chuar* from the Suket Shale and also not been reported from the Cryogenian sequence of Australia (Arouri et al 2000). The SEM and TEM studies of specimens from the Liulaobei Formation in China (Steiner 1994) did not reveal any canal structures. Talyzina (2000) compared few cavities within the ‘wall’ of *Chuar* from the Visingsö Formation with ‘radial canal’ structures reported by Jux (1977) and Amard (1992). The herein observed irregular cavities (plate 2f) occur only locally, probably caused by degradation. However, they are different from the cavities reported by Talyzina (2000) from *Chuar* of the Visingsö Formation. TEM sections of leiosphaerids, which may be related to translucent specimens of *Chuar circularis*, showed a similar ultrastructural construction as in *Chuar* (Steiner 1994; Javaux et al 2004). Porous inner zones of a compact layer may represent preservational artifacts which may be due to later degradation (compare Steiner 1994; Javaux et al 2004). The interpretation of a fine-layered construction of wall in leiosphaerids and the existence of a trilaminar structure may also be due to preservational artifacts (see Javaux et al 2004).

8. Reflectance studies

A determination of thermal maturity of pre-Silurian sedimentary rocks from a routine application of petrographic techniques is somewhat limited due to the absence of higher plant material. Incident light microscopy studies of marine fossils (e.g., chitinozoa, graptolites and scolecodonts) which are very common in Lower Paleozoic sedimentary rocks have been used for maturity studies in the last two decades (Bertrand and Héroux 1987; Hoffknecht 1991; Obermajer et al 1996). But no initiative has been made until today for maturation studies of Precambrian sediments using

Figure 5. Composite histograms showing distribution of reflectance of *Chuarina* from (a) the Suket Shale, India (sample number Ram 216); (b) the Visingsö Formation, Sweden (sample number Mul 1); (c) the Liulaobei Formation, China (sample number Llb 339b).

reflectance studies of *Chuarina*. In the present study the reflectance of *Chuarina* was investigated as a means of determining the level of thermal maturity. Altogether 10 samples of *Chuarina* were measured from the Suket Shale. For comparison, *Chuarina* from the Visingsö Formation (Sweden) and from the Liulaobei Formation (China) were also measured. The histograms of the reflectance studies of different samples are given in figure 5(a-c). The maximum value of reflectance of *Chuarina* (ChuR_0) from the Suket Shale is 3.20% and the lowest value is 2.16%. The median values of ChuR_0 ranges from 2.34% to 2.90%. Reflectance of *Chuarina* from the Visingsö Formation ranges from 1.1 to 1.24%

(figure 5b) and from 0.86% to 1.14% in the Liulaobei Formation (figure 5c). *Chuarina* from different formations shows different values of reflectance, which, in turn, probably indicates differences in their thermal maturity. The carbonaceous fossils from the Suket Shale show the highest maturity while that of the Liulaobei Formation is lowest and those of the Visingsö Formation are intermediate. Indian *Chuarina* samples and its host sediments have experienced a comparably high thermal overprinting as reflected from other black shale horizons of the Vindhyan basin which are overmatured (see Banerjee *et al*, this volume). Thermal maturity of organic remains depends on several factors

Figure 6. Total ion chromatogram resulting from Pyrolysis-GC of *Chuarina circularis*, Suket Shale, Vindhyan Supergroup, India. Each doublet corresponds to an alkene (○) and an alkane (●); selected C-numbers indicated. B, T and X indicate benzene, toluene and ethyl benzene, respectively.

during sedimentary basin evolution (Poelchau *et al* 1997; Yalçin *et al* 1997) and an analytical compilation of all these factors are beyond the scope of this paper. Here it is just concluded that reflectance studies of *Chuarina* might represent a time-temperature scale and tool to compare maturity of Precambrian sediments.

9. Molecular composition

The total ion chromatogram obtained by Pyrolysis-GC of the *Chuarina* from the Suket Shale is shown in figure 6. The pyrolysates are dominated by a bimodal distribution of *n*-alkene/*n*-alkane doublets ranging from C₇ to C₂₂ with maxima at C₇. *n*-alkene/*n*-alkane doublets are typical products of the algaenan biopolymer which occurs in the cell walls of various marine and fresh water algae (Hatcher and Clifford 1997). Aromatic compounds like benzene, toluene, ethylbenzene have been detected. Pyrolytic studies

of *Chuarina* from the Australian Centralian Superbasin were carried out by Arouri *et al* (2000), however, no GC-amenable pyrolysates were produced and thus it was concluded by these authors that the samples were highly overmature. A similar pattern is also reflected by the present pyrolytic studies of *Chuarina* as abundance of pyrolysates of this organic walled fossil is very low. But, any molecular investigation of this enigmatic fossil is essential to increase knowledge on its biological affinity. Pyrolytic degradation techniques for Precambrian kerogen are well known, but separation of indigenous molecular fossils from contaminants is sometimes difficult (see Brocks *et al* 2003). Prior to chemical investigation, the *Chuarina* samples were cleaned several times by dichloromethane, which minimizes the probability of the presence of any contaminant. Recently, Grice *et al* (2003) carried out Curie point pyrolysis of the fresh water alga *Botryococcus braunii* from Miocene/Pliocene age and found a homologous series of *n*-alkene/*n*-alkane doublets. Similarly,

Figure 7. Distribution of the *Chuaria circularis* in a palaeogeographic reconstruction of Vendian age (Paleogeographic reconstruction modified after Kirschvink 1992). (1) Chuar Group, USA (Ford and Breed 1973); (2) Uinta Mountain Group, Utah, USA (Hofmann 1977); (3) Franklinsundet Group Kapp Lord Formation, Spitsbergen (Knoll 1982); (4) Akademikerbreen Group, Svanbergfjellet Formation, Spitsbergen (Butterfield *et al* 1994); (5) Shaler Supergroup, Wynniatt Formation, Victoria Island, Canada (Hofmann and Rainbird 1994); (6) Little Dal Group, Mackenzie Mountain, Canada (Hofmann 1985b); (7) Debengdin, Khajpakh and Khatyspyt Formations, Yakutia (Vidal *et al* 1993); (8) Lachandin Formation, Uchur-Maja, Siberia (Pjatiletov 1980); (9) Tent Hill Formation, Arcoona Quartzite, South Australia (Damssa and Knoll 1986); (10) Wessel Group, Raiwalla Shale, Maningrida, Australia (Haines 1998); (11) Liulaobei and Jiuliqiao Formations, Shouxiian, China (Sun 1987); (12) Changlongshan Formation, Xinglong and Huailai, Hebei, China (Du and Tian 1985); (13) Guotun, Diaoyutai, Nanfeng Formations, S. Liaoning, China (Chen 1991); (14) Chichkan Series, Mali karatau, Kazakhstan (Ogurtsova and Sergeev 1989); (15) Shilu Group, Hainan Island, China (Zhang *et al* 1991); (16) Qingshuigou Formation, China (Dai and Peng 1987); (17) Pusa Shale, Spain (Brasier *et al* 1979); (18) Pendjari Formation, Benin and Burkina-Faso, west Africa (Amard 1992); (19) Soltanieh Formation, Chapoghlu Shale, Elburz Mountain, Iran (Ford and Breed 1973); (20) Nama Group, Namibia (Germis *et al* 1986); (21) Sierra Bayas Formation, Argentina (Baldis *et al* 1983); (22) Vindhyan Supergroup, Suket Shale, Rampura, India (Sahni 1977; Kumar 2001); (23) Vindhyan Supergroup, Rewa Formation, Jhiri Shale, India (Rai *et al* 1997); (24) Vindhyan Supergroup, Bhandar Limestone and Sirbu Shale, Maihar, India (Kumar and Srivastava 1997); (25) Vindhyan Supergroup, Rohtas Formation, Katni, India (Rai and Gautam 1998); (26) Bhima Group, Gangurthi Shale, south India (Suresh and Sundara Raju 1983); (27) Kurnool Group, Owk Shale, Andhra Pradesh, India (Sharma and Shukla 1999); (28) Robertson Bay Group, Northern Victoria Land, Antarctica (Cooper *et al* 1982); (29) Visingsö Group, Sweden (Vidal 1974); (30) Kanilov Formation, Podolia, Ukrain (Steiner 1997).

pyrolysis of the marine alga *Tasmanites* from the Permian revealed *n*-alkene/*n*-alkane doublets with tricyclic hydrocarbons (Greenwood *et al* 2000). Benzenes and alkylbenzenes were other pyrolysates detected in the pyrolysates. Low relative abundances of these aromatic compounds are also a common feature of algaenan (e.g., Derenne *et al* 1992). The alkylated aromatic products probably derive from biological precursors although pyrolysis-induced aromatisation processes can contribute to the abundance of simple aromatic hydrocarbons (see Larter and Horsfield 1993). Li *et al* (2004) carried out pyrolysis of 1.2 Ga

kerogen from the Hongshuizhuang Formation, north China and found that the pyrolytic products consist of benzene and naphthalene and that their alkylated homologs and *n*-aliphatic products occur in subordinate amounts suggesting that this kerogen originated from Proterozoic cyanobacteria. A significant aliphatic moiety was detected from the Neoproterozoic acritarchs from south Australia and it was concluded that these acritarchs were Chlorophycean algae (Arouri *et al* 1999). Very recently, Dutta *et al* (2006) carried out pyrolysis of handpicked prasinophycean algae (e.g., *Tasmanites*, *Leiosphaeridia*) from the Dadas

Formation, SE-Turkey and observed predominance of *n*-aliphatic products. It is true that migration of aliphatic moieties from matrix to fossil is a topic of considerable debate in the field of organic geochemistry (see Stankiewicz *et al* 2000; Versteegh *et al* 2004; de Leeuw *et al* in press). At the present state of our knowledge, the predominance of *n*-aliphatic pyrolysates of *Chuarina* are consistent with a highly aliphatic nature and thus provides hints towards an algal affinity. These organic remains were probably very early eukaryotic algae which appeared during Early Mesoproterozoic time in the area of Indian Platform.

10. Age and geographical distribution

Chuarina has a wide geographical distribution and is recorded from United States, Canada, Russia, Australia, China, Kazakhstan, Spain, Namibia, Benin, Iran, Argentina, India, Antarctica, Sweden and Moldova/Ukraine (figure 7). Ford and Breed (1973) considered *Chuarina* as a potential index fossil for the time range of 1000 Ma to 570 Ma. But Hofmann and Chen (1981) and Du and Tian (1985) reported *Chuarina* from sedimentary sequences of Paleoproterozoic age. Recently, a *Chuarina*–*Tawuia* assemblage has also been found from the Paleoproterozoic Changzhongou Formation in the Yanshan Range, north China (Zhu *et al* 2000). Vidal *et al* (1993) discussed the significance of the time range of the *Chuarina*–*Tawuia* assemblage with emphasis on the 700–840 Ma interval, which generally predates the Varanger glacial event. A similar conclusion was also reached by Sun (1987) mentioning that *Chuarina* occurrences fall in the time range of 700–1000 Ma. However, Steiner (1994) reported *Chuarina* from the Early Cambrian (520–545 Ma) Yanjiahe Formation at Heziao and Jijiapo, Hubei Province, south China. Based on the discoveries of fossils in an underlying unit, Amard (1997) also suggested an Early Cambrian age for *Chuarina* from the Pendjari Formation of west Africa. Therefore, the presently recorded stratigraphic range of *Chuarina circularis* seems to range from the Paleoproterozoic to Early Cambrian. Accordingly, *Chuarina circularis* cannot be used as a biostratigraphic tool for global correlation of Proterozoic sedimentary sequences.

11. Conclusions

External surface features of *C. circularis* from the Suket Shale like wrinkles and ‘opening structures’ are of taphonomic origin. Colour and/or opacity are not useful to define the genus because they depend on the wall thickness of the fossil.

The investigated material of *C. circularis* from India shows neither radial pores nor canals like those which are typical of *Tasmanites*, nor trabecular ultrastructures as observed by TEM in the topotype material of *C. circularis*. The cavities within the fossil wall occur only locally, and have therefore resulted either from previously incorporated sediments or by degradation of the specific inner part of the fossil. The reflectance of *C. circularis* represents a useful tool for comparative maturity studies of Precambrian sediments. The gas chromatographic determination of pyrolysates from *C. circularis* suggests an eukaryotic algal affinity due to the predominance of *n*-alkane/*n*-alkene doublets. Based on a review of the age and geographical distribution of *C. circularis*, it is concluded that *C. circularis* cannot be considered as an index fossil for the biostratigraphic subdivision of the Proterozoic.

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