Correlative microspectroscopy of biogenic fabrics in Proterozoic silicified stromatolites

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Abstract

Questions surrounding the biogenicity of ancient stromatolites have perplexed geobiologists for decades. Abiotic processes can produce superficially stromatolite-like structures; moreover, stromatolites frequently fail to preserve organic materials and cellular traces of their microbial architects. Using spatially correlated optical and electron microscopy coupled with Raman and FTIR microspectroscopy, we show that silicified stromatolites from the Tonian Skilloogalee Dolomite (Flinders Ranges, South Australia) contain exceptionally well preserved microbial mat fragments and microbially induced sedimentary structures. These organic-rich layers exhibit mat-like laminations with low degrees of inheritance and reflect interactions between microbial communities and their environments, i.e. growth, sediment trapping and binding, and reactions to early diagenesis, and are inconsistent with abiotic formation. Although accounting for a minor proportion of the volume of the stromatolites, these kerogenous relics are demonstrably syngenetic and comprise aromatic and aliphatic organic materials, likely preserved due to early and rapid silification. Constraining the origins of such lamination-scale features can elucidate relationships between morphogenesis and diagenesis and may assist in the resolution of controversies surrounding stromatolite biogenicity in deep time.

Introduction

Stromatolites are laminated organo-sedimentary structures archiving complex interplays between microbial mat growth, nutrient diffusion, sedimentation, mineral nucleation, and hydrological and geochemical regimes (Burne and Moore, 1987; Awramik, 2006; Hickman-Lewis et al., 2019). They provide a record of microbial ecosystems throughout almost 3.5 billion years of Earth history and are counted amongst the oldest traces of life (Awramik, 2006). Nonetheless, their geobiological significance is repeatedly challenged; indeed, Ginsburg (1991) stated that “almost everything about stromatolites has been, and remains to varying degrees, controversial.” Despite numerous compelling lines of evidence pointing to the biogenic origins of most fossil stromatolite-like structures (Awramik, 2006; Schopf, 2006), doubts endure regarding the unambiguous identification of primary biological influence in ancient examples with diverse morphologies (Lowe, 1994; Grotzinger and Rothman, 1996; Perri et al., 2013; Brasier et al., 2019). It has been theoretically and experimentally demonstrated that abiotic processes can produce laminated stromatoloids, whose macrostructures mirror those of fossil stromatolites (Buick et al., 1981; Dupraz et al., 2006; McLoughlin et al., 2008); nonetheless, truly non-biological stromatolite-like features (e.g., de Wit et al., 1982) are probably rare in the geological record.

Establishing biogenicity in ancient stromatolites is also hindered by a general lack of preservation of primary organic material and cellular microfossils (Buick et al., 1981). Kremer et al. (2012) noted that microfossil preservation in stromatolites is rare due to early post-mortem and diagenetic nanogranular calcification. Where present, organic materials in ancient stromatolites often occur as discrete particles or agglomerations, intermixed with other phases, that are impossible to associate with primary microbial communities, or as secondary, post-diagenetic hydrocarbon infiltration fabrics (Rasmussen et al., 2021).

In the absence of cellular preservation, lamination-scale mesostructural characteristics, i.e. at the scale of a well developed microbial community, could provide crucial evidence for biogenicity in ancient stromatolites with simple macrostructural morphologies. This contribution presents an example of such high fidelity preservation of organic materials within silicified carbonate stromatolites using a combination of textural, mineralogical, and spectroscopic observations that elucidate microbial mat growth processes and the preservational mechanisms of organic-rich biofabrics.

Geological Context

The studied stromatolites are from the Tonian Skilloogalee Dolomite (Burra Group) at Prince Alfred copper mine, near Cradock, Flinders Ranges, South Australia (Figs. S-1, S-2) and date to ~790 Ma
(Preiss et al., 2009). The mine is located at the east of the Nackara Arc where the Skillogalee Dolomite outcrops beneath an unconformity separating the pre-Sturtian Burra and post-Sturtian Umbertana groups (Preiss, 2000). Stromatolites from the Skillogalee Dolomite described by Preiss (1971, 1973) as *Baicalia burra* are now widely used in Neoproterozoic chronostratigraphy.

Palaeoenvironmental studies of the Skillogalee Dolomite conclude that it reflects a low energy peritidal setting associated with an inner platform reef (Preiss, 1971, 1973; Virgo et al., 2021). Sr and O isotope systematics suggest marine deposition although certain horizons enriched in $^{18}$O and $^{13}$C denote intertidal-peritidal evaporitic episodes (Belperio, 1990). Coupling sedimentological observations with trace and rare earth element (REE) geochemistry, Virgo et al. (2021) identified ripple marks and desiccation structures, superchondritic Y/Ho, light REE depletion and positive Eu anomalies consistent with a dynamic shallow water environment featuring clastic input and simultaneous marine, intertidal and fluvial influences. Although interbedded magnesite-bearing horizons may represent palaeoenvironments that were largely inclement to life (Belperio, 1990), primary dolomitized horizons evince colonisation by stromatolite-forming communities (Preiss, 1971, 1973).

## Results

The Skillogalee stromatolites feature stratiform–domical macrostructures comprising undulatory and laterally discontinuous layers (~0.5–2 mm) of micritic mudstone and packstone–boundstone (Figs. 1, S-3–S-6). Layers are primarily composed of fine grained dolomicrite and dolomicrospar (wackestone-packstone–boundstone), quartz, and rare cement-filled vugs and intraclasts (Figs. 1, S-3–S-6). SEM-EDS analyses show that, in addition to dolomite and quartz, aluminous phyllosilicates, pyrite, apatite and rare mafic phases occur throughout the matrix (Figs. 1, S-8–S-11). The stromatolites also feature organic-rich laminations with a low degree of inheritance, i.e. the topography of the underlying layers does not strongly act as a template for the overlying layers (Figs. 2d,e, S-4). Rare stylolites disconformably cross stromatolitic laminations (Fig. 1a,b). Some organic-rich laminations feature millimetre-scale (pseudo)columnar or microdомical structures (Figs. S-3, S-4 and S-6) whereas others include domains of organic-rich bindstone including fine, undulatory, wispy laminations set within a micrite/micrinite matrix (Figs. 1a,b, S-7). Isolated laminated organic fragments occur throughout the matrix (Fig. 1a,b). Many darker laminations are surrounded by pale brown–grey domains of diffuse organic material (Figs. 2c, S-7; organic staining cf. Pomoni and Karakitsios, 2016; DeMott et al., 2020). High magnification optical microscopy indicates that these diffuse organic materials occur mostly within interstitial zones of a fine grained mineral matrix (Fig. S-7). Some laminae bind grains in a pliable manner denoting original plasticity; elsewhere, carbonate particles surrounded by poorly preserved laminae form networks of oriented grains suspended within an organic matrix (Fig. 2b).

![Figure 1](https://example.com/figure1.png)

**Figure 1** Petrographic characterisation of stromatolites in thin section. (a, b) Optical photomicrographs (original and annotated, respectively) showing organic-rich stromatolitic mesostructure (green), disseminated organics (amber) and stylolite (red). (c–e) SEM image and EDS maps showing representative matrix fabric; dol = dolomite, qz = quartz. (f–h) Optical photomicrograph (f) and EDS maps (g, h) showing contact between organic-rich layer and matrix.
Raman microspectroscopy was used to map the distribution of carbonaceous materials and mineral phases associated with organic-rich laminations (Fig. 3a–d). The matrix is dominated by dolomite (Raman peaks at 175, 300, 723 and 1095 cm$^{-1}$) and quartz (peaks at 205 and 465 cm$^{-1}$), whereas the laminations are richer in carbonaceous materials (peaks at ~1340 and ~1600 cm$^{-1}$). Quartz is often concentrated in layers surrounding carbonaceous materials (Fig. 3c). Although some carbonaceous materials show weak layering (Fig. 3d), most occur as diffuse clouds (Fig. S-12d). Raman geothermometry using carbonaceous materials-based spectral deconvolution was applied to organic-rich laminations to determine peak metamorphic temperatures (Fig. 3e, Table S-1); peak thermal histories of 348 ± 50 °C (after Beyssac et al., 2002), and 346 ± 30 °C and 317 ± 50 °C (after Kouketsu et al., 2014) were calculated.

FTIR microspectroscopy was used to identify and map functional groups within the organic-rich laminations (Fig. 4, Table S-2). In the aliphatic stretching region (3000–2800 cm$^{-1}$; Fig. 4d), methylene CH$_2$, terminal-methyl CH$_3$ and alkene =C–H moieties were detected in both stromatolitic laminations and the surrounding domains of diffuse organic materials. Weak signals potentially attributable to methyne C–H were also detected in laminations. Mapping both aliphatic C–H (2850 cm$^{-1}$) and aromatic C=C (1600 cm$^{-1}$) stretches shows more intense detections within dark carbonaceous laminations and a very low abundance or absence in the surrounding matrix (Fig. 4a–c); weak organic detections occur disseminated within fine grained dolomicrospar but are absent within dolosparite (Fig. 3). Although C–H and C=C detections are strongest in dark carbonaceous laminations, a weaker ‘halo’-like signal is also present in the surrounding diffuse organic staining domains (Figs. 4, S-13).

**Discussion**

A serious impediment to establishing the biogenic origins of Precambrian carbonate stromatolites is the absence of preserved...
cellular and cell-associated organic materials and biofabrics. Stromatolites from the Skillogalee Dolomite exhibit exceptional preservation of organic material-rich laminations interpreted to represent microbial mats and microbially induced sedimentary structures (MISS); their lithofacies association implies authigenic microbialite growth on a carbonate platform and is consistent with palaeoenvironmental interpretations (Virgo et al., 2021).

By performing the first correlated optical, SEM-EDS, Raman and FTIR microanalyses of microbial mat structures in Precambrian carbonate stromatolites, we have shown systematic spatial variations in the signatures of organic and mineral phases throughout the microbial stratigraphy of *Baicalia burra* from the Tonian Skillogalee Dolomite that illuminate the morphogenetic and diagenetic history of these stromatolites.

The morphology of kerogen-rich layers is diagnostic of microbial mat growth. Non-isopachous laminations exhibiting a poor degree of inheritance are consistent with laterally variable biomass productivity and suggest complex interactions between ecosystems and local palaeoenvironments, which manifest as numerous directionally conflicting growth and decay morphogenetic vectors (Dupraz et al., 2006; Hickman-Lewis et al., 2019). Low degrees of inheritance are most common in regions containing organic material-rich laminations (Figs. 2d,e, S–4), here interpreted to be biogenic, i.e. the growth of the stromatolite-building community provided new relief, seeding topographic complexity that resulted in a sequence of layers characterised by low degrees of inheritance. Layers with a higher degree of inheritance are typically poorer in, or devoid of, organic materials, and we therefore suggest that these feature minimal biological morphogenetic components. The presence of isolated fragments of laminated organic materials in the matrix (Fig. 1a,b) may indicate either poorly formed mats or the reworking of epibenthic mats under energetic hydrodynamic regimes (Noffke et al., 2001, 2022). Sub-angular carbonate particles bound within laminae (Figs. 2b, S–12) have a plausible origin through microbially mediated carbonate precipitation under carbonate-supersaturated Neoproterozoic interglacial conditions (Hood and Wallace, 2012; Corkeron and Slezak, 2020). The orientation of these particles parallel to mat layers can be explained as an MISS: silt grade sediment baffled by vertically oriented microbial filaments was captured within upward-growing microbial biofilms, before becoming entrapped within the fossilised mat, which pushes the grains apart during biofilm growth (Noffke et al., 1997, 2001).

The dominance of aromatic moieties in Raman and FTIR microspectroscopic data (Figs. 3, 4) indicate that the kerogen composing organic laminations is thermally mature. Its peak thermal maturity (317–348 °C) is consistent with the metamorphic history of the region (greenschist facies; Preiss, 1971), strongly suggesting that the kerogen derives from primary stromatolite-building communities. Furthermore, weak but unambiguous signals from aliphatic compounds in FTIR spectra, although providing only a qualitative estimation of maturity, suggest that moderate pressures and temperatures have influenced the kerogen, consistent with the quantitative estimation of thermal history from Raman data. Correlated microspectroscopic data therefore show that the mesostructures of interest are neither purely graphitic nor entirely aromatic, but retain a small amount of primary aliphatic complexity, i.e. moderately thermally mature carbonaceous materials. The syngeneity of kerogen is further supported by domains of diffuse organic staining surrounding dark laminations (Fig. S–7), indicating early diageneric micro-scale mixing of fluids rich in finely particulate organic matter (Hips et al., 2011); such domains are known to develop from early dissolution–reprecipitation of primary organic matter (DeMott et al., 2020). The strong localisation of kerogen within microbial mat structures and its absence from matrix fractures renders secondary hydrocarbon contamination implausible.

The preservation of organic materials in these carbonate stromatolites can be explained by their early post-depositional history. The presence of microquartz immediately surrounding organic-rich layers and more broadly throughout the matrix...
(Figs. 1, 3) suggests a palaeodepositional environment supersaturated with respect to silica, which precipitated rapidly, i.e., the earliest diagenetic processes included penecontemporaneous silification. As in more ancient fossil microbialites, we interpret this early and rapid silica precipitation as contributing to the exceptional preservation of biochemical heterogeneity in the otherwise labile organic fraction; such preservation is otherwise rare in carbonates (Kremer et al., 2012).

Although constraining the origins of ancient stromatolite-like structures is challenging, demonstrably syngenetic mature organic materials exhibiting spatial distributions consistent with microbial morphogenesis and spectral characteristics consistent with thermally altered biological organic materials can allow biogenicity to be established. Such occurrences can be considered fossil lagerstätten. Identifying similar mesoscale phenomena in more ancient stromatolites using the correlated imaging–microspectroscopy approach developed herein could facilitate definitive interpretations of their morphogenesis.

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**Additional Information**

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