STROMATOLITE CONSTRUCTION, BIOFACIES AND BIOMARKERS IN THE LOWER CAMBRIAN HAWKER GROUP, ARROWIE BASIN, SOUTH AUSTRALIA

Bronwyn L. Teece*
Departments of Earth and Planetary Sciences and Biological Sciences, and Macquarie University Marine Research Centre, Macquarie University, Sydney, NSW, 2109, Australia
bronwyn.teece@hdr.mq.edu.au

Simon C. George
Department of Earth and Planetary Sciences and Macquarie University Marine Research Centre, Macquarie University, Sydney, NSW, 2109, Australia
simon.george@mq.edu.au

Glenn A. Brock
Department of Biological Sciences and Macquarie University Marine Research Centre, Macquarie University, Sydney, NSW, 2109, Australia
glenn.brock@mq.edu.au

**presenting author asterisked*

SUMMARY

Stromatolites are laminated microbial deposits, normally composed of accretionary layers of cyanobacteria and other (often anoxic) bacteria which form on the sediment-water interface. Stromatolites represent one of the earliest records of life on Earth, dating back at least 3.7 billion years. Stromatolites became extremely diverse and very abundant throughout the Archean era 4-2.5 billion years ago, eventually causing increasing levels of atmospheric oxygen on Earth, as part of the Great Oxidation Event. The emergence and radiation of bilaterian animals and the development of new and more complex food webs during the early Cambrian coincided with a sharp decline in the abundance of stromatolites, yet they continued to exist in a range of Cambrian carbonate environments. The appearance, environment, and possibly the biogeochemistry, of Cambrian stromatolites appears to have been altered after the evolutionary development of epifaunal grazing bilaterians. Stromatolites were sampled from a wide spectrum of carbonate facies in the lower Cambrian Hawker Group in the Flinders Ranges, South Australia. The appearance, construction, distribution, and biogeochemistry of stromatolites from different depositional environments, including phosphatic hardgrounds, intertidal shoals and shelf/ramp settings is being described as part of an investigation into their morphological variation and ecological association, aiding the clarification of specific stromatolitic biofacies, and taxonomic associations. There has been little previous research on the morphology, architecture, growth, and biogeochemistry of Cambrian stromatolites in the Arrowie Basin. This study is designed to provide novel data about stromatolite evolution and ecology during a period dominated by the radiation of complex animals.

Key words: Stromatolite, Cambrian, biomarkers, geochemistry, hydrocarbon

INTRODUCTION

The Cambrian Explosion represents a geologically short interval of significant change in global biogeochemistry and flourishing biodiversity, from the microbe-dominated Proterozoic to the Cambrian period with abundant macrofauna and an intricate system of radiations and extinctions (Pagès et al., 2016). The Cambrian is marked in the fossil record as a time of complex ecological change and restructuring, because within 30 million years of the Cambrian Explosion all major animal phyla had evolved (Marshall, 2006). Due to the evolution of bioturbation, and zooplankton ventilation, the ocean chemistry changed significantly, and it has been suggested that this oxygenation of the ocean may have led to the rapid diversification of animal life (Bush et al., 2011; Marshall, 2006). Microbial build-ups, termed microbialites, represent some of the earliest signals of life throughout the Proterozoic and early Palaeozoic (Tosti and Riding, 2017). Microbialite diversity and distribution was severely restricted after the evolution of metazoans (Chen et al., 2011). Microbialites are often studied as environmental proxies because their morphology is significantly affected by environmental parameters such as atmospheric conditions and seawater chemistry (Grotzinger and Knoll, 1999; Mukhopadhyay and Thorie, 2016). Reefs transitioned from being stromatolitic to metazoan-dominated during the Cambrian, but collapsed worldwide by the middle Cambrian. However, there are no clear answers as to why these changes occurred in the Cambrian (Pagès et al., 2016).

Research into the biogeochemical makeup of microbialites may yield information about the identity and relationships of extinct organisms (Brocks and Pearson, 2005). Thus, by investigating the physical and biogeochemical record of these microbialites, more information about the processes that govern these structures during ecological change and transitions can be gleaned. There have been no biogeochemical investigations of the microbialites in the Arrowie Basin, and little is understood about the hydrocarbon potential of the region (Carr et al., 2012; Youngs, 1977; Zang et al., 2004). Zang et al. (2004) took thermal alteration indexes from acritarchs across the Arrowie Basin, and determined that there had been a maximum temperature of 100–150°C. Zang et al., (2004) interpreted these data as showing that a post-Cambrian thermal event had taken place during the Permian, which may have matured the rocks for oil generation. Carr et al., (2010) showed that some areas of the basin, such as the North-west) had been subjected to heating events when the Ediacara Fault was reactivated. To investigate the biogeochemistry of the Arrowie Basin microbialites and the hydrocarbon potential of the Arrowie Basin, samples were taken from the Wirrapowie Limestone (Stage 2/3) and the Wirrealpa Limestone (Stage 4) (Figs. 1,2,3). These microbialites were examined morphologically and geochemically through petrography, fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray flourescence (XRF), and gas chromatography-mass spectrometry (GC-MS).

METHODS

The samples were prepared, solvent extracted (Bitumen I and II) and analysed by GC-MS using the same methods as described by Hoshino and George (2015). The same parameters for FTIR and Raman spectroscopy were used as documented by Baydjanova (2016). XRF was performed on the samples using the same methodology and instrumentation as Frese et al., (2017).

PRELIMINARY RESULTS

Petrographic and morphological investigations reveal the presence of micrite throughout the samples cementing peloids and other allochems in place. FTIR (Fig. 4) and Raman spectra show typical calcite peaks, and FTIR and petrographic results indicate dolomitisation in some samples, with FTIR peaks at 2511cm $^{-1}$ (Fig. 5). Some hydrocarbons have been detected by GC-MS in most samples except in TH118 and SSWTH. The hydrocarbons are dominated by aliphatic hydrocarbons including n-alkanes. The Raman spectroscopy data in Table 1 pertains to the graphite band (G) and the D_1 (defected carbonaceous material). The intensity of the D_1 band decreases relative to the G-band, and the G band becomes narrower as metamorphic temperature increases (Beyssac et al., 2002). Deconvoluted spectra were then characterised by parameters given in Table 1: integrated area, band width, full width at half maximum (FWHM), and the intensity ratios (I_{D1}/I_G) and $I_{D1}/(I_{D1} + I_G)$ *(%)* (Allwood et al., 2006; Beyssac et al., 2002; Marshall et al., 2007). The (I_{D1}/I_G) and $I_{D1}/(I_{D1} + I_G)$ values range from 0.87 to 1.99, and 47% to 67% respectively. The FWHM is known to decrease with increasing thermal maturity (Allwood et al., 2006). Samples from locality 1 have more noticeable D and G peaks in spectra, higher intensity ratios, and higher $I_{D1}/ (I_{D1} + I_G)$ percentages, and have lower FWHM values, so are suggested to be more mature. The locality 2 samples have visually less intense Raman peaks, but the degree of thermal maturity in locality 2 is still relatively high (Table 1). For instance, the rocks of the Archaean Strelley Pool Chert, which has been interpreted to have reached 200-500% thermal maturity (Allwood, 2006) has an $I_{D1}/(I_{D1} + I_G)$ *(%)* range of 50-59% and intensity ratios ranging between 0.72-1.42, the values in both localities for this study are within and above that range, meaning that they could have perhaps been heated even higher.

Some samples from the stromatolitic section (Wirrapowie Limestone) are peritidal and contain no evidence of metazoans in life position. However, one samples of an iron encrusted hard ground has a fossilised microbial mat overgrowth, indicative of a restricted lagoonal environment. This is supported by an even carbon number predominance of *n*-alkanes from GC-MS which indicate a hypersaline environment. The thrombolitic section (Wirrealpa Limestone) is similar in form to those seen by Riding (2011) at Hamelin Pool, Shark Bay, which likely form from episodic sediment supply, rather than epifaunal burrowing. This is supported by transported and fragmentary fossils which vary with stratigraphic height in the thrombolitic section. For example, no chancelloriid fossils are present at 5.2 m, but the thrombolite at 9.7 m is composed almost entirely of chancelloriids. Lastly, an oncolitic grainstone (part of the Wirrealpa Limestone) likely formed in a north-south transgression, as interpreted by Youngs (1977), as is supported by the median orientation of the major axes of the oncolites. Both fragmented fossils and oncolites are indicative of a high energy shoaling environment, which transitioned into a calmer, deeper subtidal environment as supported by the presence of microbial rinds.

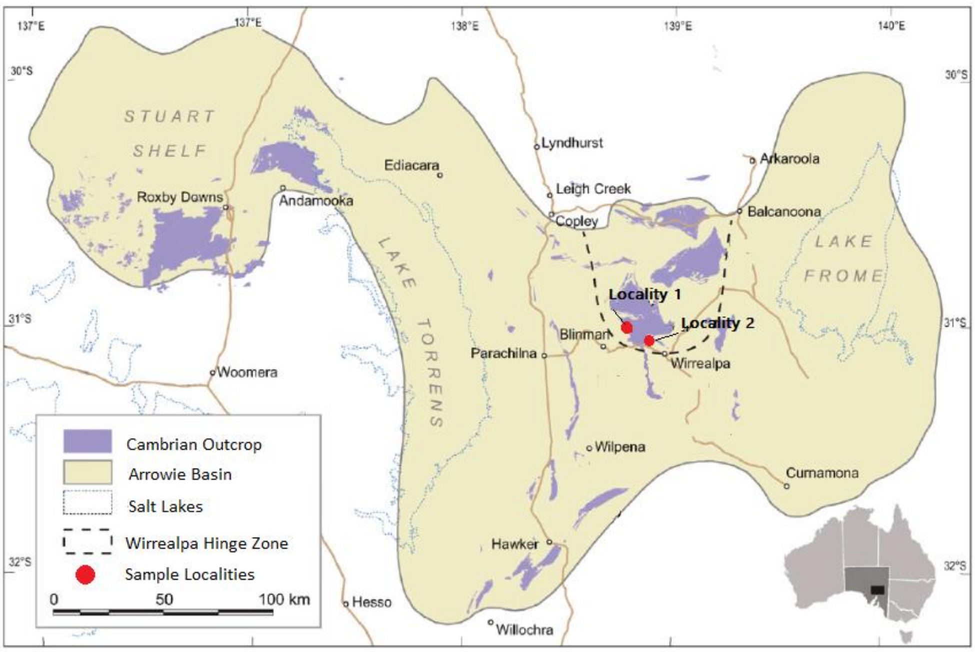

Figure 1: Map of the Arrowie Basin, detailing Cambrian outcrops and the stratigraphic section locations used in this study. Modified from Betts et al. (2016).

Figure 2: Map of where samples were taken from locality 1. Samples WP0, WP1, MM, WP2 and WAR405 were taken from spot localities on (or along strike from) the WAR stratigraphic section measured by Betts et al. (2016). Samples WP0, WP1, MM and WP2 were taken from a 25m long transect at S31°01'30.2" E138°47'59.0", whereas sample WAR405 was taken 405 m from the base of the section at S31°01'21.1" E138°47'12.3. Because sample MM was attached to sample WP2, it is not included as a separate location.

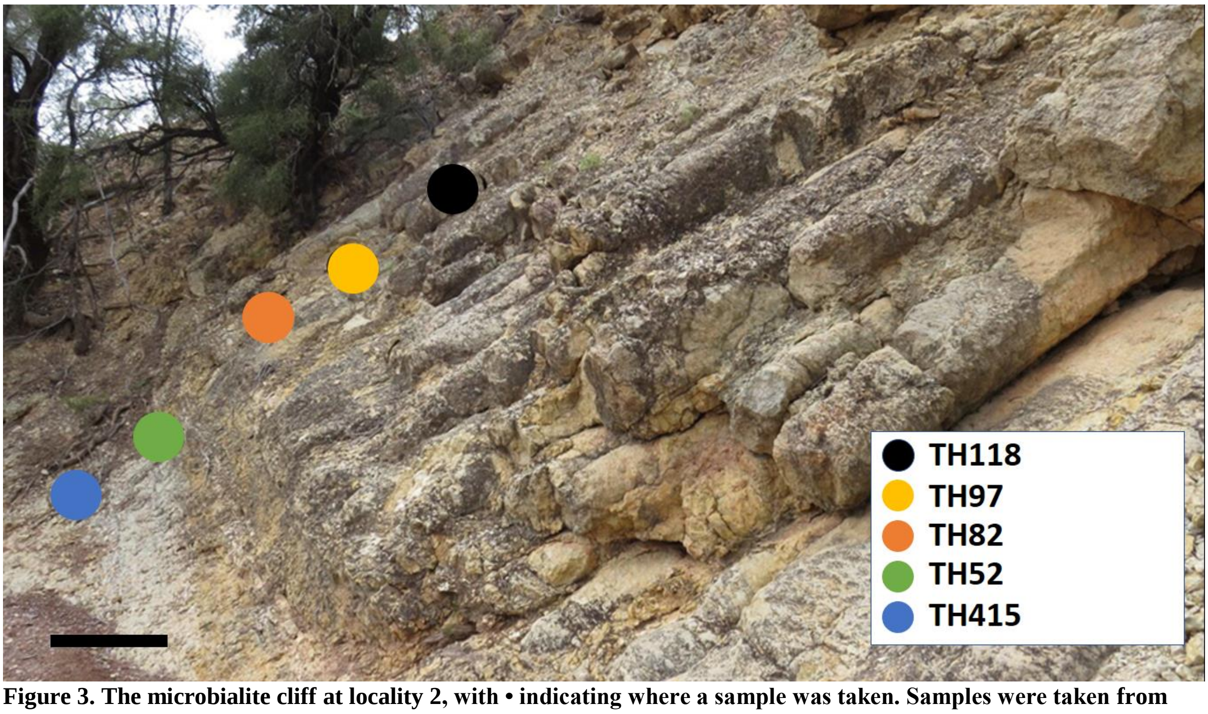

Figure 3. The microbialite cliff at locality 2, with • indicating where a sample was taken. Samples were taken from 4.15 m, 5.2 m, 8.2 m, 9.7 m and 11.8 m above the base. Scale bar = 1 m.

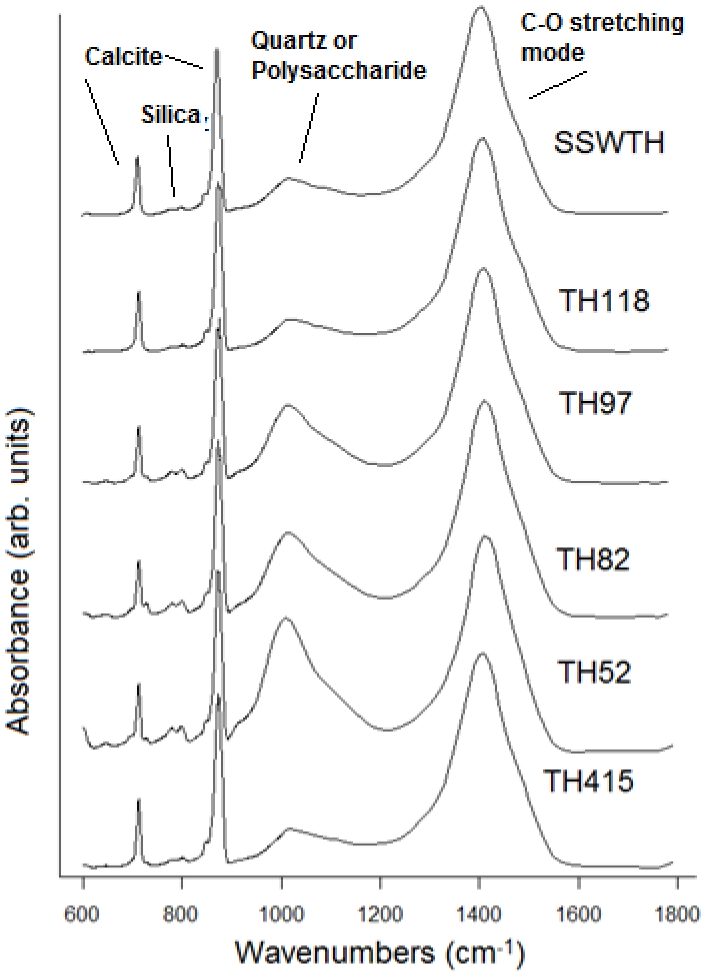

Figure 4: Representative spectra of FTIR results for samples from locality 2, peak allocations are labelled in figure.

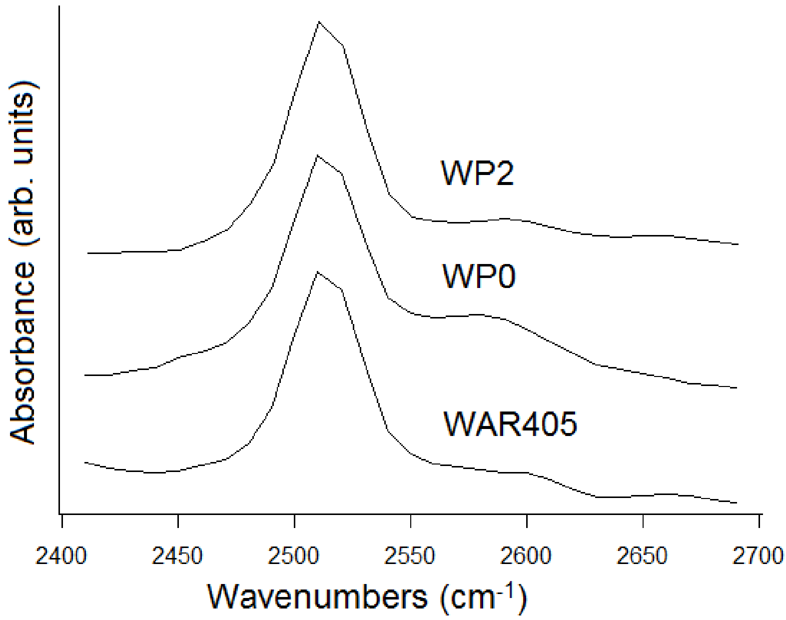

Figure 5: Representative spectra showing a dolomite peak at 2511cm^{-1}

Table 1. Raman spectral data for samples from localities 1 and 2. A representative spectrum from each thin section was deconvoluted to yield the values for the integrated areas of the D_1 and G bands, the G band width full width at half maximum (FWHM), the intensity ratio which is the integrated area of the deconvoluted D_1 peak, as a ratio with the integrated area of the G peak (I_{D1}/I_G), and the integrated area of D_1 divided by the intensity ratio [$I_{D1}/(I_{D1} + I_G)$].

Sample	Integrated Area (D_1)	Integrated area (G)	G band width (FWHM)	I_{D1}/I_G	$I_{D1}/(I_{D1} + I_G)$ (%)
WP0	29601.51	14850.68	45.2	1.99	0.67
WP1	13662.35	8475.99	57.25	1.61	0.62
WP2	26130.13	15796.63	42.09	1.65	0.62
MM	26943.73	16922.91	46.18	1.59	0.61
WAR405	13540.43	9142.88	45.41	1.48	0.60
TH415	16043.11	10217.95	68.35	1.57	0.61
TH52	19102.05	11746.73	115.49	1.63	0.62
TH97	23745.16	19600.94	86.77	1.21	0.55
TH118	15648.28	17952.73	138.88	0.87	0.47
SSWTH	48960.12	48369.07	68.5	1.01	0.50

CONCLUSIONS

Both Raman spectroscopy and FTIR show that calcite is the main mineral in all samples, with evidence of dolomitisation in some samples. The dominance of aliphatic hydrocarbons in most of the samples may be because kerogen derived from the mat-forming stromatolitic morphotypes becomes increasingly aliphatic with increasing thermal maturation (Stasiuk et al., 1993). The morphological and geochemical data support the presence of thermally over-mature sediments in this part of the Arrowie Basin, with comparable and higher values than those detected in the Archaean Strelley Pool Chert. Samples from the stromatolitic section (Wirrapowie Limestone) likely formed in a shallow marine to restricted lagoonal environment with restricted sediment supply. The thrombolites of the Cambrian Stage 5 Wirrealpa Limestone were likely deposited subtidally during a transgressive system track, wherein a low-energy, subtidal environment with high levels of $CaCO_3$ caused the precipitation of the clays. This environment is consistent with the formation of the oncolite, and is characterised by fragmented fossils that indicate a previously high energy shoaling environment that transitioned into a calmer environment at the height of the transgression.

ACKNOWLEDGMENTS

This work was funded in part by a grant from the Betty Mayne Fund from the Linnean Society of NSW. We would also like to thank Oluwatoosin Agbaje for the generous help with performing FTIR and Raman spectroscopy, Sarah Jacquet for her help with figure generation, and Matthew Kerr for short coding lessons which enabled us to produce figures far more efficiently. Thanks to Ian and Di Fargher from "Angorichina" Station for access to field sites. And lastly, we thank Timothy D. Murphy for his help with XRF and patiently sitting through endless geochemical queries.

REFERENCES

Allwood, A. C., Walter, M. R., and Marshall, C. P., 2006, Raman spectroscopy reveals thermal palaeoenvironments of c. 3.5 billion-year-old organic matter: Vibrational Spectroscopy, 41, 190-197.

Baydjanova, S., 2016, In search of the first animals. Masters of Research Thesis, Macquarie University.

Betts, M. J., Paterson, J. R., Jago, J. B., Jacquet, S. M., Skovsted, C. B., Topper, T. P., and Brock, G. A., 2016, A new lower Cambrian shelly fossil biostratigraphy for South Australia: Gondwana Research, 36, 176-208.

Beyssac, O., Goffé, B., Chopin, C., and Rouzaud, J., 2002, Raman spectra of carbonaceous material in metasediments: a new geothermometer: Journal of metamorphic Geology, 20, 859-871.

Brocks, J. J., and Pearson, A., 2005, Building the biomarker tree of life: Reviews in Mineralogy and Geochemistry, v. 59, 233-258.

Bush, A. M., Bambach, R. K., and Erwin, D. H., 2011, Ecospace Utilization During the Ediacaran Radiation and the Cambrian Eco-explosion, Evolutionary Ecology, 36, 111-133.

Carr, L., Korsch, R., Struckmeyer, H., Jones, L., Holzschuh, J., Costelloe, R., and Meizner, A., 2012, The architecture and petroleum potential of Australia's onshore sedimentary basins from deep seismic reflection data and petroleum systems maturation modelling: the Arrowie, Georgina and Darling Basins: Geoscience Australia Record 2012/36.

Chen, L., Wang, Y., Xie, S., Kershaw, S., Dong, M., Yang, H., Liu, H., and Algeo, T. J., 2011, Molecular records of microbialites following the end-Permian mass extinction in Chongyang, Hubei Province, South China: Palaeogeography, Palaeoclimatology, Palaeoecology: 308, 151-159.

Frese, M., Gloy, G., Oberprieler, R. G., and Gore, D. B., 2017, Imaging of Jurassic fossils from the Talbragar Fish Bed using fluorescence, photoluminescence, and elemental and mineralogical mapping: PloS One, 12, e0179029.

Grotzinger, J. P., and Knoll, A. H., 1999, Stromatolites in Precambrian carbonates: evolutionary mileposts or environmental dipsticks?: Annual review of earth and planetary sciences, 27, 313-358.

Hoshino, Y., and George, S. C., 2015, Cyanobacterial Inhabitation on Archean Rock Surfaces in the Pilbara Craton, Western Australia: Astrobiology, 15, 559-574.

Marshall, C. P., Love, G. D., Snape, C. E., Hill, A. C., Allwood, A. C., Walter, M. R., Van Kranendonk, M. J., Bowden, S. A., Sylva, S. P., and Summons, R. E., 2007, Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia: Precambrian Research, 155, 1-23.

Marshall, C. R., 2006, Explaining the Cambrian "explosion" of animals: Annual Review of Earth and Planetary Sciences, 34, 355-384.

Mukhopadhyay, A., and Thorie, A., 2016, Comparative study of two relatives, MISS and Stromatolites: example from the Proterozoic Kunihar Formation, Simla Group, Lesser Himalaya: Arabian Journal of Geosciences, 9, 1-23.

Pagès, A., Schmid, S., Edwards, D., Barnes, S., He, N., and Grice, K., 2016, A molecular and isotopic study of palaeoenvironmental conditions through the middle Cambrian in the Georgina Basin, central Australia: Earth and Planetary Science Letters, 447, 21-32.

Riding, R., 2011, The nature of stromatolites: 3,500 million years of history and a century of research, Advances in Stromatolite Geobiology, Springer, p. 29-74.

Stasiuk, L., Kybett, B., and Bend, S., 1993, Reflected light microscopy and micro-FTIR of Upper Ordovician Gloeocapsomorpha prisca alginite in relation to paleoenvironment and petroleum generation, Saskatchewan, Canada: Organic geochemistry, 20, 707-719.

Tosti, F., and Riding, R., 2017, Fine- grained agglutinated elongate columnar stromatolites: Tieling Formation, ca 1420 Ma, North China: Sedimentology, 64, 871-902.

Youngs, B. C., 1977, The sedimentology of the Cambrian Wirrealpa and Aroona Creek limestones, Department of Mines, Geological Survey of South Australia, 47.

Zang, W.-L., Jago, J., Alexander, E., and Paraschivoiu, E., 2004, A review of basin evolution, sequence analysis and petroleum potential of the frontier Arrowie Basin, South Australia:Eastern Australasian Basins Symposium II. Special Publications, Petroleum Exploration Society of Australia, 243-256.