

LOOKING FOR SYNGENETIC BIOMOLECULES IN ANCIENT OVERMATURE ORGANIC MATTER: IMPLICATIONS FOR ORGANIC ANALYSIS ON MARS B.L Teece^{1,2}, R. J. Baumgartner^{1,3}, E.V. Barlow^{1,4}, B. Pejčić³, G. G. Soares^{1,4}, S.C. George⁵, L. M. Barge², A. Pages⁶, M. J. Van Kranendonk¹ ¹Australian Centre for Astrobiology, University of New South Wales, Sydney Australia, ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA, ³CSIRO Mineral Resources, Kensington, Australia, ⁴ Pennsylvania State University, University Park, PA, USA, ⁵School of Natural Sciences, Macquarie University, Australia, ⁶Department of Water and Environmental Regulation, Western Australia

Introduction:

The study of organic matter (OM) and in particular, kerogen, can provide insight into how life evolved on Earth and help determine its existence elsewhere in the solar system [1] Kerogen can be found in some of the earliest rocks on Earth (i.e., Archean, > 2.5 Ga), but there are commonly questions regarding its syngeneity, biogenicity, and potential contamination (French et al., 2015). Therefore, robust synthesis of morphological, chemical, and contextual data is required for the confident interpretation of the early organic record [2]. Advances in understanding the properties of ancient and mature fossilized kerogen have been important in understanding syngeneity in ancient and astrobiologically relevant samples.

Here, we examine kerogen from a diverse assemblage of microfossils that come from distinct depositional settings within a well preserved, ~2.4 Ga microbialite reef complex of the Turee Creek Group in Western Australia [3,4]. The Turee Creek Group more broadly is composed entirely of sedimentary rocks - including three glacial diamictites - and records the onset of the Great Oxidation Event via sulfur isotopes and the oldest recorded phosphorite [5,6]. The studied reef complex is globally unique in terms of its exceptional preservation, age, and diversity of fossil forms [3,4,6,7].

The different microfossils that form the basis of this study come from cherts that have experienced the same thermal and structural history. This represents a unique opportunity to examine whether ancient, overmature OM retains any primary biological information, given that any variations detected should solely reflect the nature of the source, assuming contamination can be ruled out. To minimise the possibility of contamination, microscope-Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy were performed in situ, directly on thin section samples. By employing these in situ techniques, we can better distinguish whether the contained OM is syngenetic or comes from later fluid influx and/or contamination. For instance, Raman spectroscopy represents an essential step in ensuring that the OM analysed reflects the expected thermal maturity expected for the rocks and was not

introduced at some later time, under lower-temperature conditions [8]. Raman mapping was also performed to determine that the OM was tied to textural features. FTIR was performed on the exact same spots as those analysed by Raman spectroscopy, so as to ensure consistency between techniques. The use of multiple complementary techniques allows for increased reliability for all results. The validity of this approach was highlighted by the structure of the OM being consistent across techniques used on different samples.

Despite the high maturity of the samples, in FTIR analyses there were notable differences in the CH₃/CH₂ ratio and the presence of different aromatic compounds linked to different microfossils, while the thermal maturity of the OM remained consistent across all Raman spectroscopy measurements. Our study shows that analysing kerogen from different types of microfossils in different depositional settings within the same unit has the potential to provide increased levels of confidence that the results reflect derivation from the original organisms, as opposed to later, widespread contamination from younger geological (diagenetic, metamorphic, or hydrothermal) events.

Implications for planetary sample analysis:

The techniques chosen in this study are similar to those of the Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument aboard the Perseverance rover. Raman spectroscopy is more sensitive to the molecular framework than FTIR and is therefore more suited for the analysis of thermally mature carbonaceous and inorganic materials [9]. Thus, the combination of both techniques allows for a more robust understanding of the full range of organic compounds remaining after diagenesis and maturation. The recent detections of organic molecules in ancient Martian rocks that do not have an unambiguous biogenic origin [10–13], necessitate further research into the presence of organics in early Earth rocks.

References:

- [1] De Gregorio B. T. et al. (2011) *Earliest Life on Earth: Habitats, Environments and Methods of Detection*, 239-289. [2] Hays L. E. et al. (2017) *Astrobiology*, 17, 363-400. [3] Barlow E. V. et al. (2016). *Geobiology*, 14, 317-343. [4] Barlow E. V. and Van

Kranendonk M. J. (2018) *Geobiology*, 16, 449-475.
[5] Williford K. H. et al., (2011) *Geochim. Cosmochim. Acta*, 75, 5686-5705. [6] Soares G. G. et al. (2019) *Precambrian Res.*, 320 193-212. [7] Nomchong B. J. and Van Kranendonk M. J. (2020) *Precambrian Res.*, 338, 1-18. [8] Kouketsu Y. et al. (2014) *Isl Arc*. 23, 33-50. [9] Olcott Marshall A., Marshall C. P. (2015) *Palaeontology*, 58, 201–211. [10] Scheller E. L. et al. (2022) *Science*, 378, 1105-1101. [11] Freissinet C. et al., (2015) *J. Geophys. Res. Planets.*, 120, 495–514. [12] Eigenbrode J. L. et al. (2018) *Science*, 360, 1096–1101. [13] Millan M., et al. (2022) *Nat. Astron.*, 6, 129–40.