EXPERIMENTAL EVIDENCE FOR MINERALOGICAL CONTROL ON THERMAL ALTERATION OF ORGANIC MATTER AS MEASURED BY RAMAN SPECTROSCOPY: IMPLICATIONS FOR BIOSIGNATURE PRESERVATION. A. D. Czaja¹ and J. T. Osterhout², ¹Department of Geology, University of Cincinnati, Cincinnati, OH, 45221-0013, USA, andrew.czaja@uc.edu, ²Department of Earth, Planetary, and Space Sciences, University of California-Los Angeles, Los Angeles, CA 90095, USA

Introduction: Organic matter preserved in ancient rocks (kerogen) is one of the primary sources of information about the earliest life on Earth and would provide strong evidence for past life on other planets, such as Mars. Raman spectroscopy is a common tool used to identify the presence of organic carbon in ancient rocks. It is also typically used to assess the level of thermal alteration experienced by organic fossils and their encompassing geologic units as indicated by the kerogen molecular structure [e.g., refs 1, 2, 3]. Previous studies, however, have each focused on a single lithology. This study provides evidence for variable molecular structures of kerogen on millimeter scales within primary lithologies composed of different minerals. This evidence comes from both naturally occurring kerogen and experimentally thermally altered organic matter.

Methods: For this study, samples of Mesoproterozoic kerogen-bearing chert-carbonate microbialites from the Middlebrun Bay member of the Rossport Formation of Ontario, Canada were used. This unit was previously studied by Raman spectroscopy to measure the effect of thermal alteration on the carbon isotope composition of the kerogen by a local igneous intrusion [4]. Slabs of chert-carbonate were placed in a tube furnace and heated at various temperatures from 125 to 400°C for various lengths of time. Thin sections were made from the central portion of each slab. The molecular structure of the kerogen within individual microbialites layers was studied via Raman spectroscopy and the apparent level of thermal maturity was determined via standard spectral parameters such as D/G band intensity ratios, D-band FWHM, and Raman Index of Preservation (RIP) [1, 2, 3].

Results and Discussion: Kerogen preserved in the least altered cherts and carbonates have similar molecular structures as measured by Raman spectroscopy (Fig. 1, lower panels). The more thermally altered samples possess kerogen with molecular structures that vary with lithology/mineralogy (Fig. 1, upper panels). The measured molecular-structural variations are possibly the result of bonding of the kerogen with the various minerals that differentially shield the kerogen from thermal alteration.

Conventional wisdom states that a difference in perceived thermal alteration between a kerogenous object and the rest of the host rock is an indicator that they are not syngenetic [e.g., refs. 3, 5]. The results reported here, however, imply that this is not necessarily true and any scale of Raman thermal alteration (e.g., geothermometry, RIP) for kerogen must be calibrated to the host mineral composition. These findings have implications for positively identifying early life on Earth and also for the study of potential organic matter on Mars via the Mars 2020 SHERLOC instrument, which will use UV Raman spectroscopy to search for and identify organic matter in martian sedimentary rocks.

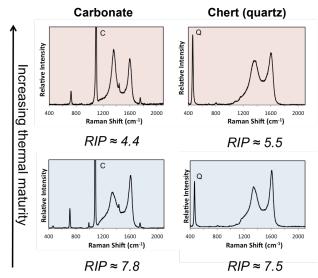


Figure 1. Raman spectra of kerogen preserved in carbonate (C, left panels) and chert/quartz (Q, right panels) from the Mesoproterozoic Middlebrun Bay Member of Ontario, Canada. Note that the measured degree of preservation (as indicated by the Raman index of preservation, RIP) decreases with increasing thermal alteration, but the change is not consistent amongst different lithologies. Adapted from [4].

References:

[1] Beyssac O. et al. (2002) J. Metamorph. Geol., 20(9), 859–871. [2] Kouketsu Y., et al. (2014) Island Arc. 23(1): 33–50. [3] Schopf J. W. et al. (2005) Astrobiology, 5(3), 333–371. [4] Osterhout J. T. (2016) University of Cincinnati, Masters Thesis, 103 pp. [5] Papineau D. et al. (2011) Nature Geosci., 4(6), 376–379.