Micro Raman spectroscopic investigations of the nature and provenance of carbonaceous material in micro-fossil bearing rocks: redefining D and G carbon band parameters for the detection of biosignatures. D. M. Bower[1], A.Steele[1] , M.D. Fries[2] and L. Kater[3], [1]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd, NW, Washington, DC, 20015, dbower@ciw.edu, [2]Planetary Science Institute, Tucson, AZ 85719, [3]WITec GmbH, Ulm, Germany.

Introduction: The identification of biosignatures and detection of extra planetary life is one of the primary goals in astrobiology. Intrinsic to this goal is the improvement of analytical techniques and protocols used to identify biosignatures. Micro Raman spectroscopy is a non-destructive method that allows for in situ analysis of samples and unambiguous identification of a wide range of minerals and compounds. One of the biggest controversies using this technique, however, is in the use of D (~1350 cm^{-1}) and G (~1580 cm^{-1}) band parameters to determine the biogenicity of carbonaceous materials in ancient rocks [4,6,7]. Not only do carbonaceous compounds from different sources often share the same spectroscopic characteristics, but the absolute nature of the D band is still unclear [1,2,9,10]. To elucidate biogenicity, young samples of known provenance are typically analyzed and used as a baseline for comparison to much older samples or samples that have experienced extreme temperatures and pressures. To this ends we used the high-resolution imaging and geochemical mapping capabilities of micro Raman spectroscopy to investigate the nature and provenance of the mineral and carbonaceous material in samples from the 400 Ma Rhynie chert, 570 Ma Duosnato phophorite, 1.9 Ga Gunflint chert, 2.7 Ga Tumbiana carbonate, and the 3.5 Strelley Pool and Apex cherts. The wide array of morphological microstructures, carbonaceous components, and mineral assemblages in these samples provide the perfect testing ground for these techniques [5, 7, 8]. To further constrain D and G band carbon characteristics, micro Raman analyses were also performed on a suite of well-characterized carbonaceous meteorites. The spectral features of each sample set were quantified and compared. The results give much needed information for biosignature identification in these and other biologically significant rocks.

Method: Raman spectra of the samples were collected using a WITEC Digital Pulse scanning near-field optical microscope (AlphaSNOM) with Scan Control Spectroscopy Plus. The Raman scans were conducted with a a frequency-doubled 532 nm YAG laser with. The laser was focused through a 25μm diameter fiber and a 100x objective lens. The scan speed was 3-5s dwell time per pixel at 30 kW cm^{-2}. Images and virtual maps of the spatial elemental and mineral composition of the microtextures were generated using Witec Project 1.99 software. The collected spectra were deconvoluted and quantified using ACD Labs 12 software.

Results: Comparisons of the Raman data from the microfossils and meteorites studied here show that G and D band parameters for both sample sets overlap, making it difficult to assign a biologic or abiolgic source for the carbonaceous material. The results of one G-band parameter comparison, however, provide a way to confirm the degree of thermal alteration of the carbonaceous matter in geologic samples. Raman spectral maps for each sample also show a wide range of microstructural features and minerals associated with the carbonaceous material.

Conclusions: While the unique mapping capabilities of micro Raman spectroscopy provide a greater view of the spatial relationships between carbonaceous materials and other features in ancient rocks, the D and G band characteristics of the carbonaceous material found in biologically associated structures are similar to those of abiologic origin. Careful analysis and deconvolution of the carbon D and G band parameters should be undertaken in any study involving the origins of carbonaceous meterials. In addition, it is necessary to explore the spatial relationships and spectral characteristics to establish biosignatures for life detection in ancient rocks on Earth and of those on other planets.

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