LIFE DETECTION LIMITATIONS DUE TO FLUORESCENCE IN RAMAN IMAGING. J.R Emry[1], A. Olcott Marshall[1] and C. P. Marshall[1], [1]Department of Geology, Lindley Hall, 1475 Jayhawk Blvd, University of Kansas, Lawrence, KS, 66045, jremry@ku.edu, cpmarshall@ku.edu, and olcott@ku.edu

Introduction: Multiple studies have revealed that abiotic features, such as fluid inclusions or veins, may be misidentified as microfossils or other biosignatures [1-4]. In an attempt to avoid this problem, researchers have proposed a variety of criteria based on morphology, context, and chemistry that they feel should all be met if a sample is to be considered a *bona fide* microfossil [2,5,6]. This has led to increased interest in the chemical composition of putative microfossils, and Raman spectroscopy has become a popular technique to study the composition of microfossils [2,3] and to detect other traces of life (see [7] and references therein). The 2018 Exomars rover includes a Raman spectrometer [8] and the 2020 NASA rover will contain two Raman instruments, SuperCam and SHERLOC [9].

Recent technological advances have allowed for advanced Raman data collection including hyperspectral imaging, which has been used to study a variety of microfossils and microfossil-like features [10-16], and to search for biomarkers [17]. Such datasets are composed of multiple spectra and must be analyzed using univariate or multivariate techniques to create Raman images. In addition to natural processes, data collection and analysis issues during Raman imaging may also mimic evidence for life in Raman images. Many factors can affect spectral quality during data collection, but autofluorescence can be a problematic issue that limits the ability to acquire useful data [18]. Depending on the analytical method used, sloping baselines caused by autofluorescence can result in Raman images that mistakenly indicate the presence carbon in regions where it is not, in fact, present.

The Apex chert: The ~3.5 Ga Apex chert contains controversial microstructures: originally, Raman imaging was used to suggest that these are microfossils composed of carbonaceous material [12-14], while a. more recent study utilizing Raman imaging illustrated that similar microstructures identified in new samples of the Apex chert are hematite-filled microveins [3]. Images presented in both studies were based on a univariate method that calculates the intensity at Raman shift value representing the presence of a diagnostic Raman band for a material of interest. Previous work showed that intensity images intended to represent carbonaceous material based on the "D" band located at 1350 cm^{-1} may result in a false-positive identification due to the colocation of a band in hematite at ~1320 cm^{-1} [3,10]. Subsequently, it has been proposed that intensity at a point based on the ~1600 cm^{-1} "G" band should be used to identify carbon.

Results and Discussion: Twenty-two hyperspectral datasets were acquired from microfractures identified in the Apex chert samples. High sloping baselines due to autofluorescence were observed in multiple spectra in every dataset, and in some cases completely overwhelmed the Raman signal. Observation of multiple spectra from the dataset verifies that the hematite microfractures typically displayed high autofluorescence compared to the quartz and carbonaceous material in the matrix. Raman intensity images from non-baseline corrected datasets representing hematite (1320 cm^{-1}) and carbon (1600 cm^{-1}) showed that the increase in intensity values due to autofluorescence in the hematite led to a false-positive signal for carbon [18].

Here, we propose that direct Classical Least squares (DCLS) analysis should be adapted as a complementary technique to verify the spatial distribution of materials, as it is less affected by autofluorescence [19].

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