SHERLOC: Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals, an Investigation for 2020.

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Introduction: The Scanning Habitable Environments with Raman & Luminescence for Organics & Chemicals SHERLOC investigation was recently proposed for the Mars 2020 integrated payload. SHERLOC enables non-contact, spatially resolved, and highly sensitivity detection and characterization of organics and minerals in the Martian surface and near subsurface. The instrument goals are to assess past aqueous history, detect the presence and preservation of potential bio-signatures, and to support selection of return samples. To do this, SHERLOC will measure CHNOPS-containing mineralogy, measure the distribution and type of organics preserved at the surface, and correlate them to textural features.

SHERLOC is an arm-mounted, Deep UV (DUV) resonance Raman and fluorescence spectrometer utilizing a 248.6-nm DUV laser and 50 micron spot size. The laser is integrated to an autofocusing/scanning optical system, and co-boresighted to a context imager with a spatial resolution of 30 μm. SHERLOC operates over a 7 × 7 mm area through use of an internal scanning mirror. The 500 micron depth of view in conjunction with the MAHLI heritage autofocus mechanisms enables arm placements from 48 ±12.5 mm above natural or abraded surfaces without the need for rover arm repositioning/movement. Additionally, borehole interiors to a depth of ~25 mm, at angles from normal incidence to ±20 degrees, can be analyzed.

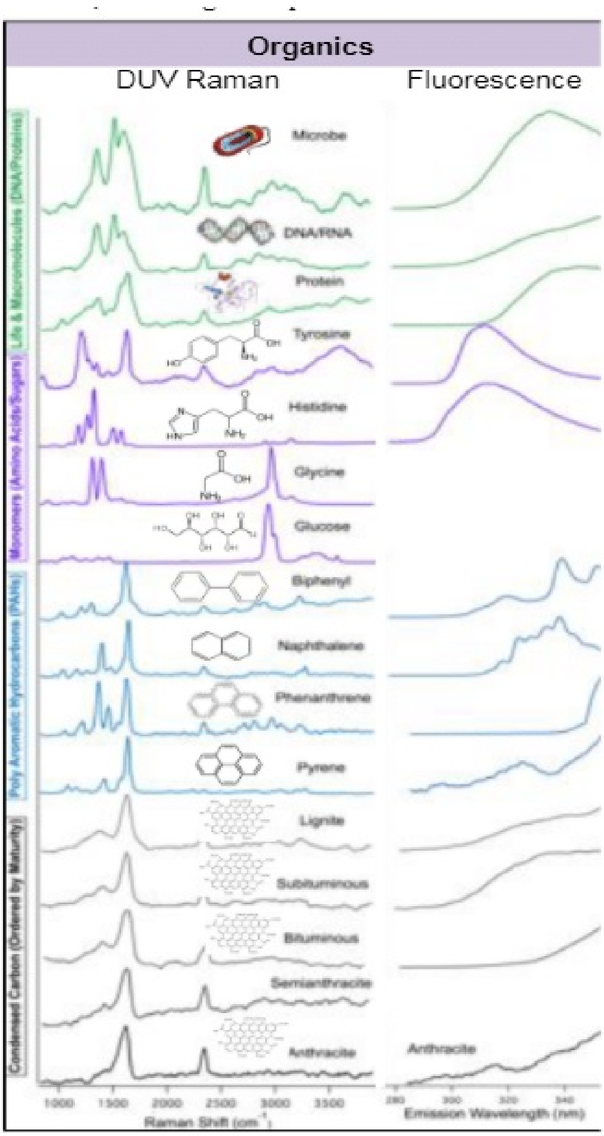
Deep UV induced native fluorescence is very sensitive to condensed carbon and aromatic organics, enabling detection at or below 10-6 w/w (1 ppm) at <100 micro meter spatial scales. SHERLOC's deep UV resonance Raman enables detection and classification of aromatic and aliphatic organics with sensitivities of 10-2 to below 10-4 w/w at <50 micro meter spatial scales. In addition to organics, the deep UV Raman enables detection and classification of minerals relevant to aqueous chemistry with grain sizes below 20 micro meter grains.

Science Goals and Objectives:

SHERLOC will Assess the habitability potential of an ancient site including understanding its aqueous history and determining the availability of key elements and energy sources for life.

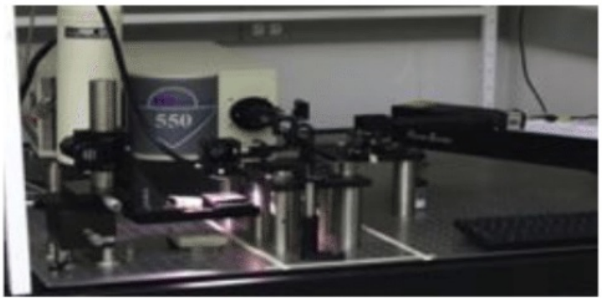
SHERLOC will determine if there are potential bio-signatures preserved by studying the nature and distribution of organic material. SHERLOC will characterize cached samples. It will interrogate the upper 25 mm of the borehole as a proxy for core interrogation.

DUV Raman and Fluorescence Advantages over other techniques. SHERLOC's investigation combines two spectral phenomena, native fluorescence and pre-resonance/ resonance Raman scattering. These events occur when a high-radiance, narrow line-width, laser source illuminates a sample. Organics that fluoresce, absorb the incident photon and reemit at a higher wavelength. The difference between the excitation wavelength and the emission wavelength indicates the number of electronic transitions which increases with increasing aromatic structures (i.e. number of rings) [1]. This is a highly efficient phenomenon, with typical cross section 105 x greater than Raman scattering and enables detection of microbial cells containing <1 pg of carbon, resulting in a powerful means to find trace organics [2].



The native fluorescence emission of organics extends from ~270 nm into the visible. Conversely any mineral fluorescence emission stemming from crystal line defects and impurities do not have strong absorption features in the deep UV resulting in mineral fluorescence that begins at ~360 nm and can continue into the NIR. The only reported fluorescence of nonorganic material in the region 250-360 nm is in non-relevant astrophysical conditions. In Over 15 years of experiments in our laboratory, there has not been any fluorescence at shorter wavelengths <360 nm that could not be attributed to organic compounds trapped in the mineral matrix. This is especially useful because it allows deep UV Raman measurements free of native fluorescence [3].

SHERLOC's narrow-linewidth 248.6 nm DUV laser also enables additional characterization aromatics and aliphatic organics and minerals by creating Raman scattered photons within the fluorescence-free region (250 – 270 nm). Excitation at DUV wavelengths enables resonance and pre-resonance signal enhancements (>100 to 10,000×) of organic/mineral vibrational bonds by coupling of the incident photon energy to the vibrational energy [3]. DUV Raman also capitalizes on the Rayleigh Law (∝1/λ4) – 20× greater scattering efficiency than 532 nm, 100× greater than 785 nm. This enables high-sensitivity measurements without requiring high-intensity of excitation photons, where DUV sensitivities are 10 to 100x greater than visible Raman systems that used 150x more energy at the sample. Thus the technique avoids damage or modifies organics by inducing reactions with species such as perchlorates.



Testbed #1 is shown in the figure above. This laboratory based instrument was developed through ASTID, NSF and NAI funds. It has the same optical parameters as the Mars SHERLOC version including components (laser and CCD), spectrometer resolution, and photon budget that has been used to collect the data presented here. A flight like version of the instrument with form and fit identical to the 2020 version is currently undergoing testing.

Example Measurement on Fig. Tree Using the SHERLOC testbed, and analysis of a piece of the astro-biologically interesting chert obtained from the Fig Tree Group [4, 5, 6] is presented. A small piece of fig tree, on the order of a few centimeters, was cleaned using O2 plasma.

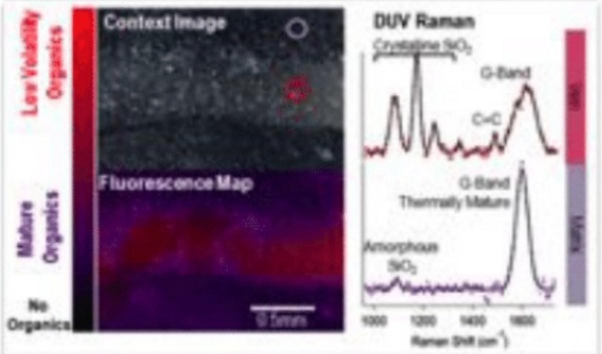
A context image of the sample is acquired.

Using the internal scanning mirror, a 50 micron laser spot is systematically rastered over the surface. On the same CCD, spectra in the range 250-360 nm are obtained. Analysis of the fluorescence region (>270 nm) identifies regions where organic material is present. Analysis of the fluorescence spectra identifies number of aromatic rings present, and identifies regions of high organic content. In order to achieve high sensitivity, multiple laser shots can then be targeted on a spot to obtain characteristic Raman spectra. The Raman spectra shown on the right are from the two circles shown in the context image.

By studying the data we can conclude that our analysis indicates that:

- The chert has not been altered uniformly—pressure/temperature exposures are evident from carbon maturity variation
- Majority of matrix is thermally mature carbon— anthracitic to sub-bituminous
- An intrusion of silica with much younger carbon invaded the main matrix

Potential for bio-signature preservation in the matrix is low due to thermal history of the sample, with high preservation in the thermally unaltered vein material.



References: [1] Bhartia et. al. (2008) App Spec. 62, 1070-1077, [2] Bhartia et. al. (2010) AEM. 76, 7231 – 7237 [3] Asher, S. and Johnson. C.R., (1984), Science, 255, 311-313 [4] Tice et al. (2004) Geology, 32, 302– 318. [5] Hoffman A. and Harris, C. (2008) Chemical Geology, 257, 221-239 [6] Schopf, J.W. and Barghoorn E.S (1967) Science, 28, 508–512.

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