

MICROSCOPIC SAMPLE INTERROGATION THROUGH MULTI-WAVELENGTH SPECTROSCOPY COUPLED WITH VARIABLE MAGNIFICATION IMAGING. M. D. Fries¹, R. Bhartia¹, L. W. Beegle¹, Y. Gursel², and G. S. Mungas², ¹Jet Propulsion Laboratory, 4800 Oak Grove Dr. Pasadena Ca, 91109. ²Fire Star Engineering 1122 Flightline Rd. #76, Mojave, CA 93501

Introduction: Non-invasive chemical imaging techniques such as Raman spectroscopy have attained mature status as laboratory instruments, allowing unprecedented multi-wavelength, high-resolution imaging of mineralogy and all known polymorphs of carbon-based compounds in samples with minimal processing. Obtaining this capability for in-situ analysis is ideal, however Raman instruments developed for either spaceflight or field deployments have been limited to a single wavelength laser source. Previous instruments also utilize point spectroscopy or line scanning methods. A single excitation source does not provide both mineralogical and trace organic analysis, although multiple wavelengths can increase instrument complexity. Novel developments in laser technology now make it possible for a field Raman instrument to include dual excitation sources from the deep UV to the NIR, which results in an instrument that is optimized for both mineralogy and organic studies.

Arguably, the goals of Raman flight instruments in an astrobiological role would be best served by requiring the capability of not only detecting organic compounds but also describing their mineralogical content so that conclusions can be drawn about the formation and alteration histories of both materials. This can be done, but multiple excitation wavelengths are realistically required.

In addition to laser optimization, contextual information (i.e. images) is necessary for meaningful measurements. Mineralogy and organic composition of a sample without spatial correlation limits the scientific utility of these measurements. As such point spectroscopy is not sufficient. State-of-the-art laboratory Raman spectrometers capable of mapping cm² areas, are co-located with visible images for additional context.

In order to describe samples of astrobiological significance in terms of both their organic and mineralogical components, we studied six different samples using three different imaging techniques. Each of these techniques are high TRL; proposed as flight instruments in the past and will be proposed in the future. This investigation allows us to study the parameter space around an arm mounted imager that would be specifically designed not only to detect organic compounds and condensed carbon with high sensitivity, but also to provide mineralogical and morphological context to understand how they were formed, alterations and their origin. The proposed instrument is a combined green (532 nm) excitation Raman imager for mineralogy imaging and deep UV (248 and/or 224nm)

Raman/fluorescence imager for high sensitivity organic compound detection, utilizing the CHAMP-SLS imaging instrument for visual imaging.

We utilized a 532 nm Raman imaging Raman spectrometer system from Horiba, a UV Raman imaging system developed at JPL, and a variable focus infinity to microscopic imager (CHAMP-SLS), to: 1) Demonstrate the utility of this combination of multi-spectral imaging analysis on martian and lunar analogue materials; 2) Demonstrate sensitivity and resolution of each imaging technique; 3) Demonstrate the identification of martian- and lunar-relevant mineralogy and potential organic compounds; 4) Demonstrate non-destructive nature of UV analysis of organic compounds.

Applicability to martian and lunar materials is a primary use of this technique and was demonstrated with suitable analogue materials, i.e. a martian meteorite (DaG 476 shergottite) thin section and actual Apollo lunar regolith.

The combination of Raman techniques presented here is also especially well suited to sample return analysis. A suite of six samples was selected and then analyzed using green (532 nm) Raman imaging, Deep UV fluorescence imaging, and visible imaging using the CHAMP-SLS imaging instrument. These samples were selected on the basis of applicability to Mars-related studies and are comprised of a sample of the MMS Mars-simulant basalt [1], a thin section of the DaG 476 martian meteorite, a cut slab of Svalbard peridotite, a fragment of the Allende carbonaceous chondrite, and a small conifer leaf fossil from Svalbard that retains kerogenous material. These samples were imaged using the CHAMP-SLS instrument and then imaged using the 532 nm LabRam Raman imaging instrument at Hiorbia and a Deep UV fluorescence mapping instrument developed at JPL.

Methods: CHAMP-SLS The camera, handlens, and microscope probe with scannable laser spectroscopy (CHAMP-SLS) is an imaging/spectroscopy instrument capable of imaging continuously from infinity down to high resolution microscopy (resolution of ~1 micron/pixel in a final camera format), the closer CHAMP-SLS is placed to a feature, the higher the resultant magnification [1,2]. Images of samples were collected at a range of magnification values for all the samples analyzed in this study.

When incident radiation interacts with a molecule multiple phenomena can occur depending on the energy of the light and attributes of the target molecule.

When incident radiation is absorbed by a molecule, its energy level becomes excited, and a fluorescence or phosphorescence event can occur. The Raman effect occurs when a photon is scattered off of a material with energy loss equal to the energy required to set up a molecular or lattice-mode vibration in the material. While aromatic molecules, bacterial spores, and rare earth minerals all fluoresce, their fluorescence spectra tends to be representative of their molecular class. By observing the ratio of 6 bands in the visible spectra it is possible to identify the type of molecule without sample preparation [6].

Green (532 nm) Raman images were collected from pertinent sections of each sample, producing Raman images of mineralogy and petrography of these samples that are deemed to be representative of whole-rock (or whole-sample) mineralogy. Raman spectroscopy provides information about chemical bonding and crystal structure. The method is relatively rapid and selective. Raman spectroscopy can be used to

identify rock forming minerals, accessory minerals, and secondary minerals [4]. The Mars Microbeam Raman Spectrometer (MMRS) was developed at JPL and is a system which has been developed for flight [5].

References: [1] Peters et al. (2008) *Icarus*, 197, 470-479. [2] Mungas G. et al. (2008) *Proc of SPIE Vol 7060* doi: 10.1117/12.792024, [3] Boynton, J. et al. (2005), IEEE Doi 10.1109/AERO.2005.1559353 631-640 [4] Wang A. et al. (2004) *J Raman Spec* 35, 504-14. [5] Wang A. et al. (2003) *JGR* 108, doi:10.1029/2002JE001902 [6] Bhartia, R. et al. (2008) *Appl Spec* 62, 1070-1077.

ACKNOWLEDGMENT: This work was performed at the Jet Propulsion Laboratory (JPL), California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA)

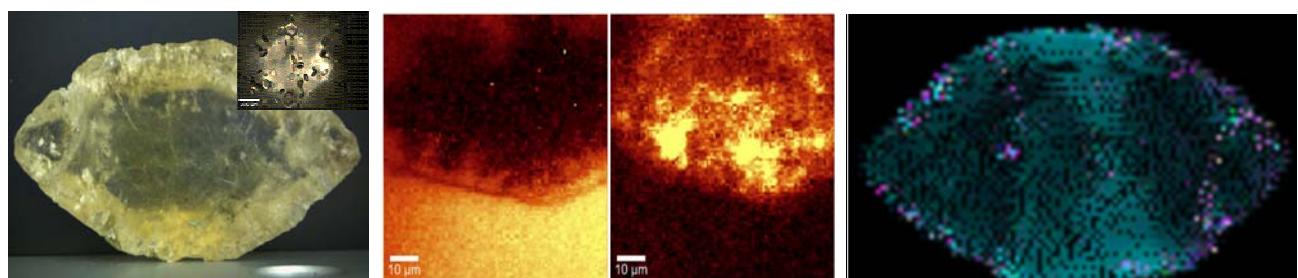


Figure 1. (Left) image of Hanksite $[KNa_{22}(SO_4)_9(CO_3)_2Cl]$ An evaporite mineral formed from slow evaporation of saturated brine and often containing mud with organics in inclusion fields (Inset). Crystal is 3 cm across. Green Raman images showing: (center left) Image of hanksite proximal to a brine inclusion, and (Center right), Visible light fluorescence of organic material trapped in an inclusion. (Right) Deep UV fluorescence image showing diffuse Organisms trapped in the hanksite crystal.

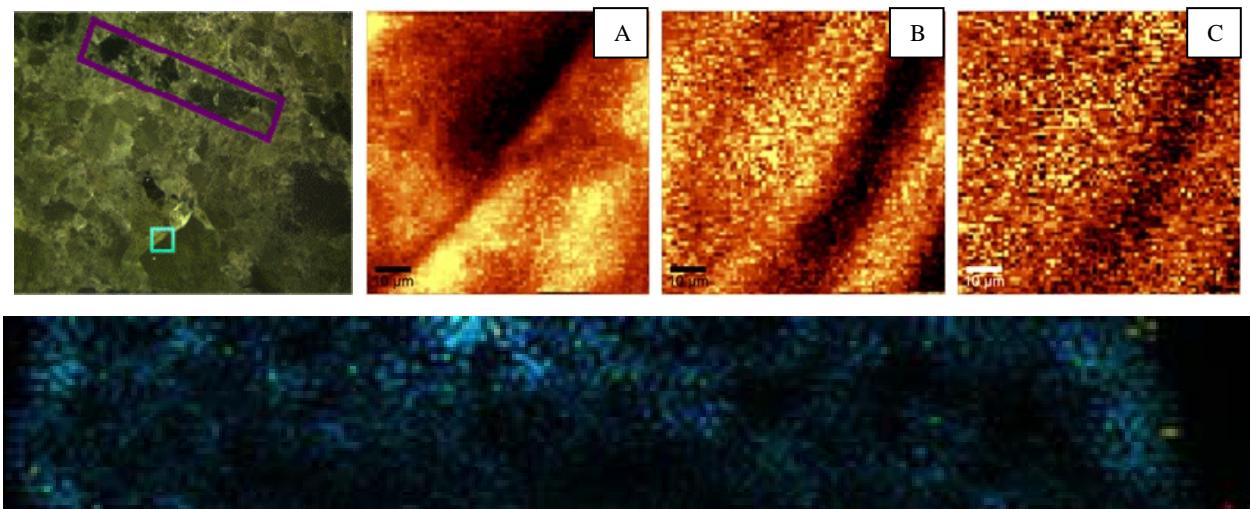


Figure 2. (Top Left) image Svalbard peridotite showing coarse-grained olivine, pyroxenes and chromium diopsides. Image is 3.5 cm wide taken with the CHAMP-SLS. The green box shows the location of the green Raman image showing A) Olivine mineral phase image B) Crystalline orientation and C) Olivine composition variation. The Purple box shows the Deep UV fluorescence image (bottom showing native carbonaceous materials condensed from mantle volatiles.