# Raman spectra identifications of mineral and organic constituents

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## Abstract

We present design, integration and test results for a field Raman spectrometer science payload, integrated into the Mars Analog Research and Technology (MARTE) drilling platform. During the drilling operation, the subsurface Raman spectroscopy inspection system has obtained signatures of organic and mineral compositions. We also performed ground truth studies using both this field unit and a laboratory micro Raman spectrometer equipped with multiple laser excitation wavelengths on series of field samples including Mojave rocks, Laguna Verde salty sediment and Rio Tinto topsoil. We have evaluated laser excitation conditions and optical probe designs for further improvement. We have demonstrated promising potential for Raman spectroscopy as a non-destructive *in situ,* high throughput, subsurface detection technique, as well as a desirable active remote sensing tool for future planetary and space missions.

## Introduction

Structural analytical methods including Raman spectroscopy, Mössbauer, mass spectrometry, and infrared (IR) spectrometry have been used to detect and analyze the samples of minerals and fossils from planetary surfaces. The detection of C-C and C=C chemical bonds or functional groups which contain such chemical compositions, could be key indicators of life. Raman spectroscopy analysis, in particular, has very large C-C, C-N scattering cross-section, yielding high sensitivity and selectivity from the *in situ* background mixture. Incorporating this analytical component yields a very powerful technique for the detection of organics and biogenic organics on the surface of Mars and other planetary analog environments. Raman spectroscopy is photon inelastic scatterings by molecules. The wavelength of the scattered light may be greater or less than the wavelength of the incidence light. These observed Raman shifts correspond to vibrational transitions of the scattering molecule. Thus, a Raman spectrum contains characteristic signatures of each target molecule species including oxyanionic minerals: carbonates, sulfides and hydroxides (Rosch et al, 2003; Jarvis, 2004, Russell et al, 1998). When the monochromatic light excites matter (solid, liquid or gas), it scatters light as the result of relaxation from the virtual states, which are short-lived and distorted by the oscillating electric field of the incident light. A photon is immediate emitted or absorbed during the scattering. Depending on higher or lower vibration states it relaxes back, stoke and anti-stoke scatterings are resulted respectively. A small percentage of light scatters the same frequency as the incident light when Fig. 1 shows the energy level diagram of the Raman and resonant Raman effect. When the incident light matches to the electronic transition states, resonance scattering occurs with the intensity up to $10^8$ over the non-resonance intensity. By using different excitation energy, the interested targets can be selectively enhanced with increased signal to noise ratio. The electronic band gap and exciton emission thus can be measured. Fig. 1 also illustrates the energy level of the resonant Raman scattering. Thus, Raman scattering is a versatile technique that enable the structure and electronic property investigated simultaneously. In addition, Raman spectroscopy sensitivity and selectivity can be further enhanced with other innovated approaches. For an example, surface enhanced Raman scattering (SERS) greatly increases the detection limit by enhancing electromagnetic field around the nanostructures. With metal particle enhancement, Raman has been shown to be capable of detecting single organic molecule (Nie and Emory, 1997).

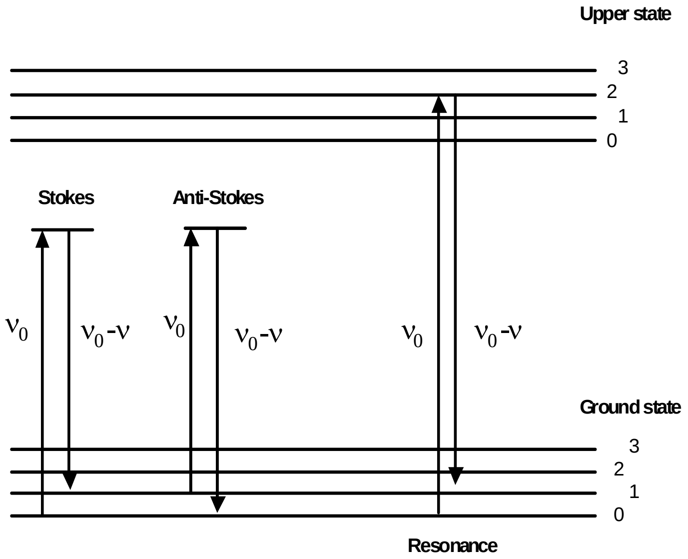

***Fig. 1*** Energy level diagram of the Raman and resonant Raman effect

Recently, Raman spectroscopy has been shown to be a very sensitive method to investigate mineral chemical compositions in various planetary samples (Ellery and Wynn-Williams, 2003; Edwards et al. 2003, Sharma, et. al., 2004, 2005). It is a powerful technique to identify aqueous minerals on the planetary surface and subsurface. In particular, Sharma et al have demonstrated the remote capability to measure the mineral spectra up to 100-meters standoff distance with a fiber optic probe attached to a laboratory spectrometer. For example, distinct mineral Raman signatures of 3064 $cm^{-1}$ and 3210 $cm^{-1}$ are used to identify hydrate groups, while 282 $cm^{-1}$, 711 $cm^{-1}$, and 1085 $cm^{-1}$ are used to characterize calcite.

*In-situ* Raman spectroscopy has several advantages over other analytic techniques for planetary sample analysis. It provides high spatial resolution that resolves morphology controversies (Schopf and Parker, 1987; Schopf et al., 2002). It can also detect trace chemical groups on the surface and inside mineral crystals and study depth profiles of soil samples to understand the environmental protection and stress effect. It permits molecular identifications on the channels, boundaries, micro sizes and shapes from a solid sample without extraction or introducing solvent and other chemical species, enabling better understand of the geochemical and environment context. Combined morphological feature, chemical stability and relative abundance information helps us understand how extreme geochemical environments affect minerals. The Raman spectrometer designed for the MARTE project aims to analyze soil samples from geochemistry affected by temperatures, pH conditions, salinity, thermal and geological stresses. Since no commercially available field spectrometer met the requirements for the MARTE drilling experiment, the MARTE Spanish engineering team constructed the Bore Hole Inspection System, BHIS based on COTS components from JY Horiba Inc.

***Fig. 2*** Illustration of Raman spectroscopy probe inside BHIS

There are several prototypes of field Raman spectrometers under development for space and planetary exploration. While they are based on similar optical design and CCD technology, the laser excitation energy and power density vary (Wang, et. al., 1998, Sharma, et. al, 2003). No field unit has been constructed so far that can achieve spectral performance comparable to that of state-of-the-art laboratory units. The major reason is that fluorescence, typically stimulated by visible laser excitations, is several orders of magnitude more intense than the Raman signal. So far, 1064 nm laser excitation yields the best quality information for mineral samples since fluorescence is avoided with such near IR excitation. However, Raman spectrometer design using 1064 nm excitation incorporates an interferometer and Fourier Transform data processing. This prototype identified four limitations: (1) Spectral quality is proportional to the light path, which requires a bulky interferometer. (2) Signal acquisition time is generally much longer than with a dispersive Raman spectrometer because of the data processing. (3) Moving parts required in the interferometer are not robust components for the field Raman spectrometer. (4) The longer excitation wavelength decreases the signal intensity since Raman intensity is proportional to the fourth power of the excitation frequency. For these reasons the MARTE Raman spectrometer incorporates a dispersive spectroscopy design that is suitable for field application.

Fiber optic probes are used to deliver light from an excitation laser and collect the light from Raman scattering. An optical fiber is a flexible wave guide for light illumination, collection, transmission, and imaging. Fiber optics may be used to produce a more robust field spectrometer design. In particular, the flexibility and point-to-point imaging capability enable optical fiber bundles to perform remote sensing and imaging. The light pathway can be flexible and yet confined inside the optical fiber (Cullum, et. al., 2000). Miniaturized collection optics can be epoxied in place in the probe head, minimizing shock-induced mis-alignment. The spectrometer thus can be compact and light, and capable for *in situ* measurement in geologically important, but hard to reach locationsm including hot springs, dry valleys, and high lakes as well as for side-on subsurface detection in borehole drilling operations. Additionally, metal coatings can be used on the fiber core to generate surface enhanc Raman scattering (SERS) and increase the signals by orders of magnitude.

## Results and discussions

### *1. Field instrument construction and design*

In the framework of the MARTE Project simulated mission, the BHIS Instrument was designed to inspect the hole drilled in the surface of the (surrogate) Martian environment. This instrument was devoted to studying the 48-mm diameter borehole as a complement to core sample analysis and was capable of measuring Raman spectra of targets on the walls of the borehole along with complementary color imagery. These field devices are highly constrained by power consumption, weight and volume. There is no commercially available spectrometer equipped with a fiber optic probe that has the required performance. Therefore, this design integrated a miniaturized Raman probe placed inside the down-hole instrument, with a Raman spectrometer and excitation laser on the lander. Two optical fibers join these two main parts: one for the transmission of the laser beam to the miniaturized probe, and the other to transmit the scattered light gathered by the probe to the spectrograph. The spectral range of this Raman spectrometer is between 200 $cm^{-1}$ to 3900 $cm^{-1}$, and the spectral resolution is 12 $cm^{-1}$. A HeNe laser, provides an excitation wavelength of 633 nm with excellent temperature stability. The spectrometer incorporates a fixed concave grating of 1200 grove/mm.

Fig. 3 shows a detailed view of the Raman probe and the laser beam in the BHIS. The Raman probe is housed inside a Pyrex window that slightly attenuates the signal. Because this window is out of the focal plane, only minimal signature from this material is registered in the spectra. In quick scan mode, this instrument requires only 10 seconds to acquire the signal photons and read the spectra from the array detector.

### *2. Raman spectroscopy measurement results*

#### 2.1 Raman spectroscopy characterization of organic matter using BHIS at Rio Tinto

The MARTE field site in the Rio Tinto region of south central Spain was selected for its relevance as a Mars analog based on a number of features, including both geological and biological factors (Stoker et al, Prieto-Ballesteros, et al, Fernandez-Remolar, et al, 2007). The MARTE BHIS Raman subsystem has provided information about mineral paragenesis of rocks as well as detection and determination of organic matter. Fig. 3 shows an example of Raman side-on spectral analysis and corresponding panoramic images taken in the bore hole depth interval between 1300mm - 2700 mm. Raman spectra have shown detectable carbon and organic carbon at 1300 cm$^{-1}$ and 1600 cm$^{-1}$ respectively, and CN composition at 1670 cm$^{-1}$. The plotted spectra signature between the wave numbers of 2600 cm$^{-1}$ - 2700 cm$^{-1}$ is indicative of plausible organic matter originating in bio-molecules such as lipids. It was noted during remote spectral monitoring that when better panoramic images of core samples were taken, we obtain correspondingly better-resolved Raman spectra.  This was likely owing to radial irregularities in the borehole wall surface that exceeded the depth of field for both the imaging and Raman optical systems.

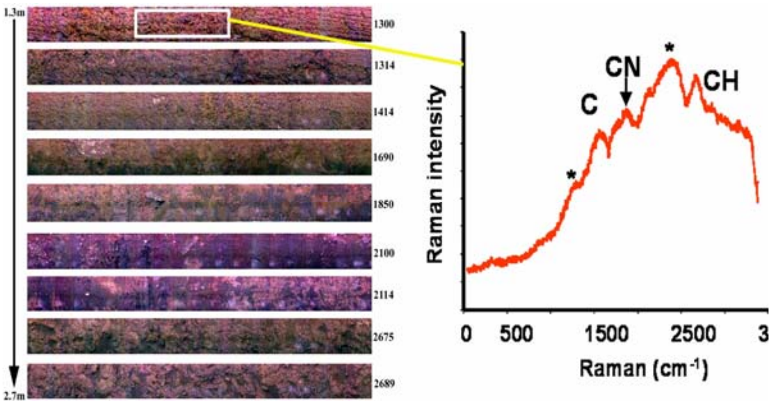

***Fig. 3*** Raman spectral analysis (*right*) of organic carbon species in the borehole inspection depth interval from 1300mm - 2700 mm. Corresponding panoramic image of core sample (*left)* at the same borehole depth.

## 2.2 Paleospring mineral field detection

A portable off-shelf instrument provided by Ocean Optics, Inc was used to study in field sites in Paleosprings in one of Arctic expeditions. Composition changes (gypsum vs. selenite) corresponding to geochemical environment are clearly shown in Fig. 4. Anhydrides not presented on the fresh samples, are detected from the eroded side samples.

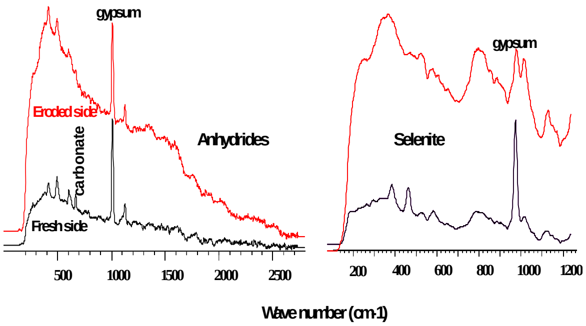

***Fig. 4*** Raman spectra in Arctic field detection (Ocean Optics, Inc). Gypsum and small amount of carbonate are detected. The Raman spectrometer is capable to measure the composition changes occurred in samples caused by geochemical processes.

## 2.2 Unprocessed field sample laboratory measurements with BHIS unit

In the state of the art laboratory Raman analysis, resonant excitation and surface enhanced Raman scattering techniques can be used to carefully examine field samples with no preparation and process. The microscopic feature can be examined without undesirable extractions and isolations from the sample pristine matrix. It can be applied equally well to materials on the surface of a rock sample or thin section and to materials below the sample surface, enclosed in an optically transparent mineral (Haskin *et al*, 1997; Pasteris, 1998; Wang *et al*, 1999). The sample can be analyzed *in situ*, and can be preserved with the material's morphology and with the petrologic context, minimizing chemical alteration in the sample processing.  In addition, *in situ* field measurements is also crucial to conduct sample characterization from unique geochemical sites. This is because taking sample back with may change its property with temperature and humidity conditions. In other cases, it is impossible to retrieve from a planetary surface and subsurface.

Prior to the BHIS deployment to the Rio Tinto drilling site, we had tested its performance with unprocessed field samples at NASA Ames Research Center. We measured mineral and organic compositions using several field samples with no processes or treatments. Some of our initial results are shown in Fig.5. Raman spectra taken from green algae line area contain high concentration of graphitic carbon (1600 cm$^{-1}$) than that taken from brown rock area where carbon constituent likely originated from carbonate group (1300 cm$^{-1}$) in Fig. 5a. Similarly, graphic carbon (1600 cm$^{-1}$) are also shown rich in the brown biogenic formation area in Laguna Verde salty sediment in Fig. 5b. We have detected key compositions from both Mojave rock and Laguna salt samples. However, we were not able to obtain Raman signals from Jarosite and Hematite minerals with this field Raman spectrometer. We attempt to use laboratory spectrometer to investigate parameters that enable mineral field measurements. In comparison, Fig. 6 shows the laboratory studies of the same Mojave rock using a laboratory micro Raman spectrometer equipped with three excitation lasers. Note the Raman signature of quartz at 130 cm$^{-1}$, 207 cm$^{-1}$, and 467 cm$^{-1}$, and that of carbonate at 1000 cm$^{-1}$. Contradictory to the results from the BHIS spectrometer, the compositions from quartz and $SiO_2$ are predominant with all three excitation lasers. However, carbon (1300 cm$^{-1}$) and organic carbon (1600 cm$^{-1}$) groups have stronger signal intensity respectively under the 514 nm laser excitation than under either the 633 nm or 785 nm laser excitations.

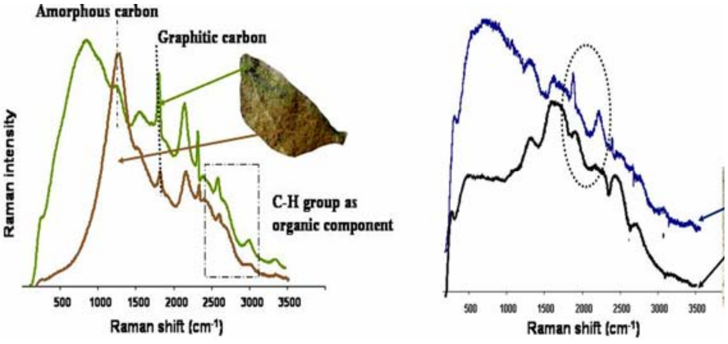

***Fig. 5*** Initial Raman spectra measured with MARTE field spectrometer at 633 nm laser excitation. a. Mojave Rock, the Raman spectra were taken from green algae line area contains high concentration of graphitic carbon (1600 cm$^{-1}$) than the brown rock area where carbon constituent likely originated from carbonate group (1300 cm$^{-1}$), and b. Laguna Verde salty sediment, where graphic carbon (1600 cm$^{-1}$) are rich in the brown biogenic formation area**.**

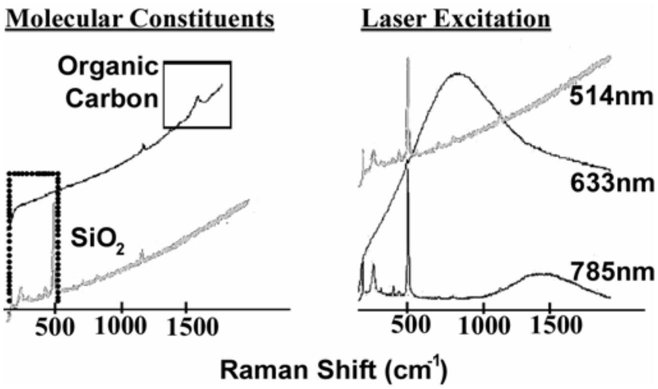

***Fig. 6*** Mojave samples analyzed with a laboratory Raman spectrometer. Left: green Algae line spectrum (upper) shows carbon peaks at 1300 cm$^{-1}$ and organic carbon peak at 1500 cm$^{-1}$, while brown rock area (lower) shows main chemical composition is quartz. Right: Mojave soils excited at three visible wavelengths. 633 nm laser in this set up does not yield strong Raman signals as 785 and 514 nm lasers.

We believe we could improve spectrometer performance by (1) improving the light coupling from the fiber optical probe to the spectrometer, (2) choosing an optimal excitation laser wavelength for resonant excitations. The improved detection capacity is similarly needed for detection and characterization of carbonate, sulfides, hydroxides and oxyanionic mineral groups. Further work is underway to use a fiber optical SERS probe in place of the currently used commercial probe in order to improve the collection efficiency of Raman signal.

### 2.3 Rio Tinto field sample measured from a laboratory instrument

We also analyzed the topsoil layer (0-1 cm depth) samples with a laboratory micro Raman spectrometer (Stoker et al, 2007). This instrument was capable of using 3 different laser excitation wavelengths, and so permitted some examination of the parametric effect of excitation wavelength. The total organic carbon analysis shows up to 11.8% of carbon and nitrogen constituents (Bonaccorsi, et al, 2007). Although our lab Raman data analysis shows very strong signatures consistent with quartz composition of $SiO_2$, it did not conclude organic carbon detections.

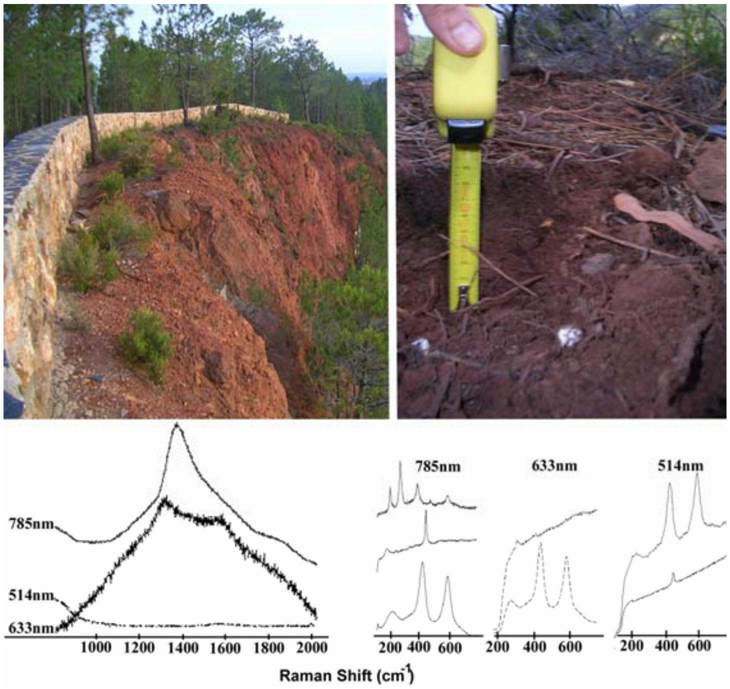

***Fig.7*** Laboratory Raman spectra studies of Rio Tinto topsoil samples. While the organic carbon are very weak, strong mineralogy features from quartz composition of $SiO_2$ (208 $cm^{-1}$, 266 $cm^{-1}$, 470 $cm^{-1}$ and 1086 $cm^{-1}$) and hematite (226 $cm^{-1}$, 293 $cm^{-1}$, 410 $cm^{-1}$ and 612 $cm^{-1}$ and 1086 $cm^{-1}$) are clearly shown.

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Fig. 7 shows Raman spectra taken with three excitations. Raman microscopic analysis within the micrometer-scale spots using the same excitation conditions reveals different chemical compositions. This is due to resonant excitation with laser energy from different constituents in the sample. Among them, the 514 nm excitation is least effective since it produces a higher fluorescence background as shown in the baselines. Spectra are optimized with 785 nm excitation. The Raman signature peaks of $SiO_2$ (208 $cm^{-1}$, 266 $cm^{-1}$, 470 $cm^{-1}$ and 1086 $cm^{-1}$) and hematite (226 $cm^{-1}$, 293 $cm^{-1}$, 410 $cm^{-1}$ and 612 $cm^{-1}$ and 1086 $cm^{-1}$) are observed respectively depending on the sample grain dispersion. On the other hand, very weak Raman peaks of carbon and organic carbon constituents have been detected at around 1400 $cm^{-1}$ and 1600 $cm^{-1}$ respectively. Note that we only observed an organic carbon Raman signature around 1600 $cm^{-1}$ with 633 nm laser excitation. These results partially explain that the BHIS is quite sensitive in detecting carbon and possible nitro groups, but not well suited for mineral composition in the field, since the spectrometer is equipped with only a 633 nm laser.

## Conclusion

We have designed and tested a field Raman spectrometer equipped with a fiber optic probe. The hardware has endured the entire MARTE drilling project including considerable exposure to vibration and mechanical impacts. We have studied minerals and organic matter in unprocessed soil and rock samples with Raman spectroscopy. *In situ* side-on inspection in the Rio Tinto field drilling experiment has shown organic carbon signatures, which are confirmed by corresponding core samples studied in the laboratory. In addition, core samples studied with a lab instrument equipped with multiple laser wavelengths clearly demonstrates mineral signatures previously undetected by the field unit. The comparison studies using this laboratory spectrometer indicate that it is possible to further improve BHIS performance to achieve better light delivery, coupling, and focusing by improving the optical probe design, and to increase signal sensitivity through optimal choice of the laser excitation source. Further systematic laboratory and field studies on different groups of carbonate, sulfite and organic constituents will determine optimal laser power and wavelength, and could eventually lead to an unprecedented active spectroscopy sensing capability in the field. The Raman analysis technique holds promising potential for future planetary exploration. It will play an important role for *in situ* mineral and organic detection.

## Acknowledgment

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