AUTOMATED CORE SAMPLE ANALYSIS BY THE MARS MICROBEAM RAMAN SPECTROMETER (MMRS) ON-BOARD THE Zoë ROVER IN ATACAMA: A TERRRESTIAL TEST FOR MARS EXPLORATION

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Introduction: Raman scattering probes the fundamental vibrations of molecules that produces fingerprint spectral patterns with sharp no-overlapping peaks. Raman spectra can be acquired from the sample, as is, i.e., it is non-invasive, non-destructive and fast. Using a focused laser beam for excitation, in situ Laser Raman spectroscopy (LRS) is a powerful technique for the detection and characterization, at fine-scale, of the major, minor and trace species in a mixture (rocks and soils), and is suitable for landed surface explorations on planets.

The Mars Microbeam Raman Spectrometer (MMRS), a LRS for flight, has been developed as a science payload instrument for landed Mars missions by a science team at Washington University in St. Louis, and an engineering team at Jet Propulsion Laboratory.[1] Further developments since then have augmented its science capability and Technical Readiness Levels. A new version of MMRS, Compact Integrated Raman Spectrometer (CIRS), is now ready for flight.

MMRS in the Atacama: The Atacama Desert is one of the driest desert on Earth [2], and an excellent analog site for Mars. Since 2012, the MMRS team has joined the NASA ASTEP Life in the Atacama (LITA) project. LITA has aimed at investigating the regional distribution of life and habitats in the Atacama Desert and also at promoting technology advances for remote exploration in terrestrial extreme environments and future Mars missions [3]. During the 2013 field season, MMRS was installed on the Zoë rover (Carnegie Mellon University). The field exploration lasted for two weeks. Zoë traveled 50 km, and was remotely directed by a science team from U.S., and locally operated by an engineering team at Atacama.[13]

The Zoë Rover, MMRS, and BUF: One of the features of the 2013 LITA field campaign was the autonomous MMRS analysis of core samples. Core samples were obtained at 10, 30 and 80 cm depths, and delivered into the sample cups (10x10x10 mm³) on a carousel that delivered the sample under the MMRS probe head (figure 1). MMRS collected Raman spectra from a sampling spot excited by a focused 532nm beam. A stepper motor within the probe moves the optical bench linearly over the sample surface in a range of 10 mm, from which Raman spectra of 20-100 spots were collected without using autofocus.

Core samples were obtained at four locales (#8-#11) on a playa. A pit was dug near each drilling hole and more samples were collected and manually put into cups for ground-truth. Additional pit samples were collected at Locales 2B, 5 and 6B, about 20 km to the west of the playa. Raman spectra were acquired by MMRS autonomously for both the core samples and the pit samples.

A BUF camera using white and UV LEDs for illumination was installed on the same carousel next to the MMRS, to obtain the context image of the sample surface examined by MMRS. The wavelength (370 nm) of the UV LEDs was selected to obtain bio-related UV fluorescence (BUF) images. The same set of field samples were taken to the WUSTL laboratory and Raman spectra were acquired with a laboratory Raman spectrometer (Kaiser Hololab 5000, 532 nm).

MMRS calibration, validation, and field robustness: MMRS spectrometer wavelength calibration was made using a Ne lamp before during and after the field campaign. In addition, reference Raman spectra of naphthalene and diamond were taken frequently during the field campaign for laser wavelength calibration, and for the evaluation of MMRS’ general performance, such as sensitivity, noise level and spectral resolution. Any changes, especially the optical alignment of MMRS affected by mechanical, optical or electronic fluctuations during the transverse of the rover, would be reflected in the reference spectra. Despite Zoë rover’s 50 km transverse on a rough terrain and a wide diurnal temperature cycle, from -6 to 27 °C, during the field campaign, the MMRS did not show noticeable performance change. On the other hand, we did notice the laser wavelength shifts, as a result of lacking adequate temperature control in the current laser unit within MMRS probe. This issue has been corrected for 2014 field season.

Minerals identifications: Multi-point Raman spectra were obtained for 31 core and pit samples. The spectral
analysis showed the presence of three groups of minerals in the Atacama samples. They are: original igneous minerals (mainly feldspar and quartz); alteration products (e.g., TiO₂ and goethite); and hydrous or anhydrous salts (sulfates and carbonates) with variable origins.

MMRS covers a Raman shift range from 100 to 4000 cm⁻¹. For clarity, the high frequency region was not shown. Typical spectra of three calcium sulfates are shown in Fig. 2a, top panel. These spectra in 400-1200 cm⁻¹ range bear similar spectral pattern as the major Raman peaks are contributed by the internal vibrations of common SO₄ group in these sulfates. The shifts in exact peak positions among these sulfates are caused by structural changes (bond length and angles) of SO₄ tetrahedra induced by the change in cation or hydration degrees. Two OH stretch Raman peaks in gypsum appeared at 3407 and 3494 cm⁻¹. The position of the strongest peak, ν₁(SO₄) symmetric stretch in gypsum and anhydrite are different by 9 cm⁻¹ and can be clearly distinguished. ν₁(SO₄) in another stable hydrated cesium sulfate, bassanite (CaSO₄·0.5H₂O), is located at 1015 cm⁻¹ [4-6], too close to make an assertive difference from this set of data due to laser wavelength shift discussed above. No Raman spectra obtained can be unambiguously assigned to bassanite at this point.

A third Ca-sulfate was found in laboratory measurement of the samples, with the strongest ν₁(SO₄) mode occurring at 1025 cm⁻¹. Based on the position details of all observed peaks, the phase was assigned to be γ-CaSO₄. [7]

Two carbonates were observed (Fig. 2b). Calcite has the major Raman peak at 1086 cm⁻¹, the sample in Fig. 2b also contained gypsum (1008 cm⁻¹) and quartz (464 cm⁻¹). The second carbonate has the strongest peak at 1066 cm⁻¹. One candidate is K₂CO₃, which has been reported to have the ν₁(CO₃) peak at 1063 cm⁻¹.[8] some other candidates are BaCO₃ and BaCa(CO₃)₂, with the peak at 1060 and 1066 cm⁻¹, respectively.[12]

Raman spectra of quartz and anatase are shown in Figure 2c. The strongest Raman peaks of feldspars fall within the narrow region of 505 to 515 cm⁻¹.[9] The three end member feldspars, K-feldspar, albite and anorthite, have the strongest Raman peaks at 513, 508 and 505 cm⁻¹, respectively.[9] The strongest Raman peaks observed are between 508 to 516 cm⁻¹, indicating dominant alkali-feldspars..

Raman peaks of carbonaceous materials were observed in a few samples (Fig. 2d). Raman spectra of graphite has 3 bands (D, G, D') at 1355, 1581 and 1620 cm⁻¹.[12] The observed band at 1605 cm⁻¹ seems to be an overlap of G- and D'-bands. Different ratios of band areas were obtained, which suggests a difference in structural order of these C-bearing phases.

Phase distributions at different depths in a playa

We used a Raman point count method [10] to extract the mineral proportions from MMRS line scan measurements on each Atacama sample. The averaged percentage proportions of quartz, gypsum, anhydrite (with bassanite), feldspars, calcite and anatase are 10, 11, 8, 7, 2 and 1.8 respectively. We found from the samples collected by drill at different depth (surface, 20 cm, 60 cm, 80 cm depth) of a playa, both anhydrite and gypsum show higher proportions at the deepest points, and almost zero percent distribution at the surface. However, at Locale 5B, an ash sample is composed almost purely of gypsum. Quartz does not have depth preference, while feldspar shows high proportion at the surface. No indication of organics was observed from both Raman spectra and BUF images from the current data analysis.

References:

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