**IN SITU LASER RAMAN SPECTROSCOPY FOR MARS SAMPLE RETURN MISSION.** Alian Wang, Dept Earth & Planetary Sciences, McDonnell Center for Space Sciences, Washington University in St. Louis (alianw@levee.wustl.edu).

Laser Raman Spectroscopy (LRS): LRS observes the spectral shifts (Raman shift $\Delta\lambda$) from a excitation laser wavelength (λ_0) caused by the molecular vibrations of chemical bonds in a sample. Therefore, LRS can work in IR, VIS, UV, and X-ray spectral ranges. The information provided by LRS include the *identification and characterization of molecular species (organic and inorganic) in the form of solid (crystals and amorphous), liquid, and gas.* The LRS laser does not vaporized the materials, thus LRS measurement is non-destructive. The laser beam and the induced Raman photons of a Vis-LRS penetrate through optically transparent windows on a sample container, thus LRS measurement can be non-invasive.

In situ LRS for flight: *Mars Microbeam Raman Spectrometer (MMRS)* has been developed by a combined team at Washington University in St. Louis and at Jet Propulsion Laboratory [1,2]. *MMRS* has a high TRL and *was ranked category one during the payload selection review for MSL*.

MMRS is an *in situ* Raman sensor to be deployed by a robotic arm and to make mineral and molecular characterization of the planetary material. It has four characters: (1) a narrow beam with linear scan capability; (2) a high spectral resolution with wide spectral range; (3) a large depth of sampling field; (4) a 532 nm excitation wavelength. We are discussing here the scientific advantages brought by these characters.

Finding minor/trace species and making molecular mapping: *MMRS* uses a narrow laser beam (tens' μm diameter) to interrogate a spot in a sample, and uses an automated linear scan to get hundreds sampling spots from an area of ~ cm diameter on a target [3, 4]. Comparing with a broad beam Raman system from which the Raman peaks of minor/trace species would likely be suppressed by the strong peaks of major phases (due to the large differences in Raman cross sections), from a narrow beam Raman system the minor/trace species in the sampling spot would contribute the major Raman signals (Fig. 1). With hundreds examed spots in a sample, the minor/trace species will have a high probability to be encountered by the laser beam and to be detected (e.g., calcite in EETA79001, [4]).

A broad beam

A narrow beam

Figure 1
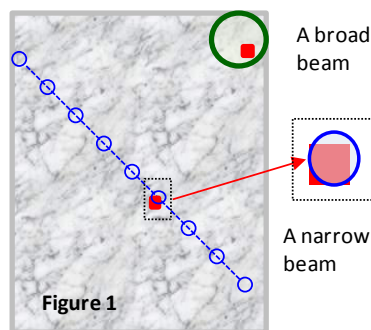
A narrow laser beam would also help fighting the fluorescent interference from some samples.

The automated linear scan is the simplest way to make *molecular map* of a target during a robotic planetary exploration. The mapping parameters can all be defined in real time during the operation, such as the line orientation, the number of lines, the number of sampling points per line, and the size of scanning step. The mapped area on a target can be selected across veins, mineral clusters, and other textural features, with additional information on mineral grain size and crystal orientations [3-6]. From those molecular maps, we will be able to find the *genetic relationship among different species* in a selected target [6].

ID of broad-range species and mineral chemistry: The fundamental Raman peaks of minerals, H_2O/OH in minerals, organics, and carbon of various structures, amino acids, and lipids occur at different Raman spectral ranges. In order to maintain the capability of detecting broad-range species during the explorations at planetary surfaces, *MMRS* provides the widest possible spectral range, and in the same time maintains an adequate spectral resolution for the purpose of getting chemistry information. Those information are extracted from the small shifts of Raman peak positions, caused by cation-substitution in mineral solid-solutions, e.g., the Mg/(Mg+Fe) ratio in olivine [7], the Mg/ (Mg+Fe+Ca) ratio in pyroxene [8], the Fe/(Fe+Ti+Cr) ratio in Fe-oxides [9], the Mg/(Mg+Fe) ratio in some phyllosilicates [10], the endmember and intermediate K-Na-Ca feldspar [11], the endmember and intermediate Mg-Ca-Fe(Mn) carbonates [12], and the hydration degree changes of Mg-, Fe-, Ca-sulfates [13, 14, 15].

High tolerance for robotic arm deployment: The optical design of *MMRS* provides a large depth of sampling field, which would enable *the measurements on rough surface* (to certain degree) of a selected target. Adding an auto-focusing system for rough surface measurements will increase the system complicity in optics-electronics-mechanics (increase of mass & volume), and the measurement time of a single-spot (increase of power). Because LRS has intrinsically a much higher tolerance (than LIBS) for the off-focus measurement, the trade-off that we would select is to use a simple system and to make many measurements.

A suitable laser wavelength for general mineralogy and long-live biomarkers: The suitability of a laser wavelength for a planetary Raman system depends on (1) its efficiency on the materials that would be commonly encountered during the explorations at

planetary surfaces and on the minor/trace species to be searched; (2) the probability of avoiding interferences from other optical signals; (3) the maturity of laser technology. We recently measured a set of five standard minerals and three amino acids using five excitation laser lines, 785 nm, 633 nm, 532 nm, 442 nm, and 325 nm on a laboratory Raman system, to re-evaluate factors (1) & (2) (Figure 2)..

We found that 785 nm excitation has a generally low Raman efficiency (I $\propto 1/\lambda^4$ rule), and quite often induces strong fluorescent peaks from basaltic glasses in 1000-2000 cm^{-1} that would interfere with C-species characterization. We also found that although 325 nm excitation can sometime avoid the fluorescent interference from bio-contaminated clays, its efficiency for general mineralogy is 1-2 magnitudes lower than those of VIS-laser excitations. The advantage of I $\propto 1/\lambda^4$ for UV-Raman is diminished by poor performances of optical components in UV and by the shallow penetration depth of UV-photons into geo-samples.

Among the VIS-laser wavelengths, 532 nm excitation not only has a great performance for general mineralogy, it also stimulates the resonance Raman (10^{3-4} times stronger than normal Raman) signals from lipids that have the longest preservation record through geologic history. These observations, plus the maturity of nowadays laser technology, all confirmed that _the 532 nm is currently the most suitable laser wavelength for planetary Laser Raman spectroscopy._

Mars Sample Return (MSR) missions: 2011 Decadal Survey for Planetary Sciences ranked the Mars Sample Return with the highest priority among NASA flagship missions for next ten years. It suggested that MSR to be conducted in three steps: the first mission to select and to collect well characterized Mars surface/subsurface samples from well characterized environments; the next two missions to bring the samples back to Earth for detailed laboratory analyses [16].

We learned from the recent surface explorations on Mars (MER and Phoenix) that Mars surface/subsurface materials are spatially heterogeneous even at very

small scale [17,18]. With a severe limitation on the total mass of the to-be-collected samples for Earth-returning, careful selection of the sampling area is absolutely essential. For that purpose, knowledge on the texture, chemistry, mineralogy, potential biomarkers must be obtained beforehand. The technical tools to gain those knowledge should be non-destructive.

Conclusion: LRS provides molecular information of major, minor, trace phase in a geological target and their genetic relationship. It is capable of detecting organics species, distinguishing variety of carbonaceous materials, and recognizing biomarkers. It is non-destructive. We believe that LRS, especially _MMRS_ with high TRL, is the suitable technology for the sample selection in the first mission of MRS.

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