A COMPACT INTEGRATED RAMAN SPECTROMETER, CIRS, FOR FINE-SCALE MINERALOGY AND BIO-SIGNATURE DETECTION IN PLANETARY SURFACE EXPLORATIONS OF OUR SOLAR SYSTEM.

Alian Wang[1], Bradley Jolliff[1], James Lambert[2], Robert Menzies[2], Ian Hutchinson[3], Jie Wei[1], Walter Goetz[4], [1]Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, [2]Jet Propulsion Laboratory, [3]University of Leicester, UK; [4]Max Planck Institute for Solar System Research, Germany. (alianw@levee.wustl.edu).

Introduction: Since 1995 [1-11], we have shown through analysis of extraterrestrial samples (returned rocks and regolith from the Moon, meteorites from Mars and elsewhere) the potential of Laser Raman spectroscopy (LRS), specifically *in-situ* green laser Raman spectroscopy, for use in definitive mineralogy and bio-signature detection relevant to planetary exploration missions. We have demonstrated the power of LRS to study the thermodynamic and kinetic properties of hydrous salts to address key questions posed by orbital and landed mission observations on Mars [12-24].

Over the same time period, we designed and built two versions of *in-situ* green laser Raman systems, the Mars Microbeam Raman Spectrometer (MMRS) [25-29] and the Compact Integrated Raman Spectrometer (CIRS), under the support of NASA PIDDP, MIDP, ASTEP, and MATISSE programs. The MMRS was field tested in the Atacama Desert as a stand-alone unit in 2012 and on the Zoe rover in its 50 km traverse in 2013. The first set of results from performance tests of the MMRS was published in *Journal Geophysical Research* in 2003 [26]. Results from the Atacama field test were reported in conferences [27-29] and a manuscript was submitted to *Journal of Raman Spectroscopy* in 2014.

Raman scattering is an intrinsically weak process. Detection requires a carefully crafted optical configuration with high optical efficiency in order to collect useful Raman signals from mineral mixtures of complicated natural materials (e.g., rocks and regolith with rough surfaces) that would be encountered during a planetary surface exploration mission. Through two decades of studies of extraterrestrial materials and tests in the laboratory and in natural geologic settings, we have come to a conclusion regarding the best configuration for a planetary Raman system to satisfy the need of fine-scale definitive mineralogy and bio-signature detection, i.e., the configuration of MMRS and CIRS. In terms of engineering, this configuration uses the simplest, most mature, and optically most effective techniques (continuous wave, low power 532 nm laser, visible optics, CCD). The robustness of this configuration was demonstrated through the 2013 field test on Zoe rover. Moreover, we have studied and demonstrated that other configurations generate either weak Raman signals or incomplete molecular information.

All of our work (and publications) to demonstrate wide planetary applications of LRS [1-24] have used *in-situ* green Raman systems, e.g., an MMRS or CIRS type of instrumental configuration. Here, we report the new development of CIRS supported by the MATISSE program, and how it can address important scientific questions in future planetary missions.

CIRS, a Compact Integrated Raman Spectrometer: CIRS is a non-optical-fiber version of MMRS, with augmented science capabilities. CIRS combines a high-quality laser Raman spectrometer (CIRS-LRS) with a Context Imager (CIRS-CI) using the LRS front optics for image collection.

CIRS-LRS retains all major technical characteristics and development maturities of the MMRS in the

Figure 1. Comparison of Raman signal strength of a feldspar sample generated using five laser lines for excitation on a commercial Raman system (inVia, by Renishaw Company) that has separated & optimized optical channels for UV, Vis, and IR-Raman.
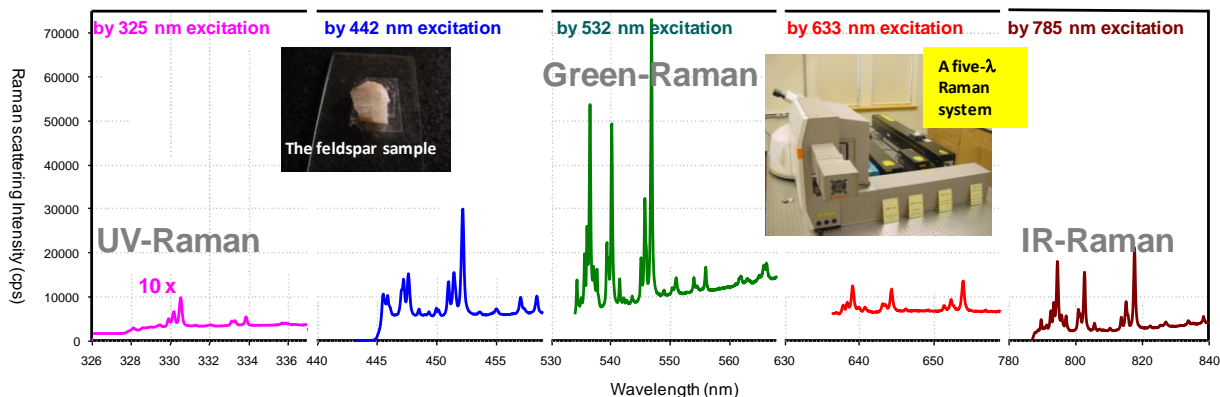
following four aspects: (1) a *narrow laser beam* (< 20 μm diameter) with *linear scan capability* (> 1 cm) for identification of the major, minor, and trace molecular species in mixtures and for mapping rock texture; (2) a *wide*

Figure 2. CIRS-LRS & CIRS-CI together

Figure 3. Two capabilities of CIRS for detecting potential fluorescence species

spectral range (200-4000 cm^{-1}) with high spectral resolution (7-8 cm^{-1}) for the detection of a broad range of molecular species and for obtaining approximate mineral chemistries; (3) A large depth of *Raman sampling field* to achieve a high tolerance for measuring rough surface of rocks and soils; (4) the *most suitable excitation laser wavelength* (532 nm) for general mineralogy and long-lived bio-markers.

Figure 1 compares the of Raman signal strength from a feldspar sample using five excitation laser lines, obtained from a commercial Raman system that has three separate optical paths for UV-, Vis-, and IR-Raman, all highly optimized. The figure shows that the strongest Raman signal strength is from a green Raman channel, and the weakest Raman signal strength is from a UV Raman channel.

CIRS has augmented science capabilities compared to MMRS in the following four aspects: (1) increased Raman signal strength by integrating the MMRS probe-head directly on the MMRS spectrometer (removal of optical fibers, Fig. 2), with a 20% improvement of overall Raman signal; (2) added context image capability (CIRS-CI) by replacing a mirror in the MMRS probe design with a filter, providing a 3 × 12 mm mosaic context image of the sample scanned by the CIRS-LRS. An image pair based on a mosaic context image and the molecular map generated by CIRS-LRS can be further nested into images with a larger field of view to gain full-scale geologic context; (3) added UV-stimulated fluorescence image capability that uses the same collecting optics as CIRS-CI, but with excitation from three UV LEDs (250 nm or 280 nm, FWHM ~ 12 nm in either case). A feasibility test was done on a set of 158 samples of terrestrial and extraterrestrial origins, and a field test was successfully done in 2013 at Atacama; (4) added capability to conduct *Shifted Excitation Raman Difference Spectroscopy* (SERDS) or Sequential Shifted Excitation Spectroscopy (SSES), using a well-characterized continuous
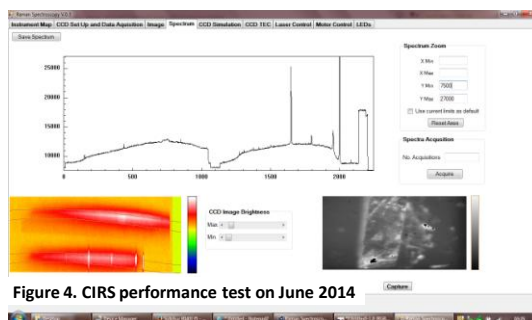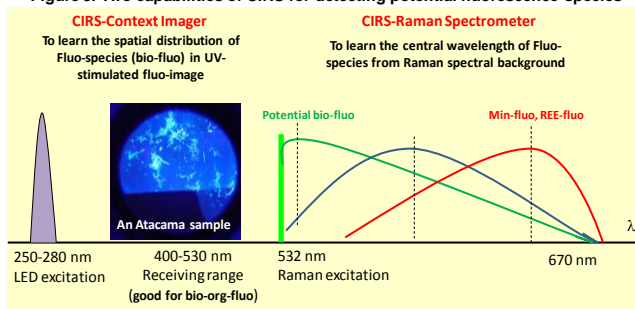

Figure 4. CIRS performance test on June 2014

wave (cw) 532 nm laser with adjustable laser line position. The purpose of this added capability is to extract Raman signals in case a high fluorescence background is generated at a specific sampling spot. A test was successfully accomplished using the cw 532 nm laser developed for CIRS [30].
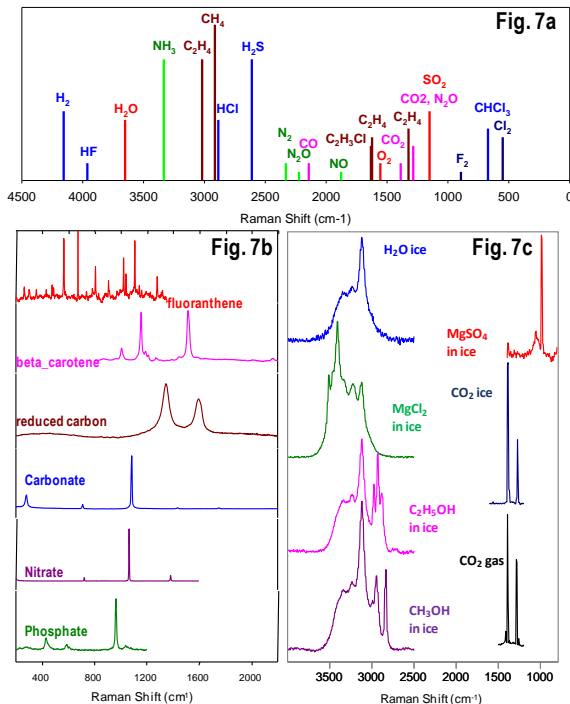
Based on following three sets of observations, we conclude that natural fluorescence would not be a major threat for LRS that uses cw green laser excitation for planetary explorations: (1) Numerous reports in the literature have suggested that the natural fluorescence emissions stimulated by UV or Vis-excitation from materials at the martian surface (Phoenix and MSL) and (2) on meteorites that are from Mars and elsewhere are low to absent [31-35]; (3) furthermore, we are reporting in this workshop a quantitative study on the fluorescence properties of extraterrestrial samples using different excitation lines, in comparison with some terrestrial materials [36], that confirms the above conclusion.

On the other hand, some extraterrestrial materials do contain organic species. Moreover, evidence of life may yet be discovered on Mars. Some of the relevant biochemical species can generate fluorescence in localized small spots in a sample during a CIRS line scan. For these spots, CIRS has two capabilities in its design to make the detection (Fig. 3): (1) detection of green-yellow-red fluorescence, stimulated by the 532 nm laser radiation, in the form of a Raman spectral background, which provides knowledge of the central wavelength of broad fluorescence bands; and (2) imagery of blue-green fluorescence stimulated by 250 nm (or 280 nm) UV LEDs, which provides knowledge of its spatial distribution in a 3×12 mm area. During a mission to a planetary body with potential habitability, a target showing strong natural fluorescence in CIRS data would be an excellent candidate for further investigation of potential biological origin.

Current status of CIRS – after one year development support by the MATISSE program, a prototype of CIRS was built and preliminary tests were done. Further optimization is in progress. Figure 4 shows one of the test results in June 2014, with both Laser Raman Spectroscopy (CIRS-LRS) and Context Imagery (CIRS-CI) functions working at the same time.

Fig. 7a

Fig. 5a

Fig. 5b

Fig. 7b

Fig. 7c
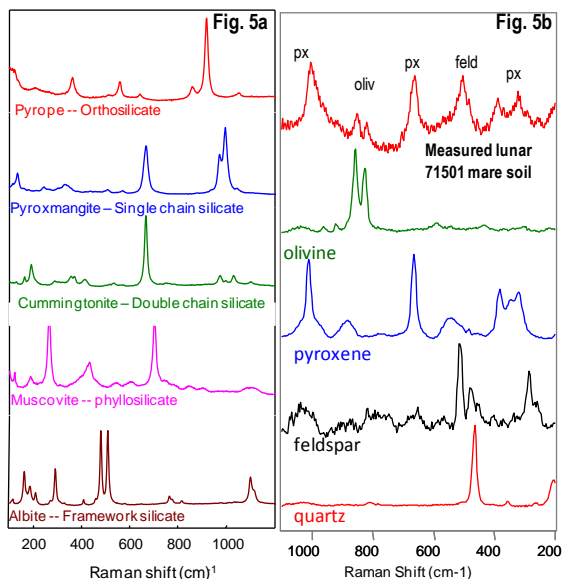
CIRS for future planetary exploration of the Solar System -- Among the missions listed in the 2013-2022 Decadal Survey, about half are landed missions or sample-return missions. This fact demonstrates the community-wide recognition of their science value. The overall science return of a landed mission will rely particularly on knowledge of the fine-scale molecular make-up of the planetary surface and subsurface materials, made by *in-situ* molecular spectroscopy. The characteristics of CIRS will enable the following three science objectives to be accomplished during a landed mission on planetary bodies in the Solar System:

Science objective #1 – **Relate igneous, hydrothermal, and sedimentary rocks to the formation and evolution of planetary bodies;** Figures 5a & 5b demonstrate the classification of different types of silicates; the identification and characterization of major igneous silicates can be achieved by straightforward inspection of raw LRS spectra of a mixture (rock & soil).

Science objective #2 – **To determine the effects of past and current climate and environments, and role of water in a planet's history;** Figures 6a, b, & c show the identification and characterization of hydrous minerals, including details of their degree of hydration, and potential S-species in Venus' surface-atmospheric interactions using LRS.

Science objective #3 – **To evaluate the inventory of organics, reduced carbon, and molecular carriers of the building blocks of life, H, C, N, O, & P, at planetary surfaces.** Figure 7a shows the Raman peak positions and peak intensities (based on Raman cross sections) of gaseous species and relevant functional groups; Figure 7b presents Raman spectra of biomarkers, re-

Fig. 6a

Fig. 6b

Fig. 6c
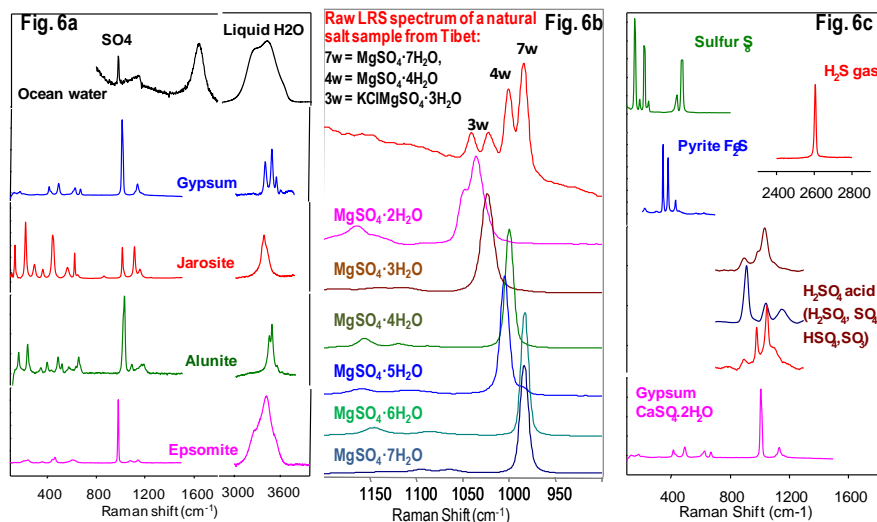
duced carbon, and molecular carriers of H, C, N, O, P that are of relevance to astrobiology (Mars, satellites of giant planets); Figure 7c shows Raman spectra of molecular species mixed with H_2O ice as might occur in the polar regions of Moon and Mars, as well as on satellites of the giant planets. Direct identification and characterization of such compounds can be made based on LRS data.

Test results on detection limits of bio-signatures by *in-situ* green Raman: As part of the MATISSE-CIRS project, we conducted a series of tests on the detection limits of bio-signatures, specifically on two groups that can have long periods of preservation in harsh environments. These include reduced carbon and chemical compounds (bio-markers) that have demonstrated preservation in ancient terrestrial rocks. We demonstrated [37] the detection of reduced carbon at 8 $\times 10^{-6}$ w/w in mixtures of an Archean chert with quartz, and the detection of four bio-markers at mole concentration from 10^{-3} to 10^{-5} in mixtures with gypsum.

In the detection of reduced carbon and biomarkers, *in-situ* green Raman compares favorably to deep UV-Raman due to the generally lower signal strength of the latter. We have observed over 100 times lower Raman signals from the UV-Raman channel during tests on two commercial Raman systems (Horiba and Renishaw), both have equally optimized UV- and Vis-Raman channels. A commonly accepted reason in the Raman spectroscopy community for the relatively poor Raman signal strength under UV-excitation is the shallow penetration depth of UV radiation into a solid sample, as well as the lower efficiency of many optical components in the UV-spectral range.

This comparison on published detection limits of bio-signatures by *in-situ* green laser Raman [37] vs. those by UV-Raman [38], and the fact that UV-Raman is rarely used in terrestrial (and geoscience) applications, suggest to us that the best configuration for a flexible planetary laser Raman system for fine-scale mineralogy and bio-signature detection is an *in-situ* green laser Raman system. CIRS, an *in-situ* green Raman unit for flight, has great science potential for future missions to the Moon, Mars, Venus, asteroids, and satellites of the giant planets.

Future plans: In the second and third years of the current MATISSE project, we will complete the environmental tests of all major optical components and we will finish optimization of the CIRS prototype and its environmental tests. We anticipate that CIRS will reach TRL 6.

References: [1] Wang et al., 1995, JGR, 100, 21189-21199; [2] Haskin et al., 1997, JGR, 102, 19293-19306; [3] Korotev et al., 1998, LPSC, abs#1797; [4] Wang et al., 1999, JGR, 104, 8509–8519; [5] Wang et al., 2004, JRS, 35, 504-514; [6]. Wang et al., 2004, Am. Minerals. 89, 665-680; [7] Kong et al., 2010, LPSC, abs# 2730; [8] Ling et al., 2011, ICARUS, 211, 101-113; [9] Takir et al., 2013, MPS, doi: 10.1111/maps.12171; [10] Haenecour et al., 2014, 11th GeoRaman, abs #5017; [11] Ling et al., 2014, 11th GeoRaman, abs #5089; [12] Wang et al., 2014, PSS; [13] Wang et al.,, 2006, GCA, V70, p6118-6135; [14] Wang et al., 2009, JGR, doi:10.1029/2008JE003266; [15] Ling et al., 2010, ICARUS, 209, 422-433; [16] Kong et al., 2011, JRS, doi10.1002/jrs.2790; [17] Wang and Ling, 2011, JGR, 116, E00F17; [18] Kong et al., 2011, Chem. Geology, 284, 333-338; [19] Wang et al., 2011, JGR, 116, E12006; [20] Wang et al., 2012, ICARUS, 218, 622-64; [21] Chou et al., 2012, JAES, dx.doi.org/10.1016/j.jseaes.2012.11.027; [22] Wang et al., 2013, ICARUS, 226, 980-991; [23]. McCollom et al., 2014, Am. Minerals, 99, 948-964; [24] Wang and Chou, 2014, ICARUS, 234, 162-173; [25] Wang et al., 1998, Appl. Spec, 52, 477-487.; [26] Wang et al., 2003, JGR, doi:10.1029/2002JE001902; [27] Wei et al.; 2013, GSA, abs #226899; [28] Wei et al., 2014, LPSC, abs #2428; [29] Wei et al., 2014, Mars-8, abs #1369; [30] Lambert et al., 2014, this volume; [31] Wang et al., 2003 LPSC, abs# 1753; [32] Goetz W et al. (2012) Planetary and Space Sci., 70, 134. [33] Edgett K S et al. (2012) Space Sci. Rev., 170, 259. [34] Minitti et al., 2014 LPSC, abs# 2029; [35] Minitti et al., 2012 LPSC, abs# 2249; [36] Wei et al., 2014, this volume; [37] Wei et al., 2014 LPSC, abs # 2847. [38] Beegle et al., 2014, LPSC, abs# 2835.