

FINE-SCALE, DEFINITIVE, AND COMPREHENSIVE MINERALOGY FOR A VENUS LANDING

MISSION, Alian Wang¹, James Lambert², Ian Hutchinson³, ¹Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, ²Jet Propulsion Laboratory, ³University of Leicester, UK. (alianw@levee.wustl.edu).

Three key questions: Among the terrestrial planetary bodies, we have the least knowledge about Venus. There isn't any meteorite that can be remotely assigned to a Venus origin. The geochemical data from Venera and Vega landing sites suggest a basaltic crust, but rich in incompatible elements (K, Th, U) similar to alkali-rich terrestrial oceanic island [1]. Venus has the youngest surface built through recent volcanic activities. With a dense atmosphere of high pressure and high temperature near the surface, Venus has the most interesting atmosphere-surface interactions. These characters make the mineralogy of the surface of Venus to be "the single most fundamental question" faced by any Venus landing mission [2]. The other two key questions are the chemical composition of the lower 22 km of Venus atmosphere, and the oxidation state of the surface of Venus [2, 3].

In situ Raman can provide the answers during a landed Venus mission: which will be described in following three aspects.

Definitive and Complete Mineralogy: *in situ* Raman measurements generate finger-print spectra for silicates, carbonates, sulfates, phosphates, oxides, sulfides, hydroxides, and etc., with sharp, non-overlapping spectral peaks thus enabling the definitive mineral identification from a spectrum of mixture (rocks or regolith). For example, thermodynamic equilibrium calculations predict many rock-forming hydrous silicates are unstable at Venus surface, but some Fe-free mica (estonite, phlogopite), some alkali-amphiboles (tremolite), and chloride-bearing scapolite might be stable [3, 4]. They all have characteristic Raman spectra that distinguish them from other silicates [5, 6]. Furthermore, it is critical during a landed Venus mission to determine whether or not the minerals which can buffer CO₂, HCl, and HF are present at surface. XRF of Venra and Vega provided indirect evidence of the present of carbonates by the mass deficits [2]. While using *in situ* microbeam Raman, direct ID of trace carbonates (calcite) was achieved in a study of martian meteorite EETA79001 [7], and F-, Cl-, and OH-bearing apatite have distinct Raman peaks [8]. The highly active volcanic processes and dense Venus atmosphere all make the sulfur-cycle to be a key player in Venus surface-atmosphere interaction. For which, to

identify and to quantify the products of S-cycle (S₈, Fe_xS_y, H₂SO₄-H₂O, HSO₃-H₂O, sulfide and sulfate minerals) in Venus surface/subsurface regolith bear great scientific significance, and they are all very strong Raman scatters (Fig. 1). For a planetary mission, a Raman system with very tight laser spot (microbeam Raman) is a necessity for the detection of trace minerals, in order to provide a complete mineralogy (major, minor, and trace minerals) for rocks or regolith.

Mineral Chemistry: Planetary Raman spectroscopy reveals cation speciation and cation ratio in a mineral through accurate Raman peak position readings, e.g., Mg/(Fe+Mg) in olivine [9]; Mg/(Fe+Mg+Ca) in pyroxene [10]; Or-Ab-An endmembers and intermediate feldspar [11]; Fe-Ti-Cr solid-solution oxides [12]; cation speciation in carbonates [13]; and the cation speciation & hydration degrees in sulfates [14]. For a planetary mission, a Raman system with spectral resolution better than 10 cm⁻¹ is required to provide the cation ratios within ± 0.1 uncertainty [9-14].

Rock Characterization: The relative peak intensities in the Raman spectrum of a rock are mainly affected by the crystal orientations of the mineral grains in the rock, which would very hard to know in most cases during a robotic planetary mission. Therefore, it is non-practical to extract the mineral proportions information on the basis of peak intensities in a Raman spectrum collected from a large sampling spot on a mixture (rock or regolith). On the other hand, this information can be extracted by using a microbeam Raman system with scan capability, i.e., on the basis of the occurring frequency of the Raman spectral pattern (or major peak)

of a mineral among > 100 Raman sampling spots. That occurring frequency is approximately proportional to the mineral proportion in a rock or regolith, the more sampling spots the higher statistical accuracy [15]. When using a highly condensed laser beam spot (6-25 μm), single mineral phase (or 2-3 phases only) would be excited that generates high S/N spectrum, which would facilitate high quality mineral ID and the extraction of mineral chemistry. Combination of these two sets of info would provide the compositional distribution a mineral phase within a rock (Fig. 2), which

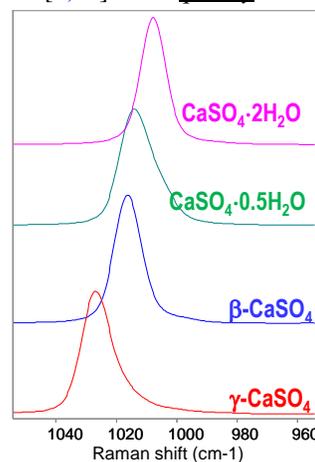


Fig 1. Ca-sulfates may exist at Venus surface

can be a direct reflection of the formation history of that rock [7]. For a Venus landing mission, a Raman system with high optical throughput that can generate a good S/N spectrum in < 1 min measurement duration (to accomplish >100 spot Raman scan in 1-2 hours) is required to provide these performances.

A high TRL microbeam Raman system for a Venus lander:

Planetary Raman spectroscopy provides rich and powerful information. However, Raman scattering is an intrinsically weak process with Raman cross sections of minerals $< 10^{-13}$. A Raman system for robotic planetary surface exploration requires carefully crafted optical configurations, with high Raman efficiency and robust optical-electronic-mechanic components/subsystems. Our studies of extraterrestrial materials and field tests led to a conclusion on the best Raman system architecture, to satisfy the need of fine-scale, definitive, and comprehensive mineralogy for planetary surface exploration.

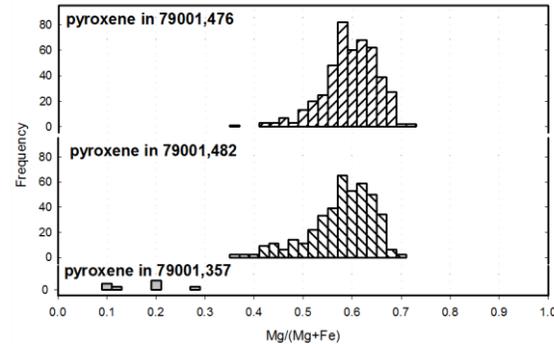
MMRS & CIRS configurations use the simplest, mature, and effective techniques, i.e. continuous wave, low power 532 nm laser, optics in visible spectral range, and conventional CCD. They both satisfy the requirements mentioned in above sections, i.e., $< 25 \mu\text{m}$ laser beam size, better than 10 cm^{-1} spectral resolution, line-scan capability, and especially, a f/2 optical chain to provide high Raman throughput.

MMRS development was supported by PIDDP, MIDP, ASTEP program and early MER mission development. It has a separate Raman probe connected through optical fiber to Raman spectrometer. MMRS was tested during three field seasons (2012-2015) in Atacama Desert, twice on Zoe rover ($> 50 \text{ km}$ traverse each time) and once stand-alone. These field studies [16] demonstrated a solid science performance and robust engineering of MMRS (TRL 5).

CIRS was developed on the basis of mature MMRS technology but having an all-optics-in-one architecture (i.e., without optical fiber). CIRS was supported by MatISSE program since 2013, with a goal to reach TRL 6. Currently, a prototype of CIRS was built and preliminary tests were done. Further system optimization is in progress. The environmental tests of major optical components (and some sub-systems) were accomplished or on-going.

Comparison with remote-Raman architecture: In the aspect science return, a microbeam *in situ* Raman architecture is much more advantageous than a remote-

Fig 2. Compositional distribution of pyroxene in martian meteorite EETA79001



Raman in following three aspects. (1) A **25-50 μm** sampling spot enables the detection of minor and trace minerals in a rock, while the large sampling spot (0.5-1 mm) of a remote-Raman allows only the detection of major or light-toned minerals. (2) The Raman photons collectivity of a f/2 optics is 10^2 to 10^4 times that of a f/20 to f/100 optics used by remote-Raman architecture.

(3) the adjustable **low power cw laser** avoids the overheating-damaging (or the generation of LIBS) of the target minerals, when compared with the pulse laser used by remote-Raman architecture.

These are exactly the reasons that the publications by WUSTL Raman team in past > 25 years were all based upon the use of microbeam Raman architecture, which demonstrated the wide and deep planetary applications. For the exactly same reason, before the realization of microbeam Raman architecture in 1980s, there were practically no geological applications of Raman spectroscopy, none for planetary applications.

A special deployment for a Venus mission: MMRS & CIRS systems both work in visible spectral range (532-675 nm), thus allow the laser excitation and Raman photon collection through a transparent window (fused silica or sapphire). This character will enable Raman measurements to be made behind a window in a Venus lander, on which Venus surface/subsurface sample could be delivered onto from outside. Depending on the desired S/N in Raman spectra, CIRS or MMRS can generate 100 spectra (spots) in **1-2 hours**.

Acknowledgement: NASA-MatISSE NNX13AM22G.

References: [1] McLennan, 2014, 45th LPSC, abs# 1868; [2] Fegley et al., 1997, in Venus II, 591-636; [3] Fegley and Treiman, 1992, in Venus and Mars: Atmosphere, Ionosphere, and Solar Wind Interaction, 7-71; [4] Zolotov et al., 1997, Icarus, 130, 475-494; [5] Wang et al., 2015, JRS, DOI: 10.1002/jrs.4680; [6] Wang et al., 1994, Appl. Spec, 48, 959-968; [7] Wang et al., 2004, JRS, 35, 504-514; [8] Shea et al., 1974, Arch Oral Biol. 19, 995; [9] Kuebler et al., 2006, GCA, 70, 6201-6222; [10] Wang et al., 2001, Am. Minerals, 86, 790-806; [11] Freeman et al., 2008, Can. Minerals, 46, 1477-1500; [12] Wang et al., 2004, Am. Minerals, 89, 665-680; [13] Herman et al., 1987, Appl. Spec., 41, 437-440; [14] Wang et al., 2009, JGR, 114, doi:10.1029/2008JE003266; [15] Haskin et al., 1997, JGR, 102, 19293-19306; [16] Wei et al., JRS, v10., DOI: 10.1002/jrs.4656;