

INVESTIGATING SURFACE MINERALOGY, ALTERATION PROCESSES, AND BIOMARKERS ON MARS USING LASER RAMAN SPECTROSCOPY Alian Wang, B. L. Jolliff, and L. A. Haskin, Department of Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, Campus Box 1169, One Brookings Drive, St. Louis, MO 63130. <alianw@levee.wustl.edu>.

Introduction: In a surface investigation of Mars, a key priority should be definitive identification and characterization of surface materials (e.g., definitive mineralogy), which will improve our understanding of Mars' evolutionary history. As used here, "definitive" mineralogy includes mineral identification and determination of key mineral chemical compositions; however, it is also important to determine the relative proportions of different minerals in a rock or soil as well as textural relationships of mineral assemblages. Because we know the chemical and physical conditions under which individual minerals form, we learn about past martian environmental conditions from such detailed mineralogical information. The record of alteration in surface rocks is expected to reach back in time from relatively recent alteration of rock surfaces, to past stream and lake environments, to hydrothermal settings of the upper martian crust, and to the planet's early igneous chemical differentiation. An assessment of whether life might have formed on Mars requires a broad understanding of the nature of the planet, with an emphasis on the presence and role of water during its evolution. With better knowledge of past and present Mars' environments, we can speculate more rationally on the possible development of life on Mars.

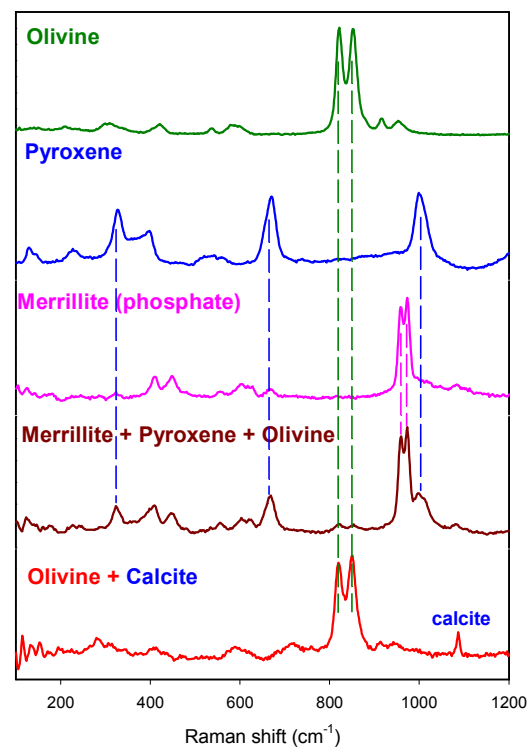
Despite a wealth of information from past and on-going missions to Mars, the capability to determine the mineralogy of surface materials and to connect mineralogy with lithologic characteristics that are diagnostic of the environment in which those materials formed remains inadequate. The 2003 Mars Exploration Rovers (MER) will carry a Mini-TES and a Mössbauer spectrometer, which will provide some detailed mineralogy information. For general characterization of minerals and/or biogenic phases (reduced carbon, PAHs, etc) on the surface of Mars, we have been developing a miniaturized laser Raman spectrometer for *in situ* analyses -- the Mars Microbeam Raman Spectrometer, MMRS [1]. We are also developing strategies to use Raman spectroscopy as a stand-alone technique and to be used synergistically with other *in situ* analysis methods in future planetary missions. Through studies of Martian meteorites and terrestrial analogs, we are gaining experience of what compositional and structural information can be obtained on key mineral groups using *in-situ* Raman measurements. We are developing methods for determining mineral proportions in rocks or soils and identifying rock types from sets of closely spaced, rapidly acquired spectra. We are studying how weathering and alteration affect the Raman and luminescence features of minerals and rocks,

and we are investigating the Raman characteristics of biogenic organisms and their remains. These studies form the scientific basis for *in-situ* planetary Raman spectroscopy, and they are being done in parallel with instrument development towards a flight version of the MMRS [1].

Planetary Raman spectroscopy. Laser Raman spectroscopy is well suited for on-surface mineralogical investigations of Mars for the following reasons:

1) It is definitive; i.e., minerals are unambiguously identified through their fingerprint spectra. Raman peaks are sharp and non-overlapping; straightforward identification of phases in a mixture can be achieved from raw spectra, spectral deconvolution in general is not required. Figure 1 shows five spectra taken from EETA79001, three single phase spectra (olivine, pyroxene, phosphate) and two mixture spectra in which the contributing phases are obvious.

Figure 1. Single-phase and multi-phase Raman spectra obtained from EETA79001 martian meteorite



2) Raman spectroscopy does not suffer from a "grain size effect." Raman peak positions and peak widths do not change even when the size of particles decreases to 1-2 μm , although overall intensity may decrease because of scattering.

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3) Analyses are rapid, requiring only a few seconds to half a minute to obtain a spectrum.

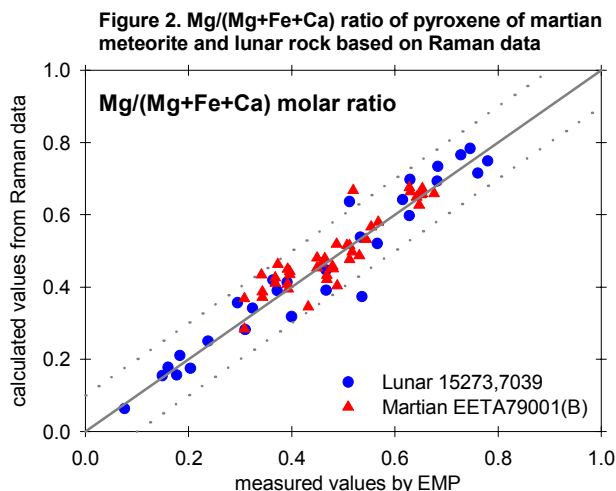
4) The analysis method requires no sample positioning, a Raman probe will send a laser beam towards sample surfaces (rock or soil), and will collect the backscattered radiation.

5) No sample preparation is required; original rough surfaces of rocks and soils give informative spectra. Freshly exposed surfaces, potentially available if the rover carries a rock abrader, are best for studying original rock mineralogy, but rock coatings are important to determining environmental effects [2].

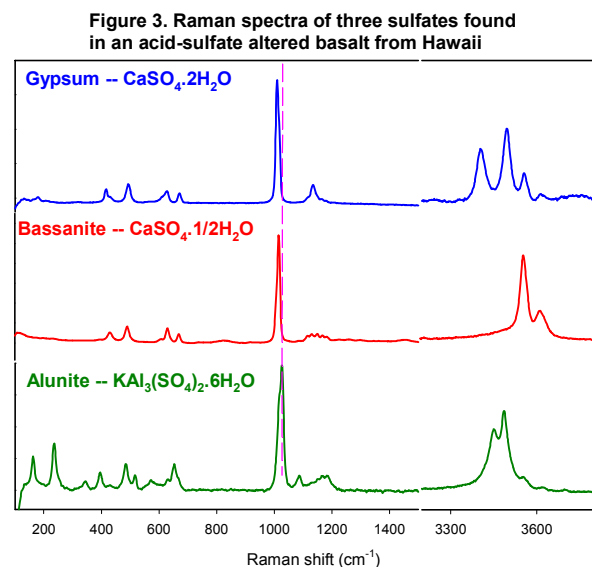
6) It provides approximate minerals modes, rock identification, and information on grain size and rock texture through our Raman “point-counting” procedure, [3, 4]. Broader-beam techniques integrate over major, minor, and trace minerals in a sampling area such that less abundant phases may not be definitively identified because the spectrum is dominated by the major phases. Minor and trace phases register strongly with the microbeam Raman technique when they fall within the small sampling area (10-30 μm) activated by the laser beam. Alteration minerals that occur in cracks and vesicles would likely be detected and identified within the linear scan (~ 1 cm) by the Raman probe (e.g., [5]). The spatial relationships within mineral assemblages are obtained in the same way; sets of juxtaposed minerals that form together at various locations within a rock can be key to discovering possible biologically mediated formation of a mineral or mineral assemblage.

In the following paragraphs, we describe examples of results from our planetary Raman spectroscopic studies that demonstrate the usefulness of this technique and the potential of the MMRS for future missions.

Silicate mineralogy. Raman spectroscopy provides straightforward identification of silicates, including ortho-, chain-, double-chain-, ring-, layer-, and framework-silicates [6]. The differences in degree of polymerization of the major silicate groups provide distinct and systematic variations in their Raman spectral patterns. Furthermore, Raman peak positions of some mafic silicate minerals provide information on cation ratios, e.g., Mg/(Mg+Fe) in olivine [7] and Mg/(Mg+Fe+Ca) in pyroxene [8], which relate directly to rock genesis. Figure 2 compares Mg/(Mg+Fe+Ca) ratios in pyroxene derived from Raman data and those analyzed by electron probe microanalysis. Based on the compositional distribution of pyroxene (and olivine) in a rock, we obtain insight on the cooling rates of parent magmas and the crystallization of that rock. The Mg/(Mg+Fe) variations in olivine and pyroxene grains along a Raman point-count traverse reveal three generations of olivine during the formation of EETA79001 martian meteorite.



Carbonates, sulfates, phosphates. Raman spectroscopy provides excellent sensitivity for oxyanionic minerals, e.g., carbonates, sulfates, and phosphates (e.g., [9]). The strong covalent bonding in CO_3 , SO_4 , and PO_4 groups provide characteristic strong and narrow Raman peaks, which are readily detected even in mixtures and at low concentrations. Major cation variations (e.g., Mg, Fe, Ca) can be determined from well resolved peak positions. Figure 3 shows Raman spectra of three sulfates found in a Hawaiian acid-sulfate altered basalt; peaks from the H_2O vibration occur in the 3200–3800 cm^{-1} region.



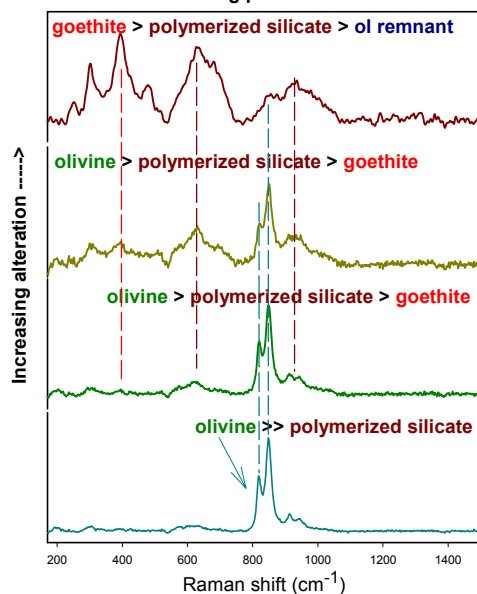
Oxides and oxyhydroxides -- Fe-oxides and oxyhydroxides have modest covalent character, and thus are relatively weak Raman scatterers. Chromite, magnetite-ulvöspinel, ilmenite-hematite and their solid solutions are, nevertheless, well characterized by the spectral patterns and positions of their major and minor Raman peaks, so they can be distinguished even based on spectra with low S/N. In some cases such as in the

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chromite series, major cation ratios can be determined from variations in Raman spectra [10, 11].

Alteration mineralogy. In addition to the main rock-forming minerals, phases formed at different stages of alteration and information about their degree of structural order can be identified. We have studied a basalt cobble from Lunar Crater Volcanic Field, NV, in which olivine grains altered to iddingsite along their edges and fractures [12]. The structure of altered olivine affects its Raman peak positions and peak widths, so it can be distinguished from unaltered phenocrystic olivine. A more polymerized structure (between chain and phyllosilicate) was formed where alteration was more intense. Goethite and hematite were identified among the products of alteration. Figure 4 shows phase variations in the alteration zone.

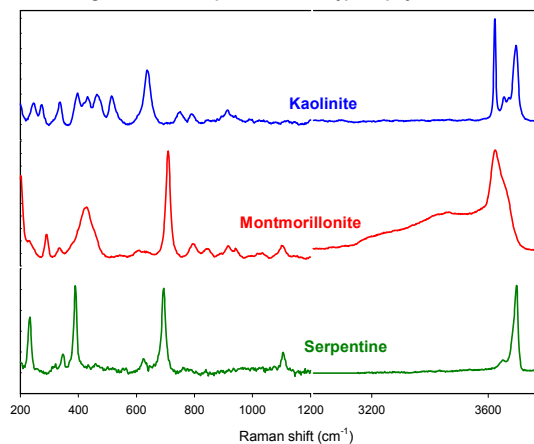
Figure 4. Raman Spectra taken in linear traverse showing phase variations



Mineralogical and other forms of H₂O. Water of all forms, ice, liquid, gaseous, bound (OH), clathrate, and unbound (H₂O) in minerals have characteristic Raman features. The Raman spectral features of hydrous phyllosilicates provide a way to distinguish their structures (di-octahedral or tri-octahedral), chemistries (Mg, Fe, Al-bearing), local site symmetry, and the types and number of crystallographically equivalent sites around OH groups [13]. Figure 5 shows Raman spectra of two di-octahedral clay minerals (kaolinite & montmorillonite) and a tri-octahedral phyllosilicate (serpentine).

Organic materials. Graphitic carbon and organic C-C, C-H, C-O, C-N, bonds are strong Raman scatterers. We detected reduced carbon in a 3.35 Ga chert from South Africa (Fig. 6) to a level of ≤ 50 ppm using the MMRS brassboard [8]. In a study of a weathered basalt cobble, we encountered a crustose lichen in a

Figure 5. Raman spectra of three typical phyllosilicates



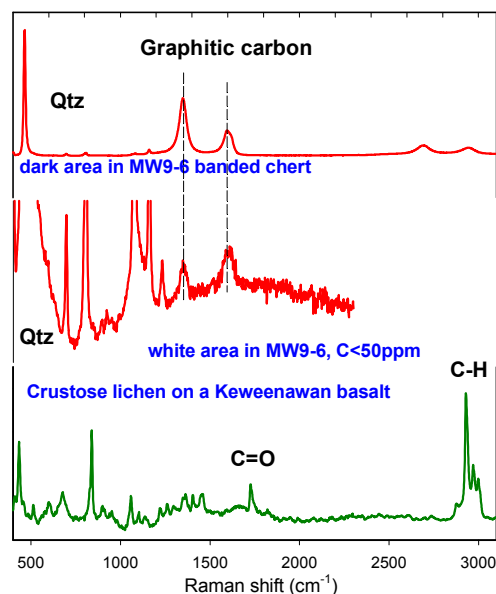
Raman point-count traverse, and its protective wax coating yielded strong Raman peaks.

Laser Raman spectroscopy for planetary surface analysis has some limitations, as follows:

Raman spectroscopy is not well suited to detect strongly ionic minerals such as halite. Simple salts with more covalent character, however, give useful spectra, e.g., fluorite, CaF₂.

Glassy materials yield relatively broad and weak spectra, and the extraction of signals for glass beneath the spectral peaks of crystalline phases is difficult. Nonetheless, basaltic glass and silica-rich glass are easily observed and can be distinguished in spectra of low background.

Figure 6. Raman spectra of reduced carbon and a crustose lichen



Some materials photoluminesce to the extent that mineral spectral features are obscured. On the other hand, intense photoluminescence carries valuable information; for example, it is commonly associated with organic matter in terrestrial materials. Inorganic photo-

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luminescence seldom prevents mineral identification, and provides additional information on mineral compositions, such as the existence of rare-earth elements and Mn^{2+} .

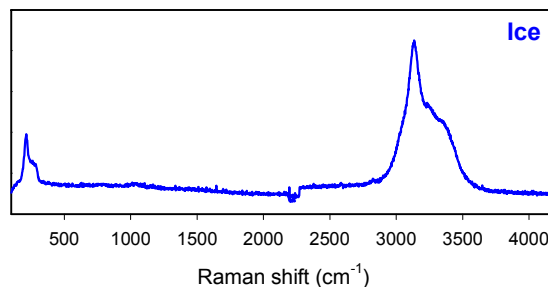
Current development status of the MMRS. The Mars Microbeam Raman Spectrometer (MMRS) was designed to achieve the desired scientific performance as described in above section, and was described in detail by [1]). The MMRS has three major parts: a Raman probe, a miniaturized spectrograph, and electronics (including the laser). The mass of the MMRS is ~2.6 kg. Operationally, the Raman probe will be positioned against the target by a robotic arm of a rover or a lander or fixed in place and samples delivered to it. A set of 50–100 spectra will be taken along a ~1 cm traverse on the target during a 1–4 hour period. Total energy usage is estimated to be ~35 Whrs per 100 spectra.

The current status of the MMRS is that an advanced brassboard (ADBB) of MMRS is accomplished this year [13]. The probe and spectrograph have been redesigned with improved optics, and the electronics have been miniaturized. The CCD detector is now cooled thermoelectrically in anticipation of eventual terrestrial field testing of the instrument. Based on measurements on a set of standard common minerals (quartz, feldspar, olivine, pyroxene and calcite), the ADBB has a detection sensitivity ~40% that of our state-of-the-art laboratory Raman system, thus twice that of the previous MMRS brassboard. The ADBB has an improved spectral resolution, and still maintains the required spectral range ($207\text{--}4325\text{ cm}^{-1}$), which to covers the fundamental vibrational bands of minerals, OH, H_2O , and organic species. The ADBB also has an improved Raman-to-photoluminescence S/N ratio, and an improved depth of sampling field. Target surfaces are likely to be rough and uneven in the field; the design of the MMRS nevertheless eschews automatic focusing for the sake of system simplicity. To compensate, the probe has a substantial depth of sampling field (DSF).—The DSF of ADBB is >12 mm for a colorless calcite and a light green olivine, and ~2 mm for a very dark pyroxene.

A whole-system cold performance test at -24°C was conducted for the ADBB system at the National Ice Core Laboratory, Denver. Raman spectra of ice and mineral grains embedded in ice were obtained (Fig. 7).

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Figure 7. Raw spectrum obtained at -24°C from ice core



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