

Remote Raman Measurements of Minerals with Mars Microbeam Raman Spectrometer (MMRS)

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Introduction: In a rover or lander-based investigation of Mars, a key priority should be detailed and definitive characterizations of minerals and impact glasses on the surface and exposed subsurfaces in craters. These mineralogical data will improve our understanding of Mars' evolutionary history. Remote Raman investigations of surface and sub-surface mineralogy in crater walls could provide information about the changes caused by (i) past stream and lake environments, (ii) hydrothermal interaction with the upper Martian crust, and (iii) the planet's early igneous chemical differentiation. An assessment of whether life might have formed on Mars calls for a better understanding of the nature of the planet, with an emphasis on the presence and role of water during its evolution. Laser Raman spectroscopy has potential for yielding better knowledge of past and present Mars' environments, by examining any organics and biominerals that may be present on Mars. With these data, we could provide a more rational view of the possible development of life on Mars. Micro-Raman [1-5] and remote Raman spectroscopy [6-9] have been demonstrated to be effective tools for investigating mineralogy of terrestrial rocks and Martian meteorites; as the Raman lines of minerals are sharp and distinct. The Raman fingerprints of minerals do not shift appreciably and remain distinct even in sub-micron grains and so can be used for mineral identification in fine-grained rocks [e.g., 10]

In order to use the remote Raman spectrograph for space mission, it is essential to minimize the size, weight, and power consumption of the instrument. Toward this goal, we have measured remote Raman spectra of various minerals with the UH remote Raman receiver interfaced with the miniaturized Mars microbeam Raman spectrometer (MMRS), conceived and developed at Washington University, St. Louis [11].

Equipment: A photograph of the Washington University/JPL MMRS prototype instrument interfaced to the remote Raman receiver is shown in Fig. 1. The remote Raman receiver was interfaced with a 500 micro-meter fiber to the MMR spectrometer. The Raman receiver is a modified version of an earlier instrument [8] developed at the University of Hawaii. The receiver system consists of a 127mm telescope (Meade ETX-125 Maksutov Cassegrain, 125mm clear aperture, 1900mm focal length), and a frequency doubled mini Nd:YAG laser source (Model ULTRA CFR, Big

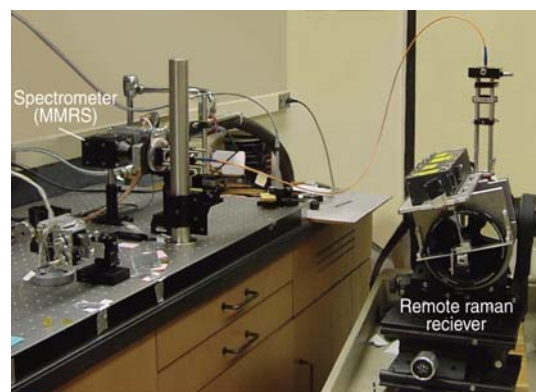


Fig. 1. Photograph of the remote pulsed Raman set up. The pulsed laser is mounted on the top of 125mm telescope. The Fiber-Optic (FO) cable transmits the Raman signal to the MMRS spectrograph equipped with a CCD detector.

Sky Laser, 532nm, 35mJ, 20Hz). The width of the laser pulse was approximately 8ns, and the beam divergence of the central laser spot was less than 0.8 mrad. The fixed slit width of MMRS is 50 μ m, and the instrument was used without any modification. Details of MMRS for micro-Raman measurements are described elsewhere [11]. A conductively cooled CCD detector was used for recording Raman spectra. The remote Raman measurements were made at 8.5 m, limited by the space available in the laboratory. All measurements were made in the dark.

Samples: Mineral samples from the Washington University collection were used for remote Raman measurements. These samples included quartz, pink quartz, microcline, potassium feldspar, tremolite, calcite, gypsum and barite. The mineral samples were used without any cutting or polishing. In addition Raman spectra of water, and acetone were also recorded. All experiments were conducted at the Raman Laboratory of Washington University.

Results and Discussion: Figure 2 depicts typical remote Raman spectra of calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), α -quartz, and K-feldspar (KAlSi_3O_8) measured from a distance of ~ 8.5 m. These spectra are collected with integration time of 60 s to improve signal to noise ratio. In Fig. 2 the Raman fingerprints of carbonate ions at 1085 cm^{-1} in the calcite spectrum,

and of sulfate ions at 1009 cm^{-1} in the gypsum spectrum are present. The 464 cm^{-1} , $\nu_s(\text{Si-O-Si})$ symmetric stretching modes of the 6-membered rings of SiO_4 tetrahedra in α -quartz, and the Raman fingerprints of the $\nu_s(\text{T-O-T})$ modes of 4-membered rings of TO_4 tetrahedra, where $\text{T} = \text{Si}$ or Al , are clearly visible in the spectra of these silicates (Fig.2) The assignments of these Raman bands of α -quartz and K-feldspar both in crystalline and glassy phases are discussed

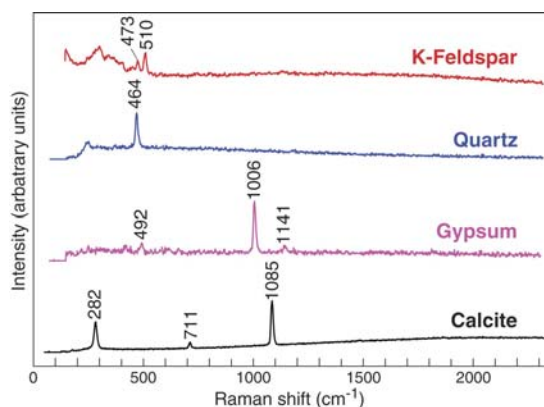


Fig. 2. Telescopic unpolarized Raman spectra of a variety of minerals measured at a distance of ~ 8.5 m. Laser power 35mJ/pulse @ 532nm, integration time 60 s, slit $50\text{ }\mu\text{m}$

elsewhere [6, 11-12]. The $\nu_s(\text{T-O-T})$ and $\nu_{as}(\text{T-O-T})$ Raman bands are also known to be sensitive indicators of shock amorphization of plagioclase crystals, as well as to shock history of the glasses [3]. These fingerprint Raman bands can be used to estimate the peak shock pressure of the shocked materials on a planetary surface. The telescopic Raman spectra thus have potential to be used for distinguishing between glasses formed by volcanic processes and glasses formed by impact processes.

In addition, we measured successfully remote Raman spectra of pink quartz, microcline, potassium feldspar, tremolite, calcite, gypsum and barite with the remote Raman-MMRS system. All of these minerals spectra have characteristic Raman fingerprints. We also successfully recorded Raman spectra of water and water ice, and acetone with the remote Raman-MMRS system. Both in the low-frequency region as well as in C-H and O-H stretching regions.

Our data clearly show that remote Raman measurements can be made with a miniaturized Raman spectrometer such as MMRS. As compared with the laboratory based system, the spectra with the Remote Raman-MMRS instrument are weaker in intensity. One possible reason is the narrow $50\text{ }\mu\text{m}$ fixed slit of the MMRS as compared to the 100 to $160\text{ }\mu\text{m}$ slit used

with the laboratory based remote Raman spectrometers [6-9]. We were not able to record the remote Raman spectra of olivine and of rocks that have low Raman cross-sections because of this mismatch. Since the MMRS is not specifically designed for remote Raman spectroscopy, it was difficult to interface efficiently the light from telescope with MMRS's entrance slit resulting in high coupling losses at the interface.

The current CCD detector of the MMRS operates in continuous wave (CW) mode and cannot be gated. This restricts the use of the existing MMRS in the dark or at night time only. We are in process of developing fast gating of the light in the optical fiber as well as acquiring a CCD with fast electronic shutter so that day and night time measurements can be made with remote Raman spectrometer. It is anticipated that the optical coupling system and the CCD detector of MMRS can be optimized so that it can be used both for micro-Raman and remote Raman measurements.

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