

Remote Sensing with a Spatial Heterodyne Raman Spectrometer for Mineralogical Analysis at 5 Meters. M. J. Egan¹, S. K. Sharma¹, and S. M. Angel², ¹Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, HI 96822, USA, Email: eganm@hawaii.edu, ²Dept. of Chem. & Biochem., University of South Carolina, Columbia, SC 29208, USA, Email: smangel0@mailbox.sc.edu

Introduction: Modern planetary missions typically require spectroscopic tools capable of unambiguously identifying organics, inorganics and biomarkers. Raman spectroscopy is ideally suited to fulfill these requirements due to its selectivity to chemical environments and ease of analysis due to its narrow spectral features. Recently, Harlander^[1] invented a new type of interferometer, the spatial heterodyne spectrometer, which is capable of measuring Raman spectra^[2] with high resolution in a compact, light footprint system. A spatial heterodyne Raman spectrometer (SHRS) is a Michelson interferometer variant in which the mirrors of a Michelson are replaced with two stationary diffraction gratings. The light entering SHRS is incident upon the diffraction gratings, and the diffracted wavefronts recombine as crossed wavefronts at the beam-splitter, creating an interference pattern in space, which is imaged by an intensified charge-coupled device (ICCD) camera. The resulting interference pattern is Fourier transformed, yielding a Raman spectrum. The purpose of the present work is to test the efficacy of SHRS on a relatively large (25 mm diameter spot) area of carbonate, sulfate and silicate minerals at a distance of 5 meters that might be useful for planetary exploration.

Samples: The rock-forming minerals (calcite, dolomite, smithsonite, gypsum, anhydrite, barite, plagioclase, quartz, and forsterite) were purchased from Ward's Natural Science Establishment Inc. (Rochester, NY USA). All samples were measured without cutting or polishing. The carbonate minerals calcite, dolomite, and smithsonite were from Chihuahua Mexico, Bamble Norway, and Arizona USA, respectively. The sulfate minerals gypsum, anhydrite and barite were obtained from Utah USA, Windsor Nova Scotia Canada, and Missouri USA, respectively. Finally, the silicate minerals plagioclase, α -quartz, and forsterite were from Colorado USA, Minas Gerais Brazil, and North Carolina USA, respectively. The average composition of the plagioclase feldspar was $Ab_{23.5}An_{75.96}Or_{0.39}$ as measured with electron microprobe, where $Ab = NaAlSi_3O_8$, $An = CaAlSi_2O_8$ and $Or = KAlSi_3O_8$.

Experimental: The SHRS instrument design used in this work is similar to the design described by Gomer^[2]. The light source is a diode-pumped Nd:YAG laser operating at 532 nm, 100 Hz and 8.6 mJ per pulse. The laser beam is expanded to 25 mm diameter spot with a 2x Ronar-Smith beam expander, reflected

off a mirror and directed onto a sample 5 meters away. The light is scattered off the sample and collected by a Questar 100 mm telescope. The collected light is then filtered with two 532 nm long-pass filters that reject Rayleigh scattered light. The filtered beam of light is then split 50/50 by a cube silica glass cube beam splitter and directed onto a 150 grooves per mm diffraction gratings. The diffracted wavefronts recombine at the beam-splitter and the interference pattern is imaged by a Nikon f/1.8 lens and a Princeton Instruments ICCD camera. The FT of this interferogram is taken, which results in a Raman spectrum

Results and Discussion: The following spectra were collected with the experimental setup described above. The accumulation time for the carbonate and sulfate minerals was 10 seconds with a camera gain of 150; the accumulation time for the silicate mineral spectra was 30 seconds with a camera gain of 250. The reason for the longer accumulation time and higher camera gain for the silicate minerals is that the silicate minerals have a lower Raman scattering efficiency and so could not be measured with adequate signal to noise ratio (SNR) in 10 seconds and 150 camera gain.

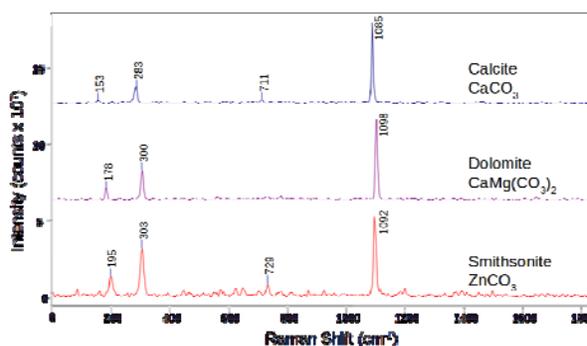


Fig. 1 Raman spectra of carbonate minerals calcite, dolomite and smithsonite taken at 5 meters.

Figure 1 illustrates the Raman spectra of three carbonate minerals – calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and smithsonite ($ZnCO_3$). The characteristic features of carbonate ions in these minerals are the symmetric stretching (ν_1) and antisymmetric bending (ν_4) of the carbonate anion present between 1085-1100 cm^{-1} and 710-730 cm^{-1} , respectively. Another important feature is the lattice vibrations^[3-5] that occur in the Raman spectrum between 150-300 cm^{-1} that distinguish one carbonate mineral from another. For example, the lattice modes of calcite appear at 153 and

283 cm^{-1} , the lattice modes for dolomite are observed at 173 and 300 cm^{-1} and at 193 and 303 for smithsonite. The change in chemical environment for each of these carbonate minerals causes a shift in the vibrational wavenumber of these modes, which is quantified by the Raman spectrum.

Figure 2 depicts the Raman spectra of three sulfate minerals – gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4) and barite (BaSO_4). The most prominent feature of the vibrational spectra of sulfate ions in these minerals^[6-8] is the symmetric stretch (ν_1) of the sulfate anion that appears between 990-1020 cm^{-1} . Other important features include the symmetric (ν_2) and antisymmetric bending (ν_4) modes of the sulfate anion that appear between 400-500 cm^{-1} , and 600-700 cm^{-1} , respectively. In the spectrum of gypsum the sulfate symmetric stretching mode appears at 1009 cm^{-1} , which is lower than the corresponding Raman line of anhydrite due to the excess of hydrogen bonding of the SO_4^{2-} ions with water molecules.

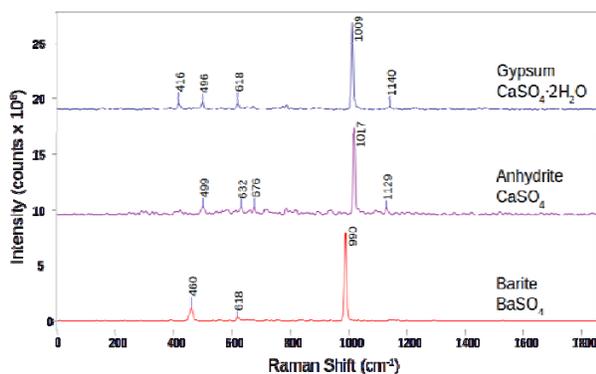


Fig. 2 Raman spectra of sulfate minerals gypsum, anhydrite and barite taken at 5 meters.

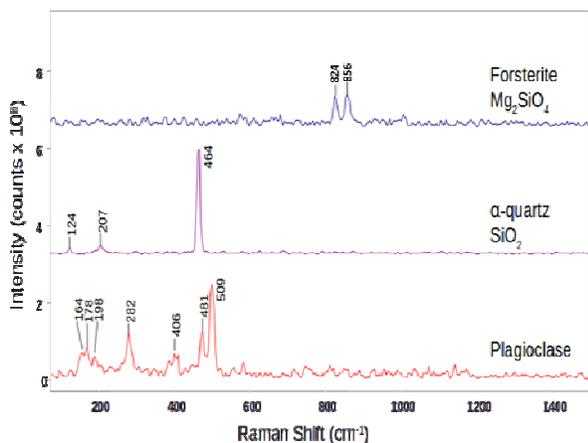


Fig. 3 Raman spectra of silicate minerals forsterite, α -quartz and plagioclase measured from 5 meter distance.

Figure 3 shows the Raman spectra of silicate minerals – forsterite (Mg_2SiO_4), α -quartz ($\alpha\text{-SiO}_2$) and

plagioclase ($\text{Ab}_{23.5}\text{An}_{75.96}\text{Or}_{0.39}$). The most striking and identifiable features of forsteritic-rich olivines is the doublet consisting of Raman lines at 824 and 856 cm^{-1} . This doublet originates from the $\text{Si-O}_{\text{non-bridging}}$ bond stretching in the $[\text{SiO}_4]^{4-}$ tetrahedra and has a mixed character of ν_1 and ν_3 modes^[9-11]. The Raman line at 464 cm^{-1} in the spectrum of α -quartz, originates from the symmetric stretching mode of the six-membered ring SiO_4 tetrahedra. The Raman lines at 207 and 464 cm^{-1} are the Raman fingerprints of α -quartz, and can be used to distinguish this mineral with high certainty. The most distinctive features of the feldspar mineral spectrum are the 4-membered TO_4 , where T = Si or Al, tetrahedral ring breathing modes located between 450-520 cm^{-1} in the Raman spectrum. In the highly ordered microcline polymorph of KAlSi_3O_8 , the three Raman lines at 475, 484 and 513 cm^{-1} are observed¹³.

Summary: Spectra of low Raman efficiency minerals olivine and plagioclase feldspar with SHRS are measured for the first time. The spectra presented in this work demonstrate the efficacy of SHRS in measuring Raman spectra of carbonate, sulfate and silicate minerals over a diameter of 25 mm without scanning at a distance of 5 meters.

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