

**LASER RAMAN SPECTROSCOPIC DETERMINATION OF MINERAL PROPORTIONS IN ROCKS ON PLANETARY SURFACES.** LARRY A. HASKIN, ALIAN WANG, BRADLEY L. JOLLIFF, RANDY L. KOROTEV, KAYLYNN M. ROCKOW, AND KAREN M. VISKUPIC, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130 (lah@levee.wustl.edu)

Identifying rock types and understanding the conditions of rock and soil origin by on-surface planetary remote sensing requires characterization of the component minerals of the rocks and soils. First-order aspects of characterization are mineral identification, mineral compositional determination (obtaining mineral end-member proportions), and mineral quantification (determining the proportion of the mineral in the rock or soil). Laser Raman spectroscopy can be used to identify unambiguously major, minor, and accessory lunar minerals (silicates, phosphates, some oxides); Raman spectra of these minerals have sharp peaks that do not overlap with each other [1, this work]. It can also determine approximate  $\text{Mg}^{2+}/\text{Fe}^{2+}$  ratios for olivines and pyroxenes from peak shifts. Pyroxene compositions are obtained to first order by identifying structural type (orthopyroxene, clinopyroxene, and pyroxenoid), which yields information about  $\text{Ca}^{2+}$  concentrations, and  $\text{Mg}^{2+}/\text{Fe}^{2+}$  ratios can be constrained by using peak shifts [2]. The work described here shows how to quantify the relative abundances of minerals in a rock or soil using small-beam ( $\leq$  tens of  $\mu\text{m}$ ) laser Raman spectroscopy.

For a polyphase target such as a rock or a soil, a broad, fairly representative area might be sensed a spectroscopic method and the fraction of that area occupied by a mineral could be related quantitatively to the peak intensities for that mineral. This procedure does not seem feasible for on-surface Raman spectroscopy for two reasons: (1) Laser beam diameters for planetary Raman spectroscopy need to be small in order to provide high power density for good signal-to-noise ratio at low total laser power. A narrow beam does not sample a representative area of a rock surface, however. (2) Numerous, mostly uncontrollable factors affect Raman peak intensities. In spectroscopy of single crystals or multicrystal systems, important factors are frequency of the exciting laser, Raman cross section of the mineral (which depends on the strength of the covalent bonding), crystal orientation relative to the direction of laser polarization, and long-range chemical and structural ordering in the crystal lattices. Especially for multigrain samples, experimental factors affect peak intensities; these include laser power density to the sample and effective sampling volume. Laser power density depends on laser power, beam diameter, and angle of incidence on the sample. Effective sampling volume depends on both the depth and the diameter of the region of excitation and scattering. These are functions of laser focus position, mineral grain size, mineral transparency to both incident beam and scattered radiation, reflections and refractions associated with grain boundaries (and thus indices of refraction), and roughness of sample surface. All of these factors combine to prevent any simple relationship between relative intensities of Raman scattered radiation and mineral concentrations, even if the laser spot is broad enough to illuminate a large number of mineral grains.

Under practical conditions of planetary surface remote sensing, a single laser spot may excite only one mineral grain of a rock, and in most rocks and soils not more than several grains. With a modern Raman spectrometer, the spectrum of a single spot can be obtained rapidly, probably less than two minutes per spectrum on a planetary surface. We can take advantage of the high spatial resolution and short acquisition times for both qualitative and quantitative analysis by obtaining spectra from, say, 100 separate points on each sampling area of interest. This provides definitive identification of most minerals and useful information about mineral compositions and textures of a rock or soil in just a few hours. We can obtain detailed characterizations of individual mineral grains from the individual spectra, which will have high signal-to-noise ratio because of high laser power density, and we can estimate mineral proportions in the rock from the fraction of the spectra in which the characteristic peaks for each mineral appear. This technique is analogous to the well established procedure of "point counting" used by petrographers. To demonstrate the value of this technique, and to evaluate the ability of Raman analysis to determine mineralogy on a rough, unprepared surface, we have done a 100-point analysis by Raman spectrometry on a lunar rock fragment (sample 15273,7039) taken from a lunar soil, with each laser spot centered on a strict geometric grid.

The sample, 15273,7039, was a previously unstudied, 32-mg fragment from regolith sample 15270, from station 6, Apollo 15 on the Apennine Front. Under the binocular microscope it appeared to be a fine-grained igneous rock with a basaltic texture. Prior to analysis, it was rinsed ultrasonically with acetone. For Raman analysis, it rested in a shallow well ( $\sim 0.5 \text{ cm} \times 2 \text{ mm}$  deep) drilled into an aluminum block, which was placed on the microscope stage of a laboratory micro-Raman spectrometer (Jobin-Yvon S3000<sup>TM</sup>). The block was moved in fixed increments ( $\sim 330 \mu\text{m}$ ) along the X axis of a traveling stage until the width of the sample had been traversed, then it was moved by one increment in the Y direction and the next line of points obtained. The microscope was brought into rough focus at each point. Typical spectra are shown in Fig. 1. Signals from two minerals were observed in the spectra from 29 of the points and signals from three minerals were observed in the spectra from 2 of the points. The 100 points analyzed yielded 131 identifiable mineral signals. Two points that fell on fine-grained areas that were steeply sloped along the axis of the laser beam yielded no peaks. Mineral phases in six spectra remain unidentified.

Results of the 100-point modal analysis obtained by Raman spectroscopy are compared in Table 1 to results obtained by petrographic examination of an interior polished section made after the Raman analysis. The proportion of plagioclase obtained from the Raman analysis is lower than

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that found by petrographic analysis, but the polished section revealed that plagioclase is heterogeneously distributed. Proportions of total pyroxene agree between the rock surface and the polished section, but the fraction that is orthopyroxene is higher in the Raman analysis. This discrepancy occurred because the pyroxenes are strongly zoned, and Raman points and petrographic points did not coincide perfectly. The Raman analysis also yielded a higher proportion of cristobalite than the petrographic analysis, but cristobalite, like plagioclase, is heterogeneously distributed. The sum of the proportions of the four major minerals (plagioclase, ortho- and clinopyroxene, and cristobalite) is 89% for the Raman analysis and 90% for the petrographic analysis. The petrographic point count of the interior section yielded ~4% ilmenite and 7% mesostasis. This compares well with the combined 13 points for K-feldspar, whitlockite, apatite, unknowns, and “no peaks” in the Raman analysis. The identification of the rock type, basalt, is evident from the mineralogy as determined by the Raman experiment. The characteristics of the pyroxenes and the high proportion of phosphate and cristobalite indicate an evolved lithology, namely, a KREEP basalt.

Considering that the rock was collected in a mixed mare-highlands terrain, it could have been a mare basalt, a KREEP basalt (which it is), or a crystalline melt rock. This work confirms the potential value of Raman spectroscopy for silicate mineral analysis for use on a planetary surface. It is clear from the experiments described above that quantifying proportions of minerals on the basis of their Raman peak

intensities would be highly imprecise at best. Our study of point counting suggests we can successfully circumvent this problem, at least in the common, straightforward case of a rock yielding good spectra from most analyzed points.

References: [1] Wang et al., J. Geophys. Res 100, 21,189 - 21,199, 1995; Wang et al., this volume.

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Table 1: Results of modal analyses of KREEP basalt rocklet 15273,7039.

	TS	Raman	single	mixed
	(%)	(%)	(N)	(N)
	1	2	3	4
plagioclase	50	42	29	26
orthopyroxene	9.5	16	11	11
clinopyroxene	25	18	13	11
K-feldspar		2		4
cristobalite	4.5	10.5	6	9
whitlockite		2.5	2	1
apatite		1		2
ilmenite	4.1			
unidentified		6	6	
no peaks		2	2	
mesostasis	6.9			
total	100	100	69	64

Col. 2: modal analysis of a rock face by Raman spectroscopy, 100 grid points; Col. 1: modal analysis of polished section of the rock; Col. 3, occurrences as single mineral in spectrum; column 4, occurrences in bi- or tri-mineralic spectra.

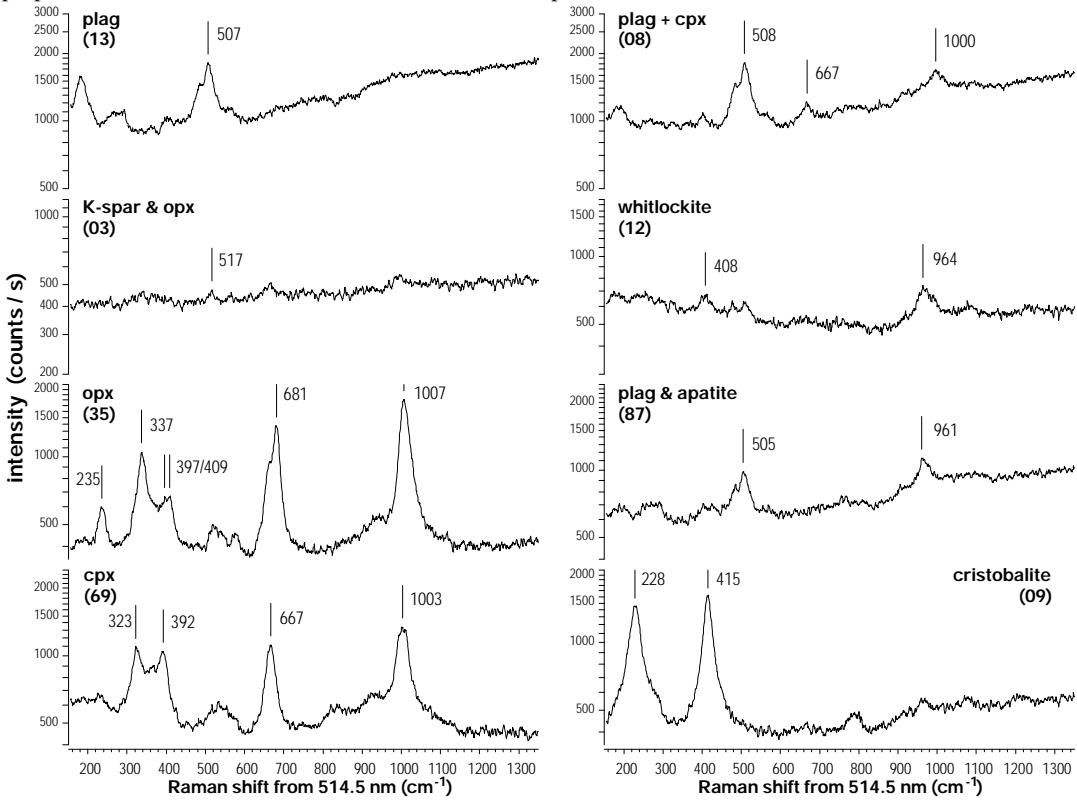


Fig. 1. Representative (not the best) spectra obtained from rocklet 15273,7039. (Grid point No. in parentheses.)