

## NEW APPROACHES TO THE IN-SITU STUDY OF MARTIAN SURFACE MINERALOGY

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With the upcoming Surveyor missions to Mars, including the Sojourner rover scheduled to be launched in December, 1996, and plans for future lander and rover missions, there will be many opportunities for in-situ study of Martian rocks. There is evidence from Earth-based reflectance spectra for the presence of amorphous gel-like coatings, rich in  $\text{Fe}^{3+}$ , on Martian surface materials [1,2,3]. Additional evidence for the presence of coatings is seen in Viking Lander images, which show specular reflections due to forward scattering from boulders [4,5,6]. Given the presence of rock coatings, the question is, will it be necessary to break rocks open or drill into them in order to analyze underlying materials, or will it be possible to use spectroscopic techniques to see beneath the coatings? To test the idea that spectroscopy can be used to infer the mineralogy of coatings and underlying materials, we are analyzing a varnished basalt from the arid environment of Lunar Crater Volcanic Field, Nevada with a laser Raman spectrometer.

Desert varnish is a thin (typically 1 - 100  $\mu\text{m}$ ) discontinuous layer of amorphous material containing Fe and Mn oxides which is deposited on desert rocks [7]. Varnish is derived primarily from external sources, not from the host rock [8] and its contact with the underlying rock is generally sharp. The potential analogy of desert varnish to probable coatings on Martian rocks make this sample a good starting point for exploring the capabilities of Raman spectroscopy. Unlike  $^{57}\text{Fe}$  Mössbauer spectroscopy, which provides information on only iron-bearing species, Raman spectroscopy is well-suited for detecting all types of silicates, carbonates, and sulfates [9,10]. Additionally, Raman spectra consist of sharp, nonoverlapping peaks, making for easier identification of minerals in a mixture than from infrared spectra [9]. The instrument used in this study is an S3000 triple spectrometer Raman microprobe with an intensified diode multichannel array detector, using the 514.5 nm  $\text{Ar}^+$  laser line. The preliminary data discussed in this abstract were obtained using a low-power (20x) objective, with the purpose of increasing the sampling area to about 50  $\mu\text{m}$  and laser power at sample level of < 7mW at the sample surface.

Analysis of the rock sample in thin section using both a petrographic microscope and an electron microprobe reveals phenocrysts of plagioclase, olivine, clinopyroxene, and ilmenite set in a fine-grained matrix of the same minerals (figure 1). Olivine is strongly altered to iddingsite, and secondary calcite fills many vesicles. Quartz grains are embedded in the surface of the rock, but do not occur within. The bulk-rock composition is that of andesine basalt with minor normative nepheline. Electron microprobe analyses of the varnish reveal an inhomogeneous mixture in which  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  account for roughly half the composition. Manganese (~2-23 wt.% as  $\text{MnO}$ ), iron (~6-11 wt.% as  $\text{FeO}$ ) and calcium (~1-22 wt.% as  $\text{CaO}$ ) are also present. These compositions are similar to those reported in other studies of desert varnish on a variety of host rock types [8,11,12,13,14]. Figure 1 illustrates the sharp contact between the layered varnish and the substrate. The varnish, which in this region ranges from a thickness of ~7  $\mu\text{m}$  to ~35  $\mu\text{m}$ , tends to accumulate most heavily in local depressions in the rock surface, whereas local protrusions have little or no varnish. This uneven mode of accumulation leads to the varying thicknesses [11] and the discontinuous nature of desert varnish.

Preliminary Raman spectroscopic analyses were done on the varnished surface of a piece of the basalt to determine the feasibility of identifying the underlying mineralogy of the rock. The strong, unique Raman spectra of the pertinent minerals (figure 2), as obtained from Raman microprobe analyses under ideal analytical conditions, indicate the inherent usefulness of the technique. The spectrum of the varnished surface in figure 3 was acquired under conditions (see above) chosen to simulate a possible configuration in a small, portable spectrometer deployed on a planetary surface. The laser spot size was comparable to the average grain size, although smaller than many phenocrysts (e.g. figure 1). Figure 3, a spectrum averaged from two spots, shows that even under these purposely degraded analytical conditions, strong peaks for plagioclase (most notably at 509  $\text{cm}^{-1}$ ) are recorded from the varnished surface. Other analyses show that the varnish itself has a Raman spectrum consistent with silicate glass. If the varnish was detected in the region analyzed in figure 3, its signature would be lost in the background of this spectrum due to the strength of the plagioclase peaks and fluorescence from plagioclase. Because minerals of the host rock are evident in this spectrum, the varnish at these points is either optically thin, or not present. Depth of penetration of the laser in this study is dependent on the wavelength of the excitation laser line (514.5 nm) and on the optical properties of the coatings. Our future research will make better use of the Raman microprobe's full capabilities to identify minerals, characterize glassy/amorphous phases in the rock and varnish, and identify the maximum varnish thickness that permits detection of the underlying rock's mineralogy. We will model the depth of penetration of the laser beam into the varnish and extrapolate these results to in-situ measurements of Martian rocks.

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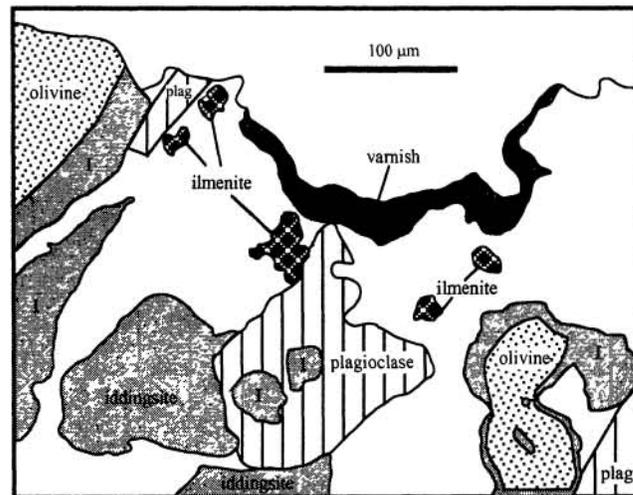


Figure 1: Sketch of a thin section of the basalt sample based on petrographic microscope and back-scattered electron image observation. Phenocrysts are mostly olivine or altered olivine/iddingsite (I), and plagioclase. The gray background represents the rock matrix containing smaller grains of ilmenite, pyroxene, plagioclase, and accessory minerals.

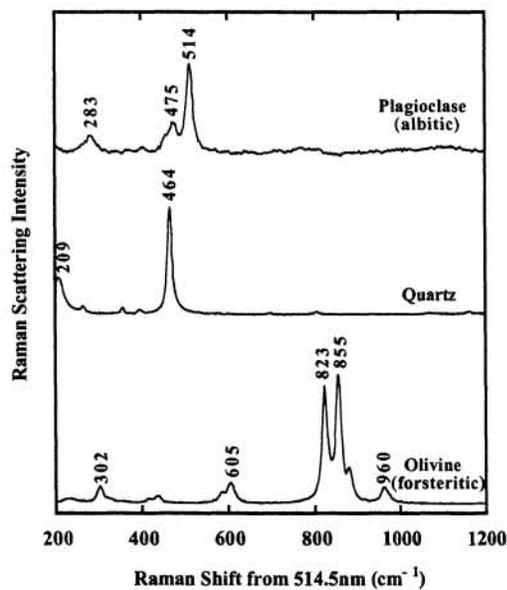


Figure 2: Raman spectra of individual grains of plagioclase, quartz, and olivine (as labeled) taken under typical analytical conditions for laboratory-based laser Raman microprobe: 1  $\mu\text{m}$  beam diameter, 10 mW at sample surface.

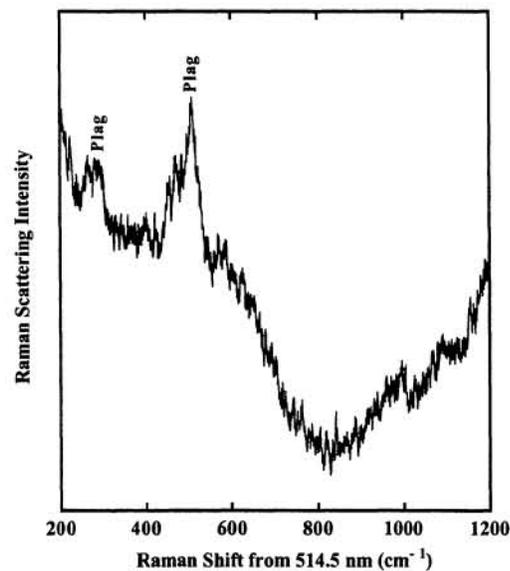


Figure 3: Raman spectrum of the basalt sample taken on the varnished surface. Spectrum acquired in about two minutes under degraded analytical conditions chosen to simulate those from a portable rover-based spectrometer. Plagioclase peaks dominate the spectrum. The varnish spectrum is not evident, but may be lost in the background.