Some Grain Size Effects on Raman Scattering Intensity for In Situ Measurements on Rocks and Soils Experimental Tests and Modeling. Alian Wang, Dept. Earth & Planetary Sciences and McDonnell Space Science Center, Washington University, St. Louis, MO 63130. (alianw@levee.wustl.edu)

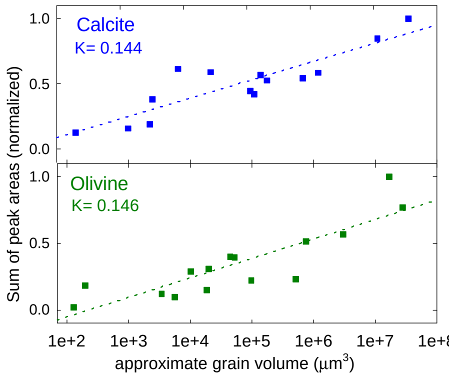
Most targets of a flight Raman system in future explorations on planetary surfaces for *in situ* mineral characterization are likely to be the surface rocks and soils scanned without sample preparation [1]. The surface roughness of these targets and the deployment of the instrument by a robotic arm require a simple flight Raman system to gather data from locations a few millimeters on either side of the focal plane of the excitation laser beam. How to provide adequate “depth of sampling field” was discussed in our previous study [2]. The actual depth of the sampling field, and thus the strength of the Raman signal, in a particular measurement is determined not only by instrument optics, but by the properties of the rock and soil targets. These include optical properties such as Raman cross section (σ), refractive index (n), absorption coefficient (α), and physical properties such as grain size, porosity, surface relief, and internal heterogeneity of mineral grains.

Factors that cause an intrinsic reduction in Raman photon production — To a first order approximation, Raman scattered radiation can be considered to arise from the emissions by oscillating dipoles in molecules, located within the small volume of the target illuminated by the laser beam. The intensity of the Raman radiation depends on the intrinsic strength of the oscillating dipole of the target mineral, i.e., by its Raman-cross-section σ. The intensity also depends on the number of molecules within the volume irradiated by the laser beam. In this sense, Raman scattering strength is volume dependent, so reduction of the irradiated volume reduces the number of excited molecules and thus the Raman signal strength. A fine-grained rock or a soil sample can have a lower volume to surface ratio than a bulk crystal, especially if porous or if grains of different minerals are present within the irradiated volume, and thus there would be fewer molecules of a given mineral that could interact with the laser photons within a given irradiated volume. The Raman signal strength from a unit volume of a fine-grained rock or soil sample is thereby reduced. The internal heterogeneity in a mineral grain, fracture, chemical zoning, and vitrification, has a similar effect on Raman scattering intensity for more complicate reasons.

Factors that cause a loss in collection of Raman photons — Multiple reflections at various surfaces within and near the excitation volume is the most important factor that reduces the collecting efficiency of Raman photons. Surfaces that may scatter Raman photons away from the collecting objective include target surface relief, grain boundaries within the irradiated volume, and changes of index of refraction caused by chemical or structural heterogeneity within a mineral grain. Even though the laser beam intensity may be kept constant, the penetration depth of the beam is reduced by multiple reflections at a rough target surface and at internal boundaries within the target. In addition, the shape of the volume irradiated by the remaining laser light that does penetrate is changed adversely by reflections from multiple grain boundaries, spreading the laser photons more broadly, so that some of the Raman photons produced by them would emerge from the sample outside of the collecting solid angle of the Raman system. The number of collectable Raman-scattered photons produced within the irradiated volume is thus decreased. Also, The Raman-scattered photons themselves suffer multiple reflections on exiting from the sample, directing more of them outside of the collecting solid angle of the Raman system. The term "grain size effect " is often used to describe the combined influences of the above factors (grain size, porosity, inner-heterogeneity, multi-reflection at boundaries, etc.) on the detectable Raman signal.

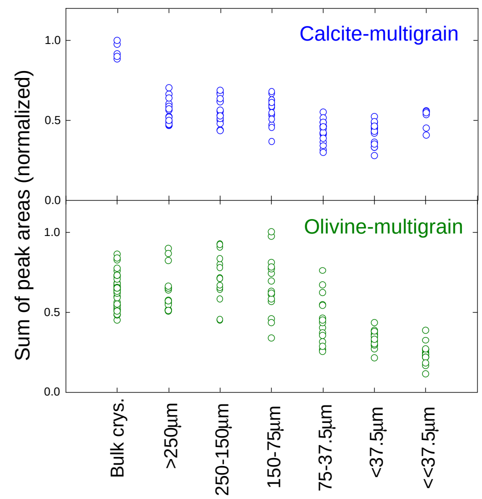
Experimental tests of grain size effect — Pure crystals of calcite and olivine were used as test samples. They were ground, and then sieved wet into the following ranges of grain sizes: >250 μm, 250-150 μm, 150-75 μm, 75-37.5 μm, <37.5 μm, and <<37.5 μm. The grains for <<37.5 μm category were obtained from the decantate of the suspending liquid. Raman spectra were obtained by using a HoloLab-5000 Raman spectrometer (Kaiser Optical System Inc.) with the 632.8nm line of a He-Ne laser as excitation source. A 20x objective (0.4 NA) was used, which condenses the laser beam to d <2μm at focal plane. Each measurement was made over a ≥4 minute time period to ensure that any fluctuations in laser power or from other sources would be averaged out. Three types Raman measurements were made. Type I was done on individual, isolated grains of different sizes. The results in Figure 1 show that the Raman radiation decreases monotonically as the function of grain volume. This test mainly represents the effect of decreasing volume ratio (sample volume to laser irradiation volume) on Raman radiation intensity, which is presumably the reason for the very similar slopes of both the olivine and calcite data.

Figure 1. Measurement results on single grains: the sum of Raman peak areas (normalized using the data from bulk crystal) decreases as a function of grain volume (as estimated from microscopic images of the grains).



Type II measurements were made on multi-grain samples, but in each case the laser beam was focused on a single grain whose top surface was perpendicular to the laser beam. In this test, the effects of volume ratio, volume to surface ratio, presence of internal boundaries, and porosity are all included; only effects of the surface tilt and roughness were minimized. About 15 measurements, each focused on a different crystal, were made for each grain size category. Figure 2 shows the Raman signal as a function of grain size for multigrain samples, normalized to the strongest signal obtained in the series. Results for each grain size category show considerable spread, a result of heterogeneity in grain orientation, grain-grain packing, local porosity, and differences in optical and physical properties of each targeted grain. For calcite, the strongest signal was obtained from the single, bulk crystal of ~1 cm, and relative to it, all smaller grain sizes samples have significantly reduced signal, down to roughly half for >250µm category and perhaps even more reduction at the smallest grain sizes. The relative decrease is greater for calcite than for olivine. The strengths of the Raman signals for olivine are essentially the same for grain sizes down to 75 µm for the first four categories, then drop toward the <37.5µm grain size. We have observed a similar pattern in many of our Raman measurements on actual rock and soil samples: Olivine shows a less strong grain size effect than calcite. The effects of grain size in multigrain samples, as seen in Figs. 1 and 2, have practical importance for planetary surface Raman studies. For both calcite and olivine, the signal strength relative to that of a large crystal is high enough for sensitive observation even at the lowest grain sizes of these tests. Type III measurements were done along linear traverses on the surface of multi-grain samples, with the focusing plane of laser beam adjusted and set at the first spot of each traverse. Thus, surface effects (tilt and roughness) were included in the results. The results were qualitatively the same, except the range of signal strengths for each grain size category was increased.

Figure 2. Measurement results on multigrain samples: the sum of Raman peak areas (normalized to the strongest signal obtained in the series) shown as a function of grain size



A simple model for understanding the grain size effect — As a contribution toward understanding the reasons for the difference in grain size effect for different minerals, we have considered a simple model based on the concept of an effective sampling volume (ESV). The ESV is a virtual volume within the sample, defined as that part of the laser-irradiated volume from which all Raman photons generated penetrate back to the sample surface and fall within the collecting solid angle of the Raman system. The relative ESV of a mineral is estimated as the function of the density of internal boundaries (basically, grain thickness along the path of the laser beam), the index of refraction of the mineral (n), and the absorption coefficient (α). Calculations based on this model suggest a strong grain-size effect for calcite but a weak one for olivine, qualitatively consistent with our experimental observations.

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References: [1] Squyres S. et al., (1998) *LPS XXIX*, [2] Wang A. et al. (1998) *Applied Spectroscopy 52*, 477-487.