Mineralogy of Three Lunar Soil Endmembers by Raman, Mid-IR, and Vis-NIR Spectroscopic Studies.
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Introduction: As we come into a new era for lunar exploration, it will be beneficial to examine the returned Apollo and Luna samples by various modern analytical techniques and newly developed methodologies. Laser Raman spectroscopy (LRS) has been proposed for lunar surface robotic exploration to provide definitive mineralogical information, including mineral identification [1], mineral proportions [2], and major mineral chemistry [3-7]. Mid-IR spectroscopy yields additional information on fundamental vibrational modes under different selection rules. Vis-NIR spectroscopy (commonly used for orbital remote sensing) offers information on overtone and combinational modes, and electronic transition modes. A combination of these three spectroscopic methods will not only provide a comprehensive set of information at atomic and molecular levels of lunar samples, but will also contribute to a direct link between *in situ* surface exploration and orbital remote sensing.

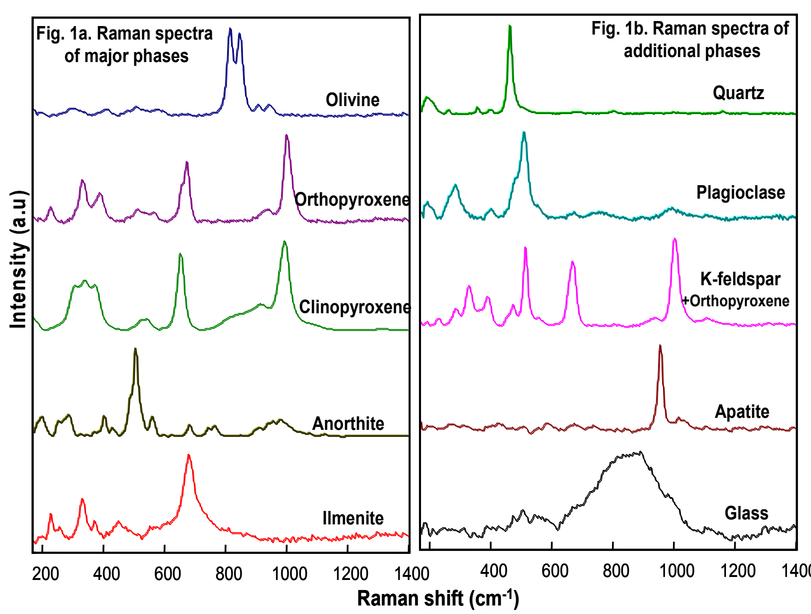
Lunar soils were selected for this study because they are the major contributors to orbital remotely sensed data. Furthermore, the mineral chemistry of individual grains in a lunar soil sample bears important information on its formation and history. Combined spectroscopic studies, especially laser Raman spectroscopy, provide the potential for in-situ determination of key information. This capability is developed through a set of systematic studies by establishing calibrations to extract compositional information from spectroscopic data, such as Mg/(Mg+Fe+Ca) and Ca/(Mg+Fe+Ca) in pyroxene [3], Mg/(Mg+Fe) in olivine [6], classification of Or-Ab-An feldspars [7], and discrimination of phosphate species [4] and Fe-Ti-Cr oxides [5].

Apollo Samples: Three lunar soils, 14163, 67513, and 71501, were selected for this study. They represent three endmembers in lunar soil chemistry, with enrichments of KREEP impact-melt breccias, feldspathic crustal materials, and high-Ti mare basalt, respectively. Soil 14163 was collected at the end of Apollo 14 EVA-1 on the Fra Mauro Formation. The sample contains abundant impact-melt breccia and includes several unusual lunar lithologies such as alkali anorthosite, granite, and monzogabbro [8]. Apollo 16 sample 67513 was collected at station 11 on the rim of the very fresh North Ray Crater. The Apollo 16 mission was the only manned mission to obtain samples from a region of the ancient heavily-cratered highland crust [9]. Apollo 17 sample 71501 was collected at station 1, 15 m northeast of a 10 m diameter crater with blocky ejecta [10].

Using the video camera of our laser Raman spectrometer, the diameter of each soil grain under examination can be measured. Analyzed grains are mainly in the 10-40 μm size range. Soil 67513 (typically ~30 μm) is the coarsest, whereas soil 14163 is the finest (typically 10-20 μm) among the three members. These measurements agree with the distribution of lunar soil grain size given in the Lunar Soils Grain Size Catalog [11].

Spectroscopic measurements: LRS measurements were made by using a HoloLab 5000-532nm Raman system with an automatic scanning stage. A Raman point-counting procedure [2] was applied over a 10×10 sampling grid with about 100 μm intervals. Manual adjustment of laser focus was made at each spot with a 6 μm beam size. A Nicolet Nexus 670 FTIR spectrometer was used to make ATR (attenuated total reflectance) measurements of the three Apollo soils, using a diamond anvil. An Analytical Spectral Device (ASD) was used to obtain the Vis-NIR reflectance spectra of the three lunar soils.

Results and Discussion: More than 100 LRS meas-



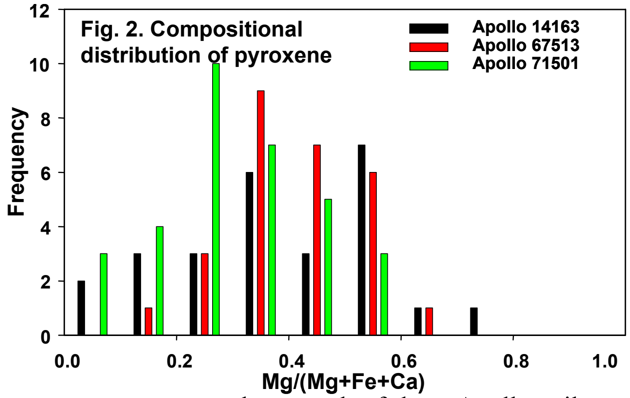


Fig. 2. Compositional distribution of pyroxene

urements were made on each of three Apollo soil samples. Figure 1a shows the typical Raman spectra of major minerals, and Figure 1b shows those of accessory minerals. These typical lunar minerals all have characteristic non-overlapping spectral peaks, thus mineral identification(s) can be made at each sampling spot. However, multiphase spectra (such as K-feldspar and pyroxene in Fig 1b) were obtained in most spots during the point-counting procedure from which the mineral proportions were extracted. Raman point-counting results indicate that plagioclase is the most abundant mineral in all three soils, with 67513 highest and 71501 lowest. These plagioclase proportions agree well with the fact that soil 67513 is a feldspathic endmember and soil 71501 is a high-Ti mare basalt soil. Plagioclase grains in soil 67513 almost all belong to "low temperature" anorthite [7]. In soil 71501, we find considerable amounts of high-T anorthite and shocked anorthite grains. Soil 67513 contains more orthopyroxene and soil 71501, more clinopyroxene. Soils 14163 and 71501 have higher amounts of glassy materials than soil 67513. We found three characteristic spectra of crystalline quartz (SiO_2 with space group $P3_121$, but not cristobalite, coesite, or tridymite) among 174 spectra taken from soil sample 14163. Feldspar grains in soil 14163 have the highest Na contents. This observation agrees well with the fact that Apollo 14 samples include igneous lithologies with evolved compositions such as granite and quartz monzodiorite (monzogabbro) [7,12].

Figure 2 shows the compositional distribution of pyroxene grains from three lunar soils, in terms of Mg/(Mg+Fe+Ca). Pyroxene grains in grains in 67513 (anorthositic highland soil) are slightly richer in Mg; and pyroxene grains in 71501 (mare soil) are richer in Fe and Ca, with more augite grains than pigeonite. For sample 14163, the compositional distribution of pyroxene is scattered more widely than the other two.

Figure 3 shows the mid-IR (ATR) spectra for the three soils. Compared with the spectrum of soil 67513, the spectra of soils 71501 and 14613 both have a wide ν_3 band with much less spectral detail, which suggests low crystallinity, thus higher soil maturity. Among the three soils, 67513 has the lowest maturity [14].

Vis-NIR spectra of the three soils are given in Figure 4. The soil 67513 shows the highest albedo, with a strong orthopyroxene absorption band near 938 nm. This observation is consistent with Raman analyses, i.e., a higher proportion of orthopyroxene. Spectra from soil 14163 and 71501 both have lower spectral contrast than soil 67513, a reflection of their maturity.

Conclusions and Future work: This study presents definitive mineralogical information that can be obtained through a set of intrinsically related spectroscopic investigations. We demonstrate the feasibility of using this set of technologies, especially LRS, for mineral characterization and in-situ resource utilization (ISRU) in future lunar exploration [13]. A fourth soil endmember, a low-Ti mare basalt soil 15273 was measured and data analyses is on-going. A comparison with literature data on soil chemistry and lithology will be conducted, and be presented at LPSC.

Acknowledgements: This study was initiated by a collaboration between Dept. Space Sciences and Applied Physics at Shandong University and Dept. Earth and Planetary Sciences at Washington University, and supported by both institutions. We thank R. Korotev, J. Freeman, R. Zeigler, and K. Kuebler for science advice and lab assistance.

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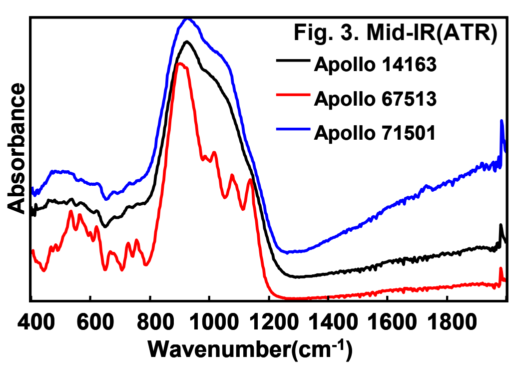

Fig. 3. Mid-IR(ATR)

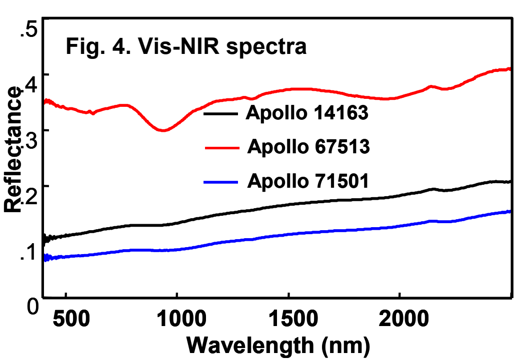

Fig. 4. Vis-NIR spectra