# QUANTITATIVE RAMAN SPECTROSCOPIC STUDIES OF TERNARY LUNAR SILICATE MIXTURES.

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**Introduction:** Raman spectroscopy is more often associated with the determination of the molecular structure and qualitative analysis than quantitative analysis. Especially in terms of planetary Raman spectroscopy, there is still a dearth of robust models to quantify silicate minerals with Raman spectra acquired from different set-ups. Hence, considering the crucial role that mineral modes play in understanding the local lithological properties, quantitative Raman spectroscopic studies on lunar analogs are conducted.

**Sample Preparation:** Previous petrological and mineralogical analyses show that silicate is the dominant mineral on the lunar surface, mainly feldspar, pyroxene, and olivine. These three kinds of silicate minerals are commonly mixed in lunar soils and lunar rocks. Terrestrial analog minerals including feldspar (Fsp), olivine (Oli) and augite (Aug) were ground to prepare lunar regolith simulants with grain size less than 38 μm. Monomineralic powders were mixed in different mass fractions (Table 1) to obtain 15 polymineralic mixtures. Afterwards, the mixed powders were compacted under a pressure of 340 MPa for 120 s in the mold.

Table 1. Mineral mass fractions in lunar soil analogs studied.

| No. | Sample ID | Mineral proportions (wt.%) | | |
| --- | --- | --- | --- | --- |
| | | Feldspar | Olivine | Augite |
| 1 | FOA-118 | 0.1015 | 0.1029 | 0.7956 |
| 2 | FOA-217 | 0.2018 | 0.1003 | 0.6979 |
| 3 | FOA-316 | 0.3011 | 0.0992 | 0.5997 |
| 4 | FOA-415 | 0.3988 | 0.1021 | 0.4992 |
| 5 | FOA-514 | 0.4999 | 0.1005 | 0.3996 |
| 6 | FOA-613 | 0.5993 | 0.0998 | 0.3009 |
| 7 | FOA-712 | 0.6989 | 0.0998 | 0.2013 |
| 8 | FOA-811 | 0.7270 | 0.0913 | 0.1817 |
| 9 | FOA-127 | 0.1005 | 0.1999 | 0.6996 |
| 10 | FOA-136 | 0.1002 | 0.3013 | 0.5984 |
| 11 | FOA-145 | 0.1033 | 0.3943 | 0.5025 |
| 12 | FOA-163 | 0.1003 | 0.5995 | 0.3002 |
| 13 | FOA-181 | 0.1003 | 0.7990 | 0.1007 |
| 14 | FOA-226 | 0.2002 | 0.2024 | 0.5974 |

**Acquisition of Raman Spectra and Data Preprocessing:** Raman spectra of these lunar soil analogs were acquired using an inVia® Raman system (Renishaw company) equipped with an automated 3D scanning stage at Shandong University, Weihai. Samples were analyzed with a 532 nm frequency-doubled Nd: YAG laser in the back-scattering geometry. Moreover, a 50× objective with long focus length (Numerical Aperture (N.A.) = 0.55) was used to focus the laser on the sample to a spot diameter of ~2.0 μm

and collect the scattered Raman photons. A grating with 1800 lines/mm was used and the spectral repeatability and spectral resolution were ± 0.1 cm⁻¹ and better than 0.8 cm⁻¹, respectively.
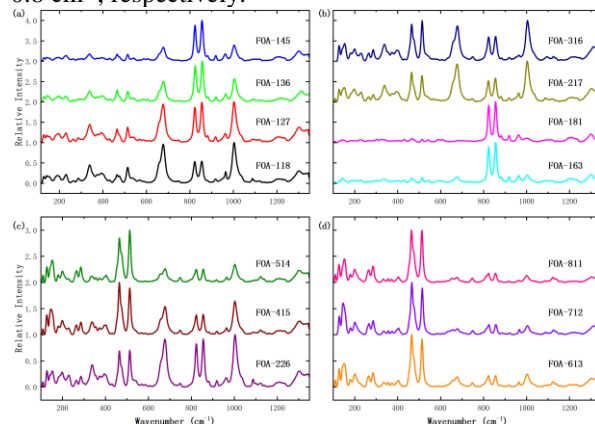


Fig. 1. Raman spectra of all ternary mixtures.

We conducted Raman imaging measurements on mixtures using the Streamline™ mode [1]. Besides, a crystalline Si wafer with the known band position of ~520.7 cm⁻¹ was used to calibrate the Raman shift dimension of CCD array before measurements. Raman imaging measurements were conducted in four square regions of 500 μm × 500 μm (the XY step size was 100 μm), with a laser power of 9.5 mW at the sample surface and an exposure time of 7 s for each measurement. Eventually, 144 Raman spectra in the range of 104.745 - 1348.09 cm⁻¹ (1005 bands) were recorded for each sample.
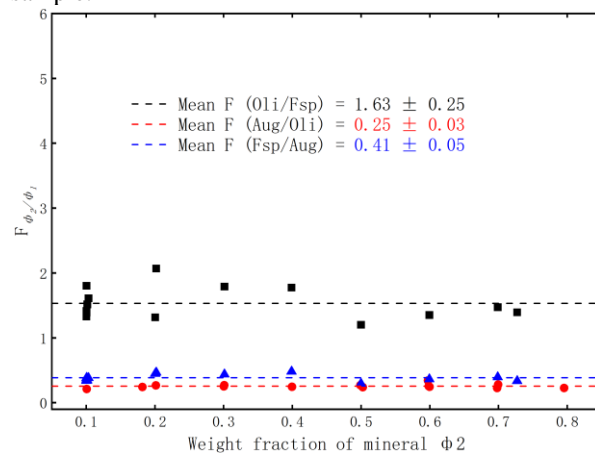


Fig. 2. $F_{\Phi2/\Phi1}$ factors calculated from feldspar-olivine-augite mixtures, represent the relative apparent Raman scattering efficiencies of these minerals.

Features in the spectra caused by cosmic ray incident on the detector were manually removed using the Renishaw WiRE 3.4™ software. Then, a Savitzky–Golay filter [2] of order one and 5-points window was applied to smooth these spectra. Subsequently, the baselines of these spectra were estimated using a small-window moving average-based method and removed [3]. Moreover, the 144 spectra of each sample were averaged (Fig. 1) and then normalized using a correction factor $F_{\Phi2/\Phi1}$[4] (Fig. 2). The accurate Raman peak positions and peak areas were obtained by spectral deconvolution using a mixed Gaussian-Lorentzian algorithm.

**Results and Discussions:** It was demonstrated in a number of studies that the intensities of diagnostic peak within a Raman spectrum would simplistically be proportional to concentrations of certain species. However, an important question regarding this is that Raman peak intensities are affected by complex factors (e.g., crystal orientation, the incident and emission angle, roughness, mineral grain size, mineral transparency) [5] which introduce uncertainties to the estimates of peak intensity. These factors may lead to weak robustness of the quantitative calibration curve. In addition, only photon counts in a single channel was used when peak intensity was employed. Therefore, in addition to controlling the characteristics of the sample and using appropriate normalization methods to correct measurement and instrument artifacts, peak areas were used instead.

Raman bands at 512 cm$^{-1}$ for feldspar, 855 cm$^{-1}$ for olivine, and 668 cm$^{-1}$ for augite were used to construct calibration curves. By plotting the calculated band area versus the mineral proportion in the samples listed in Table 1, the calibration curves presented in Fig. 3 were obtained. The peak area versus mineral abundance plot shows a good correlation between the samples used as reference. The final calibration curves were constructed by using the Leave-One-Out Cross Validation method. This method guarantees the robustness and repeatability of the calibration curves, although it requires tedious calculations.

The correlation coefficients ($R^2$) are 0.952, 0.9779, and 0.992 for augite, olivine, and feldspar, respectively (Fig. 3). We denote the $X_{Fsp}$, $X_{Oli}$, $X_{Aug}$ as the relative content of feldspar, olivine, and augite, respectively. The final equations describing the feldspar-olivine-augite calibration curves to calculate the proportion as a function of relative band areas $Area_{Fsp/FOA}$, $Area_{Oli/FOA}$, and $Area_{Aug/FOA}$ are as follows:

$$X_{Oli} = -0.1274 + 0.8511 \cdot Area_{Oli/FOA} + 0.1778 \cdot Area_{Fsp/FOA} \quad (1)$$
$$X_{Aug} = 1.1397 - 0.8788 \cdot Area_{Oli/FOA} - 1.2165 \cdot Area_{Fsp/FOA} \quad (2)$$
$$X_{Fsp} = 1 - X_{Aug} - X_{Oli} \quad (3)$$

**Conclusions:**

We prepared a series of lunar soil analogs with ternary minerals and conducted quantitative Raman studies with the intent to optimize the scientific outcome of the planetary Raman payloads. Calibration curves for calculating relative mineral proportions from Raman peak areas were obtained. The robustness of our simulations is asserted by the significant correlation coefficients and small standard deviations.

**References:** [1] Wang A. et al. (2015) *Planet. Space Sci., 112,* 23-34. [2] Savitaky A. and Golay M. J. E. (1964) *Anal. Chem., 36,* 1627-1639. [3] Schulze H. G. et al. (2012) *Appl. Spectrosc., 66,* 757-764. [4] Demaret L. et al. (2021) *Analyst, 146,* 7306-7319. [5] Haskin L. A. et al. (1997) *J. Geophys. Res. Planets, 102,* 19293-19306.
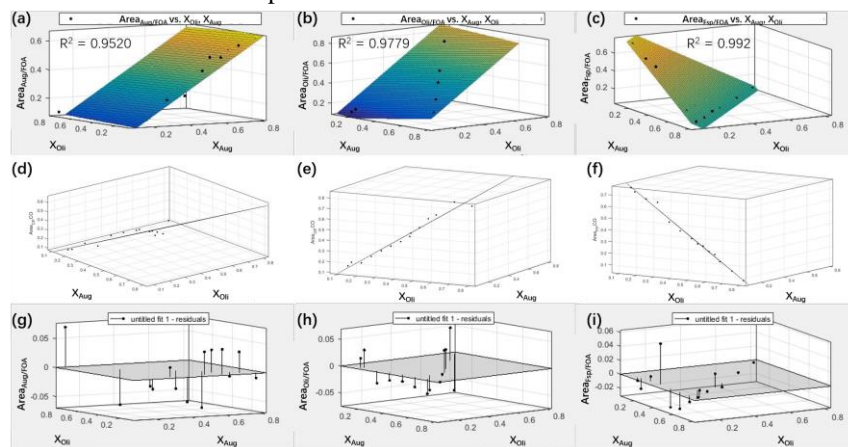


Fig. 3. Relationships between abundance and the relative band areas for (a, d) augite, (b, e) olivine and (c, f) feldspar; Residual diagram of (g) augite, (h) olivine and (i) feldspar.