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cy, we report here a sample library (**Figure 1**) and spectral database consisting of fine-grained binary mixtures using 38 pure mineral phases. We then test how well individual mineral abundances can be determined using multivariate analysis.

Background: Quantitative relationships between peak area and mineral abundance are obscured by many complicating factors in Raman spectroscopy: the exciting laser wavelength, the Raman cross-section of the minerals (dependent on the strength of covalent bonding and polarizability of the molecule), crystal orientation relative to laser polarization, and long-range chemical and structural ordering in the crystal lattices [5]. Even if the Raman laser interrogates a broad area to avoid crystal orientation, variable Raman cross-sections of minerals prevent quantitative assessment of mineral abundances in mixtures. Until a theoretical model for unmixing of Raman data is developed, empirical methods such as multivariate analysis and/or use of Raman Coefficients [6] are needed.

Methods: Hand samples of 38 Mars-analog minerals were obtained from various vendors, as listed in Figure 1 [6]. Chemical analyses from electron micro-

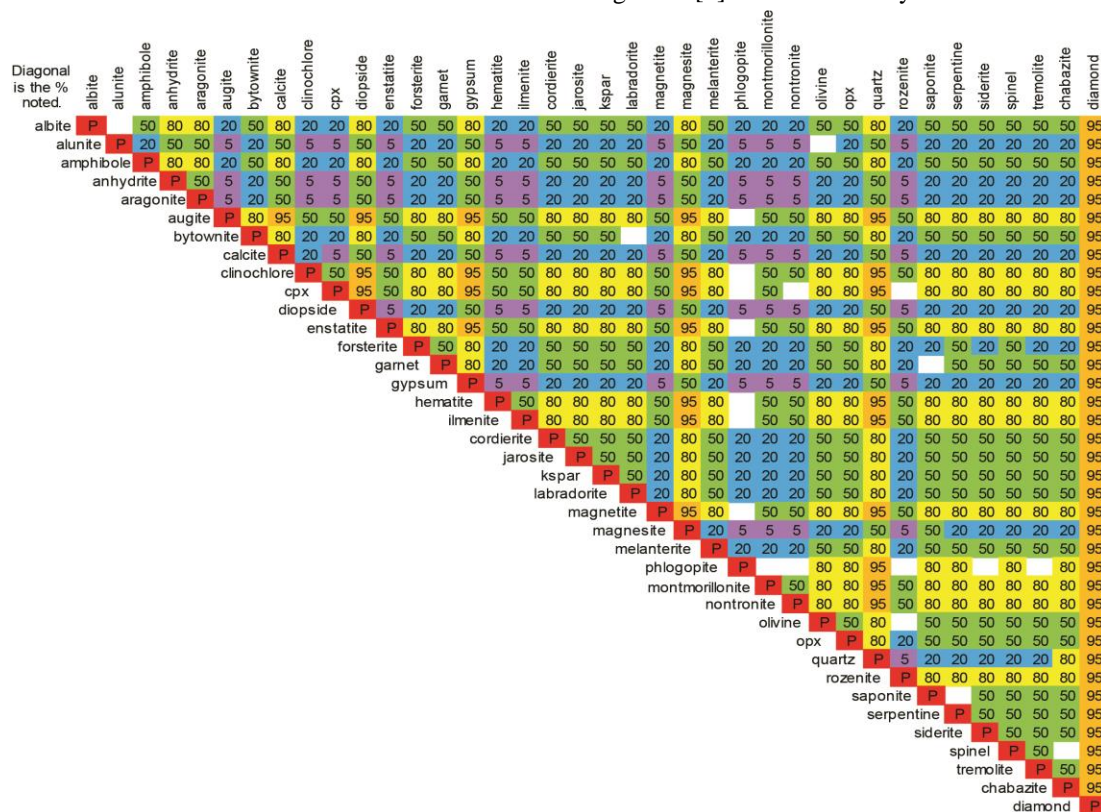


Figure 1. Diagram of binary mineral mixtures with volume abundances noted in each square. The numbers give the percentage of the mineral written on the diagonal and “P” is an indication of pure minerals.

probe were used to calculate the density of each mineral comparing against literature values. Samples were crushed, handpicked for purity, and sieved, producing roughly 10g of each sample divided among grain size fractions of <25, 25-45, 38-125 and 45-125 μm . Mixtures were paired such that samples of the same grain size were used. Samples were then weighed into ratios of 50:50, 20:80, and 95:5 volume % depending on the Raman cross-sections of the paired phases. Mixtures were customized for each pair to ensure that each phase would have characteristic bands with sufficient peak areas to aid the multivariate analysis models.

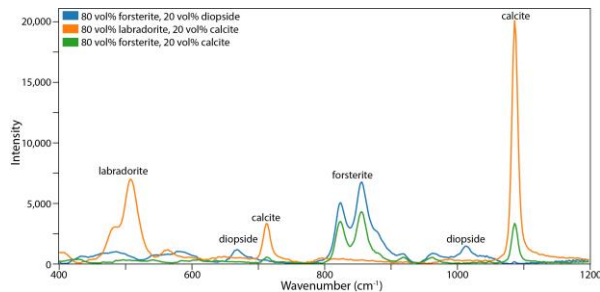


Figure 2. Spectra of three binary mixtures consisting of forsterite, calcite, labradorite, and diopside.

Spectra were acquired on a Bruker Optics BRAVO Raman spectrometer using dual laser excitation and a patented fluorescence mitigation strategy involving successive laser heating [7]. Three scans were obtained per spectrum using an integration time of 10s over the wavenumber range of 300-3200 cm^{-1} .

Results: All data show the expected nonlinearity of peak areas relative to their volumetric abundances in mixtures (e.g., **Figure 2**). Each individual band responds according to the Raman cross-section of the associated bond and other factors noted above.

The multivariate techniques of partial least squares (PLS) and least absolute shrinkage operator (Lasso) were utilized to build models to predict mineral abundances in each mixture. The PLS method regresses one response variable against multiple explanatory variables (intensity at each channel of the spectra), assigning coefficients to every single channel. As a result, when predicting an individual mineral abundance, coefficients of the PLS model should generally mirror the fingerprint of the Raman spectrum of that mineral, as observed for the San Carlos forsterite sample. In contrast, Lasso uses continuous shrinkage to reduce coefficients of spectral channels to as low as zero [8] if they do not contribute to the model. Thus channels used in Lasso models should track known peaks of each mineral but not necessarily include all of them.

Leave-one-out cross-validated root mean square error (LOO RMSE-CV) for predictions of mineral abundances are given in **Table 1** as a proof of concept for

several mineral species using PLS and Lasso in units of the mineral volume %. Both techniques produce comparable results for each of the four phases. Accuracy for predicting mode is ca. ± 4 volume %, comparable to errors associated with unmixing of reflectance spectra. Ongoing work will predict modes of the remaining minerals. Our expectation is that minerals with highly ionic bonding and correspondingly low Raman cross sections will have higher prediction errors.

Table 1. Multivariate prediction error of minerals in mixtures ($n = 275$) on Bruker's BRAVO Raman spectrometer.

Mineral	C/ α	Model	Internal R^2	LOO RMSE-CV
anhydrite	5	PLS	0.84	4.4
	0.019	Lasso	0.96	4.5
calcite	3	PLS	0.86	4.3
	0.002	Lasso	0.99	4.2
diopside	10	PLS	0.87	6.2
	0.008	Lasso	0.99	5.2
magnesite	7	PLS	0.87	4.1
	0.007	Lasso	0.98	3.7

Note: Wavenumber range of 300-1200 cm^{-1} , C/ α = components for PLS models and α for Lasso models.

Discussion and Future Work: Multivariate results were obtained here from a dataset of 275 spectra, but more data are still needed. Diversifying the mixtures beyond the three ratios utilized here by expanding the abundance ranges and filling in gaps for each mineral phase would likely improve each multivariate model. We are also working to expand the number of phases present in the mixtures, though this is a formidable undertaking given the requirement of high purity and large volumes of mineral separates.

These mineral mixtures represent a huge advance in the number of intimate mixtures available for further study of Raman unmixing. As *ExoMars* and *Mars 2020* approach, analyses of these samples on equivalent instruments to those of the missions should enhance our ability to identify minerals within mixtures on Mars and constrain the error of those predictions. This work underscores the need for the creation of additional mineral mixtures to prepare for Mars exploration uses, as well as to pursue the unmixing problem computationally through software development.

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