QUANTIFYING MINERAL ABUNDANCES IN MIXTURES USING RAMAN SPECTROSCOPY: CREATING MINERAL MIXTURES.
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Introduction: Excitement is building over the imminent arrival of three different styles of Raman instruments on the surface of Mars. The *ExoMars* mission carries an RLS instrument inside the analytical laboratory of the rover [1]. It will use a 532 nm laser to probe powdered samples obtained by a drill. *Mars 2020*'s SHERLOC will utilize deep ultraviolet (DUV) resonance to scan habitable environments with both Raman and luminescence for organics and chemicals [2]. It is an arm-mounted instrument with a 248.6 nm DUV laser. Finally, Super-Cam on *Mars 2020* will probe Mars surface materials at distance up to 12 m [3] using a pulsed doubled Nd:YAG laser (532 nm, 10Hz, 10 mJ/pulse) to produce Raman emission at energies up to 4,200 cm^{-1} [4] and footprints of 0.67 mrad (1.3 mm at 2 m distance; [3]). Although the implementations differ, these instruments share a common capability to fingerprint surface minerals and inform Martian geology and geochemistry.

The ability of all these instruments to successfully do their job depends on the availability of appropriate databases and software for phase identification *at the relevant scales*. The ~50 μm beam sizes of RLS and SHERLOC are small enough to probe mostly individual mineral phases, but the 1.3 mm beam size of Super-Cam and the powdered samples presented to RLS are likely to produce mixed-mineral spectra. Unlike the situation for unmixing algorithms developed for reflectance spectroscopy of visible to mid-infrared wavelengths in planetary science, the larger Raman community lacks any methodology for estimating quantitative abundances of minerals in mixtures. In fact, Raman spectra of mixed phases with known quantitative molar abundances do not exist in any public libraries. To begin to address this deficiency, we report here on the creation of a sample library and spectral database consisting of intimate binary mixtures of 23 minerals created in volume percentages and accompanying Raman spectra. These data lay the foundation for models of molar abundance in mixtures such as [5] to be developed.

Background: In Raman spectroscopy, quantitative relationships between peak intensity and mineral abundance are obscured by many complicating factors: the frequency of the exciting laser, the Raman cross section of the mineral (which depends on the strength of the covalent bonding and the polarizability of the molecule), crystal orientation relative to the direction of laser polarization, and long-range chemical and structural ordering in the crystal lattices [6]. There is as yet no analog to "Hapke modeling" of reflectance spectra that allows these factors to be mitigated or even understood. Even if the Raman laser interrogates a broad area to avoid crystal orientation, variable Raman cross-sections of minerals confound estimation of quantitative mineral abundances from mixtures using Raman spectra. Until a theoretical model for unmixing is developed, it is necessary to pursue empirical methods such as multivariate analysis [5] for unmixing spectra. This project provides spectra to form the basis for such models.

Methods: We obtained large hand samples of Mars-analog minerals for this study from various vendors. The 23 minerals species used include alunite, anhydrite, augite (clinopyroxene), bytownite (feldspar), calcite, clinochlore (chlorite), diopside (clinopyroxene), enstatite (orthopyroxene), forsterite (olivine), gypsum, hematite, ilmenite, jarosite, rozenite, labradorite (feldspar), magnesite, magnetite, montmorillonite, nontronite, saponite, siderite, tremolite, and chabazite (zeolite) [7]. Chemical analyses were obtained using electron microprobe, and all samples were crushed, handpicked for purity, and sieved to grain
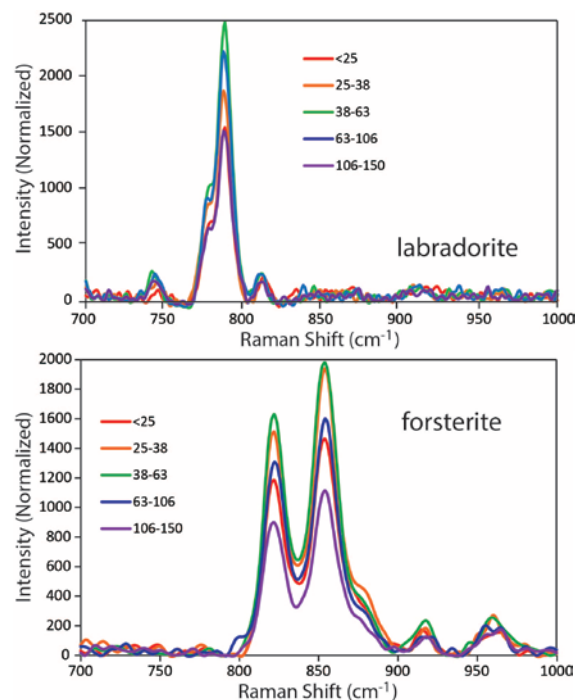

Figure 1. Spectra of pure minerals with variable grain sizes (in microns) used to choose the appropriate grain size for mineral mixtures.

diagonal is the % noted	Alunite	Anhydrite	Augite	Bytownite	Calcite	Clinochlore	Diopside	Enstatite	Forsterite	Gypsum	Hematite	Ilmenite	Jarosite	Labradorite	Magnetite	Magnesite	Montmorillonite	Nontronite	Rozenite	Saponite	Siderite	Tremolite	Chabazite
Alunite	P	50	5	20	50	5	50	5	20	50	5	5	20	20	5	50	5	5	5	20	20	20	20
Anhydrite		P	5	20	50	5	50	5	20	50	5	5	20	20	5	50	5	5	5	20	20	20	20
Augite			P	80	95	50	95	50	80	95	50	50	80	80	50	95	50	50	50	80	80	80	80
Bytownite				P	80	20	80	20	50	80	20	20	50		20	80	20	20	20	50	50	50	50
Calcite					P	5	50	5	20	50	5	5	20	20	5	50	5	5	5	20	20	20	20
Clinochlore						P	95	50	80	95	50	50	80	80	50	95	50	50	50	80	80	80	80
Diopside							P	5	20	50	5	5	20	20	5	50	5	5	5	20	20	20	20
Enstatite								P	80	95	50	50	80	80	50	95	50	50	50	80	80	80	80
Forsterite									P	80	20	20	50	50	20	80	20	20	20	20	20	20	20
Gypsum										P	5	5	20	20	5	50	5	5	5	20	20	20	20
Hematite											P	50	80	80	50	95	50	50	50	80	80	80	80
Ilmenite												P	80	80	50	95	50	50	50	80	80	80	80
Jarosite													P	50	20	80	20	20	20	50	50	50	50
Labradorite														P	20	80	20	20	20	50	50	50	50
Magnetite															P	95	50	50	50	80	80	80	80
Magnesite																P	5	5	5	50	20	20	20
Montmorillonite																	P	50	50	80	80	80	80
Nontronite																		P	50	80	80	80	80
Rozenite																			P	80	80	80	80
Saponite																				P	50	50	50
Siderite																					P	50	50
Tremolite																						P	50
Chabazite																							P

Table 1. Diagram of binary (two-phase) mineral mixtures created for this project, with volume abundances noted in each square. "P" indicates pure minerals, and numbers give the percentage of the mineral noted on the diagonal.

sizes <64 μm, producing roughly 10g of each sample that is divided among grain size fractions from 25-45 μm and 45-125 μm. This grain size was chosen on the basis of experiments on six different minerals in which spectra of five different size fractions were measured (**Figure 1**).

X-ray diffraction was used to confirm the homogeneity of each pure phases. Samples were then weighed into binary mixtures in ratios of 50:50, 20:80, and 95:5 volume percent depending on the Raman cross sections of the paired phases (**Table 1**). The mixtures were customized for each pair to ensure that each phase would have characteristic peaks with sufficient volume to yield accurate data on the mixture.

Spectra were acquired on a Bruker Optics, Inc. BRAVO Raman spectrometer, which uses dual laser (758 and 852 nm) excitation and a patented fluorescence mitigation strategy involving successive heating of the laser [8]. With a scan time of 10s and wavenumber range of 300-3350 cm^{-1}, each sample was run three times and the spectra were averaged. The BRAVO produces baseline-subtracted data.

Results: All the data show the expected nonlinearity of the mineral peak areas relative to their volumetric abundances in mixtures. Each individual peak responds according to the Raman cross-section of the associated bond.

Discussion: Our results are limited by the small number of phases used in this proof-of-concept study. However, they represent a huge advance in the number of mineral mixtures available for further study. They underscore the need for creation of additional mineral mixtures to prepare for Mars exploration uses, as well as accompanying software development to pursue the unmixing problem computationally.

References: [1] Rull F. et al. (2014) *8th Intl. Mars Conf.*, Abstract #1277. [2] Beegle L. W. et al. (2014) *11th Intl. GeoRaman Conf.*, Abstract #5101. [3] Maurice S. et al. (2015) *LPS LXXVII*, Abstract #2818. [4] Clegg S. M. et al. (2015) *LPS LXXVI*, Abstract #2781. [5] Carey CJ (2016) *LPS LXXVII,* Abstract #2626. [6] Haskin L. A. et al. (1997) *JGR*, *102*, 19293-19306. [7] Breitenfeld L. B. (2016) *LPS LXXVII,* Abstract #2186. [8] Cooper J. B. et al. (2014) *Spectroscopy*, 29, 38-42.