

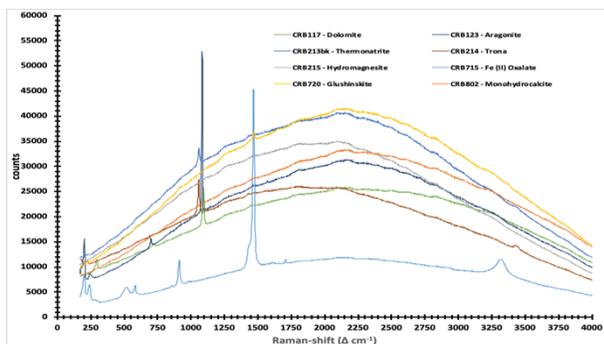
**ASTROBIOLOGY- AND HABITABILITY-RELEVANT MATERIALS CHARACTERIZED BY 532 NM LASER RAMAN SPECTROSCOPY.** J. C. Kuik<sup>1\*</sup>, D. M. Applin<sup>1</sup>, M. Ramirez, and E. A. Cloutis<sup>1</sup>. Dept. Geography, University of Winnipeg, 515 Portage Ave., Winnipeg, MB, Canada R3B 2E9; \*[kuikjessec@gmail.com](mailto:kuikjessec@gmail.com).

**Introduction:** Raman spectroscopy will be an important analytical tool in mineralogical exploration and the search for signs of past or present life on Mars. In 2020 both ESA and NASA are sending rovers to Mars with payloads utilizing Raman spectroscopy.

The ExoMars rover will host the Raman Laser Spectrometer (RLS), part of the Pasteur payload. The RLS is expected to cover the spectral range of 200-3800  $\Delta\text{cm}^{-1}$  with a nominal spectral resolution of 6-8  $\Delta\text{cm}^{-1}$ , and a laser spot size of  $\sim 50 \mu\text{m}$ . The RLS objectives will be to characterize mineral phases produced by water-related process, water/geochemical environment as a function of depth, characterize igneous minerals with possible alteration products, identify mineral products and indicators of biologic activities, and identify organic compounds and search for extinct or extant forms of life. [1].

SuperCam will host a stand-off Raman system that is similar to RLS in many facets, including similar science objectives. The Raman spectrometer will cover the spectral range of 150 – 7000  $\Delta\text{cm}^{-1}$  with a  $<9 \Delta\text{cm}^{-1}$  FWHM resolution [2]. The Raman spectrometer is part of an integrated instrument that has capabilities to perform Laser-Induced Breakdown Spectroscopy and VNIR reflectance. The Raman spectrometer will utilize time-gating (down to 40 ns exposures) to limit the amount of fluorescence signal induced by the laser.

This study assesses the capabilities of a 532 nm laser Raman spectroscopy without fluorescence mitigation techniques for the characterization of astrobiologically relevant materials. The suite of samples included in this study that are relevant to astrobiology and include clays, carbonates, sulfates, hydroxides, sulfides, silicas, nitrates, nitrites, oxalates, borates and phosphates.



**Figure 1.** Raman spectra of carbonate and oxalate minerals.

**Methods:** A BWTek iRaman spectrometer with a 532 nm laser was used to characterize powders, rocks,

and pellets. The systems covers the spectral range of 175 to 4000  $\Delta\text{cm}^{-1}$  and has a nominal spectral resolution of 4  $\Delta\text{cm}^{-1}$ . The laser spot diameter while in focus is  $\sim 80 \mu\text{m}$ . Various laser power levels from 1 to 50 mW, and various integration time were used, depending on the Raman scattering of the samples.

**Table 1.** Minerals and other materials used in this study, including the number of each type that was characterized by 532 nm laser Raman spectroscopy.

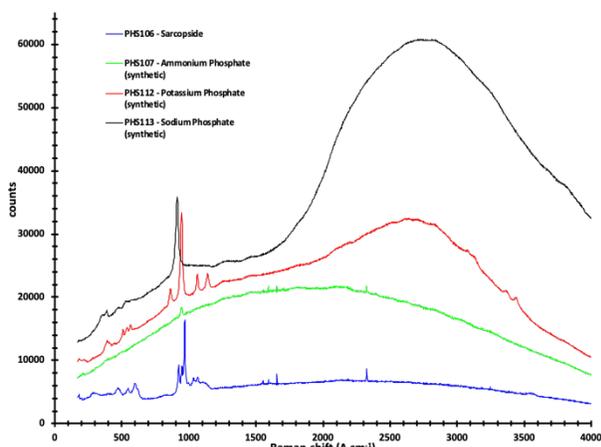
Sample type	number of samples
Phyllosilicates	15
Oxides	5
Hydroxides	3
Sulfates	5
Sulfides	3
Carbonates	15
Oxalates	5
Borates	2
Nitrates	4
Nitrites	1
Phosphates	4
Chlorides	2
silica (opal, quartz, sinters)	6
Oil sands	2
Oil shales	3
Carbon-rich	8
Endoliths	4

**Results and Discussion:** This study focuses on the characterization of a comprehensive suite of Mars-relevant minerals and organic-bearing materials. Here we look at the capabilities of the 532 nm laser Raman to characterize four types of minerals in our sample suite; carbonates, oxalates, phosphates, and nitrates.

Figure 1 shows several carbonate and oxalate minerals that are astrobiology- and habitability-relevant to Mars. Laser-induced fluorescence is present in all of these spectra, at various intensities. For some of these minerals, this has the effect of masking potential Raman-scattered peaks. This phenomena has often hindered Raman spectroscopy in mineralogical and biological studies, where fluorescence mitigation tech-

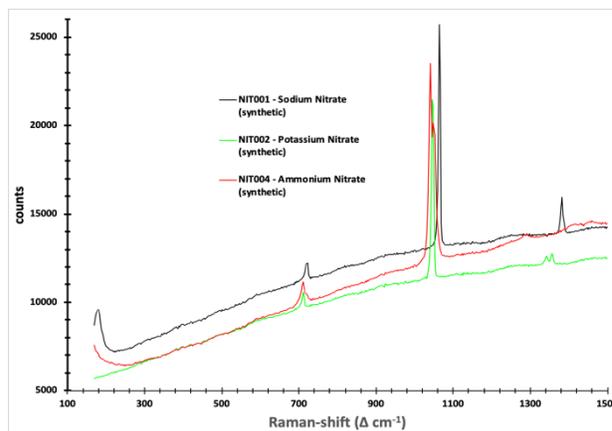
niques are not used. [4]. Nonetheless, Raman spectroscopy can identify the strongest Raman signals from most of these minerals. As an example, the prominent bands in dolomite due to  $\text{CO}_3^{2-}$  and its four vibrational modes of asymmetric and symmetric stretching, and asymmetric and symmetric deformation [5] are shown in Figure 1 at 1435, 1086, 724 and  $290 \Delta \text{cm}^{-1}$ . Trona, another carbonate in this study, exhibited strong fluorescence, yet the Raman signal at  $1058 \Delta \text{cm}^{-1}$  was strong enough to be observed. The characteristic O-H band around  $3400 \Delta \text{cm}^{-1}$  was discernable from the fluorescence in trona and humboldtine.

The phosphate mineral suite consisted of one naturally occurring mineral, PHS106 (sarcopside) and three synthetic phosphates, ( $\text{NH}_4$ , Na, K). In the naturally-occurring sarcopside, the most prominent band occurs around  $970 \Delta \text{cm}^{-1}$ , likely due to vibrational symmetric stretching [6]. The shift of this peak in wavelength space highlights the capabilities of Raman spectroscopy for phase discrimination. PHS107 (ammonium phosphate) shows this band to occur at  $946 \Delta \text{cm}^{-1}$ . PHS112 (potassium phosphate) shows this band to have a hypsochromic shift from PHS107, as it is positioned around  $918 \Delta \text{cm}^{-1}$ . PHS113 (sodium phosphate) shows this band at  $910 \Delta \text{cm}^{-1}$ .



**Figure 2.** Raman spectra of a four phosphate samples, sarcopside, ammonium phosphate, potassium phosphate and sodium phosphate minerals.

The nitrate samples were synthetically created compounds ( $\text{NH}_4$ , K, Na). Figure 3 shows the most prominent features in the 175 to  $1500 \Delta \text{cm}^{-1}$  wavenumber region. The strongest bands that occurs in this region are situated between  $1041\text{-}1064$ , and are due to the  $\nu_1$  symmetric stretching [7]. The analysis of these nitrate minerals again shows the capability of Raman spectroscopy for phase discrimination, and specific mineralogical identification.



**Figure 3.** Raman spectra of three nitrate minerals, sodium nitrate, potassium nitrate, and ammonium nitrate.

**Conclusions and future work:** Collectively these results suggest that fluorescence can be a problem when not using any form of mitigation techniques, i.e. time-gating.

However, there are a significant amount of minerals that exhibit Raman scattering stronger than fluorescence with the 532nm excitation source. This allows for their detection and characterization.

From these results, it appears that the RLS and SuperCam instruments will be able to detect and characterize astrobiological and habitability-relevant materials in many cases.

Raman spectra have been collected on the entire sample suite and the results will be presented at this conference.

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