SUPERCAM'S TIME-RESOLVED RAMAN AND LUMINESCENCE SPECTROSCOPY ONBOARD THE PERSEVERANCE ROVER

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Introduction: The SuperCam instrument onboard the NASA Perseverance rover will combine multiple investigation techniques to study Jezero crater [1,2]. These techniques include Laser Induced Breakdown Spectroscopy (LIBS), Time-Resolved Raman (TRR) and Luminescence (TRL) spectroscopy in addition to VISIR, a microphone and a remote micro-imager (RMI). This versatile remote-sensing instrument will provide chemical and mineralogical information from the same spot on the target at a sub-mm to mm scale. Here, we present the Raman and luminescence part of the instrument as well as Raman and luminescence spectra acquired by Super-Cam during development and testing.

Instrument description: SuperCam is composed of a mast unit (MU) and a body unit (BU), which are connected by an optical fiber, and a set of calibration targets. The MU is at the top of the rover mast and includes a laser, a telescope, an IR spectrometer, the RMI, and electronics. The BU contains a demultiplexer, two reflection spectrometers for LIBS and VIS, and a transmission spectrometer for LIBS, Raman, TRL, and VIS spectroscopy. For Raman spectroscopy, the excitation source is a pulsed, frequency doubled Nd:YAG laser, operating at 532 nm with a 4 ns pulse width, 10 mJ pulse energy and 10 Hz pulse repetition rate. The laser is collimated on the target illuminating a surface of a few mm^2 in extent. Irradiance at the sample location ranges from 10^{10} to 5.10^{10} W m^{-2}. The telescope collects light within the laser footprint with a collection area ranging from $\approx$1.5 mm in diameter at 2 m to $\approx$5.2 mm at 7 m: this is the analytical footprint. Light is then transferred to the optical fiber by several optics including a soft notch filter removing 95% of the reflected and Rayleigh scattered laser light. In the BU, light for TRR and TRLS is directed to a transmission spectrometer by an optical demultiplexer including an edge filter to remove the Rayleigh light (cutoff $\approx$140 cm^{-1}). The transmission spectrometer is a new compact design including diffraction gratings, an intensifier, and relay optics that focus light onto an ICCD. This configuration yields a spectral resolution better than 12 cm^{-1} for the Raman window and allows collection of luminescence emission signal from 535 to 850 nm. Wavelength calibration will be obtained from reference LIBS spectral lines, but two calibration targets were specifically designed for Raman: a diamond to assess the instrument integrity (intensity for alignment, FWHM for resolution...) and an organic target to monitor the detection of organics on Mars and possible irradiation effects on the Raman signature (Fig. 1). Detailed description of the calibration targets is given by [3].

How does SuperCam's Raman spectrometer differ from commercial instruments? SuperCam's Raman spectrometer differs from commercial laboratory instruments in two fundamental ways. First, SuperCam remotely-senses Raman signal with a telescope at large distances (routinely 2 to 7 m) with large laser spot sizes (i.e. a mm in diameter or greater) while commercial laboratory instruments detect Raman signal at short distances (i.e., ~ mm) with small spot sizes (i.e., ~ μm) by using a microscope. Hence, SuperCam Raman will likely probe a population of mineral phases depending on the target's grain size while laboratory instruments generally targets a single phase. Second, SuperCam utilizes a pulsed excitation source combined with a gated detector, while commercial laboratory instruments typically employ continuous-wave (CW) excitation sources and detectors. The idea is that Raman signal (lifetime $\approx 10^{-14}$ s) is only produced during the excitation pulse, while other signals like luminescence (lifetime $>10^{-9}$ s) are excited by the pulse but continue to decay after it. Using a short gate (100 ns for SuperCam) that is synchronized with the laser pulse allows efficient rejection of overlapping parasitic signals, like luminescence or daylight entering the telescope, and optimized collection of the Raman signal. TR spectroscopy further allows collection of only the luminescence signal by opening the detector gate just after the laser pulse: the Raman signal by then is absent while the luminescence is still present. Compared to CW instruments, SuperCam Raman benefits from signal intensification and filtering in the time-domain but uses considerably less excitation, hence receives less signal because of the non-continuous excitation.

Testing SuperCam Raman (TRR): SuperCam's Raman spectrometer has been tested during several campaigns at LANL using various configurations (EQM: engineering qualification model, FM: flight model): EQM-MU/EQM-BU in 2018 and EQM-MU/FM-BU in 2019. The final FM-MU/FM-BU was tested after integration onto the rover at JPL during summer/fall 2019. For most Raman activities, the number of shots is set at 100-200, the gate at 100 ns and the optimal distance to target is estimated to be from 2 to 5 m. To improve the signal-to-noise ratio, it will be possible to do more shots on some targets, up to 1,000 shots by repeating the nominal activity.

Various mineral targets were tested (Fig. 2): silicates, phosphates, sulfates, carbonates and accessory phases (e.g. oxides). Most targets consisted of raw single crystals but some were prepared as powder pellets. Some organics and natural rocks were also tested during the campaigns.

TRR spectra are generally high-quality for phosphates, sulfates and carbonates with clear detection of internal molecular modes and lattice vibrations. Notably, (i) polymorphs can be unambiguously distinguished (e.g. calcite vs.

aragonite), (ii) OH/H$_2$O is clearly detected/specified in relevant phases (e.g. gypsum, hydromagnesite) and (iii) spectral resolution is sufficient to detect differences in subtle Raman shifts of main peaks due to compositional variations (e.g. Mg vs. Ca carbonates). Some silicates (e.g. olivine, pyroxene, talc) yield good spectra as well with similar information, while others are challenging to analyze (e.g. some phyllosilicates). Accessory phases like opaque minerals are not detectable. For these and other challenging phases, it is mostly due to the high value of their optical absorption coefficient that prevents volumetric analysis and/or to their poor Raman efficiency (even with CW lab instruments!). Some organics like some amino-acids yielded strong signal.

Preliminary tests with mineral powders with various grain sizes and natural rocks show that fine-grained rocks will be challenging for Raman analysis while coarse-grained rocks will be more favorable. Further tests are also needed to assess (i) the sensitivity and detection levels of organics or accessory minerals in rocks and (ii) the respective Raman contributions of various minerals in the case of mineral mixtures.

Analyzing luminescence (TRLS): SuperCam's time-resolution capabilities efficiently remove most mineral luminescence when acquiring Raman spectra. On the other hand, SuperCam can efficiently remove Raman signals in order to isolate a luminescence signal. For example, luminescence may be used to detect emission centers at trace concentrations like Mn^{2+} in carbonates, Fe^{3+} in feldspars, or rare-earth elements (REEs) in various mineral matrices like apatite and zircon. An example of TR spectra is depicted for REE detection in Durango apatite in Fig.3.

Synergy with other techniques: LIBS will be used first to remove dust on the target's surface as dust is detrimental for Raman and IR analysis. Owing to the much larger analytical footprint of Raman compared to LIBS spots, we do not anticipate any Raman spectral artefacts due to the prior LIBS ablation [4]. Combining Raman with VISIR and LIBS will allow performing a petrochemical characterization of rocks, soil/regolith and even dust all along the M2020 prime and extended missions.

Conclusion: SuperCam Raman performs very well with many mineral phases of high interest for Jezero crater (e.g. carbonates, sulfates). Alternatively, some minerals/rocks are inherently hard to detect with Raman. SuperCam TRLS is an interesting new tool as it can efficiently detect and identify trace elements like REEs in some accessory minerals. By the time of the conference, SuperCam should have acquired Raman data from the martian surface, which will be the focus of the poster, in comparison with reference data acquired on Earth.

References: [1] Wiens R.C. et al. (2020) Space Science Reviews 10.1007/s11214-020-00777-5. [2] Maurice S. et al. (2020) Space Science Reviews SPAC-D-20-00069R1. [3] Manrique J.A. et al. (2020) Space Science Reviews 216, 138, 10.1007/s11214-020-00764-w. [4] Fau A. et al. (2019) Spectrochimica Acta B, 160, art. 105687.
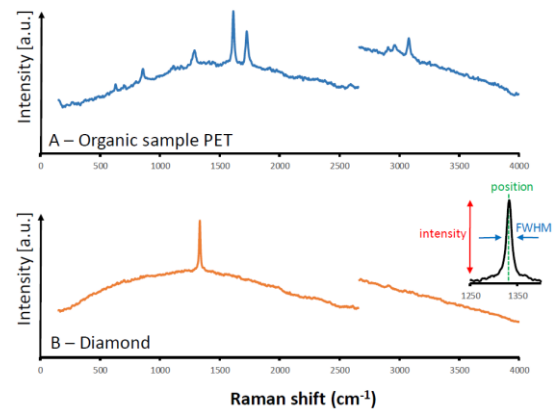

Fig. 1 Spectra acquired during rover tests (10 shots) of the organic PET (A) and diamond (B) onboard targets. Luminescence background from the adhesive under the diamond piece can be seen. Parameters used for checking the instrument health are depicted in the right inset. Figure modified from [3].
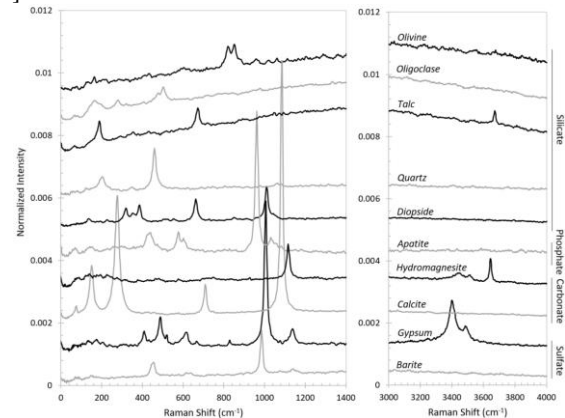

Fig. 2 Raman spectra of various minerals obtained with SuperCam's Raman. Figure modified from [1].
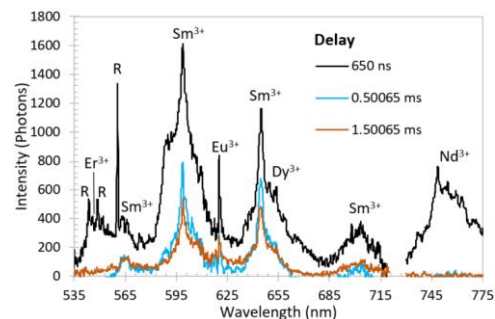

Fig. 3 Time-resolved luminescence spectroscopy of REEs in Durango apatite with various delays for the synchronization between laser and ICCD. "R" indicates Raman features collected with the luminescence. Figure modified from [1].