COMBINATION OF REMOTE RAMAN-LIBS DATA: NOVEL MINERAL DISCRIMINATION STRATEGIES TO SUPPORT SUPERCAM ON MARS

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Introduction: The SuperCam instrument onboard the NASA/Perseverance rover will offer the unprecedented opportunity to collect both Raman and LIBS spectra from remote targets on Mars [1-4]. By collecting complementary molecular and elemental information from the same spot of analysis, SuperCam spectroscopic datasets will optimize the geochemical and mineralogical characterization of Martian rocks and soils over spectroscopic systems used in previous missions.

The combination of Raman and LIBS data has been successfully used in previous works to optimize the discrimination of mineral phases [5,6]. However, it should be noted that many of these studies are based on the treatment of spectra gathered by state-of-the-art analytical instruments, the analytical features of which are not comparable to instruments built for space exploration.

To overcome this issue, this study proposes tailored analytical strategies based on the combination of LIBS and Raman data remotely collected by a SuperCam-representative standoff Raman-LIBS prototype.

Taking into account the mineralogy of the landing site and the main objective of the Mars2020 mission, Raman-LIBS combination strategies were applied to the study of carbonate minerals.

Carbonate units at Jezero Crater: Carbonate-rich geological units detected from orbit at the landing site are scientific targets of paramount importance for the M2020 mission. In detail, the enrichment of carbonates detected at the margins of Jezero crater suggests that their deposition occurred during the closed-basin phase of the lake sequence (lacustrine shoreline deposits) [7]. Knowing that a) carbonates that precipitated in the near-shore environments on Earth are often biologically mediated [8], and b) carbonate precipitation is widely recognized as an excellent mechanism for biosignature preservation [9,10], Jezero's marginal carbonates represent an optimal scientific target to search for biomarkers. As presented elsewhere [7], the strongest carbonate signatures detected at the margins of Jezero Crater are consistent with Mg-rich phases (e.g magnesite). Additionally, variations in band parameters (position of maximum intensity, peak symmetry and relative intensity ratio) suggested the occurrence of local Fe- and Ca- substitutions.

If these features are clearly detected from orbit, it can be deduced that on-ground spectroscopic analysis performed at a microscopic scale could potentially reveal the presence of even richer complex mineral assemblages, where intermixed carbonates and intermediate phases (e.g. dolomite) could be either detected.

In light of to the (plausible) forthcoming exploration of this geological environment by the Perseverance Rover, it is important to investigate to what extent the combination of Raman and LIBS data could optimize the discrimination of carbonate minerals.

Analyzed samples: A wide variety of carbonate minerals were selected from the ADaMM collection (Analytical Database of Martian Minerals [9]). The list of samples analyzed in this study is presented in Table 01:

Table 01: Carbonate mineral phases and mixtures

Ca-Fe-Mg ternary system		Other carbonates	
Name	**Formula**	**Name**	**Formula**
calcite	$CaCO_3$	rhodochrosite	$MnCO_3$
aragonite	$CaCO_3$	strontiatite	$SrCO_3$
magnesite	$MgCO_3$	cerusite	$PbCO_3$
siderite	$FeCO_3$	smithsonite	$ZnCO_3$
dolomite	$CaMg(CO_3)_2$	gaspeite	$NiCO_3$
ankerite	$CaFe(CO_3)_2$	witherite	$BaCO_3$
huntite	$Mg3Ca(CO_3)_4$	barytocalcite	$BaCa(CO_3)_2$
calcite-magnesite (50-50%)		Nahcolite	$NaHCO_3$
calcite-siderite (50-50%)		bismutite	$Bi_2O_2CO_3$
magnesite-siderite (50-50%)		gaylussite	$Na_2Ca(CO_3)_2{\cdot}5H_2O$
		malachite	$Cu_2CO_3(OH)_2$
		azurite	$Cu_3(CO_3)_2(OH)_2$

The Raman analysis of all carbonate samples was caried out to investigate how vibrational features vary according to cationic substitution.

Raman analysis of minerals within the Ca-Mg-Fe ternary diagram was then combined to LIBS data to 1) understand the capability of SuperCam to discriminate mineral phases potentially present at the landing site, and 2) define to which extent Raman-LIBS data combination strategies facilitate the proper discrimination of mixed mineral phases.

Employed instruments: Several concepts of stand-off Raman and LIBS instruments have been presented by the ERICA (Raman and Infrared Spectroscopy applied to Cosmogeochemistry and Astrobiology) research group over the past two decades [12]. As a result of these developments, a remote spectroscopic system was recently assembled to reliably simulate the scientific outcome of SuperCam. This instrument uses a Nd:YAG laser, frequency doubled, to provide a 532 nm excitation source.

The laser is delivered to the sample collimated, providing a "constant" irradiance with distance. Raman and LIBS were collected at the same spot of analysis, from samples located at 5 meters distance. The Raman signal was collected by a two-track spectrometer going from 0 to 4000 cm^{-1}, while LIBS spectra were recorded by an echelle spectrometer in a range between 200 and 980 nm. Remote Raman spectra were then compared to those gathered from a bench-top Raman instruments, ensuring a higher spectral resolution.

Results: Raman and LIBS data were separately analyzed to determine, in different scenarios, pros and cons of each technique in the discrimination of carbonate phases.

In detail, the spectral data gathered from bench-top and remote Raman setups was compared. As both systems use the same spectrometer, the impact of the loss of resolution (due to the wider laser in one hand, and the use of the intensifier in the other) in the remote detection of key spectroscopic features was assessed, thus gathering valuable information to reliably estimate the potential scientific outcome of SuperCam.

Afterwards, Raman-LIBS data combination strategies were applied to evaluate to which extent the proposed data processing methods could serve to overcome the limitations presented by mono-analytical interpretations.

On one hand, the remote Raman-LIBS study of mineral phases within the Ca-Mg-Fe ternary diagram helped define strengths and weaknesses of both analytical methods in the identification of mineral phases and/or assemblages that are expected to be found at Jezero Crater (Figure 01).

On the other hand, Raman-LIBS data combination strategies proved to enhance the discrimination of mineral phases over mono-analytical methods, especially in the case of mineral mixtures.

Beyond the proposed scenario, this work suggests Raman-LIBS data combination strategies could be used to enhance the scientific outcome of SuperCam operating in further geological contexts considered to be relevant to the Mars 2020 mission. Therefore, further laboratory experiments are recommended.

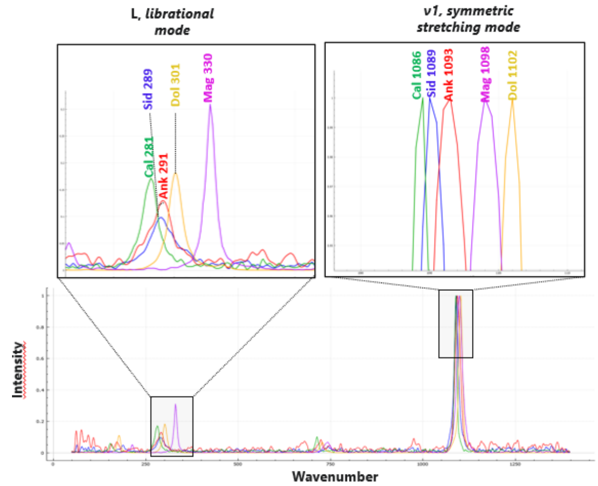

Figure 01: Remote Raman spectra of calcite (green), siderite (blue), ankerite (red), dolomite (yellow) and magnesite (blue).

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