

**SEMI QUANTIFICATION AND IDENTIFICATION OF CARBONATE MIXTURES USING A COMBINATION OF LIBS AND RAMAN TECHNIQUES.** S. Julve González<sup>1</sup>, J.A. Manrique<sup>1,2</sup>, M. Veneranda<sup>1</sup>, C. Prieto<sup>1</sup>, J.A. Sanz<sup>1</sup>, E. Lalla<sup>3</sup>, M. Konstantinidis<sup>3</sup>, F. Rull<sup>1</sup>, G. Lopez-Reyes<sup>1,2</sup> <sup>1</sup>ERICA research group (Universidad de Valladolid), Spain, <sup>2</sup>Department of Theoretical Physics (Universidad de Valladolid), <sup>3</sup>Centre for Research in Earth and Space Science, York University, Toronto, Ontario, Canada. (sofia.julve@alumnos.uva.es).

**Introduction:** The family of spectroscopic techniques used in planetary exploration has new members added recently, thanks to the inclusion of Raman spectroscopy in different instruments for robotic exploration [1-5].

On the other hand, the combined use of two data sources from different spectroscopic techniques can improve the ability to characterize different targets, as different techniques can provide information of different features of the sample, or redundant information if looking at the same feature, in any case the increase of information leads to a better characterization. In this study, we have focused on the combination of LIBS and Raman which will allow us to determine both of the elemental and molecular composition and microstructure of the samples. Using this combination we will evaluate semiquantitative calculations from binary mixtures of different carbonates using combined and individual data sets from LIBS and Raman spectra.

We focused on this type of compounds due to their great interest in astrobiology, as they are linked to water activity. Also, our study might be relevant on the current context of the Perseverance Rover, which is located in a former lake with an extremal rim where different carbonates precipitated and have been detected from orbit [6, 7].

**Materials and methods:** The samples are binary mixtures in different concentrations of calcium, iron and magnesium carbonates ( $\text{CaCO}_3$ ,  $\text{FeCO}_3$ ,  $\text{MgCO}_3$ ). That samples have been mixed using pure reagents from the laboratory, and mixing by grinding the powder in a mortar. Structurally they correspond to pure calcite, siderite and magnesite.

Natural samples of different Ca-Fe-Mg carbonates were also studied, as calcite, aragonite, dolomite, magnesite, siderite, huntite or ankerite. Although Raman spectra are different to the pure reagents mixtures, as the molecular structures are different, LIBS data from the laboratory mixtures can be used to build calibration curves to provide semiquantitative information of these natural samples.

LIBS spectra were taken with an instrument that uses the second harmonic of a Nd:YAG pulsed laser (120mJ per pulse) for the ablation. The spectra were acquired using an Echelle spectrometer (200 to 850 nm

attached to an intensified camera synchronized with the laser, with the ability to tune gate width and delays.

On the other hand, two different instruments have been used for Raman measurements (both using 532nm as excitation source). The first one is a top-bench instrument, providing laboratory-grade spectra in a range between 0 and 4000  $\text{cm}^{-1}$  with resolution under 6  $\text{cm}^{-1}$ , this is using a two-track spectrometer and cooled (-70 °C) CCD. Secondly, we have used the RLS-Sim [7], an instrument that mimics the RLS instrument onboard Rosalind Franklin Rover, including the acquisition constraints. This last instrument provides spectra closer in terms of quality to those we may receive from RLS.

With these datasets we will evaluate the combination of different processed data to obtain a semiquantification tool based on Artificial Neural Networks. Evaluating performance in each case. This approach is to be used in the natural samples, taking advantage of the developed LIBS calibration curves, and ad hoc univariate methods to evaluate Raman spectra. The objective is to evaluate how the characterization of the targets is improved thanks to the use of combined data sets.

**Results:** Starting with Raman data set solely, we use univariate analysis techniques, in which different indicators based in the position and intensity of different bands are calculated for each compound. Based on this we can calculate a polynomial regression based on these spectral features to obtain the concentration of different carbonates in the binary mixtures.

Calculations using LIBS spectra were done using multivariate methods. In particular, we used the intensities of different atomic lines of Ca, Fe and Mg (5 to 7 main spectral lines) as inputs to build a model based on Artificial Neural Networks. Different models were calculated for binary mixtures (providing two outputs) and a global model calculating the abundance of the three carbonates. These model were later used in the characterization of natural samples (previously characterized by XRD) and evaluated for their accuracy.

Finally models using ANN were created introducing the different features from both techniques, and the models were evaluated for accuracy.

**Conclusion:** Analyzing the data obtained with both techniques, we notice that the Raman data of the RLS-Sim provided the lowest performance given the low

signal to noise ratio, especially, in the samples with a higher Fe concentration that present a lower Raman cross section than the other carbonates evaluated. Anyway, this is due to a known instrumental issue that is being currently corrected.

In particular, using this instrument, the available spectral features for calculations, either univariate or multivariate, is the main Raman band of the carbonates, as weaker features were barely appreciable in the collected spectra. This, of course, have a negative impact in the final results of our model, as the identification relies only in one feature. The Raman spectra are improved with the first mentioned instrument thanks to its greater range and spectral resolution, as well as its ability to collect spectra with higher SNR, not being affected by operational constraints as RLS-sim, and having a detector less noisy.

The results of the LIBS method are much more accurate in distinguishing between different cations in the carbonate, although it may not distinguish between aragonite or calcite, as expected.

A rapid combination of both techniques has been shown to improve slightly the semiquantification of the binary mixtures when compared to LIBS.

In addition, to estimate the concentration of the natural samples, we see how the calculations done using LIBS data, and the model developed with binary mixtures (using ANN), are close to the concentration measured using mass spectroscopy.

However, when it comes to Raman spectra obtained with RLS-Sim, it is difficult to distinguish the different natural samples based only on the main peak of each compound as these are, in many cases, very close to each other. Identification using the top bench instrument is easier and demonstrates how it can distinguish between different structures (polymorphs).

The combination of both inputs demonstrated how the semiquantification of mixtures was improved, and all the aspects of certain targets can be better known using this framework. Mixtures of more compounds are to be evaluated, as situations in which carbonates are present in combination with silicates in the same analyzed area. Anyhow, the ability to combine different techniques in a single instrument encourages frameworks as SuperCam, or the combination of different instruments with the possibility to measure on the same area, such as PIXL/SHERLOC or the Pasteur Analytical Laboratory of Rosalind Franklin's Rover.

627-654 [6] B. Horgan et al. (2020) *Icarus*, 339, 113526, [7] Clave E. et al (2022), *this conference*, [8] G. Lopez et al. (2021), *J Raman Spectrosc*, 1.

**References:** [1] Wiens R.C. et al. (2021) *Space Sci Rev*, 217, 4. [2] Maurice S. et al. (2021) *Space Sci Rev*, 217, 47. [3] Manrique J.A. et al. (2020) *Space Sci Rev*, 216, 138. [4] Bhartia R. et al. (2021) *Space Sci Rev*, 217, 58. [5] Rull F. et al. (2107) *Astrobiology*, 17, 6-7,