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INFRARED, TIME-RESOLVED RAMAN AND LUMINESCENCE SPECTROSCOPY OF CARBONATES: PREPARING FOR MARS 2020 SUPERCAM INSTRUMENT.
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Introduction: All three remaining landing sites (NE Syrtis [1], Jezero [2] and Gusev [3]) for the Mars 2020 rover have shown occurrences of carbonate minerals detected either by orbital IR spectroscopy or *in situ* by the rover Spirit at Gusev [4]. Carbonates are key players in the Martian Carbon cycle and they may constitute a major rocky shallow carbon reservoir which has likely interacted with the Martian atmosphere through time [5]. Carbonates are also tracers of shallow or deeper fluid-rock interactions (hydrothermalism) identified on Mars [6], in particular at Gusev and NE Syrtis. Last but not least, one of the main objectives of the Mars 2020 mission is the identification of past or present life on Mars. Carbonates being frequently formed by biological processes on Earth in lacustrine environments possibly similar to Jezero, they are also excellent candidates to trace Life on Mars surface.

Orbital IR spectroscopy by diffuse reflectance is used in a specific spectral range to identify carbonates. On Mars, carbonates of various chemical composition between the Ca-, Fe- and Mg- endmembers were identified, some of them being potentially hydrated, e.g. Mg-hydrocarbonates [7]. This has been confirmed by the analysis of carbonates in martian meteorites and *in situ* analysis by Spirit at Gusev. Although such IR data are very powerful and useful to detect carbonates, clear identification of mineralogy and/or chemistry remains challenging for this technique due to strong overlapping of the main carbonates absorbtion bands with bands from other mineral phases (e.g. serpentines, phyllosilicates), but also due to a lack of spectral resolution for most IR planetary instruments.

The SuperCam instrument will combine Laser Induced Breakdown Spectroscopy (LIBS), time-resolved Raman and luminescence spectroscopy in addition to IR, a microphone and advanced imagery onboard the NASA Mars2020 rover [8]. This versatile remote sensing instrument is very promising to detect and characterize carbonates as Raman spectroscopy is very sensitive to distinguish carbonates polymorphs as well as the various structures of carbonates including the water they can incorporate. Chemistry of major (Raman) and trace (luminescence) elements will also be accessible by SuperCam Raman instrument and will complement the chemical information retrieved by SuperCam LIBS. Here, we present a combined IR, time-resolved Raman and luminescence study of reference carbonate mineral phases and discuss some expected contributions from the Mars 2020 SuperCam instrument.

Methodology: A series of reference carbonate minerals were analyzed including Ca-, Fe-, Mn- and (hydro)Mg-carbonates and some compositions in between. These minerals were first characterized by X-ray diffraction and their chemistry was analyzed when necessary: some of them are not completely pure and exhibit traces of other mineral phases and/or organic matter. Raman measurements were carried out at IMPMC (Paris, France) using a homemade time-resolved Raman/luminescence instrument with both microscopic and remote macroscopic analysis working at 532 nm [9]. This instrument can be operated in a SuperCam-like configuration in terms of irradiance (in the range 10^{10}-10^{11} W. m^{-2}) and data collection (ICCD gating of 100 ns, spectral resolution of Ca. 12 cm^{-1}). Figure 1 summarizes some information that can be obtained from Raman spectroscopy for carbonates, *i.e.* mineralogy and chemistry. Diffuse reflectance IR spectra were obtained by using a Nicollet 6700 in the range 1.3-2.6 μm.
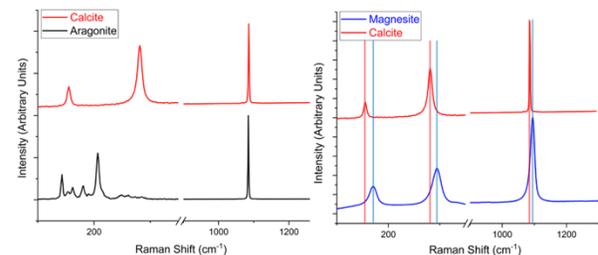

Figure 1: Left: Raman spectra of polymorphs calcite and aragonite showing different lattice vibrations (range 100-400 cm^{-1}) due to different structures, but similar internal modes (Ca. 1085 cm^{-1}) due to same chemistry (Ca-carbonates both). Right: Raman spectra of magnesite and calcite with similar lattice vibrations and internal modes (same structure) but shifted due to the different chemical composition (peak positions indicated by red line for calcite and blue line for magnesite).

Results and discussion:
Selected IR diffuse reflectance spectra are displayed in Figure 2. Raw spectra as well as positions of the 2.3 and 2.5 μm bands are in good agreement with existing data (e.g. [7]) . Figure 3 depicts Raman spectra for a series of hydrated Mg-carbonates obtained with (i)

conventionnal continuous wave configuration and (ii) our time-resolved Raman instrument in SuperCam configuration. Monocrystals of pure endmembers (e.g. calcite, aragonite, magnesite, siderite, rhodocrosite) are easy to analyze and yields high-quality Raman spectra for both configurations.
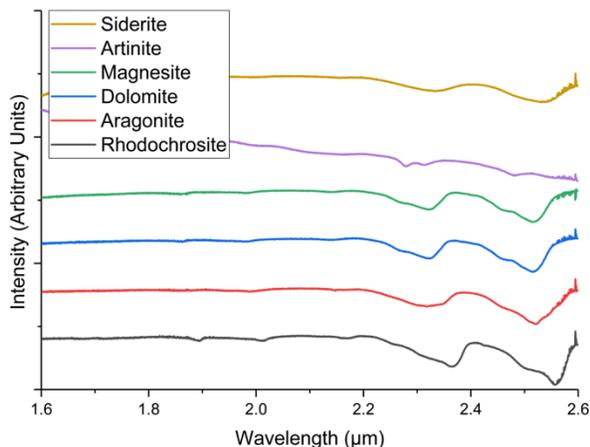

Figure 2: Infrared spectra for various carbonates obtained in diffuse reflectance mode. The main carbonate absortion bands stand at 2.3 and 2.5 μm.
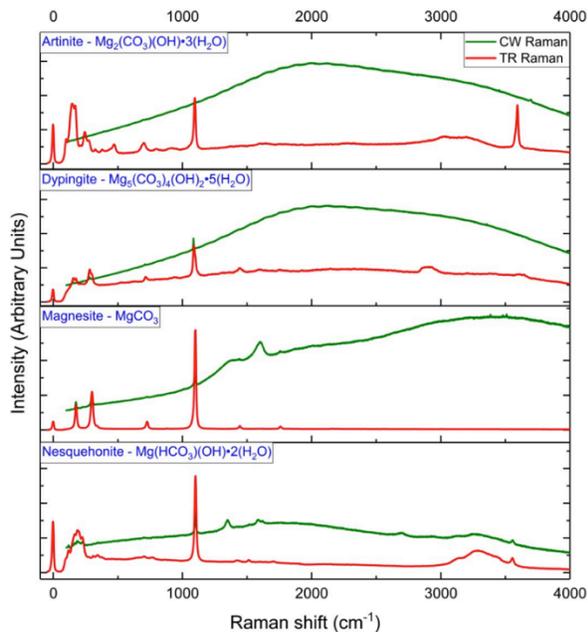

Figure 3: Raman spectra for various (hydrated or not) Mg-carbonates acquired in continuous wave (green) and time-resolved (red) Raman spectroscopy at 532 nm. Note that the strong background present in the green spectra and masking the Raman signal can be significantly removed thanks to the time-resolution. Note that the presence of OH or H_2O in the structure generates bands in the range 3000-4000 cm^{-1}.

In contrast, all fine-grained carbonates analyzed with the continuous wave mode were characterized by an intense background often masking the Raman peaks. Similarly, most (hydro-) Mg carbonates exhibit such a background when using the continuous wave configuration. Alternatively, using the time-resolution instrument and closing the ICCD gate around the laser pulse allows to significantly decrease this background and in most case to retrieve good quality Raman spectra. Interpretation of this background (often considered abusively as luminescence) requires further work and is likely due to a combination of laser diffusion in fine-grained materials with intrinsic luminescence by various possible emission centers (defects, trace elements).

Altogether, our work constitutes a first consistent spectral database of IR and time-resolved Raman spectra for the SuperCam instrument. More generally, this database complements existing database (e.g. RRUF for Raman) by adding new minerals or spectra for some minerals that were difficult or even impossible to analyze with continuous wave Raman at 532 nm.

Conclusion:
The SuperCam time-resolved Raman instrument should be able to detect carbonates and should have sufficient spectral resolution not only to distinguish polymorphs (calcite/aragonite) but also to give first insight into the chemical composition of the analyzed carbonate target including its possible water incorporation by analyzing the shift of the main Raman modes. More work is needed to assess the sensitivity of time-resolved Raman in a SuperCam configuration for the analysis of carbonates in relevant real rocks, *i.e.* within various mineral matrix.

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