LISTENING TO LASER PLASMAS OF MINERALS: RESEARCH ACTIVITIES TOWARDS THE ANALYTICAL EXPLOITATION OF THE MICROPHONE ONBOARD SUPERCAM FOR THE MARS 2020 ROVER.

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Introduction: One of the main problems that researchers must to tackle with to utilize atomic and ionic emission lines intensities of particular elements to quantify the different species in Mars rocks and soils through their laser-induced breakdown spectroscopy (LIBS) measurements is the matrix effect: Two rocks with the same elemental content may report LIBS spectra with different intensities for the corresponding emission lines while two rocks with different content of particular elements may report LIBS spectra with identical intensities for the associated emission lines. This non-linear relationship between spectral lines intensities and elemental contents creates a significant complication to an accurate quantitative analysis.

In order to reduce the interference matrix and to improve the calibration models, LIBS spectra can be normalized using a parameter representative of the actual plasma conditions. One of the main standardized methods of data normalization for the proposition of univariate and multivariate regression models for the direct analyses of rocks and soils by LIBS to compensate for the differences among sample matrices is the use of a reference signal.[1,2] Thus, in connection with the SuperCam/Mars Microphone scientific investigation,[3] the acoustic signals associated with the plasma formation during analysis of a set of mineral phases using a specifically designed LIBS setup coupled with acoustic test bench under ambient terrestrial atmosphere is studied.

Set-up and Materials:

SonoLIBS system. At this preliminary phase of the research a laboratory scale prototype has been considered. The acoustic sensor consisted of a Q-switched Nd:YAG (neodymium-doped yttrium aluminum garnet) laser (532 nm, 50 Hz, 70 mJ/pulse−1, 13 ns pulse width, flat top hat distribution intensity) as excitation source. Laser pulses at low repetition rate (1 Hz) were directly focused on the target surface through a 30 cm focal length plane-convex quartz lens, thereby reaching a spot diameter of ca. 400 μm. Acoustic signals launched into ambient atmosphere were captured using a 6 mm pre-polarized condenser microphone (20 Hz–19 kHz frequency response, Omni-directional polar pattern, 14 mV/Pa sensitivity, TR-40 Audix model) located coaxial to the source-receiver path at a fixed distance of 100 cm. Transduced sounds were digitized using a 24-bit/192 kHz audio interface (Roland UA-55 Quad-capture model) at the standard sampling rate of 96 kHz.

Targets were housed inside a purpose-built hemi-anechoic chamber (70 × 40 × 40 cm3, L × W × H) on top of a Y-axis linear translation stage to refresh the sampling position into the target. Polyurethane foam pyramid-shaped panels (80 mm thickness, 23.0 ± 2.0kg/m³ density) were used to form the absorbing boundaries inside the chamber to reduce echoes as well as vibrations and noise contributions from outside. A total of one hundred audible events (recording time was 100 s) were laser-stimulated in each of the acoustic trials. To diagnose the acoustic differences time-domain waveforms were resolved into frequency components spectra of data using fast Fourier transform (FFT) methods.

The optical emission spectra of the plasma sources launched in parallel with the acoustic events were also gathered. The plasma light emitted was collected orthogonally through a collimating lens coupled to the tip of a 600 μm optical fiber (tri-furcated cable, 3×600 μm fibers, all legs SMA terminated, total 2 m long, splitting point in the middle) which guided the light to the entrance of a tri-channel miniature Czerny-Turner spectrograph (75 mm focal length). Spectrometers were each one fitted with CCD detectors. LIBS spectra that span from 350 nm to 900 nm were achieved. Plasma light was acquired using a 1.1 ms gate width at 1.28 μs delay from the external trigger input (zero-time position) supplied by the laser Q-switch output signal to the activation of the detector device.

Materials. LIBS analyses have been accomplished on 4 different minerals whose evidences on Mars have been discovered. A pair of carbonate minerals, aragonite (one of the three most common naturally occurring crystal forms of CaCO3) and siderite (FeCO3), which have very important implications on the possibility that life developed there has been considered. Furthermore, pyrite (FeS2) and goethite (α-Fe3+O(OH), an iron-bearing hydroxide mineral normally formed under oxidizing conditions as a weathering product of the first, have been tested.
Results: Fig. 1 shows typical examples of the LIBS spectra measured from carbonate minerals together with the Fast Fourier Transforms (FFTs) of recorded waveforms on the corresponding plasmas. As seen, acoustic signal accompanying laser plasmas changes not only its intensity but also its frequency spectrum depending on the ablation performance over each mineral.

![Fig. 1: LIBS spectra measured from aragonite and siderite together with the Fast Fourier Transforms (FFTs) of recorded waveforms on the corresponding plasmas.](image)

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Fig. 2 shows the FFTs of recorded waveforms on the laser-induced plasmas of selected minerals. As seen, acoustic response during μplasma formation can be employed to identify iron-based minerals chosen (cases in which different samples may practically provide identical LIBS spectra whose differences are solely due to variations in the relative intensity of Fe lines according to the ablation rate of each material.

The difference in acoustic responses confirm that acoustic signals can be used as an identifier of targets and considered as a core asset to normalize the spectral intensities [4,5,6] obtained under the same experimental conditions from different minerals due to properties such as hardness/density and roughness.

![Fig. 2: FFTs for waveforms detected simultaneously by a microphone during laser ablation of absorbing minerals in air at atmospheric pressure.](image)

Conclusions: The frequency analysis of the audible signals detected during the laser ablation of different minerals have revealed valuable differences that could be usefully exploited for identification purposes. These differences are supposed to be linked to different disturbances on the surrounding air because the distinct microstructural vibrations forced on each mineral's surface.

Despite these findings, however, one should not lose sight of the fact that rocks are intrinsically inhomogeneous since they are a mixture of different particles of minerals. Rocks usually may present several degrees of surface texture and/or grain size, which may make acoustic responses for the rocks conditional on the involved mineral phases. Thus, research is ongoing for improving the analytical capabilities for determining acoustic responses of the different geological samples obtained. In addition, future acoustic analysis of these samples under Martian conditions are being considered.

References: