

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) ANALYSIS OF ORGANIC-BEARING MARS ANALOGUE SAMPLES. J.C. Kuik¹, E. A. Cloutis¹, V. Latendresse², and R.V. Kruezeleky². ¹ Dept. Geography, University of Winnipeg, 515 Portage Ave., Winnipeg, MB, Canada R3B 2E9; kuikjessec@gmail.com. ² MPB Communications Inc. Pointe Claire, QC, Canada.

Introduction: Building on the success of the ChemCam instrument on the Mars Science Laboratory (MSL) rover, the NASA Mars2020 rover will host a refinement of the instrument, known as SuperCam. SuperCam will host four remote sensing techniques [1] that can help explore and characterize an astrobiologically relevant ancient environment and search for signs of extant or extinct life [2]. SuperCam will utilize a laser-induced breakdown spectrometer (LIBS), an updated Raman spectrometer, time-resolved fluorescence, as well as a vis-NIR reflectance spectrometer [3]. These remote sensing techniques will work together to investigate the geological, mineralogical and elemental composition of Mars.[3]

We are investigating the capabilities that a 1064 nm Nd:YAG LIBS[1] has on detecting organics in a laboratory environment. LIBS is a spark spectrochemical technique which utilizes a laser pulse to ablate material on the surface of the target, generating a high-temperature plasma. As this plasma cools, any excited atomic ionic and molecular fragments present will emit radiation as they reconfigure to an electronic ground state. The radiation emitted shows the elemental makeup of the surface of the sample being analyzed via emission lines that are element-specific [4].

An investigation of the LIBS capabilities in detecting organic elements was performed on a suite of organic-bearing Mars analog samples. Analysis was performed in a laboratory environment with an integrated LIBS and DUV Raman instrument (LiRS), developed by MPB Communications Inc. [5]. The focus of this study is to understand LIBS ability to detect organic elements in a suite of Mars analog samples. Preliminary findings are reported in this paper.

Samples: The suite of samples analyzed in this study was a mix of solid rocks, and powders compressed into pellets, from a variety of Mars analog sites. Thirty-nine samples were analyzed ranging from full rock samples comprising biofilms, endoliths, stromatolites, oil sands, and various organic-bearing geological materials and laboratory-created organic-bearing mixtures. The use of pellets for the powdered samples was necessitated by the need to mount samples vertically for the LIBS measurements.

Experimental/Results: The instrument used for this study was a modular breadboard of integrated LIBS and DUV Raman spectroscopy techniques,

(LiRS) [5]. The LIBS integration utilized a 16mJ pulse miniature 1064nm Nd:YAG laser. The integration time for analysis was 200ms. Samples were individually positioned to obtain the greatest intensity of peaks. Optimum sample placement was guided by using the acoustic signal of the LIBS-induced sample ablation. Pulse durations were 265 μ s, with laser pulse frequency set to 10Hz. A suite of detectors covered the wavelength range from 240nm to 830nm, with a spectral resolution of 0.08 nm FWHM at 250nm to 0.3nm near 830nm [5].

Analysis of samples was performed in ambient terrestrial conditions of atmospheric pressure and temperature. The points of interest on each sample were determined through visual identification of features that indicated the presence of organics on the surface of each sample. For example, sample ANT-EN5 showed melanized fungi striations just below the surface of the rock. In cases where visual evidence of organics was not detected, random points on sample surfaces were measured.

The emission spectra were analyzed for the presence of emission lines associated with organic elements. The C emission line at 723.8 nm is chosen because it not affected by iron features like many that are found in the UV [6]. The peak of interest was likely found (near 721 nm), and is likely due to carbon (wavelength calibration of the LiRS instrument is ongoing). Figure 1 is a zoom of a carbon peak of interest.

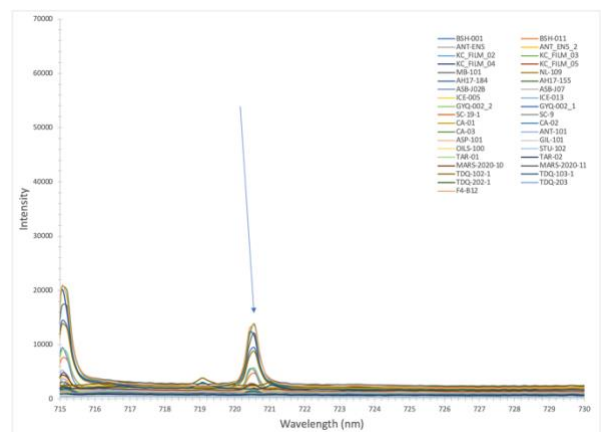


Figure 1: LIBS spectra of all samples. Zoomed in to identify carbon peak at 723.8 nm. The likely carbon peak is positioned at 720.5 nm.

A nitrogen emission line of interest at 500.5 nm is also present in the samples and has been found in LIBS analysis of N-bearing organic compounds in various Mars-relevant mixtures [6]. Figure 2 shows the emission spectra of all samples in this wavelength region. From the figure the sharp peaks indicated are powder samples of a mixture of nontronite + adenine, and nontronite and adenine. The broader hump upon which these narrower peaks are superimposed is due to atmospheric nitrogen.

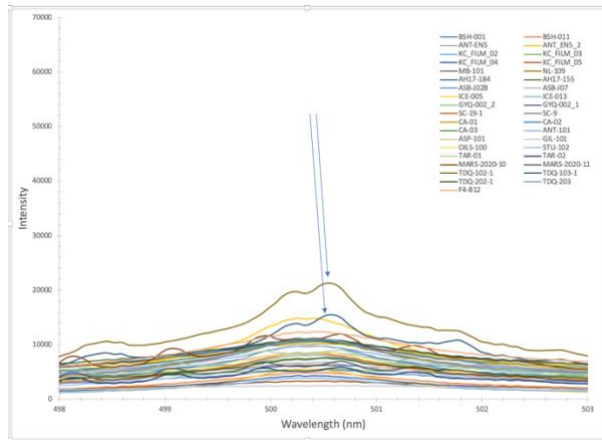


Figure 2: LIBS spectra of all samples. Zoomed in on the nitrogen emission line at 500.5 nm. Indicated humps are samples TDQ-102-1 (99.4% hematite + 0.6% adenine TDQ-202-1 (nontronite 99% + adenine 0.1%).

An oxygen feature present at 777 nm is present in all sample spectra. Identification of this peak shows LiRS capability of detecting oxygen, whether due to the atmosphere or the sample [7], but also suggests that LiRS calibration is more complicated than a simple linear wavelength offset (the cause is currently being investigated). Figure 3 shows the zoomed in spectra in the region of the oxygen peak.

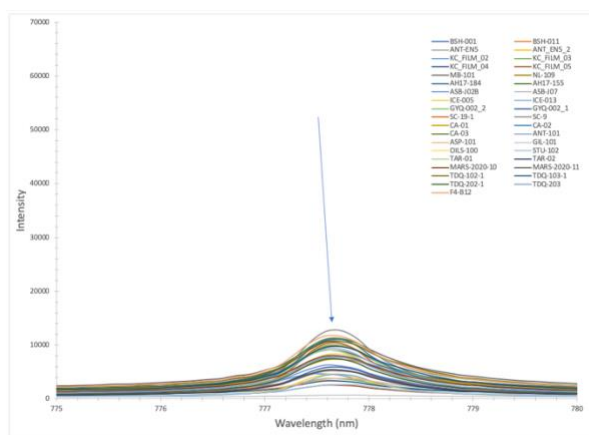


Figure 3: LIBS spectra of all samples. Zoomed in on the oxygen emission line at 777.7 nm.

Our preliminary results show that LIBS on the LiRS instrument is capable of detecting organics in a diverse suite of organic-bearing Mars analogue samples via detection of a nitrogen peak, and possibly a carbon peak, and that oxygen peaks can also be discerned. The expected carbon feature was not detected at 723.8 nm, but is likely present at slightly shorter wavelength than expected for reasons that are still being investigated.

Discussion/Implications: LIBS, with its ability to identify elemental bioindicators in emission spectrum, will be capable of identifying organic-bearing targets of interest similar to those included in this study [7]. NASA's upcoming plans to land the Mars2020 rover at Jezero crater will provide the opportunity to explore a deltaic environment for which analysis of samples in this terrain will rely upon SuperCam as a means of detecting biosignatures based upon elemental composition and abundances, furthering our understanding of Mars history. Therefore it is important to be informed as to the instrument's capabilities and limitations in regard to *in situ* sample analysis.

Conclusions and further work: LIBS is capable of detecting elements of interest related to the presence of organic molecules and potential biosignatures. Further work on a larger suite of organic-bearing samples from diverse terrestrial Mars analog environments will further improve our understanding of LIBS's ability to interrogate and characterize organic-bearing lithologies on Mars.

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References: [1] Wiens, R.C. et al. (2017) *Spectroscopy*, 32, 50-55 [2] Mustard, J.F. et al. (2013) *Report on Mars2020, SDT*, 1-154. [3] Perez, R., et al. (2016) *ICSO*, 105622K. [4] Harmon, R.S. et al. (2005) *G.E.E.A*, 5(1), 21-28. [5] Latendresse, V. et al. (2018). *ASCE*, paper 121. [6] Dequaire, T. et al. (2017). *Spectrochimica Acta Part B*. 131. p 8-17. [7] Tran, M. et al. (2001), *Journal of Analytical Atomic Spectrometry*. 16(6), 628-632.