COMBINED MEASUREMENTS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY AND LASER-INDUCED MOLECULAR SPECTROMETRY FOR PLANETARY EXPLORATION.

E. A. Lalla[1], M. G. Daly[1], A. Quaglia[2], S. Walker[2], G. Flynn[2], G. Levy[2], E. Sawyers[1], G. Lopez-Reyes[3], and M. Konstantinidis[1,4]. [1]Department of Earth & Space Science & Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada, (elalla@yorku.ca). [2]Sciencetech Inc, 1450 Global Drive, London, Ontario, Canada. [3]Unidad Asociada UVA-CSIC-CAB. C/ Francisco Valles 8, 47151, Boecillo, Spain. [4]Dalla Lana School of Public Health, University of Toronto, 155 College St. Toronto, Canada.

Introduction: The Canadian Space Agency (CSA) is providing financial support, as part of the effort from the Government of Canada, to Canadian Companies for increasing their competitiveness in the space sector [1]. The STPD Program from the CSA supports basic research and development (R&D) in new space technologies that encourage innovation and increase Canadian industrial capabilities [1]. These efforts are paramount to increase the role of the Canadian Space industry as key collaborators in planetary missions and further industrial applications. LABEISS funding received from CSA is in the second year. For our current status, we finished Phase 0 study, which is being used as a roadmap for future instrument and science development for possible flight on a planetary mission in the near future. At this conference, we will report on the latest results of the current project. We will start the Abstract with an overview of the LABEISS techniques used, the LABEISS project and the breadboard, and current results [2, 3].

Overview of LIBS-LAMIS. Laser-Induced breakdown spectroscopy (LIBS) has become one of the most efficient and reliable techniques onboard different rovers such as ChemCam and the more recently evolved system SuperCam, onboard NASA's Mars2020 Perseverance [2, 3]. LIBS is a rapid technique for obtaining analytical results of major and minor elements in geological samples, soil samples, and surface cleaning (with repetitive laser ablation). LIBS, like many other methods (e.g., Raman Spectroscopy or X-Ray Diffraction), presents some limitations in its ability to characterize the geological origin of a sample and several features can be lost (e.g., geochronology, isotopic features, and possible origin of organic matter). To address these limitations, LAMIS has emerged as a promising complementary technique to cover some of the limitations of LIBS. LAMIS is based on the isotopic shift (so-called isotopologues) from the molecular emission at a time delay defined in terms of when the plasma and atoms associate during the laser ablation [4, 5].

Laser ABlation Elemental ISotopic Spectrometer (LABEISS): This project is being undertaken and led by Sciencetech Inc. (SCI) and the Planetary Exploration Instrumentation Laboratory (PIL) at York University. The LABEISS project is focused on providing new insight into a putative instrument that combines the LIBS and LAMIS technologies. Moreover, the project is aligned to provide basic R&D of space technology to be used in future missions while exploring extraterrestrial environments such as moons asteroids and other minor bodies in the solar system. It will provide isotopic analyses with a precision that can help our understanding of how these bodies came to be, their continuing dynamics, and even give clues to biologically related processes for understanding the evolution of organic molecules in a planetary context. Furthermore, LABEISS can obtain quantitative and qualitative information on the sample's composition (elemental and isotopic) for different planetary surfaces. Also, the combined techniques are aligned with CSA research priorities for future planetary exploration that include Planetary Science, Astrobiology, Planetary Geology, Geophysics and Prospecting, Planetary Space Environment, and Space Health [4]

The LABEISS system was undertaken via two parallel and interrelated tasks: "Science" and "Engineering." The scientific objective of LABEISS was to determine the best implementation by which to combine the LAMIS method with LIBS to determine isotopic elemental composition and quantification for different targets. This challenge included scientific research and characterization of the selected targets of planetary interest (space simulant, meteorites, and certified isotopic samples) such as: 1) understanding the relationship between line intensity in the spectrum and the concerned isotopic mass fractions in the samples; 2) research of the electronically, vibrationally, and rotationally excited "isotopologues" of dimers, oxides, nitrides, or halides in plasma reactions of the ablated sample of atomized matter.

The engineering challenge of the proposal included developing a robust system that can be applied in future planetary space exploration and other fields such as geology and archeology, among other emerging needs of the marketplace. Our engineering and design approach started with a baseline i nstrument. We are determining and selecting the spectroscopic (Spectrometer + gated camera) system, laser system, and optics, according to the technical and scientific requirements of LIBS and LAMIS.

LABEISS breadboard configuration. The proposed configuration for the LABEISS Breadboard is shown in Figure 1. It employs a 1064 and 532 Quantel pulsed dual laser (the output power, pulse duration, and frequency adapted to the sample). The incoming beam is delivered through a beam Nd:YAG coated Galilean expander, where the beam is increased 3 times in diameter. Subsequently, the ablation scattering is delivered to an Nd:YAG coated off-axis parabolic mirror and focused onto the sample at 20 cm. The light created from the plasma is collected by a 7.5 cm diameter refractive system with two lenses (f = 25 cm and f = 15 cm). The light is coupled into fiber optics and delivered to the Spectrometer and Camera. Finally, we set up the LABEISS breadboard with the selected optimized mechanical and optical configuration system (Laser, test Spectrometer, camera, optical configuration, and sensing distances). Furthermore, we characterized the breadboard with respect to key characteristics such as required laser power, sensing distance, spectrometer configuration (delay time, acquisition time, delay-width), and calibration methods (intensity and wavelength) [3].

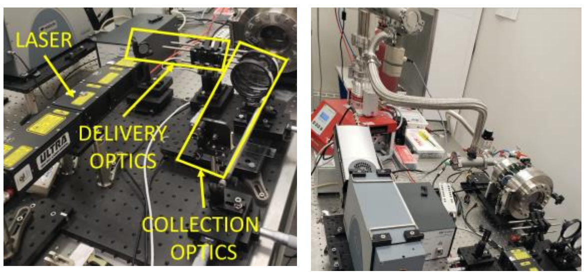

Figure 1. Sketched configuration of the LABEISS breadboard system (more details on the Poster).

To fulfill the scientific requirements and establish a better approach to emulate real, in-situ measurements under planetary conditions, we developed several augmentations. We have thereby addressed the scientific and technical limitations of the LABEISS breadboard in advance, which will increase the chances of developing a successful future flight instrument. The augmented version included a vacuum X-Y LIBS-LAMIS scanning mode for 1x1cm^2 capable of mapping 20 points per sample. Future measurements, at the end of the project, would result in high-fidelity to real missions . The augmentation on the LABEISS system was the installation of a Nano-Chamber, designed to be as small and light as possible with a volume of 5000 cm^3 with a custom add-a-door equipped with a sapphire window allowing light excellent transmission in the visible region where the X-Y stages for mapping have been installed inside. Furthermore, the Mini-Chamber allows obtaining ultra-high vacuum in approximately 30 minutes for emulating Moon environment installed on a heavy-duty translation stage. The Nano-chamber presents a pressure and atmospheric monitoring system that allows control over the pressure and atmospheric composition for different planetary atmospheres like Earth or Mars. The samples can be monitored with a context camera that will be used to ensure the stability of the sample before and after each measurement [3].

Currently, we are using ^{12}C and ^{13}C standards to estimate the LIBS and LAMIS spectroscopic. Figure 2 shows the spectral evolution of the plasma ablation for ^{12}C and ^{13}C at 500 ns time delays. Figure 2 shows the so-called carbon Swan molecular spectrum from both carbon isotopes (^{13}C and ^{12}C).

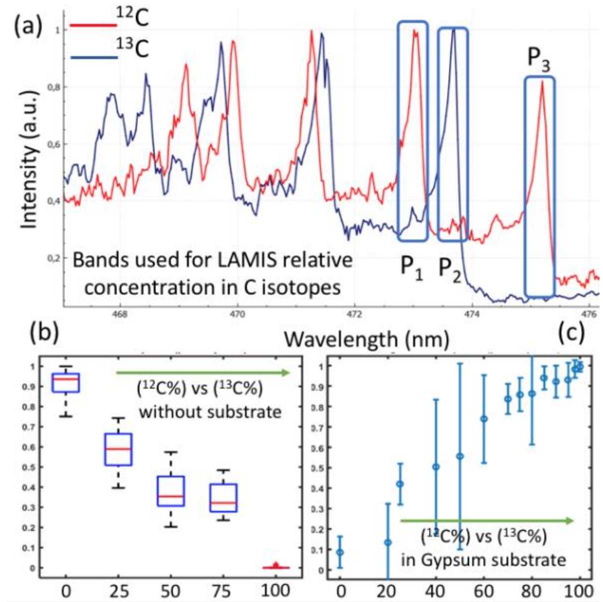

Figure 2. LIBS-LAMIS spectra of $^{12}C/^{13}C$ sample. (a) LAMIS spectra at 500 ns of Swan molecular spectrum of ^{12}C and ^{13}C. (b) Evolution of pelletized samples at different % ^{12}C and ^{13}C samples without substrate , using $\left[\frac{P_1}{P_2+P_1}\right]$. (c) Evolution of pelletized samples at different % of ^{12}C and ^{13}C samples in 80% gypsum substrate using $\left[\frac{P_2}{P_2+P_3}\right]$.

Spectrometer Design: We are starting to evaluate the results from commercial spectrometers and cameras, enabling the most suitable combination for possible system miniaturization and future integration into the LABEISS breadboard. These measurements have enabled us to prototype the most suitable spectrometer, which will be integrated into the LABEISS breadboard at the end of the project [3].

Acknowledgments: We wish to acknowledge the support provided by the CSA through their STDP. This study is partially supported with funding from Sciencetech Inc and York University.

References:[1] STDP Program [2] Weins R. C. et al. (2013) *Spectrochim. Acta Part B 82: 1–27*. [3] Lalla et al (2021) *52nd LPSC*, Abstract #2266. [4] CSA Priorities. [5] Bol'shakov et al. (2016) *J. Anal. At. Spectrom* 31, 119-134.