OVERVIEW OF THE LABEISS BREADBOARD FOR PLANETARY EXPLORATION. E. Sawyers[1], M. G. Daly[1], A. Quaglia[2], S. Walker[2], J. Freemantle[1], G. Flynn[2], G. Levy[2], E. A. Lymer[1], A. Barlow[3], G. Lopez-Reyes[4] and E. A. Lalla[1,5]. [1]Department of Earth & Space Science & Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada, [2]Sciencetech Inc, London, Ontario, Canada. [3]University of Waterloo, Waterloo, Ontario, Canada. [4]Unidad Asociada UVA-CSIC-CAB, Boecillo, Spain. [5]Canadensys Aerospace Corporation, Bolton, Ontario, Canada

Introduction: The Laser ABlation Elemental ISotopic Spectrometer System (LABEISS), is a breadboard instrument that features two primary techniques – Laser-Induced breakdown spectroscopy (LIBS) and Laser Ablation Molecular Isotopic Spectrometry (LAMIS). Furthermore, LABEISS is capable of Raman Spectroscopy, Laser-Induced Fluorescence and Passive Reflectance as supporting techniques. LIBS has become a staple technique in planetary exploration, most notably as ChemCam and SuperCam instruments, the latter recently launched onboard NASA's Mars2020 Perseverance rover [1, 2, 3]. LIBS is a rapid method for obtaining analytical results of major and minor elements in geological samples, soil samples, and surface cleaning (with repetitive laser ablation). Compared to LIBS, LAMIS is based on 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]. LAMIS has emerged as a promising complementary technique to LIBS because it can characterize the isotopic features of the targets providing isotopic differentiating. Raman spectroscopy (RS) occurs when a molecule is excited by a source of excitation and creates inelastic scattering by the vibration, rotation, or stretching of molecular bonds or crystal lattices. Each band corresponds to a different Raman shift in wavenumber from the excitation wavelength of a molecular bond and can be used to identify or "fingerprint" many kinds of materials.

RS and LIBS are very similar in terms of their instrumentation requirements but differ in their laser power and exposure time. By decreasing the laser power for the Raman mode, we can activate the crystal and molecular vibration. Thus, RS will give LABEISS a significant advantage over other 532 nm systems by using a Pulsed laser instead of a Continuous Wavelength Raman System.

Laser-induced fluorescence (LIF) is the broadband re-emission of absorbed electromagnetic energy provided by a laser. The LIF and Raman modes of LABEISS share the same excitation source. The only differences between LIF and Raman acquisition are the exposure and gate width. RS is based on a short exposure up to 10 ns and perfect synchronization with the Laser source, while LIF uses a longer exposure of between 20-100 ns and occurs several ns after the laser pulse.

Furthermore, time-gated cameras allow us to carry out Time-Resolved (TR)-LIF. TR-LIF allows us to measure the time duration of the fluorescence (lifetime), which permits the identification and discrimination between minerals and organics [6]. The TR-LIF could be an important addition to an instrument that uses techniques such as LAMIS, the objective of which is the investigation of isotopes in planetary exploration and the possible habitability of another planet. As such, TR capabilities can assist in identifying locations on a sample most likely to present possible organic material and complement the LAMIS-LIBS measurements.

In this regard, LIBS-LAMIS, with other supporting techniques such as RS, LIF and TR-LIF, has converted LABEISS into a combined multi-spectroscopic instrument capable of several applications in planetary exploration. Moreover, we are currently investigating the best combination procedure for collecting passive reflectance measurements and context imaging in the system.

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 designed to provide basic research and development of space technologies in future missions while exploring extraterrestrial environments such as the Moon and asteroids and astrobiological applications. It will provide isotopic analyses with a precision that can help our understanding of how planetary bodies came to be, and their continuing dynamics and give clues to biologically related processes to understand the evolution of organic molecules in the planetary context. Furthermore, LABEISS can obtain elemental and isotopic information on a sample's composition for different planetary surfaces. Overall, at full development, the LABEISS system is expected to deliver additional capabilities in line with the CSA's research priorities for future planetary exploration (e.g., Astrobiology, Planetary Geology, Geophysics and Prospecting, Planetary Space Environment, and Space Health) [4]

The LABEISS system has two interrelated objectives: 1) Science and 2) 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 simulants, meteorites, and certified isotopic samples), such as 1) understanding of the relationship between line intensity in the spectrum and relevant isotopic mass fractions in the samples and 2) research of the electronically, vibrationally and rotationally excited "isotopologues" of dimers, oxides, nitrides or halides in plasma reactions of the ablated sample atomized matter.

The engineering objective 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 instrument. 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 nm and 532 nm 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 Gaussian expander, where the beam is increased three 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 then coupled into a fibre 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 wavelengths) [3]. We developed several augmentations to fulfill the scientific requirements and establish a better approach to emulate real, in-situ measurements under planetary conditions. The augmented version included a vacuum X-Y LIBS-LAMIS scanning mode for 1x1cm^2 capable of mapping 20 points per sample. In addition, a Nano-Chamber was installed, designed to be as small and light as possible with a volume of 5000 cm^3 and a custom add-a-door equipped with a sapphire window. This allows excellent light transmission in the visible region. The Nano-Chamber allows ultra-high vacuum conditions to be obtained in about 30 minutes (this is particularly useful for emulating the environment of the Moon). The Nano-chamber includes a pressure and atmospheric monitoring system, thus allowing high-fidelity emulation of relevant planetary conditions (e.g., Mars or the Moon). Additionally, samples can be monitored with a context camera to ensure the stability of the sample before and after each measurement [3].

Currently, we are using Carbon, Boron and OH standards with the corresponding isotopes to estimate LIBS and LAMIS spectroscopic features with the supporting techniques.

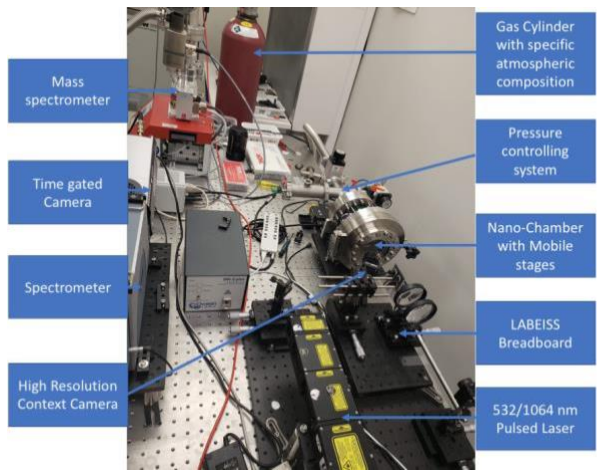

Figure 1. LABEISS breadboard with several of the modification described above.

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 to 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] Lalla et al. (2022) *Astrobiology 22 (4), 416-438* [2] Weins R. C. et al. (2013) *Spectrochim. Acta Part B 82: 1–27*. [3] Lalla et al (2021) *52nd LPSC*, Abstract #2266. [4] Bol'shakov et al. (2016) *J. Anal. At. Spectrom* 31, 119-134. [5] Jiang et al (2019) *J. Anal. At. Spectrom. 34, 1838*