LASER-   INDUCED FLUORESCENCE, CONTEXT IMAGING, PASSIVE REFLECTANCE, AND RAMAN SPECTROSCOPY AS SUPPORTING TECHNIQUES FOR THE LABEISS SYSTEM.

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Introduction: A team at York University, in partnership with ScienceTech Inc in London Ontario, has developed an integrated LIBS system capable of elemental and i sotopic capabilities. LIBS is one of the most successful techniques in planetary exploration that utilizes **J** laser pulse energies for the excitation of plasma emission. LIBS is a rapid methodology for obtaining analytical information of major and minor elements in geological samples, soil samples, and surface cleaning (with repetitive laser ablation). As detailed in other work, we have combined LIBS with a new emerging techniques that will expand the LIBS capabilities to isotopic detection quantification, namely, Laser Ablation Molecular Isotopic Spectrometry (LAMIS).

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. Despite the richness of information provided by the combined capabilities of LIBS and LAMIS, there nevertheless exists major limitations in their ability to characterize a target to the necessary degree for planetary interest (e.g., molecular structure, organic context, and alteration before and after the shots). To address these limitations, we are extending the LABEISS capabilities to include Raman Spectroscopy (RS), Passive Reflectance (PS), and Time-R esolved Laser-I nduced Fluorescence (TR-LIF). In this regard, knowing elemental-isotopic, structural, and molecular information of the targets, from LIBS-LAMIS and supporting techniques (RS, PS, and TR-LIF) will allow us to identify rocks and minerals, and organic signatures.

Laser Ablation Elemental Isotopic Spectrometer (LABEISS) Overview. This project is being undertaken and le d by Sciencetech Inc. (SCI) and the Planetary Exploration Instrumentation Laboratory (PIL) at York University. The project was funded by the Canadian Space Agency (CSA), as part of the effort from the Government of Canada to increase their competitiveness in the space sector under the STPD program [1]. The LABEISS project is focused on providing new insight into a putative instrument that combines LIBS and LAMIS technologies. Moreover, the project is aligned to provide b asic R&D of space technology to be used in future missions while exploring extraterrestrial environments such as the Moon and asteroids. It will provide isotopic analysi s

with a precision that can help our understanding of how these bodies came to be, their continuing dynamics, and give clues to biologically related processes for the understanding of the evolution of organic molecules in the planetary context. Furthermore, during the development of the LABEISS breadboard system, we carried out several augmentations (**Figure 1**): 1) a Nano-chamber with X-Y mapping capabilities to simulate different environments (Pressure ($< 8\text{x}10^{-4}$ hPa) and composition), 2) a context Camera to observe, in situ, the status of the samples (before and after each shot), 3) a mass spectrometer to measure the loss of samples during the measurements, and 4) a heavy-duty translation stage for the Nano-chamber that allows us to mimic a defocusing system (i.e., simulating as flight instrument on a rover).
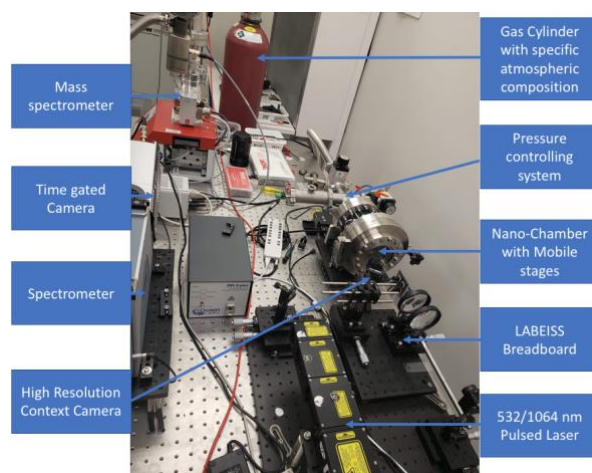

Figure 1. LABEISS breadboard with several of the modification described above.

Experimental Instrumentation. The LABEISS system utilizes a dual 532/1064 nm laser to provide LIBS and LAMIS. The dual beams (one at the time) are overlapped at a Galilean beam expander, which is used to increase the beam diameter by ~3 times. The expanded beam is directed and focused using an off-axis parabolic mirror to the target. Light from the sample is collected by a refractive telescope coupled into an optic fiber and delivered to a combined spectrograph and ICCD system. Both the beam expander and the focusing stage are calibrated at a 20 cm sensing distance for the 1064 and 532 beams. The Mechelle spectrograph and camera allow for a wide spectral range (200-850 nm)

and a high resolution (0.04-0.16 nm) with a 50 μm slit. It is worth noting that while other Spectrographs like Shamrock allow for a higher resolution for LAMIS (0.01-0.05 nm), they result in a lower spectral range. The ICCD is connected to a computer where data from the detector is received and converted to a spectrum.

Access to the chamber is via a hinged door with a window allowing quick exchange of target. Chamber pressure can be reduced to at least 8×10^{-4} hPa with the use of a Hi Cube 80 Eco turbo pump. Qualitative analysis of gas composition is done using a PrismaPro QMG 220 F1 mass spectrometer. A context camera has been added that can be used to take images of the samples on the target stage

Secondary techniques for LABEISS. RS scattering occurs when a molecule is excited by a source of excitation and creates the vibration, rotation, or stretching of molecular bonds or crystal lattice. Each band corresponds to a different Raman shift of a chemical structure and can be used to identify or "fingerprint" any kind of material.

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 in 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.

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 difference between LIF and Raman is the exposure and gating time. RS is based on a short exposure up to 10 ns and a perfect synchronization with the Laser source, while LIF uses a longer exposure between 20-100 ns and occurs several ns after the laser pulse.

Furthermore, time-gated cameras also allow us to carry out 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 is using techniques such as LAMIS, the objective of which is the investigation of isotopes in planetary exploration and possible habitability of another planet. As such, time-resolved capabilities can assist in identifying locations on a sample most likely to present possible organic material and complement the LAMIS-LIBS measurements.

Another useful technique is passive reflectance, which is used to study the surfaces and atmospheres of solar system objects. It has become one of the most important techniques because it provides first-order information on the presence and amounts of certain ions, molecules, and minerals on a surface or in an atmosphere. For example, the ChemCam instrument employs passive visible/near-infrared reflectance (VNIR) spectroscopy for collecting first-order information of a target.

In this regard, these supporting techniques will help to improve the capabilities of LABEISS. We are currently investigating the best combination procedure for collecting passive reflectance measurements and context imaging. We will then proceed to evaluate the other non-destructive techniques such as RS, LIF, and TR-LIF.

We will use LIBS and LAMIS to evaluate the target (elementally and isotopically). Furthermore, synergistic capabilities will provide a set of resulting data that could give us elemental-isotopic and mineral identification, quantification, possible organic identification, passive reflectance properties, a physical image of the target, and the ability to observe the samples before and after the LIBS-LAMIS measurements.

Conclusion. We have presented an overview of possible extended capabilities of the LABEISS system. These supporting techniques, coupled with LABEISS present a synergistic framework by which a comprehensive geochemical, biochemical, and geochronological understanding of planetary samples may be obtained.

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. [6] Lymer et al. (2021) *Astrobiol. 21, 11.*