LASER ABLATION MOLECULAR ISOTOPIC SPECTROMETRY AND TIME-RESOLVED LASER-INDUCED BREAKDOWN SPECTROSCOPY: IMPLICATIONS FOR PLANETARY EXPLORATION. M.

Konstantinidis[1,2], E. A. Lalla[1], G. Lopez-Reyes[3], E. A. Lymer[1], J. Freemantle[1], M. G. Daly[1]. [1]Department of Earth & Space Science & Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada, (menelaos@my.yorku.ca). [2]Dalla Lana School of Public Health, University of Toronto, 155 College St. Toronto, Canada. [3]Unidad Asociada Universidad de Valladolid-CSIC-CAB, C/Francisco Valles 8, 47151 Boecillo, Valladolid, Spain

Introduction: The LIBS Raman Sensor (LiRS) instrument [1,2] is a breadboard design for future planetary exploration missions. It features two laser sources – 1064 nm for Laser-induced Breakdown Spectroscopy (LIBS), and 266 nm for Raman Spectroscopy, Laser-induced Fluorescence Spectroscopy (LIF), and Time-resolved LIF (TR-LIF). These combined techniques allow for an in-depth geochemical and biochemical characterization of surface and sub-surface samples both *in situ* and for sample return missions similar to OSIRIS-REx and Mars2020. In particular, the LiRS instrument has been found to provide 1) elemental identification, 2) elemental quantification, 3) mineral identification, 4) relative mineral quantification, and 5) organic identification. Furthermore, and in of particular interest here, the LiRS instrument is also capable of time-resolved LIBS, and Laser Ablation Molecular Isotopic Spectrometry.

Background: The LIBS mode uses energetic laser pulses to ablate a target sample, thereby creating plasma [2]. The resulting spectrum from the plasma, can then in principle, be correlated to elements, thus providing a framework by which to predict the concentration of major and trace elements in a geological sample. Moreover, the resulting information can also be used to compliment inferences gained from other techniques such as Raman Spectroscopy and LIF.

While powerful with its baseline capabilities, the present work demonstrates that the LiRS instrument can be used to generate additional valuable insights. In particular, we note the ability to conduct Time-resolved LIBS (TR-LIBS) and investigate the Laser Ablation Molecular Isotopic Spectrometry (LAMIS) measurements.

TR-LIBS: An extension of LIBS, TR-LIBS may be obtained by measuring LIBS spectra at sequentially increasing time-gates, enabled through a gated ICCD camera. Several benefits have been identified for the use of TR-LIBS. In particular, 1) a decrease of continuum emission due to Bremstraulung radiation after plasma formation, 2) the possibility of avoiding spectral interferences between species (during the plasma decay), and 3) improvement in spectral resolution as a result of the minimization in the Stark effect contribution [3]. Cumulative, the aforementioned

capabilities are particularly important features for the identification and possible quantification of isotopes – Carbon-12 (^{12}C) and Carbon-13 (^{13}C).

LAMIS: Laser Ablation Molecular Isotopic Spectrometry (LAMIS) is a form of spectrometry by which laser-induced plasma emissions can be used for isotopic inferences. The characterization of isotopic behaviours is based on isotopic shifts (isotopologues) from molecular emissions due to the association of free molecules in the "plasma afterglow" [4]. By quantifying the spectral intensity and shift, it is possible to estimate the relative abundance between elemental isotopes (e.g., $^{13}C/^{12}C$). Such capabilities are naturally attractive in the planetary exploration context where geochronology (enabled by isotopic analyses) of planetary bodies is of interest [5].

LiRS Instrument: In order to conduct TR-LIBS and LAMIS, the LIRS instrument uses an active Q-switched laser at 1064 nm with a 290-kW peak power, and laser pulse width of ~560 ps with a repetition rate of 10 kHz. The beam diameter at the different sensing distances (20 to 50 cm) varies between 21 to 50 μm. The maximum intensity at the target point is between 41 and 8.3 GW/cm^2 over the sensing distance. The beam is delivered to samples through a multicomponent optical system. Firstly, the beam is collected by a motorized beam expander used to focus the light on the target at different sensing distances. Subsequently, the output from the beam expander is collected by a double-mirror (tip/tilting automatic alignment) before focusing the outcoming beam through an off-axis parabolic mirror. The backscattered light from the ablation is collected by a motorized telescope with a 10 cm primary mirror and delivered to a fiber-connected Echelle spectrograph equipped with an ICCD system. The spectral range of the system is 200-850 nm with a resolution of 0.04-0.16 nm? with 50 μm slit. The detailed configuration of the LIRS system can be found on [2].

Results: For both the TR-LIBS and LAMIS analyses, we have conducted preliminary measurements on pure standards of ^{13}C and ^{12}C. In case of TR-LIBS measurements, the spectra at each time step were integrated. The resulting trend over the time-steps (Figure 1) for ^{13}C follows an exponential decay (as

expected). A similar phenomenon is observed for ^{12}C, albeit with a different rate of decay.
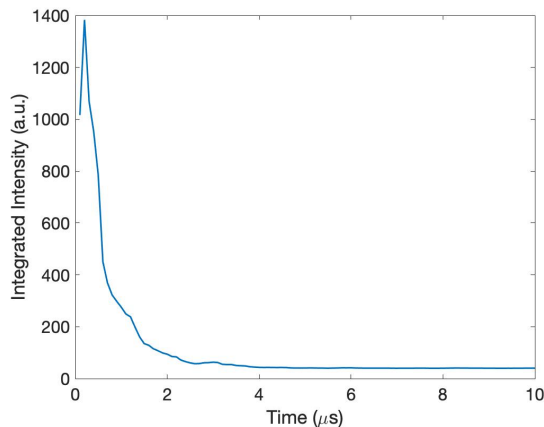

Figure 1. Intensity decay of integrated TR-LIBS spectra from pure ^{13}C sample.

Moreover, we investigated the relationship between the integrated intensities of both ^{12}C and ^{13}C (over the time-steps). This was plotted (Figure 2) and an ordinary least squares regression was conducted between the two. We find that there is a strong linear relationship between the integrated TR-LIBS spectra of ^{12}C and ^{13}C ($p<0.00001$), with an R-squared value of 0.95. Visual inspection indicates that the spectra at lower integral values are highly linear, with some asymmetry above 550 (arbitrary units) – see below for discussion. The fit suggests a linear relationship with an intercept of -138.48 and a slope of 1.4499.
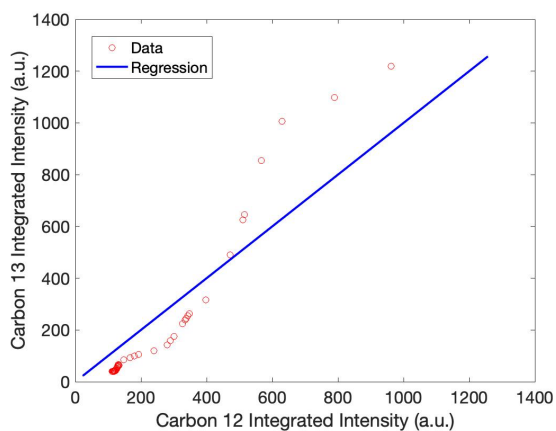
Figure 2. Linear relationship between the integrated TR-LIBS spectra of ^{12}C and ^{13}C.

Additionally, Figure 3 demonstrates the relationship in the LIBS spectra between ^{12}C and ^{13}C.
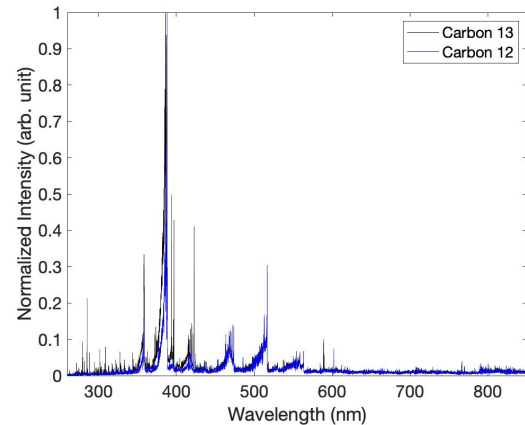
Figure 3. LIBS spectra of pure ^{13}C and ^{12}C samples at a gate delay of 1000 ns.

Discussion:

TR-LIBS: While it is true that the present results for TR-LIBS are in the preliminary stages, it is nevertheless clear that there is potential for isotopic measurements and possible geochronology. With that in mind, several refinements still need to be made. From the data side, it is necessary that when plotting the integrated spectra between ^{12}C and ^{13}C, the starting point be at the maximum integrated value. Referring back to Figure 2, this discrepancy also contributes to the outlier values above 550 arb. units. With respect to the instrument itself, the acquisition parameters have not yet been optimized for TR-LIBS or LAMIS measurements. Thus, in order to obtain optimal results, this must first be ensured. Moreover, several matrix effects may be present, possibly resulting from 1) amount of ablated material per pulse and 2) subsequent changes the delay time for ion-recombination in Carbon species [7] – these need to be investigated.

References: [1] M. Konstantinidis et al. (2020) *Icarus*, 114113. [2] K. Cote et al. (2019) *IAC LXX,* AC-19-A3.3B.12. [3] D.A. Cremers, L. J. Radziemski. 2013. Handbook of Laser-induced Breakdown Spectroscopy. Oxford (Oxon): John Wiley & Sons Ltd. [4] J.M. Vadillo and J. J. Laserna. (1996) *Talanta*, 43, 1149-1154. [5] A. A. Bol'shakov et al. (2016) *J. Anal. At. Spectrom*, 31, 119-134. [6] B. A. Cohen et al. (2019) *Astrobiology*, 19, 11, 1303-1314 [7] S. Brown et al. (2014) *SSA*, 101, 204-212.