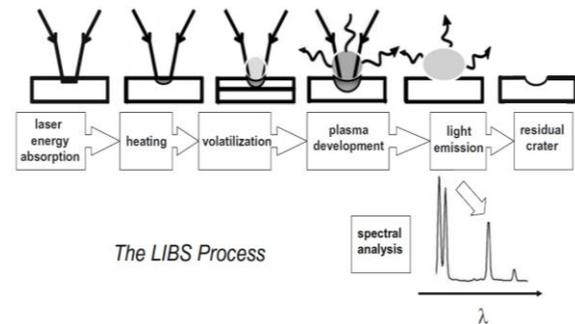


**LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AS A SIMULATED STAND-OFF GEOCHEMICAL ANALYSIS INSTRUMENT IN THE CANMARS 2016 MSR ANALOGUE MISSION.** M. J. O. Svensson<sup>1</sup>, M. Maloney<sup>1</sup>, S. Duff<sup>1</sup>, G. R. Osinski<sup>1, 2</sup>, <sup>1</sup>Centre for Planetary Science & Exploration / Dept. Earth Sciences, University of Western Ontario, 1151 Richmond Street N. London, Ontario, Canada, N6A 5B7 ([mjsvens@uwo.ca](mailto:mjsvens@uwo.ca)), <sup>2</sup>Department of Physics and Astronomy, University of Western Ontario, London, Ontario, Canada.

**Introduction:** The CanMars 2016 Mars sample return (MSR) rover analogue mission [1] is a collaborative program developed by the Canadian Space Agency (CSA), and the Centre for Planetary Sciences and Exploration (CPSX) at the University of Western Ontario (UWO) as part of the NSERC CREATE project “Technologies and techniques for Earth and space explorations” (<http://create.uwo.ca>). Participants included representatives from the University of Western Ontario, McGill University, University of British Columbia, Memorial University, York University, University of Winnipeg, the CSA and NASA. A Mars analogue field site in Utah was analyzed using a suite of stand-in and integrated instruments on board the CSA Mars Exploration Rover (MESR). Results from the CanMars 2016 mission are a continuation of those from the 2015 MSR mission [1] allowing for further characterization of the field site in Utah. Consequently, the 2016 campaign began on Sol 12, with the rover starting at the location where it ended at the end of the 2015 mission. The objectives of this mission were to assess current hardware and software capabilities and workflow, to test the detection capabilities of biosignatures and to field test the sampling capabilities of the rover [2]. The laser induced breakdown spectrometer (LIBS) was a stand in instrument used to simulate the ranged geochemical analysis capabilities of Mars Science Laboratory’s (MSL) ChemCam and the similar SuperCam instrument that will be on the Mars 2020 rover. LIBS effectively served as a replacement for 2015’s stand-off X-ray Fluorescence (XRF) instrument [3]. As such, the purpose of the LIBS in 2016 was to perform stand-off geochemical measurements of outcrops and regolith in support of the mission’s science objectives. Here we report the results of the LIBS instrument used in the 2016 MSR simulation and compare it with the XRF used in 2015 to highlight the usefulness of LIBS in remote field studies.

**LIBS (2016) Data Collection:** The LIBS instrument used to simulate the ChemCam instrument on board MSL was the SciAps Z-500 contact LIBS. The data collection process occurs in six main steps detailed in Fig 1 [4]. A high-power laser is optically focussed at a point in short pulses, instantaneously heating the target causing vaporization and atomization generating a plasma [4, 5]. Nanograms of the target material are vaporized within the plasma [4, 5].



**Figure 1:** Schematic diagram of the steps involved in LIBS data collection [4]

The light intensity emitted from the plasma is spectrally and temporally analyzed to produce an elemental composition [4]. The use of the Z-500 as a stand-off instrument was simulated by allowing the analysis of targets at a maximum range of 7 m from the rover as per the restrictions of ChemCam. Prior to each analysis the remote micro-imager (RMI) provided context images, which were then annotated with LIBS rasters. Three point rasters (~50 $\mu$ m analysis spots) [5] were most frequently used as they provided a good compromise between energy consumption and data acquisition. Before each target was analyzed, a “cleaning shot” was fired at each point followed by two analyzing shots, which were averaged to produce a set of data.

LIBS is designed to collect a full spectrum of geochemical data with each point in a raster [4, 5]. The data return came in two forms: (1) .csv files for each raster containing quantitative elemental data, and (2) .csv files containing wavelength and intensity data. When used in conjunction with the SciAps – Utility software package, the wavelength – intensity data produced emissions spectra allowing qualitative analysis of each point in the raster. The data was imported into a geochemical data analysis software package called ioGAS, which allowed rapid data interpretation primarily through X-Y plots and ternary diagrams.

With a full suite of geochemical data there are relatively few restrictions imposed on LIBS measurements. However, due to the 50 $\mu$ m sample size, acquiring an exact context for the data acquired by the LIBS was difficult. Elements that have a high degree of trace element variability are problematic for LIBS. Similar to MSL, it is also difficult to predict the exact composition of a remote field site’s samples prior to each anal-

ysis. Difficulty in acquiring representative standards prevented the LIBS instrument from providing extensive geochemical data while the mission was active, so a very limited and unreliable range of geochemical measurements were returned. Analyzing new lab standards and incorporating them into the Z-500 database required a rigorous comparison between two measurements: (1) measurements taken by the Z-500 on the new standards, and (2) measurements of the new standard taken using laboratory instruments. Comparisons between the Z-500 measurements and lab measurements were done to ensure they match in terms of resolution, wave-length and spectral range, etc. This required a joint effort between specialists at SciAps and the CanMars 2016 field team that continued long after the end of the mission.

#### Discussion:

**Capabilities.** Selecting a site to study in depth and possibly sample prompts meticulous stand-off science via imagery and geochemical analysis. As both XRF (2015) and LIBS (2016) were used as stand-off instruments they are especially useful guides for sampling decisions. These instruments enabled remote environmental characterization complimenting long range imagery of regional stratigraphy, providing contextual interpretations of the field site. In addition, they complement m to cm scale images providing contextual interpretations of a specific target. The science team could then use these data to make informed decisions regarding which targets to sample.

Similar to the LIBS instrument used in 2016, the XRF was modeled after MSL's LIBS [3]. Context images from RMI and in some cases PanCam were used to select targets where due to the small sample size it was also difficult to acquire a highly precise context [3]. Although XRF could detect a wide range of geochemical data it was not sensitive to light elements, significantly sodium [3]. While a large set of analytical techniques were available with these data, more could be carried out with 2016's LIBS as it was capable of detecting a full suite of elements. This is especially useful as it enables more precise geochemical classification of different units. A full geochemical suite enables calculations of the chemical index of alteration (CAI),  $\text{CaO} + \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{K}_2\text{O}$  ternary plots, and various X-Y plots such as  $\text{Al}_2\text{O}_3$  vs  $\text{K}_2\text{O}$ . Geochemical trends in  $\text{CaO} + \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{K}_2\text{O}$  ternary plots could be used as a method to delineate the degree of chemical weathering in a particular sample. X-Y plots such as  $\text{Al}_2\text{O}_3$  vs  $\text{K}_2\text{O}$  are useful for identifying geochemical signatures of different types of clay such as illite, kaolinite and montmorillonite. CAI measurements can complement both X-Y and ternary plots as they can also be used to interpret the degree of chemi-

cal weathering and infer the presence of different mineral phases [6].

**Field Use.** The full geochemical suite provided by the LIBS served as a tool for acquiring a detailed geochemical characterization of the depositional environment. On Sol 13 the LIBS targeted bright white amorphous material to determine whether it formed in an alkaline environment by searching for  $\text{MgCO}_3$ , which can occur in microcrystalline material in evaporites or basinal brines leftover from alkaline and hypersaline lakes and mudflats [7]. Occurrences of Mg-sulfates would also be difficult to detect using LIBS, but would suggest the environment has a restricted capability to support life as they could indicate acidic saline lakes. LIBS was also used on multiple red coloured layers to detect iron oxides as their presence could suggest the existence of iron-oxidizing bacteria in the paleo-environment. As LIBS can also detect the spectrum of elements encompassed by XRF (2015) it could also be used to perform similar analyses such as sediment chemical maturity plots, clay-carbonate quartz trends, A-CN-K feldspar and clay weathering trends, and provenance studies [3].

**Conclusion:** LIBS' usefulness comes from its ability to measure all elements in target rocks, minerals, and soils in real time with minimal sample preparation. Harmon et al. (2009) have shown that LIBS has the ability to distinguish between structurally similar minerals with a high degree of accuracy based on their dominant elements coupled with the use of a library for the sample and a statistical analysis approach. LIBS requires a precise and well defined database of standards in order to acquire meaningful results. This can be difficult in remote studies where the nature of the field site is unknown. Challenges arise in developing an appropriate database for each study thus complicating data interpretation. The LIBS' ability to accurately measure the geochemical composition of its target with virtually no sample preparation is an invaluable tool for remote studies and is likely to play an important role in future Mars missions.

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