THE USE OF 266 NM LASER-INDUCED FLUORESCENCE (LIF) SPECTROSCOPY FOR DETECTION OF ORGANIC BIOSIGNATURES IN MARTIAN ANALOGUE VOLCANIC ROCKS. C. H. Ryan[1] , M. G. Daly[1], A. L. Brady[2] , G. F. Slater[2] , and D. S. S. Lim[3], [1]Centre for Research in Earth and Space Science, Lassonde School of Engineering, York University, Toronto, ON (email: chryan@yorku.ca), [2]Environmental Organic Geochemistry Lab, School of Geography and Earth Sciences, McMaster University, Hamilton, ON, [3]NASA Ames Research Center, Moffett Field, CA.

Introduction: The search for life on other planets has been a primary goal of space exploration since its inception; accordingly, the NASA BASALT (Biologic Analog Science Associated with Lava Terrains) Research Project aims to simulate manned Mars missions with the goal of studying geology and astrobiology in volcanic environments [1]. BASALT has completed three field deployments to date: one at Craters of the Moon National Monument, Idaho, in 2016; and two within Hawai'i Volcanoes National Park in 2016 and 2017 [1].

Our research focuses on the detection of biosignatures – organic molecules known to be the products of past or present life – in rock samples collected during BASALT deployments using a prototype Raman and Laser-Induced Fluorescence (LIF) spectroscopy instrument designed for use in future planetary surface missions.

Background: Raman and LIF spectroscopy are used primarily to detect and differentiate molecular species present in a sample. These methods are non-destructive and do not necessitate sample preparation, a critical advantage in the search for *in situ* astrobiological signatures [2]. LIF spectroscopy, the capability explored here, offers lower-resolution immediate detection of organic and mineral fluorescence, as well as time-resolved data showing growth and decay of fluorescence signals [3 - 5]. For the purposes of this research, LIF results provide us with useful precursers to determining the Regions Of Interest for subsequent Raman analyses.

The purpose of this research is to detect and characterize biosignatures and their relationships within the rock to physical and chemical characteristics such as alteration, vesicularity, and mineralogy. Understanding the distribution of biosignatures with respect to these physical properties allows us to better understand the potential habitability of Martian volcanic rocks, especially in regards to the emplacement and subsequent alteration of the sample.

Methods: The primary tool of investigation in this project is an experimental Raman/LIF spectroscopy instrument, developed at York University [4], which is being used to study rock samples from the 2016 BASALT deployment to Mauna Ulu, Hawai'i [1]. A 266 nm-wavelength laser excites samples to produce both Raman and LIF spectra. This method has been proven effective for the detection of organic molecules and the separation of the Raman and LIF effects in the spectrum produced [6].

Three measurement modes are used: time-resolved, surface mapping, and spectral analysis. For mapping measurements, the instrument is set up to create a 2D raster of an ROI on the rock surface. The resulting map, showing the intensity of fluorescence at a given wavelength on the surface, is combined with a microscopic image of the sample. Initially, a straight transect of a long axis of the surface is taken to identify any strongly-fluorescing ROIs (figure 1), followed up by more detailed measurements at these significant points. Time-resolved measurements show the time-evolution of the fluorescence spectra as the laser excites the material. This not only aids in the discrimination between shorter-lived organic fluorescence, but decay-time analysis can be used to further narrow the identification of specific materials [5]. Finally, LIF spectra can be referenced to spectra of known samples, giving the identities of any excited species.

Results: Initial tests show areas of peak fluorescence intensity at a number of different wavelengths correspond spatially to distinct grains (fig. 1).

Further Work: In-depth analyses of priority samples (4-6 samples each) from all three BASALT deployments will continue over the coming year, including the LIF methods described above and similar methods for Raman measurements. These results will represent a range of different environmental conditions and alteration of samples, giving a better understanding of which conditions provide the best habitability and biosignature preservation. This work will be done in collaboration with other members of the BASALT team in order to provide a comprehensive picture of astrobiology in Martian volcanic environments.

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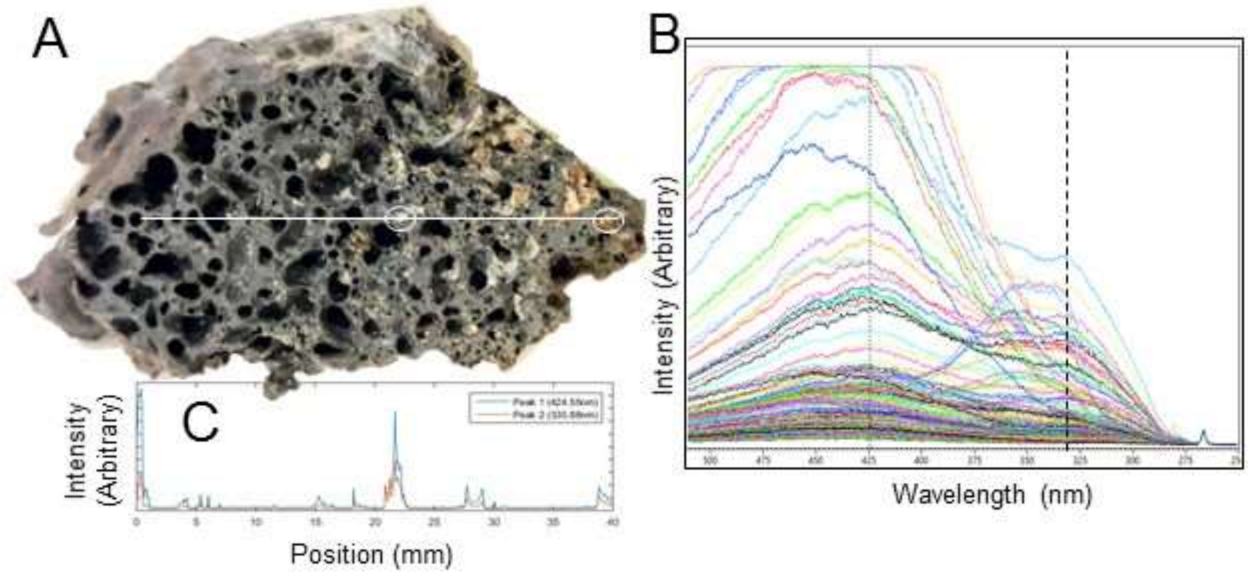

Figure 1: *(A) Image of a slice of sample MU 100620 from the Hawai'I 2016 BASALT deployment. The white line represents the trace of the path of the laser over the surface, with measurements taken every 0.05mm for a total of 800 measurements (40mm). Each spectrum at (B) is a single measurement from this transect; when stacked together, they show that the two most common peaks measured were at approximately 425nm and 331nm. The plot (C) shows the exact position along the transect where these peaks, 425nm (blue) and 331nm (orange), were at highest intensity, meaning that these points (circled in (A)) were strongly fluorescent at these wavelengths and should be considered as ROIs for further LIF and Raman measurements*.

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