THE DISTRIBUTION OF ORGANIC MATERIAL WITHIN MARTIAN-ANALOGUE VOLCANIC ROCKS MEASURED THROUGH LASER-INDUCED FLUORESCENCE SPECTROSCOPY.

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Introduction: The search for life on Mars is a crucial element of the NASA Mars Exploration Program Analysis Group [1] and the Canadian Space Exploration Workshop Steering Committee [2]. Accordingly, the NASA BASALT (Biologic Analog Science Associated with Lava Terrains) Research Project was developed to simulate crewed missions to Martian volcanic environments, with a goal of understanding the biologic potential of these environments [3]. BASALT has completed three mission deployments: two to Hawai'i Volcanoes National Park, Hawai'i, USA (2016, 2017) and one to Craters of the Moon National Monument, Idaho, USA (2016) [4]. On these missions, basalt samples were collected by astronauts during simulated extra-vehicular activities. Samples were returned to Mission Control and ultimately distributed to the participating laboratories, including at York University and McMaster University.

Our research focuses on characterizing the distribution of organic material in these basalt samples using a prototype Laser-Induced Fluorescence (LIF) spectroscopy instrument designed for use in future planetary surface missions. LIF, used in conjunction with Raman and Laser-Induced Breakdown Spectroscopy, will be included as a technique on Mars 2020's SuperCam instrument [5].

Background: Laser-Induced Fluorescence Spectroscopy is a technique where a laser is used to excite a sample. The target molecule absorbs the incoming light and becomes excited to a higher energy state. It transfers the energy internally through non-radiative means before relaxing to its ground state, releasing a photon of a higher wavelength than the incident photon. Many organic molecules are strongly fluorescent when incident light is in the UV range [6-8]. The detected wavelengths of emitted photons are characteristic of chemical bonds and can be used to fingerprint the organic species present. Additionally, molecules show a distinct growth and decay of their fluorescence signature over time, with organic substances having a much shorter (< 10 ns) decay period than minerals [6-8]. Hence, with a sub-nanosecond time-gated and time-delayed intensified CCD detector, this fluorescence decay can be measured and used to distinguish between organic materials and minerals in a heterogeneous sample.

Methodology: Samples were collected using sterile techniques in the field during BASALT deployments in 2016, and kept frozen during transport. They were then freeze-dried so they could be used at room temperature. The rocks were cut into slices approximately 1 cm thick using a sterile, dry rock saw to prevent contamination. Slices were taken at various orientations in the rock in order to maximize the ability to measure different micro-environments within each sample. Each slice was then mounted to a glass slide using epoxy (Fig. 1a).

At York University, we have an experimental instrument designed to simulate *in situ* LIF and Raman measurements on a Mars mission. It uses a 266 nm Nd:YAG laser pulsed at 1 kHz and an Andor iStar iCCD detector with 1.5 ns time-gating abilities coupled to an Andor Shamrock spectrograph. The details of this instrumental configuration are discussed in [9, 10], although some subsequent modifications have been made.

LIF mapping was conducted by choosing a 1 cm^2 window on the sample surface (Fig. 1a), then setting up the slide on a motorized stage system designed to move the stage in 0.25 mm increments after each LIF measurement was taken, creating a 40*40 raster within the window. Eighty readings were gathered and integrated at each point, with a gate delay of 4-6 ns (depending on initial tests for best delay per sample to get highest intensity) and gate width of 10 ns. Map locations were chosen within the samples to best represent sample heterogeneity and included at least one window touching an exposed edge and one far within the interior of the slide.

Map data were converted to images with relative colour maps representing fluorescence intensity at each measurement point (Fig. 1c), and overlain on microscope images of the slide (Fig. 1b). Points of interest (POIs) were chosen on each map based on highest observed fluorescence intensity compared to background. POIs were then measured using time-resolved LIF (TRLIF). With each laser pulse, the detector took a 3 ns-width snapshot at an increasing delay of 0.5 ns, creating a 3D measurement of intensity per wavelength over a time period of 10 ns (Fig. 1d-g).

Results: One representative sample from Mauna Ulu, Hawai'i Volcanoes National Park, is illustrated in Fig. 1, below.

Our results show the following correlations:

i. Highly fluorescent material (FM) tends to concentrate with white crystalline material located in vesicles.

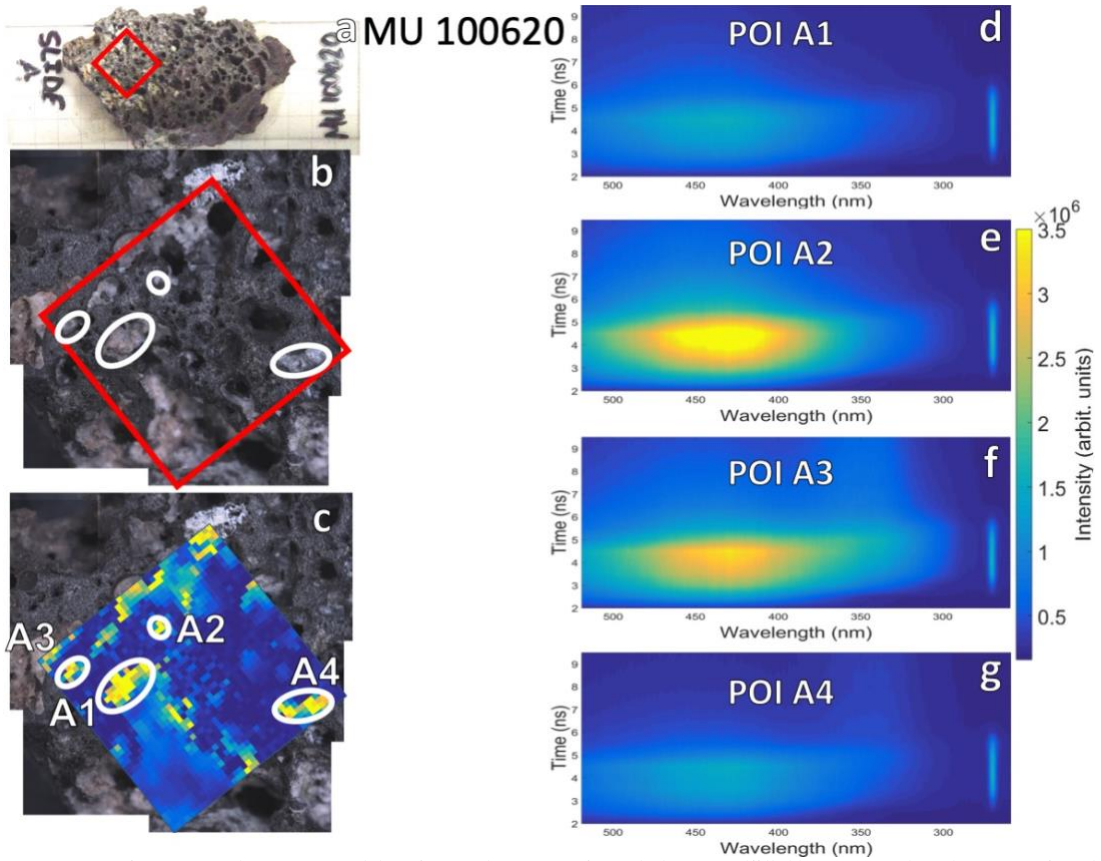

Fig. 1. *LIF measurements of HI2016 sample MU 100620, slide A, from a relict meteoric fumarole deposit. Red/filled boxes in [a-c] have dimensions of 1 cm*1 cm. [a] Image of sample slide A mounted. [b] Composite microscopic image of slide with outline of mapped area, including POIs. [c] LIF map with outlines and labels of POIs. Colourmap is scaled relative to sample, with yellow representing highest fluorescence intensity and blue representing lowest/background. Note how POIs correlate to vesicles filled with white crystalline material, as seen in [b]. [d-g] Absolute (scale on right) heat maps of fluorescence intensity over time across the entire measured spectral range. (Note that the narrow bright band located at the far right of each spectrum represents excess laser light [266 nm] entering the detector.)*

ii. There was significantly more FM in the Hawai'i 2016 samples vs the Idaho 2016 samples, and more FM in samples collected from active or relict meteoric fumaroles within the HI 2016 suite.
iii. Samples that were more porous showed higher distribution of FM, as FM was mostly concentrated within vesicles.
iv. Of the FM measured with TRLIF, many of the spectra showed higher intensity and fast (< 10 ns) decay peaks around the 425 nm wavelength, and lower intensity, long (>10 ns) decay peaks around the 325 – 350 nm wavelength. Spectra with higher-intensity, long-decay peaks tended to be found in low-alteration samples with lower porosity.

Discussion and Future Work: Our data show that most of the examined POIs likely contain a mixture of strongly-fluorescent, short-excitation organic material and weakly-fluorescent, long-excitation mineral or inorganic material. Further data have been collected with scanning electron microscopy (SEM) and electron-dispersive x-ray spectroscopy (EDS) with the goal of confirming the presence of organic carbon and determining the mineralogy of the white crystalline material. Additionally, accurate measurements of sample porosity are being conducted in order to demonstrate how strong the correlation is between porosity and FM distribution.

This work is a contribution to the BASALT project and to our understanding of the habitability of volcanic material as a whole. As astrobiologists seek to understand which environments best support and preserve organic material, and instrumental techniques are developed for planetary exploration, our research is crucial for ground-truthing new exploration hypotheses.

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