ALTERATION-ASSOCIATED SPATIAL DISTRIBUTION OF ORGANIC BIOSIGNATURES IN MARS-ANALOGUE VOLCANIC ROCKS. C. H. Ryan[1,2*], M. G. Daly[1], A. L. Brady[3], G. F. Slater[3], and D. S. S. Lim[4], [1]Centre for Research in Earth and Space Science, Lassonde School of Engineering, York University, Toronto, ON, [2]Institute for Earth and Space Exploration and Department of Earth Sciences, Western University, London, ON (*current affiliation email: cryan73@uwo.ca), [3]School of Geography and Earth Sciences, McMaster University, Hamilton, ON, [4]National Aeronautics and Space Administration Ames Research Center, Moffett Field, CA.

Introduction: Understanding the distribution of trace organic material in a rocky environment is a key to constraining the material requirements for sustaining microbial life. We used an ultraviolet laser-induced fluorescence (LIF) spectroscopy instrument to characterize the distribution of organic biosignatures in basalts collected from two Mars-analogue environments.

Mars-Analogue Environments: These samples were collected during the 2016 deployments of the NASA Biologic Analog Science Associated with Lava Terrains (BASALT) project [1, 2] to the volcanic environments of Hawai'i Volcanoes National Park, HI, USA (HI2016 samples), and Craters of the Moon National Monument, ID, USA (ID2016 samples) [3]. Samples represent a diversity of alteration conditions found in these two environments, including active and relict fumaroles [3]; these variances in alteration styles affect physical or geochemical properties that may be important for biological colonization and biomass production [4-10]. In particular, it is hypothesized that samples that are highly-altered have readily-available chemical energy needed for microbial metabolism, and fumarolic deposits are known to be habitable [11]–[13].

LIF: Previous research has demonstrated the applicability of UV-LIF with sub-ns time-resolved fluorescence (TRF) capabilities for detecting organics in rocks and characterizing the organics present, with the goal of developing a future Mars rover-deployable instrument [14]–[17]. TRF especially is an invaluable technique, as organic molecules are known to fluoresce for a much shorter time-frame (<10 ns) than minerals (μs – ms) [15]. However, these previous studies did not utilize LIF mapping of samples for initial detection of organic material, and thus lacked a focus on characterizing the spatial distribution of organics within the whole-rock environment. Our work concentrated on this aspect of organic detection, expanding our understanding of rock habitability to influence future sample-site selection and sample measurement procedures.

Methods: Samples from HI2016 and ID2016 were classified *in situ* on the basis of their perceived alteration: HI2016 included samples collected from active meteoric fumaroles, relict fumaroles, and unaltered, while ID2016 included high-T alteration (syn-alteration), low-T (ambient) alteration, and unaltered. Samples were collected with sterile tools, and freeze-dried upon return to the laboratory. At York University, they were cut into flat slices approx. 1 cm thick and adhered to glass slides. In total, four samples from HI2016 (ten slides; 1 – 3 slides/sample) and five samples from ID2016 (eighteen slides; 3 – 4 slides/sample) were mapped with the UV-LIF instrument.

UV-LIF measurements were completed using an instrument modified from [18, 19]. 1 cm^2 raster maps of sample surfaces were created by combining the stepwise movement of a motorized sample stage with spectral measurements of the wavelength range from 255 – 515 nm. Raster pixels were processed to produce absolute colour-scaled maps, with each pixel colour representing fluorescence intensity integrated across the wavelength range. Pixels classified as "high" (yellow) or "very high" (red) fluorescence intensity (based on the maximum and minimum pixel values from all maps) were deemed points-of-interest (POIs), and further investigated.

LIF time-resolved measurements were taken from these POIs to evaluate the decay times of fluorescence intensity. Further, measurements of POIs were completed with scanning electron microscopy (SEM) and electron-dispersive x-ray spectroscopy (EDX) to determine mineralogy of POI material and possible carbon content.

Results: In Figure 1, an example LIF map is presented from one slide of one HI2016 relict fumarole sample.

Of the 28 slides mapped, twelve sample slides representing six samples – only those with LIF maps that contained POIs – were further examined with TRF and SEM-EDX. All POIs were associated with white crystalline minerals (WCM) located in sample vesicles; these were determined through EDX analyses to be zeolites, clays, or calcite, all common secondary alteration materials in volcanic environments. Additionally, all POIs showed short (~ 7 ns) growth and decay periods of fluorescence intensity - consistent with organic molecule presence - in these locations.

Fluorescence evidence (maximum intensity and number of red + yellow pixels per map), along with carbon content estimations from EDX, were compared with the alteration styles of the samples to determine if there were any correlations. This indicated that HI2016 samples overall showed much greater evidence for organic material than ID2016 samples, and in particular, the relict fumarole sample from HI2016 showed the

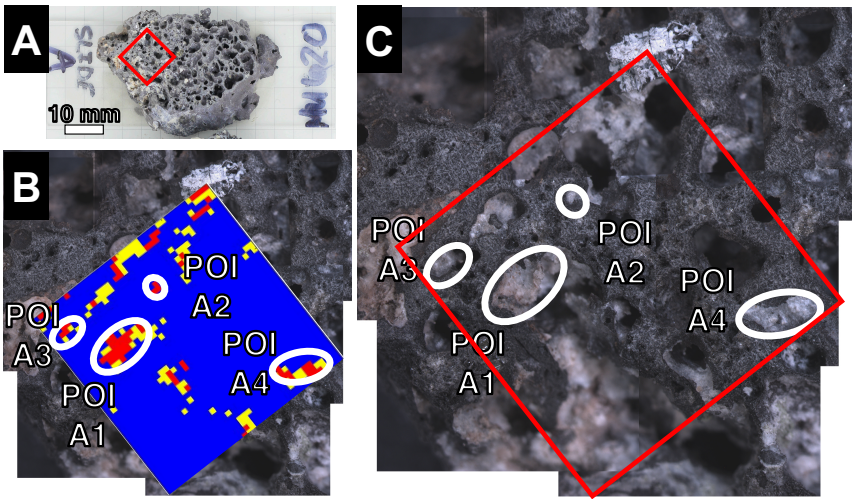

Figure 1: LIF mapping results from one slide of a relict fumarole sample from HI2016. [A] Sample slide with map location outlined in red. All red boxes in image are 1 cm². [B] Microphotograph of mapped area with absolute-scale fluorescence map overlain. Four clusters of red (very high-intensity fluorescence) and yellow (high-intensity fluorescence) pixels were chosen as POIs for further analyses. [C] Microphotograph of mapped area. Note how POIs (and all highly-fluorescent material) correspond to white crystalline mineral (WCM) deposits in sample vesicles; WCM in this sample was determined with SEM to be zeolite and chlorite.

highest evidence; although one unaltered sample from ID2016 had comparable fluorescence attributes to the HI2016 samples.

Further, POI locations with respect to a sample's interior or weathered exterior edges were examined, and showed that there is a slight preference for sample edges as sites of sites of organic material deposition. Porosity was also compared to these parameters, with no correlations shown.

Discussion: A study using replicates of our HI2016 samples [20] was conducted to estimate biomass and biodiversity in these samples. They showed complementary results, with high biomass estimates for relict fumarole and unaltered samples. The findings of our study when compared with theirs suggest that the young, hydrothermally-active, primitive, water-adjacent lavas of Hawai'i are readily colonized by microbial life, even if these lavas are not extensively altered. Conversely, the older, non-fumarolic, evolved, high-desert environment of Craters of the Moon show less evidence for wide distribution of organic material.

Moreover, our evidence shows that secondary mineral deposits within the vesicles of these rocks are the primary targets for microbial colonization, rather than the rock itself. These minerals have been extensively reported as support structures for microbial habitation in basaltic environments, both in the surface and sub-surface [21]–[24]. The sample from ID2016 showing the highest evidence of organic material was field-classified as unaltered, but contained deposits of calcite that showed similar fluorescence characteristics to the zeolite and clay deposits in the vesicles of the HI2016 samples, suggesting that some alteration had occurred. This emphasizes the importance of alteration conditions that facilitate the deposition of these secondary minerals, rather than lava geochemistry, in promoting the habitability of volcanic rocks; and further suggests basaltic rocks with identifiable alteration features such as secondary minerals are potential high yield targets for astrobiology investigations.

The small-scale variations in organic material distribution, along with weak correlations between organics and physical properties, demonstrate the need for the collection and analysis of a large and diverse sample suite during Mars exploration. Visual interpretation at the outcrop scale or measurements taken from a remote instrument are insufficient for fully assessing the potential for past inhabitation and preservation of organic biosignatures. The LIF/TRF mapping technique utilized here, in contrast, is especially suited to this task. Millimeter-scale mapping of a sample or outcrop surface can reveal concentrated areas of fluorescent material, highlighting the heterogeneous distribution of potential biosignatures. TRF measurements can subsequently be used to distinguish between organic and inorganic fluorescence. From there, more detailed chemical and biological analyses are needed to confirm the presence of biosignatures in a rock.

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