MAKING AND MAINTAINING LIPID BIOSIGNATURES IN A GLACIOVOLCANIC SETTING. E. F. Gibbons[1*], R. J. Léveillé[1], K. Berlo[1], and G. Slater[2]. [1]McGill University; Department of Earth and Planetary Sciences, CA, [2]McMaster University; School of Earth, Environment & Society, CA (*erin.f.gibbons@gmail.com)

Introduction: Volcano–ice interactions produce an array of environments (e.g., meltwater lakes, fumaroles, and hot springs) with equally diverse mineralogical deposits [1]. This diversity provides a wealth of options for life to establish itself and for biosignature preservation, thereby motivating astrobiological attention. Such glaciovolcanic environments likely existed on Mars during the Noachian (4.1-3.7 Ga), and may have become more common as the climate cooled [2]. Wet subglacial niches potentially existed late into the Hesperian (3.7-2.9 Ga), and may have represented habitable niches after Mars lost much of its surface water [2]. Characterizing terrestrial glaciovolcanic deposits can help identify similar processes on Mars.

Here, we study a glaciovolcanic system in Iceland, where the Vatnajökull icecap partially overlies the active volcano, Kverkfjöll (subsurface temperatures of the thermal system are ~300°C [3]). Freshwater hydrothermal fluids (sourced from local precipitation) circulate through the Fe-rich tholeiitic basalt, generating a range of geothermal surface environments in direct contact with snow/ice [4,5]. This site thus offers a natural laboratory to study communities supported by basalt-derived metabolic redox pairs and polar hydrothermal conditions that could have existed on Mars. Further, the high-altitude and lack of overland inputs enables investigation of a well-isolated, relatively pristine microbial ecosystem and its associated biosignature record unperturbed by complex signatures from outside the system.

Objectives: We aim to: (1) characterize the mineralogy and geochemistry to help identify analogous sites on Mars, (2) characterize the suite of lipid biosignatures produced by the in situ microbial communities to investigate trends in biomass and community structure, and (3) characterize the recalcitrant geolipids present/deposited within the local sediments to understand the potential of these glaciovolcanic sedimentary environments to capture, preserve, and/or alter biosignatures.

Methods: *Field Site:* Water, sediment, and biomass samples were collected using aseptic techniques from the Kverkfjöll caldera (~64°39′5.4″N, -16°43′16″W). The sampling area is dominated by an ice-damned meltwater lake where the only overland inflow is a small stream over flowing from a hot spring ~60 m north of the lake shore; samples were collected along a transect from the hot spring, along the overflow stream, and throughout the lake. Adjacent to the lake, but elevated on a sediment mound, meltwater from ice/snow interacts with fumarolic ground to form mud pots and pools; samples were collected from mud pots with variable surface activity. Samples were kept cold with snow before storing at -4°C in laboratory freezers.

Analytical Methods: Temperature, pH, conductivity, and dissolved oxygen (DO) were measured in-situ with a YSI Pro meter. Water chemistry was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (cations) and Ion Chromatography (anions). Duplicate sediment samples were collected for geological and lipid measurements. Geological samples were oven dried and ground to <45 μm using an agate mortar. Mineralogy was measured by X-ray Diffraction (XRD) using a scan range of 5-83 2θ on a Bruker D8 Discover equipped with a cobalt source. Biological samples were freeze-dried, homogenized, and solvent extracted using a Bligh & Dyer protocol [6]. Total lipids were separated into different classes using eluants of increasing polarity through silica gel: F1– hexane containing hydrocarbons; F2– dichloromethane containing neutral lipids and glycolipids; and F3– methanol containing phospholipids. Here, the hydrocarbons and phospholipid fatty acids (PLFA; derivatized as fatty acid methyl esters) were analyzed by gas chromatography-mass spectrometry.

Preliminary Results: *Environmental Observations and Geological Analyses:* Physicochemical traits vary across the geothermal field. The subaerial hot spring water measured ~87˚C, a neutral pH, severely dysoxic levels of DO (0.52 mg/L), high dissolved SO_4^+ (69.1 mg/L), and a relative enrichment in dissolved Si^{4+}, Na^+, and K^+. Rocks in the vicinity of the hot spring were encased in calcite. Water temperatures and pH decreased, while DO increased away from the spring, producing steep physicochemical gradients across a small spatial scale (~75 m). Where the outflow stream measured 30-47˚C, mats of green filamentous bacteria grew.

Within the lake, the dissolved cation load decreased, but dissolved sulfate increased marginally (76.9 mg/L). Temperature (9.4˚C average) and pH (pH=6) were generally consistent along the transect from shoreline to lake-center, and throughout depth (4.5 m at center), suggesting a well-mixed system. A few measurements saw temperatures between 65-75˚C at the lake-floor, indicating the presence of subaqueous hot springs. Sediment dredged from the bottom of the lake revealed a transition from heterogenous gravel-sized grains at the shoreline to visually homogenous blue-grey mud-sized grains at the lake center. Surprisingly, the mineralogical profile did not alter substantially along the transect from the hot spring to the lake (with the exception of calcite observed exclusively at the spring source), or across the grain-size transition from gravel to mud, suggesting that physical weathering drives the variability in sediment expression. Indeed, all samples in the transect contained primary basalt minerals and alteration minerals, including heulandite (Ca/Na zeolite), dioctahedral swelling clay, quartz, pyrite, and anatase (the clay content precluded quantification of minerals in the bulk samples).

The active mud pots ranged from quiescent pools (42˚C, pH=3.3) to energetically bubbling pots (72˚C, pH=2.9). The solutions within mud pots contained a greater proportion of total dissolved solids enriched in Si^{4+}, Ca^{2+}, Mg^{2+}, Fe_T and Mn^{2+}. We also observed relict mud pots in various stages of desiccation with polygonally cracked surfaces. The pots were dominated by mud to fine-sand grains with a similar mineralogical assemblage as that of the spring-lake system, but with minor evaporitic minerals (e.g., gypsum) and acidic alteration minerals (e.g., jarosite).

Lipid Profile: PLFAs decay rapidly after cell death and thus offer insight into the community structure and the production of lipids from active organisms. All PLFA profiles were consistent with a bacterial origin: the majority of fatty acids were within the C_{14}-C_{20} range and several specific domain markers were identified, including terminally-branched PLFA common in Gram-negative bacteria, mid-branched PLFA associated with actinomycetes, and unsaturated PLFA typical of cyanobacteria and gram-negative bacteria [7]. Relatedly, we did not observe lipids diagnostic of plants or eukarya, such as long chain PLFA ($>C_{20}$), abundant polyunsaturated PLFA, sterols, or wax esters [7].

Whereas PLFA decay rapidly, hydrocarbons are more resistant to decay and are known to be stable on Earth over billion-year timescales [8]. All samples were dominated by low molecular weight alkanes, mostly *n*-$C_{16-18,}$ often associated with the degradation of similarly short-chained (cyano)bacterial or algal PLFA; hydrocarbons characteristic of plants (e.g., long chain *n*-alkanes, steroids) were not observed in abundance [8]. Specific markers and patterns of life were also observed throughout the system, including hopanes (synthesized by bacteria) and an odd-over-even preference (OEP) in carbon chain length (from enzymatic synthesis of biomolecules) in most samples [9]. Samples from the hot spring, stream, and lake all contained unresolved complex mixtures (UCM) of branched and cyclic hydrocarbons, with a single peak between from *n*-C_{18} and *n*-C_{20}; UCMs were not observed in the mud pots. UCMs may result from microbial activity or catagenic alteration of organic matter [10]. Biologically-mediated UCMs commonly show a mode near *n*-C_{17} or *n*-$C_{22,}$ while catagenic UCMs are usually characterized by a maximum near *n*-C_{25} [10]. Microbial activity thus appears to contribute to the UCM. However, the UCM is most appreciable in the sample taken at the hot spring, where the biogenic OEP ratio is also near 1 (insignificant), suggesting that alteration by hydrothermal fluids may also contribute/overlap the biogenic signals here. However, biogenic markers (specific compounds) and patterns (odd-over-even preference) are preserved within downstream sediments and within the mud pots, despite the thermal setting. Thus, we can conclude that refractory biosignatures are indeed preserved through the initial stages of diagenesis throughout a diversity of glaciovolcanic deposits.

Lastly, we note that both the PLFA and hydrocarbon profiles differed between the mud pot and fluviolacustrine samples, as well as along the spring-lake transect, indicating variations in microbial diversity, biomass, and preservation potential.

Conclusions: The key to glaciovolcanic habitability lies in the generation of sustained liquid water and geothermal heat. We report on the geology and organic geochemistry of a remote glaciovolcanic site to better understand its geological signature, habitability, and biosignature preservation potential. We identify an assemblage of minimally re-worked basalt products and hydrated alteration minerals (clays, zeolites); future work will focus on clarifying a geological signature. The PLFA profile revealed a bacterially-dominated community with variations in biomass and community structure throughout the system, reflecting the wide-range of putative habitats generated by glaciovolcanic interactions and underscoring the habitable potential of such settings. Further, the lack of lipid signatures from complex organisms confirmed that Kverkfjöll is a suitable analogue within which to study biosignature preservation potential relatively unbiased by more complex inputs. Lastly, the refractory hydrocarbon profile retains biogenic patterns preserved through the initial stages of diagenesis, which often sees the majority of lipid degradation, demonstrating that glaciovolcanic settings are both habitable and suitable for preservation of geologically-significant biosignatures.

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