COLLECTION OF SAMPLES FOR ORGANICS ANALYSES AT ICELAND SINTER SITES.

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Introduction: Throughout its history, volcanism and water on Mars likely produced habitable regions below the surface, where geothermal energy interacted with the hydrosphere [1]. The Nili Patera caldera in the Syrtis Major volcanic province exhibits mound morphology and silicic sinter deposits indicating past hydrothermal activity [2] and conditions for a habitable conduit from the potential deep biosphere to the surface. Similar geologic activity could have formed the silica deposits at Home Plate in Gusev Crater [3]. These sinters provide ideal locations to concentrate and preserve potential biosignatures that could be targets for future planetary exploration.

A NASA Planetary Science and Technology Through Analog Research (PSTAR) project, Seeking Signs of Life in Nili Patera (SSLNP), traveled to 3 hydrothermal sinter sites in Iceland in July-August 2016 and employed several exploration methodologies including: spectroscopic, mineralogic, microscopic, molecular, and geophysical to investigate the biological, environmental and volcanic history of the analog sites. Our part was to determine if molecular biosignatures, such as lipids, are 1) preserved in the sinter and 2) detectable with a benchtop version of the TMAH (tetramethylammonium hydroxide) wet chemistry experiment on the SAM (Sample Analysis at Mars) instrument on the Curiosity rover. With these data we can also begin to deconvolve the microbial ecology within these sinter deposits.

Methods: Samples were collected using organically clean methods from each of the Icealanic hydrothermal sinter sites. Site activity ranged from inactive/relict to active with fumeroles and hot springs. Surface, S, and subsurface, I, samples were collected at 3 locations: 1) near vent, V, 2) mid-apron, M, and 3) distal apron, D. Samples were stored in solvent washed and ashed glass vials on ice until analysis in the lab.

Sinter samples were ground to a powder with an ashed mortar and pestle and parsed into aliquots in solvent cleaned vials. Samples underwent pyrolysis at a 1mg:1uL ratio with TMAH to hydrolyze and methylate fatty acids potentially bound in macromolecules. This process makes fatty acids volatile and detectable to GCMS. The fatty acids were then analyzed by pyro-GCMS using a SAM-like heating ramp (35°C/min) on a Frontier pyrolyzer and Agilent GCMS instrument.

Results and Discussion: In general, greater FAME diversity and abundance was observed in surface versus subsurface samples (Table 1). Monounsaturated fatty acids were lost at depth, indicative of early diagenesis [4]. Odd carbon number saturated FAMEs were also lost at depth, while those with even carbon numer were preserved. FAMEs >C_{20} indicate input from terrestrial plants [4] and are only found in surface samples. The presence of $C_{18:2}$ may be linked to cyanobacteria or fungi [4] and again are only in the surface samples. In general, there is an even-over-odd carbon number preference, possibly indicative of a more modern bacterial community [5]. Our results indicate that fatty acids are preserved at depth in the modern and relic Icelandic sinter and are detectable with a benchtop version of the SAM TMAH wet chemistry experiment.

References: [1] *Michalski et al.* (2013), *Nat. Geosci.*, *6*(2), 133; [2] *Skok et al.* (2010), *Nat. Geosci.*, *3*(12), 838; [3] *Ruff et al.* (2011), *J. Geophys. Res.*, *116.* [4] *O'Reilly et al. (2016), Geobiol., 1-19.* [5] *Wilhelm et al. (2017) Org. Geochem., 103, 97-104.*

Table 1. FAME detection in Mars-analog Icelandic sinter deposits.

		*	C_6	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	$C_{16:1}$	C_{17}	C_{18}	$C_{18:1}$	$C_{18:2}$	C_{20}
Site 1 Gunnuhver Hot, recent but ceased spring activity	A1	V, S	--	x	x	x	--	x	--	x	--	--	--	--	x	--	--	--
	A2	V, I	x	--	x	x	--	x	--	--	--	--	--	--	--	--	--	--
	B1	M, S	x	x	x	x	x	x	x	x	x	x	--	--	x	--	--	--
	B2	M, I	--	x	x	x	--	x	--	x	--	x	--	--	x	--	--	--
	C1	V, S	x	x	x	x	--	x	--	x	x	x	--	--	--	--	--	--
	C2	V, I	No FAMEs															
	D1	D, S	--	x	x	x	--	x	x	x	x	x	--	x	x	x	--	--
	D2	D, I	--	--	x	--	--	x	--	--	--	--	--	--	--	--	--	--
Site 2 Hveravellir Active with hot springs	E1	D, S	--	x	x	x	--	x	x	x	x	x	--	--	x	--	--	--
	E2	D, I	--	--	--	--	--	x	x	x	x	x	--	--	x	--	--	--
	F1	V, S	x	x	x	x	x	x	x	x	x	x	x	x	x	x	--	--
	F2	V, I	--	x	x	x	x	x	x	x	x	x	--	x	x	--	--	--
	G1	M, S	x	x	--	--	--	--	--	x	x	x	--	x	x	x	--	x
	G2	M, I	--	--	x	x	--	x	--	x	x	x	x	--	x	x	--	--
Site 3 Lysuholl Relict	H	V(?), I	--	x	x	x	x	x	x	x	x	x	x	x	x	--	--	--
	I1	V, S	x	x	--	x	--	x	--	x	x	x	x	x	x	x	x	--
	I2	V, I	x	x	x	x	x	x	x	x	x	x	--	--	x	--	--	--

* D = distal apron

M = mid-apron

V = near vent

S = surface sample

I = interior sample