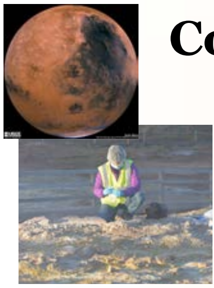


Collection of Samples for Organic Analyses at Iceland Sinter Sites

Kathleen L. Craft, Kate.Craft@jhuapl.edu, JHU Applied Physics Laboratory
Amy Williams, ajwilliams@towson.edu, Towson Univ./NASA GSFC
J.R. Skok, jrskok@seti.org, SETI Institute

Introduction

Surface features and spectroscopic analyses indicate volcanism and water activity on Mars likely occurred throughout its history, leading to the idea that habitable regions would have been produced in the subsurface, where magma sourced heat interacted with the hydrosphere [1]. 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, compositional, microscopic and geophysical to study the biological, environmental and volcanic history of the analog sites.

Nili Patera (Fig. 1a) caldera in the Syrtis Major volcanic province exhibits:

- Mound morphology → Indicates past hydrothermal activity [2]
- Silicic sinter deposits → 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** [3,4]. These **sinters provide ideal locations to concentrate and preserve potential biosignatures** that could be targets for future planetary exploration.

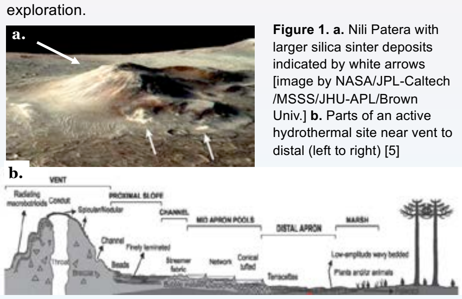
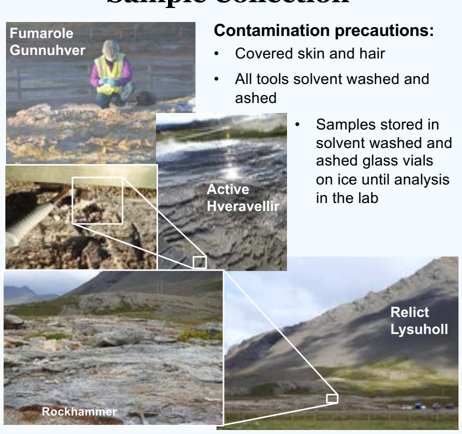


Figure 1. a. Nili Patera with larger silica sinter deposits indicated by white arrows [image by NASA/JPL-Caltech /MSSS/JHU-APL/Brown Univ.] **b.** Parts of an active hydrothermal site near vent to distal (left to right) [5]

Objectives:

1) Collect samples at 3 sites: Relict, Recently active-Fumarole, and Active
2) Determine if molecular biosignatures, such as lipids, are:
   a) Preserved in the sinter and
   b) 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
3) Deconvolve the microbial ecology within these sinter deposits

Sample Collection



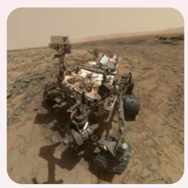
Contamination precautions:

- Covered skin and hair
- All tools solvent washed and ashed
- Samples stored in solvent washed and ashed glass vials on ice until analysis in the lab

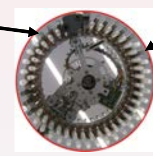
Methods – Sample Analyses SAM-like TMAH

- Ground sinter samples to a powder with an ashed mortar and pestle
- Parsed into aliquots in solvent cleaned vials

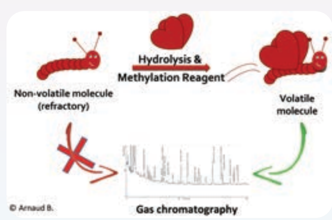
Curiosity Rover with SAM instrument– Sample Analyses at Mars



Two TMAH cups for low temperature extraction targeting less volatile organic compounds



- 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 coupled to an Agilent GCMS instrument.

Results

FAME detection in Mars-analog Icelandic sinter deposits

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

- Generally greater FAME diversity in surface (S) vs. interior (I) samples
- Monounsaturated fatty acids lost at depth
- Odd carbon number saturated FAMEs also not observed at depth
- Even carbon number saturated FAMEs were preserved

Special thanks to PSTAR Project SSLNP and the American Philosophical Society (APS) for funding sample collection

Discussion

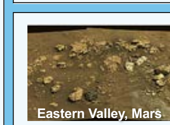
- As **monounsaturated fatty acids were lost at depth** - suggests **early diagenesis** [6]
- Observations of even carbon numbered saturated FAMEs at depth and loss of odd carbon numbered FAMEs indicates **even carbon number preservation preference**
- The presence **of $C_{18:2}$ may be linked to cyanobacteria or fungi** [6] and again are only in the surface samples
- **FAMEs >C_{20} indicate input from terrestrial plants** [6] and are **only found in surface samples**
- In general, the **observed preference of even vs. odd carbon** numbered FAMEs **could indicate a more modern bacterial community [7]**

Active vs. Recently Active vs. Relict *Interior samples*

1) The **active and relict systems contained wide ranges of FAMEs** with both even and odd length chains represented.
   – **may indicate a microbial succession or recolonization of the relict system** with organisms not native to the active hot spring environment
2) The **fumarole system exhibits either a similar range of FAMEs to the active system or a more limited range** (C_6 to C_{12}), with the notable loss of odd numbered or long chain length FAMEs. One sample contained no detectable FAMEs.

* Results indicate that **fatty acids are preserved at depth** across the active, recently active - fumarole, and relic Icelandic sinter systems and are **detectable with a benchtop version of the SAM TMAH** wet chemistry experiment *

Future Work



1) Compare SAM like data to sample optimized analyses (e.g. flash pyroloysis) to better resolve fatty acids.
2) Correlate with physical biosignature preservation being performed by SSLNP team members (e.g. J. Farmer and M. Juarez Rivera).
3) Explore any possible correlations with vent, mid-apron, distal apron locations
4) Link to the opportunity to send GCMS systems on future planetary missions to environments showing evidence of silica hot springs such as Nili Patera and Gusev Crater/Columbia Hills (potential Mars2020 mission)

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] Ruff and Hamilton (2017), *American Mineralogist, in press;* [5] Campbell et al., (2015), *Astrobiology, 15:10, 858;* [6] O'Reilly et al. (2016), *Geobiol.,* 1-19; [7] Wilhelm et al. (2017), *Org. Geochem., 103,* 97-104.