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► **To cite this version:**

Maeva Millan, Amy Williams, Amy Mcadam, Jennifer Eigenbrode, Caroline Freissinet, et al.. Organic Molecules Revealed in Glen Torridon by the SAM Instrument. 52nd Lunar and Planetary Science Conference, Mar 2021, Online, Unknown Region. pp.LPI Contribution No. 2548, id.2039. insu-04464305

**HAL Id: insu-04464305**

**<https://insu.hal.science/insu-04464305v1>**

Submitted on 18 Feb 2024

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## ORGANIC MOLECULES REVEALED IN GLEN TORRIDON BY THE SAM INSTRUMENT.

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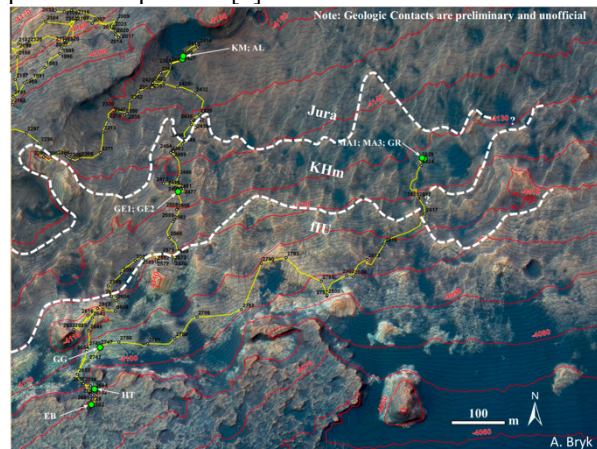
**Introduction:** Curiosity is analyzing the stratigraphic rock layers at Gale crater, in order to find clues to Mars' environmental history and habitability [1]. The Sample Analysis at Mars (SAM) instrument suite onboard Curiosity (Figure 1) is primarily dedicated to the search for organic molecules in near surface samples. SAM performs *in situ* evolved gas analysis (EGA) and pyrolysis-gas chromatograph-mass spectrometry analysis (pyro-GC-MS) by heating solid samples collected by Curiosity up to ~900°C. These experiments allow the detection, separation, and identification of the volatile inorganic and organic compounds released from the samples during heating. SAM can also extract and detect a broader range of less volatile organics using two wet chemistry reagents: *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide and dimethylformamide (MTBSTFA:DMF 4:1) and tetramethylammonium hydroxide (TMAH) in methanol [2]. The derivatization with MTBSTFA allows the detection and identification of complex, polar and/or refractory molecules by transforming molecules into volatile derivatives easily amenable to GC-MS analysis. MTBSTFA reacts with organics of astrobiological interest—such as nucleobases, amino acids, carboxylic acids, and sugars—while preventing degradation of their chemical structure. TMAH thermochemolysis allows the extraction of polar molecules (e.g., acids, amines, and thiols) bound in macromolecules and monomers chemically bound to mineral phases, making them detectable via GC-MS after methylation.



**Figure 1.** The Sample Analysis at Mars (SAM) instrument suite aboard the Curiosity rover, overlooking at Mount Sharp, Gale Crater, Mars.

## Glen Torridon, Mineralogy and SAM analyses:

During its exploration of the Glen Torridon (GT) clay-bearing unit over the past two years, SAM has analyzed the following samples: Kilmarie (KM) from the Jura member; Glen Etive (GE), Mary Anning (MA), and Groken (GR) from the Knockfarril Hill member (KHm); Glasgow (GG) from the Fractured Intermediate Unit (FIU), and Hutton (HU) from near the unconformity between the FIU and overlying the Greenheugh Pediment (GP) (Figure 2). X-ray diffraction of GT samples by CheMin showed large abundances of smectite clay minerals, feldspar, calcium sulfates and lower amounts of well-crystalline hematite [3]. Mineralogy constraints from SAM EGA results indicated that the rocks from GT experienced a complex authigenic/diagenetic history involving fluids with varying pH and composition [4].



**Figure 2.** Location of the samples collected by Curiosity at Glen Torridon and analyzed by the SAM instrument. Unit names are preliminary. Credit: A. Bryk

Laboratory analyses suggest clay and sulfate minerals can preserve organic matter [5,6] and organic matter has been detected in some clay-rich samples within Gale crater despite irradiation and diagenetic events over geological time scales [7]. To evaluate whether organic molecules were preserved within the minerals of the GT rock samples with SAM, we performed a total of five pyro-GC-MS experiments on KM, GE, MA, GG, and HU, two MTBSTFA derivati-

zation experiments on GE and MA, and a TMAH thermochemolysis experiment on MA.

Importantly, different pyrolysis temperature cuts were used to analyze these samples. Temperature cuts represent the portion of gas sent to the SAM hydrocarbon trap and the GC during pyrolysis and target the extraction of organics from minerals during thermal breakdown. KM and GE were analyzed using low temperature cuts (<500°C) whereas high temperature cuts (>500°C) were analyzed for MA, GG and HU.

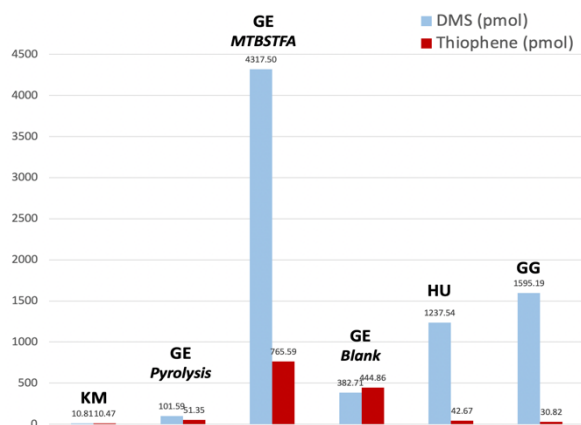
**EGA and Pyrolysis-GC-MS results:** Diverse and abundant organic molecules have been detected in chromatograms extracted from analyses of the GT samples. EGA indicated results within the medium to high molecular weight ranges of masses, suggesting the presence of a complex mixture of compounds. The diversity of aromatics seems consistent with recalcitrant organic materials such as macromolecules [7].

N-bearing and O-bearing organics were detected in all the samples and are likely derived from the MTBSTFA:DMF background present within SAM's Sample Manipulation System (SMS). Chlorinated organics, including chloromethane, dichloromethane and chlorobenzene, were detected at background level. Most of these chlorohydrocarbons are likely produced from reactions between martian chlorides and/or HCl (detected in EGA) and organics from SAM internal sources [8,9]. KM did not show clear evidence of the presence of indigenous organic molecules.

S-bearing organics were detected in the GT samples (Figure 3). GE and HU showed the highest abundance of S-bearing organic compounds, including aliphatic and aromatic compounds: dimethylsulfide, thiophene, and likely ethanethiol and dithiapentane. Because the pyrolysis experiments on GE and HU were preceded by wet chemistry experiments, the origin of the S-bearing organics is unclear and remains under investigation. MA indicated the presence of three previously unidentified S-organics: dithiapentane, dithiolane, and trithiane. The most diverse S-organic molecules, however, were extracted from GG, including a number of aliphatics (dimethylsulfide, propanethiol (or methylthioethane), diathiapentane) as well as aromatic (thiophene, methyl-thiophene and dithiolane). The S-bearing organics from MA and GG may be indigenous to Mars, as they were released at high temperature (>600°C) consistent with recalcitrant organic materials within the sample. Further, some organic fragments could have been structurally modified upon thermal release in the oven. The evolution temperatures of CO<sub>2</sub>, and evolution of CO, in EGA also indicate the likely presence of oxidized carbon.

**Wet chemistry results:** EGA and GC-MS data from the GE MTBSTFA experiment showed much less saturation of the wet chemistry solvents due to improvements in the analytical method based on lessons

learned from the 1<sup>st</sup> wet chemistry experiment performed on the Ogunquit Beach sample [10]. High molecular weight compounds were detected in GE. The highest abundance of sulfur-bearing organics ever measured by the SAM instrument was recovered in both the pyrolysis and wet chemistry runs of GE. The derivatization and first thermochemolysis experiment performed on MA liberated a wide range of aromatic organic molecules including methylated polycyclic aromatic hydrocarbons (methyl-naphthalene), a potential methylated ester carboxylic acid (benzoic acid) and benzothiophene, all detected for the first time on Mars [11]. However, no amino acids or fatty acids have been identified in any of the wet chemistry experiments.



**Figure 3.** Abundances of the S-bearing organics dimethylsulfide/ethanethiol (DMS) and thiophene in the GT samples.

**Conclusion and future work:** The SAM pyrolysis and wet chemistry experiments performed in the Glen Torridon clay-bearing unit revealed the highest diversity and abundance of organic molecules ever detected on Mars. Experiments are ongoing to obtain the retention times of the molecules detected and will help confirm other organic molecule identifications. Pathways of formation of sulfur-bearing and aromatic compounds are under investigation through laboratory experiments on SAM breadboards to ascertain their most likely source, either from the SAM internal background or as indigenous to Mars.

**References:** [1] Grotzinger, J.P. et al. (2013) *Sci Express* 343, 1242771-1242714. [2] Mahaffy P.R. et al. (2012) *Space Sci Rev*, 401-478. [3] Rampe et al., this meeting, [4] McAdam et al., this meeting [5] Millan, M. et al. (2018) *LPSC meeting* [#1558]. [6] Williams, A. et al. (2019) *Astro-bio*. 19, 522-546. [7] Eigenbrode et al. (2018) *Science*. [8] Glavin, D.P. et al. (2013) *Science*. [9] Millan et al. (2020) *JGR: Planets*. [10] Millan et al. (under revisions) *Nature Astronomy*. [11] Williams et al. this meeting.

**Acknowledgements:** M.M. and S.S.J. thank the funding from the NASA-GSFC grant NNX17AJ68G. The authors thank the SAM and MSL Operations, Engineering, and Science teams.