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RESEARCH ARTICLE
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Special Section:
The Curiosity rover's investigation of Glen Torridon and the surrounding area

Sedimentary Organics in Glen Torridon, Gale Crater, Mars: Results From the SAM Instrument Suite and Supporting Laboratory Analyses

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Abstract The Sample Analysis at Mars (SAM) suite instrument on board NASA's *Curiosity* rover has characterized the inorganic and organic chemical composition of seven samples from the Glen Torridon (GT) clay-bearing unit. A variety of organic molecules were detected with SAM using pyrolysis (up to ~850°C) and wet chemistry experiments coupled with evolved gas analysis (EGA) and gas chromatography-mass spectrometry. SAM EGA and GCMS analyses revealed a greater diversity and abundance of sulfur-bearing aliphatic and aromatic organic compounds in the sediments of this Gale crater unit than earlier in the mission. We also report the detection of nitrogen-containing, oxygen-containing, and chlorine-containing molecules, as well as polycyclic aromatic hydrocarbons found in GT, although the sources of some of these organics may be related to the presence of chemical reagents in the SAM instrument background. However, sulfur-bearing organics released at high temperature (≥600°C) are likely derived from Martian sources (e.g., igneous, hydrothermal, atmospheric, or biological) or exogenous sources and consistent with the presence of recalcitrant organic materials in the sample. The SAM measurements of the GT clay-bearing unit expand the inventory of organic matter present in Gale crater and is also consistent with the hypothesis that clay minerals played an important role in the preservation of ancient refractory organic matter on Mars. These findings deepen our understanding of the past habitability and biological potential of Gale crater.

Plain Language Summary Organic molecules are essential to all life as we know it. Clay minerals are known on Earth for their high organic preservation potential and can be key indicators of past habitable environments. On Mars, the Glen Torridon (GT) region in Gale crater was first identified from orbit as a priority target for the Mars Science Laboratory mission due to its abundant clay minerals. To evaluate the organic preservation potential of this region, seven rock samples were collected and characterized using the Sample Analysis at Mars (SAM) instrument onboard the *Curiosity* rover. The SAM investigation indicated the presence of various organic compounds, including the first observation on Mars of some sulfur-containing and ring-structured organics and the highest abundance of sulfur organics observed to date. Our investigation of the sources of these organics revealed that while some of the sulfur-bearing organics are likely Martian, a portion may also be related to the presence of chemical reagents carried in SAM, making attribution to a definitive source challenging. Nevertheless, these new SAM results confirm that ancient organic matter is preserved in the clay mineral bearing sediments of GT. Its origin—either meteoritic, abiotic or biotic—has yet to be established.

Key Points:

- *Curiosity* explored the Glen Torridon region of Gale crater, which has a smectite-rich mineralogy with high organic preservation potential
- The greatest diversity and abundance of sulfur-bearing organics to date were detected in the solid samples by the SAM instrument
- S-bearing organics extracted ≥600°C and some aromatic compounds likely come from martian refractory organic matter

†Deceased 28 January 2021.

Supporting Information:

Supporting Information may be found in the online version of this article.

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Writing – review & editing: R. E. Summons

1. Introduction

Between 2019 and 2021 (sols 2300 to 3067), the Sample Analysis at Mars (SAM) instrument suite onboard the *Curiosity* rover investigated one of the primary targets of the Mars Science Laboratory (MSL) mission: the clay-bearing Glen Torridon (GT) region (Figure 1) (Grotzinger et al., 2012, 2015). The SAM instrument suite (Mahaffy et al., 2012) is designed to investigate the past habitability and biological potential of Gale crater. This includes a search for organic molecules and an examination of their potential source(s) and origin(s). SAM is a miniaturized analytical chemistry laboratory that can characterize the volatile chemical composition of near-surface (~6 cm) sand and rock samples scooped and drilled by *Curiosity*. Since the beginning of the MSL mission, a variety of organic molecules from both martian and instrument background sources have been extracted and analyzed by SAM evolved gas analysis (EGA) and gas chromatography mass spectrometry (GCMS) (Eigenbrode et al., 2018; Freissinet et al., 2015, 2019; Glavin et al., 2013; Millan et al., 2021; Szopa et al., 2020).

Organic molecules detected by SAM-EGA and GCMS include chlorine and sulfur-bearing organic compounds, fragments of alkyl and aromatic compounds, and medium-chain length alkanes produced from organic matter preserved in the mudstones and sandstones of Gale crater. Despite the irradiation and diagenetic processes that have affected these rocks over 3 billion years (Pavlov et al., 2022), Martian organic molecules have been detected (Eigenbrode et al., 2018; Freissinet et al., 2015, 2019; Szopa et al., 2020). The detection of ancient organic molecules in Gale crater, in tandem with favorable environmental conditions ~3.5 billion years ago, indicates the presence of "habitable" environments, meaning that all the ingredients necessary to life as we know it were likely present.

SAM has the capability to extract and detect polar and complex organic molecules of potential astrobiological interest using two wet chemistry experiments: (a) *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide and its solvent dimethylformamide (MTBSTFA:DMF 4:1 by volume) and (b) 25 wt% tetramethylammonium hydroxide (TMAH) in methanol. The derivatization efficiency of MTBSTFA was demonstrated for the first time on Mars on the Ogunquit Beach (OG) scooped dune sample (Millan et al., 2021). In the OG experiment, several derivatized molecules, including benzoic acid, phenol, ammonia and phosphoric acid structure-related compounds, were detected. Possible sources of these species include organic molecules that were oxidized under the harsh conditions of the Martian surface/subsurface (e.g., contact with reactive oxygen-containing species and radiation) and/or molecules produced from the MTBSTFA reagent present in the SAM background, or both. The efficiency of the TMAH technique has been tested in the laboratory on Mars analogs and has shown to recover fatty acid biomarkers from analogs containing a wide variety of minerals similar to those that can be found in martian materials (He, Buch, Szopa, Williams, et al., 2021; Williams et al., 2019). Results of the first thermochemolysis analysis on the GT samples are summarized elsewhere (Williams et al., 2021) and will be detailed in a future paper.

Laboratory analyses of terrestrial samples indicate that clay and sulfate minerals can enhance the preservation of organic molecules, including biomarkers that can be precious indicators of past habitable environments and biological communities (Johnson et al., 2020; Millan et al., 2018; Williams et al., 2019). These results are particularly relevant for the exploration of GT since it is the most clay- and sulfate-rich region that has yet been explored by *Curiosity* (Bennett et al., 2022; Thorpe et al., 2022). This article reports the nature and abundances of organic molecules detected in seven drilled samples from the GT region with the SAM pyrolysis and wet chemistry experiments. The most likely source(s) and origin(s) of these organic molecules were investigated utilizing supporting laboratory experiment data.

2. Methods

2.1. SAM Flight Experiments

2.1.1. The Glen Torridon Samples

During *Curiosity*'s exploration of the GT *clay-bearing* region, the following samples were analyzed with the SAM instrument suite: within the Murray formation, Kilmarie (KM) was obtained in the Jura member; within the Carolyn Shoemaker formation, Glen Etive (GE), Mary Anning (MA), and Groken (GR) were drilled in the Knockfarril Hill member (KHm); and Glasgow (GG), Hutton (HU) and Nontron (NT) from the Glasgow member (Gm) (Figure 1). KM was the first sample of the GT analyzed by SAM, followed by GE, HU, GG, MA, GR, and NT. X-ray diffraction (XRD) of the GT samples by CheMin indicated higher abundances of smectite clay

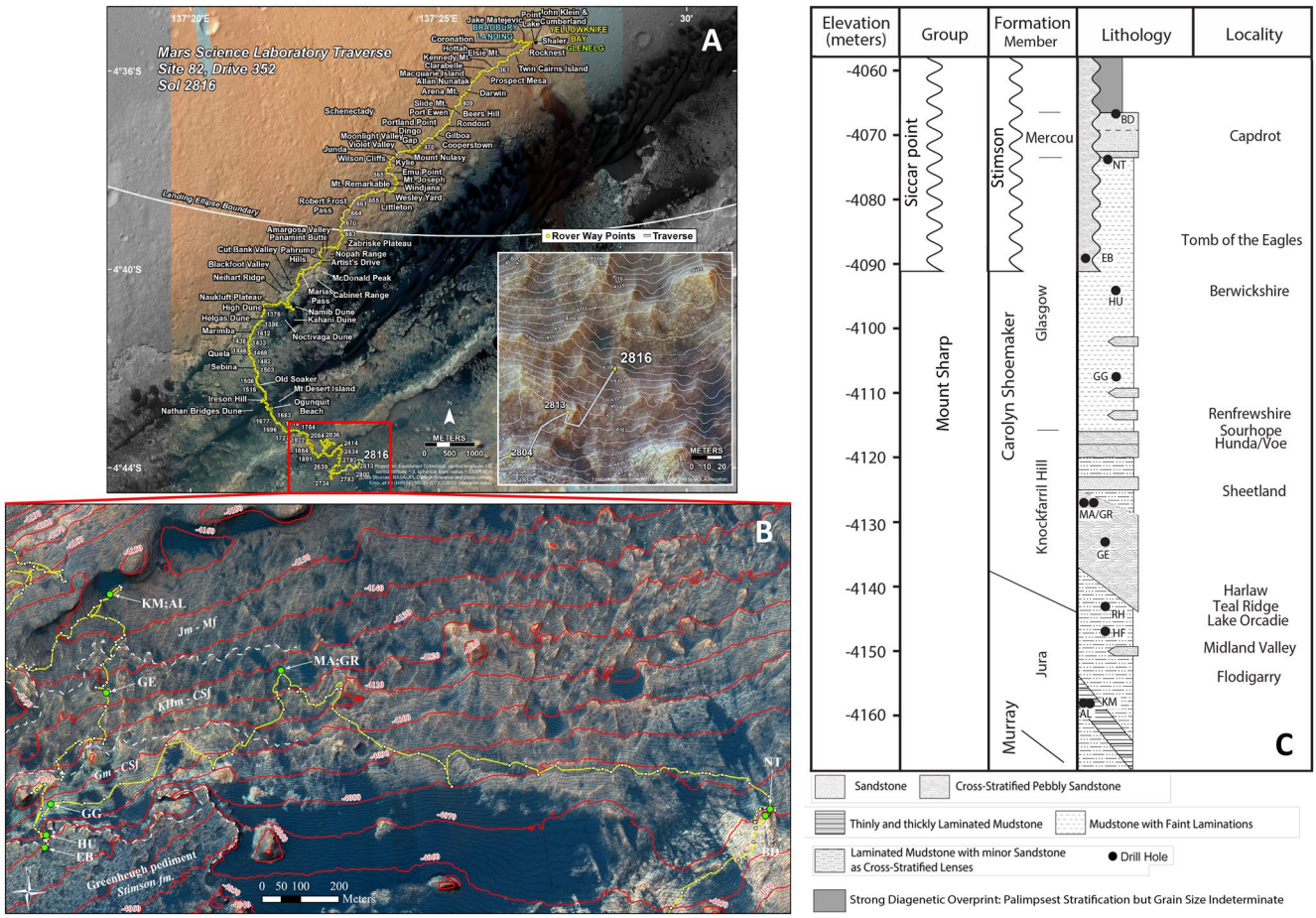


Figure 1. (a) *Curiosity*'s traverse (yellow line) as of sol 2816, overlain on an image acquired by the High Resolution Imaging Science Experiment (HiRISE) camera. The red square indicates the location of the Glen Torridon region. Inset image (bottom right) is a zoom of *Curiosiy's* location, sol 2816 (b) The Glen Torridon region that was analyzed between sols 2300 to 3067. Credit: NASA/JPL-Caltech/MSSS. (c) Stratigraphic column showing drill samples acquired during the Glen Torridon campaign. The samples from Glen Torridon discussed in this article and represented on the figure are the following: Kilmarie (KM), Glen Etive (GE), Mary Anning (MA), Groken (GR), Glasgow (GG), Hutton (HU) and Nontron (NT). Jm: Jura member, KHm: Knockfarril Hill member, CSf: Carolyn Shoemaker formation, Gm: Glasgow member. Column credit: Fedo et al., 2022.

minerals, feldspar, calcium sulfates and lower amounts of well-crystalline hematite compared to the nearby Vera Rubin ridge (VRR) (Bristow et al., 2021; Thorpe et al., 2022) (Table 1).

2.1.2. SAM Pyrolysis and Wet Chemistry Experiments

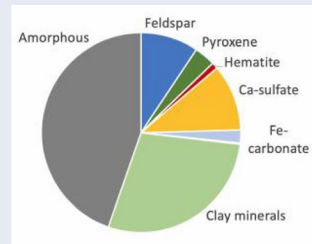
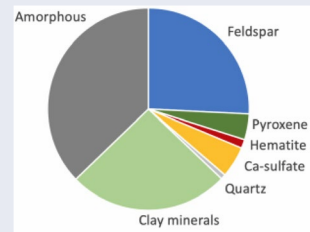
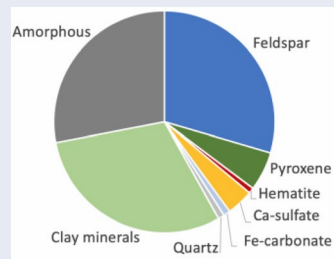
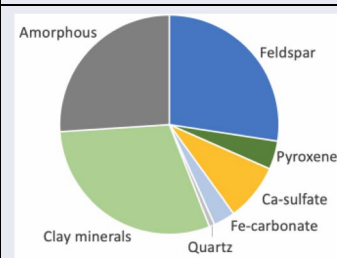
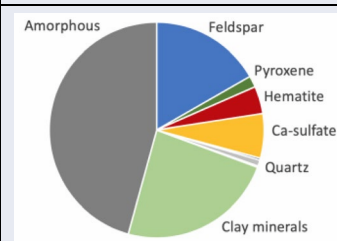
Drilled samples collected by *Curiosity* were each dropped into one of the 74 cups of the Sample Manipulation System (SMS) inside SAM. Samples were then heated to ~850°C at 35°C.min^{-1} under He flow to desorb and release all the volatiles into the three SAM instruments: the gas chromatograph (GC), the mass spectrometer (MS), and the tunable laser spectrometer (TLS) connected through a solid sample and gas processing system. In this article, we focus on the solid sample analyses. SAM can analyze the molecules released during pyrolysis using three modes: (a) EGA, (b) EGA plus GCMS, and (c) wet chemistry with EGA and GCMS. To evaluate whether organic molecules were contained and preserved within the smectite-bearing GT rock samples, we performed a total of seven pyrolysis-GCMS experiments on KM, GE, MA, GR, GG, HU and NT, two MTBSTFA derivatization experiments on GE and MA, and a TMAH thermochemolysis experiment on MA.

2.1.2.1. Evolved Gas Analysis (EGA)

During EGA, the volatiles evolved during the pyrolysis of solid samples were sent directly to the MS for detection. This mode allowed tracking of the temperature(s) at which volatiles were released, which could be used to characterize the chemical composition of each sample. Data from the EGA mode was employed to

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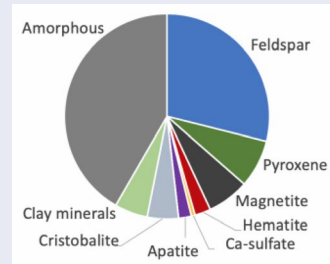
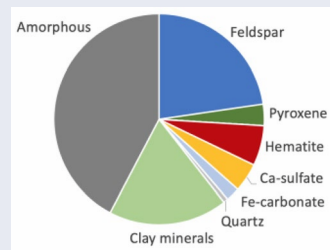
Table 1
Mineralogy of the Samples Analyzed by SAM as Measured by the CheMin Instrument

Geological Formation	Geological Member	Sample name (Abbreviation)	Mineralogy (CheMin)
Murray formation	Jura member (Jm)	Kilmarie (KM)	
Carolyn Shoemaker formation	Knockfarril Hill member (KHm)	Glen Etive (GE)	
		Mary Anning (MA)	
		Groken (GR)	
	Glasgow member (Gm)	Glasgow (GG)	

select the temperature ranges of evolved gases that would be chosen for subsequent analysis by GCMS. These "ranges" were designated "Temperature cuts" (T cuts). The selection of these T cuts depended on the organics and minerals targeted (e.g., organic molecules that may have been contained in a specific mineral) and the need to limit the amounts of certain volatiles introduced into the trap(s) and GC to prevent column saturation and/or degradation (e.g., HCl, SO_2).

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Table 1
Continued

		Hutton (HU)	
		Nontron (NT)	

2.1.2.2. Temperature Cuts

One temperature cut was chosen for the pyrolysis-GCMS analyses of KM (279°C–647°C), GE (195°C–574°C) and HU (303°C–604°C). These ranges were selected in order to target a broad range of trapped organic molecules including those potentially released from the smectites and the sulfur-mineral(s) which started to decompose at the beginning of the SO_2 release as observed in EGA (~600°C).

Two T cuts were selected for the pyrolysis analysis of GG, MA, and GR. A low/intermediate temperature cut (from 265°C to 556°C for both MA and GR and from 299°C to 425°C for GG) was used to capture any organic molecules that could be related to the evolved CO_2 and CO observed in EGA, and a high temperature cut (701°C–822°C for MA and GR and 600°C–825°C for GG) to capture the organic molecules that could be related to the CO evolved at high temperature. These temperatures also limited major interferences with evolved SO_2 that could saturate and/or damage the SAM components (e.g., column, trap(s)). A high T cut (700°C–820°C) was selected for the analysis of NT in an attempt to only capture the organic molecules potentially trapped in sulfur-bearing minerals such as S-bearing organics.

For the wet chemistry experiments, the GE and MA samples were heated from ~30°C to ~850°C. However, only portions of the gases were selected at different intervals during pyrolysis and were sent to the trap(s) and columns, to avoid saturation by the reagents as described in Millan et al. (2021). The temperature ranges chosen for each sample are illustrated in the diagram below (Figure 2).

2.1.2.3. Wet Chemistry: Derivatization and Thermochemolysis

Nine of the 74 cups present in the SAM SMS were designed to perform in situ wet chemistry experiments using MTBSTFA derivatization and thermochemolysis. The first nominal MTBSTFA derivatization experiment on the scooped sand from the OG location allowed optimization of the derivatization sequence (Millan et al., 2021). Therefore, the amount of chemical reagents transferred to the analytical system for the wet chemistry analyses of GE and MA was significantly reduced and subsequently improved the detection and identification of the chemical species. This improvement was observed on the peaks related to MTBSTFA-DMF byproducts, which appeared much sharper compared to the OG analysis.

"Clean-ups" were performed after each pyrolysis and derivatization experiment to control contamination and clean the system (traps, column, and MS). To do so, the analytical sequence that was used to analyze the sample is repeated but without sample nor pyrolysis.

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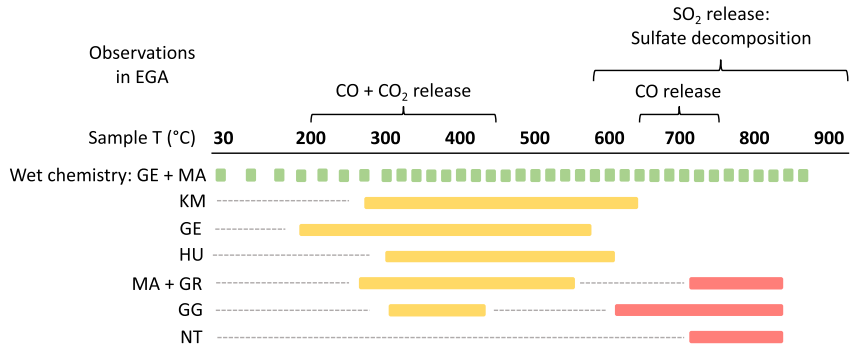


Figure 2. Illustrative diagram representing the temperature ranges or "cuts" chosen for each sample. Except for the wet chemistry experiments, in which only a portion of the gases was sent to the traps and columns (green), the temperature ranges (medium in yellow and high in red) were selected based on the gases released from the samples, as observed in the evolved gas analysis data. Sample abbreviations: GE: Glen Etive, MA: Mary Anning, KM: Kilmarie, HU: Hutton, GR: Groken, GG: Glasgow, NT: Nontron.

2.1.3. GCMS Operating Conditions

During the GT campaign, the samples were analyzed using three of the six GC columns available on SAM: the MXT-20 (Restek) or "GC1", MXT-5 (Restek) or "GC2" and Chirasil-β Dex (Agilent) or "GC4" (Mahaffy et al., 2012). Each column has the following dimensions: 30 m × 0.25 mm with a film thickness of 0.25 μm. For each experiment, two columns were used in parallel to maximize the range of molecules to be separated and detected, although this strategy decreased the abundance of molecules sent on each channel. The choice of the GC4 column for the GT campaign was deliberate since it was the only remaining SAM column preceded with an injection trap (IT) after the clogging of the MXT-CLP or "GC5" that we were primarily using.

The KM and GE samples were analyzed by pyrolysis GCMS (KM) and MTBSTFA derivatization GCMS (GE), respectively, while sequentially using GC1 and GC4 (dual-column experiment). MA was analyzed by both pyrolysis GCMS and thermochemolysis GCMS using the MXT-20 (GC1) and Chirasil-β Dex CB (GC4) channels. However, the absence of peaks in the GC4 chromatogram and pressure sensor housekeeping data led to the conclusion that the IT from the GC4 channel likely clogged during the MA experiment. GG and HU were analyzed with pyrolysis using GC1 and GC4, and GR and NT were analyzed using GC1 and GC2 (Table 2).

2.1.4. Strategies for Molecular Identification and Quantification

Identification of the molecules detected in the GCMS analyses is achieved by comparison between the SAM mass spectra extracted from the flight chromatograms and mass spectra from the National Institute of Standards and Technology (NIST) library. To confirm the preliminary identifications of the molecules made in flight with the MS, the retention times of the molecules suspected to be present in the flight data are measured in the laboratory under simulated SAM flight conditions (column temperature and carrier gas flow rate) and compared to the retention times of the equivalent standard molecules analyzed in the laboratory using an identical spare column mounted on a commercial instrument. The abundances of the molecules were calculated using a method that has been used previously and is described elsewhere (e.g., Szopa et al., 2020) as well as in the Supplementary Material.

2.1.5. Criteria and Level of Confidence to Attribute a Martian Origin to a Compound

Establishing a definitive Martian origin to the organic molecules detected in the SAM evolved gas, pyrolysis and wet chemistry GCMS analyses is challenging. Indeed, the internal SAM instrument organic source(s) are known to contribute to the signals of some of the organics detected and, in most cases, compound specific isotopic analyses and chirality measurements are not possible with SAM. Therefore, several other criteria are used to determine our level of confidence that a molecule detected by SAM is more likely derived from the Martian sample rather than from internal instrument derived sources:

1. A high confidence level that molecules are derived from Martian organic matter is when they are not observed in SAM procedural blanks or in SAM-like laboratory experiments, and a variation in the relative abundances of the detected molecules is observed across different Martian samples.

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Table 2
Samples Analyzed by Sample Analysis at Mars (SAM) and Details of Each Experiment Including Their Geological Unit, Designated Name, the SAM Test Experiment Identification Number, the Type of Experiment (Pyrolysis, MTBSTFA Derivatization, or TMAH Thermochemolysis), the Temperature Cut(s) Sent to the Hydrocarbon Trap, the Chromatographic Columns Used (MXT-20/GC1, MXT-5/GC2, and Chirasil-β Dex/GC4), the Date of Analysis and the Sols of the Mission

Geological formation	Geological member	Sample name (Abbreviation)	TID	Experiment	T cut (°C)	Column(s)	Date of analysis	Sol of the mission
Murray formation	Jura member	Kilmarie (KM)	25517	Pyrolysis	279–647	GC1 + GC4	May 2019	2398
Carolyn shoemaker formation	Knockfarril Hill member	Glen Etive (GE)	25533	Pyrolysis	195–574	GC1 + GC4	August/September 2019	2501
			25544	MTBSTFA	31–827[a]	GC1 + GC4		2540
		Mary Anning (MA)	25600	Pyrolysis	265–556; 701–822[b]	GC1 (GC4 failure[c])	August/September 2020	2850
			25608	TMAH	31–828[a]	GC1 + GC2		2878
			25613	MTBSTFA	31–849[a]	GC1 + GC2		2885
		Groken (GR)	25622	Pyrolysis	265–556; 701–822[b]	GC1 + GC2	November 2020	2918
	Glasgow member	Glasgow (GG)	25582	Pyrolysis	299–425; 600–825[b]	GC1 + GC4	May 2020	2771
		Hutton (HU)	25568	Pyrolysis	303–604	GC1 + GC4	February 2020	2682
		Nontron (NT)	25639	Pyrolysis	700–820	GC2 + GC1	March 2021	3067

Note. The specific mineralogy of each sample, as measured by CheMin, is summarized in Table 1.

[a]Wet chemistry venting to Mars mode: subset of this temperature range material was sent to the hydrocarbon trap during pyrolysis. [b]Two temperature ranges were selected during which the material released from the pyrolysis of the sample was sent to the hydrocarbon trap. [c]GC4 channel likely clogged during the experiment resulting in no detection of chemical species with the MS.

2. A medium confidence level of a Martian origin is when compounds are detected in SAM procedural blanks and not in laboratory analog experiments, but they are present at elevated abundances above the SAM instrument background with variations in relative abundances across different Martian samples. In this case, compounds could be derived from SAM internal sources, from Martian organic matter, or both.
3. A low confidence level of a Martian origin is when the compounds are present in SAM procedural blanks as well as laboratory analog experiments and we observe a similar distribution of molecules across multiple Martian samples. In this case, the compounds detected are most likely derived from SAM internal organic sources.

2.2. Laboratory Experiments

The potential for reactions between organic molecules and oxychlorine or sulfate minerals during SAM pyrolysis motivated a new series of laboratory experiments. These experiments were performed to better understand the SAM results obtained at GT and support the interpretation of the most likely precursors and sources of the organics detected.

2.2.1. Samples and Chemical Reagents

Pyrolysis experiments were performed on synthetic sulfur- and chlorine-containing Mars analog materials. Jarosite samples were synthesized at 18°C using a method adapted from (Driscoll & Leinz, 2005), with 10 mg of phthalic acid or valine added to the standard starting reagents (17.2 g of ferric sulfate hydrate and 5.6 g of potassium hydroxide dissolved in 100 mL deionized water) (Lewis et al., 2017). Jarosite was selected as an example sulfate mineral due to its presence in some of the Gale crater samples (Rampe et al., 2020). Additionally, sulfur in the GT samples observed in EGA is primarily sourced from iron sulfate (Table 1) and (McAdam et al., 2022; Wong et al., 2022). Phthalic acid and valine represent chemical families that are likely to be found on Mars. Valine was selected as it is a common amino acid found in terrestrial biology and is also found in carbonaceous meteorites (Callahan et al., 2013; Glavin et al., 2018). Phthalic acid is a potential oxidation product of aromatic organic matter delivered to Mars (Benner et al., 2000; Poch et al., 2013). It may also be a chemical precursor of some of the chlorohydrocarbons that have been detected in several Gale crater drill samples (Freissinet et al., 2020; Miller et al., 2016).

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2.2.2. Laboratory Pyrolysis and Wet Chemistry Experiments

Two types of experiments were conducted; SAM-like pyrolysis experiments (temperature ramp from 35°C to 850°C at 35°C.min^{-1}) and flash-pyrolysis (temperature ramp from 35 to 850°C at a 100°C.s^{-1}). Flash-pyrolysis experiments were performed as a "worst-case" scenario of SAM oven reactions at high temperature. Flash-pyrolysis experiments are usually more favorable to the chemical reactivity, in comparison to SAM-like pyrolysis, they simulate the highest pyrolysis temperature that can be reached during the pyrolysis on Mars. The jarosite/organic mixtures were pyrolyzed in multiple modes: (a) on their own, (b) in the presence of 1 wt% calcium perchlorate (estimated average Martian oxychlorine concentrations), and (c) in the presence of 1 wt% calcium perchlorate and 2 µL of the MTBSTFA-DMF (4:1) wet chemistry reagent used in the SAM instrument (Glavin et al., 2013).

The laboratory pyrolysis-GCMS experiments were conducted using a commercial CDS5100 pyroprobe (CDS Analytical). Samples were powdered and aliquots (~10–30 mg) were loaded into an organically clean quartz tube packed with glass wool on each side. The interface temperature between the pyrolyzer and the GC was set at 250°C. During the SAM-like pyrolysis experiments, the volatiles released from the samples were flushed under helium and trapped by a hydrocarbon trap filled with Tenax® TA adsorbent and set at 50°C. To desorb the molecules, the trap was heated up to 320°C and the helium flow was reversed from the trap to the GC. No trap was used during the flash-pyrolysis experiments. To ensure that the system was free of contamination and to clean the system between each analysis, blanks were performed in which the pyrolyzer was flash-heated at 850°C for several minutes. The GCMS injector, column, transfer line and ion source were also regularly cleaned by heating (cycles of 30 min at 300°C). The pyrolysis products were analyzed and identified by GCMS using the Xcalibur software from ThermoFisher.

2.2.3. GCMS Operating Conditions

The GCMS experiments were conducted on a Trace 1310 GC coupled to an ISQ quadrupole MS (ThermoFisher). The GC was equipped with a Restek capillary MXT-5 column similar to the SAM GC2 column (30 m long × 0.25 mm internal diameter bonded with a 0.25 µm thick stationary phase) which allows us to analyze and separate a wide range of molecules (~C_5-C_{30}). For consistency, and to help the comparison of the results, the operating conditions of the GCMS were kept identical for all the pyrolysis experiments. The column temperature was programmed as followed: an initial temperature of 40°C held for 5 min followed by a 6°C.min^{-1} heating ramp up to a final temperature of 300°C held for 1 min to bake out the column before the next analysis. The helium carrier gas (99.9999%) was set at a constant 1.5 mL.min^{-1} flow rate with split flow ranging from 10 to 50 mL.min^{-1}. The MS ion source and transfer line were both set at 300°C and ions produced by the 70 eV electron ionization source were scanned with mass-to-charge ratios (m/z) comprised between 10 and 535 with a scan time of 0.2 s.

3. SAM Results

3.1. Evolved Gas Analysis (EGA)

EGA results indicated the presence of several medium to high molecular weight (HMW) organic compounds released during the pyrolysis and wet chemistry experiments, including aromatics such as methylnaphthalene (Eigenbrode et al., 2020). The diversity of aromatic compounds seemed consistent with the presence of recalcitrant organic materials in the samples, such as macromolecules (e.g., kerogen-like material) as inferred to be present in previous analyses of mudstone samples collected in Gale crater (Eigenbrode et al., 2018).

CO_2 and CO evolutions observed during SAM EGA of the GT samples (Figure 3) were largely consistent with those produced by organic salts, such as oxalates, during SAM-like EGA in the laboratory (Lewis et al., 2021). Organic salts such as oxalates can produce CO_2 and CO evolutions in the temperature ranges labeled "oxalates (CO)" and "oxidized organic C (CO_2)" in Figure 3, which show clear peaks in the data from all the GT samples. The oxidation of more reduced organic compounds (indigenous to the sample or from the SAM background) could also have produced some of the observed CO and CO_2 throughout the temperature range. In addition, CO_2 evolved at temperatures above 360°C may have resulted from decomposition of small amounts of carbonate detected during CheMin XRD analysis of some samples (Bristow et al., 2021) (Figure 3). CO_2 evolved below ~200°C is attributed largely to adsorbed atmospheric CO_2.

The GT samples all evolved SO_2, indicating variable abundances of Fe sulfate/sulfide and Mg sulfate. The samples acquired at lower stratigraphic levels, KM and GE, indicated evidence for Mg sulfates (based on high

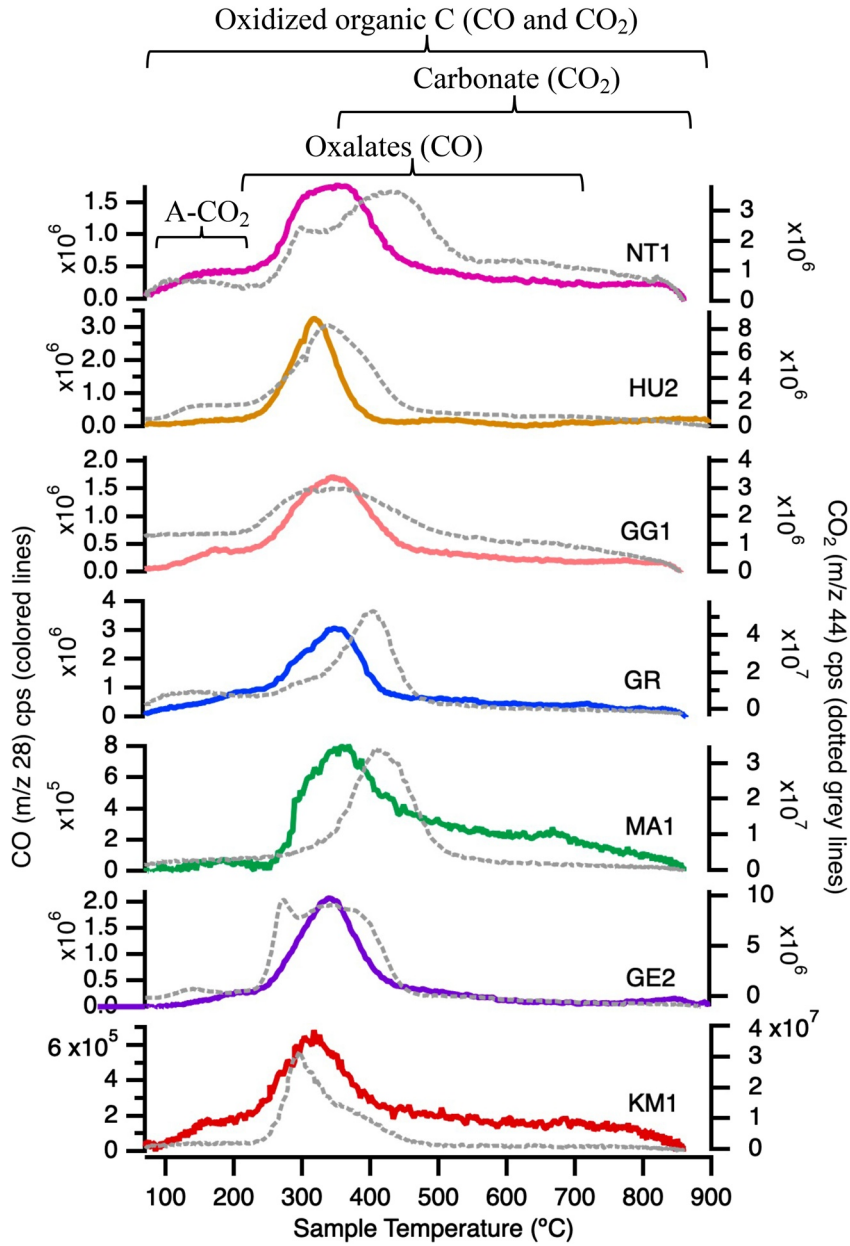


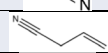
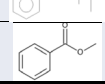
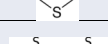
Figure 3. (a) Evolved CO and CO_2 versus the sample temperature (°C) as observed in evolved gas analysis. The samples analyzed are as followed: NT1: Nontron, HU2: Hutton, GG1: Glasgow, GR: Groken, MA1: Mary Anning, GE2: Glen Etive, KM1: Kilmarie. The temperatures for sources of evolved CO_2 and CO are indicated with brackets. A-CO_2 indicates adsorbed atmospheric CO_2.

temperature SO_2 releases), unlike the other GT samples, which suggested a possible change in fluid chemistry (McAdam et al., 2022). Most of the mid-temperature (~500°C) SO_2 evolved by GT samples was consistent with an Fe sulfate source based on an analysis of peak SO_2 release temperatures, statistical comparisons to laboratory analog data, and $\delta^{34}S$ calculations (Wong et al., 2022). KM was the only sample found to show strong evidence for the presence of a sulfide mineral, which was consistent with Jura member VRR samples (Wong et al., 2020). Additionally, the GT samples continued the trend of low/no oxychlorine species since sol 1058 with the exception of the Rock Hall sample (McAdam et al., 2020).

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Table 3
Summary of the Main Molecules That Have Been Identified in the Glen Torridon Samples

Chemical family	Name of the molecule	Raw chemical formula	Molecule	Sample and type of analysis										Origin(s) of the organic molecules detected in GT
				KM	GE		MA			HU	GG	GR	NT	
				Pyr	Pyr	MTBSTFA	Pyr	TMAH	MTBSTFA	Pyr	Pyr	Pyr	Pyr	
Inorganics	CO and/or N_2	CO/N_2	C≡O / N≡N	X	X	X		X		X	X			martian atmosphere
	O_2	O_2	O=O	X	X	X				X	X			
	H_2O	H_2O		X	X	X	X	X		X	X			
	NO	NO	N=O	X	X					X	X			Nitrates
	H_2S	H_2S		X	X					X	X			Sulfates, sulfides
	COS	COS	O=C=S	X	X	X				X	X			
	SO_2	SO_2		X	X		X	X	X	X	X		X sat.	
	CS_2	CS_2	S=C=S		?	X				X	X			
	CO_2	CO_2	O=C=O	X		X	X	X		X	X	X sat.		Oxidized organics and carbonates
	HCN	HCN	N-C≡N		X	X				X	X			MTBSTFA-DMF and/or indigenous
Hydrocarbons	methylpropene isomers	C_4H_8		X	X	X (1)				X (1)	X (1)			MTBSTFA
	Pentene isomers	C_5H_{10}				X (2)				X (1)	X (1)			
N-bearing organics	acetonitrile	C_2H_3N		X	X	X				X	X			MTBSTFA-DMF and/or indigenous
	methacrylonitrile	C_4H_5N				X								
	Propenenitrile (acrylonitrile)	C_3H_3N		X	X	X				X	X			
	propanenitrile	C_3H_5N			X					X	X			
	butenenitrile	C_4H_5N			X						X			
	isocyanate t-BDMS	$C_7H_{15}NOSi$				X								MTBSTFA-DMF
	isocyanomethane	C_2H_3N								X	X			
	dimethylbenzenamine	$C_8H_{11}N$						X						TMAH + organic
	trimethylbenzenamine	$C_9H_{13}N$						X						TMAH + organic
	tetramethylbenzenamine	$C_{10}H_{15}N$						X						
	benzonitrile	C_7H_5N							X			X	X	Potentially indigenous
O-bearing organics	acetone	C_3H_6O			X									MTBSTFA and/or DMF
	methylpropenal	C_4H_6O			X					X	X			MTBSTFA-DMF + minerals and/or indigenous
	methylpropanal	C_4H_8O								X	X			
	Potential oxygen-bearing aromatic	?	?								X			
	benzoic acid t-BDMS	$C_{13}H_{20}O_2Si$							X			X		Oxidized organics and/or MTBSTFA + trap(s)
	benzoic acid methyl ester	$C_8H_8O_2$						X						
Cl-bearing organics	chloromethane	CH_3Cl		X	X	X	?			X	X			MTBSTFA + chlorides or HCl
	dichloromethane	CH_2Cl_2			X		?			X	X			
	chloromethylpropane	C_4H_9Cl			X									Likely indigenous
	chloromethylpropene	C_4H_7Cl			X (1)					X	X			MTBSTFA + chlorides or HCl
	chlorobenzene	C_6H_5Cl			(X)		(X)			?	X			Likely indigenous
	chlorodimethylethylsilane	$C_4H_{11}ClSi$		X	X					X	X			MTBSTFA + chlorides or HCl
S-bearing organics	ethanethiol	C_2H_6S		(X)	X	X	?			X	X			Likely indigenous
	thiophene	C_4H_4S		(X)	X	X	?			X	X			
	dithiapentane	$C_3H_8S_2$			?		X			?	X			
	dithiolane	$C_3H_6S_2$					X				X			Likely indigenous

3.2. GCMS Pyrolysis and Wet Chemistry

The nature of the main compounds detected in the analyses of the GT samples and the specific samples/analyses where they were detected are summarized in Table 3 and below.

Table 3
Continued

	trithiane	$C_3H_6S_3$					X				?				
	benzothiophene	C_8H_6S						X							
	alkyl-thiophene	?	?					X							
	propanethiol	C_3H_8S									X				
	methylthiophene	C_5H_6S									X				
Aromatics	benzene	C_6H_6		X	X	X		X		X	X			Trap(s)	
	toluene	C_7H_8		X	X	X		X		X	X				
	phenol t-BDMS	$C_{12}H_{20}OSi$		X	X	X			X	X		X	X	Trap(s) + MTBSTFA	
	phenol	C_6H_6O		X	X					X				Trap(s)	
	xylene	C_8H_{10}									X				
	phenylethyne	C_8H_6			X	X				X	X				
	styrene	C_8H_8		X	X	X				X	X				
	biphenyl	$C_{12}H_{10}$		X	X				X	X	X	X			
	diphenylmethane or methylbiphenyl	$C_{13}H_{12}$						X	X						
	methylindene	$C_{10}H_{10}$						?						Trap(s) and/or indigenous	
	phthalic acid t-BDMS	$C_{20}H_{34}O_4Si_2$							X			X		Trap(s) + MTBSTFA	
	naphthalene	$C_{10}H_8$						X	?			?		Potentially indigenous	
	fluoronaphthalene (IS)	$C_{10}H_7F$						?	?			?	?	SAM Internal standard	
	tetramethylbenzene	$C_{10}H_{14}$						X						Trap(s) and/or indigenous	
	dihydronaphthalene	$C_{10}H_{10}$						?							
	methylnaphthalene	$C_{11}H_{10}$						X (1)						Likely indigenous	
Others	mono-silylated water (MSW)	$C_6H_{16}OSi$		X	X	X	X			X	X			MTBSTFA + H_2O	
	bi-silylated water (BSW)	$C_{12}H_{30}OSi_2$		X	X	X	X	X	X	X	X	X	X		
	t-butyldimethylfluorosilane	$C_6H_{15}FSi$		X	X	X				X	X		X	MTBSTFA byproduct	
	trifluoromethylacetamide (TFMA)	$C_3H_4F_3NO$		X	X	X			X		X	X			
	boric acid 3-TMS	$C_9H_{27}BO_3Si_3$						X	X			X	X	MTBSTFA + silica beads	
	dimethyltrifluoroacetamide	$C_4H_6F_3NO$			X					X	X			MTBSTFA byproduct	
	MTBSTFA (unreacted)	$C_9H_{18}F_3NOSi$				X								MTBSTFA	
	DMF (unreacted)	C_3H_7NO				X	?							DMF	

Note. The molecules that were not identified were not listed. Legend: (X) at background level. The number in parenthesis indicates the number of isomers that were detected in the analysis. ? compound potentially detected but such the identification was not confirmed. Sample abbreviations are as followed: KM: Kilmarie, GE: Glen Etive, MA: Mary Anning, HU: Hutton, GG: Glasgow, GR: Groken, and NT: Nontron.

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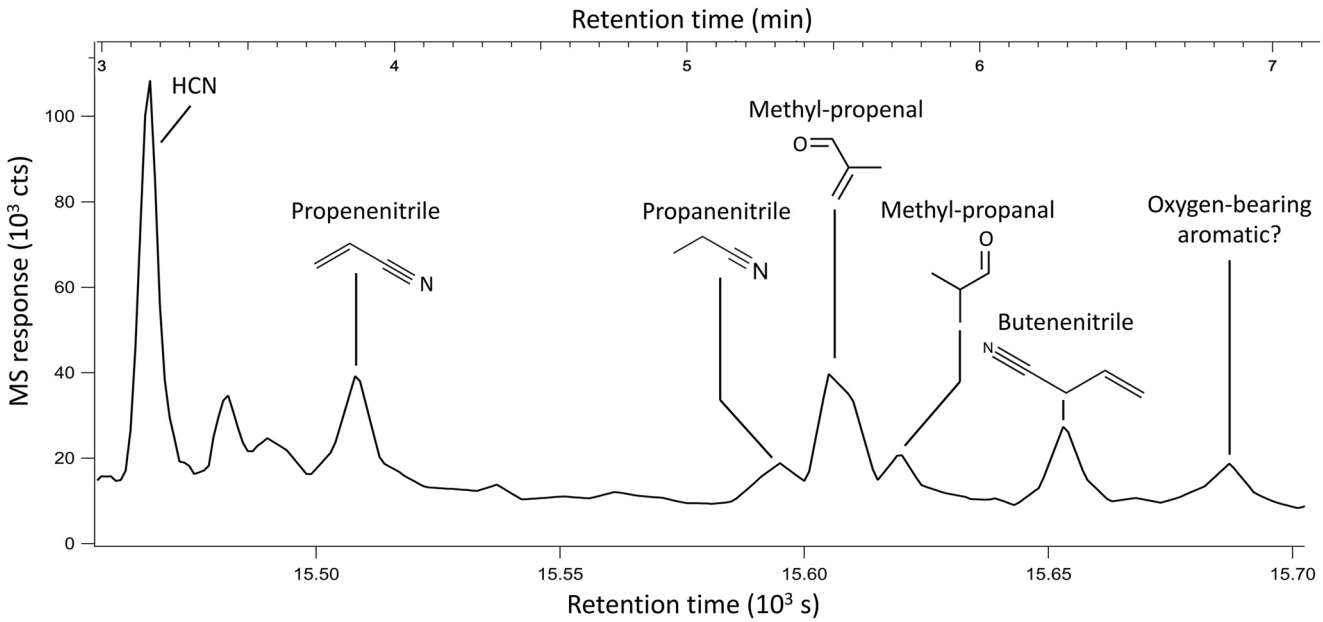


Figure 4. Reconstructed chromatogram of the first eluted nitrogen- and oxygen-bearing organics detected in the analysis of the Glasgow sample obtained with the Chirasil-β Dex column (GC4) and plotted as such: m/z 54 + m/z 57 + m/z 67 + m/z 70 + m/z 72. The Reverse Match Factor (RSI) of the last molecule of the chromatogram was insufficient to strictly identify it (RSI < 600), however its extracted mass spectra indicated the presence of a potential oxygen-bearing aromatic.

3.2.1. Nitrogen-, Oxygen- and Chlorine-Bearing Compounds

Nitrogen-bearing organic molecules were detected in most analyses and included nitriles and amines (Figure 4). Acetonitrile and propenenitrile (acrylonitrile) were detected in the KM, GE (pyrolysis and MTBSTFA), HU, and GG analyses. Methacrylonitrile (or methylpropenenitrile) and derivatized isocyanate were only detected after the MTBSTFA experiment performed at GE. Propanenitrile and butenenitrile were detected in the analyses of GE, HU and GG. Benzonitrile was detected in the MA (MTBSTFA), GR and NT analyses. Isocyanomethane was detected in the HU and GG analyses. Dimethyl-, trimethyl- and tetramethylbenzenamine were only detected after the TMAH analysis on the MA sample.

Oxygen-bearing organics were only detected in a few analyses (Figure 4). Acetone was present after the pyrolysis of GE. Two new aldehydes, were detected. Methylpropenal was identified for the first time in GE, GG, and HU, and its saturated homolog, methylpropanal was detected in HU and GG as well as potentially furyl-butanone or another oxygen-bearing compound with a similar structure. Derivatized benzoic acid was potentially present in the MTBSTFA and pyrolysis analyses of MA and GR, respectively, and as benzoic acid methyl ester in the TMAH analysis. The identification of both benzoic acid derivatives was confirmed with their retention time measured using laboratory instruments under SAM-flight conditions.

Chlorohydrocarbons included chloromethanes and chlorobenzene, detected above background in some samples (>10 pmol), two chloromethylpropene isomers, chloromethylpropane and chlorodimethylethylsilane (Figure S1 in Supporting Information S1 and Table 3). Details regarding the specific analysis where they were detected and their abundances can be found in the Supplementary Materials.

3.2.2. Sulfur-Bearing Compounds

Sulfur-bearing organic molecules were present in most samples and include compounds that had not been observed previously. Ethanethiol (or its isomeric equivalent form dimethylsulfide) and thiophene were detected after the pyrolysis of all the samples except KM, GR, and NT, and potentially in MA (pyrolysis), regardless of the temperature cut. They were detected in the analysis of GE, for which a medium T cut (200°C–600°C) was used, and in HU and GG, which both included a high T cut (>600°C). Ethanethiol and thiophene were present with an abundance of ~10 pmol in KM, between 100 and 1500 pmol for ethanethiol, and at an average of ~40 pmol for thiophene in the pyrolysis analyses of GE, HU and GG (Figure 5). However, their highest abundances were observed after the MTBSTFA derivatization analysis of GE with amounts of ~4,300 pmol and ~765 pmol

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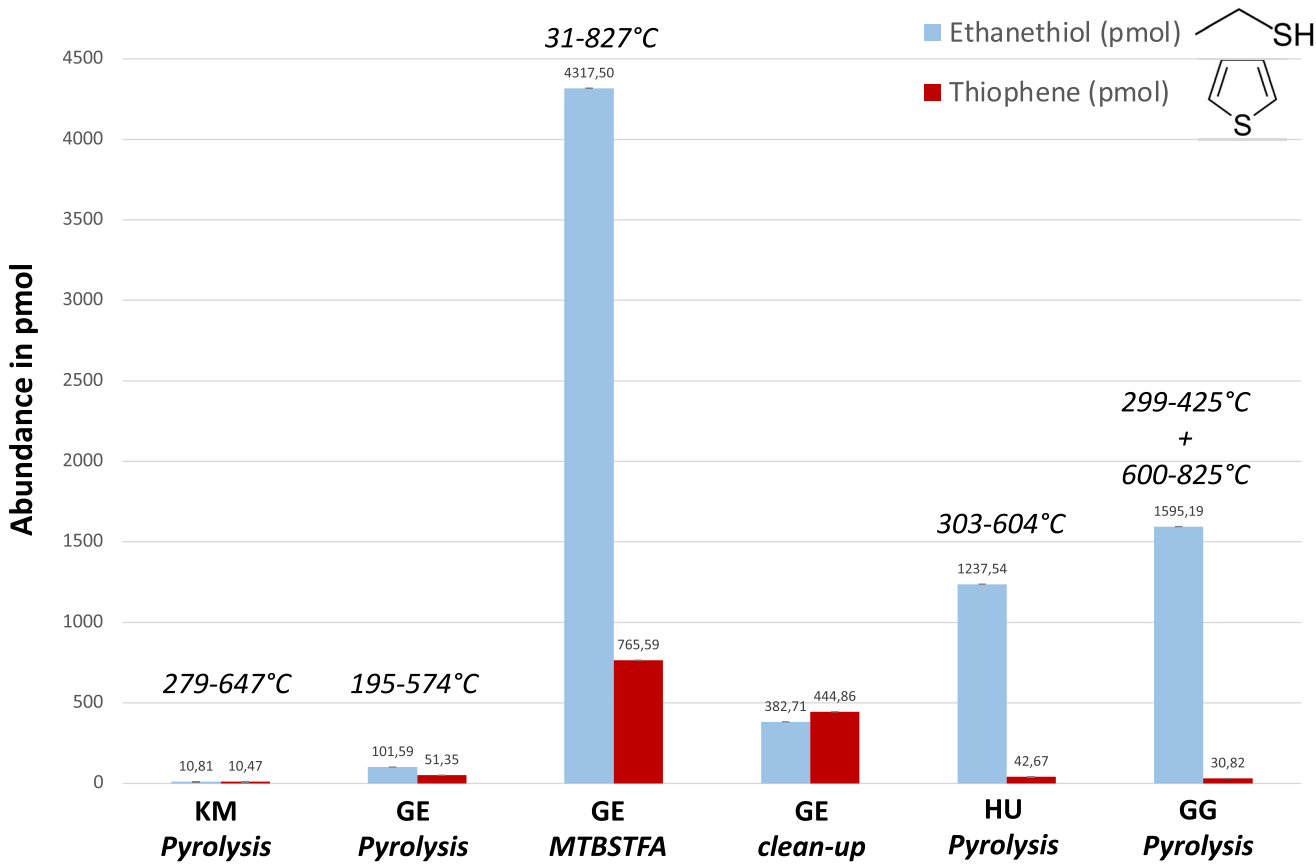


Figure 5. Abundances of the sulfur-bearing organic molecules ethanethiol and thiophene measured in the chromatograms obtained with the Chirasil-β Dex (GC4) column and extracted from the Kilmarie (KM), Glen Etive (GE) pyrolysis and MTBSTFA analyses and following clean-up, Hutton (HU) and Glasgow (GG) samples. The temperature cuts selected for GCMS analysis are represented in italic. The method used to calculate the abundances is described elsewhere (Szopa et al., 2020) and in Supporting Information S1.

for ethanethiol and thiophene, respectively (Figure 5). The clean-up analysis performed after the derivatization experiment of GE still showed elevated abundances of ethanethiol and thiophene of ~382 and ~444 pmol, respectively.

The pyrolysis GCMS analysis of GG, with its highest T cut, produced the greatest diversity of S-bearing organic molecules (Figure 6). Methylthiophene was detected in addition to ethanethiol and thiophene as well as sulfur organics that were detected for the first time with SAM including two aliphatics: propanethiol (or its isomeric equivalent methylthioethane) and 2,4-dithiapentane, and two aromatics: 1,3-dithiolane and 1,3,5-trithiane (Figure 6). 2,4-dithiapentane, has been previously suspected in the Cumberland (CB) sample (Yellowknife Bay region) analyzed early on in the mission. The clear detection of 2,4-dithiapentane in GG confirmed its previous detection in CB. 2,4-dithiapentane, 1,3-dithiolane and 1,3,5-trithiane were also detected in the pyrolysis analysis of MA with the GC1 column only since the analysis of MA led to the clog of the GC4 IT channel. The identification of these molecules was confirmed with their retention times measured in laboratory in SAM-flight conditions and by comparison of their flight mass spectra with the mass spectra from the NIST library (Figures 6 and 7). Retention time measurements in the laboratory also allowed for the identification of which dimethylsulfide/ethanethiol and propanethiol/methylthioethane isomers were most likely present. Ethanethiol and propanethiol were identified as the primary isomers, and they are designated as such in the rest of the paper.

After the detection of the new sulfur-bearing molecules in GG, a search for their major ion mass fragments was conducted in earlier analyses (KM, GE, and HU) and indicated that ethanethiol and dithiapentane were likely present but in lower abundance (~10 pmol) compared to GG. Benzothiophene, a sulfur-heterocycle, and an alkyl-thiophene were detected in the thermochemolysis analysis of MA (Figure 8). Except dithiapentane, which

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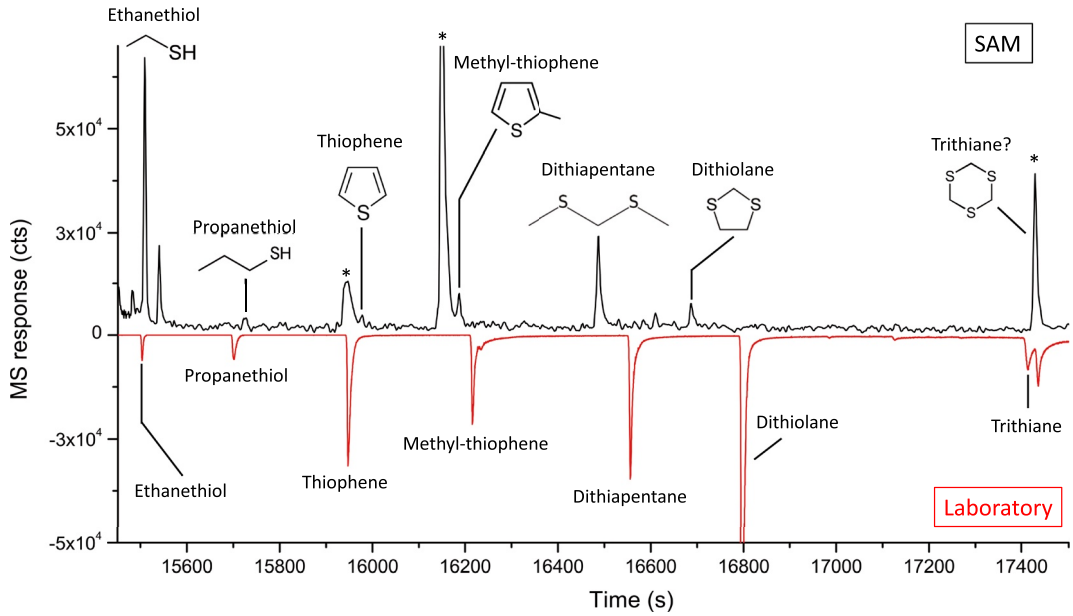


Figure 6. Sample Analysis at Mars gas chromatography mass spectrometry (SAM GCMS) identifications of the sulfur-bearing molecules detected in the Glasgow sample compared with laboratory results from a SAM-like experiment (Top) Reconstructed chromatogram from the Chirasil-β Dex (GC4) column and plotted as such: m/z 61 + m/z 84 + m/z 97 + m/z 106. (Bottom) Chromatogram from the SAM-like GC analysis performed in laboratory. 1,3,5-trithiane, detected in the chromatogram from GC1, may also be present in GC4, but co-elutions with other compounds made it difficult to confirm its identification. The differences in the retention times of some molecules may be due to minor variations between the flight and laboratory ramp temperatures, and the manufacturing process of the stationary phase of the SAM and spare columns. *Organic molecules from SAM background.

might be more ubiquitous on Mars as shown by its detection in CB, these new sulfur-bearing molecules were detected only in the samples that were analyzed using a high pyrolysis temperature (GG and MA).

3.2.3. Aromatic Compounds

Aromatic compounds, including compounds new to SAM up to two carbon rings, were detected in the analyses of the GT samples. Benzene, toluene, phenol (derivatized and underivatized), xylene, phenylethyne, styrene, and biphenyl were detected in most of the pyrolysis analyses. One xylene isomer was detected in the GG analysis. However, the largest number of aromatic compounds was observed in the analysis of the MA sample after the first TMAH experiment (Figure 7) and in higher relative abundance compared to the derivatization analysis that chronologically followed. Analysis of this complex chromatogram is ongoing and will be the subject of an upcoming manuscript. The most abundant aromatics detected so far in the thermochemolysis analysis include: methylindene, naphthalene and/or fluoronaphthalene (the internal standard contained in the MTBSTFA derivatization cups) which may be co-eluting in the chromatogram, benzoic acid methyl ester, tri-, tetra-, and pentamethylbenzene, the two methylnaphthalene isomers that were also detected in EGA and likely dihydronaphthalene and dihydromethylnaphthalene. Some of these molecules were also detected in the MTBSTFA derivatization of MA and pyrolysis analysis of GR (e.g., biphenyl, benzonitrile, fluoronaphthalene, and/or naphthalene) but were not present in NT. We also note the detection of derivatized phthalic acid in the MTBSTFA analysis of MA and in the GR and NT analyses.

3.2.4. Other Compounds

Inorganic compounds were detected in most of the pyrolysis analyses and include CO and/or N_2, CO_2, O_2, H_2O, S-bearing volatiles such as H_2S, COS, SO_2 and CS_2, and nitrogen-bearing compounds such as NO and HCN. Other compounds detected in most analyses include t-butyldimethylsilanol and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxane commonly designated mono-silylated water (MSW) and bi-silylated water (BSW), respectively, t-butyldimethylfluorosilane, *N*-methyl-2,2,2-trifluoroacetamide (TFMA), tris(trimethylsilyl)borate derivative (boric acid 3-TMS), dimethyltrifluoroacetamide, unreacted MTBSTFA and DMF (Table 3) and

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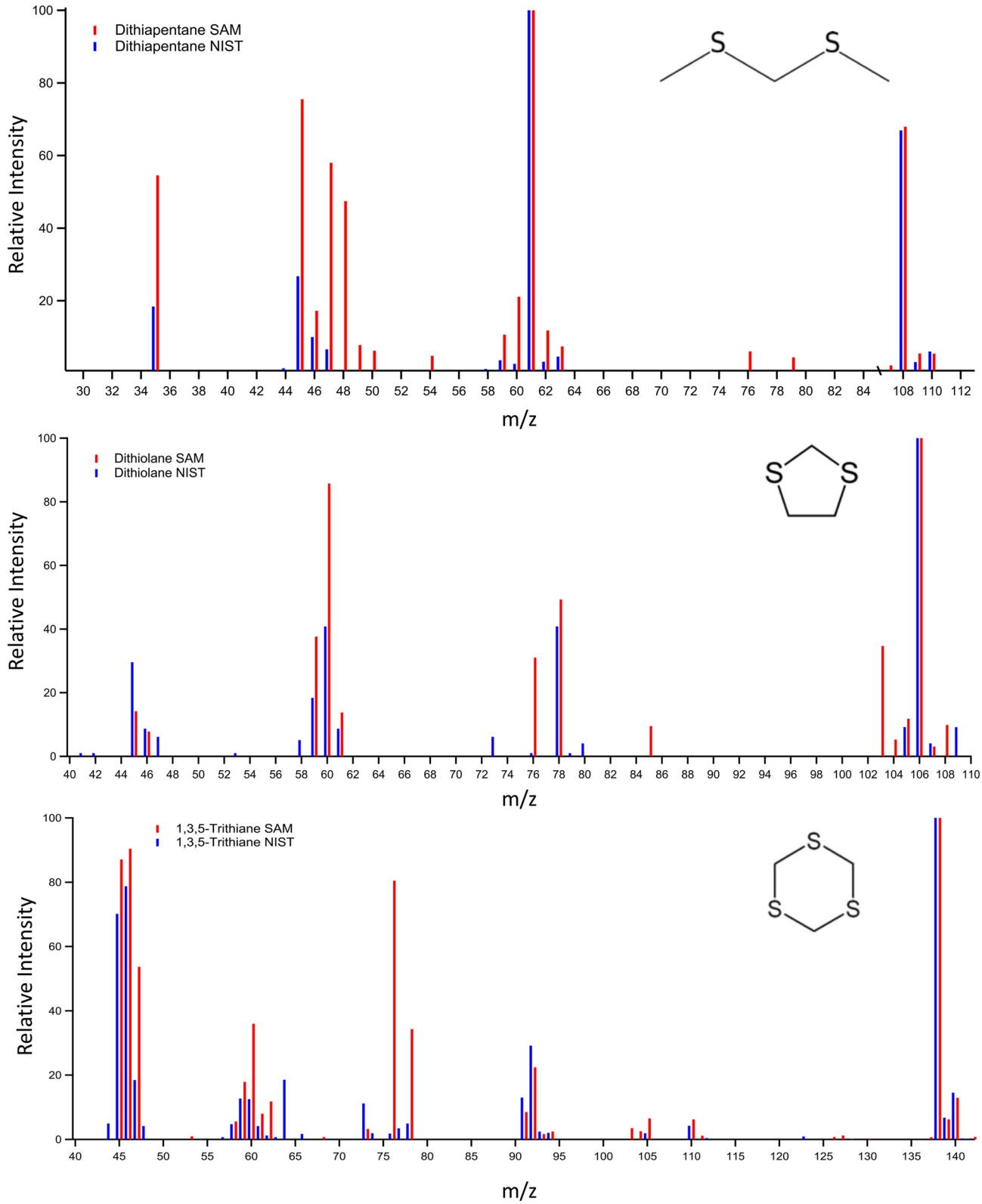


Figure 7. Flight mass spectra of the new sulfur-bearing organic molecules detected with Sample Analysis at Mars (red): 2,4-dithiapentane (top), 1,3-dithiolane (center) and 1,3,5-trithiane compared to the mass spectra extracted from the NIST Mass Spectral Database (blue). Other molecules present in the background had m/z 76 and 78 which contributed to the signal of the 1,3,5-trithiane molecule and modified the ratios.

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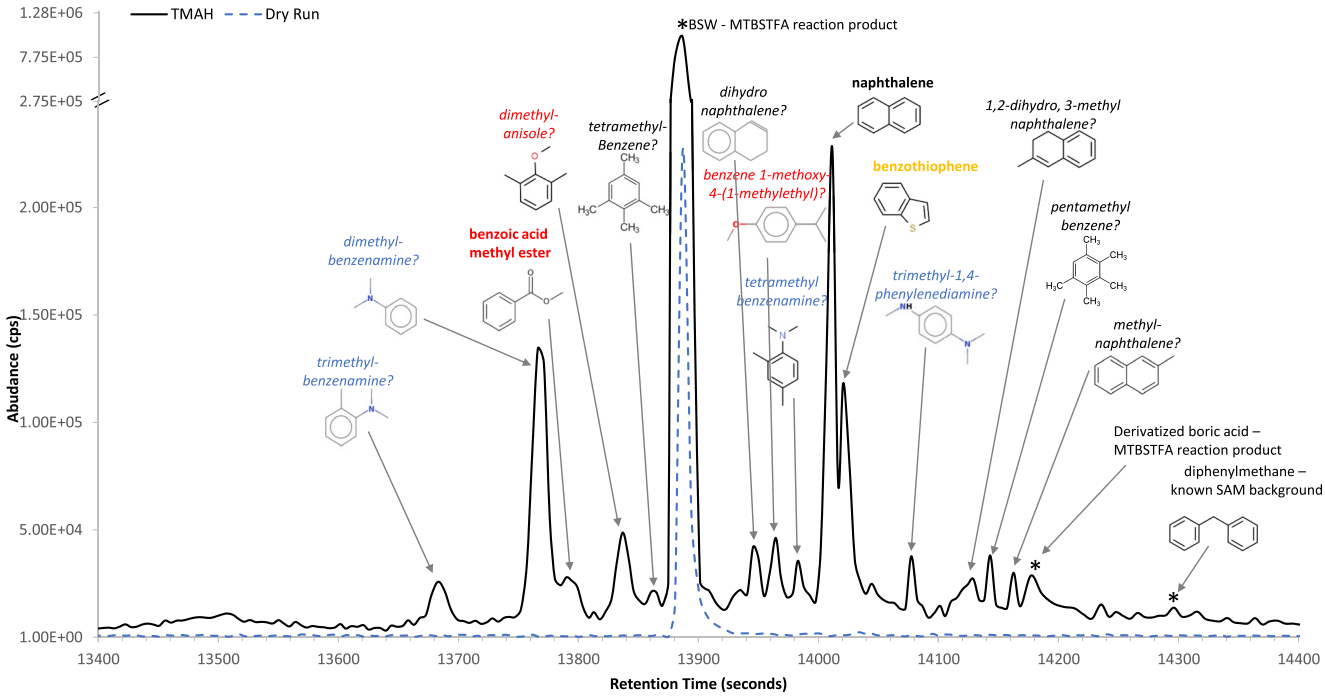


Figure 8. Reconstructed chromatogram of some of the organic molecules detected in the Mary Anning TMAH wet chemistry experiment obtained with the GC2 column and plotted as: m/z 121 + 128 + 130 + 134 + 135 + 136 + 142 + 144 +148 + 149 + 150. Sulfur-bearing, oxygen-bearing, and nitrogen-bearing are represented in yellow, red, and blue, respectively. The identification of the organics that was confirmed by retention time are represented in bold. The identification of the organics with a question mark have not yet been confirmed. *Organic molecules from Sample Analysis at Mars background.

trimethylamine (TMA). Two types of hydrocarbons were detected: the two methylpropene isomers in the pyrolysis analyses of KM and GE, one methylpropene isomer in the MTBSTFA derivatization analysis of GE and the pyrolysis analyses of HU and GG, two pentene isomers in the MTBSTFA experiment at GE, and one pentene isomer in HU and GG.

Mass spectra matching methylphosphonic anhydride t-BDMS (major ion m/z 155) and decanoic acid t-BDMS (major ions m/z 229–231 and 271) were detected in both GC1 and GC4 chromatograms extracted from the GE sample and in their highest abundance since their first detection in the opportunistic derivatization experiment (Freissinet et al., 2019). However, the tentative identifications of these compounds through laboratory experiments in SAM-like conditions failed to match the flight and laboratory retention times (Millan et al., 2021). These compounds may have also been correctly identified but their retention times shifted due to the saturation of the MTBSTFA-DMF. We note that neither amino acids nor fatty acids were detected in either the MTBSTFA or TMAH analyses.

4. Results of the Laboratory Experiments

To help interpret the SAM data, laboratory experiments were performed on synthetic Mars analogs to which selected organics were incorporated (phthalic acid and valine). The nature of the thermal decomposition product(s) obtained after pyrolysis is described below.

4.1. SAM-Like Pyrolysis of Phthalic Acid in Jarosite With Perchlorate and MTBSTFA-DMF

The chromatograms obtained after the SAM-like pyrolysis of phthalic acid in jarosite, in the presence of calcium perchlorate and in the presence of both calcium perchlorate and the MTBSTFA-DMF derivatization reagent are presented in Figure 9, in black, orange, and green respectively.

The primary compounds detected after the pyrolysis of phthalic acid in jarosite were inorganic compounds such as CO_2, SO_2, H_2O and two sulfur-aromatic compounds: S_6 and S_8. Phthalic acid was detected with its

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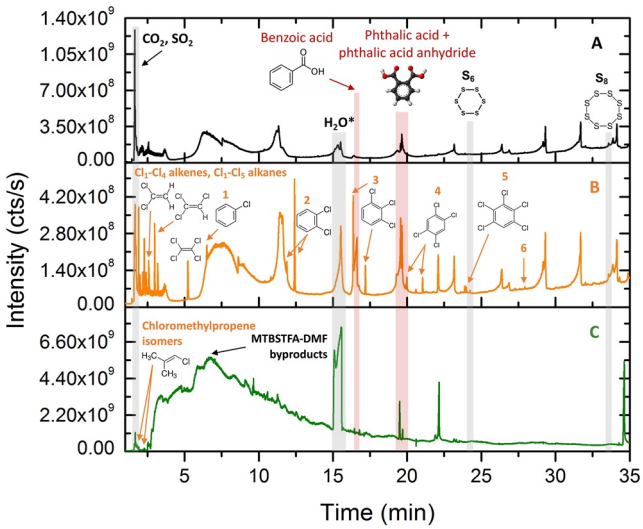


Figure 9. Gas chromatograms of the total ion current (TIC) recorded after the Sample Analysis at Mars (SAM)-like pyrolysis (40°C–850°C at a 35°C.min^{-1} rate) of phthalic acid in jarosite (a) as is, (b) with 1 wt% calcium perchlorate, and (c) with both 1 wt% calcium perchlorate and MTBSTFA-DMF in black, orange, and green respectively. *Derivatized molecules. MTBSTFA-DMF byproducts include mono- and bi-silylated water, trifluoromethylacetamide (TFMA), DMF (unreacted), and *tert*-butyldimethylfluorosilane. Cl_1-Cl_4 alkenes: chloroethene, dichloroethene, trichloroethene and tetrachloroethene, Cl_1-Cl_5 alkanes: chloromethane, dichloromethane, trichloromethane, tetrachloromethane and pentachloroethane, 1: chlorobenzene, 2: 2x dichlorobenzene isomers, 3: 2x trichlorobenzene isomers, 4: 2x tetrachlorobenzene isomers, 5: pentachlorobenzene, 6: hexachlorobenzene.

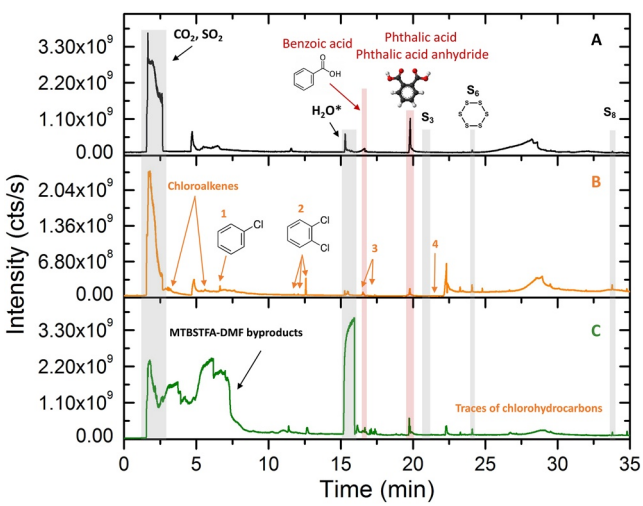


Figure 10. Gas chromatograms recorded after the flash-pyrolysis (~850°C, 1 min) of phthalic acid in jarosite (a) as is, (b) in the presence of 1 wt% calcium perchlorate, and (c) in the presence of both 1 wt% calcium perchlorate and MTBSTFA-DMF in black, orange, and green respectively. 1: chlorobenzene, 2: three dichlorobenzene isomers, 3: two trichlorobenzene isomers, 4: two tetrachlorobenzene isomers.

two main thermal decomposition products—phthalic anhydride and benzoic acid—resulting from its dehydration and decarboxylation, respectively. In the presence of calcium perchlorate, Cl_1-Cl_4 chloroalkenes, Cl_1-Cl_5 chloroalkanes, chloroacetaldehyde, Cl_1-Cl_6 aromatics (chlorobenzene to hexachlorobenzene) and Cl_1-Cl_3 chlorophenol were detected. In the presence of both calcium perchlorate and MTBSTFA-DMF, only the two chloromethylpropene isomers were detected as well as MTBSTFA-DMF byproducts. Phthalic acid, its decomposition products (phthalic anhydride and benzoic acid) and S_6 and S_8 were still present despite the presence of perchlorate and MTBSTFA-DMF reagents. To ensure that no sulfur-bearing compounds were present in all three analyses other than S_6 and S_8, we searched for the specific major ion mass fragments of the S-organics detected with SAM: thiophene, ethanethiol, propanethiol, dithiapentane, dithiolane, and trithiane, and found that none of those were present in the laboratory analyses.

4.2. Flash-Pyrolysis of Phthalic Acid in Jarosite With Perchlorate and MTBSTFA-DMF

The chromatograms obtained after the flash-pyrolysis of phthalic acid in jarosite, in the presence of calcium perchlorate only and with both calcium perchlorate and MTBSTFA-DMF are shown in Figure 10, in black, orange, and green respectively.

The main compounds detected after the flash-pyrolysis of phthalic acid in jarosite were inorganic compounds such as CO_2, SO_2, H_2O and three sulfur aromatic compounds (S_3, S_6, and S_8). S_3 was not detected after SAM-like pyrolysis. Phthalic acid and its two main thermal decomposition products—phthalic anhydride and benzoic acid—and the sulfur aromatic compounds were still detected after all three pyrolysis analyses, which is consistent SAM-like pyrolysis. However, the abundances of phthalic acid, benzoic acid, S_6 and S_8 were relatively higher compared to SAM-like pyrolysis. In the presence of perchlorate, fewer chlorohydrocarbons were detected compared to SAM-like pyrolysis including chloroalkenes and all Cl_1-Cl_4 chlorobenzenes isomers. In the presence of calcium perchlorate and MTBSTFA-DMF, wet chemistry byproducts were also detected. Once again, no sulfur-containing organic compounds were detected despite a rigorous search for the specific major ion mass fragments of the S-organics detected with SAM.

4.3. SAM-Like and Flash-Pyrolysis of Valine in Jarosite With Perchlorate and MTBSTFA-DMF

Since no major differences were observed between the SAM-like and flash-pyrolysis experiments, only the chromatograms obtained after SAM-like pyrolysis of valine in jarosite are presented in Figure 11.

The main pyrolysis products detected after pyrolysis of valine in jarosite were long-chain alkene isomers, ketones and phthalimides. The phthalimides were the only compounds detected after the pyrolysis of valine hosted in jarosite, regardless of the presence of calcium perchlorate or MTBSTFA-DMF and likely result from the thermal decomposition of valine and pyrolysis byproducts reactions (Millan et al., 2020; Moldoveanu, 2009). SO_2, S_3, S_6, and S_8 were detected in all three analyses. In the presence of perchlorates, hexathiepane (CH_2S_6) and methylphthalimide, which were not present after the pyrolysis of phthalic acid with perchlorate, were detected. A search for the major ion mass fragments of the chlorohydrocarbons detected with SAM was conducted and allowed the detection of a few chloroalkanes and chloroben-

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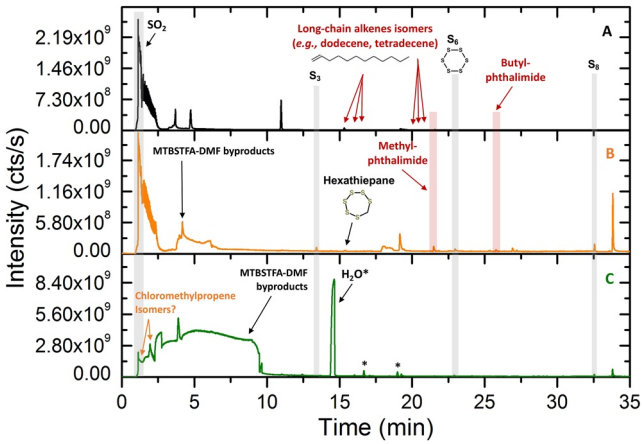


Figure 11. Gas chromatograms recorded after the Sample Analysis at Mars (SAM)-like pyrolysis (40°C–850°C at a 35°C.min^{-1} rate) of valine in jarosite (a) as is, (b) in the presence of 1 wt% calcium perchlorate and, (c) in the presence of both 1 wt% calcium perchlorate and MTBSTFA-DMF in black, orange, and green respectively. *Derivatized molecules. MTBSTFA-DMF byproducts include monosylilated water, trifluoromethylacetamide (TFMA), DMF (unreacted), *tert*-butyldimethylfluorosilane (b and c), and chloro-*tert*-butyldimethylsilane (b).

zene, but in low abundances compared to phthalic acid, which is consistent with previous studies (Millan et al., 2020; Szopa et al., 2020). In the presence of both calcium perchlorate and the MTBSTFA-DMF reagents, the two chloromethylpropene isomers that were detected after SAM-like pyrolysis of phthalic acid were detected. However, the high background induced by the amount of wet chemistry byproducts introduced in the system and released during pyrolysis prevented the clear identifications of the products present in the 0–10 min retention time range. As with phthalic acid, no sulfur-containing organic compounds were detected.

5. Discussion

5.1. Possible Origin(s) of the Organic Molecules Detected in Glen Torridon

5.1.1. Organic Molecules Likely Indigenous to the Martian Samples

5.1.1.1. S-Bearing Organic Compounds

Ethanethiol and thiophene were detected in all the GT samples analyzed by pyrolysis with GC4. The fact that they were not present in MA, GR, or NT is likely due to the difference in the columns used for these analyses: GC1 and GC2, which are not coupled to an IT and do not have the capability to retain the most volatile compounds. Less volatile sulfur-bearing compounds were detected in MA with the GC1 column and are discussed further.

Ethanethiol and thiophene were present as is in the sample or formed during pyrolysis by chemical reactions between martian organic matter and the inorganic sulfur species (e.g., SO_2, COS, CS_2, H_2S) released from the sulfur minerals (e.g., sulfates, sulfides) (Francois et al., 2016; Wong et al., 2020). Ethanethiol and thiophene were previously detected at Pahrump Hills in Gale crater, (Murray formation, sol 826) and were interpreted as being indigenous to the martian samples and fragments of refractory organic macromolecules from different possible sources: biological, geological, and/or brought by exogenous sources (Eigenbrode et al., 2018).

The low abundance of ethanethiol and thiophene in KM (~10 pmol) is consistent with the pyrolysis temperature (<650°C) which was insufficient to decompose any macromolecules presumably present in the sample. They were detected in higher abundance in GE (50–100 pmol), which was analyzed using a lower temperature cut compared to KM (Figures 2 and 5). The high abundances of MTBSTFA-DMF byproducts in GE indicate that significative amounts of wet chemistry reagents were present, and seem correlated to the high abundance of ethanethiol and thiophene. The MTBSTFA derivatization experiment performed on the GE sample tends to confirm this hypothesis since the highest abundance of ethanethiol and thiophene so far measured with SAM.

The lack of correlation between evolved reduced gases (e.g., CH_4) and BSW in most of the GT samples supports the notion that MTBSTFA has not significantly reacted with sulfates during pyrolysis to produce ethanethiol and thiophene (see details and Figure S2 in Supporting Information S1). In addition, results from the laboratory experiments indicated that despite the presence of a high amount of MTBSTFA-DMF and sulfur inorganics released from the jarosite (SO_2, S_3, S_6, and S_8) (Figures 9–11), ethanethiol and thiophene were not produced in the conditions tested for this study. Hexathiepane (CH_2S_6) was the only S-bearing organic detected and was likely formed by reactions between the S-inorganics released during pyrolysis and the valine decomposition products (Millan et al., 2020; Moldoveanu, 2009). These results indicate that phthalic acid, valine and the MTBSTFA-DMF wet chemistry reagents are unlikely the precursors of the ethanethiol or thiophene detected on Mars. At low pyrolysis temperatures (<500°C), a portion of thiophene might be produced from reaction between MTBSTFA's thermal organic fragments (e.g., methylpropene) and sulfur released from the minerals. However, the formation of thiophene at high temperature (>500°C) in the presence of MTBSTFA byproducts has not yet been demonstrated and is unlikely. This is consistent with the EGA data, which indicate that most MTBSTFA byproducts (e.g., chloromethane) were released at low temperatures, whereas the sulfur-bearing organic and inorganic compounds were released at high temperatures (Eigenbrode et al., 2018; Freissinet et al., 2015). Therefore, the EGA and laboratory results support the hypothesis that the hydrocarbon source of thiophene is not related to

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the MTBSTFA-DMF reagents. MTBSTFA-DMF may have helped in another way by (a) enhancing the extraction of these compounds, and/or (b) reacting primarily with the oxidizing species present in GE instead of the sulfur-bearing organics, and thus protected them from oxidation and degradation (Kenig et al., 2016). The correlation between the high amount of chemical reagents and the high abundances of ethanethiol and thiophene remains intriguing. Further laboratory experiments are necessary to better understand the possible relationship(s) between the wet chemistry reagents and the S-bearing organics detected on Mars. Different organic molecules, salts, and minerals than the ones presented in this study could be tested, as well as natural Mars analogs and higher amounts of reagents (see details in Supporting Information S1 in the section "Detection, abundances and origin(s) of the sulfur-bearing organics").

On Earth, thiophenes, alkyl-thiophenes and benzothiophene are part of the macromolecular component of kerogens, coal, stromatolites and microfossils (Heinz & Schulze-Makuch, 2020). Laboratory studies using pyrolysis-EGA and GCMS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) of martian and carbonaceous meteorites such as Tissint and Murchison, as well as kerogen-bearing terrestrial sediments, indicate that thiophenes are common pyrolysis fragments associated with the refractory phase of the samples (Derenne & Robert, 2010; Eigenbrode et al., 2018; Matthewman et al., 2013; Steele et al., 2018). This supports the idea that the thiophenes detected on Mars are related to the thermal decomposition of macromolecules from different possible sources:

1. Exogenous sources such as meteorites (e.g., carbonaceous chondrites) and interplanetary dust particles (IDPs) which have been constantly delivered at the surface of Mars since its formation. Non-sulfur-containing organic matter may also have been delivered to the surface of Mars and the sulfur was incorporated later on during diagenesis.
2. Abiotic syntheses. Sulfur could have been incorporated during the electrochemical reduction of CO_2 to organic material on corroding sulfide minerals (Steele et al., 2018). This mechanism is akin to that proposed for organic synthesis at deep sea hydrothermal vents on early Earth (Vladimirov et al., 2004). Another process well known on Earth is the post-diagenesis incorporation of sulfur through interaction with an oxidizing and acidic S-bearing fluid as suggested in the Pahrump Hills region of Gale crater (Rampe et al., 2017).
3. Biosynthesis. In this scenario, sulfates would transform into sulfides by bacterial sulfur reduction (e.g., jarosite to H_2S). Biological sulfur reduction has been suggested as a plausible metabolic pathway on ancient Mars and in the modern subsurface (Heinz & Schulze-Makuch, 2020; Summons et al., 2011).

Four new S-bearing organic molecules were clearly detected in addition to ethanethiol and thiophenes: propanethiol, 2,4-dithiapentane, 1,3-dithiolane, and 1,3,5-trithiane. Their detection in GG and MA at high pyrolysis temperature (>700°C) combined with their detection in these two samples specifically leans toward a martian origin of these molecules. As for the thiophenes, these molecules are likely related to the thermal decomposition of recalcitrant organic materials within the sample, and are consistent with the decomposition products of kerogens and meteorites (Steele et al., 2018). They might also have been formed during pyrolysis by chemical reaction between H_2S and aldehydes and ketones, indeed present in the GCMS data. For instance, trithiane can be produced by reaction of formaldehyde with hydrogen sulfide, dithiapentane can be formed by reaction of formaldehyde with methanethiol, and dithiolane can be formed by reaction of 1,2-ethanedithiol with ketones. To further evaluate the formation of these molecules and identify their precursors, laboratory experiments in SAM-flight conditions and using different organic molecules than those tested for this study, are required.

In summary, the S-bearing organic molecules were not detected in laboratory experiments, were exclusively present in a sub-set of Martian samples, and had variations in relative distributions dependent on the pyrolysis temperature. These lines of evidence support the idea that the S-bearing organics detected at GT are most likely indigenous to the Martian samples, whose specific lithologies and mineralogies favored organic preservation.

5.1.1.2. Chlorohydrocarbons

Chlorobenzene and chloromethylpropane (detected exclusively in GE) are not known pyrolysis products from reactions between MTBSTFA-DMF and calcium perchlorate (Glavin et al., 2013). Chlorobenzene is likely derived from reactions between oxychlorines and an organic precursor indigenous to the martian samples (e.g., benzenecarboxylates). The EGA results indicated the absence of perchlorates and chlorates salts in GE (McAdam et al., 2022). However, laboratory experiments have demonstrated that chlorides produce lower amounts of chlorobenzene compared to perchlorates/chlorates salts, which could explain its absence or lower amounts (~pmol level in the background) in the GT samples compared to Yellowknife Bay (Szopa et al., 2021). Similar

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chemical reactions may occur between martian organic matter and chlorides to produce chloromethylpropane. In addition, trichloromethylpropane has been detected in some martian mudstones (Szopa et al., 2020). Therefore, chlorobenzene and chloromethylpropane are more likely indigenous to the samples.

SAM-like laboratory experiments demonstrated that polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and phenanthrene are possible precursors of trichloromethylpropane and dichloromethylpropane, the latter of which has only been detected in laboratory experiments (Millan et al., 2020; Szopa et al., 2020). The pyrolysis of phthalic acid with calcium perchlorate led to the detection of numerous aliphatic and aromatic chlorohydrocarbons (Figure 9) and confirmed that aromatic carboxylic acids are the preferred precursors of the chlorohydrocarbons detected on Mars (Freissinet et al., 2020; Millan et al., 2020).

5.1.1.3. Aromatic Compounds

The wet chemistry analyses of MA liberated a wide range of aromatic organic molecules. The nitrogen-bearing amines—dimethyl-, trimethyl-, and tetramethyl-benzenamine—may be derived from reactions with the nitrogen from the TMAH reagent and carbon from an unknown source. The PAHs—naphthalene and/or fluoronaphthalene and the two methylnaphthalene isomers—were detected for the first time with SAM in both the EGA and GCMS data. No PAHs larger than 2 rings have been identified by SAM to date which may be related to GC analytical conditions that are not favorable for the elution of heavier aromatic compounds (Millan et al., 2016). The formation of naphthalene derivatives through reactions with the SAM chemical reagents has not been demonstrated in SAM-like laboratory experiments (Buch et al., 2019; He, Buch, Szopa, Millan, et al., 2021). Naphthalene derivatives (e.g., methylnaphthalene) and benzenamines have been found in martian meteorites where they are related to the presence of macromolecular material (McKay et al., 1996; Mojarro et al., 2021; Steele et al., 2012). These results indicate that the aromatic compounds detected with SAM are most likely derived from martian macromolecules. This is consistent with the detection of benzonitrile and sulfur-bearing organics in MA, GG and HU, which are all likely related to preserved indigenous macromolecules. Further TMAH thermochemolysis experiments and pyrolysis experiments on Murchison meteorite are ongoing, and results thus far are consistent with the variety of molecules present in Murchison meteorite when thermochemolyzed with TMAH.

5.1.2. Organic Molecules With Possible Contributions From Both SAM and Mars

Numerous nitrogen-bearing and oxygen-bearing organic molecules were detected in the GE, GG, and HU analyses.

5.1.2.1. N-Bearing Organic Compounds

Saturated and unsaturated aliphatics (C_1-C_4) included acetonitrile, methacrylonitrile, propenenitrile, propanenitrile, butenenitrile, and the benzonitrile aromatic (Figure 4). Methacrylonitrile was detected exclusively in the GE derivatization experiment whereas the other nitriles were detected in the analysis following the first full cup derivatization experiment performed on the OG sample (Millan et al., 2021). Therefore, these nitriles could be partially or fully related to the thermal and/or chemical degradation of the MTBSTFA-DMF reagents or aided by the reduced chlorine species (e.g., chlorides) present in GE, GG and HU. Laboratory experiments have been conducted to study the nature of the organics formed after the pyrolysis of the MTBSTFA and DMF reagents at different temperatures (He, Buch, Szopa, Millan, et al., 2021). These studies indicated that nitrile aromatic compounds such as benzonitriles are only produced after the flash-pyrolysis of MTBSTFA at high temperature (850°C). In addition, benzonitrile has been identified in the Martian meteorite Nakhla but its provenance as indigenous to the sample was ambiguous (Sephton et al., 2002). Therefore, a portion of the benzonitrile detected in the derivatization analysis of MA, GR and NT, may be related to the presence of Martian macromolecular material.

Propenenitrile, propanenitrile, and butenenitrile were present in the analyses of GE, HU, and GG, which all included a low T cut (<500°C). Their absence in the wet chemistry analysis where large amounts of reagents were introduced indicate that they might not be entirely related to the decomposition of SAM reagents. Laboratory studies seem to confirm this hypothesis since none of these compounds were detected during the thermal and chemical degradation of MTBSTFA-DMF in the presence or absence of perchlorate salts (He, Buch, Szopa, Millan, et al., 2021).

Part per million levels of nitrogen-bearing organics containing imino, nitrile, N-heterocycles, amide, and/or amino groups have been identified in a variety of terrestrial and Martian meteorites and could have been brought to the surface of Mars by these exogenous sources (Koike et al., 2020; Steele et al., 2018). Amino acids of

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Martian origin were detected in Martian meteorite RBT 04262, but no nucleobases or other N-heterocycles have been identified in any Martian meteorite to date (Callahan et al., 2013) on the contrary of carbonaceous chondrites (Oba et al., 2022). Nevertheless, no amino acids were detected in our wet chemistry analyses, including the 3-fluorovaline internal standard present in each derivatization cup. This is consistent with the results from the derivatization experiment performed on the OG sample but could be due to current technical SAM-flight limitations (Millan et al., 2016, 2021). N-bearing molecules could have also been formed by in situ geological processes, in the presence of nitrogen minerals such as nitrates which have been detected in Gale crater (Stern et al., 2015, 2017).

In conclusion, even if we cannot definitely rule out a contribution from the SAM reagents, some of the nitrogen-bearing molecules are likely indigenous to the sample. In this case, they would have been desorbed from the surface of the minerals during the low pyrolysis temperature step.

5.1.2.2. O-Bearing Organic Compounds

Aldehydes, were identified for the first time in GE, GG, and HU. The fact that methylpropanal was not detected in GE in addition to the potential detection of an oxygen-bearing aromatic in GG, seems to indicate that these molecules were extracted or formed during the highest temperature range of pyrolysis (>550°C). This is consistent with the CO release at high temperature observed in EGA for these three samples and suggest the presence of oxidized organics (Figure 3).

Laboratory pyrolysis studies of the thermal decomposition of amino acids have indicated the release of O-bearing and N-bearing organics such as ketones, aldehydes, nitriles, and amines. The release of methylpropanal and methylpropenal combined was for instance observed after the pyrolysis of valine, and nitriles are common pyrolysis products of small amino acids (Moldoveanu, 2009). Although these studies are insufficient to identify the parent molecules of the compounds detected with SAM, the detection of a combination of several new N- and O-bearing compounds might be related to the presence of N- and/or O-bearing organic compounds indigenous to the sample. Nevertheless, methylpropenal was detected in our laboratory experiments after the pyrolysis of pure jarosite (without organics) with calcium perchlorate and MTBSTFA-DMF. These results indicate that methylpropenal could be formed through reactions between calcium perchlorate and MTBSTFA-DMF in the presence of jarosite. Therefore, we do not exclude that the oxygen compounds are fully or partially derived from the MTBSTFA-DMF reagents, although they were not detected after pyrolysis of pure MTBSTFA-DMF, in the presence or absence of perchlorates (He, Buch, Szopa, Millan, et al., 2021).

Benzoic acid derivatives were detected in both MA wet chemistry analyses and after the first full cup derivatization experiment on Mars on the OG sample (Millan et al., 2021). Benzoic acid may be produced through the oxidation of organic molecules present in the martian regolith and/or the thermal decomposition of the Tenax® TA adsorbent present in the SAM trap(s) (Benner et al., 2000; Millan et al., 2021). Benzoic acid is one possible precursor of the chlorobenzene that has been detected on Mars in the CB sample (Freissinet et al., 2020). Although a portion of benzoic acid may still be related to the decomposition of Tenax®, its non-detection in GE, where similar analytical conditions were applied, suggests a potential martian origin. Carbon/oxygen functionality has been detected by soft transmission X-ray microscopy (STXM) and attributed to the refractory aromatic rich phases in the Tissint meteorite, indicating that carbonyl and carboxyl compounds are a component of organic material in martian materials (Steele et al., 2018).

Further laboratory experiments are required in order to discriminate the possible contributions from the SAM internal organic sources to the nitriles and oxygen-bearing organic molecules that were detected at GT. These experiments include the study of the degradation of the MTBSTFA and DMF reagents using different analytical parameters than those from previous laboratory studies (e.g., temperature of pyrolysis, amounts of reagents, use of relevant Mars mineral matrices). Evaluating the chemical and thermal degradation of complex N- and O-bearing organic molecules as well as the potential chemical interaction between organic molecules and martian salts and minerals (e.g., nitrates, oxalates) should also be considered.

5.1.3. SAM-Derived Organic Molecules

5.1.3.1. Compounds Derived From the Wet Chemistry Reagents

Acetone, acetonitrile, and alkenes (methylpropene and pentene isomers) have been detected since the beginning of the mission, in the analysis of the Rocknest sample (sol 93), as well as in SAM blanks and laboratory exper-

iments. They are then likely related to the degradation of the MTBSTFA and/or DMF wet chemistry reagents present in the SAM's SMS (Glavin et al., 2013).

The aliphatic chlorohydrocarbons were likely derived from reactions between Martian chlorides and/or HCl (detected in EGA) and organics from SAM internal sources (Freissinet et al., 2015; Glavin et al., 2013; Miller et al., 2016; Szopa et al., 2021). Laboratory experiments confirmed this hypothesis since dichloromethane and chloromethylpropene were mainly produced from chemical reactions between jarosite-organic with perchlorate and MTBSTFA-DMF (Figure 9c). It is notable that chloromethane, dichloromethane and chlorobenzene have been detected as pyrolysis products of the soils analyzed by the Viking GCMS instruments which did not contain MTBSTFA (Biemann et al., 1976, 1977; Guzman et al., 2018), and in Martian meteorites (Steele et al., 2018). Although we cannot rule out the possibility that a portion of the chloroalkanes was derived from Martian organic matter, especially in runs where chloromethylpropene (a common chlorination product of MTBSTFA) was not detected, their presence in SAM blanks and formation in SAM-like laboratory experiments makes it very difficult to firmly establish their source. Chlorohydrocarbons abundances can be found in Supporting Information S1.

Other compounds detected in most of the analyses or exclusively in wet chemistry experiments originate from side reactions with the chemical reagents or are products of the derivatization reaction: MSW and BSW, t-butyldimethylfluorosilane, TFMA, boric acid 3-TMS, dimethyltrifluoroacetamide, and unreacted MTBSTFA and DMF (Table 3) (Buch et al., 2019; He, Buch, Szopa, Millan, et al., 2021). Derivatized isocyanate, isocyanomethane, methacrylonitrile, propenenitrile, and TMA are also known breakdown products of MTBSTFA-DMF and TMAH (Buch et al., 2019; He, Buch, Szopa, Millan, et al., 2021). The detection of TMA alongside with a newly elevated background after the TMAH analysis, indicate that the TMAH cup was properly punctured and that the thermochemolysis analysis was successful (Williams et al., 2020, 2021).

5.1.3.2. Compounds Derived From the Trap(s)

Aromatic organic molecules included benzene, toluene, styrene, xylene phenol (derivatized and underivatized), phenylethyne, diphenylmethane and biphenyl and are all known degradation products of the adsorbents used in the SAM hydrocarbon and ITs (Buch et al., 2019; Miller et al., 2015). We note that benzene, toluene, phenol, and a C_2-alkylbenzenes have been identified in the Nakhla martian meteorite (Sephton et al., 2002) and two- to six-ringed PAHs were detected in ALH 84001 and several other martian meteorites (McKay et al., 1996; Steele et al., 2012). However, because these molecules are systematically released by the SAM trap(s) in all of the analyses regardless of the pyrolysis temperature and in similar abundances, including in martian and laboratory blanks, we cannot attribute them to a potential indigenous origin.

5.2. Preservation of Organic Molecules in Glen Torridon

5.2.1. Lithologies of the Samples

The organic molecules indigenous to the GT samples, specifically the sulfur-bearing molecules and the aromatics (e.g., methylnaphthalene, benzothiophene, benzonitrile) are consistent with the presence of macromolecular material such as those found in martian meteorites and terrestrial kerogens (McKay et al., 1996; Mojarro et al., 2021; Steele et al., 2012). These molecules were primarily found in the samples from the Carolyn Shoemaker formation, and specifically in MA, GG and HU, where the lithology is composed of thinly laminated mudstones (GG and HU), or cross-stratified sandstone (MA) (Figure 1c). The higher abundance of sulfur-bearing organic compounds in GG and HU compared to the other samples suggests that these specific lithologies may have played a role in the preservation of the organic molecules. These results are consistent with previous organic detections in Gale crater, and confirmed that mudstones are a favorable preservation environment (Eigenbrode et al., 2018; Freissinet et al., 2015).

A lack of organic molecules was clearly observed in the KM, GR, and NT samples. The nature of the few organics that were detected in KM (e.g., chloromethane) is consistent with an origin primarily from the thermal decomposition of the MTBSTFA-DMF wet chemistry reagents and chemical reactions with chlorides (Glavin et al., 2013). The lack of organics in KM, including compounds that are usually present in the background (e.g., chlorobenzene), may be related to characteristics of the KM rocks that derive from their proximity to the diagenetically altered VRR. Indeed, it is possible that diagenesis may have been facilitated in this region, resulting in fewer chlorides and a lack of clear native reduced organics detected in pyrolysis-GCMS experiments. The lack of organics in GR and NT could be explained by technical biases, as explained below.

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The sedimentary rocks of GT have experienced a complex authigenic/diagenetic history involving fluids with varying pH and redox composition (McAdam et al., 2022). Diagenetic fluid chemistry could have influenced the change in sulfur mineralogy from KM and the GE/MA drill samples up-section to the Glasgow member, which includes the GG and HU samples.

5.2.2. Source(s) of the Martian Organic Molecules

Laboratory experiments have shown that some of the organic compounds detected by SAM in Gale crater rocks could be produced within the instrument's ovens during pyrolysis. Chemical reactions such as combustion, decarboxylation, aromatization, chlorination, and sulphurization may occur between organic molecules indigenous to the sample and the inorganic volatile compounds released from minerals undergoing thermal decomposition, or by the heat itself. The inorganic compounds detected in SAM include O_2, chlorine species such as HCl and Cl_2, and sulfur-bearing species such as SO_2, COS, H_2S and CS_2 (Archer Jr et al., 2015; McAdam et al., 2020; Sutter et al., 2017). The minerals detected on Mars that provide these compounds include perchlorates, chlorates, chlorides, sulfides, or sulfates. These salts and their thermal breakdown products can induce the formation of chlorine- and sulfur-containing aliphatic and aromatic molecules including the chlorohydrocarbons and sulfur-bearing compounds that were detected in GT and previous samples collected in Gale crater (Eigenbrode et al., 2018; Freissinet et al., 2020; Millan et al., 2020; Szopa et al., 2020).

Constraining the source(s) of the Martian macromolecules (exogenous vs. endogenous) is challenging using SAM measurements because of the similarities between the pyrolysis products derived from carbonaceous meteorites (e.g., Murchison) and terrestrial kerogens (Matthewman et al., 2013). The lack of certain organic molecules in meteorites, such as the aliphatic O- and N-bearing organics detected in the GT samples, prohibits their exclusive attribution to Martian endogenous sources or constrain their processes of formation. In addition, the composition of ancient organic matter is likely to change over time through radiation and oxidizing processes, and would confer a composition unique to Mars which could explain the differences observed between the nature of the organics on Mars and those present in carbonaceous chondrites and terrestrial kerogens (Pavlov et al., 2012, 2014).

5.2.3. Preservation Mechanisms of Organics in Clay and Sulfate Minerals

The greatest diversity of martian organic molecules was found in GG, which is among the samples with the highest proportion of clay and calcium sulfate minerals combined (24 wt% and 6 wt%, respectively) (Table 1). Phyllosilicate clay minerals are known to help preserve organic molecules, especially in redox-active Fe and Mn environments such as GT (Gasda et al., 2022). The spectral signatures of the phyllosilicates from GT indicated that they were dominantly iron-rich dioctahedral smectites consistent with nontronite present within mudstone deposits (He et al., 2022). A mixed-layer phyllosilicate phase consistent with talc/minnesotaite and serpentine or greenalite (Bristow et al., 2021; Dehouck et al., 2022; Thorpe et al., 2022) was also detected in several of the GT samples analyzed by *Curiosity*. These results are consistent with more open-system hydrologic environments in the depositional/diagenetic environment, and/or sediment source region, compared to the depositional environments recorded in the several smectite-bearing rocks analyzed earlier in the mission (Bennett et al., 2022).

Smectites are the phyllosilicates with the highest surface area and cation exchange capacity. Terrestrial studies indicated that several parameters can play a role in the preservation of organic molecules in phyllosilicates through long geological time scales (Broz, 2020 and references therein): (a) interlayer spaces provide a physical protection for the organics, (b) their charged surface area easily sorbs and retains organic molecules, (c) they are more resistant to desorption compared to other minerals and thus hinder the organics and clays to be separated, (d) the sorption of organics, facilitated by the binding between the smectite interlayers, acts as a retention mechanism that can protect the organics from degradation by the harsh martian conditions such as oxidation and radiation, (e) other parameters such as crystal edges and chemically reducing microenvironments have been suggested and can also "protect" the organics from degradation. The abundance of clays, the composition and abundance of amorphous materials, redox-state of the soil, and sulphurization, discussed in details below, are other factors that can influence organic preservation (Broz, 2020).

Curiosity reached the clay-sulfate transition in 2021 after exploration of GT, and is heading toward the Layered Sulfate-bearing unit (LSu). The exploration of the LSu, the most recently targeted region of Gale crater by MSL, will help us understand potential major changes in Mars' geology, climate history and habitability. Orbital mapping of the LSu indicated the presence of hydrated sulfate minerals, interfingering with the clays (Sheppard et al., 2021). XRD and SAM EGA analyses from *Curiosity* confirmed that clays are disappearing and that the sulfates are

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mostly rich in Mg (Clark et al., 2022; Rampe et al., 2022). The organic molecules detected in GT indicated that salts are still influencing the organic preservation and transforming organics into secondary products (e.g., chloroalkanes). Discriminating the precursors of these organics, and subsequently, their source(s) remains challenging in rocks and soil containing high amounts of salts such as GT. In addition, laboratory studies have shown that iron oxide minerals such as magnetite and hematite, which are widespread on Mars, may induce catalytic effects and favor chemical reactions with these salts. However, sulfate minerals such as kieserite can shelter organic molecules from deleterious reactions and facilitate the identification of their precursors (Francois et al., 2016). Future SAM analyses on samples that will be collected in the LSu will thus be key to further understanding organic preservation on Mars, and specifically whether organics can be incorporated within the sulfate minerals and protected from chemical interaction with salts and oxidants. Sulphurization has been proposed in the past as a preferred mechanism that has aided the preservation of organic molecules in the sedimentary rocks of Gale crater (Eigenbrode et al., 2018). The high diversity and abundance of sulfur-bearing organics in GT confirms that sulfur may enhance organic preservation and shelter them from degradation by diagenesis, oxidation, and radiation.

These new SAM results confirm that both Martian phyllosilicate and sulfate minerals can preserve organic molecules, which is consistent with laboratory analyses of terrestrial samples (Johnson et al., 2020; Millan et al., 2018; Williams et al., 2019).

5.2.4. SAM Technical Biases and Limits of Sample Comparisons

The lack of sulfur-bearing molecules in GR and NT, which were analyzed using a high temperature cut, is likely due to experimental factors, rather than their mineralogy. Some of the organic compounds may have been masked because of (a) the higher wet chemistry background due to the preceding MTBSTFA and TMAH wet chemistry experiments that may have covered up the signal from compounds in lower abundance, or (b) the range of organics detectable with dual-column analysis without an IT (GC1 and GC2). Without the use of an IT, some of the most volatile sulfur compounds such as dithiolane or trithiane may have eluted prior to GCMS analysis. We also note that none of the S-bearing inorganic compounds detected in our laboratory experiments and released from the jarosite (S_3, S_6, or S_8) were detected in Gale crater. A possible explanation is that they eluted beyond the time limit of the SAM analysis due to the thermal constraints of the chromatographic columns (Millan et al., 2016).

6. Conclusion

In search of evidence of preserved ancient organic molecules, the *Curiosity* rover explored the clay-rich GT region of Gale crater from 2019 to 2021 (sols 2300 to 3067 of the mission) with the SAM instrument suite. SAM conducted a total of seven pyrolysis-GCMS experiments in GT on seven samples (KM, GE, GG, HU, MA, GR, and NT), including three wet chemistry experiments (optimized MTBSTFA-derivatization on the GE and MA samples and the first TMAH thermochemolysis experiment at MA). The SAM pyrolysis and wet chemistry experiments (derivatization and thermochemolysis) revealed the greatest diversity and abundance of sulfur-organic molecules and aromatic compounds yet discovered on Mars. Other organic molecules included nitrogen-containing, oxygen-containing, and chlorine-containing molecules.

Pathways of formation of sulfur-bearing organic compounds, chlorohydrocarbons, and aromatics were investigated through SAM-like laboratory experiments to understand their most likely origin(s). Laboratory experiments included the study of the reactivity of oxychlorine and sulfates minerals with organic molecules and the MTBSTFA-DMF wet chemistry reagents. These experiments so far have not only illuminated the nature of the sulfur-bearing molecules and chlorohydrocarbons and that can be formed in SAM-flight conditions in analog environments, but they also helped us constrain the parameters for future laboratory experiments. While some molecules may indeed be sourced from the SAM wet chemistry reagents and components (e.g., traps, columns), the sulfur-bearing organics from the MA, GG, and HU samples, are likely indigenous to Mars, as they were extracted at high temperature (≥600°C), and do not seem to be formed through reactions between species released from sulfur-minerals and the SAM chemical reagents.

Based on the first nominal derivatization experiment performed on the OG sample from the Bagnold Dune sands on Mars, we were able to optimize the analytical parameters and reduce the saturation of wet chemistry reagents, which helped the detection and identification of the organic molecules in the wet chemistry analyses. No amino acids or fatty acids were identified in any of the wet chemistry experiments. However, the derivatization and first thermochemolysis experiment performed on MA liberated a wide range of aromatic organic molecules including methyl-

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ated PAHs (methylnaphthalene), a potential methylated ester carboxylic acid (benzoic acid) and benzothiophene, all detected for the first time on Mars, and which may also be indigenous to the sample. Both the sulfur-bearing organic and aromatic compounds are consistent with the presence of recalcitrant macromolecular materials within the sample, where preservation was likely enhanced by the presence of clay and sulfate minerals. Another hypothesis is that some organic fragments were structurally modified upon thermal release in the oven and formed by reactions between indigenous organic molecules and the S-inorganic compounds released during pyrolysis.

These new SAM results indicate that GT is the most (sulfur-)chemically diverse region of Gale crater that has been explored by *Curiosity* so far and that organic molecules could be widespread and well preserved within 3.5-billion-year-old martian sedimentary rocks containing a significant portion of clay minerals and sulfates. However, their origin—either meteoritic, abiotic, or biotic—has yet to be established.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data from the SAM experiments used in this study are available in the Planetary Data System (Mahaffy, 2013). Data from the laboratory experiments are publicly available in the Mendeley repository (Millan, 2022).

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