

1 *Analysis of organic molecules extracted from Mars analogues and influence of their*  
2 *mineralogy using N-methyl-N-(tert-butyldimethylsilyl)trifluoroacetamide derivatization*  
3 *coupled with gas chromatography mass spectrometry in preparation for the Sample Analysis*  
4 *at Mars derivatization experiment on the Mars Science Laboratory mission*

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16  
17 **Abstract**

18 The search for complex organic molecules on Mars, including important biomolecules  
19 such as amino acids and carboxylic acids will require a chemical extraction and derivatization  
20 step to transform these organic compounds into species that are sufficiently volatile to be  
21 detected by gas chromatography mass spectrometry (GCMS). We have developed a one-pot  
22 extraction and chemical derivatization protocol using N-methyl-N-(tert-  
23 butyldimethylsilyl)trifluoroacetamide (MTBSTFA) and dimethylformamide (DMF) for the  
24 Sample Analysis at Mars (SAM) experiment on the Mars Science Laboratory (MSL). The  
25 temperature and duration of the derivatization reaction, pre-concentration of chemical  
26 derivatives, and gas chromatographic separation parameters have been optimized under SAM  
27 instrument design constraints. MTBSTFA/DMF extraction and derivatization at 300°C for  
28 several minutes of a variety of terrestrial Mars analogue materials facilitated the detection of  
29 amino acids and carboxylic acids in a surface soil sample collected from the Atacama Desert and  
30 a carbonate-rich stromatolite sample from Svalbard. However, the rapid reaction of MTBSTFA  
31 with water in several analogue materials that contained high abundances of hydrated minerals  
32 and the possible deactivation of derivatized compounds by iron oxides, as detected by XRD/XRF  
33 using the CheMin field unit Terra, proved to be highly problematic for the direct extraction of

1 organics using MTBSTFA. The combination of pyrolysis and two different chemical  
2 derivatization methods employed by SAM should enable a wide range of organic compounds to  
3 be detected by GCMS if present on Mars.

4

## 5 **1. Introduction**

6 Mars remains a key target of astrobiological interest since its past environmental  
7 conditions are thought to have been more favorable for the emergence of life. Since 2004,  
8 several missions to Mars, including the Mars Exploration Rovers Spirit and Opportunity, the  
9 Mars Express probe, the Mars Reconnaissance Orbiter, and the Phoenix lander, have provided  
10 mineralogical data that indicate a past sustained presence of liquid water on Mars, probably  
11 during the first 500 million years of the planet's history (Squyres et al., 2004, Bibring et al.,  
12 2006). During this period, Mars was bombarded by asteroids, comets, and their fragments  
13 (Cottin et al., 1999, Botta and Bada, 2002, Pizzarello et al., 2006), which would have delivered  
14 organic matter, including compounds potentially useful for the emergence of a prebiotic  
15 chemistry or even the origin of martian life to the surface of the planet (Chyba and Sagan, 1992).

16 Even if life never arose on Mars or became extinct, the cooling of Mars and the lack of  
17 extensive plate tectonic recycling may have enabled the preservation of molecular evidence of  
18 prebiotic and/or biotic activity in ancient sediments (Morrison, 2001). Future *in situ* exploration  
19 of the Mars surface will include specific experiments to detect organic molecules that may  
20 represent chemical fingerprints of a prebiotic chemistry or biological activity, past or present.  
21 While the detection of trace concentrations of the only organic compound, methane, is debated in  
22 the martian atmosphere from both orbital and Earth based observations (Formisano et al., 2004,  
23 Krasnopolsky et al., 2004, Mumma et al., 2009), more complex nonvolatile organic compounds  
24 trapped in the regolith, such as carboxylic acids or amino acids, cannot be detected remotely and  
25 will require direct *in situ* measurements of the regolith at the surface.

26 To date, the only *in situ* experiment devoted to the search for complex organic  
27 compounds in the martian regolith was the Gas Chromatograph-Mass Spectrometer (GCMS)  
28 experiments of the Viking missions in 1976. In these experiments, several surface samples,  
29 collected down to approximately 10 cm depth, were heated to temperatures of up to 500°C, and  
30 the gases released were analyzed directly by GCMS. No organic molecules of martian origin  
31 were detected at the two different landing sites within the detection limits of the instruments

1 (Biemann et al., 1976, Biemann et al., 1977). Although, the Viking GCMS instruments did detect  
2 chloromethane and dichloromethane at part-per-billion (ppb) levels at both landing sites in the  
3 surface regolith samples, it was argued that these chlorohydrocarbons were derived from  
4 cleaning solvents used on the instrument hardware (Biemann et al., 1977). Several explanations  
5 for the lack of organics in surface materials on Mars have been proposed including the  
6 destruction of hydrocarbons by UV and ionizing radiation (Oro and Holzer, 1979, Stoker and  
7 Bullock, 1997, Ten Kate et al., 2005, Dartnell et al., 2007, Stalport et al., 2008, Stalport et al.,  
8 2009, Stalport et al., 2010) and/or other oxidation processes (Chun et al., 1978, Pang et al., 1982,  
9 Yen et al., 2000, Clancy et al., 2004, Encrenaz et al., 2004). Recent *in situ* data obtained from the  
10 Northern polar region of Mars by the *Phoenix* mission showing high concentrations of  
11 magnesium perchlorate (Hecht et al., 2009), and laboratory thermal volatilization GCMS  
12 measurements of Atacama Desert soils containing perchlorate suggest that a significant amount  
13 of organic carbon in the martian regolith (up to part-per-million levels) may have been converted  
14 to chlorohydrocarbons during high temperature pyrolysis (up to 500°C) due to the possible  
15 presence of perchlorates in the soils analyzed by *Viking* (Navarro-González et al., 2010). It is  
16 also been suggested that significant amounts of non-volatile products such as amino acids and  
17 carboxylic acids, would not have been extracted by the Viking pyrolysis procedure or would  
18 have been destroyed prior to GCMS detection (Glavin et al., 2001, Benner et al., 2000).  
19 Therefore, future GCMS analyses of complex organic compounds on Mars may require lower  
20 temperature extraction protocols, such as chemical derivatization, that can transform less volatile  
21 and less thermally stable organic compounds into molecules that can be readily detected  
22 (Meunier et al., 2007, Buch et al., 2009).

23 NASA and ESA are planning a series of new robotic missions to Mars and other  
24 destinations that will incorporate *in situ* wet chemistry experiments. Chemical derivatization  
25 using dimethylformamide-dimethylacetal (DMF-DMA) has already been incorporated into the  
26 Cometary Sampling and Composition (COSAC) evolved gas experiment on ESA's Rosetta  
27 Lander and will provide amino acid detection and enantiomeric measurements on the surface of  
28 comet 67P/Churyumov-Gerasimenko in 2014 (Meierhenrich et al., 2001, Szopa et al., 2003,  
29 Goesmann et al., 2007). The use of multiple chemical derivatization agents including MTBSTFA  
30 and DMF/DMA are also under consideration for inclusion in the Mars Organic Molecule  
31 Analyzer (MOMA) instrument on the 2018 ExoMars rover mission (Buch et al., 2009). The

1 NASA Mars Science Laboratory (MSL) mission, which is scheduled to land on Mars in early  
2 August 2012, is carrying the Sample Analysis at Mars (SAM) instrument suite designed to detect  
3 a wide range of chemical biosignatures, organic and inorganic, that could provide evidence of a  
4 habitable environment and possibly signs of life (Cabane et al., 2004, Mahaffy et al., 2010).  
5 The SAM instrument suite includes a gas chromatograph quadrupole mass spectrometer (GCMS)  
6 that will enable the separation and direct analysis of volatile species in the atmosphere and  
7 released from solid samples heated up to 1000°C. In addition, SAM will employ a lower  
8 temperature ( $\leq 300^\circ\text{C}$ ) chemical extraction and derivatization step using sealed metal cups filled  
9 with a mixture of MTBSTFA and DMF that will target less volatile and less-thermally stable  
10 organic compounds such as amino acids and carboxylic acids that cannot be readily extracted  
11 and detected by high temperature pyrolysis and GCMS analysis alone.

12 MTBSTFA was originally selected as a derivatizing agent for the SAM wet chemistry  
13 experiment since the reaction can occur in a single step (Knapp, 1979), MTBSTFA is less  
14 susceptible to hydrolysis compared to other reagents, and it does not require separation of the  
15 derivatives prior to GC analysis. In addition, MTBSTFA will rapidly react with a wide range of  
16 organic compounds with acidic hydrogen atoms including amino acids, carboxylic acids,  
17 nucleobases, primary and secondary amines, alcohols, and amides (Buch et al. 2006).  
18 Furthermore, the derivatization yields for pure amino acid and carboxylic acid standards are high  
19 and typically in the range of 90-100% (Rodier et al. 2001). SAM also has the ability to extract  
20 and detect higher molecular weight organic matter, including fatty acids, by thermochemolysis at  
21 temperatures  $>340^\circ\text{C}$  using tetramethylammonium hydroxide (TMAH). Thermochemolysis was  
22 not investigated in this study, but TMAH protocols and experiments have been tested previously  
23 using Mars analogue materials from the Atacama Desert (Geffroy-Rodier et al., 2009).

24 Here we report the first GCMS results of amino and carboxylic acids that were extracted  
25 from a suite of terrestrial Mars analogue materials using a derivatization test-bed that  
26 approximates the front end extraction capabilities of the SAM flight instrument. MTBSTFA  
27 derivatization experiments were not run using the actual SAM flight instrument to avoid  
28 contamination of the flight instrument by the analogue materials and derivatization agents  
29 themselves. The primary goal of this study was to understand the influence of minerals on the  
30 efficiency of MTBSTFA derivatization of amino and carboxylic acids using the SAM one-pot  
31 extraction approach. Since SAM flight hardware components were not available for this study,

1 we did not focus on optimization of the derivatization process that will be used on Mars by SAM  
2 which will be done on the SAM testbed instrument when it becomes available. The experimental  
3 results described here will be used to guide SAM testbed derivatization operations, help  
4 formulate a sample selection strategy for the SAM derivatization experiment on Mars, and  
5 enable a more accurate interpretation of the *in situ* derivatization GCMS results obtained by  
6 SAM.

## 8 **2. Experimental**

### 9 **2.1 Analogue Samples and Preparation**

10 Five terrestrial Mars analogue samples, one meteoritic sample and one procedural blank  
11 were selected for this study and represent a diverse set of the types of samples that could be  
12 encountered on Mars (Table 1). Understanding the potential interferences of different analogue  
13 materials on the extraction of organics will permit more accurate interpretations of *in situ*  
14 derivatization data obtained by SAM on Mars.

15 Two soil samples were collected in 2006 from Site #3 (27°20.2'S, 70°42.4'W) in the  
16 Atacama Desert in Chile using a sterile metal scoop (personal communication, K. Snook). The  
17 surface sample collected at 0-1 cm depth (hereafter, Atacama-01) and a subsurface sample  
18 collected from ~10 cm depth (hereafter, Atacama-02) were stored in solvent cleaned Teflon  
19 capped glass vials. Although the Atacama Desert region has been characterized as a reasonable  
20 Mars analogue due to the extremely dry climate, oxidizing environment, and soil mineralogy  
21 (Navarro-Gonzalez et al., 2006), it should be noted that samples analyzed in this study from Site  
22 #3 were collected from a coastal region of the Atacama where fog events are much more  
23 common than in the more arid core of the Atacama Desert.

24 We also analyzed a sample of precipitated sediment collected in 2003 from the Rio Tinto  
25 "Headwaters Spring A" collection site (hereafter, RioTinto-01). The Rio Tinto sample was  
26 collected with stainless steel tongs and stored in a Whirl-Pak polyethylene bag (personal  
27 communication, Mary Sue-Bell). Rio Tinto is a highly acidic environment and is another  
28 plausible terrestrial Mars analogue because of the presence of jarosite and other sulphate  
29 minerals similar to those that have been identified on Mars by the Mars Exploration Rover  
30 Opportunity at Meridiani, Planum (Fernández-Remolar et al., 2005, Squyres et al., 2004).

1 A Mars regolith simulant used in this study, called JSC Mars-1, is a palagonitic tephra  
2 (glassy volcanic ash) collected from the Pu'u Nene Cinder Cone on the island of Hawaii (Allen  
3 et al., 1998). JSC Mars-1 is a close spectral analog to the bright regions of Mars (Morris et al.,  
4 1993), and has a chemical composition that is similar to the soils analyzed by Viking (Clark et  
5 al., 1982).

6 A carbonate-rich stromatolite collected during the 2005 ASTEP Mars Analogue Svalbard  
7 Expedition (AMASE) was also included in this study (hereafter, Carbonate-01). Carbonate  
8 minerals have been observed from orbit in the Nilli Fossae region on Mars (Ehlmann et al.,  
9 2008) and calcium carbonate has recently been identified in the polar regolith by the Phoenix  
10 mission (Boynton et al., 2009).

11 Although not a terrestrial sample, a fragment of the CM2 carbonaceous meteorite  
12 Murchison (USNM 6650.2; hereafter Murchison) was also selected for this study as an analogue  
13 since it contains a wide variety of soluble organic molecules including amino acids and  
14 carboxylic acids of abiotic origin (Cronin et al., 1993), and it has been estimated that material  
15 from carbonaceous meteoritic infall could account for between 2 and 29% of the total mass of  
16 the martian surface regolith (Flynn and McKay, 1990).

17 As a control, a fused silica quartz glass powder (FS 120, < 150  $\mu\text{m}$  size fraction, Reade  
18 Advanced Materials) that had been heated to 900°C for 7 hours in air to remove organic  
19 contamination was processed in parallel with the analogue samples (hereafter Quartz-01). A  
20 similar fused silica material, called the Organic Check Material (OCM), will be carried on board  
21 the 2011 MSL rover and used as an end-to-end procedural blank to monitor organic  
22 contamination from the sample handling system.

23 All of the glassware and tools used to prepare the analogue and blank samples were  
24 pyrolyzed at 500°C in air overnight. The samples (~ 5-10 g each) were crushed and using a  
25 ceramic mortar and pestle inside a Class 100 High Efficiency Particulate Air (HEPA) laminar  
26 flow hood and the resulting sample powders then passed through a 150  $\mu\text{m}$  stainless steel sieve  
27 and homogenized by mixing. The same sample size fraction (< 150  $\mu\text{m}$ ) will be delivered by the  
28 MSL Sample Acquisition/Sample Processing and Handling (SA/SPaH) directly to the SAM  
29 instrument via solid sample inlet funnels on the top of the rover deck. All of the sample  
30 powders were stored inside clean Teflon capped glass vials. For this study, aliquots of each  
31 powdered sample were carried through a SAM-like derivatization and GCMS analysis to

1 measure the distribution and abundance of amino and carboxylic acids, as well as other  
2 compounds that react with MTBSTFA.

## 4 2.2 Chemicals

5 A concentrated stock solution ( $1 \times 10^{-3}$  M) of 3-fluoro-DL-valine (Fluka, >99% purity,  
6 hereafter, 3-FV) was prepared by mixing the amino acid standard in Millipore water (18.2 M $\Omega$ , <  
7 5 ppb total organic carbon). 3-FV is used as an internal standard for the SAM derivatization  
8 experiment since this synthetic fluorinated amino acid is unlikely to be found on Mars and will  
9 not interfere with the detection of any indigenous valine, if present. The derivatization chemical  
10 used in this study was *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA,  
11 Sigma-Aldrich, 97% purity), a silylating agent that rapidly reacts with amines, carboxylic acids,  
12 alcohols, amino acids, sugars, and nucleobases at moderate temperatures (Fig. 1).  
13 Dimethylformamide (Pierce, > 99% purity, hereafter, DMF) does not react with MTBSTFA and  
14 was used only as a solvent to assist with the extraction of organic compounds from the samples.  
15 Pyrene (C<sub>16</sub>H<sub>10</sub>), a polycyclic aromatic hydrocarbon (Sigma-Aldrich, 100 ng/L in cyclohexane, >  
16 99% purity), also does not react with MTBSTFA, and was used as an internal standard for *in situ*  
17 verification of the SAM derivatization experiment and to determine the relative abundance of  
18 any derivatized compounds, if present.

## 20 2.3 SAM Derivatization Experiment

21 A schematic illustrating the SAM derivatization procedure for Mars is shown in Fig. 2.  
22 The SAM instrument contains 74 cups located in two concentric rings inside the Sample  
23 Manipulation System (SMS) carousel, nine of which contain solvents needed for chemical  
24 derivatization or thermochemolysis. 3-FV is used as an internal derivatization standard inside  
25 seven of the cups that are dedicated to the MTBSTFA derivatization experiment (Fig. 3). Since  
26 the purpose of the 3-FV is to test the reaction efficiency of MTBSTFA (Fig. 1) under martian  
27 conditions, the dried internal 3-FV standard must be isolated from the MTBSTFA until the  
28 derivatization experiment is carried out on Mars. To achieve this, the solid 3-FV is located inside  
29 a separate foil capped reservoir that is hermetically sealed under vacuum by a pinch off tube (<  
30  $10^{-4}$  mbar) and separated from the MTBSTFA and DMF solvents that are present in the outer  
31 volume of the SAM derivatization cup (Fig. 3). The total amount of dry 3-FV standard

1 hermetically sealed inside each SAM derivatization cup is ~40 nmol. The sealed internal  
2 reservoir prohibits any exposure and reaction of the 3-FV standard with MTBSTFA fluid until  
3 the foil caps are punctured and the experiment is carried out *in situ* on Mars. The outer volume of  
4 each cup contains ~0.5 ml of a mixture of four times freeze-pump-thaw degassed  
5 MTBSTFA/DMF (4:1 by volume), including pyrene (25 nmol) dissolved in solution. Pyrene  
6 does not react with MTBSTFA and is used as a second internal standard for the SAM  
7 derivatization experiment to determine that the cup was properly punctured and the solvent  
8 carried into the GCMS. Prior to receiving sample fines from the MSL Sample  
9 Acquisition/Sample Processing and Handling (SA/SPaH) system, both foil caps on a  
10 derivatization cup are opened using a puncture pin and the 3-FV internal standard is then  
11 exposed to the derivatization solvents.

12 After foil cap puncture, the cup can be filled with martian regolith or powdered drill fines  
13 through the SAM solid sample inlet tube up to a volume of 0.79 cc, the total volume of the outer  
14 reservoir of the derivatization cup. Since the sample acquisition system on MSL will deliver ~  
15 0.05 cc volume aliquots of powder to the SAM derivatization cups, we selected 100 mg as the  
16 sample mass for our experiments which assumes a density of the martian regolith of ~ 2 g/cc.  
17 After the sample is loaded into the cup, the sample and fluids are heated up to a maximum  
18 temperature of 300°C inside the SAM pyrolysis oven for several minutes to initiate  
19 derivatization and drive volatile products to the hydrocarbon trap (Carbosieve, Tenax TA  
20 (porous 2,6-diphenylene oxide), and glass beads packed inside a glass tube, refer to Fig. 2 and  
21 discussion in Section 2.4). Previous experiments by Buch *et al.* (2009) have shown that heating  
22 to 300°C for several minutes is needed to desorb amino acids and carboxylic acids bound to the  
23 mineral matrix prior to chemical derivatization with MTBSTFA. Helium carrier gas flows at a  
24 rate of  $\sim 5 \times 10^{-2}$  atm.cc/sec from the bottom of the cup through the pyrolysis oven and over the  
25 SAM hydrocarbon trap which can be cooled to a temperature of -50°C. The internal pressure  
26 inside the SAM pyrolysis oven at ambient temperature under these flow conditions is ~30 mbar.  
27 After the derivatization products are transferred from the pyrolysis oven to the hydrocarbon trap,  
28 the SAM trap is heated to a maximum of 300°C to flush the derivatized products under helium  
29 flow to the inlet of one of six SAM GC columns (MXTU, MXT20, MXT5, MXTCLP,  
30 Carbobond, Chirasildex CB) where the compounds are separated using a programmed column  
31 ramp. Derivatized compounds eluting from the GC column are then ionized by electron impact



1 and identified by their unique mass fragmentation patterns using the SAM quadrupole mass  
2 spectrometer (mass range 2-535 m/z). Quantitation of derivatized 3-FV by the SAM GCMS will  
3 indicate the extraction efficiency of the MTBSTFA/DMF reaction on Mars, including evidence  
4 for possible side reactions (e.g. MTBSTFA reactions with the mineral matrix or oxidizing  
5 materials) that could inhibit the reaction of MTBSTFA with any organics present in the martian  
6 sample. For the procedural blank and each analogue sample, we performed multiple (~6 to 10)  
7 derivatization experiments and GCMS analyses of the hydrocarbon trap and the average  
8 recoveries of the both the pyrene and 3-FV internal standards for each sample were determined.

#### 10 **2.4 Derivatization Test-Bed and GCMS Protocol**

11 In order to carry out one-pot MTBSTFA/DMF extraction of organic compounds from the  
12 analogue samples using the SAM chemical derivatization approach, a front-end gas processing  
13 system was assembled at NASA Goddard Space Flight Center that included a sample reactor  
14 oven, gas transfer line, and hydrocarbon trap assembly (Fig. 2). Although the derivatization test-  
15 bed used in this study does not include actual SAM flight hardware components (specifically, the  
16 flight pyrolysis oven and metal cup assembly), we have made every effort to assemble and  
17 operate the derivatization test-bed using materials and experimental conditions (including helium  
18 gas flow rates, pressure, temperature, solvent volumes and concentrations, and analogue sample  
19 volumes) that are similar to SAM. Additional optimization of the SAM derivatization experiment  
20 using a flight-like oven and metal cup assembly will be required when the SAM test-bed  
21 instrument becomes available for derivatization testing in 2012.

22 The entire test-bed assembly was operated inside a chemical fume-hood. This  
23 derivatization test-bed was designed to similar specifications as the SAM gas processing system,  
24 including the gas path and flow rates from the pyrolysis oven to the hydrocarbon trap, the  
25 transfer line dimensions (length and internal diameter) and the chemical composition of the SAM  
26 hydrocarbon trap fill material. The glass beads and tube used in the hydrocarbon trap assembly  
27 were first conditioned and heated in air at 500°C for 2 hours in a furnace. Prior to each  
28 derivatization experiment, the loaded hydrocarbon trap was conditioned overnight at 300°C  
29 under helium gas flow (flow rate = 1.6 ml/min) using a commercial pyroprobe instrument (CDS  
30 Analytical, Pyroprobe 5200) to remove any hydrocarbon contaminants. The masses and volumes  
31 of the 381 micron non porous silica glass beads ( $V = 0.32 \text{ cm}^3$ ,  $m = 0.49 \text{ gram}$ ), Tenax TA 60/80

1 mesh ( $V = 0.32 \text{ cm}^3$ ,  $m = 0.08 \text{ gram}$ ), and Carbosieve G 60/80 mesh ( $V = 0.32 \text{ cm}^3$ ,  $m = 0.11$   
2 gram) used in the test-bed hydrocarbon trap are similar to the volumes of material in the SAM  
3 flight hydrocarbon trap (within  $\pm 10\%$ ). The silica glass beads act as a filter at the front of the  
4 hydrocarbon trap and can effectively trap solids at room temperature and higher boiling  
5 compounds. Tenax TA has a low affinity for water, but will readily trap medium to high  
6 molecular weight volatile organic compounds ( $C_6$  to  $C_{10}$  and higher) that can be readily released  
7 when heated to temperatures of up to  $350^\circ\text{C}$  (Cao and Hewitt, 1992). Finally, carbosieve has a  
8 very high capacity and breakthrough volume for low boiling point, low molecular weight  
9 compounds including  $C_2$  to  $C_6$  volatile hydrocarbons and noble  
10 gases (<http://www.sisweb.com/index/referenc/bv-hyd.htm>). The MTBSTFA and DMF fluids used  
11 in this study as well as a wide range of hydrocarbons and MTBSTFA derivatives extracted from  
12 the Mars analogue samples are readily trapped using these materials.

13 The derivatization test-bed vacuum manifold consists of the following components: i) an  
14 active pumping system (Drytel 1025 roughing pump) and a  $\text{CO}_2$  gas tank to simulate the gas  
15 composition and average pressure at the martian surface ( $\sim 6\text{-}10 \text{ mbar}$ ), ii) a helium gas tank with  
16 flow restrictor set at  $5 \times 10^{-2} \text{ atm.cc/sec}$  to flush and purge derivatization solvents and other  
17 gaseous products generated inside the oven during heating to the hydrocarbon trap, and iii) a  
18 transfer line heated up to  $170^\circ\text{C}$  from the pyrolysis oven to the hydrocarbon trap, the maximum  
19 temperature tested on the SAM flight instrument. The hydrocarbon trap itself was maintained at  
20 approximately  $30^\circ\text{C}$  during the entire derivatization experiment. Most of the plumbing was  
21 connected using Swagelok Tube Fittings, however the pyrolysis cell and hydrocarbon trap  
22 manifold that were opened between each experiment were sealed using Swagelok metal gasket  
23 fittings. When dynamically pumped with no carrier gas flow, the derivatization test-bed vacuum  
24 system achieved an internal pressure of  $< 0.1 \text{ mbar}$ .

25 For each derivatization experiment, the Inconel 625 test-bed reactor cell (used as a proxy  
26 for the SAM derivatization cup and oven) was preloaded with  $40 \text{ nmol}$  3-FV and  $25 \text{ nmol}$  of  
27 pyrene by pipetting the appropriate volumes of the internal standards into the oven and then  
28 evaporating the solutions to dryness under  $\text{N}_2$  gas flow. A similar total abundance of these  
29 internal standards are present in each of the seven SAM flight MTBSTFA derivatization cups.  
30 We then added  $150 \mu\text{l}$  of a solution of MTBSTFA/DMF (4:1) directly to the oven containing the  
31 dried internal standards. The volume of solvent used in these experiments ( $150 \mu\text{l}$ ) is lower than

1 the total volume of MTBSTFA/DMF (~ 500  $\mu$ l) loaded inside the SAM flight cups. We found  
2 through testing that volumes of MTBSTFA/DMF in excess of 150  $\mu$ l can lead to severe  
3 oversaturation and degradation of the hydrocarbon trap, as well as clogging of the GC column  
4 after subsequent trap heating. As pyrene is dissolved into the MTBSTFA/DMF mixture inside  
5 the SAM flight cups, we performed evaporations tests with the setup in order to understand the  
6 evaporation rate of MTBSTFA, DMF, and pyrene. Unlike MTBSTFA and DMF, we observed  
7 that the pyrene did not evaporate from the oven during the evaporation step after heating at 75°C  
8 for several minutes at 7 mbar, which is not surprising given the very low vapor pressure of  
9 pyrene of ~0.12 mbar at 125°C (Smith et al., 1980) and the high boiling point of pyrene (404°C)..  
10 For the actual SAM analysis, it will be necessary to evaporate a large fraction of the  
11 MTBSTFA/DMF solvent from each cup through the SAM exhaust vent prior to the actual  
12 derivatization experiment to avoid solvent oversaturation and possibly damage to the  
13 hydrocarbon trap and/or GC columns. After the solvent was added to the reactor cell,  
14 approximately 100 mg of each sample was weighed, transferred into the reactor oven and the  
15 oven then sealed to the VCR fitting connected to the vacuum manifold (Fig. 2). The reactor oven  
16 containing the solid sample was sealed under ~7 mbar CO<sub>2</sub> (to simulate martian surface  
17 atmospheric pressure in the SAM experiment) using a valve and then heated up to 300°C. After  
18 three minutes, the valve of the reactor oven and the helium tank were opened simultaneously to  
19 allow helium to flow through the cell. The MTBSTFA/DMF solvent and derivatized volatiles are  
20 transferred to the hydrocarbon trap (trap temperature ~30°C). After five minutes, the valve of the  
21 hydrocarbon trap is closed and removed from the test-bed manifold and inserted into a  
22 commercial pyroprobe system for GCMS analysis.

23 The pyroprobe was interfaced to a Thermo-Finnigan Trace GC and DSQ quadrupole  
24 mass spectrometer (DSQ) for analyses of the derivatized products released from the hydrocarbon  
25 trap. Data analysis was performed with The DSQ was operated in quadrupole detection mode  
26 (50--550 m/z) with the detector voltage set at 1 kV. The GCMS was equipped with a splitless  
27 injector set at a temperature of 300°C. The GC inlet is used in splitless mode to maximize the  
28 quantity of derivatized species desorbed from the hydrocarbon trap onto the GC column. For  
29 each GCMS analysis, the pyroprobe trap was heated to 300°C for 10 minutes under an optimized  
30 helium carrier gas flow of 1.6 ml/min to release the derivatized products and transfer them  
31 directly to the inlet of the GC column (Restek RTX 5 MS capillary column, 95%

1 dimethylpolysiloxane, 5% diphenyl, 30 m, x 0.25 mm x 0.25  $\mu$ m). The commercial GC column  
2 used in all of these experiments was similar to one of the six GC columns used in the SAM  
3 instrument (MXT 5). This column is efficient for a wide range of organic molecules such as  
4 amines, amino acids, and carboxylic acids. The initial temperature of the column was kept at  
5 140°C to avoid condensation and clogging of the GC column by excess MTBSTFA and DMF  
6 from the hydrocarbon trap. After 10 minutes at 140°C, the GC oven was ramped to 300°C at a  
7 rate of 10°C/min. The final temperature of the column was maintained at 300°C for 10 minutes.  
8 A mass spectrometer solvent delay of 10 minutes from the time of GC injection was included to  
9 minimize saturation of the DSQ detector by excess MTBSTFA and DMF.

## 11 2.5 CheMin XRD/XRF Technique

12 The CheMin X-Ray Diffraction/X-Ray Fluorescence (XRD/XRF) instrument, can  
13 determine the bulk mineralogy of rocks and soil that are provided to it by the MSL SA/SPaH. A  
14 detailed description of the CheMin flight instrument and capabilities has been discussed  
15 previously (Blake et al., 2010). Several prototype instruments have been built, one of these  
16 instruments (Terra) was used for this study. Unlike in CheMin, the XRF capabilities of Terra are  
17 limited due to absorption occurs by the beryllium windows of the CCD detector preventing  
18 detection below 3 keV. The instrument uses a Co X-ray tube, has a range of 5-55° 2 $\theta$  and a full  
19 width at half maximum of 0.3° 2 $\theta$ . The CCD detector is sensitive to X-rays between about 2.3  
20 KeV and 8 KeV (Cl K $\alpha$  to Cu K $\alpha$ ). All samples were received as vials of powder, sieved to <  
21 150  $\mu$ m grain size. Approximately 65 mm<sup>3</sup> aliquots of sample material were poured into the  
22 sample holder of the instrument and samples were analyzed continuously for 6 hours,  
23 approximating the flux intensity and data collection rates anticipated for MSL. Quantitation of  
24 the mineral abundances from XRD patterns by Rietveld refinement and other full pattern fitting  
25 techniques are generally accurate to  $\pm$ 10% of the amount present, with the exception of clays and  
26 amorphous materials (Bish and Post, 1993, Chipera and Bish, 2002). Detection limits range from  
27 1% for highly crystalline materials, to 5-10% for clays and amorphous materials. Amorphous  
28 and disordered minerals such as clay minerals (e.g., smectites) are not quantifiable by Rietveld  
29 refinement.

## 31 3. Results and Discussion

### 3.1 Bulk Mineralogy Measurements

The XRD pattern and XRF spectrum for the Atacama Desert surface soil sample (Atacama-01) is shown below (Fig 4). Similar XRD/XRF measurements were made on the fused silica procedural blank and the other analogue samples selected for this study (data not shown). The mineral abundances in the samples determined from the Terra instrument spectra after Rietveld refinement and fitting are shown in Table 1. XRD data from the FS120 fused silica sample was monotonically amorphous quartz (100% SiO<sub>2</sub>); no mineral impurities in the sample were detected.

The mineral composition of the two Atacama Desert soil samples analyzed (Atacama-01 and Atacama-02) were similar to previous analyses of soil from the Atacama Desert (Sutter et al., 2007). However, some differences in bulk mineralogy between the surface and subsurface samples were observed (Table 1). The presence of quartz, albite, and anorthite in both samples suggest that their parent rocks were felsic or granitic in composition. The presence of secondary minerals such as calcite suggests that alteration occurred in the presence of groundwater, particularly in the case of the subsurface sample Atacama-02 where calcite is a major constituent (~30%). Substantially different clays (kaolinite in the surface sample and palygorskite in the subsurface sample) are found in the two soil layers. Since kaolinite is typically a weathering or hydrothermal alteration product of felsic minerals, it follows that it is likely a product of the breakdown of the locally abundant felsic parent rocks. The palygorskite clay found in the lower horizon is present at a much higher abundance (18.5%) than kaolinite at the surface (2.5%) and suggests a different formational or diagenetic environment relative to the upper horizon, possibly a buried soil horizon from an earlier time. Palygorskite clays can occur in a wide range of environments such as marine and lacustrine sediments, soils, paleosols and calcretes. The structure of palygorskite lends itself to adsorption of water and organic molecules (in structural channels in the mineral). This would be a likely place for organic molecules to persist if they had been present in the original environment, and a likely place for organic molecules to be trapped should ground water containing organic compounds have passed through this horizon.

The mineral composition of the Mars regolith simulant, JSC Mars-1 is similar to previous XRD measurements (Allen et al., 1998, Perko et al., 2006). The JSC Mars-1 sample analyzed in this study was dominated by plagioclase (62% anorthite and 27% augite), with lower abundances

1 of forstetite (~ 9%), and trace abundances (~ 1%) of chromite and ilmenite. We did not detect  
2 any magnetite in this JSC Mars-1 sample, although previous XRF measurements of JSC Mars-1  
3 have identified 10-15 wt% magnetite ( $\text{Fe}_2\text{O}_3$ ). Iron Mossbauer spectroscopy measurements of  
4 JSC Mars-1 has shown that the majority of iron (64%) in this sample is present as nanophase  
5 ferric oxide particles (Morris et al., 1993, Allen et al., 1998), however this phase was not  
6 identified in this study. We did not identify any phyllosilicates in this sample (< 1 wt%) which is  
7 consistent with previous analysis (Allen et al., 1998).

8 The Rio Tinto headwater sample (Rio Tinto-01) is a red-orange colored sample formed at  
9 low pH (~ 1) with a mineralogy dominated by hydrated aluminium and iron sulphate minerals  
10 including alunogen (40 wt%) and jarosite (36 wt%). Lower abundances (~12 wt% each) of  
11 copiapite and amarantite were also identified in this sample. Previous XRD measurements of  
12 samples from the Rio Tinto headwaters have revealed similar mineralogies (Fernández-Remolar  
13 et al., 2005). This sample is a very good soil analogue for the acid-sulphate chemistry and  
14 mineralogy observed by the Mars Exploration Rover Opportunity at Meridiani Planum, Mars  
15 (Fernandez-Remolar et al., 2004, Klingelhöfer et al., 2004).

16 The calcium and magnesium rich carbonate sample collected during the 2005 AMASE  
17 Svalbard campaign (Carbonate-01) is a stromatolite. Stromatolites are layered accretionary  
18 structures formed in shallow waters by the cementation of sedimentary grains by biofilms of  
19 microorganisms. XRD analyses of this sample showed that it consisted predominately of  
20 dolomite (99 wt%) with trace amounts of quartz (1 wt%).

21 Finally, the Murchison meteorite contained a highly diverse distribution of minerals  
22 dominated by olivine (forsterite, 43 wt%), serpentine (lizardite, 19 wt%), and pyroxenes (10 wt%  
23 augite, 8 wt% diopside, and 6 wt% enstatite). Lower abundances (< 5 wt%) of chromite, calcite,  
24 and tochilinite) were also identified. This meteorite is a fragment of an exceedingly complex  
25 extraterrestrial parent body that has a mix of high temperature and low temperature phases and  
26 exhibits extensive hydrothermal or aqueous alteration (Lauretta and McSween, 2006). Despite  
27 the large number of published studies, very few XRD results have been reported. This is perhaps  
28 because of the complexity of the rock and the fine-grained nature of some of the components. It  
29 is possible that other fragments of the Murchison meteorite will contain additional minerals not  
30 reported here, and there are likely fine-grained phases that are “X-ray amorphous” and not  
31 detectable by this technique.

### 3.2 Derivatization and GCMS Analysis of Organic Compounds

The first goal of this study was to verify the ability of the SAM-like derivatization test-bed to efficiently extract and concentrate the two internal standards, 3-FV and pyrene using the oven and the hydrocarbon trap. The experimental sequence discussed in Section 2.4 was optimized by varying both the oven temperature and duration of heating to maximize the recovery of the two internal standards (3-FV and pyrene). The total extraction recoveries of both internal standards placed inside the reaction oven and carried through the entire test-bed derivatization experiment were determined based on the areas of the peaks compared to the areas obtained by direct injection of similar quantities of the standards in the GCMS. From the analysis of fifteen individual experiments using these pure standards in an empty oven, we calculated a maximum extraction recovery of approximately  $30\pm 2\%$  for 3-FV and  $10\pm 2\%$  for pyrene after heating to  $300^\circ\text{C}$  for 3 minutes followed by transfer to the hydrocarbon trap under helium carrier gas flow. We found that higher oven temperatures and longer heating times did not improve the recovery yields for these two internal standards. Based on these findings, subsequent derivatization extraction experiments for the analogue samples were all carried out at  $300^\circ\text{C}$  for 3 min.

The low recoveries of the internal standards after one-pot extraction and subsequent trapping of the compounds on the hydrocarbon trap could be due to oversaturation of the hydrocarbon trap with excess MTBSTFA/DMF and the relatively low transfer line temperature of  $170^\circ\text{C}$  used. For 3-FV, we believe that the relatively large ( $150\ \mu\text{l}$ ) volume of MTBSTFA/DMF used in the experiments saturates the hydrocarbon trap which inhibits the adsorption of 3-FV on the hydrocarbon trap. For pyrene, the saturation could also explain the low recovery, however we also note that due to the low vapor pressure of pyrene of  $\sim 2.2\ \text{mbar}$  at  $170^\circ\text{C}$  (Smith et al., 1980), a large fraction of pyrene would condense on the interior surfaces of the transfer line from the oven to the hydrocarbon trap which were kept at a temperature of  $\sim 170^\circ\text{C}$  under He carrier flow at a pressure of 30 mbar for the duration of the experiment. This temperature represents the maximum temperature that the transfer lines can safely be heated to in the SAM instrument. We confirmed in subsequent experiments that much higher transfer line temperatures ( $\geq 250^\circ\text{C}$ ) were required to transfer the remaining pyrene to the hydrocarbon trap under helium carrier gas flow.

1 GCMS analysis of the hydrocarbon trap after derivatization extraction of the fused silica  
2 procedural blank clearly show peaks and mass fragmentation patterns corresponding to the  
3 MTBSTFA derivative of 3-FV (retention time ~ 12.4 min) as well as a smaller peak at ~18.2 min  
4 corresponding to pyrene. Although the 3-FV standard used in this experiment is chiral (racemic  
5 mixture, D/L = 1), we were unable to obtain separate peaks for the D- and L-enantiomers of 3-  
6 FV under the conditions employed. Other prominent peaks in the GC chromatogram are clearly  
7 observed in Fig. 5 and can be attributed to derivatization artifacts and other unidentified  
8 derivatized species that formed from the reaction of MTBSTFA with the hydrocarbon trap  
9 material and/or internal metal surfaces of the test-bed setup. A very wide GC peak is also visible  
10 at the beginning of the chromatogram (10-12 minutes) as well as others peaks corresponding to  
11 polysiloxane fragments from the GC column itself. Due to the extremely high solvent  
12 background and the relatively high initial starting temperature of the GC column (140°C), more  
13 volatile MTBSTFA derivatives including glycine and alanine will be difficult to detect above  
14 background, especially if these amino acids are only present at trace abundances in a martian  
15 sample (the detection limit for these amino acids under these conditions is ~1 nmol). However,  
16 assuming there are no side reactions with the mineral matrix from a sample on Mars, heavier less  
17 volatile amino and carboxylic acids should be identified by GCMS after MTBSTFA chemical  
18 derivatization if present in the martian regolith. Finally, we determined that starting the oven  
19 ramp at 140°C was important to minimize clogging of the GC column at the inlet with a high  
20 flow of solvent from the hydrocarbon trap.

21 GCMS analysis of the hydrocarbon trap after extraction of the Atacama-01 in Fig. 6  
22 showed the presence of both pyrene and 3-FV which indicated that the MTBSTFA derivatization  
23 reaction occurred during the experiment. We also identified two carboxylic acids, hexadecanoic  
24 acid and octadecanoic acid (stearic acid) based on their mass fragmentation patterns that matched  
25 the fragmentation of their MTBSTFA derivatives from standards we injected for comparison and  
26 the NIST spectral library. These two carboxylic acids have been previously identified in a  
27 different Atacama Desert soil sample using one-pot MTBSTFA derivatization and GCMS  
28 analysis (Buch et al., 2009). However, Buch *et al.* reported a much wider range of MTBSTFA  
29 derivatized compounds in different Atacama Desert soils including 9 carboxylic acids, 2 hydroxy  
30 acids, and 3 amino acids (glycine, alanine, and valine) at concentrations ranging from 0.5 to 9  
31 nmol per gram. This is likely due to non-SAM like extraction methods and GCMS conditions



1 such as a pre-extraction sonication step using water and isopropanol or a thermal desorption step  
2 prior to MTBSTFA.

3 In contrast to the surface sample, we were unable to identify any amino acids or  
4 carboxylic acids originating from Atacama-02. Although pyrene and some 3-FV was detected in  
5 the extract, the absolute intensity of the 3-FV peak was twelve times smaller than observed in the  
6 extract from Atacama-01 which indicates that the derivatization was inhibited in the subsurface  
7 soil. Since Atacama-02 contains a much higher abundance of hydrated minerals (Sutter et al.,  
8 2007), water bound in the palygorskite clay may have reacted preferentially with the MTBSTFA  
9 or hydrolyzed the labeled organics. Thus, reaction of MTBSTFA with free or bound water  
10 presented in the clays in the Atacama-02 sample could explain the reduced intensity of the  
11 derivatized 3-FV peak in GCMS analysis of the Atacama-02 sample.

12 We were unable to detect the 3-FV internal standard or any other derivatized organic  
13 compounds in JSC Mars-1 and Rio Tinto-01 samples (Fig. 7 and Fig. 8). However, we did detect  
14 the internal standard pyrene in both samples which suggests that any organics of similar or lower  
15 volatility extracted from the samples should have been collected on the hydrocarbon trap during  
16 the experiment and detected by GCMS. The lack of amino acids extracted from the JSC Mars-1  
17 analogue is surprising since a wide range of amino acids have previously been found in this  
18 sample with concentrations ranging from ~2 to 35 parts-per-million as measured by high  
19 performance liquid chromatography (Garry et al., 2006). JSC Mars-1 contains no evidence for  
20 hydrated minerals, but iron oxide minerals such as  $\text{FeTiO}_3$  are present (Table 1) (Allen et al.,  
21 1998) which could inhibit derivatization or deactivate derivatized species at 300°C. Deactivation  
22 of the MTBSTFA could result in a reverse chemical reaction producing lower volatility  
23 compounds that cannot be extracted from the sample under the conditions employed..

24 Rio Tinto contain evidence of a variety of microorganisms (González-Toril et al., 2003),  
25 and abundant lipids (Fernández-Remolar et al., 2005) and microcapillary electrophoresis  
26 analyses of subcritical water extracts from Rio Tinto-01 was observed to have a variety of amino  
27 acids present at part-per-million (ppm) concentrations [Stockton et al. 2010]. Given the high  
28 abundances of amino acids and lipids present in the sample and the lack of detection of the 3-FV  
29 internal standard, we believe that the MTBSTFA reagent probably reacted with the iron and  
30 aluminium rich hydrated sulfate minerals during the extraction experiment in preference to the  
31 organics known to be present.

1 The Murchison meteorite contains a wide variety of extraterrestrial organic matter,  
2 including both amino acids and carboxylic acids at great than ppm concentrations that are readily  
3 extracted and detected using standard GCMS analysis protocols (Cronin and Chang, 1993).  
4 However, the low intensity of 3-FV and the lack of any other identifiable derivatized amino acids  
5 or carboxylic acids in Murchison (Fig 10) suggest that the MTBSTFA reaction with these  
6 compounds is being inhibited by the mineral matrix or possibly non-volatile macromolecular  
7 organic matter. We believe that the most likely source of interference is the hydrated magnesium  
8 silicates (e.g. lizardite) in the Murchison sample that act to deactivate the MTBSTFA reagent.  
9 The other peaks in the chromatogram were detected in Quartz blank and are polysiloxanes from  
10 the GC column bleed and unidentified products resulting MTBSTFA reacting with the  
11 hydrocarbon trap.

12 The most promising results obtained in this study were from Carbonate-01. GCMS  
13 analysis of this sample after extraction revealed a strong 3-FV peak indicating that MTBSTFA  
14 derivatization occurred (Fig. 9). Although we were unable to identify any carboxylic acids in the  
15 sample, we were able to identify the MTBSTFA derivatives of two common protein amino acids,  
16 leucine and proline based on our own database and the NIST library. Since these amino acids  
17 were not detected in any of the procedural blanks, these amino acids were extracted from the  
18 stromatolite sample itself and are likely derived from biological organic matter in the sample.  
19 Other common protein amino acids such as glycine and alanine are also likely present in the  
20 stromatolite sample, however these amino acids are more volatile and are not easily detected  
21 under these conditions since they elute with the MTBSTFA and DMF solvents. At least two  
22 other peaks corresponding to derivatized compounds (though not in our data base neither in the  
23 NIST library) were detected in the sample and not the blank. Unlike many of the other analogue  
24 samples tested in this study, Carbonate-01 is a nearly pure dolomite and lacks hydrated minerals  
25 and iron oxides that are present in the other samples. Therefore, for carbonate rich samples, our  
26 results suggest that MTBSTFA will not be inhibited by the mineral matrix and will readily react  
27 with free amino and carboxylic acids present in the sample.

28

#### 29 **4. Conclusion**

30 Here we report on the first analyses of a suite of Mars analogue samples using the  
31 MTBSTFA extraction protocol being developed for the SAM instrument under “flight-like”

1 experimental conditions. The results obtained from this study showed that the extraction and  
2 detection of both amino acids and carboxylic acids using a SAM-like instrument protocol is  
3 possible for some analogue materials. The most promising result we obtained was the GCMS  
4 detection of two derivatized protein amino acids, leucine and proline, that were extracted from  
5 the carbonate-rich stromatolite sample using the “one-pot” MTBSTFA derivatization procedure  
6 and preconcentration using a SAM-like hydrocarbon trap. Carbonate minerals, such as those  
7 recently detected on Mars by the Phoenix lander and the Mars Reconnaissance Orbiter may  
8 represent the best targets for MTBSTFA extraction of organic compounds using the SAM  
9 instrument.

10 In contrast to the carbonate stromatolite sample, we found that reactions of the  
11 MTBSTFA derivatization solvent with the mineral matrix during the one-pot derivatization  
12 extraction was highly problematic, and based on the extraction efficiency of the 3-FV internal  
13 standard, the extraction of amino acids and carboxylic acids from the analogue samples was  
14 clearly inhibited. For some samples, no indigenous amino and carboxylic acids could be  
15 identified by GCMS after the samples were extracted in MTBSTFA and DMF at 300°C for  
16 several minutes, even though these samples are known to contain high concentrations of soluble  
17 organic compounds. We believe that the most probable inhibitor to the MTBSTFA derivatization  
18 reaction is the presence of hydrated minerals and/or iron oxides in the analogue samples.  
19 Additional derivatization testing on pure minerals will be required to further understand these  
20 effects.

21 The influence of the mineral matrix and chemical composition on derivatization,  
22 especially the presence of hydrated minerals and oxides in martian samples, will likely be a  
23 major constraint in the ability for SAM to detect amino and carboxylic acids using MTBSTFA.  
24 Additional testing will be required to understand if the derivatization extraction efficiency can be  
25 improved using a multi-step procedure where the sample is first heated to high temperatures to  
26 extract and concentrate organic compounds on the hydrocarbon trap, followed by exposure of the  
27 hydrocarbon trap directly to MTBSTFA in a second step. Although a large fraction of the amino  
28 and carboxylic acids originally present in the sample could be destroyed during the first heating  
29 step, this approach would avoid direct exposure of the rock sample with MTBSTFA. SAM also  
30 contains two cups with a second derivatization agent, tetramethylammonium hydroxide  
31 (TMAH). Thermochemolysis using TMAH is much more resistant to the presence of water and

1 would be a good alternative for the extraction of organic compounds in samples containing  
 2 abundant hydrated minerals. The results from this martian analogue study provide an important  
 3 framework for the sample selection and organic compound detection strategy for the SAM  
 4 derivatization experiment on the 2011 Mars Science Laboratory (MSL) mission as well as ESA's  
 5 current ROSETTA mission scheduled to arrive at comet 67P/Churyumov-Gerasimenko mission  
 6 in 2014 which includes a similar derivatization experiment as part of the Cometary Sampling and  
 7 Composition experiment (COSAC).

8

## 9 6. Tables and Figures

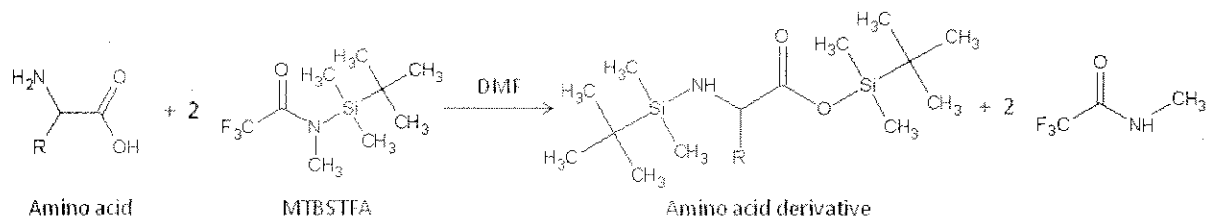
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11 Table 1: Description of the samples analyzed in this study including the organic compounds  
 12 identified and bulk rock compositions.

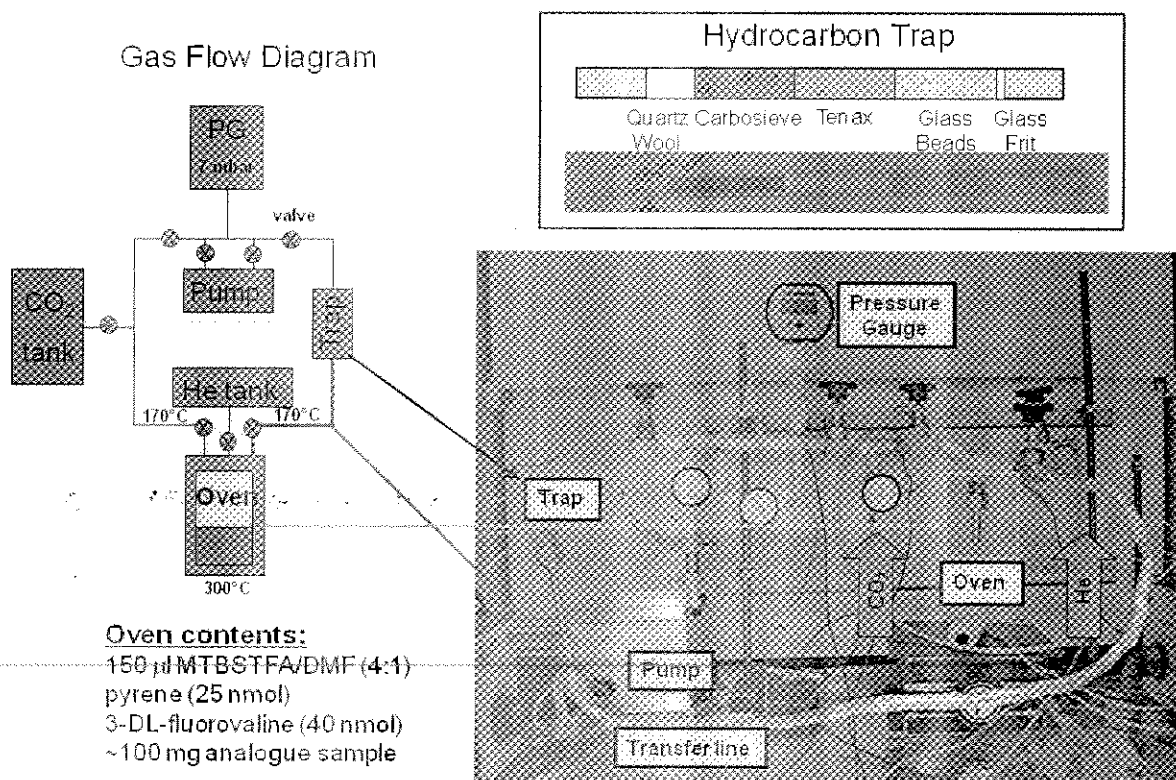
Sample	Description	Internal Standards Detected (percent recovery)	Organics Detected (concentration)	Mineralogy Deduced (wt %)
Quartz-01	Procedural blank, fused silica (FS 120)	3-FV (30%), Pyrene (10%)	None	100% Quartz (SiO <sub>2</sub> )
Atacama-01	Atacama Desert surface soil sample, Chile (0-1 cm depth)	3-FV (24%), Pyrene (11%)	Hexadecanoic acid (0.05 nmol/g) octadecanoic acid (0.04 nmol/g), several unidentified compounds	37.0% Quartz (SiO <sub>2</sub> ) 4.1% Calcite (CaCO <sub>3</sub> ) 27.2% Albite (NaAlSi <sub>3</sub> O <sub>8</sub> ) 24.5% Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ) 4.7% Hematite (Fe <sub>2</sub> O <sub>3</sub> ) 2.5% Kaolinite (Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> )
Atacama-02	Atacama Desert subsurface soil sample, Chile (10 cm depth)	3-FV (2%), Pyrene (9%)	None	21.0% Quartz (SiO <sub>2</sub> ) 29.7% Calcite (CaCO <sub>3</sub> ) 30.3% Albite (NaAlSi <sub>3</sub> O <sub>8</sub> ) 18.5% Palygorskite clay ((Mg, Al) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH)·4H <sub>2</sub> O) 0.5% Hematite (Fe <sub>2</sub> O <sub>3</sub> ) 62.1% Anorthite (CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ) Augite 27.3% (Ca,Mg,Fe) <sub>2</sub> (Si,Al) <sub>2</sub> O <sub>6</sub> ) 8.8% Forstetite (MgSiO <sub>4</sub> ) 1.0% Chromite (FeCr <sub>2</sub> O <sub>4</sub> ) 0.9% Ilmenite (FeTiO <sub>3</sub> )
JSC Mars-1	Mars regolith simulant, Mauna Kea, Hawaii, USA	Pyrene (10%)	None	36.2% Jarosite (KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> ) 11.6% Copiapite (Fe <sub>3</sub> [OH(SO <sub>4</sub> ) <sub>2</sub> ] <sub>2</sub> ·20(H <sub>2</sub> O)) 40.1% Alunogen (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·17(H <sub>2</sub> O)) 12.0% Amaranthite (FeSO <sub>4</sub> ·OH·3(H <sub>2</sub> O)) 99.0% Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> ) 1.0% Quartz (SiO <sub>2</sub> )
Rio Tinto-01	Rio Tinto	Pyrene (8%)	None	1.0% Quartz (SiO <sub>2</sub> )
Carbonate-01	Carbonate rich stromatolite from Svalbard	3-FV (27%), Pyrene (10%)	Leucine (0.02 nmol/g), proline (0.01 nmol/g), several unidentified compounds	
USNM 6650.2	Murchison Meteorite	3-FV (1%), Pyrene (8%)	None	43.3% Forstetite (MgSiO <sub>4</sub> ) 19.2% Lizardite (Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ) 9.5% Augite ((Ca, Mg, Fe) <sub>2</sub> (Si, Al) <sub>2</sub> O <sub>6</sub> ) 7.5% Diopside (Ca,MgSiO <sub>3</sub> ) 5.7% Enstatite (MgSiO <sub>3</sub> ) 3.5% Chromite (FeCr <sub>2</sub> O <sub>4</sub> ) 4.1% Calcite (CaCO <sub>3</sub> ) 4.9% Tochilinite (Fe <sub>3-6</sub> (Mg,Fe) <sub>5</sub> (OH) <sub>10</sub> S <sub>6</sub> )

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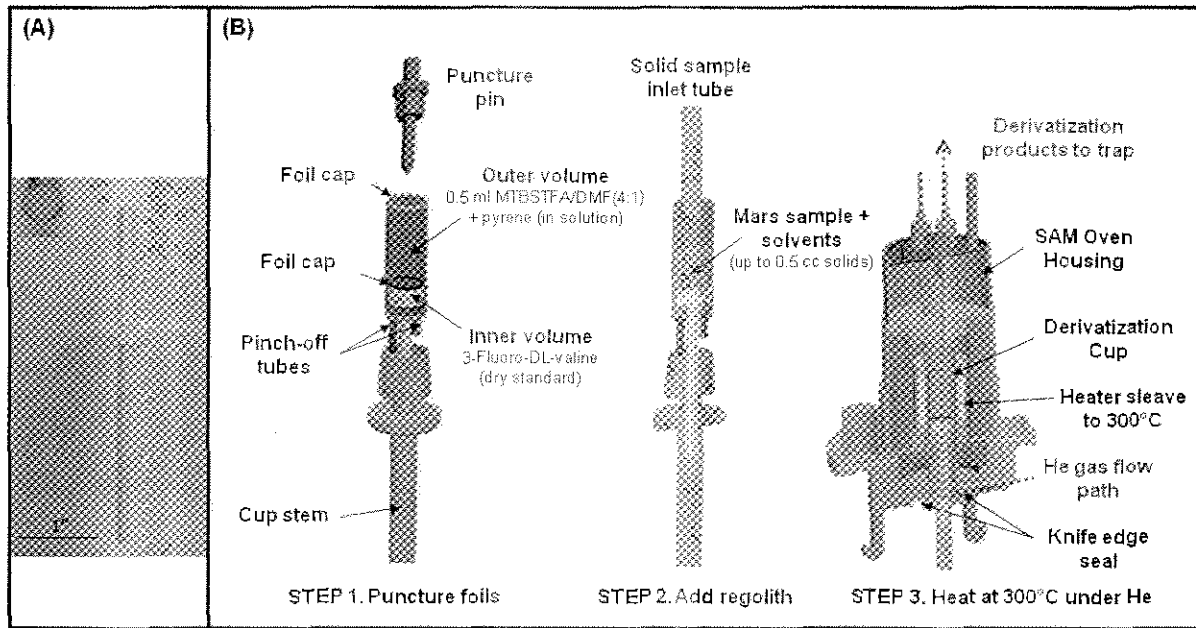
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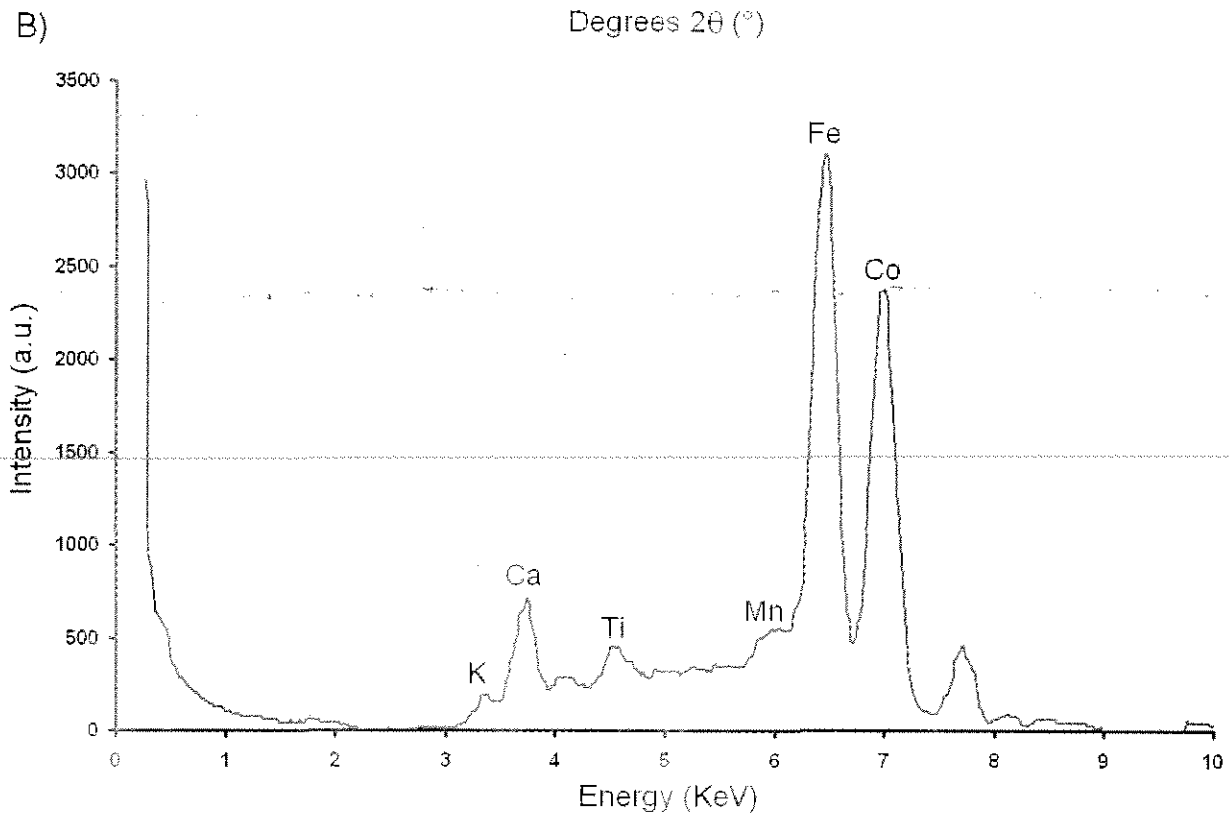
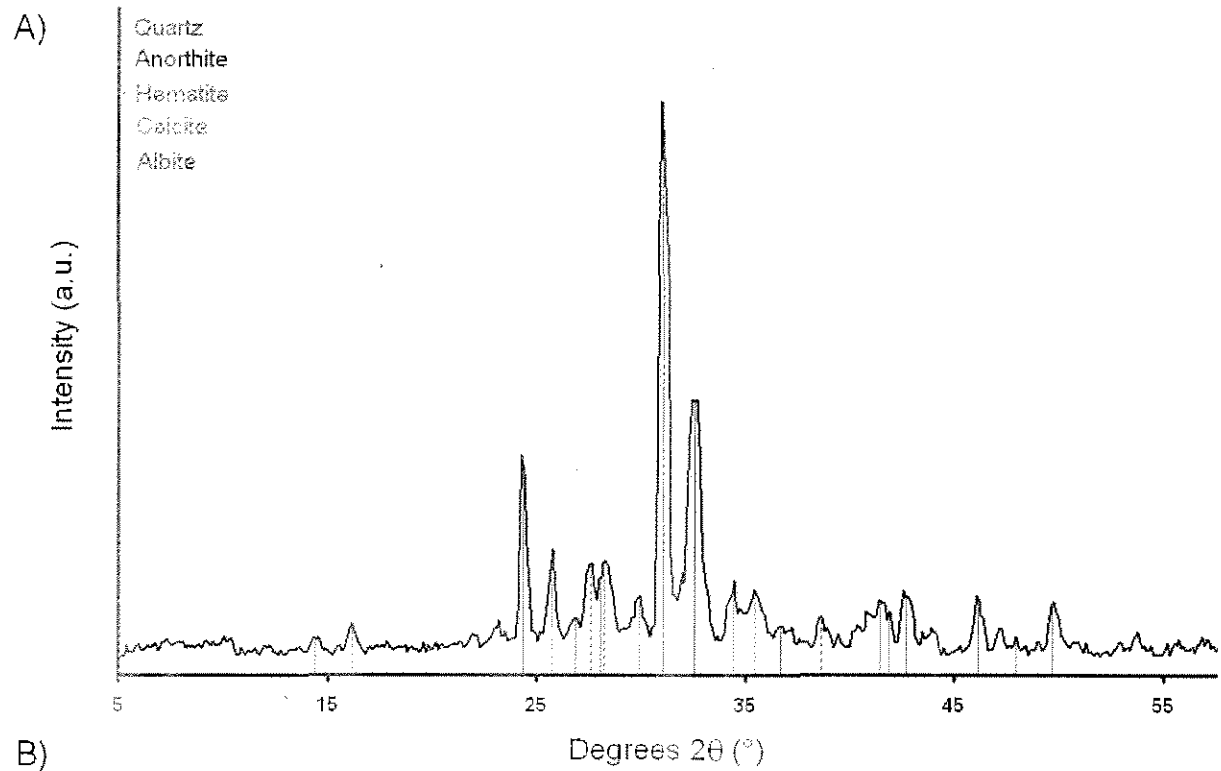
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4 **Figure 1:** Scheme of the derivatization reaction between a generic amino acid and MTBSTFA. A  
5 similar reaction will occur for carboxylic acids. DMF is used as the solvent.  
6



7  
8 **Figure 2:** Flow diagram and photo of the experimental setup used in this study to extract organic  
9 compounds from Mars analogue materials and concentrate the MTBSTFA derivatization  
10 products on a SAM-like hydrocarbon trap for GCMS analyses (commercial pyrolysis GCMS  
11 instrument not shown).  
12



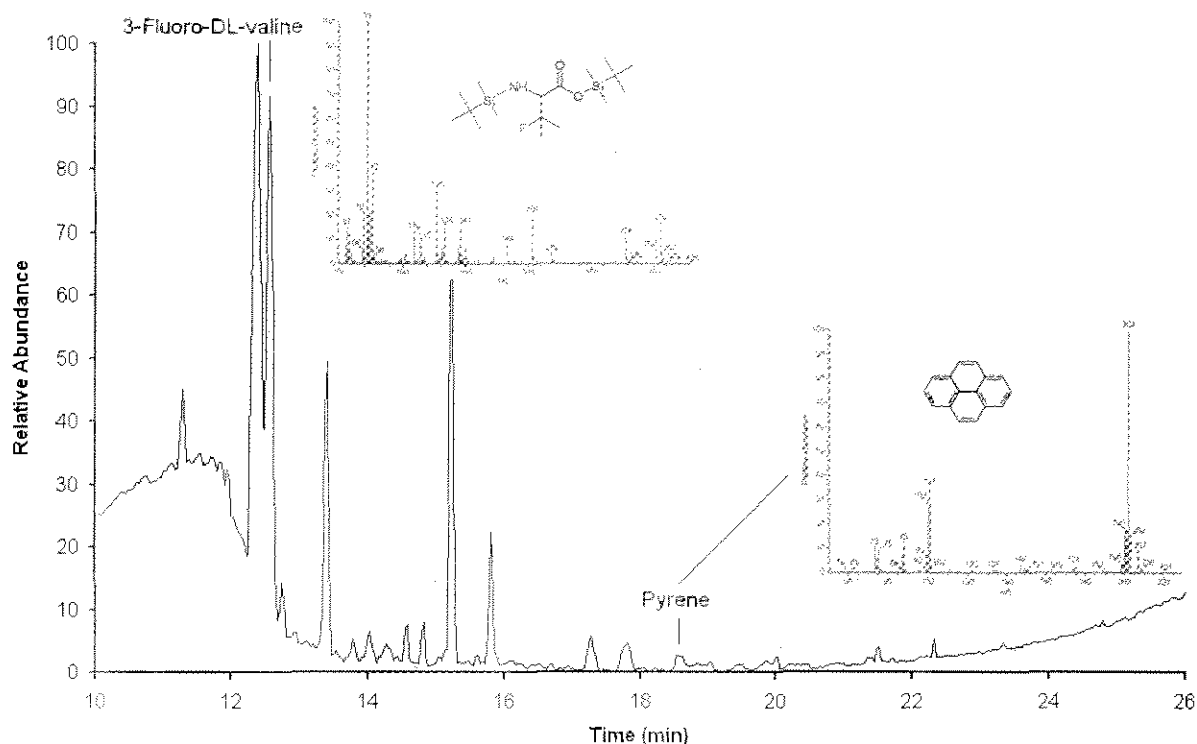
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 2 **Figure 3:** Photo of one of the SAM derivatization solvent filled cups (A) and a diagram of the  
 3 metal derivatization cup and pyrolysis oven illustrating the interior contents of the cup and the  
 4 extraction process for the SAM derivatization experiment on Mars (B).  
 5



1  
2 **Figure 4:** (A) XRD pattern, with quantitative analysis by Rietveld refinement, for the Atacama  
3 Desert surface soil sample (Atacama-01). Colored markers at the bottom of the plot show the

1 positions of the peaks for each mineral. (B) Elemental composition determined from the X-ray  
2 fluorescence spectrum obtained by summing a total 100 frames of the X-ray photons detected by  
3 the CCD. A brief discussion of the patterns and the quantitative mineral abundances for each  
4 sample is provided in the text.

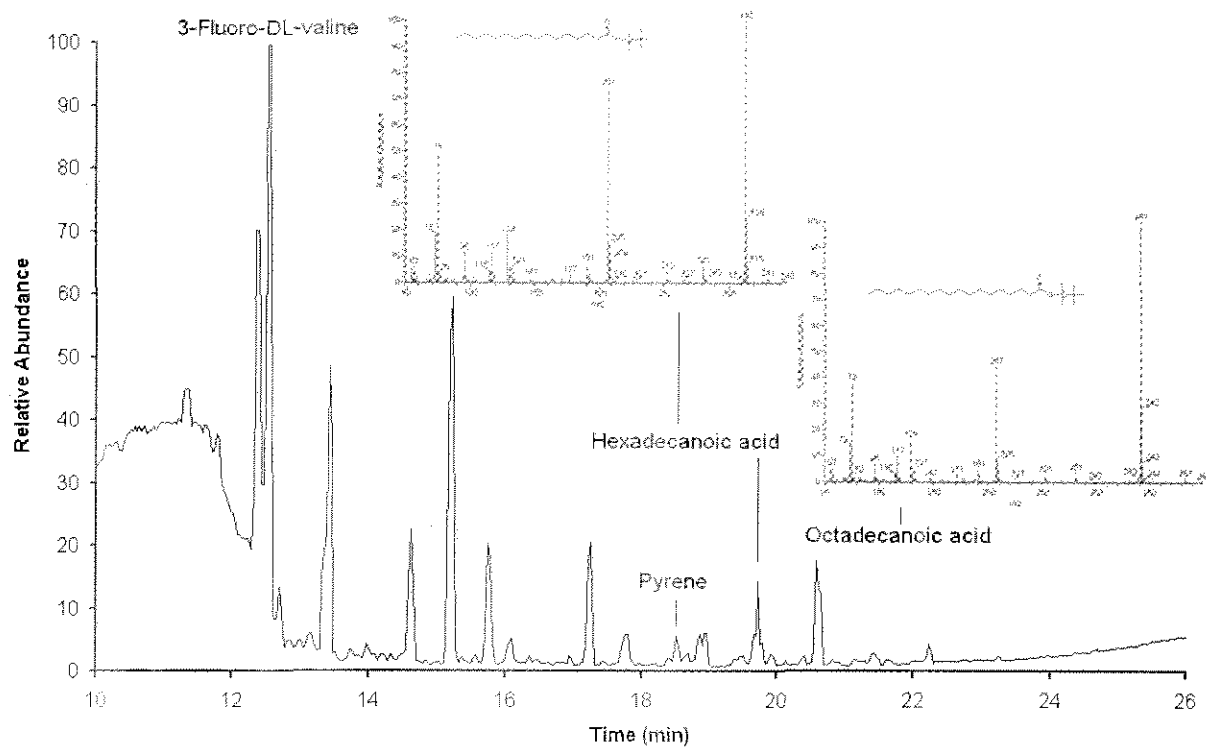
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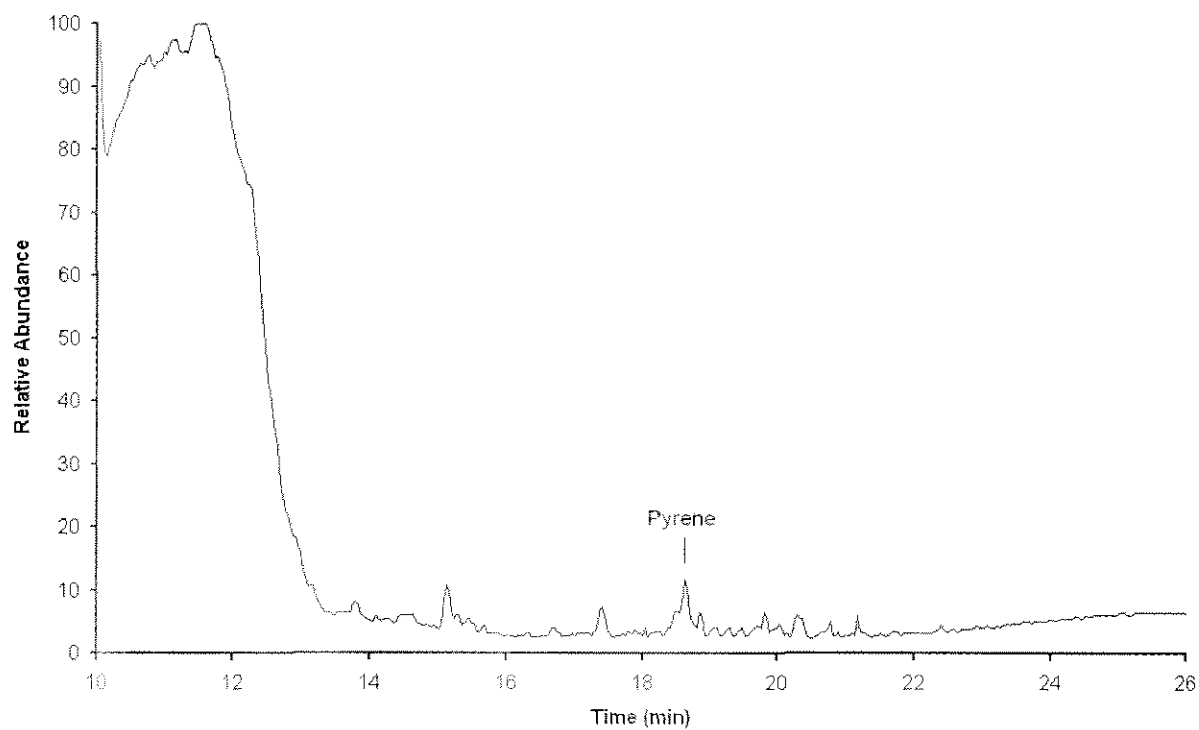
6  
7 **Figure 5:** GCMS analysis of the hydrocarbon trap after derivatization of the fused silica  
8 procedural blank (Quartz-01) with 150  $\mu$ l of MTBSTFA-DMF at 300°C for 3 minutes. The  
9 others peaks are also present in the blank (MTBSTFA/DMF only, no 3-FV) and are  
10 polysiloxanes or reaction products from the hydrocarbon trap. Top and right: mass spectrum of  
11 3-FV derivative and pyrene extracted from sample.

12

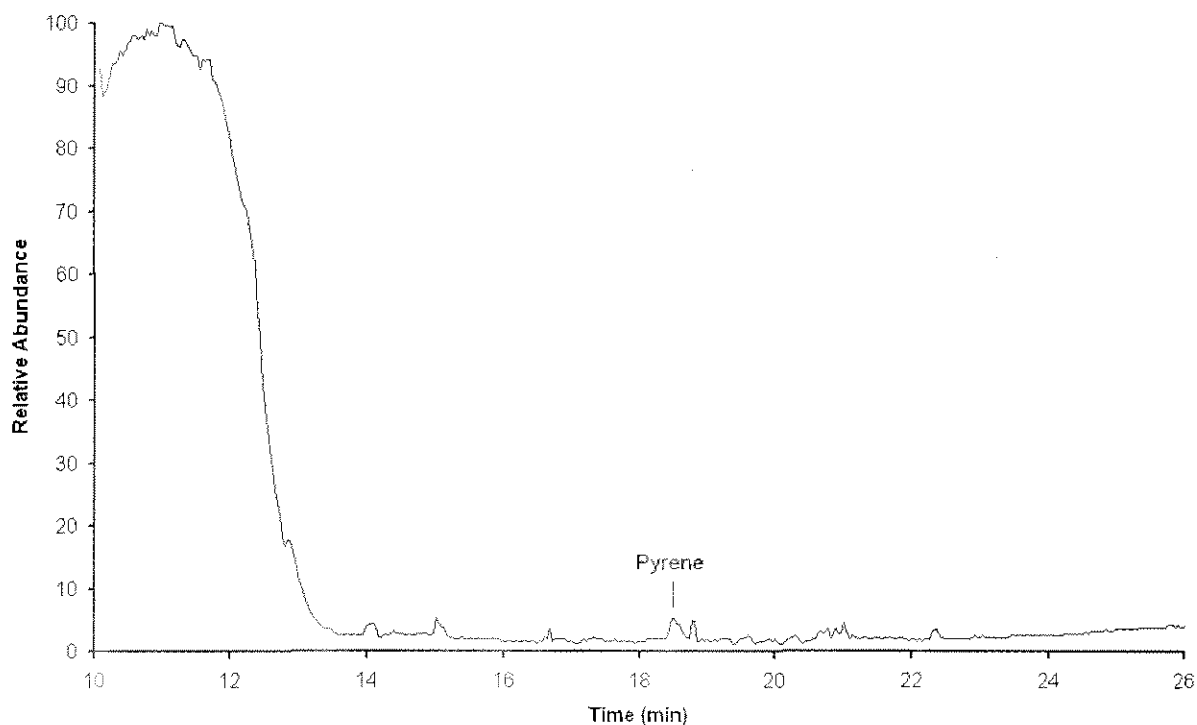




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 2 **Figure 6:** GCMS chromatograms of the hydrocarbon trap after one-pot extraction and  
 3 derivatization of the Atacama Desert surface (Atacama-01) soil at 300°C. Top and right: mass  
 4 fragmentation pattern of octadecanoic acid and hexadecanoic acid derivatives extracted from  
 5 sample. Fragmentation patterns for MTBSTFA/DMF, 3-FV and pyrene not shown.  
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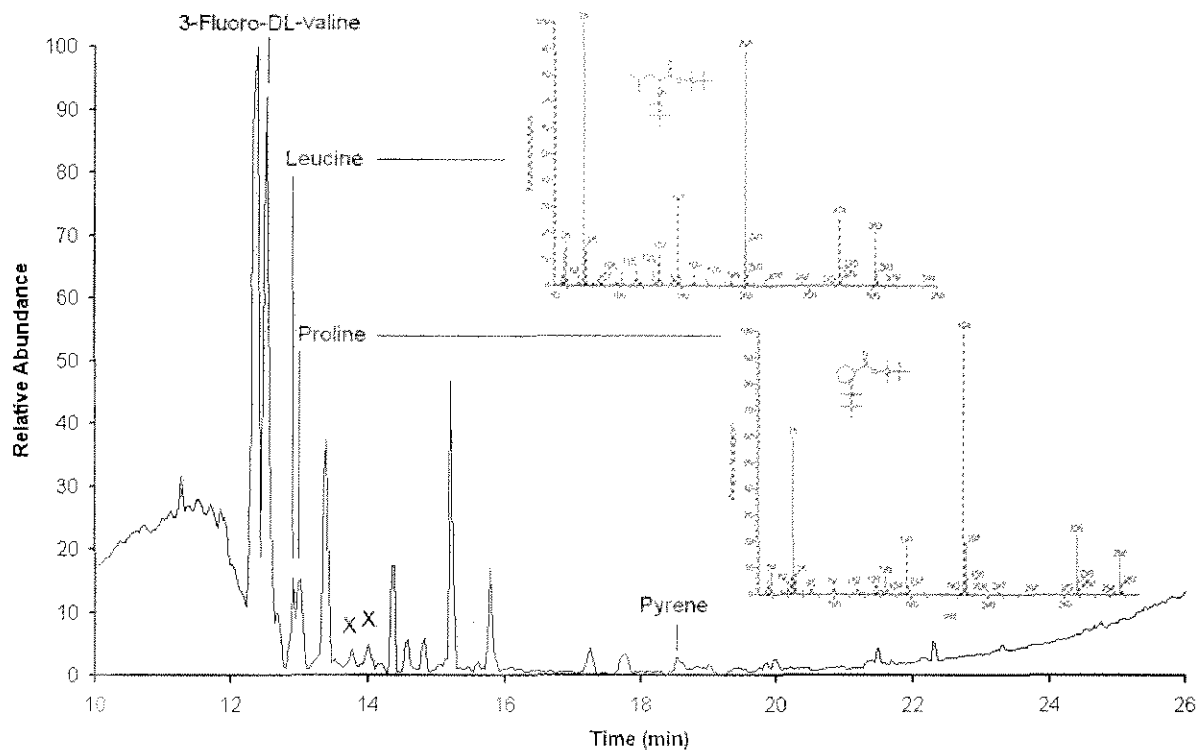


1  
2 **Figure 7:** GCMS analyses of the hydrocarbon trap after extraction and derivatization of JSC  
3 Mars 1 at 300°C. The only compound that could be identified by mass fragmentation pattern in  
4 these samples was pyrene. Mass fragmentation pattern data for pyrene not shown.  
5



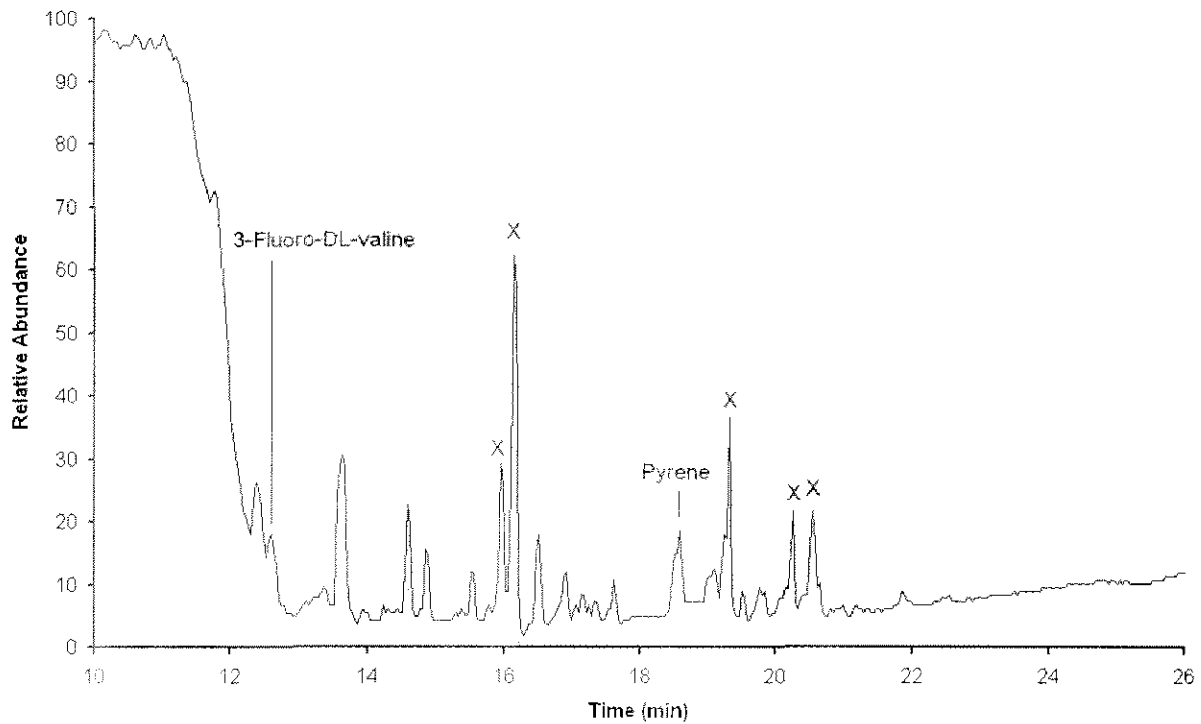
1  
2 **Figure 8:** GCMS analyses of the hydrocarbon trap after extraction and derivatization of the Rio  
3 Tinto (Rio Tinto-01) headwaters sample at 300°C. The only compound that could be identified  
4 by mass fragmentation pattern in these samples was pyrene. Mass fragmentation pattern data for  
5 pyrene not shown.

6



1  
 2 **Figure 9:** GCMS analysis of the hydrocarbon trap after MTBSTFA extraction and derivatization  
 3 of the carbonate-rich stromatolite (Carbonate-01) sample at 300°C. Right: mass fragmentation  
 4 pattern of corresponding to the MTBSTFA derivatives of leucine and proline. Mass  
 5 fragmentation pattern of pyrene and 3-FV not shown. The peaks with a “X” mark are  
 6 unidentified compounds not present in the procedural blank.

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 2 **Figure 9:** GCMS analyses of the hydrocarbon trap after extraction and derivatization of the  
 3 Murchison meteorite (USNM 6650.2) at 300°C. Mass fragmentation pattern of pyrene and 3-FV  
 4 not shown. The peaks with a “X” mark are unidentified compounds not present in the procedural  
 5 blank.

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7 **7. References**

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 15  
 16 Allen, C. C., Morris, R. V., Jager, K. M., Golden, D. C., Lindstrom, D. J., Lindstrom, M. M. and  
 17 Lockwood, J. P. (1998) Martian Regolith Simulant JSC Mars-1 *Lunar and Planetary*  
 18 *Institute Science Conference Abstracts*, **29**, 1690.  
 19 Benner, S. A., Devine, K. G., Matveeva, L. N. and Powell, D. H. (2000) The missing organic  
 20 molecules on Mars *PNAS*, **97**, 2425-2430.  
 21 Bibring, J.-P., Langevin, Y., Mustard, J. F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B.,  
 22 Mangold, N., Pinet, P. and Forget, F. (2006) Global Mineralogical and Aqueous Mars  
 23 History Derived from OMEGA/Mars Express Data *Science*, **312**, 400-404.

- 1 Biemann, K., Oro, J., Toulmin, P., III, Orgel, L. E., Nier, A. O., Anderson, D. M., Flory, D.,  
2 Diaz, A. V., Rushneck, D. R. and Simmonds, P. G. (1976) Search for organic and volatile  
3 inorganic compounds in two surface samples from the Chryse Planitia region of Mars  
4 *Science*, **194**, 72-76.
- 5 Biemann, K., Oro, J., Toulmin, P., Orgel, L. E., Nier, A. O., Anderson, D. M., Simmonds, P. G.,  
6 Flory, D., Diaz, A. V., Rushneck, D. R., Biller, J. E. and Lafleur, L. (1977) The search  
7 for organic substances and inorganic volatile compounds in the surface of Mars *Journal*  
8 *of Geophysical Research*, **82**, 4641-4658.
- 9 Bish, D. L. and Post, J. E. (1993) Quantitative Mineralogical Analysis Using the Rietveld Full-  
10 Pattern Fitting Method *American Mineralogist*, **78**, 932-940.
- 11 Blake, D. F., Vaniman, D., Anderson, R., Bish, D., Chipera, S., Chemtob, S., Crisp, J.,  
12 Desmarais, D. J., Downs, R., Farmer, J., Feldman, S., Gailhanou, M., Ming, D., Morris,  
13 R., Stolper, E., Sarrazin, P., Treiman, A. and Yen, A. (2010) In *Lunar and Planetary*  
14 *Institute Science Conference Abstracts*, Vol. 41, pp. 1898.
- 15 Botta, O. and Bada, J. L. (2002) Extraterrestrial Organic Compounds in Meteorites *Surveys in*  
16 *Geophysics*, **23**, 411-467.
- 17 Boynton, W. V., Ming, D. W., Sutter, B., Arvidson, R. E., Hoffman, J., Niles, P. B., Smith, P.  
18 and Team, P. S. (2009) Evidence for Calcium Carbonate at the Phoenix Landing Site  
19 *Lunar and Planetary Institute Science Conference Abstracts*, **40**, 2434.
- 20 Buch, A., Sternberg, R., Szopa, C., Freissinet, C., Garnier, C., Bekri, E. J., Rodier, C., Navarro-  
21 Gonzalez, R., Raulin, F., Cabane, M., Stambouli, M., Glavin, D. P. and Mahaffy, P. R.  
22 (2009) Development of a gas chromatography compatible Sample Processing System  
23 (SPS) for the in-situ analysis of refractory organic matter in martian soil: preliminary  
24 results *Advances in Space Research*, **43**, 143-151.
- 25 Cabane, M., Coll, P., Szopa, C., Israel, G., Raulin, F., Sternberg, R., Mahaffy, P., Person, A.,  
26 Rodier, C., Navarro-Gonzalez, R., Niemann, H., Harpold, D. and Brinckerhoff, W.  
27 (2004) Did life exist on Mars? Search for organic and inorganic signatures, one of the  
28 goals for "SAM" (sample analysis at Mars) *Advances in Space Research*, **33**, 2240-2245.
- 29 Cao, X.-L. and Hewitt, C. N. (1992) Trapping efficiencies of capillary cold traps for C<sub>2</sub>-C<sub>10</sub>  
30 hydrocarbons *Journal of Chromatography A*, **627**, 219-226.
- 31 Chipera, S. J. and Bish, D. L. (2002) FULLPAT: a full-pattern quantitative analysis program for  
32 X-ray powder diffraction using measured and calculated patterns *Journal of Applied*  
33 *Crystallography*, **35**, 744-749.
- 
- 34 Chun, S. F. S., Pang, K. D. and Cutts, J. A. (1978) Photocatalytic oxidation of organic  
35 compounds on Mars *Nature*, **274**, 875-876.
- 36 Chyba, C. F. and Sagan, C. (1992) Endogenous production, exogenous delivery, and impact-  
37 shock synthesis of organic molecules: an inventory for the origins of life *Nature*, **355**,  
38 125-132.
- 39 Clancy, R. T., Sandor, B. J. and Moriarty-Schieven, G. H. (2004) A measurement of the 362  
40 GHz absorption line of Mars atmospheric H<sub>2</sub>O<sub>2</sub> *Icarus*, **168**, 116-121.
- 41 Clark, B. C., Baird, A. K., Weldon, R. J., Tsusaki, D. M., Schnabel, L. and Candelaria, M. P.  
42 (1982) Chemical composition of Martian fines *Journal of Geophysical Research*, **87**,  
43 10059-10067.
- 44 Cottin, H., Gazeau, M. C. and Raulin, F. (1999) Cometary organic chemistry: a review from  
45 observations, numerical and experimental simulations *Planetary and Space Science*, **47**,  
46 1141-1162.

- 1 Cronin, J. R. and Chang, S. (1993) Organic matter in meteorites: molecular and isotopic analyses  
2 of the Murchison meteorite. *The Chemistry of Life's Origins*, 209-258.
- 3 Cronin, J. R., Pizzarello, S., Epstein, S. and Krishnamurthy, R. V. (1993) Molecular and isotopic  
4 analyses of the hydroxy acids, dicarboxylic acids, and hydroxydicarboxylic acids of the  
5 Murchison meteorite *Geochimica et Cosmochimica Acta*, **57**, 4745-4752.
- 6 Dartnell, L. R., Desorgher, L., Ward, J. M. and Coates, A. J. (2007) Modelling the surface and  
7 subsurface Martian radiation environment: Implications for astrobiology *Geophysical  
8 Research Letters*, **34**, 02207.
- 9 Ehlmann, B. L., Mustard, J. F., Murchie, S. L., Poulet, F., Bishop, J. L., Brown, A. J., Calvin, W.  
10 M., Clark, R. N., Des Marais, D. J., Milliken, R. E., Roach, L. H., Roush, T. L., Swayze,  
11 G. A. and Wray, J. J. (2008) Orbital Identification of Carbonate-Bearing Rocks on Mars  
12 *Science*, **322**, 1828-.
- 13 Encrenaz, T., Bézard, B., Greathouse, T. K., Richter, M. J., Lacy, J. H., Atreya, S. K., Wong, A.  
14 S., Lebonnois, S., Lefèvre, F. and Forget, F. (2004) Hydrogen peroxide on Mars:  
15 evidence for spatial and seasonal variations *Icarus*, **170**, 424-429.
- 16 Fernandez-Remolar, D., Gomez-Elvira, J., Gomez, F., Sebastian, E., Martiin, J., Manfredi, J. A.,  
17 Torres, J., Kesler, C. G. and Amils, R. (2004) The Tinto River, an extreme acidic  
18 environment under control of iron, as an analog of the Terra Meridiani hematite site of  
19 Mars *Planetary and Space Science*, **52**, 239-248.
- 20 Fernández-Remolar, D. C., Morris, R. V., Gruener, J. E., Amils, R. and Knoll, A. H. (2005) The  
21 Río Tinto Basin, Spain: Mineralogy, sedimentary geobiology, and implications for  
22 interpretation of outcrop rocks at Meridiani Planum, Mars *Earth and Planetary Science  
23 Letters, Sedimentary Geology at Meridiani Planum, Mars*, **240**, 149-167.
- 24 Flynn, G. J. and McKay, D. S. (1990) An assessment of the meteoritic contribution to the  
25 Martian soil *Journal of Geophysical Research*, **95**, 14497-14509.
- 26 Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N. and Giuranna, M. (2004) Detection of  
27 Methane in the Atmosphere of Mars *Science*, **306**, 1758-1761.
- 28 Garry, J. R. C., Loes Ten Kate, I., Martins, Z., Nånberg, P. and Ehrenfreund, P. (2006)  
29 Analysis and survival of amino acids in Martian regolith analogs *Meteoritics and  
30 Planetary Science*, **41**, 391-405.
- 31 Geffroy-Rodier, C., Grasset, L., Sternberg, R., Buch, A. and Amblès, A. (2009)  
32 Thermochemolysis in search for organics in extraterrestrial environments *Journal of  
33 Analytical and Applied Pyrolysis*, **85**, 454-459.
- 34 Glavin, D. P., Schubert, M., Botta, O., Kminek, G. and Bada, J. L. (2001) Detecting pyrolysis  
35 products from bacteria on Mars *Earth and Planetary Science Letters*, **185**, 1-5.
- 36 Goesmann, F., Rosenbauer, H., Roll, R., Szopa, C., Raulin, F., Sternberg, R., Israel, G.,  
37 Meierhenrich, U., Thiemann, W. and Muñoz-Caro, G. (2007) Cosac, The Cometary  
38 Sampling and Composition Experiment on Philae *Space Science Reviews*, **128**, 257-280.
- 39 González-Foril, E., Gómez, F., Rodríguez, N., Fernández-Remolar, D., Zuluaga, J., Marín, I. and  
40 Amils, R. (2003) Geomicrobiology of the Tinto River, a model of interest for  
41 biohydrometallurgy *Hydrometallurgy Biohydrometallurgy: Fundamentals, Technology  
42 and Sustainable Development*, **71**, 301-309.
- 43 Hecht, M. H., Catling, D. C., Clark, B. C., Deflores, L., Gospodinova, K., Kapit, J., Kounaves, S.  
44 P., Ming, D. W., Quinn, R. C., West, S. J. and Young, S. M. M. (2009) In *Lunar and  
45 Planetary Institute Science Conference Abstracts*, Vol. 40, pp. 2420.

- 1 Klingelhöfer, G., Morris, R. V., Bernhardt, B., Schröder, C., Rodionov, D. S., de Souza, P. A.,  
2 Yen, A., Gellert, R., Evlanov, E. N., Zubkov, B., Foh, J., Bonnes, U., Kankleit, E.,  
3 Gütlich, P., Ming, D. W., Renz, F., Wdowiak, T., Squyres, S. W. and Arvidson, R. E.  
4 (2004) Jarosite and Hematite at Meridiani Planum from Opportunity's Mössbauer  
5 Spectrometer *Science*, **306**, 1740-1745.
- 6 Knapp, D. R. (1979) Handbook of Analytical Derivatization Reaction *Wiley, New York*.
- 7 Krasnopolsky, V. A., Maillard, J. P. and Owen, T. C. (2004) Detection of methane in the martian  
8 atmosphere: evidence for life? *Icarus*, **172**, 537-547.
- 9 Laurretta, D. S. and McSween, H. Y., Jr. (2006) *Meteorites and the Early Solar System II*.
- 10 Mahaffy, P. R., Glavin, D. P., Eigenbrode, J. L., Franz, H., Stern, J., Harpold, D. N.,  
11 Brinckerhoff, W. B., Cabane, M., Coll, P., Szopa, C., Conrad, P. G., Webster, C. R. and  
12 Team, S. (2010) In *Lunar and Planetary Institute Science Conference Abstracts*, Vol. 41,  
13 pp. 2130.
- 14 Meierhenrich, U. J., Thiemann, W. H.-P., Muñoz Caro, G. M., Schutte, W. A. and Greenberg,  
15 J. M. (2001) Simulated cometary matter as a test for enantiomer separating  
16 chromatography for use on comet 46P/wirtanen *Advances in Space Research*, **27**, 329-  
17 334.
- 18 Meunier, D., Sternberg, R., Mettetal, F., Buch, A., Coscia, D., Szopa, C., Rodier, C., Coll, P.,  
19 Cabanec, M. and Raulin, F. (2007) A laboratory pilot for in situ analysis of refractory  
20 organic matter in Martian soil by gas chromatography mass spectrometry *Advances in*  
21 *Space Research*, **39**, 337-344.
- 22 Morris, R. V., Golden, D. C., Bell III, J. F., Lauer Jr., H. V. and Adams, J. B. (1993) Pigmenting  
23 agents in martian soils: Inferences from spectral, Mössbauer, and magnetic properties of  
24 nanophase and other iron oxides in Hawaiian palagonitic soil PN-9 *Geochimica et*  
25 *Cosmochimica Acta*, **57**, 4597-4609.
- 26 Morrison, D. (2001) The NASA Astrobiology Program *Astrobiology*, **1**, 3-13.
- 27 Mumma, M. J., Villanueva, G. L., Novak, R. E., Hewagama, T., Bonev, B. P., DiSanti, M. A.,  
28 Mandell, A. M. and Smith, M. D. (2009) Strong Release of Methane on Mars in Northern  
29 Summer 2003 *Science*, **323**, 1041-.
- 30 Navarro-Gonzalez, R., Navarro, K. F., Rosa, J. d. I., Iniguez, E., Molina, P., Miranda, L. D.,  
31 Morales, P., Cienfuegos, E., Coll, P., Raulin, F., Amils, R. and McKay, C. P. (2006) The  
32 limitations on organic detection in Mars-like soils by thermal volatilization-gas  
33 chromatography-MS and their implications for the Viking results *PNAS*, **103**, 16089-  
34 16094.
- 35 Navarro-Gonzalez, R., Vargas, E., de la Rosa, J., Raga, A. C. and McKay, C. P. (2010)  
36 Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on  
37 Mars *Journal of Geophysical Research (Planets)*, **115**, 12010.
- 38 Oro, J. and Holzer, G. (1979) The Photolytic Degradation and Oxidation of Organic Compounds  
39 Under Simulated Martian Conditions *Journal of Molecular Evolution*, **14**, 153-160.
- 40 Pang, K. D., Chun, S. F. S., Ajello, J. M., Nansheng, Z. and Minji, L. (1982) Organic and  
41 Inorganic Interpretations of the Martian Ultraviolet Infrared Reflectance Spectrum  
42 *Nature*, **295**, 43.
- 43 Perko, H. A., Nelson, J. D. and Green, J. R. (2006) Mars soil mechanical properties and  
44 suitability of mars soil simulants *Journal of Aerospace Engineering*, **19**, 169-176.



- 1 Pizzarello, S., Cooper, G. W. and Flynn, G. J. (2006) The Nature and Distribution of the Organic  
2 Material in Carbonaceous Chondrites and Interplanetary Dust Particles *Meteorites and*  
3 *the Early Solar System II*, 625-651.
- 4 Smith, N. K., Stewart, R. C., Osborn, A. G. and Scott, D. W. (1980) Pyrene: vapor pressure,  
5 enthalpy of combustion, and chemical thermodynamic properties *J. Chem.*  
6 *Thermodynamics*, **12**, 919-926.
- 7 Squyres, S. W., Arvidson, R. E., Bell, J. F., Brückner, J., Cabrol, N. A., Calvin, W., Carr, M. H.,  
8 Christensen, P. R., Clark, B. C., Crumpler, L., Des Marais, D. J., d'Uston, C., Economou,  
9 T., Farmer, J., Farrand, W., Folkner, W., Golombek, M., Gorevan, S., Grant, J. A.,  
10 Greeley, R., Grotzinger, J., Haskin, L., Herkenhoff, K. E., Hviid, S., Johnson, J.,  
11 Klingelhöfer, G., Knoll, A. H., Landis, G., Lemmon, M., Li, R., Madsen, M. B., Malin,  
12 M. C., McLennan, S. M., McSween, H. Y., Ming, D. W., Moersch, J., Morris, R. V.,  
13 Parker, T., Rice, J. W., Richter, L., Rieder, R., Sims, M., Smith, M., Smith, P.,  
14 Soderblom, L. A., Sullivan, R., Wänke, H., Wdowiak, T., Wolff, M. and Yen, A. (2004)  
15 The Opportunity Rover's Athena Science Investigation at Meridiani Planum, Mars  
16 *Science*, **306**, 1698-1703.
- 17 Stalport, F., Coll, P., Szopa, C., Cottin, H. and Raulin, F. (2009) Investigating the Photostability  
18 of Carboxylic Acids Exposed to Mars Surface Ultraviolet Radiation Conditions  
19 *Astrobiology*, **9**, 543-549.
- 20 Stalport, F., Coll, P., Szopa, C. and Raulin, F. (2008) Search for organic molecules at the Mars  
21 surface: The "Martian Organic Material Irradiation and Evolution" (MOMIE) project  
22 *Advances in Space Research*, **42**, 2014-2018.
- 23 Stalport, F., Guan, Y. Y., Coll, P., Szopa, C., Macari, F. d. r., Raulin, F. o., Chaput, D. and  
24 Cottin, H. (2010) UVolution, a Photochemistry Experiment in Low Earth Orbit:  
25 Investigation of the Photostability of Carboxylic Acids Exposed to Mars Surface UV  
26 Radiation Conditions *Astrobiology*, **10**, 449-461.
- 27 Stoker, C. R. and Bullock, M. A. (1997) Organic degradation under simulated Martian  
28 conditions *Journal of Geophysical Research*, **102**, 10881-10888.
- 29 Sutter, B., Dalton, J. B., Ewing, S. A., Amundson, R. and McKay, C. P. (2007) Terrestrial  
30 analogs for interpretation of infrared spectra from the Martian surface and subsurface:  
31 Sulfate, nitrate, carbonate, and phyllosilicate-bearing Atacama Desert soils *Journal of*  
32 *Geophysical Research (Biogeosciences)*, **112**.
- 33 Szopa, C., Sternberg, R., Raulin, F. and Rosenbauer, H. (2003) What can we expect from the in  
34 situ chemical investigation of a cometary nucleus by gas chromatography: First results  
35 from laboratory studies *Planetary and Space Science*, **51**, 863-877.
- 36 Ten Kate, I. L., Garry, J. R. C., Peeters, Z., Quinn, R., Foing, B. and Ehrenfreund, P. (2005)  
37 Amino acid photostability on the Martian surface *Meteoritics and Planetary Science*, **40**,  
38 1185.
- 39 Yen, A. S., Kim, S. S., Hecht, M. H., Frant, M. S. and Murray, B. (2000) Evidence That the  
40 Reactivity of the Martian Soil Is Due to Superoxide Ions *Science*, **289**, 1909-1912.

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