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**INVESTIGATING THE ORIGIN OF CHLOROHYDROCARBONS DETECTED BY THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT AT ROCKNEST.** D. Glavin[1], D. Archer[2], A. Brunner[1], A. Buch[3], M. Cabane[4], P. Coll[5], P. Conrad[1], D. Coscia[4], J. Dworkin[1], J. Eigenbrode[1], C. Freissinet[1], P. Mahaffy[1], M. Martin[1,6], C. McKay[7], K. Miller[8], D. Ming[2], R. Navarro-González[9], A. Steele[10], R. E. Summons[8], B. Sutter[2], C. Szopa[4], S. Teinturier[4], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771 (daniel.p.glavin@nasa.gov), [2]NASA Johnson Space Center, Houston TX 77058, [3]Ecole Centrale Paris, 92295 Chatenay-Malabry, France, [4]LATMOS, Univ. Pierre et Marie Curie, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, [5]LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, [6]Catholic University of America, Washington DC 20064, [7]NASA Ames Research Center, Moffett Field, CA 94035, [8]Massachusetts Institute of Technology, Cambridge, MA 02139, [9]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [10]Carnegie Institution of Washington, Washington, DC 20015.

**Introduction:** The search for organic compounds on Mars, including molecules of either abiotic or biological origin is one of the key goals of the Mars Science Laboratory (MSL) mission. Previously the Viking and Phoenix Lander missions searched for organic compounds, but did not find any definitive evidence of martian organic material in the soils. The Viking pyrolysis gas chromatography mass spectrometry (GCMS) instruments did not detect any organic compounds of martian or exogenous origin above a level of a few parts-per-billion (ppb) in the near surface regolith at either landing site [1]. Viking did detect chloromethane and dichloromethane at pmol levels (up to 40 ppb) after heating the soil samples up to 500°C (Table 1), although it was originally argued that the chlorohydrocarbons were derived from cleaning solvents used on the instrument hardware, and not from the soil samples themselves [1]. More recently, it was suggested that the chlorohydrocarbons detected by Viking may have been formed by oxidation of indigenous organic matter during pyrolysis of the soil in the presence of perchlorates [2]. Although it is unknown if the Viking soils contained perchlorates, Phoenix did reveal relatively high concentrations (~ 0.6 wt%) of perchlorate salt in the icy regolith [3], therefore, it is possible that the chlorohydrocarbons detected by Viking were produced, at least partially, during the experiments [2,4].

The Sample Analysis at Mars (SAM) instrument suite on MSL analyzed the organic composition of the soil at Rocknest in Gale Crater using a combination of pyrolysis evolved gas analysis (EGA) and GCMS. One empty cup procedural blank followed by multiple EGA-GCMS analyses of the Rocknest soil were carried out. Here we will discuss the results from these SAM measurements at Rocknest and the steps taken to determine the source of the chlorohydrocarbons.

**SAM Measurement Protocol:** Prior to the analysis of the soil, a procedural blank run using an empty quartz cup was carried out to characterize the background of the SAM instrument. A quartz cup was sealed inside the pyrolysis oven and heated to ~835°C at a rate of 35°C/min under He carrier gas flow. A small fraction of the gas released from the cup was measured directly by electron impact quadrupole mass spectrometry (QMS mass range 2-535 Da). A larger fraction of the gas was sent to a hydrocarbon trap (Silica beads/Tenax TA/Carbosieve G) at an initial temperature of 5°C. The trap was subsequently heated to a temperature of ~300°C for 4 min under He flow and the volatiles released were sent to the Tenax TA injection trap on the GC column. Trapped compounds were separated on the MXT-CLP column (30 m x 0.25 mm I.D.) set at an initial temperature of 50°C followed by heating to 220°C at 10°C/min. Eluting compounds were detected by thermal conductivity [5] and by the QMS using a smart scanning mass algorithm and identified by their retention time and comparison of the mass fragmentation pattern to the NIST11 library.

A sample of the Rocknest soil (scoop #5) collected by Curiosity's solid sample acquisition and handling system called CHIMRA was sieved (< 150 μm fraction), portioned (< 76 $mm^3$), and a single portion delivered to a preconditioned SAM quartz cup *via* the SAM solid sample inlet tube. The mass estimates of the Rocknest portions delivered to SAM remain uncertain [6]. EGA-GCMS analyses of the individual Rocknest soil portions were performed using conditions similar to those that were used for the blank.

**SAM Pyrolysis GCMS Results:** Several chloromethanes including chloromethane ($CH_3Cl$), dichloromethane ($CH_2Cl_2$), and trichloromethane ($CHCl_3$) were detected by SAM GCMS above blank levels (Fig. 1). Individual *m/z* values in counts per second comprising each peak were Gaussian fitted in IGOR [7] and each compound was identified by the mass fragmentation pattern generated from the peak fits (Fig. 1, inset). The total abundance of each compound was estimated by calculating the sum of the area of each *m/z* value and comparing the total area to known concentrations of hexane that were analyzed by GCMS on the SAM flight instrument during pre-flight calibration. Differences in the relative molar response of hexane and the chloromethanes were accounted for.

The abundances of the chloromethanes detected by SAM in the Rocknest soil analyses #1 and #2 ranged from ~0.02 to 2.4 nmol and were all well above blank levels (Table 1). These abundances are much higher than the pmol values for chloromethane and dichloromethane previously measured by Viking (Table 1). The low levels of chloromethanes measured in the Rocknest soil#3 sample is due to the fact that the GCMS measured the high sample temperature cut (533-822°C) during a time when no chloromethanes were released from the sample based on EGA.

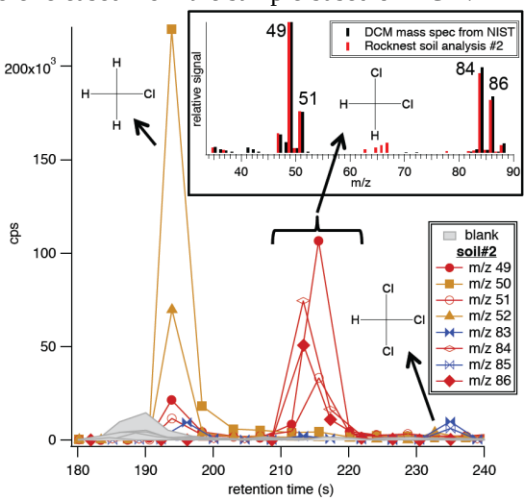


**Figure 1.** SAM GCMS analysis #2 of the Rocknest soil showing the peaks corresponding to $CH_3Cl$, $CH_2Cl_2$, and $CHCl_3$. The compounds were identified by retention time and comparison of the mass spectra (inset) to the NIST library and were present well above blank levels.

**Discussion:** There are three possible explanations for the source of chlorohydrocarbons detected by SAM acting either individually or together in unknown proportions including: (1) reaction of martian soil Cl with terrestrial organics from the sample handling chain during pyrolysis and/or chlorohydrocarbons in the sample handling chain, (2) reaction of martian soil Cl with terrestrial organics in SAM during pyrolysis and/or chlorohydrocarbons in SAM, and (3) reaction of martian soil Cl with martian organics during pyrolysis and/or martian chlorohydrocarbons in the soil. The possible detection of perchlorate [6,8] and the correlation between the evolution of $O_2$ and the production of chloromethanes at cup temperatures above 200°C measured in SAM EGA mode [9], strongly suggest that these chlorohydrocarbons are being produced during combustion. The lack of any chlorohydrocarbons in the SAM procedural blank run indicates that the chlorohydrocarbons themselves are not contaminants from the SAM instrument. It is possible that the chlorohydrocarbons were derived from contamination in the sample handling chain, although it is important to note that CHIMRA was scrubbed with the soil multiple times prior to the first SAM soil analysis and the surfaces were found to be organically clean prior to launch [9,10]. Analysis of the MSL organic check material is needed to further assess this possibility. Terrestrial *N*-methyl-*N*-(*t*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) and associated reaction products from the SAM wet chemistry experiment were identified in both the blank and soil EGA-GCMS analyses [11,12]. Based on laboratory pyrolysis GCMS experiments, combustion of MTBSTFA during SAM pyrolysis and reaction with martian Cl can explain the presence of the chloromethanes and a chloromethylpropene also detected by SAM [9]. Furthermore, these are the two chlorohydrocarbon classes expected by MTBSTFA combustion. Thus, at this time, while MTBSTFA contamination can explain all of the chlorohydrocarbons observed, we cannot exclude the possibility that traces of martian organics contributed to the chloromethanes measured by SAM.

**Table 1.** Comparison of the abundances of chloromethanes detected by the Viking and SAM GCMS instruments.

| Sample | Temp | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ |
|---|---|---|---|---|
| ***Viking (VL1)[a]*** | | | | |
| Blank | 500°C | ND | ND | ND |
| Soil#1 | 200, 500°C | 30 pmol | ND | ND |
| Soil#2 | 200,350,500°C | ND | ND | ND |
| ***Viking (VL2)[a]*** | | | | |
| Blank | 500°C | ND | ND | ND |
| Soil#1 | 200,350,500°C | ND | 2 - 16 pmol | ND |
| Soil#2 | 200,350,500°C | ND | 0.05 - 47 pmol | ND |
| ***MSL-SAM[b]*** | | | | |
| Blank | 144-533°C | 0.2 ± 0.1 nmol | < 0.03 nmol | < 0.01 nmol |
| Soil#1 | 144-533°C | 1.3 ± 0.5 nmol | 0.8 ± 0.3 nmol | 0.02 ± 0.01 nmol |
| Soil#2 | 98-425°C | 2.4 ± 0.8 nmol | 0.9 ± 0.3 nmol | 0.04 ± 0.01 nmol |
| Soil#3 | 533-822°C | 0.2 ± 0.1 nmol | 0.04 ± 0.01 nmol | < 0.01 nmol |

[a]Viking data in pmol calculated from [1] assuming 100 mg samples; ND = not determined; [b]SAM cup temperature range indicates temperature cut where volatiles were collected on the hydrocarbon trap for GCMS analysis. SAM Soil#1 and Soil#2 abundances in nmol were corrected for the gas fraction sent to the hydrocarbon trap using EGA data. Errors determined by the standard deviation of the average of five separate hexane calibration runs on SAM.

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