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Investigating organic molecules in MSL's SAM Wet Chemistry experiments using *de novo* mass spectrometry interpretation. L. Chou^{1,2}, C. Malespin¹, A. McAdam¹, D. Glavin¹, M. Millan^{3,2}, C. Freissinet³, C. Szopa³, A.J. Williams⁴, J. Lewis¹, J. Eigenbrode¹, S. Teinturier^{1,5}, J. Y. Bonnet⁶, B. Prats^{1,7}, W. Brinckerhoff¹, S. S. Johnson², and P. Mahaffy¹. ¹NASA Goddard Space Flight Center, Planetary Environments Lab (luoth.chou@nasa.gov; 8800 Greenbelt Rd, Greenbelt, MD 20771), ²Georgetown University, ³LATMOS/CNRS, ⁴University of Florida, ⁵Goddard Earth Science Technology Research, ⁶Telespazio France, ⁷eINFORMe, Inc.

Introduction: For the past decade, the Sample Analysis at Mars (SAM) instrument suite onboard the Mars Science Laboratory (MSL) *Curiosity* Rover has served as a critical payload for characterizing the chemical composition of Mars, helping to elucidate its past and present geochemical environments and habitability [1,2]. The SAM instrument suite includes evolved gas analysis (EGA) and pyrolysis-gas chromatography (pyro-GC), coupled to mass spectrometry (MS), all of which has been used to conduct *in situ* chemical characterization of Martian sediments. While SAM can detect a wide range of volatile organic compounds via thermal volatilization, it was also designed to extract and analyze less volatile and more polar organic molecules by derivatization using two wet chemistry reagents: N-methyl-N-(tert-butyl-dimethylsilyl) trifluoroacetamide in dimethyl formamide (MTBSTFA:DMF 4:1) and tetramethylammonium hydroxide (TMAH) in methanol [3]. Polar compounds such as amino acids, fatty acids, or nucleobases are some of the important astrobiological targets that can be revealed by SAM wet chemistry experiments. To date, SAM has conducted several MTBSTFA derivatization experiments on Mars, three of which were full cup derivatization experiments, and three others were "opportunistic derivatization" (OD) experiments using MTBSTFA vapor that leaked into SAM's Sample Manipulation System earlier in the mission [4]. Those experiments were conducted on samples *Curiosity* obtained from Yellowknife Bay (sample: Cumberland OD x2), Bagnold Dunes (Ogunquit Beach), Vera Rubin ridge (Rock Hall OD), and the Glen Torridon region (Glen Etive and Mary Anning) of Gale crater. In those MTBSTFA wet chemistry experiments, several high mass and high abundance compounds were tentatively identified based on mass fragmentation patterns and supporting evidence from SAM-like pyro-GC-MS laboratory analyses. These compounds likely resulted from the derivatization reaction of possible MTBSTFA byproducts (e.g., silanol) with MTBSTFA itself (i.e., SAM-internal species), but may also include potentially F-bearing mineral species on Mars. We investigate the possible formation pathways of these compounds and discuss the implications of their findings for future MTBSTFA wet chemistry experiments (four remaining cups) as MSL traverses the sulfate-bearing region of Gale crater in the next decade.

Methods: Sample delivery. The SAM wet chemistry experiments involve a series of analytical sequences that is further detailed in [5]. Briefly, the SAM gas processing system (GPS) is conditioned prior to the EGA/GC-MS analysis. The metal cup containing MTBSTFA:DMF is then punctured and moved to the SAM inlet to receive powdered sample from the rover. The cup is then moved to the SAM oven and incubated at 100°C for 100 s prior to analysis.

Pyrolysis EGA and GC-MS: The samples are pyrolyzed starting at ambient temperature to ~900°C at 35°C/min while SAM subsamples ("sniffs") the evolved gas with different cadences (cycles of 5-20 seconds) as the oven heats up to avoid oversaturating the hydrocarbon (HC) and injection traps, as well as the GC columns with MTBSTFA. The HC trap itself is kept at 80°C as the EGA temperature approaches ~250°C to further allow for MTBSTFA and some of its byproducts to bypass the trap, and then cooled to 0°C at higher EGA temperatures (>250°C) to collect higher molecular weight molecules, including derivatized products. After pyrolysis, the HC trap is flash heated to 320°C and the compounds sent into one, or split into two of the six GC columns for separation and analysis by MS. The GC temperature program is slightly different for various runs and can be further found in [5].

Laboratory pyrolysis-GC-MS: Laboratory experiments were conducted to aid in the identification of compounds found in the SAM data. For this study, we pyrolyzed 10 µL of MTBSTFA that was deposited on ~1 mg of quartz wool in a quartz cup to understand the potential byproducts of MTBSTFA under SAM-like conditions. The pyrolysis ramp rate was 35°C/min, starting at 100°C for 100s, ramping to 900°C and held isothermally for 2 mins. A SAM-like HC trap was utilized to mimic SAM sample processing, which was kept cooled at -10°C, and once pyrolysis completed, compounds were desorbed at 300°C for 2 minutes prior to introduction into the GC. A SAM-like GC column (RXT-CLP, similar to GC5) was used for this analysis. The laboratory MS had a mass range of 2-535 Da, like the mass range for the SAM quadrupole mass spectrometer (QMS).

Results: In nearly all the SAM MTBSTFA experiments (including OD experiments), MTBSTFA byproducts such as trifluoro-N-methylacetamide (TFMA), trifluoroacetamide (TFA), mono-silylated water (MSW), and bi-silylated water (BSW), etc., were observed. Several compounds were also present that

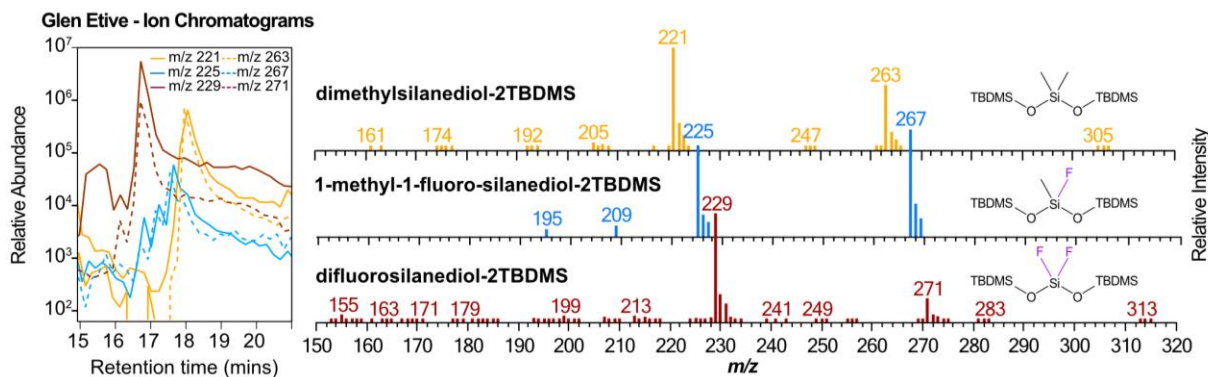


Figure 1: (Left) Ion chromatograms of the Glen Etive MTBSTFA wet chemistry experiment showing ion traces for major masses in the 3 compounds identified in this study. (Right) Respective mass spectra of those compounds and their identification.

contained mass ions with very high signals relative to other MTBSTFA byproducts. The mass spectra of these compounds show a common neutral loss of 42 Da, indicating that they may contain similar molecular moieties. Those compounds, with pairs of masses 221/263, 225/267, and 229/271, all show similar abundance distributions patterns that differ from each other by 4 D (Figure 1). Based on numerous previous studies of mass fragmentation patterns of MTBSTFA derivatized molecules (*-t*-BDMS products) [6] and data from our laboratory experiments (not shown here), we tentatively identify these compounds as dimethylsilanediol-2*t*-BDMS, 1-methyl-1-fluoro-silanediol-2*t*-BDMS, and difluoro-silanediol-2*t*-BDMS. The 4 Da differences indicate substitutions of methyl groups with fluorine.

Discussion: The three compounds identified were doubly-derivatized on the -OH groups by MTBSTFA to form the respective -2*t*-BDMS derivatives, suggesting that the wet chemistry experiments conducted on SAM proceeded as expected (also see [5]). Dimethylsilanediol is a silanol that is a common monomer of the gas chromatograph stationary phase, (poly)dimethyl-siloxane, which is a component of MXT[®] 20 WCOT (GC1), MTX[®] 5 WCOT (GC2), and MXT[®] CLP (GC5). Therefore, the most logical source of dimethylsilanediol is likely the GC column of the SAM instrument. However, it cannot be completely ruled out that the compounds with *m/z* 221 and *m/z* 229 derived from Mars since they were also present (at low abundances) in the EGA pyrogram, and materials analyzed by EGA-MS do not pass through the GC columns. Other sources of dimethylsilanediol could potentially be silica in the samples, though the methylation mechanism is unknown.

The fluorination process of dimethylsilanediol to form difluorosilanediol prior to derivatization is still currently under investigation. One possible source of F is MTBSTFA that has been pyrolyzed to liberate F⁻ ions, which can then be stuck in the GPS of SAM, and further reacted with dimethylsilanediol during GC-MS

analysis. Another possibility is that F can derive directly from F-bearing minerals in Martian sediments.

Conclusion: The SAM wet chemistry experiments on the *Curiosity* Rover offer a great opportunity to observe and characterize non-volatile organics on Mars. However, the SAM instrument background convolutes our full interpretation of wet chemistry data. Nevertheless, *de novo* mass spectrometry interpretation can help elucidate the structure of organic molecules that may not be present in standard mass spectral libraries (e.g., NIST). In addition, SAM-like laboratory analyses are not only useful, but necessary, for optimizing future SAM wet chemistry experiments as well as in the pursuit of searching for organics on Mars.

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