LESSONS LEARNED FROM THE FULL CUP WET CHEMISTRY EXPERIMENT PERFORMED ON MARS WITH THE SAMPLE ANALYSIS AT MARS INSTRUMENT.

M. Millan[1,2], C. A. Malespin[1], C. Freissinet[3], D. P. Glavin[1], P. R. Mahaffy[1], A. Buch[4], C. Szopa[3,5], A. Srivastava[1], S. Teinturier[1,6], A. J. Williams[7,1], A. McAdam[1], D. Coscia[3], J. Eigenbrode[1], E. Raaen[1], J. Dworkin[1], R. Navarro-Gonzalez[8] and S. S. Johnson[2]. [1]NASA Goddard Space Flight Center, Greenbelt, MD, 20771 maeva.millan@nasa.gov, [2]Georgetown University, [3]Laboratoire Atmosphères, Milieux, Observations Spatiales (LATMOS), UVSQ, France, [4]Laboratoire de Genie des Procedes et Materiaux, CentraleSupelec, France, [5]Institut Universitaire de France, [6]Goddard Earth Science Technology and Research, Universities Space Research Association, [7]Dept. of Geological Sciences, University of Florida, [8]Universidad Nacional Autónoma de México

Introduction: The Curiosity Rover is ascending Mount Sharp, analyzing stratigraphic rock layers to find clues to Mars' environmental history and habitability [1]. The Sample Analysis at Mars (SAM) instrument suite onboard Curiosity includes a pyrolyzer coupled to a gas chromatograph-mass spectrometer (pyro-GCMS) mostly dedicated to the search for organic molecules on Mars. SAM is able to perform *in situ* molecular analysis of gases evolved from heating solid samples collected by Curiosity up to ~900°C. SAM can then detect, separate, and identify volatiles inorganic and organic compounds released from the gas phase of the solid samples.

SAM also carries nine sealed wet chemistry cups to allow for a new capability to be employed at Mars' surface, opening the possibility for a larger set of organics to be detected. Seven of the cups contain a 0.5 mL mixture of *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide and dimethylformamide (MTBSTFA:DMF 4:1) for derivatization and the two others contain tetramethylammonium hydroxide (TMAH), 25% in methanol mixture for thermochemolysis [2]. The cups also contain standards of organic molecules (36.2 nmol of 3-fluorovaline and 24.2 nmol of pyrene in the MTBSTFA cups) (Figure 1) for calibration and validation purposes.

The derivatization with MTBSTFA allows the detection and identification of complex, polar and/or refractory molecules. In this silylation method, the labile hydrogen of the targeted molecule is replaced by the MTBSTFA silyl group, transforming molecules into volatile derivatives easily amenable to GCMS analysis (Figure 1). Thus MTBSTFA reacts with organics of astrobiological interest—such as nucleobases, amino acids, carboxylic acids, and sugars—while preventing degradation of their chemical structure.

Early in the mission, one of the MTBSTFA cups inadvertently leaked into SAM. While the team was able to use the leaked vapors to complete an opportunistic derivatization experiment [3], none of the seven cups were punctured to perform a full-cup derivatization until December 2017, when the first full-cup wet chemistry experiment was completed on the Ogunquit Beach sand sample from the Bagnold dune field.

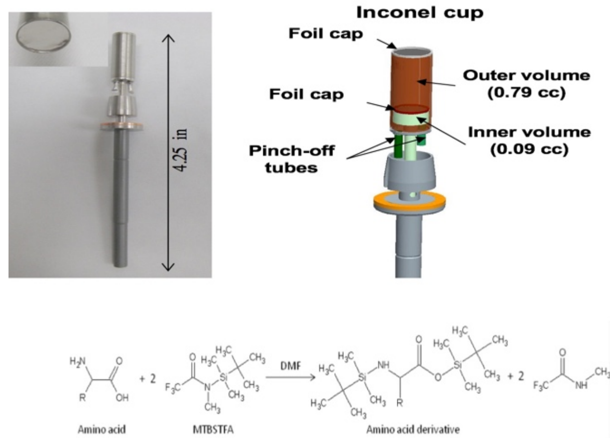

Figure 1. The MTBSTFA derivatization cup (top) and an example of the MTBSTFA reaction with an amino acid that displaces the labile hydrogens with a *tert*butyldimethylsilyl group to produce a volatile amino acid derivative (bottom).

Here we describe the results of this first derivatization experiment that includes the puncture of one of the MTBSTFA cups, detailing the lessons learned as well as ways to optimize future wet chemistry experiments that will soon be performed on Mars.

Experimental procedure: The SAM wet chemistry experiment was based on the "standard" SAM EGA/GCMS, divided into three sequential parts, occurring in one sol.

Part 1. Prep and background. The manifolds and pipes were heated and pumped out to clean SAM. The MS then took background readings of both the MS alone and of the manifolds prior to the introduction of MTBSTFA fluid/vapor and sample volatiles.

Part 2. Cup puncture and sample drop-off. Since, the MTBSTFA will slowly evaporate after the cup is punctured, it is important to heat the sample as quickly as possible after drop-off. Just prior to receiving the sample, the wet chemistry cup was punctured using two puncture needles (Figure 1). The cup was then moved to the inlet to accept a sample from Curiosity's arm and placed into the SAM oven for analysis.

Part 3. Pyrolysis EGA and GCMS of sample. The sample was pyrolyzed up to ~900°C at 35°C•min^{-1}. To prevent the saturation of the SAM hydrocarbon trap (HC) with MTBSTFA-DMF fluid, only a portion of the evolved gas was trapped for analysis while the remaining gas was vented out to the Mars' atmosphere. During the low temperature (< 250°C) portion of the pyrolysis step, the SAM HC trap was kept at 80°C. Laboratory experiments have shown that the MTBSTFA is not efficiently trapped at this temperature, preventing saturation and clogging of the traps and columns from the MTBSTFA, while still allowing complex derivatized organics to be collected. After most of the MTBSTFA has evaporated, the trap was cooled down to 0°C to trap evolved derivatized and non-derivatized molecules. The HC trap was then heated to 320°C to desorb trapped gases which were then split between two of the six SAM columns for GCMS analysis: Columns 1 (MXT-20) and 4 (Chirasil-Dex). The latter allows medium to high molecular weight compounds, including chiral molecules, to be analyzed and separated.

Summary of SAM results: EGA and GCMS of a the Ogunquit Beach scooped sample have been analyzed and the detailed results will be discussed in a forthcoming paper. Several compounds of interest represented by medium to high molecular masses were detected, including derivatized molecules as well as varying amounts of various MTBSTFA by-products, such as *N*-methyl-2,2,2-trifluoroacetamide (TFMA) and 1,3-bis(1,1-dimethylethyl)-1,1,3,3-tetramethyldisiloxanetetramethyldisiloxane (bi-silylated water), along with the whole MTBSTFA molecule. These results indicate that the derivatization reagent was in excess, as reactions clearly occurred and produced derivatized compounds. Data processing and laboratory experiments on martian analog samples are still ongoing to identify a subset of organics that have mass spectra missing from common MTBSTFA libraries and to further understand the type of environments where they can be found.

Optimization of future runs: Following this experiment on Mars, a series of laboratory experiments were conducted to improve the detection of derivatized organic molecules with SAM in future runs. Tests included the analysis of multiple organic mixtures (e.g. amino acids, carboxylic acids, etc.) under SAM-like operating conditions (e.g. temperature, helium flow) and varying the operating temperature of the GC columns. So far, these runs have shown that by measuring the signal of compounds that continue to elute while the column is cooling down, we can extend the effective range of heavy molecules that can be detected in comparison to previous SAM measurements (Figure 2). Laboratory experiments have also now shown that successive column cleanups after the sample GCMS experiment can release heavier compounds that may not have been released in the original experiment. Testing on the SAM testbed are ongoing to validate that this new approach will allow SAM to detect molecules that continue to elute, even after the column has stopped heating.

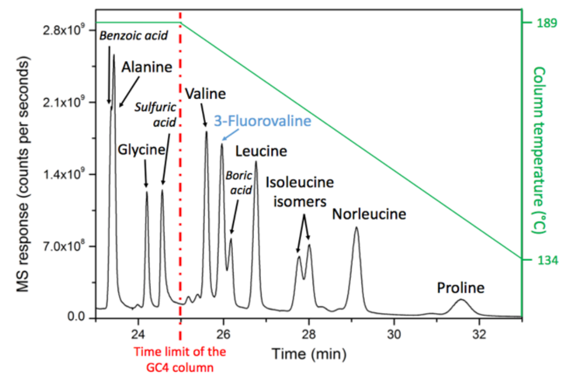

Figure 2. Gas chromatogram obtained with a spare GC4 column of a 22 amino acids standards mixture analyzed in the laboratory. Only alanine and glycine would be detectable within the current SAM-flight operating conditions used for the GC4 column on the SAM flight model instrument. However, this laboratory experiments shows that recording the signal while the temperature is cooling down on Mars could allow the detection of heavier molecules such as the amino acids targeted for this study.

As Curiosity just reached Glen Torridon (the 'Clay-Bearing Unit'), the SAM team is preparing to perform a new set of experiments. Laboratory experiments performed on terrestrial clay minerals suggest that clays may be a strong reservoir for organic molecules [4,5], thus representing a key target lithology for SAM. SAM activities in Glen Torridon will include an EGA/GCMS analysis, a new MTBSTFA derivatization experiment, potentially followed, depending on the results, by the first TMAH experiment to be performed on Mars, a run that may allow the detection of fatty acids biosignatures if they are present in the solid samples collected by the rover [4,5].

References: [1] Grotzinger, J.P., et al. (2013) *Sci Express 343*, 1242771-1242714. [2] Mahaffy P.R. et al. (2012) *Space Sci Rev*, 401-478. [3] Freissinet, C. et al. (2017) LPSC meeting [#2687]. [4] Millan, M. et al. (2018) LPSC meeting [#1558]. [5] Williams, A. et al. (2019) *Astrobio.* 19, 522-546.

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