PRESERVATION OF ORGANIC MOLECULES IN MARS-ANALOG SAMPLES USING PYROLYSIS AND DERIVATIZATION GCMS EXPERIMENTS FROM THE SAM INSTRUMENT. M. Millan[1,2], A. J. Williams[2, 3], A. Buch[4], A. Bai[1], C. Freissinet[5], C. Szopa[5], J. L. Eigenbrode[2], D. P. Glavin[2], R. Navarro-González[6], P. Mahaffy[2], S. S. Johnson[1]
[1]Georgetown University, 37th and O street NW, Washington DC 20057 (mm4385@georgetown.edu), [2]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [3]Dept. of Physics, Astronomy, and Geosciences, Towson University, Towson, MD, [4]Ecole Centrale Supelec, Grande Voie des Vignes, 92290 Châtenay-Malabry, France, [5]LATMOS (Laboratoire Atmosphère, Milieux, Observations Spatiales), 11 bvd d'Alembert, 78280, Guyancourt, France, [6]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico.

Introduction: The Curiosity rover is currently at the base of Mount Sharp, analyzing its stratigraphic rocks layers to find hints of Mars' habitability [1]. The Sample Analysis at Mars (SAM) instrument suite aboard Curiosity is a pyrolyzer coupled to a gas chromatograph-mass spectrometer (pyro-GCMS) essentially dedicated to the search for organic molecules on Mars [2]. SAM is able to perform *in situ* molecular analysis of gases evolved from the heat (up to 850°C) of the solid samples collected by Curiosity. SAM can then detect, separate and identify volatiles inorganic and organic compounds released from the samples. SAM also carries two derivatization reagents to perform wet chemistry experiments in order to extract non-volatile compounds so they can be analyzed by GCMS. The N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) is one of the two chemistry reagents carried by SAM and allows the separation, detection, and identification of complex, polar and/or refractory molecules. The method, called derivatization, is a silylation method where the labile H of the targeted molecule is replaced by the MTBSTFA silyl group transforming molecules into volatile derivatives easily amenable to GCMS analysis (**Figure 1**). The MTBSTFA is then able to react with many organics of astrobiological interest such nucleobases, amino acids, carboxylic acids, sugars, etc while preserving their chemical structure from degradation.

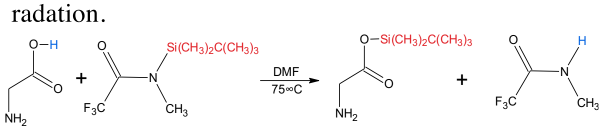

Figure 1: Chemical derivatization reaction between MTBSTFA and glycine. The amino function is silylated by the reagent in addition of DMF solvent when heated for a few minutes at 75°C. The labile hydrogen is replaced by the silyl functional group.

For the first time on Mars, a full derivatization experiment was successfully performed on the Ogonguit Beach (OG) sand sample before being analyzed by SAM [3]. This OG analysis is challenging because it led to the production of numerous MTBSTFA by-products coming from reactions between the organics, inorganics, and minerals present in the sample and high mass derivative species yet non identified.

Objectives: To evaluate the efficiency of the MTBSTFA derivatization on Martian samples and better understand the precursors and origins of the organic compounds detected by SAM to date [4,5], we are conducting laboratory experiments on a set of fifteen martian analogs. The nature and content in organics present in those analogs are evaluated to highlight the best preservation environments and types of minerals. It will help target the most fruitful solid samples to be analyzed by SAM, as well as future instruments such the Mars Organic Molecular Analyzer (MOMA), the next pyro-GCMS instrument that will be sent to Mars onboard the ESA Exomars rover. To characterize the potential limits and biases of the flight-like pyrolysis/derivatization experiments on Mars, experiments were performed in differents steps. Steps include the characterization of the samples by laboratory procedures and flight-like analyses.

Sample targeted: The rock samples have been collected in various Earth environment and represent similar mineralogies to those detected on Mars by remote and in-situ measurements. The fifteen samples studied include: an Antartic Paleolake containing C-bryophytes, used as the organic-rich control sample (OM2); iron oxides from a modern mineral precipitate and older oxidized surface gossan at Iron Mountain, CA; ancient acid saline lake sediments from Australia; siliceous sinter hot springs from a modern near-vent site and an inactive deposit from Iceland; a modern carbonate ooids from Pigeon Cay, The Bahamas; and an organic-rich shale from Messel, Germany [6].

Pyrolysis and derivatization GCMS experiments: Samples were analyzed in three steps. First, they were analyzed in flash and SAM-like pyrolysis to highlight the most promising samples in terms of organic content (step 0). We then performed solid-liquid extractions with water:isopropanol, followed by derivatization with MTBSTFA and direct injection in the GCMS (step 1). The last step is a "one-pot/one step" MTBSTFA derivatization procedure where the organics from the solid samples are extracted and derivatized at the same time to then be pyrolyzed using a SAM-like ramp temperature (step 2). Laboratory experiments were performed on a Agilent (?) GCMS with an MXT-1 column and a Frontier Lab pyrolyser mounted upstream of the GC column, in the injector. A cold-trap was used to trap the volatiles compounds during the SAM-like pyrolysis ramp temperature experiments.

Results: First results from the OM2 sample (**Figure 2**) analysed in SAM-like pyrolysis (step 0) indicated the presence of more than 300 organic compounds including alkanes, alkenes, alkynes, ketones, aromatic hydrocarbons, alcohols, nitriles and N-, O- and S-heteocycles. They could come from a variety of organic molecules of interest including amino acids, carboxylic acids, polycyclic aromatic hydrocarbons, etc. OM2 is then a good organic control sample and a very promising sample in terms of organic content. The step 1 and step 2 analysis allowed to discriminate the nature of organic present. It led to the detection of mainly carboxylic and dicarboxylic acids from 1 to 17 carbon atoms. Laboratory experiments and data treatment of the fourteen other samples are ongoing to highlight the differences between the mineralogies selected and the step analyses.

Conclusions: This ongoing work will help us identify the MTBSTFA by-products present in the SAM chromatograms and the high molecular derivatives detected in the last OG run. The investigation will also enable a better minerals target selection for the preservation of organic molecules on Mars and help the identification of the precursors of the organics detected on Mars. These experiments will also be helpful to better understand the limits and biases of the flight-like experiments to prepare th efuture analyses and the best pyrolysis and derivatization procedures to be done with the SAM and MOMA pyro-GCMS instruments.

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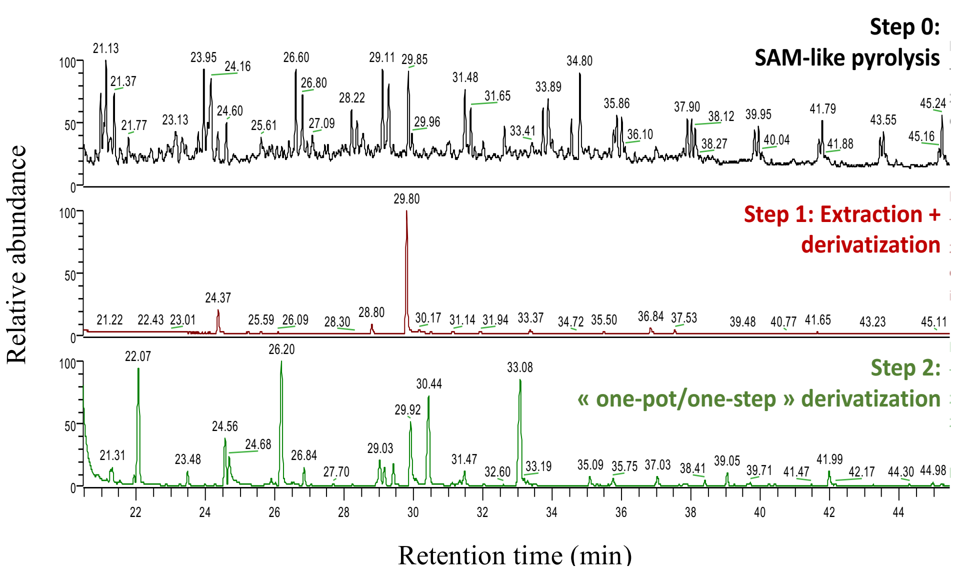

Figure 2: Comparison of the chromatograms obtained after the analysis of the OM2 sample in three steps: SAM-like pyrolysis: Step 0, solid-liquid extraction + MTBSTFA derivatization: step 1, "one-pot/one-step" extraction + derivatization (step 2).