DETECTION OF LONG-CHAIN HYDROCARBONS ON MARS WITH THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT C. Freissinet[1], D. P. Glavin[2], A. Buch[3], C. Szopa[1], S. Teinturier[2], P. D. Archer[4], A. J. Williams[2,5], R. Williams[2], M. Millan[2,6], A. Steele[7], R. Navarro-Gonzalez[8], C. H. House[9], C. A. Malespin[2], P. Mahaffy[2]
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Introduction: The wet chemistry experiments on the Sample Analysis at Mars (SAM) instrument were designed for the extraction and identification of refractory organic chemical components in solid samples using gas chromatography-mass spectrometry (GCMS) [1]. One of the chemical derivatization agent used, *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA), was sealed inside seven Inconel metal cups present in the SAM Sample Manipulation System (SMS). Before any of these foil-capped derivatization cups had been punctured on Mars for a wet chemistry experiment, data from SAM showed that some MTBSTFA vapor leaked into the SMS and was detected mostly as its reaction product with water in both empty cup blank runs and solid sample experiments [2]. Although the preliminary efforts were focused on decreasing the abundance of MTBSTFA and byproducts on the samples, the versatility of the SAM instrument allowed the team to subsequently optimize a gas chromatography mass spectrometry (GCMS) experiment for the detection of MTBSTFA derivatized organic compounds and other molecules present in the martian samples, in a so-called "opportunistic derivatization" (OD) experiment. OD was performed in a two-step multi-sols experiment, where the sample was first heated to release the oxygen from oxychlorine decomposition, placed back into SAM sample carrousel for the readsorption of MTBSTFA, and reheated to the maximum temperature (~850 °C) for the derivatization GCMS analysis. The resulting data are presented in this paper.

Methods: The experiment was performed on a Cumberland (CB) sample, drilled on Sol 279, but kept into SAM for about 1260 sols before we designed and run the OD experiment. The first step (ODa) consisted of a medium temperature heating of the sample from ambient to ~475-525 ºC to decompose perchlorates and other oxychlorine compounds in the sample. The second step (ODb) utilized a higher temperature heating from ambient to ~850 ºC to perform pyrolysis and derivatization of molecules in the sample that evolve at elevated temperatures, with much less O_2 available in the sample for combustion of organics. Both pyrolysis and derivatization occurred during ODb. Four temperature cuts along the sample heating were diverted to the hydrocarbon trap for an analysis in gas chromatography-mass spectrometry (GCMS).

Results and discussion: Results from ODb GCMS showed the presence of decane and dodecane in the CB sample, and a tentative detection of undecane (Fig. 1), the latter partially co-eluting with other compounds from the background. The identification of decane and dodecane was confirmed by both their mass spectrum and their retention time. The mass spectrum was plotted and compared to the NIST mass spectral database, which confirmed a highly probable match to medium- to long-chain hydrocarbons. The retention times of a C_{10} to C_{30} alkane mixture were then tested for correlation with OD analysis on the SAM Testbed [3], a replica of SAM available at NASA GSFC, and determined the length of the HC chains detected on Mars as being C_{10} and C_{12}, and tentatively C_{11} (Fig. 1). The hydrocarbons from CB sample are likely released from the second temperature cut, *e.g.* between 320 and 550 °C. This temperature are well in excess of the boiling point of these compounds and may correspond to their release from a carrier mineral phase. This temperature range for example corresponds to the beginning of the Fe-sulfate (jarosite) decomposition [4]. Sulfates are known to release trapped organics, at the temperature they start decomposing [5], and there has been tentative identification of alkanes associated with sulfates in Mars meteorites [6]. The result is thus in line with an alkane release from the sulfates present at CB.

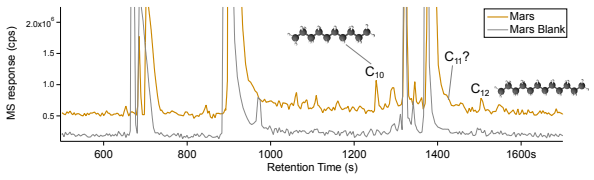

Figure 1. GCMS run of ODb experiment, showing the detection of decane and dodecane in CB sample, the tentative

detection of undecane, and their absence in the subsequent blank.

However, the origin of these long-chain hydrocarbons is unknown at this point. Initially we are pinpointing every effort to remove sources of possible contamination from the signal. The SAM team has spent years characterizing background contamination inputs into the analyses. At this time we are continuing to assess any and all possible internal or sample preparation inputs to the sample. However, the absence of alkanes in the subsequent blank ODb experiment, run in identical conditions than the CB-ODb experiment, in presence of high abundance of MTBSTFA, supports the premise that the origin of the alkanes cannot be internal to SAM, e.g. neither the Tenax adsorbent from the traps, nor the MTBSTFA itself.

One possible source of the alkanes may be from the decomposition of decomposition of higher chain length carboxylic acids, that are known to decarboxylate at high temperature when adsorbed or embedded into a mineral matrix. Laboratory experiments showed this effect when the molecules are adsorbed to clays or embedded in sulfate [J. Lewis and C. Freissinet, personal communications] and efforts are ongoing to clarify the fate of these molecules during an analysis with SAM. We are continuing to assess the data for the presence of the carboxyl form of decane and dodecane in the CB sample. Thus, undecanoic acid could be the precursor of decane, and tridecanoic acid the precursor of the observed dodecane. Undecanoic and tridecanoic acids are fatty acids, and fatty acids are of high interest in the search for biosignatures, as they are a primary constituent of terrestrial cellular membranes. The detection of an odd-over-even fatty acid preference also has implications for the biogenicity of the fatty acids, as abiotic carboxylic acid genesis is associated with no carbon number preference. However, the experimental conditions may also explain the carbon distribution.

Conclusion: Medium- to long-chain hydrocarbons, C_{10}-C_{12} alkanes, were detected on Mars with SAM thanks to a two-step procedure specifically designed to limit the combustion of organics from the O_2 from oxychlorine. This procedure is considered for future samples to remove the O_2 contribution from martian samples. The alkanes detected have an unknown origin, however, their structure is not incompatible with the presence of long-chain carboxylic acids in CB. In addition to the detection of the highest molecular weight molecule to date on Mars, this discovery shed new light on the possible detection of biosignatures with the SAM instrument.

References: [1] Mahaffy, P. R. *et al.* (2012)*, Space Sci Rev,* DOI 10.1007/s11214-012-9879-z. [2] Glavin, D. P. *et al.* (2013), *JGR :Planets,* Vol. 118, 1955–1973. [3] Malespin, C. A. *et al.* (2016) 47th *LPSC, Abstract #2615.* [4] Sutter, B. *et al.* (2017), *JGR: Pla*nets, doi:10.1002/2016JE005225. [5] François, P. et al. (2015), JGR: Planets, doi:10.1002/ 2015JE004884. [6] Steele, A. et al. (2018) Sci. Adv. Vol. 4, 1°, eaat5118