

FIRST *IN SITU* WET CHEMISTRY EXPERIMENT ON MARS USING THE SAM INSTRUMENT: MTBSTFA DERIVATIZATION ON A MARTIAN MUDSTONE. C. Freissinet^{1,2}, D. P. Glavin¹, A. Buch³, C. Szopa⁴, M. Millan⁴, S. Kashyap⁵, H. B. Franz¹, J. L. Eigenbrode¹, W. B. Brinckerhoff¹, R. Navarro-González⁶, S. Teinturier¹, C. A. Malespin¹, B. D. Prats¹, P. R. Mahaffy¹ and the SAM and MSL science teams. ¹NASA Goddard Space Flight Center, Greenbelt, MD, caroline.freissinet@nasa.gov, ²NASA Postdoctoral Program, Oak Ridge Associated Universities, TN, ³Ecole Centrale Paris, Chatenay-Malabry, France, ⁴LATMOS-UPMC, Paris, France. ⁵University of Massachusetts Amherst, Amherst MA 01003, ⁶Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico.

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]. 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). Although none of these foil-capped derivatization cups have been punctured on Mars for a wet chemistry experiment, data from SAM has shown that some MTBSTFA vapor leaked into the SMS [2]. Here we report preliminary results from an MTBSTFA derivatization (MD) GCMS experiment that was optimized for the detection of MTBSTFA residual vapor reaction products with refractory organic compounds and other molecules present in the Cumberland (CB) mudstone sample, known to contain organic molecules [3].

Discussion: MTBSTFA can react with a broad range of molecules containing a labile hydrogen such as alcohols, primary and secondary amines, carboxylic acids and amino acids in the free form. The silyl ester products of these molecules are typically much more volatile than the original non-derivatized molecule, which enables the transfer of the MTBSTFA derivatives for GCMS analysis [4]. In the MD2 experiment, the initial abundance of MTBSTFA released from the Cumberland "doggy bag" triple portion was found to be in the μmol range. In Figure 1, several key masses detected by GCMS that correspond to potential high molecular weight MTBSTFA reaction products are plotted. Several masses up to m/z 358 (the highest yet detected after pyrolysis of a sample by SAM on Mars) are observed in the MD2 GCMS analysis of the CB triple portion mudstone sample, but were not identified above background level in the twice-heated CB residue analysis that served as a blank (e.g. m/z 281 at retention time 13.1 min, Fig. 1). Numerous peaks were detected by GCMS above background and we are continuing to work to identify the derivatized compounds. Our preliminary results from MD2 compared to the control experiment indicate that several MTBSTFA derivatized aromatic hydrocarbons may be present in

the sample. Chlorobenzene, a chlorohydrocarbon that is not derived from MTBSTFA-perchlorate reactions [3] was also detected by GCMS in the MD experiments. This chlorobenzene may originate from reactions between oxychlorine species and metastable oxidized aromatic hydrocarbons in the Cumberland sample [5].

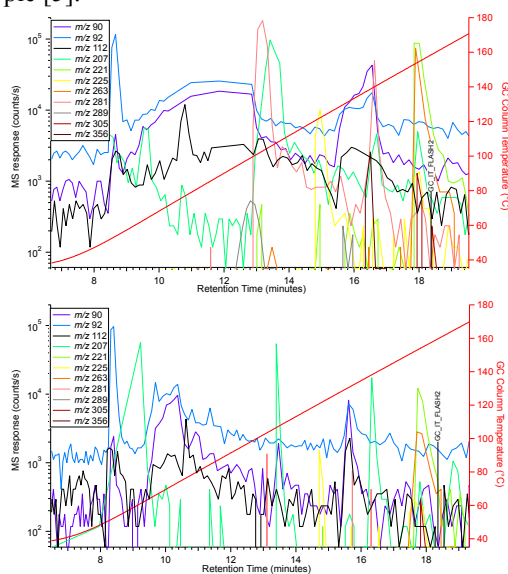


Figure 2: Comparison of some specific high masses for (top) the CB sample and (bottom) the CB blank for MD2 experiments, after the sample has been cleaned out of part of its O_2 in MD1.

Conclusion: These experiments represent the first successful MTBSTFA derivatization experiment on Mars. Several MTBSTFA reaction products were generated during reactions with the Cumberland mudstone sample at elevated temperatures, with some products containing mass fragments up to m/z 358. We are continuing the analysis of this interesting data set to identify these derivatization products that should shed additional light on the chemical nature of the organic matter present in the CB mudstone.

References: [1] Mahaffy, P. *et al.* (2012) *Space Sci Rev*, 170, 401-478. [2] Glavin, D. *et al.* (2013) *JGR Planets*, Vol. 118, 1–19. [3] Freissinet *et al.* (2015) *JGR Planets*, *accepted*. [4] Buch, A. *et al.* (2006) *PSS*, 54, 1592-1599. [5] Glavin *et al.* (2015), *LPSC abstract*.