ANALYSIS OF ORGANIC MOLECULES WITH PYROLYSIS GAS CHROMATOGRPAHY MASS SPECTROMETRY IN THE PRESENCE OF CHLORIDES : POSSIBLE IMPLICATIONS FOR MEASUREMENTS PERFORMED WITH THE SAM EXPERIMENT IN GALE CRATER.

C. Szopa[1,2], C. Freissinet[1], A. Buch[3], M. Millan[4,5], B. Sutter[6], M. Cabane[1], D.P. Glavin[4], R. Navarro-Gonzalez[7],and P. Mahaffy[4], [1]LATMOS UVSQ/SU/CNRS, Guyancourt, France, [2]Institut Universitaire de France, Paris, [3]LGPM CentraleSUpelec, Gif sur Yvette, France, [4]NASA GSFC, Greenbelt, MD, [5]Georgetown University, Washington D.C., [6]Jacobs Technology, Inc., Johnson Space Center, National Aeronautics and Space Administration, Houston, Texas, [7]Instituto de Ciencias Nucleares, UNAM, Mexico city, Mexico.

Introduction: Results from Checam, SAM, and APXS instruments onboard the Curiosity rover indicate that chlorides are present on Mars at Gale Crater, [1,2]. Even if no evaporitic layer of chlorides was found, these chemical species could represent a non-negligible fraction of chlorine bearing inorganic molecules present at the near surface of the crater floor. Laboratory analog studies have demonstrated that oxychlorine phases in Gale Crater material could serve as an O_2 and HCl source that causes the oxidation and chlorination of organic molecules present in samples analyzed by pyrolysis. SAM analysis detected chlorine bearing organic molecules in the Cumberland sample pyrolyzed at low temperatures (<400°C) [3,4]. This demonstrated that salts can interact with organic molecules present in a sample analyzed by pyrolysis. Total Cl from APXS analysis is always greater than SAM detected total Cl from oxychlorine phases indicating that chlorides likely dominate Cl in the Gale Crate4r materials. The goal of this work was to evaluate Mars analog chloride reactions with organic molecules to determine if the SAM detected chlorinated organics would form.

Moreover, other studies showed that other salts, as sulfates, can play a role of protection against the effect of oxychlorines during the pyrolysis [5,6,4]. Indeed, those salts start decomposing at higher temperatures than oxychlorines. Thus, organic molecules embedded in the salt matrix can be isolated from the gases released at low temperatures, preventing their reaction and alteration. Then, their protective role toward the effect of oxychlorine can be a key for detecting organic molecules indigenous to Mars.

The understanding of those reaction could also be a key to understand the organic molecule detected by SAM.

For these reasons, our team performed a systematic study in the laboratory of the possible influence of different chlorides on the analysis and detection of organic molecules. Then we performed pyrolysis gas chromatography mass spectrometry analysis, in order to assess their possible role in the analyses performed with the SAM experiment in Gale crater, and potentially future in situ experiments that would use such an analytical technique.

Experimental procedure: NaCl and $MgCl_2$ were used as the reference chlorides. Their thermal behavior was studied using thermal gravimetry (TG) and evolved gas analysis (EGA). More particularly their thermal decomposition was characterized as a function of the temperature up to about 900°C. Both chloride was then mixed with different organic molecules of interest for study of the Mars surface, i.e. polyaromatic hydrocarbons, amino acids, and carboxylic acids. Each mixture was submitted to two different pyrolytic treatments : i. a SAM like pyrolysis heating the sample from the ambient temperature up to 850°C at a 35°C.min^{-1} rate; ii. a flash pyrolysis at 850°C. The products of pyrolysis were analyzed using gas chromatography mass spectrometry (GCMS) and compared.

Implications: The products of pyrolysis identified are compared to those detected with the SAM experiment. In particular, an emphasis will be done on the chlorinated organic molecules identified with SAM when analyzing the Cumberland sample collected in the Yellow Knife bay area early in the mission. Conclusions about the possible influence of chlorides on GCMS analyses of Mars surface samples will be done.

Acknowledgments: NASA Mars Exploration Program supported for the development
and operations of SAM. The French National
Space Agency, the Centre National d'Etudes Spatiales (CNES), supported the development and operations of the SAM gas chromatograph.

References: [1] Sutter et al., , , JGR, , 1 (2017).
[2] N.H. Thomas et al., GRL, 46 (2019) 10754-10763.
[3] C. Freissinet et al., JGR 120 (2015) 2014JE004737.
[4] C. Szopa et al.,, Astrobiology, (In press). ; [5] P. Francois et al., JGR., 121 (2016) 61-74.[6] M.T.J. Lewis et al., Astrobiology, (2015).