INFLUENCE OF OXYCHLORINE PHASES DURING THE PYROLYSIS OF ORGANIC COMPOUNDS AND THE QUEST OF ORGANICS ON MARS WITH THE SAM INSTRUMENT.

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Introduction: One of the main objectives of the Sample Analysis at Mars (SAM) instrument is the *in situ* molecular analysis of gases evolving from the heat of the solid samples collected by Curiosity. To do so, **SAM** [1] uses a gas-chromatograph coupled to a quadrupole mass spectrometer (GC-QMS) for the separation and identification of volatile compounds. SAM detected oxychlorine phases that were also detected at the Phoenix landing site and may be prevelant over the martian surface [2]. SAM also detected chlorohydrocarbons attributed to chemical reactions on sample heating between the oxychlorines and organic compounds coming from SAM background [3] and Mars indigenous organic material [4]. The identification of the organics precursor of the chlorohydrocarbons is difficult due to the complexity of the reactions occurring during the pyrolysis. A series of laboratory experiments were performed to help understanding the influence of the oxychlorines on organic molecules during SAM pyrolysis, and try to define the possible organics parent to the species detected.

Sample selection and GC-QMS experiments: Organic molecules and perchlorates and chlorates have been chosen for their potential presence in martian samples. To focus on the reactivity between those compounds only, solid samples were simulated using fused silica as an inert sample matrix to which the oxychlorines and organics were added. Laboratory Experiments were performed on a GC-QMS and a pyrolyser mounted upstream of the GC column. Samples were pyrolyzed in flash-pyrolysis (900°C) and under SAM-pyrolysis conditions using a 35°C.min^{-1} ramp. The ratio of organic molecules to oxychlorine were varied to evaluate how ratio changes could influence the amount, nature and type of reaction products.

Results: The reaction products detected in both pyrolysis modes were analyzed and identified by GC-MS. The destruction and/or evolution of the organics by the oxychlorines depends on the nature of both organic and inorganic compounds and the pyrolysis mode used. The figure 1 shows that the naphthalene is still detected, even after its interaction with calcium perchlorates (Ca-PCL). It is sometimes possible to correlate the reaction products and the parent chemical family and/or the organics. Chloronaphthalene were detected after the pyrolysis of the oxychlorines with the naphthalene in both pyrolysis modes. This data also demonstrates that some of the molecules studied could be the precusors of the chlorohydrocarbons detected. For example, some chlorobenzene and C1 to C4 chloroalkanes are detected after the pyrolysis of the PAH with oxychlorines such Ca-PCL with naphthalene (figure 1), depending on the pyrolysis mode used.

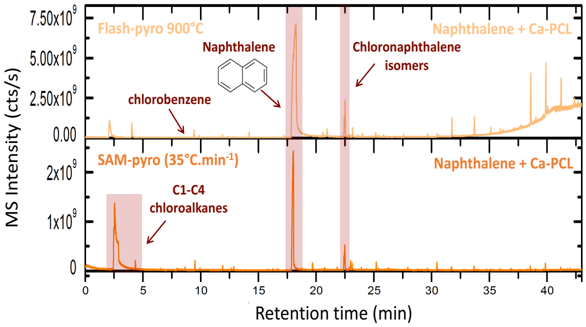

Figure 1: chromatograms obtained after the pyrolysis of the naphthalene mixed with the calcium perchlorates (Ca-PCL) at 1wt.%.

Conclusion: This work facilitates the interpretation of the SAM detections, especially regarding the chlorinated compounds found on Mars. The reaction products obtained after the pyrolysis of the sample improved the understanding of the behavior of organic matter during SAM pyrolysis experiments on Mars where chlorination, oxidation or oxychlorination are taking place. These experiments are also helpful to prepare future analyses and the best pyrolysis procedures to be done with the MOMA GC-MS experiment that will be onboard the Exomars 2020 mission.

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