

INFLUENCE OF OXYCHLORINE PHASES DURING THE PYROLYSIS OF ORGANIC MOLECULES: IMPLICATIONS FOR THE QUEST OF ORGANICS ON MARS WITH THE SAM EXPERIMENT ONBOARD THE CURIOSITY ROVER.

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Introduction: One among the main objectives of the Sample Analysis at Mars (SAM) experiment is the *in situ* molecular analysis of gases evolving from solid samples heated up to ~850°C, and collected by Curiosity on Mars surface/sub-surface in Gale crater. With this aim, SAM [1] uses a gas-chromatograph coupled to a quadrupole mass spectrometer (GC-QMS) devoted to separate, detect and identify both volatile inorganic and organic compounds.

SAM detected chlorinated organic molecules [2, 3] produced in evolved gas analysis (EGA) experiments. Several of these were also detected by the Viking experiments in 1976 [4]. SAM also detected oxychlorine compounds that were present at the Phoenix landing site. The oxychlorines may be prevalent over much of the martian surface [5].

The C1 to C3 aliphatic chlorohydrocarbons (chloromethane and di- and trichloromethane) detected by SAM were attributed to reaction products occurring between the oxychlorines phases and the organic compounds coming from SAM instrument background [2]. But SAM also showed the presence of a large excess of chlorobenzene and C2 to C4 dichloroalkanes among the volatile species released by the Cumberland sample of the Sheepbed mudstone. For the first time in the history of the Mars exploration, this proved the presence of Mars indigenous organic material at the Mars' surface [3]. However, the identification of the precursor organic compounds of these chlorohydrocarbons is difficult due to the complexity of the reactions occurring during the sample pyrolysis.

Laboratory pyrolysis experiments have demonstrated that oxychlorines phases such as perchlorates and chlorates, decomposed into dioxygen and volatile

chlorine bearing molecules (HCl and/or Cl₂) during the pyrolysis. These chemical species can then react with the organic molecules present in the martian solid samples through oxidation, chlorination and oxychlorination processes [2, 6, 7].

Objectives: Previous laboratory analog work has examined a limited set of organic-chlorine reactions that may explain the SAM detected chlorinated hydrocarbons such the chlorobenzene [7]. But the small number of chemical species investigated, including some carboxylic acids and hydrocarbons, does not exclude others parent molecules. Therefore, we performed a series of systematic laboratory experiments to help understanding the influence of oxychlorine phases on organic molecules during SAM pyrolysis, and try to define the possible organic molecules parent to the species detected by SAM.

Sample selection and preparation: Three types of organic molecules potentially present on Mars were evaluated: polycyclic aromatic hydrocarbons, amino acids, and carboxylic acids. The organics were mixed with various perchlorates and chlorates salts (Fe, Ca, Mg, K and Na), that may be present in martian solid samples. To focus on the reactivity between oxychlorines and organic compounds only, solid samples were simulated using fused silica as an inert sample matrix and 1wt.% of both oxychlorines and organics were added to the silica. The perchlorate and chlorate salts concentration correspond to Gale Crater mean value detected by SAM [3]. The solid volume analyzed is also similar to the one analyzed by the SAM experiment.

Pyrolysis-GC-QMS experiments: Laboratory Experiments were performed on a GC-QMS using a Restek Rxi-5 column (30 m x 0.25 mm x 0.25 μ m) and a Frontier pyrolyser. The pyrolyser is mounted upstream of the column, in the GC injector. Simulated samples were pyrolyzed in flash-pyrolysis up to 900°C and under SAM-pyrolysis conditions using a 35°C.min⁻¹ ramp temperature. This covers the SAM pyrolysis temperature range and enables a comparison of both pyrolysis modes. 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 (flash and ramp pyrolysis) were analyzed and identified by GC-MS. It is evident that the destruction and/or the evolution of the organic compounds by the oxychlorine phases depends not only on the nature of both organic and inorganic compounds (perchlorate and chlorate) but also on the pyrolysis mode used. The figure 1 shows the chromatogram obtained after the pyrolysis of naphthalene mixed with 1wt.% of calcium perchlorates (Ca-PCL). We observed that the naphthalene is still detected, even after its interaction with the Ca-PCL (**Figure 1**).

These results show that it is sometimes possible to correlate the reaction products and the parent chemical family and/or the organics. For example, we detected chloronaphthalene after the pyrolysis of the oxychlorines with the naphthalene by using both pyrolysis modes (**Figure 1**).

This data also demonstrates that some of the molecules, or molecular families studied, could be the precursors of the chlorohydrocarbons detected by both Viking and SAM experiments. Some chlorobenzene is detected after the flash-pyrolysis of the organic compounds mixed with the oxychlorines such naphthalene with Ca-PCL for example (**Figure 1**). Moreover, C1 to C4 chloroalkanes are only formed after the SAM-like pyrolysis of PAH and amino acids mixed with the oxychlorine phases (**Figure 1**).

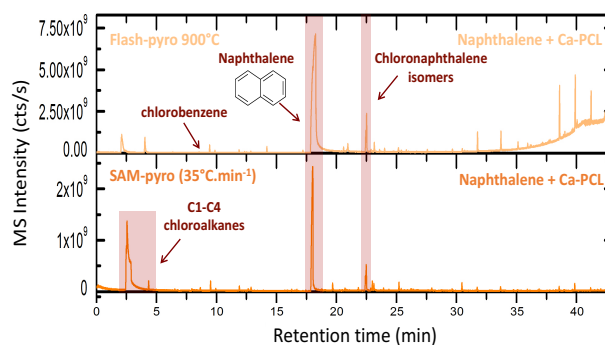


Figure 1: chromatograms obtained after the pyrolysis of the naphthalene mixed with the calcium perchlorates (Ca-PCL) at 1wt.%. Pyrolysis parameters (flash-pyrolysis and ramp temperature at 35°C.min⁻¹) are represented in light and dark orange respectively. The nature of some chlorohydrocarbons formed depends on the pyrolysis modes used.

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 organics mixed with the perchlorates and/or chlorates 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.

References: [1] Mahaffy, P. et al. (2012) Space Sci Rev, 170, 401-478. [2] Glavin, D. et al. (2013), JGR, 118, 1955-1973. [3] Freissinet, C. et al. (2015) JGR. [4] Biemann, K. et al (1977) JGR, 82, 4641-4658. Science. [5] Hecht, (2009), Science, 325 64-67. [6] Leshin L. et al. (2013). [7] Miller et al. (2016), JGR 121, 296-308.

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