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EFFECT OF THE PRESENCE OF CHLORATES AND PERCHLORATES ON THE PYROLYSIS OF ORGANIC COMPOUNDS: IMPLICATIONS FOR MEASUREMENTS DONE WITH THE SAM EXPERIMENT ONBOARD THE CURIOSITY ROVER.

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Introduction: The Mars Science Laboratory (MSL) **Curiosity** Rover carries a suite of instruments, one of which is the Sample Analysis at Mars (SAM) experiment. **SAM** is devoted to the in situ molecular analysis of gases evolving from solid samples collected by Curiosity on Mars surface/sub-surface. Among its three analytical devices, **SAM** has a gas-chromatograph coupled to a quadrupole mass spectrometer (GC-QMS) [1]. The GC-QMS is devoted to the separation and identification of organic and inorganic material. Before proceeding to the GC-QMS analysis, the solid sample collected by Curiosity is subjected to a thermal treatment thanks to the pyrolysis oven to release the volatiles into the gas processing system. Depending on the sample, a derivatization method by wet chemistry: MTBSTFA of TMAH can also be applied to analyze the most refractory compounds. The GC is able to separate the organic molecules which are then detected and identified by the QMS (**Figure 1**).

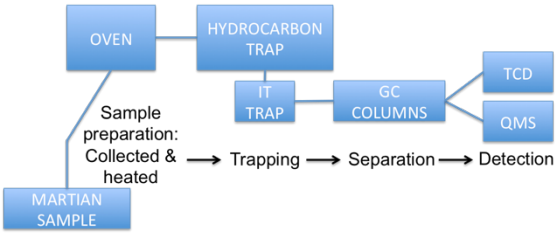


Figure 1: simplified analytical channel from sample collection to the detection and identification of the organic molecules.

For the second time after the Viking landers in 1976 [2], SAM detected chlorinated organic compounds with the pyrolysis GC-QMS experiment [3, 4]. The detection of perchlorates salts (ClO_4^-) in soil at the Phoenix Landing site [6] suggests that the chlorohydrocarbons detected could come from the reaction of organics with oxychlorines. Indeed, laboratory pyrolysis experiments have demonstrated that oxychlorines decomposed into molecular oxygen and volatile chlorine (HCl and/or Cl_2) when heated which then react with the organic matter in the solid samples by oxidation and/or chlorination processes. [3, 5, 7, 8].

Objectives: During the SAM pyrolysis, samples are heated to 850°C which favors chemical reactions between oxychlorine phases, probably homogeneously distributed at Mars's surface [6], and potential organic material in martian sediments. The first chlorohydrocarbons (chloromethane and di- and trichloromethane) detected by SAM were entirely attributed to reaction products occurring during the pyrolysis experiment between these oxychlorines and organic carbon from SAM instrument background [3], leading to chlorination or oxychlorination.

But SAM discovered for the first time in the Sheepbed mudstone of Gale crater, chlorobenzene and C2 to C4 dichloroalkanes produced by reaction between Mars endogenous organic compounds with oxychlorines [4]. The potential organic precursors of these chlorinated compounds are currently under investigation in the laboratory under SAM-like operating conditions [9]. To help understanding of the influence of perchlorate and chlorate salts on organic matter during SAM pyrolysis, we systemically study the reaction products formed during pyrolysis of various organic compounds from different chemical families mixed with various perchlorates and chlorates.

Selected samples and preparation: We selected various organic compounds from simple molecule

forms as for instance hydrocarbons, PAHs and amino acids to more complex material (> 30 carbon atoms) such as kerogen.

The perchlorates and chlorates and the organics are first prepared in silica to simulate the remaining soil. The perchlorate and chlorate salts are prepared at 1 wt % concentration, which is slightly higher than SAM abundances (*e.g.*, 0.2 to 0.5 wt % at Rocknest [3]). The organics are then mixed with the oxychlorines at various concentrations to study the potential qualitative and/or quantitative effects.

Pyrolysis-GC-QMS experiments: The experiments are performed on a laboratory GC-QMS with a Restek Rxi-5 column (30m x 0.25mm x 0.25µm) and an Intersciences pyrolyser mounted on the injector upstream the column. The mixture is pyrolyzed at different temperatures up to 900°C to cover the SAM temperature range. Different experiments are done to discriminate the pyrolysis products directly coming from the organic, and those produced from the reaction with oxychlorine. This series of experiments is under progress and should bring key information on the potential to identify Mars organic molecules when pyrolyzing solid samples.

Conclusion: The products obtained during the pyrolysis of pure organic matter and mixed with various perchlorates and/ or chlorates is expected to improve the understanding of the behavior of organic matter during SAM pyrolysis experiments on Mars subject to oxidation or oxychlorination. Depending on the organic families studied, we may find reccuring molecules which are potentially present in Mars' surface samples. This work could thus hightlight some organic precursors of the chlorinated compounds found on Mars, and support the interpretation of the SAM measurements.

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