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# Searching for Martian Organics with the Mars Organic Molecule Analyzer (MOMA) aboard ExoMars-2018

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## Abstract

The ExoMars-2018 rover mission will likely combine both in-situ analysis of Martian subsurface material and caching of samples to be returned to Earth at a later time. The Mars Organic Molecule Analyzer (MOMA) aboard the rover will assume the important task to characterize subsurface samples in terms of their organic content and thereby support the sample selection process for caching. While previous Mars missions (Viking Landers, Phoenix) largely failed in their search for organic material on Mars, MOMA will use a modified pyrolysis technique (similar to the SAM instrument of Mars Science Laboratory, MSL) next to Laser Desorption and Ionization (LDI) coupled to a Mass Spectrometer (MS).

## 1. Search for Martian organics

There ought to be organic compounds in the Martian soil: Flynn [1] calculated an annual influx of 2.4 $10^6$ kg of micrometeoritic material (particles up to 1000 µm in diameter) with the original carbonaceous material intact. Assuming constant influx over 4.6 Gyr, no degradation of organic material over time, and a global regolith thickness of 50 m, that regolith should contain 100 ppmw organic carbon atoms within organic compounds. Martian meteorites that likely come from some depth below the surface contain organic carbon at strongly varying abundance (1-100 ppmw depending on meteorite, [2]). Previous missions (Viking Landers and Phoenix) did search for, but did not find clear evidence for organic material in the soil. While the analysis of Viking [3-4] as well as TEGA/Phoenix [5] pyrolysis data is still ongoing, the detection of perchlorate at the PHX landing site [6] has provided new insight into the oxidation potential of Martian soil that needs to be taken into account by current instrument design. Perchlorates appear to decompose and oxidize Martian organics during pyrolysis. However, perchlorates are largely inert up to temperatures of ~300ºC [5]. How does MOMA respond to these findings? Figure 1 shows an overview of the different MOMA modules. MOMA has two fundamentally different operational modes: (1) Pyrolysis involving oven, tapping station, GC, and MS, and (2) LDI (Laser Desorption and Ionization) involving refillable sample container, laser, and MS. Operational mode (1) can be further split up into two types: (1a) Pyrolysis with ordinary ovens (similar to Viking and TEGA/Phoenix), and (1b) Pyrolysis with ovens that contain a derivatization agent (probably dimethylformamide dimethylacetal (DMF-DMA)). The agent will be released during oven heating at low temperatures (< 250ºC) vaporizing potential Martian organics before perchlorate becomes active.

## 2. Case Study: Pyrolysis of benzoic acid in the presence of perchlorate

In order to understand the interaction between Martian organics and perchlorate, experiments were performed with molecules that might occur on the surface of Mars, either as part of its indigenous organic inventory, or as part of vaporized molecules generated during pyrolysis. Ming et al [5] showed that one such candidate molecule, mellitic acid, does not evolve detectable organic fragments during pyrolysis. Here we describe the pyrolysis of a mixture of virtually organic-free powdered basalt (Hohen Hagen, Göttingen, Germany), 0.05 wt% benzoic acid, and 0.6 wt% magnesium perchlorate as found by WCL/Phoenix [6]. This corresponds to 345 ppmw organic carbon. Perchlorate molecules are in excess over organic C atoms (all part of the benzoic acid) by a factor of ~1.3. We also describe pyrolysis

of the same sample without perchlorate. Both experiments were performed with a Pyrola 2000 unit connected to a Varian 3800 GC with MXT-5 column and Varian 4000 ion trap MS with internal ionization. The samples were heated to 600 ºC within ~10 ms. Figure 2 shows the results of these experiments and clearly demonstrates the complexity introduced by the presence of perchlorate. The original molecule (benzoic acid, BA) can be seen during both pyrolysis experiments. However, in the presence of perchlorate numerous other molecules (in particular chlorinated benzene and phenol) appear, while the BA peak becomes accordingly smaller.

## 3. Summary

Some molecules, such as benzoic acid, provide complex pyrolysis data as recorded by GC-MS, while other molecules, such as mellitic acid [3], are almost undetectable in the presence of perchlorate. For the detection of the latter type of molecules alternative techniques are needed and will be available as part of the MOMA instrument (pyrolysis coupled with derivatization and LDI).

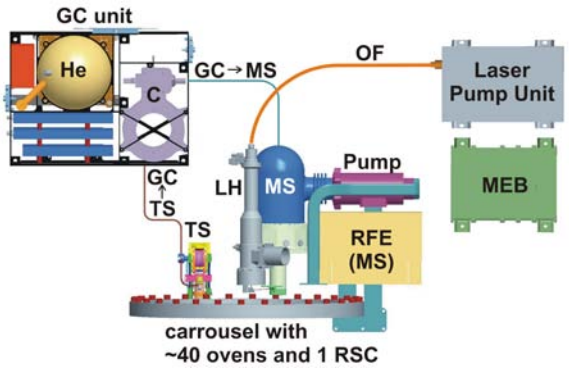


**Figure 1**: Overview of MOMA instrument modules. Operational modes are described in the text. Abbreviations: RSC = Refillable Sample Container, TS = Tapping Station, GC = Gas Chromatograph, C = GC columns (4x, including 1 enantioselective stationary phase), LH = Laser Head, MS = Mass Spectrometer (including ion guide and 2D ion trap), RFE = RF Electronics, MEB = MOMA Electronics Box, OF = Optical Fiber.

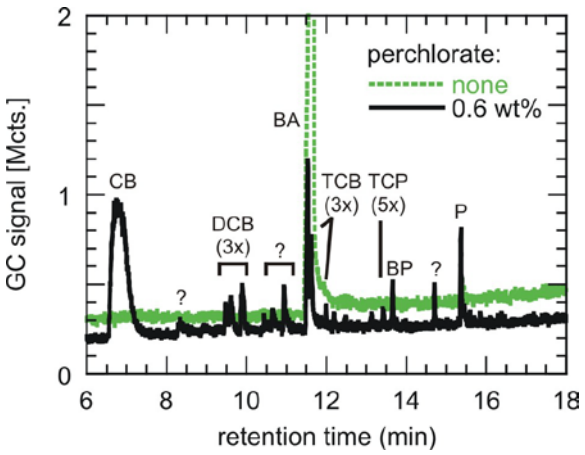


**Figure 2**: Gas chromatogram recorded during pyrolysis of benzoic acid in presence (black solid line) and absence (green dotted line) of magnesium perchlorate. The presence of the latter has a major impact on the type of molecules released during pyrolysis. Abbreviations (with approximate masses [Dalton] as measured by the MS post ionization): BA = Benzoic Acid (122), CB = ChloroBenzene (112), DCB = DiChloroBenzene (147), TCB = TriChloroBenzene (184), TCP = TriChloroPhenol (246), BP = BiPhenyl (154), P = plasticizer (diethylphthalate, 222). The number of isomers is specified in parenthesis (e.g. "3x").

## Acknowledgements

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