

CHARACTERIZATION OF ORGANIC COMPOUNDS IN MARTIAN SEDIMENTS: A CASE STUDY IMITATING MOMA PYROLYSIS & DERIVATIZATION ONBOARD THE EXOMARS ROVER.

H. Mißbach^{1,2}, H. Steininger¹, V. Thiel² and W. Goetz¹, ¹Max Planck Institute for Solar System Research, Justus-von-Liebig-Weg 3, 37077 Göttingen, Germany, missbach@mps.mpg.de, ²Geobiology, Geoscience Centre, Georg-August-University Göttingen, Goldschmidtstraße 3, 37077 Göttingen, Germany.

Introduction: Since biology experiments have been performed by the Viking Landers [1], the search for past or present life is still one of the main goals of Mars exploration (e.g., [2]). Searching for organic (bio-) signatures and therefore (traces of) life on Mars is a main objective of the Mars Organic Molecule Analyzer (MOMA) instrument onboard the ESA/Roscosmos ExoMars rover [3, 4]. However finding these signatures and discriminating whether they are biogenic or abiogenic is challenging (see e.g., [2, 5]). Therefore analog studies could help to better understand certain features and are an important prerequisite to support data interpretation.

The goals of this study are to understand the effects of MOMA-like gas chromatography - mass spectrometry (GC-MS) methods on different sample types, the differences between MOMA flight analog system (FAS) and conventional GC-MS analyses, the differences between stepwise and direct pyrolysis, the influence of magnesium perchlorate on measurements and problems related to particular sample types. It is important to mention here that this is an ongoing and long-term study in preparation of the ExoMars rover mission.

Materials: Experiments were carried out on three different samples: 1) an organic-lean (C_{org} 0.49%) silica-dominated black radiolarian chert from the Holy Cross Mountains in central Poland (Silurian age, for details see e.g., [6, 7]); 2) a Fischer-Tropsch type (FTT) product synthesized in the laboratory under hydrothermal analog conditions (see e.g., [8]) and deposited on silica gel (SiO_2), and 3) a standard mixture consisting of 8 different functionalized compounds (alkan-1-ols, alkan-2-ols, alkanic acids) deposited on silica gel. The latter sample serves both as a GC-MS standard and as a surrogate for FTT products.

Experimental setup and methods: The experiments were performed on our analog setup (MOMA FAS) that consists of a small oven to perform pyrolysis or in-situ derivatization/thermochemolysis, a tapping station and an adsorption trap (for MOMA GC-MS principle see [3, 4, 9]). The FAS was connected to a Varian CP-3800 gas chromatograph that in turn was coupled to a Varian 240-MS/4000 mass spectrometer. Experimental conditions were set as close as possible to those envisioned for MOMA

surface operations taking practical constraints in the laboratory into consideration.

3.5 to 4.5 mg of pre-dried sample (80°C for 10 min) were used for each experiment. Pyrolysis was performed by heating directly to 700°C and stepwise to 300°C, 500°C and 700°C and holding the sample at the respective temperature for 10 s. For in-situ derivatization and thermochemolysis experiments 3.5 µL of the following reagents were added directly to the sample: MTBSTFA/DMF (3:1, V:V), DMF-DMA and TMAH (25% in methanol). Reaction temperatures and times for each one of these reagents were, respectively, 250°C for 10 min, 140°C for 4 min and 600°C for 40 s (setup and methods are described in detail in [4]). Additionally some experiments were carried out under the same conditions with addition of magnesium perchlorate to the sample prior to drying.

Extracts of all samples were also analyzed by a conventional GC-MS setup (Thermo Fisher Trace 1300 Series GC coupled to a Thermo Fisher Quantum XLS Ultra MS) prior to the MOMA FAS experiments.

Pyrolysis: The first pyrolysis experiments have shown that the black chert contains several aliphatic and aromatic hydrocarbon compounds, e.g., alkanes/alkenes in the range of C_5 to C_{19} [4]. Aromatic compounds increased in abundance during stepwise pyrolysis possibly as a result of heating [4]. The production of unsaturated compounds during open-system pyrolysis as well as aromatization of hydrocarbon moieties during heating of organic-bearing samples is well known (e.g., [10, 11]). Furthermore, pyrolysis of samples containing functionalized compounds (FTT organics and standard mixture) led to artifacts (e.g., alkene production) and massive cross contamination. For a satisfying analysis of samples containing functionalized compounds a derivatization is necessary.

Addition of magnesium perchlorate to the sample led to production of chlorinated compounds during pyrolysis, like e.g., chlorobenzene, which was also observed on Mars by the SAM instrument (Sample Analysis at Mars) onboard the Curiosity rover [12].

Derivatization/Thermochemolysis:

Derivatization and thermochemolysis of the black chert were unsuccessful. Beside some alkanic acid contamination and cross contamination from previous analyses no functionalized compounds could be

identified, which is probably due to the fact that the sample has already gone through intensive thermal alteration [4]. On the other hand, the different derivatization/thermochemolysis methods gave proper results for the analysis of functionalized compounds contained in the standard mixture and the FTT sample (i.e. alkanols, alkanolic acids).

Summary: We performed MOMA-like GC-MS measurements on a black chert, on abiogenic FTT organics and on a standard mixture (containing alkanols and alkanolic acids) to get insights on the general performance as well as advantages and disadvantages of the methods envisioned for MOMA surface operations. Pyrolysis in MOMA ovens worked well for an organic-lean, thermally mature black chert containing aliphatic and aromatic hydrocarbons whereas in-situ derivatization and thermochemolysis produced sound results for samples containing alkanols and alkanolic acids.

References: [1] Levin G. V. and Straat P. A. (2016) *Astrobiology*, 16, 798-810. [2] Westall F. et al. (2015) *Astrobiology*, 15, 998-1029. [3] Goetz W. et al. (2016) *Int. J. of Astrobiology*, 15, 239-250. [4] Goesmann F. et al. (in revision) *Astrobiology*. [5] Westall F. et al. (2011) *Planet. and Space Sci.*, 59, 1093-1106. [6] Kremer B. and Kazmierczak J. (2005) *J. Sed. Res.*, 75, 895-904. [7] Bauersachs T. et al. (2009) *Org. Geochem.*, 40, 149-157. [8] McCollom T. M. et al. (1999) *Origins of Life and Evol. of the Biosphere*, 29, 153-166. [9] Morisson M. et al. (2016) *LPS XLVII*, Abstract #2159. [10] Huizinga B. J. (1988) *Energy & Fuels*, 2, 74-81. [11] Saiz-Jimenez C. (1994) *Naturwissenschaften*, 81, 451-453. [12] Freissinet C. et al. (2015) *J. Geophys. Res. Planets*, 120, 495-514.