

Pyrolysis of Organic Material and Perchlorate. H. Steininger¹, F. Goesmann¹, and W. Goetz¹, ¹Max Planck Institute for Solar System Research, Max-Planck-Strasse 2, 37191 Katlenburg-Lindau, Germany, (steininger@mps.mpg.de).

Introduction: The ESA-led Mars rover ExoMars (launch in 2018) will carry a suite of instruments, one of which is the Mars Organic Molecule Analyzer (MOMA). Organic material in Martian soil including drill samples as deep as 2 m will be either pyrolyzed at temperatures of up to 1000°C and separated by gas chromatography, or volatilized with the help of a UV laser. A mass spectrometer will be the detector for both methods.

Chlorinated methane derivatives like chloromethane and dichloromethane have been detected in pyrolysis GC-MS experiments on Mars two times. The first time was during the Viking mission in 1976 [1]. For a long time the results were interpreted as contamination by cleaning solvents [1]. The discovery of perchlorates by the Phoenix mission and subsequent analysis of pyrolysis in the presence of perchlorates gave rise to the suggestion that chloromethane derivatives are produced during pyrolysis by the chlorine produced from the decomposition of perchlorate [2,3]. The reinterpretation of Viking data in light of those new results was refuted by the principal investigator of the Viking GC-MS experiment. The peer reviewed discussion included three publications ([3], [4], [5]) and has yet to lead to a clear conclusion.

With the results of the Sample Analysis on Mars (SAM) instrument onboard the Curiosity rover the situation changed again. The first samples analyzed were surface sand. The sample was intended to represent uniformly distributed Mars sand as well as serve as a pre-cleaning test of the rover's sampling system. The pyrolysis products contained mono-, di- and trichloromethane. These results indicate that perchlorates and organic material are present. The similar results of Viking and Curiosity when analyzing surface sand might lead to the conclusion that both instruments detected traces of organics which reacted with the perchlorates. The source of the chloromethanes is however unclear lacking an unambiguous reaction mechanism leading to them. Inorganic sources for the carbon are discussed and even the decomposition of organic contamination is possible [6].

A better understanding of the influence of perchlorates on the pyrolysis is necessary. The pyrolysis of spiked analog samples and the pyrolysis of terrestrial rock samples can significantly aid understanding. With the spiked rock samples the exact starting material is known making it easier to determine the reaction mechanism. The drawback is that the distribution of the

spiked material is not the same as a naturally-deposited sediment sample. On the other hand, terrestrial rocks reflect natural deposition patterns but the exact composition of the contained organic material is unknown and pyrolysis gives only the fragments of the original molecules.

Our spiked-sample pyrolysis results have been published [7] and indicate that the oxidation of organic compounds dominates the reaction and even very stable aromatic hydrocarbons are readily oxidized. Small aromatic ring systems with C-H bonds have a chance to get transformed into chlorobenzenes [7].

Pyrolysis of black shale: The natural black shale was pyrolyzed and the resulting plot shows a complex mixture of aromatic and aliphatic hydrocarbons. Most of the smaller products are created by the breakup of complex organic compounds. Those simple compounds are too volatile to stay in the rock over a geologic time frame. The addition of perchlorates changes the GC-MS plot significantly: mostly the long chain hydrocarbons vanish while the aromatic hydrocarbons survive, unless large amounts of perchlorates are added. In these experiments the perchlorate is added as a solution of magnesium perchlorate in water resulting in an intimate mixture of the organics and the perchlorate. The reaction can already take place between the organic material and the perchlorate. Both materials are not very volatile and need to be transformed into more volatile compounds. In a second experiment, perchlorate is not mixed with the sample but only soaked into pulverized basalt and placed next to the black shale sample. In this case only the gaseous decomposition products of the magnesium perchlorate, mostly oxygen and chlorine, react with the gaseous pyrolysis products of the black shale. This reaction takes place in the gas phase above the sample. The resulting reaction products are dominated by small organic molecules with one or two carbon atoms and a varying amount of chlorine and hydrogen attached.

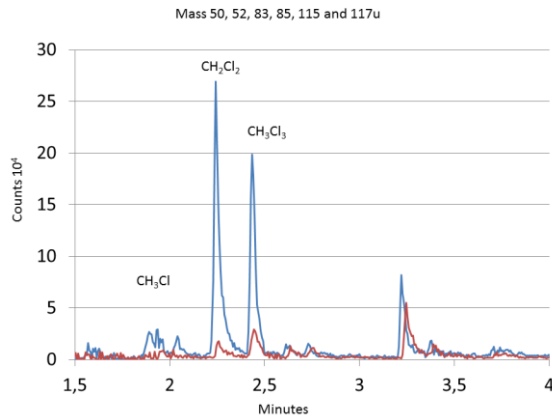


Figure 1: The blue curve shows the amount of CH₃Cl CH₂Cl₂ and CHCl₃ created during pyrolysis when the perchlorate is not in close contact with the black shale, while the red line shows the amount created when the perchlorate is in close contact with the black shale.

Conclusion: The separation of organics and perchlorates creates much larger amounts of the small chlorinated hydrocarbons than the pyrolysis in close contact. With a sample similar to the black shale large amounts of small chlorinated hydrocarbons would indicate that the perchlorates were separated from the organics. This experiment might help in the interpretation of the Viking and Curiosity results which also yielded chloromethane derivatives.

References: [1] Biemann K., Oro J., Toulmin III P., Orgel L. E., Nier A. O., Anderson D. M., Simmonds P. G., Flory D., Diaz, A. V., Rushneck D. R., Biller J. E. and Lafleur A. L. (1977) *JGR*, 82, 4641–4658. [2] Hecht M. H., Kournaves S. P., Quinn R. C., West S. J., Young S. M. M., Ming D. W., Catling D. C., Clark B. C., Boynton, W. V., Hoffman J., DeFlores L. P., Gospodinova K., Kapit J. and Smith P. H. (2009) *Science*, 325 64-67. [3] Navarro-González R., Vargas E., de la Rosa J., Raga A. C. and McKay C. P. (2010) *JGR*, 115, E12010. [4] Biemann K. and Bada J. L. (2011) *JGR*, 116, E12001. [5] Navarro-González R. and McKay C. P. (2010) *JGR*, 116, E12002. [6] Grotzinger J. P., Blake D., Crisp J. A., Edgett K. S., Gellert R., Gomez-Elvira J., Hassler D. M., Mahaffy P. R., Malin M. C., Meyer M. A., Mitrofanov I., Vasavada A. R. and Wiens R. C., (2011) *AGU Fall Meeting* U13A-01 [7] Steininger H., Goesmann F., Goetz W. (2011) *Planet. & Space Sci.*, 71, 9-17.

Acknowledgments: This work was funded by DLR (FKZ 50QX1001)