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Influence of the sample mineralogy on the nature of the organic compounds detected by the SAM experiment analysis condition at Gale Crater.

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1 Introduction

1.1 Structure and aim of SAM

Sample Analysis at Mars (SAM) is one of the instruments of the MSL mission. It is devoted to analyze the composition in volatile species contained in solid samples collected by the Curiosity rover. To do it, it is composed of 3 complementary analyzers : the Tunable Laser Spectrometer (TLS), the Gas Chromatography (GC) and the Mass Spectrometer (MS) (Mahaffy et al., 2012).

Solid samples can be treated by different ways to extract the volatile compounds and inject them in the analyzers : **(a)** a pyrolysis system, **(b)** wet chemistry: MTBSTFA and TMAH **(c)** the hydrocarbon trap (silica beads, Tenax® TA and Carbosieve G) and the injector trap (Tenax® GR) (Mahaffy et al., 2012).

1.2 Definition of pyrolysis and derivatization

Pyrolysis is the thermal degradation of chemical compounds with the aim is to reduce the sizes of molecules to increase their volatilities to analyze them by GC-MS and those in the absence of oxidant like oxygen (Stauffer, 2003).

Pyrolysis has the advantage of being easily implemented because it does not require the use of solvent contrary to thermochemolysis and pyrolysis. However, this technique has the inconvenience to bring about a large number of products (pyrolysats). The molecules produced by pyrolysis are function of the pyrolysis conditions (Moldoveanu, 1998, 2010).

Derivatization replaces labile hydrogens (e.g. present in a group -OH, -COOH, =NH, -NH2) with apolar groups. Polarity of the targeted molecule decrease and the volatility is increased (Orata, 2007)**.** On SAM wet chemistry unit, the N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA) is used as derivatization agent (Mahaffy et al., 2012).

1.3 Interaction of organic matter with minerals during pyrolysis - Generalities

During pyrolysis, minerals may have several effects on the organic material: degradation, transformation or preservation (François, 2014).

Degradation of organic matter can be catalyzed by solid phase minerals or be triggered by the formation of secondary products coming from the thermal degradation of minerals such as oxygen.

Pyrolysis of mineral may also transform the organic material such as sulfuration caused by sulfates.

Some minerals have the ability to maintain organic matter in specific conditions. During the pyrolysis, the minerals will degrade at various temperatures. Thus, the thermal degradation of a mineral does not affect the organic material enclosed in another mineral which have a higher thermal decomposition temperature.

1.4 Interaction of organic matter with minerals during pyrolysis – Example of perchlorates

The measurements done with the SAM experiment on Mars have already proved the impact of minerals on the molecules detected. Indeed, the presence of perchlorates has been demonstrated. When this salt is exposed to a thermal energy, it is decomposed and leads to the production of oxygen O_2, hydrogen chloride Cl_2 (Kirillov & Svynko, 1988) or chlorine HCl when water is present.

Thermal degradation products of perchlorates react with organic molecules and the products of this reaction have been highlighted by SAM: some aliphatic chlorinated species have been detected. In fact, these chlorinated aliphatic compounds are produced by the reaction between perchlorates and degradation products of the derivatizing agent (MTBSTFA) by the reactions of chlorination, hydrochlorination and oxychlorination (Glavin et al., 2013; Ming et al., 2014).

In conclusion, the mineralogy is an essential parameter to be taken into account in the interpretation of GC-MS analysis.

1.1 Mineralogy on Gale Crater and result of pyrolysis of organic compound with kieserite in SAM condition

Gale Crater contains a wide variety of minerals which are divided into strata and whose evolution of composition is influenced by the deposition environment. Among these minerals, we can cite silicates, clays, sulfates, iron oxides and perchlorates (Ming et al., 2014; Vaniman et al., 2014) .

Kieserite is a hydrated sulfate ($MgSO_4.H_2O$). When it is thermally decomposed, kieserite generates sulfur dioxide (SO_2) and dioxygen (O_2) which could interact with organic matter by oxidation and sulfidation (addition of sulfur) (Lau, Cubicciotti, & Hildenbrand, 1977). When the kieserite is pure, the thermal decomposition of kieserite occurs around 1000°C (Scheidema & Taskinen, 2011) but in the presence of reducing species, this temperature may decrease.

From the work of François et al. (2014) we know that the degradation of kieserite impacts the organic matter. Indeed, two molecules were tested: phthalic acid and alanine. The production of a large number of aliphatic and aromatic compound has been observed, and those either in the presence of phthalic acid and alanine. Among pyrolysates, we can cite phenol, benzofuran and octathiocane for phthalic acid and pyridine and benzonitrile for alanine.

Then, during the SAM pyrolysis of sample containing kieserite, the thermal degradation products of kieserite and MTBTFA will likely initiate the formation of various compounds.

1.5 Objectives

The objective of our study is to identify and list all the compounds that can be produced by the interaction of MTBSTFA and kieserite at high temperature to help for the interpretation of SAM results.

2 Experiments and methods

Upstream of the GC-MS (thermo ISQ) is placed a pyrolyzer (CDS Pyroprobe 5150) able to reproduce the SAM conditions.

Pyr-GC-MS. GC-MS is equipped with a Rtx-5Sil MS column (30 m×0.25 mm×0.25 µm) with a helium flow in the column of 1.1ml/min with a split of 15 mL/min. The sample placed in the pyrolyzer is heated to 35°C/min from 40°C to 850°C. During pyrolysis, the compounds are trapped in the injector by cryogenic trap at -30°C. The transfer line between the pyrolyzer and GC-MS is heated to 250 ° C.

Three samples are analyzed under pyrGCMS conditions of SAM: MTSBTFA, kieserite and the mixture of the two.

Table 1: Samples analysed by pyr-GC-MS reproducing the SAM GC-MS analysis

N°	Name	Composition
1	WCM	0.2mg MTBSTFA
2	MgS	20mg of $MgSO_4.H_2O$
3	WCM_MgS	20mg of $MgSO_4.H_2O$ + 1%wt of MTBSTFA

3 Results and interpretation

All the aliphatic and aromatic molecules detected will be presented and the phenomenon involved on the pyrolysis of samples will be shown. From these results we will be able to better understand the origin of the organic molecules detected with SAM.

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