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Constraining the source of chlorinated hydrocarbons detected on Mars with the SAM experiment onboard Curiosity

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1. Introduction

1.1 Interest of exploration on Mars

Organic molecules have been at the origin of the prebiotic chemistry that led to the emergence of life on Earth. Therefore, they are one of the key ingredients required to assess the habitability in environments of the solar system. On Mars, no endogenous organics were found until very recently (1) whereas they are expected to be present in the soil, either because they were kept safe in rocks since the early history of the planet, or because they are still brought to the Mars surface by exogenous sources. Because of their importance for astrobiology, efforts are still ongoing to search for these species in the Gale crater by the Curiosity rover, and especially the SAM experiment on its board.

1.2 Structure and aim of SAM

Sample Analysis at Mars (SAM) is one of the instruments of the MSL mission. It is devoted to characterize the composition in volatile species of the atmosphere and the soil samples collected by Curiosity, and more particularly the organic molecules. Three analytical devices are onboard SAM: the Tunable Laser Spectrometer (TLS), the Gas Chromatography (GC) and the Mass Spectrometer (MS) (*2*).

Solid sample preparation: To adapt the nature of a sample to the analytical devices used, a sample preparation and gas processing system implemented with **(a)** a pyrolysis system, **(b)** wet chemistry: MTBSTFA and TMAH **(c)** the hydrocarbon trap (silica beads, Tenax® TA and Carbosieve G) which is employed to concentrate volatiles released from the sample prior to GC-MS analysis.

1.3 Detection of chlorinated hydrocarbons

Viking landers (1976): The origin of chloromethane and dichloromethane was explained at the time by terrestrial contamination from the instruments (*3*). In a recent paper from Navarro-González (*4*), these results have been reinterpreted and chlorinated compounds could have been the product of the reaction of perchlorates identified by Phoenix (*5*) with organic materials in the sample.

MSL (2011): Abundant chlorinated hydrocarbons have been detected with the SAM experiment when analyzing samples collected in several sites explored by the Curiosity rover (Table 1). Most of these chlorohydrocarbons are produced during the pyrolysis of the solid sample by the reaction of Martian oxychlorine compounds present in the soil with organic carbon from a derivatization agent (MTBSTFA) used in SAM (*6*, *7*). Chlorobenzene cannot be formed by the direct reaction of MTBSTFA with perchlorates (*6*) and two other reaction pathways for chlorobenzene were therefore proposed : ***(1)*** reactions between the volatile thermal degradation products of perchlorates (e.g. O_2, Cl_2 and

Viking	MSL		
	RN	JK	CB
CH_3Cl	CH_3Cl	CH_3Cl	CH_3Cl
CH_2Cl_2	CH_2Cl_2	CH_2Cl_2	CH_2Cl_2
nd	$CHCl_3$	$CHCl_3$	$CHCl_3$
nd	CCl_4	CCl_4	CCl_4
nd	nd	nd	C_3H_6Cl
nd	C_4H_7Cl	nd	nd
nd	C_6H_5Cl	C_6H_5Cl	C_6H_5Cl

Table 1: chlorinated hydrocarbon molecules detected during Viking and MSL missions (nd: Non Detected)

HCl) and Tenax® and ***(2)*** the interaction of perchlorates (T>200°C) with OM from Mars's soil such as benzenecarboxylates (*8*, *9*).

1.4 Objectives

This study aims at evaluating the potential of several chemical pathways to form chlorinated hydrocarbons by specifically looking for: **(a)** all the organic products coming from the interaction of Tenax® and perchlorates, **(b)** also between some soil samples and perchlorates and **(c)** sources of chlorinated hydrocarbon precursors. This study should allow to improve the discrimination between chlorohydrocarbons formed with SAM internal organics and those produced with organics present in the soil samples analyzed.

2 Experiments and methods

To answer some of our remaining questions, laboratory experiments have been done in several solid matrixes which have been brought into direct contact with perchlorates and heated.

2.1 Solid matrix

Three solid matrixes have been analyzed.
Fused silica: It is used as a free organic sample.
Tenax®GR: This polymer absorbent can release organic compounds under high temperature (*11*).
JSC-Mars1: JSC-1 is Martian regolith simulant collected in volcanic active area in Hawaii (*12*).

2.2 GC-MS analysis

In this work, we have performed a (A, Table 2) direct (i.e. solid matrix and perchlorates are mixed together in the injector) and (B, Table 2) indirect (i.e.

Composition of sample		
Direct contact (A)		
A1	25mg Fused silica + 24 mg $CaClO_4$	
A2	25mg Tenax® GR + Various amount of $CaClO_4$	
A3	132mg JSC-Mars1 + $CaClO_4$ (9 wt%)	
Indirect Contact (B)		
	Reactor	Injector
B1	24mg $CaClO_4$	25mg Fused silica
B2	Various amount of $CaClO_4$	24mg Tenax®GR

Table 2: Samples use in GC-MS studies

perchlorate is in the reactor which is upstream from the injector where the solid samples are placed). The abundances of Ca-perchlorate used in these experiments are much higher than SAM perchlorate abundance estimates of 0.3-0.5 wt% at Rocknest (6). The GC-MS is a Thermo Trace GC Ultra with a Restek Rtx-5 Sil-MS column (30m×0.25mm×0.25µm), coupled to the MS (Thermo DSQII). The helium flow was maintained constant at 1mL/min (split 10mL/min). The temperature of the column was started at 35 °C maintained 8min then increased at 7 °C/min to a final temperature of 300 °C for another 2 min.

3 Results and discussions

Martian origin Once the OM and perchlorates raise a higher temperature than 400°C; chlorinated compounds are produced including linear (chlorinated alkane derivatives) and aromatic compounds (chlorinated phenyl derivatives). Among these aromatic compounds we have detected chlorobenzene (Table 1) which has already been detected with no ambiguity at the Mars surface by SAM. Then precursors of chlorinated hydrocarbons might be preserved on the surface of Mars notably by the phyllosilicates.

4 Conclusion

Chlorinated compounds highlighted by SAM on Mars could have several origins: from perchlorate and/or MTBSTFA oxidation, from Tenax® degradation with or without presence of perchlorate and/or Martian organics. We have established a list of all the compounds likely to be produced by SAM contamination and compared it with all the compounds detected by SAM.

References: 1. C. Freissinet et al., (2015) JGR Planets 2. P. R. Mahaffy *et al.* (2012) *Space Sci. Rev.* **170**, 401–478. 3. K. Biemann (1977) *JGR* **82**, 4641–4658. 4. R. Navarro-González *et al.* (2010) *JGR* **115**, E12010. 5. M. H. Hecht *et al.* (2009) *Science* **325**, 64–67. 6. D. P. Glavin *et al.*(2013) JGR **118**, 1955–1973. 7. L. a Leshin *et al.* (2013) *Science* **341**, 1238937. 8. C. Freissinet *et al.* (2014) LPSC XXXXV Abstract 2796. 9. H. Steininger *et al.* (2012) *Planet. Space Sci.* **71**, 9–17. 10. D. T. Vaniman *et al* .(2014) *Science* **343**, 1243480. 11. A. Buch *et al.* (2014 LPSC XXXXV Abstract 2886. 12. C. C. Allen *et al.*

(1997) LPSC XXVII Abstract 1797, 13. C. Freissinet *et al.* (2015) JGR 120, 495-514.