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► **To cite this version:**

A. Buch, Imène Belmahdi, Cyril Szopa, Caroline Freissinet, Daniel Glavin, et al.. Determination of the Possible Sources of Chlorinated Hydrocarbons Detected During Viking and MSL Missions. 46th LPSC Lunar and Planetary Science Conference 2015, Mar 2015, The Woodlands, United States. hal-01815527

HAL Id: hal-01815527

<https://hal.science/hal-01815527>

Submitted on 14 Jun 2018

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Determination of the Possible Sources of Chlorinated Hydrocarbons Detected During Viking and MSL Missions.

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Interest of exploration on Mars

Mars is interesting given that its early history is similar to one on the Earth. In fact, volcanoes were still active, the environment was wetter and warmer and the magnetosphere still existed.

Source of organic Mars: Various sources of endogenous organic matter (OM) could have existed including (a) abiotic production *via* hydrothermal vents, volcanism and atmospheric synthesis and (b) biotic synthesis. Currently, the sources of extraterrestrial organic compounds that should be delivered to Mars are known: carbon-rich meteorites, micrometeorites, comets and interstellar dust particles.

Stabilization of the OM takes place through three mechanisms described in the article of Lützow (1): (1) First, the selective preservation of OM is described as a phenomenon of accumulation of some compounds because of their resistance against the environment. (2) The second path which allows the persistence of OM is the space isolation of OM from environmental stress. (3) The last way to stabilize the OM is intermolecular interactions between minerals or metal ions with OM. One of the primary objectives of the Mars Science Laboratory (MSL) mission is to search for environments on the Martian surface that have preserved OM.

Structure and aim of SAM

Sample Analysis at Mars (SAM) is one of the instruments of the MSL mission. Three analytical devices are onboard SAM: the Tunable Laser Spectrometer (TLS), the Gas Chromatograph (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 the GC-MS analyses.

Detection of chlorinated hydrocarbons

All chlorinated hydrocarbons detected during the Viking I and II missions and MSL (Rocknest (RN), John Klein (JK), Cumberland (CB) and Confidence Hill (CH)) are listed in Table 1.

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 martian organic carbon present in the sample or terrestrial organic carbon in the instrument or sample handling chain.

MSL (2011): A diverse range of chlorinated hydrocarbons have been detected with SAM after GCMS analysis of samples collected from several sites explored by Curiosity rover (Table 1). Some of these chlorohydrocarbons are produced during pyrolysis by the reaction of martian oxychlorine compounds in the samples with terrestrial carbon from a derivatization agent (MTBSTFA) present in SAM (6, 7). Chlorobenzene (CBZ) cannot be formed by the reaction of MTBSTFA and perchlorates (6) and two other reaction pathways for CBZ were therefore proposed: (1) reactions between the volatile thermal degradation products of perchlorates (*e.g.* O₂, Cl₂ and HCl) and Tenax® and (2) the interaction of perchlorates (T > 200 °C) with OM from Mars's soil such as benzenecarboxylates (8, 9).

Viking	MSL			
	RN	JK	CB	CH
CH ₃ Cl	CH ₃ Cl	CH ₃ Cl	CH ₃ Cl	CH ₃ Cl
CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂	CH ₂ Cl ₂ nd
nd	CHCl ₃	CHCl ₃	CHCl ₃	nd
nd	CCl ₄	CCl ₄	CCl ₄	nd
nd	nd	nd	C ₃ H ₆ Cl ₂	C ₄ H ₇ Cl
nd	C ₆ H ₇ Cl	nd	C ₄ H ₇ Cl	C ₆ H ₅ Cl
nd	C ₆ H ₅ Cl	nd	C ₆ H ₅ Cl	C ₆ H ₅ Cl

Table 1: major chlorinated hydrocarbon detected during the Viking and MSL mission. MXT-CLP column (nd: not detected).

Among all the sample analyzed by SAM, JK and CB sites are interesting; smectites (phyllosilicates - 18 to 22 wt %) and quartz (0.1 to 1 wt %) were detected at the two sites (10) and could have an important role in the preservation of OM (1).

Objectives

This study investigates several hypotheses for chlorinated hydrocarbon formation by looking for: (a) all products coming from the interaction of Tenax® and perchlorates, (b) products between various soil sample and perchlorates and (c) sources of chlorinated hydrocarbon precursors.

Experiments and methods:

To answer some of our remaining questions, laboratory experiments were done in several solid matrices which

were brought directly in contact with perchlorates and heated.

Solid matrices

Four solid matrices were analyzed.

Fused silica: It is used as an organics-free sample.

Tenax®: This polymer absorbent can release organic compounds when heated to temperatures > 300 °C (11).

JSC-Mars1: JSC-1 is a martian regolith simulant collected in volcanic active area in Hawaii (12).

Fontainebleau Sand: Fontainebleau sand is almost pure silica (quartz). This sand has been previously heated to 700 °C during 24 h in our laboratory.

Experiments

GC-MS Analysis

In this work, we have performed a direct (*i.e.* solid matrix and perchlorates are mixed together in the injector) and indirect (*i.e.* perchlorate is in the reactor which is upstream from the injector where the solid samples are placed). The abundances of Ca-perchlorate (3 or 9 wt %) used in these experiments are much higher than SAM perchlorate abundances estimated to be 0.3-0.5 wt % at Rocknest (6). The GC-MS used in experiment is a Thermo Trace GC Ultra with Restek Rtx-5 Sil-MS column (30m×0.25mm×0.25µm), its injector is Optic 3 from ATASGL, and the MS is a Thermo DSQII. The helium flow was maintained constant at 1 mL/min (split 10 mL/min). The temperature of the column was started and held 8 min at 35 °C, then increased at 7 °C/min to a final temperature of 300 °C and held 2 min at this temperature.

Composition of sample		
Direct contact		
A1	132 mg Fused silica + CaClO ₄ (9 wt %)	
A2	132 mg Tenax® GR + CaClO ₄ (9 wt %)	
A3	132 mg Fontainebleau Sand + CaClO ₄ (9 wt %)	
A4	132 mg JSC-Mars1 + CaClO ₄ (9 wt %)	
Indirect Contact		
	Reactor	Injector
B1	CaClO ₄ (9wt %)	132 mg Fused silica
B2	CaClO ₄ (3wt %)	50 mg JSC-Mars1

Table 2 : Samples use in GC-MS studies

Results and discussions:

In the light of the results presented in Table 3, we can conclude that the chlorinated hydrocarbons can originate from two origins:

Martian origin Once the OM and perchlorates are raised to high temperature, chlorinated compounds are produced, even in the sample which contains 3 wt % (B2). Precursors of chlorinated hydrocarbons might be preserved on the surface of Mars as the persistent molecules found in the sample of Fontainebleau's sand (A3).

SAM origin Chlorobenzene is also product by the reaction of perchlorates and Tenax® as other compounds (e.g. No. 9-24)

No	Compounds	A1	A2	A3	A4	B1	B2
1	chloromethane	nd	nd	✓	✓	nd	nd
2	dichloromethane	nd	nd	✓	✓	nd	nd
3	trichloromethane	nd	nd	nd	✓	nd	nd
4	chloroethylene	nd	nd	nd	✓	nd	nd
5	dichloroethylene	nd	nd	nd	✓	nd	nd
6	trichloroethylene	nd	nd	nd	✓	nd	nd
7	tetrachloroethylene	nd	nd	nd	✓	nd	nd
8	chlorobenzene	nd	✓	✓	✓	nd	×
9	dichlorobenzene	nd	✓	nd	✓	nd	nd
10	trichlorobenzene	nd	✓	✓	✓	nd	nd
11	tetrachlorobenzene	nd	✓	✓	✓	nd	nd
12	pentachlorobenzene	nd	✓	✓	✓	nd	nd
13	hexachlorobenzene	nd	✓	✓	✓	nd	×
14	dichlorophenol	nd	✓	nd	nd	nd	nd
15	trichlorophenol	nd	✓	nd	nd	nd	nd
16	tetrachlorophenol	nd	✓	nd	nd	nd	nd
17	pentachlorophenol	nd	✓	nd	nd	nd	nd
18	chlorobenzenediol	nd	✓	nd	nd	nd	nd
19	dichlorobenzenediol	nd	✓	nd	nd	nd	nd
20	chloroterphenyl	nd	✓	nd	nd	nd	nd
21	dichloroterphenyl	nd	✓	nd	nd	nd	nd
22	benzoyl chloride	nd	✓	nd	nd	nd	nd
23	chlorobenzoic acid	nd	✓	nd	nd	nd	nd
24	chloroacétophenone	nd	✓	nd	nd	nd	nd

Table 3: Chlorinated compounds detected in laboratory.

Conclusion. Chlorinated compounds highlighted by SAM on Mars could have several origins: from perchlorate oxidation of MTBSTFA, Tenax® and/or Martian organics. However, due to the higher concentration of chlorobenzene in the Mars sample compared to the blank, this compound is interpreted to be from martian origin. The other line of supporting evidence for a martian chlorobenzene source is the detection of m/z 112 and 114 at ~3:1 ratio in the EGA data that is attributed to CBZ. Based on the SAM gas flow design the CBZ released from the sample cannot be attributed to reaction products from Tenax and the hydrocarbon trap. Then, to determine the origin of chlorobenzene, it is necessary to go further in laboratory investigations by using other way of analyses (13).

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