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RESEARCH ARTICLE
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**Key Points:**
- A systematic study reveals the influence of calcium perchlorate during the pyrolysis of organic compounds from various chemical families
- Some parent organics can be identified after thermal extraction as well as through the production of characteristic pyrolysis product(s)
- The precursors of the chlorohydrocarbons detected on Mars with the SAM instrument could originate from the three chemical families studied

**Supporting Information:**
- Supporting information S1

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# Influence of Calcium Perchlorate on Organics Under SAM-Like Pyrolysis Conditions: Constraints on the Nature of Martian Organics

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**Abstract** Most of the organics detected on Mars so far are aliphatic and aromatic organo-chlorine compounds. The smallest were first identified by the thermal treatment of the solid samples by Viking in 1976; although at the time, they were attributed to contamination. Since 2012, a larger variety of structures have been identified by the Sample Analysis at Mars experiment aboard the Curiosity rover. Evidence suggests that the chlorohydrocarbons formed during pyrolysis of sedimentary materials. Laboratory experiments show that heating of samples containing oxychlorines, such as chlorates ($ClO_3^-$) and perchlorates ($ClO_4^-$), along with organic matter present at Mars' surface is the logical source of these compounds. Nevertheless, this discovery of indigenous organic matter in the Mars regolith raises important questions: How do the oxychlorines influence the pyrolysis of organics? What are the organics precursors of the organo-chlorinated molecules detected on Mars? Is there a way to identify the parent molecules in a sample after pyrolysis? This paper presents the results of systematic laboratory experiments of the products formed during the pyrolysis of organic compounds from three chemical families—polycyclic aromatic hydrocarbons, amino acids, and carboxylic acids—in presence of calcium perchlorates. Results show that the polycyclic aromatic hydrocarbon parent molecules and most of the carboxylic acids are still detectable after pyrolysis in presence of calcium perchlorate and that the degradation and/or evolution of all parent molecules mostly depends on their chemical nature. In addition, we demonstrate that the chlorohydrocarbons detected on Mars by the Sample Analysis at Mars instrument could come from the three chemical families studied.

**Plain Language Summary** Organic molecules are the building blocks of life as we know it, and detecting them on the surface of Mars has been one of the major goals of Mars exploration. Viking landers in 1976, followed by the Curiosity rover in 2012, discovered simple chlorine-bearing organics on Mars. These chlorohydrocarbons are known to be mainly produced by the instrument itself, through chemical reactions at high temperatures between other organic molecules thermally extracted from solid rock and soil samples that react with the oxidizing minerals present on Mars (e.g., perchlorates). Studying the influence of the minerals like perchlorates on the thermal extraction of different parent molecules requires thorough experimental studies like this one. Our work constrains the potential parent molecules of the chlorohydrocarbons detected on Mars in the presence of calcium perchlorate, thereby shedding light on the past and present habitability of Mars.

## 1. Introduction

The first space missions dedicated to the search for biological activity and organic compounds at the Mars' surface were the Viking missions of 1976. Even though no unequivocal traces of life were detected with the experiments designed to detect biological activity (Klein, 1998, and references therein), the analyses of the pyrolyzer gas-chromatograph mass-spectrometer (pyro-GCMS) identified aliphatic organo-chlorinated compounds such as chloromethane and dichloromethane. However, until recently, these were attributed to contamination from the solvents used to clean the instruments prior to construction of the spacecraft

(Biemann et al., 1976, 1977). A few decades later, the Phoenix lander detected magnesium perchlorates ($Mg(ClO_4)_2$) in the soil at its landing site at a high northern latitude (Hecht et al., 2009). More recently, the SAM instrument suite onboard the Curiosity rover detected oxychlorines such as perchlorates and chlorates (Glavin et al., 2013; Sutter, Quinn, et al., 2016), which opened new interpretations regarding the chlorinated compounds detected by Viking. Indeed, it has been suggested that the chlorohydrocarbons detected by the Viking spacecraft were, instead, produced by chemical reactions (chlorination, oxidation, or oxychlorination) occurring during the high temperature pyrolysis (>200 °C) between the perchlorates and traces (typically at the ppm level) organics molecules present in the Martian regolith (Guzman et al., 2018; Mißbach et al., 2019; Navarro-Gonzalez et al., 2010; Steininger et al., 2012). Additional organochlorine compounds have been detected and identified in several solid samples analyzed by Sample Analysis at Mars (SAM) (Freissinet et al., 2015; Glavin et al., 2013; Szopa et al., 2019). These chlorohydrocarbons are reaction products between the inorganic species released from the thermal decomposition of the perchlorates: dioxygen ($O_2$), hydrogen chloride (HCl), and chlorine ($Cl_2$) likely ubiquitous on Mars' surface and organic compounds from various possible origins:

1. the chemical reagent carried into SAM's cups to analyze polar and refractory molecules,
2. organic molecules produced from trap's adsorbents, and
3. organic molecules indigenous to Mars' samples

Some of the $C_1$–$C_3$ aliphatic chloroalkanes are likely produced from reactions with the terrestrial organic compounds carried within the SAM sample manipulation system (SMS) (Glavin et al., 2013) even if other contributions cannot be excluded. The $C_2$–$C_4$ dichloroalkanes and the majority of chlorobenzene are likely coming from reactions between oxychlorines and organic molecules indigenous to the Martian sediment samples (Adande et al., 2007; Freissinet et al., 2015). Only a fraction of the chlorobenzene would come from reactions between the minerals and the materials present in the hydrocarbon traps within SAM (Buch et al., 2019; Miller et al., 2015). One previous empirical study using Mars analog soils identified functionalized organic molecules such as alcohols and carboxylic acids as potential precursors of the chlorohydrocarbons detected by SAM (Miller et al., 2016). In another study, benzene (Benner et al., 2000): acetic acid, benzoic acid, phthalic acid, and mellitic acid were suggested as possible precursors. These molecules have been pyrolyzed under SAM-like operating conditions with 1 wt% of hydrated calcium perchlorates ($(CaClO_4)_2 \bullet nH_2O$) or hydrated magnesium perchlorates ($(MgClO_4)_2 \bullet nH_2O$) in a Mars analog sample comprising iron oxides. These experiments demonstrated the formation of aliphatic and aromatic chlorohydrocarbons such as 1,2-dichloropropane and chlorobenzene. Although this study shed some light on potential precursors of the chlorohydrocarbons detected on Mars, it did not exclude the fact that other molecules or chemical families from an endogenous or indigenous origin could also source these compounds.

Identifying the precursors of the organics present in Mars samples is possible in the laboratory through GCMS analysis of pyrolysis products. Their nature, abundance, and temperature of formation largely depend on the minerals present and the pyrolysis parameters such as the temperature program, the nature of the carrier gas, and its pressure (Moldoveanu, 1998). To identify new organic molecules indigenous to the solid samples with SAM and in the longer term with the Mars Organic Molecule Analyzer (MOMA) GCMS instrument that will be on the Rosalind Franklin ExoMars 2022 rover, studies of the influence of the oxychlorines during pyrolysis of organic compounds are essential.

The main goals of this paper are as follows: (1) characterize the effect of perchlorate on the degradation and/or evolution of the organic molecules and their decomposition products during pyrolysis, (2) identify the organic compounds that can be precursors of the chlorohydrocarbons detected in the Martian samples. and (3) identify chlorohydrocarbons that have not been detected so far but which be detected in the future SAM and MOMA flight experiments.Here we present and discuss the results of our systematic study of the effects of calcium perchlorate on pyrolysis of suites of organic molecules potentially present at Mars' surface.

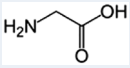
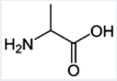
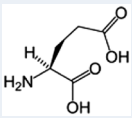
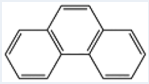
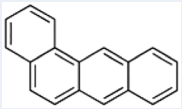
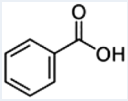
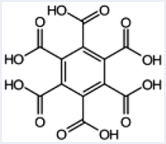
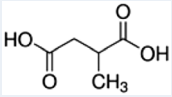
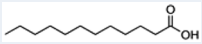
## 2. Material and Methods

### 2.1. Samples

#### 2.1.1. Oxychlorines: Calcium Perchlorate

The perchlorate anion ($ClO_4^-$) was first detected in the Mars regolith by the Thermal and Evolved Gas Analyzer (TEGA) instrument onboard Phoenix at a concentration of 0.4 to 0.6 wt% (Hecht et al., 2009).

**Table 1**
*Structures and Physical Properties of the Organic Molecules Targeted for This Study*

| Chemical family | Compound | Raw chemical formula | Representation | Molar mass (g.mol$^{-1}$) | Boiling point (°C) | Purity (%) |
|---|---|---|---|---|---|---|
| Amino Acids | Glycine | $C_2H_5NO_2$ |  | 75.07 | 233 | ≥99% |
| | Alanine | $C_3H_7NO_2$ |  | 89.09 | 295 | ≥98% |
| | Glutamic acid | $C_5H_9NO_4$ |  | 147.13 | 199 | ≥99% |
| PAH | Napththalene | $C_{10}H_8$ | | 80.26 | 218 | 99% |
| | Phenanthrene | $C_{14}H_{10}$ |  | 178.23 | 336 | 98% |
| | Benzanthracene | $C_{18}H_{12}$ |  | 228.28 | 438 | 99% |
| Carboxylic Acids | Benzoic acid | $C_7H_6O_2$ |  | 122.12 | 249 | 99.5% |
| | Mellitic acid | $C_{12}H_6O_{12}$ |  | 342.16 | 678 | 99% |
| | Methylsuccinic acid | $C_5H_8O_4$ |  | 132.11 | 117 | 99% |
| | Dodecanoic acid | $C_{12}H_{24}O_2$ |  | 200.31 | 298 | 98% |

Various cations contribute to this signal: $Mg^{2+}$, $Na^+$ and $K^+$, and $Ca^{2+}$ at a lower concentration. Results of the Wet Chemistry Laboratory (Phoenix) identified the presence of $Mg^{2+}$ and $Ca^{2+}$ without excluding contributions from other cations (Cull et al., 2010; Elsenousy et al., 2015). These detections are consistent with the temperature release of $O_2$ for calcium perchlorate between 325 and 625 °C (Hecht et al., 2009). The SAM instrument also confirmed these detections in the samples collected in Gale crater, showing perchlorates are likely widespread on Mars' surface. Their abundance is estimated to be in the 0.3 and 0.5 wt% range in the Rocknest sample (Archer et al., 2014; Leshin et al., 2013) and up to 1.3 wt% in the Cumberland (CB) sample (Ming et al., 2014). Laboratory studies of the decomposition temperature of different perchlorates have constrained the nature of the oxychlorines present in Mars samples. Without excluding the contribution of other cations and/or another anion such as chlorate ($ClO^{3-}$), the most likely candidate for Rocknest is calcium perchlorate: Ca $(ClO_4)_2$ (Archer et al., 2014; Glavin et al., 2013; Sutter, McAdam, et al., 2016), and accordingly, we chose it as the oxychlorine of reference for this study.

### 2.1.2. Organic Compounds

Organic compounds (see purity in Table 1) from three different chemical families were selected:

1. Amino acids for their astrobiological interest and their known presence in meteorites and, potentially, comets. Among the amino acids, we chose glycine ($C_2H_5NO_2$), alanine ($C_3H_7NO_2$), and glutamic acid ($C_5H_9NO_4$) (Altwegg et al., 2016; Glavin et al., 1999; Glavin et al., 2004; Sephton, 2012).
2. Polycyclic aromatic hydrocarbons (PAHs) were chosen for their abundance in meteorites, including Martian ones, and in interplanetary dust particles. We chose naphthalene ($C_{10}H_8$), phenanthrene

($C_{14}H_{10}$), and benzanthracene ($C_{18}H_{12}$) (Flynn et al., 2008; Sephton, 2012; Steele et al., 2012), respectively, composed of 2, 3, and 4 fused rings, to gauge the impact of molecular size.

3. Carboxylic acids as potential oxidation products of macromolecular organic matter under Mars surface environmental conditions (Benner et al., 2000; Poch et al., 2013) and potential precursors of some chlorohydrocarbons detected on Mars (Miller et al., 2016). Benzoic acid ($C_7H_6O_2$), mellitic acid ($C_{12}H_6O_{12}$), dodecanoic acid ($C_{12}H_{24}O_2$), and methylsuccinic acid ($C_5H_8O_4$) were chosen to provide structural variety (Martins, 2011) as summarized in Table 1.

The potential presence of contaminations of the pure compounds was assessed by GCMS and no significant contaminants were detected.

### 2.2. Sample Preparation

As the primary goal of this study was to characterize the molecules produced through the pyrolysis of perchlorate with organics, we excluded the use of minerals other than perchlorate. Catalytic effects of minerals such as iron oxides (magnetite and hematite) and/or protector minerals such as sulfates (e.g., the kieserite) have been previously studied (Francois et al., 2016) and will be partly compared to this work. To discriminate the pyrolysis products resulting from the effect of the oxychlorines to those resulting from the thermal decomposition of the pure molecules, the analyses were performed in two steps:

1. Pyrolysis of calcium perchlorate and organic compounds individually.
2. Pyrolysis of calcium perchlorate mixed with each organic molecule separately.

In order to facilitate the cross comparison between the results obtained with different molecules, the organics to calcium perchlorate mass ratio were the same for each organic molecule studied, as well as the mass of sample pyrolyzed. The abundances of organic compounds present in Mars' regolith were unknown. Hence, we must rely on estimates based on prior detections of organochlorine compounds in Gale crater. For the CB sample, these were ~90 to ~180 pmol of chlorobenzene and ~26 pmol of dichloroalkanes (Freissinet et al., 2015) and in the Mojave and Confidence Hill samples where the total organic carbon was estimated at ~91.4 and ~60.2 pmol, respectively (Eigenbrode et al., 2018). However, because these concentrations are too low to achieve a complete characterization of all the molecules produced in the pyrolytic process and because of the need for sample preparation to be reproducible, we chose 0.5 wt% (5,000 wtppm) as the higher limit concentration in organics might be found on Mars.

As mentioned earlier, calcium perchlorate is in the order of 0.07 to 1.3 wt%. Knowing the low organics amount in the Martian regolith compared to the oxychlorine salts, we chose a perchlorate concentration to be twice that of the organics namely 1 wt%, a value consistent with the average concentration detected by SAM in the Cumberland samples. Except for the pyrolysis of pure compounds, pure fused silica powder was used to prepare the samples containing the correct concentrations of calcium perchlorate and organic molecules. Fused silica was also chosen for analytical reasons at it is supposed to be chemically inert during pyrolysis (Schulten & Leinweber, 1993) and chemically and physically stable within the temperature range of pyrolysis (40 to 850 °C).

The practical sample preparation was achieved in a series of steps:

1. The silica ($SiO_2$), fused synthetic quartz supplied by Sigma-Aldrich (~44 μm grains size powder) was conditioned at 900 °C for 48 hr in an ashing oven to remove any potential organic contamination.
2. Calcium perchlorate and organic compounds were crushed separately using a ceramic mortar and pestle. As calcium perchlorate is extremely hygroscopic, a preheating step was mandatory to dehydrate before crushing and this was done in an oven heated at 80 °C. The crushing step was then conducted in a hot mortar to limit the reabsorption of water during this step. Coulometric Karl Fisher measurements were done on a sample and less than 1% of water was measured when using this preparation technic (Buch et al., 2019).
3. Calcium perchlorate and organic molecules were diluted individually in silica powder in their solid state, at 2 and 1 wt%, respectively. These values allowed final concentrations of 1 and 0.5 wt% of organics and calcium perchlorate, respectively, when mixed together. The scale used is precise at 0.001 and the silica was slowly incorporated in 4 ml vials containing the compounds and vortexed at each incorporation.
4. For the evolved gas analysis (EGA), the samples were prepared separately, at a concentration of 10 wt% in the fused silica.

**Table 2**
*Analytical and Pyrolysis Conditions Used for the EGA and Pyro-GCMS Laboratory Experiments Compared to Those Used in the SAM Instrument*

| | | EGA | Pyro-GCMS | SAM conditions |
|---|---|---|---|---|
| Pyrolyzer | Initial temperature (°C) | 80 | 40 | ~30 |
| | Final temperature (°C) | 850 | 850 | 850–900 |
| | Ramp temperature (°C.min$^{-1}$) | | 35 | |
| | Cryotrap temperature (°C) | NA | - 180 | NA |
| | Interface temperature (°C) | 250 | | NA |
| | Carrier gas flow rate (mL.Min$^{-1}$) | 0.5 | 1 | 0.9 |
| Injector | Temperature (°C) | | 250 | |
| | Split flow rate (mL.min$^{-1}$) | 20 | 10 | NA |
| | Cryotrap temperature (°C) | NA | - 190 | NA |
| GC | Column | Stainless steel tube (2.5 m, 0.15 mm ID) | Rxi 5Sil MS w/5 m integra-guard (30 m, 0.25 m, 0.25 μm) | MXT-CLP (30 m, 0.25 m, 0.25 μm) |
| | Carrier gas | | Helium | |
| | Carrier gas flow rate (mL.min$^{-1}$) | 0.5 | 1 | 0.9 |
| | Temperature program | 250 °C isothermal | $T_i$ = 33 °C for 3 min, 6 °C.min$^{-1}$ then 10 °C.min$^{-1}$ rate, $T_f$ = 300 °C for 1 min | Ti ~ 40 °C to 190 °C at 10 °C.min$^{-1}$ rate |
| MS | m/z range scanned | 10–80 | 40–500* | 10–535 |
| | Voltage filament (eV) | | 70 | |
| | Ion source temperature (°C) | | 350 | |
| | Transfer line temperature (°C) | 300 | | 135 |

*Note*. For some analyses, the scan range was initiated at m/z 30 to highlight the HCl. As HCl is saturating in the analyses, the scan range was fixed at an initial m/z of 40 for most of them. HCl is then not detected and has not disturbed the identification of the lighter volatiles eluting at the same time.

5. For the pyrolysis-GCMS of the organic/calcium perchlorate mixture, 5 mg of organic diluted in fused silica and 5 mg of perchlorate diluted in silica were collected and deposited in the cup, corresponding to a final sample weight of 10 mg. To obtain an intimate mixture of organics and oxychlorines, the powder was packed prior to pyrolysis by tapping the cup. Note that the order of deposit in the cup: perchlorates or organics first or the mix of both phases prior to deposit in the cup has been tested and does not influence the result.

## 2.3. Analytical Methods

### 2.3.1. EGA

EGA enables detection of the chemical species degassing from a sample as a function of the pyrolysis temperature. EGA was performed using an EGA/PY-3030D microoven pyrolyzer (FrontierLab) mounted on the split/splitless injector of a GC Trace gas chromatograph coupled to an ISQ mass spectrometer (ThermoFisher). Analyses require a short GC column without stationary phase so there is no interaction with the volatiles analyzed. The metallic column chosen for these experiments was 2.5 m long and 0.15 mm internal diameter. The carrier gas (helium, purity > 99.9998%, Air Liquide) flow rate was set to 0.5 ml min$^{-1}$. Calcium perchlorate was analyzed pure (0.5 mg ± 0.1 mg) and diluted in fused silica (5 mg at 10 wt%) to check the possible effect of silica on the thermal decomposition temperature of perchlorate. The weak intensity variations observed do not influence the EGA interpretation, and the intensity ratios of the peaks were reproducible from one species to another. The released temperature ranges of the species of main interest for the interpretation of the pyrolysis-GCMS results were also reproducible. Organic compounds were analyzed pure and individually (0.2 to 0.5 mg). Analyses, as described in Table 2, were performed in triplicate, interspersed with blanks, to ensure reproducibility.

The detection of volatile compounds is done either by monitoring the MS signal for all the ions produced within the 10–80 Da range or by monitoring the ions characteristics of the studied species. We use the first method to process the EGA of the organics in order to highlight their characteristic fragments. For calcium perchlorate, we chose the second method and focused only on the species that could influence the organic molecules such as water ($H_2O$, m/z 18), oxygen ($O_2$: m/z 32), hydrochloric acid (HCl: m/z 36), and chlorine ($Cl_2$: m/z 70).

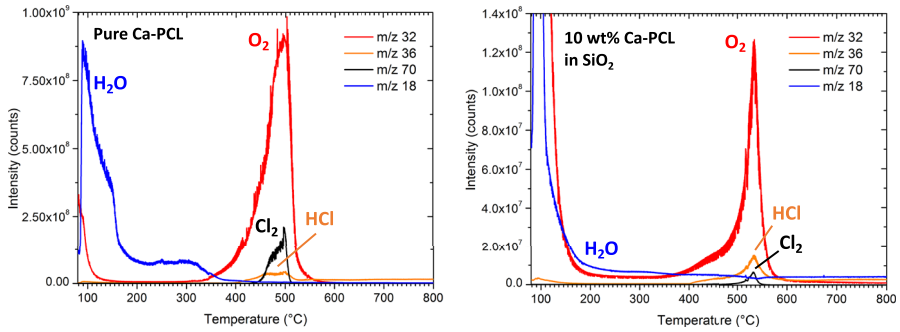



**Figure 1.** Thermally evolved gas analysis of (left) pure calcium perchlorate and (right) 10 wt% of calcium perchlorate diluted in silica. Compounds are as follows: m/z 32: Oxygen ($O_2$), m/z 36: hydrochloric acid (HCl), m/z 70: chlorine ($Cl_2$), and m/z 18: water ($H_2O$). Differences are observed within the range of releasing temperatures of the species considered. More $Cl_2$ is released when calcium perchlorate is pyrolyzed pure as shown with a peak intensity of $2.10^8$ counts compared to a peak intensity of $0.5.10^7$ counts when calcium perchlorate is diluted in the silica. The mass of calcium perchlorate was the same in each case and equals to 0.5 mg.

#### 2.3.2. Pyrolysis-GCMS

Pyrolysis-GCMS provides the means to identify the pyrolysis products and was performed using the same commercial instrument as for EGA. The analytical parameters of the pyrolyzer were chosen to be as close as possible to the SAM's pyrolyzer temperature program (Table 2). As the pyrolysis performed with SAM is slow (~30 min to rise to its maximum temperature), a liquid nitrogen cryotrap (−190 °C) was installed at the chromatographic column inlet in order to condense the compounds degassing from the samples throughout pyrolysis. Once pyrolysis was complete, the cryotrap was stopped so that the trapped species quickly evaporated prior to chromatographic separation. The analytical conditions are described and compared to the SAM pyrolysis conditions in Table 2.

For the separation, a Restek Rxi-5Sil MS (30 m, 0.25 mm i.d., and 0.25 μm stationary phase thickness) column, including a 5 m long integra-guard tube, was utilized. It was selected for its capability to separate a wide range of organic compounds and its robustness against the corrosive gases released from the thermal decomposition of calcium perchlorate. The carrier gas flow rate and the column temperature program were set to optimize the column's efficiency and achieve an efficient separation of the pyrolysis products (Table 2).

Pure silica was first pyrolyzed to assess potential contamination and provide a control blank (Figure S1 in the supporting information). As for EGA, control blanks for pyrolysis-GCMS analysis were performed between each sample analysis to identify and remove and potential contamination from previous analyses and repeated as necessary. Peaks present in the total ion current (TIC) or evident in the extracted ion chromatograms (EIC) were identified using the Xcalibur software package (Thermofisher) and comparison to the National Standard Institute of Technology mass spectra database and, in some cases, to the compound elution times.

## 3. Results and Discussion

### 3.1. Thermal Behavior of Calcium Perchlorate and the Organic Molecules

Few differences were observed between the EGA of calcium perchlorate pure versus calcium perchlorate diluted in silica meaning the silica partly influences the release of the species targeted ($O_2$, HCl, $Cl_2$, and $H_2O$). To evaluate this influence, we focused on (1) the nature of the species released, (2) the peaks and the temperature range the species of the release, and (3) the intensity of the peaks. The thermograms of the gases released by calcium perchlorate/organics during pyrolysis are presented in Figures 1 and 2.

#### 3.1.1. Thermal Behavior of Calcium Perchlorate

EGA analyses of calcium perchlorate were performed in previous studies (Sutter, Quinn, et al., 2016), and results are discussed below. However, to correctly interpret the results of our study, it was necessary to acquire those data under the experimental conditions as described above.

Figure 1 shows the comparison of the EGA performed with pure calcium perchlorate and calcium perchlorate diluted in silica. Species released from ambient temperature up to 100 °C, except for water, were not

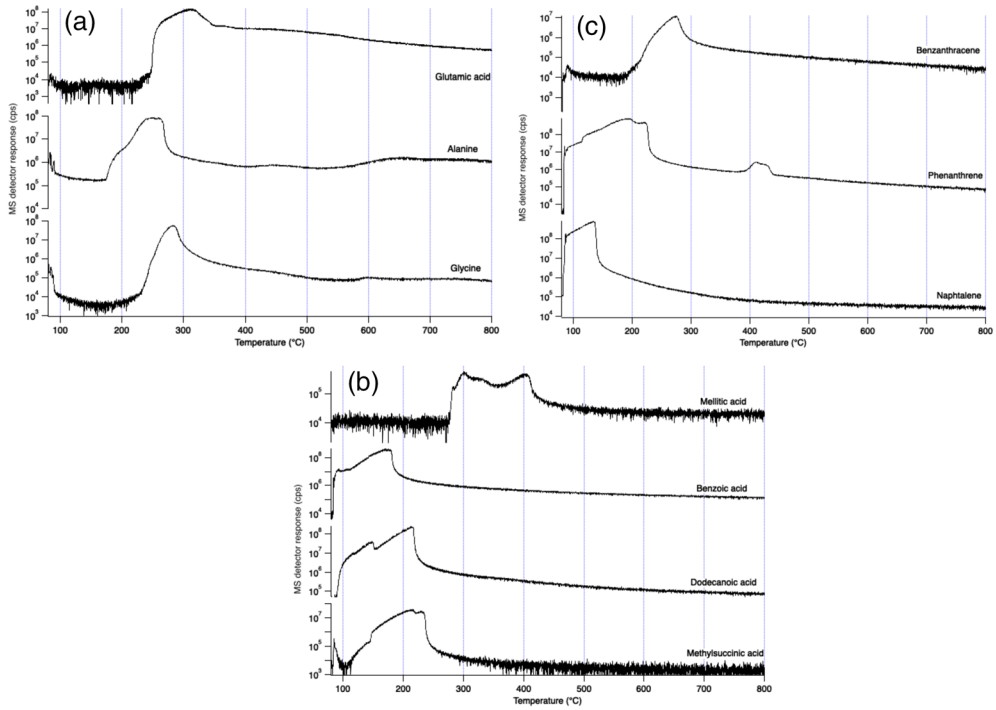



**Figure 2.** Thermally evolved gas analysis of the organic molecules diluted in silica and followed with a specific ion, that is, (a) amino acids (glycine with m/z 30, alanine m/z 44, and glutamic acid m/z 84), (b) carboxylic acids (mellitic acid with m/z 174, benzoic acid m/z 122, dodecanoic acid m/z 73, and methylsuccininc acid m/z 114), and (c) PAHs (naphthalene with m/z 128, phenanthrene m/z 178, and benzanthracene m/z 228.

considered since they mostly represent volatiles entering the helium stream as the cup is dropped into the pyrolyzer oven.

Water released by the sample is mainly observed up to 200 °C. Despite precautions taken to prevent atmospheric water adsorption on the samples during their preparation, it is likely that water adsorbed on the silica or calcium perchlorate during the time it takes to transfer the sample to the pyrolyzer. This water can be attributed to the desorption from calcium perchlorate and silica. This hypothesis is confirmed by the diminution of the $Cl_2$ peak in the presence of silica. A proportion of the $Cl_2$ can indeed react with water to form HCl at low temperature and also detected in this analysis (Sutter, Quinn, et al., 2016). This is consistent with SAM's Mars data where $Cl_2$ is not detected in EGA whereas HCl is. The EGA of pure silica showed some water release confirming ready hydration of silica during the analyses. The dehydration of calcium perchlorate, followed by its thermal decomposition, lead to the production of $O_2$ and the formation of chloride (Sutter, Quinn, et al., 2016). These reactions and the species released are consistent with those observed in calcium perchlorate thermograms. These trends changed slightly when calcium perchlorate is diluted in silica.

The comparison between the EGA of pure calcium perchlorate and diluted in silica (Figure 1) shows the release of the four species considered. At 500 °C, $O_2$, HCl, and $Cl_2$ peaks are detected. Results are similar for both samples except that a shift of 40 °C through the high temperatures is observed for $H_2O$, $O_2$, and $Cl_2$ when calcium perchlorate is diluted in silica. HCl is released around 400 °C in both cases, but the range is expanding to 620 °C for calcium perchlorate/silica, whereas it ends at 530 °C when pyrolyzed alone. Intensities also decreased of an order of magnitude for calcium perchlorate diluted in silica. The only exception is observed for HCl, where 2 orders of magnitude more in presence of silica. The thermal decomposition of calcium perchlorate occurs in several steps consistent with data from previous studies (Francois et al., 2016; Migdał-Mikuli & Hetmańczyk, 2008):

1. Water is released between 80 and 150 °C. The hydrated calcium perchlorate melts around 85 °C, and all the water adsorbed is released. It is also possible that part of the water release comes from the dehydration of silica.

**Table 3**
*Temperatures Related to EGA Measurements of Organics and Calcium Perchlorate in Silica*

| | Minimum temperature sublimation is observed (°C) | Maximum temperature of the peak of sublimation (°C) | Sublimation tail |
|---|---|---|---|
| Glycine | 230 | 330 | Small |
| Alanine | 180 | 280 | Almost not |
| Glutamic Acid | 250 | 350 | Significant |
| Naphthalene | 80 | 150 | Almost not |
| Phenanthrene | 80 | 230 | Small Second peak 390–430 °C |
| Benzanthracene | 200 | 280 | Small |
| Methylsuccinic Acid | 110 | 240 | Almost not |
| Decanoic Acid | 90 | 220 | Small |
| Benzoic Acid | 80 | 180 | Small |
| Mellitic Acid | 270 | 420 | Almost not |
| Calcium Perchlorate | 400 | 560 | Almost not |

2. In presence of silica, a portion of water is constantly released to 850 °C. It is likely that a portion of the water released by calcium perchlorate during step 1 was first adsorbed by the silica and then released at a higher temperature during the its dehydration.
3. At 416 °C, the dehydrated calcium perchlorate melts. This step is not observed in our results because it cannot be observed by EGA (Francois et al., 2016; Migdał-Mikuli & Hetmańczyk, 2008).
4. $O_2$ is released between 380 and 570 °C with a maximum around 535 °C. It shows the production of $O_2$ and the thermal decomposition of calcium perchlorate. The $O_2$ release is correlated with the $Cl_2$ release in agreement with the following mechanism of decomposition:

$$\mathbf{3}\mathrm{Ca(ClO_4)_2\ (liquid)} \rightarrow \mathbf{2}\mathrm{CaO(solid)} + \mathrm{CaCl_2(solid)} + \mathbf{11}\mathrm{O_2(gas)} + \mathbf{2}\mathrm{Cl_2(gas)}$$

The $Cl_2$ peak at 500 ± 10 °C with a maximum at 550 °C is correlated with a HCl release observed between 400 and 650 ± 20 °C the latter formed from the water and $Cl_2$ release. A portion can also be produced from calcium chloride ($CaCl_2$) formed via the previous reaction. Taking into account its high vapor pressure, it can partly sublime itself (Dow, 2003). $Cl_2$ and HCl are released in lower abundance compared to $O_2$ during the thermal decomposition of calcium perchlorate.

In conclusion, silica seems to play a role on the thermal decomposition of calcium perchlorate by absorbing a part of the heat provided by the pyrolyzer. This process leads to an increase of the peak widths and release temperature ranges of the species that take more time to extract themselves from the samples. Moreover, they are released in lower amounts in presence of silica. This phenomenon can be increased if the volatiles are adsorbed onto the silica's surface which becomes a substrate than a solid matrix diluting calcium perchlorate. In that case, the adsorbed volatiles on the silica would require higher energy to desorbed from the surface, which could explain the temperature shift observed.

To interpret the results in the following sections, only the EGA data of calcium perchlorates diluted in silica has been considered since all species have been diluted in silica for the pyrolysis-GCMS experiments.

#### 3.1.2. Thermal Behavior of the Organic Molecules

For all the studied compounds, a peak of maximum sublimation is observed in a given range of temperature. It can be observed early in the EGA at lower temperatures (for phenanthrene, naphthalene, benzoic acid, dodecanoic acid, and methylsuccinic acid) or at higher temperatures (all three amino acids, benzanthracene, and mellitic acid). After the major peak and depending the compound, two behavior modes are observed: (1) The sublimation stops quickly with the temperature increase, and (2) the sublimation continues at higher temperatures (i.e., glutamic acid). A unique exception is observed for phenanthrene, which shows a second peak, smaller than the first one, in the 400–440 °C temperature range (Table 3).

### 3.2. Influence of Calcium Perchlorate on the SAM-Like Pyrolysis of Organic Molecules Potentially Present on Mars in Presence of Silica

The influence of calcium perchlorate was evaluated for each organic compound from the same chemical family, all diluted in silica prior to the analysis. The pyrolyzates formed through the action of calcium

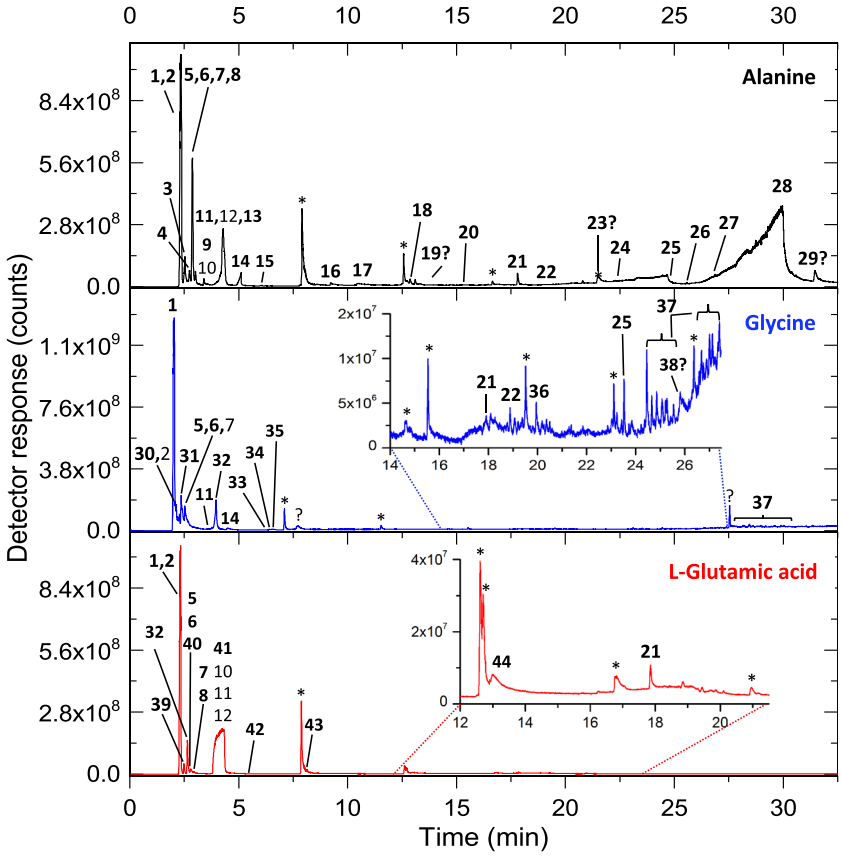



**Figure 3.** Chromatograms recorded after the pyrolysis of each amino acid diluted at 0.5 wt% in fused silica with 1 wt% of calcium perchlorate under SAM-like pyrolysis conditions. The identification and structures of the compounds represented by the numbers can be found in the supporting information Table S2. (*) Compounds related to column bleeding and (?) compound identification not confirmed. The compounds not represented in bold were found only by EIC.

perchlorate were identified including the compounds potentially oxidized, chlorinated and oxychlorinated (Table S1). The relative abundance of the parent molecule (when it was detected) and of the pyrolysis products directly resulting from the thermal decomposition of the parent molecule was semiquantitatively estimated.

### 3.2.1. Influence of Calcium Perchlorate on Amino Acids in Presence of Silica

The chromatograms obtained after the pyrolysis of alanine, glycine, and glutamic acid in presence of calcium perchlorate, all diluted in silica, are presented in Figure 3 and Table S2.

#### 3.2.1.1. Influence of Calcium Perchlorate on Alanine

As expected, alanine itself (not derivatized) is not detected after the SAM-like pyrolysis since it has a poor affinity with the stationary phase of the column due to its polarity (Buch et al., 2006) and decomposes during pyrolysis. But alanine anhydride, 3,6-dimethylpiperazine-2,5-dione, is detected in presence of calcium perchlorate (for a ratio of alanine to calcium perchlorate of 1:2) It is released in abundance as shown by the 4 min wide fronting peak reaching a maximum around 30 min, which is typical of a quantitative saturation of the stationary phase (Figure 3). The 3,6-dimethylpiperazine-2,5-dione was detected after pyrolyzing pure alanine under SAM-like pyrolysis conditions in a previous study (Francois et al., 2016) and in flash-pyrolysis at 900 °C (Moldoveanu, 2009). Thus, this compound is produced from the dehydration and decarboxylation of alanine (Moldoveanu, 2009) with no influence from calcium perchlorate.

Other pyrolysis products included $CO_2$, nitriles (e.g., acetonitrile), aromatic hydrocarbons (e.g., benzene), long chain alkanes (e.g., hexadecane and 2,3,6-trimethyl-decane), aldehydes (e.g., acetaldehyde), and oxygen-containing compounds such as heterocycles and carboxylic acids (formic, acetic, and propanoic acid). These compounds are related to the thermal decomposition of alanine from pyrolysis and their

recombination into heavier compounds from chemical reactions happening in the pyrolysis oven at high temperature (Millan et al., 2017; Moldoveanu, 2009). Our results also showed oxygen-bearing compounds detected only in presence of calcium perchlorate: one potential alcohol and aromatic ketones (1,4-anthraquinone and 2-methyl-anthraquinone or their isomers) that are likely alanine oxidation products.

Finally, both aromatic and alkyl chlorine-bearing organic compounds were detected when pyrolyzing alanine with calcium perchlorate. Two aromatics, pentachlorobenzene and potentially 1,1-dichloro-2-ethyl-2-methyl-cyclopropane (identification not confirmed), and five aliphatics, chloromethane, chloroethane, dichloromethane, trichloromethane, and tetrachloromethane, with chloromethane and chloroethane are the most abundant of all. These aliphatic organochlorine compounds are produced by chlorination reactions from calcium perchlorate on the pyrolysis products of alanine. Aliphatic compounds were more numerous in this study compared to flash-pyrolysis experiments (Moldoveanu, 2009). The detection of aliphatic chlorohydrocarbons directly related to the pyrolysis fragments of alanine such the chloroalkanes confirms the chlorination action of calcium perchlorate on the alanine's pyrolysis products, in this case on the straight and methylated alkanes. Chloromethane and chloroethane can be formed via the chlorination of methane and ethane (released during the thermal decomposition of alanine) by calcium perchlorate. The other aliphatic chloroalkanes are then formed through successive chlorination by $Cl_2$, releasing some HCl at each step. The detection of pentachlorobenzene and not of its other homologous aromatics ($Cl_1$-$Cl_4$ bearing chlorobenzene) is intriguing but could be related to the low gradian of the oven ramp temperature, which implies a longer time of residence, allowing chloride compounds to be available for successive chlorination. Thus, the concentration of low chlorinated compounds decreases under the limit of detection.

Because most of the compounds detected in our study are also observed in previous studies (e.g., Moldoveanu, 2009), it confirms the limited influence of calcium perchlorate during pyrolysis. This can be partly explained by the fact that alanine starts subliming and decomposing at lower temperature (180–280 °C with almost no sublimation tail) compared to calcium perchlorate (400–580 °C) (see EGA Figures 1 and 2 and Table 3). The amount of alanine available to react with calcium perchlorate is therefore limited resulting in a lower number of pyrolyzates compared to glycine and glutamic acid.

#### 3.2.1.2. Influence of Calcium Perchlorate on Glycine

After the pyrolysis of glycine with calcium perchlorate, $CO_2$, 2-cyanoacetamide, aromatic hydrocarbons (benzene, naphthalene, and benzanthracene), 2,4-dimethyl-3-pentanone, acetic acid, aliphatic alkanes ($C_9$, $C_{10}$ and $C_{16}$), methylated long-chain alkanes (2, 3, 4-dimethyl-heptane or isomer, trimethyl-tridecane, trimethyl-tetradecane, and a few others difficult to identify only with their MS), and long-chain alkanes bearing phenyl aromatic group (Figure 3) were detected. Most of these compounds are likely from the thermal decomposition of glycine and their reconstitution in longer chains at higher temperature, methylated or bearing a phenyl group or not (Millan et al., 2017; Moldoveanu, 2009).

Only two chlorinated organics, chloromethane and dichloromethane, were detected which is much less compared to alanine and glutamic acid. Moreover, these compounds were only detectable when analyzing extracted ion chromatograms, showing their minor abundance. Although they are certainly coming from the chlorination action of calcium perchlorate on glycine's pyrolysis products, their weak detection associated with the detection of alkanes resulting from the thermal decomposition of glycine and their recombination in bigger molecules indicate a weak impact of calcium perchlorate on glycine compared to the other amino acids studied. These results do not seem to be related to the temperature of sublimation of glycine (230–330 °C with a small sublimation tail ending around 500 °C) occurring in a range closer to the release temperature of calcium perchlorate (400–580 °C) compared to alanine and suggest that other parameters are at play.

#### 3.2.1.3. Influence of Calcium Perchlorate on Glutamic Acid

After the pyrolysis of glutamic acid with calcium perchlorate, the main compounds detected are $CO_2$, two nitriles (2-propenenitrile, a common fragment with alanine and 2-butenenitrile), aromatic hydrocarbons, 1H-pyrrole-2,5-dione ketone, and butane. The 1H-pyrrole-2,5-dione could be generated by water elimination from glutamic acid. It is also produced by water removal from its related amino acid, aspartic acid. In the case of glutamic acid, this reaction is generally associated with $CO_2$ removal, leading to pyrrole instead of 1H-pyrrole-2,5-dione (Moldoveanu, 2009), which is not the case in our results. Most of these compounds are common pyrolysis products of all three amino acids. The $CO_2$, nitriles, and aromatic hydrocarbons are

characteristic of the thermal decomposition of amino acids and are not specific to the thermal decomposition of one particular amino acid.

Seven chlorohydrocarbons are produced after pyrolysis of glutamic acid with calcium perchlorate: chlorine cyanide (ClCN), chloroacetonitrile (detected in EIC), dichloroacetonitrile, and $C_1$ to $C_4$ chloroalkanes. These compounds are consistent with the chlorination of glutamic acid and its thermal decomposition products (nitriles and alkanes). It is also consistent with the desorption temperatures of glutamic (250–350 °C with a significant sublimation tail to ~800 °C) acid compared to the calcium perchlorate as they mostly overlap and the presence of one more reactive COOH carboxyl group compared to glycine and alanine.

#### 3.2.1.4. Discussion: Influence of Calcium Perchlorate on Amino Acids

Using a SAM-like pyrolysis ramp temperature reduces the number of compounds detected compared to previous studies using flash-pyrolysis at high temperature (Millan et al., 2017; Moldoveanu, 2009). The number of aliphatic compounds detected also increases significantly. A slower temperature ramp leads to less reaction and compound recombinations, limiting the possibilities of cyclisation and aromatization. This explains why fewer aromatics are formed in ramp compared to flash-pyrolysis, even if the same final temperature is reached. Most aliphatic compounds come from the thermal decomposition of the amino acids. Except the detection of the diketopiperazines of alanine and glycine, both coming exclusively from their thermal decomposition, the pyrolysis products are characteristic of the thermal decomposition of the general amino acid chemical family and are not helpful to retrieve the specific parent amino acid. For alanine and glycine, detecting 3,6-dimethylpiperazine-2,5-dione and 2,4-dimethyl-3-pentanone in SAM-flight chromatograms could help retrieve the nature of the amino acid that was present in the sample before pyrolysis. The 1H-pyrrole-2,5-dione is characteristic of the thermal decomposition of both the aspartic and glutamic acids and could constrain the nature of amino acids present in a Martian sample, if detected. Acetic acid is observed after the pyrolysis of alanine and glycine and is a thermal decomposition product produced from deamination of amino acids ($-NH_2$). Glutamic acid was degraded in only 10 nonchlorinated compounds after pyrolysis compared to 35 and 30 for alanine and glycine, respectively. These results demonstrate that glutamic acid is the most thermally stable. Added to the thermal stability, the size of the molecule, specifically the number of carbon atoms, seems to play a role in the number of nonchlorinated compounds formed after pyrolysis and resulting from the thermal decomposition of the molecules. Alanine has one more $CH_3$ group compared to Glycine and subsequently decomposes in a higher number of pyrolyzates. Therefore, the desorption temperatures of glutamic acid and glycine, which overlap with the release temperature of calcium perchlorate, do not seem to be the main parameter leading to the degradation of the molecule.

Only two chlorohydrocarbons, the chloromethane and dichloromethane, are detected after the pyrolysis of glycine with calcium perchlorate and in lower abundances compared to alanine and glutamic acid. Glycine is then the less reactive amino acid studied in terms of chlorination. Because glycine is the smallest and simplest proteinic amino acid that exist, it decomposes in a fewer number of pyrolyzates compared to the others, therefore limiting the chlorination possibilities. Glutamic acid, with the highest number of chlorohydrocarbons detected (7), is the most reactive in terms of chlorination, followed by alanine and glycine. This result shows that not only the size of the molecule but also its reactivity plays an important role in the chlorination. Even though glutamic acid is the most thermally stable, it is the biggest of the amino acids studied and contains a supplementary carboxyl group compared to the other amino acids. The presence of a reactive function such as COOH provides more available sites for HCl and $Cl_2$ to react and is another important factor to consider in the process of chlorination. Additionally, this phenomenon is likely increased by the fact that the desorption temperatures of glutamic acid and calcium perchlorate overlap (EGA Figures 1 and 2 and Table 3). However, the thermal desorption temperatures of glycine also slightly overlap with calcium perchlorate (Figures 1 and 2 and Table 3) but did not induce the formation of many chlorinated compounds. Desorption temperatures are then not the most significant degradation and chlorination factors impacting the amino acids. Other parameters should be considered such as the thermal stability of the molecule, its number of carbon, and its reactivity potential induce by the presence of specific chemical group(s).

The chlorinated compounds detected are mostly aliphatic and come from the chlorination of the aliphatic amino acids pyrolyzates. The nature of the chlorohydrocarbons is correlated with the size of the amino acid and the nature of the pyrolyzates. Chlorohydrocarbons are mostly common to all three amino acids: $C_1$–$C_2$ chloroalkanes are present in all three, followed by $C_3$–$C_4$ present in both alanine and glutamic acid, with

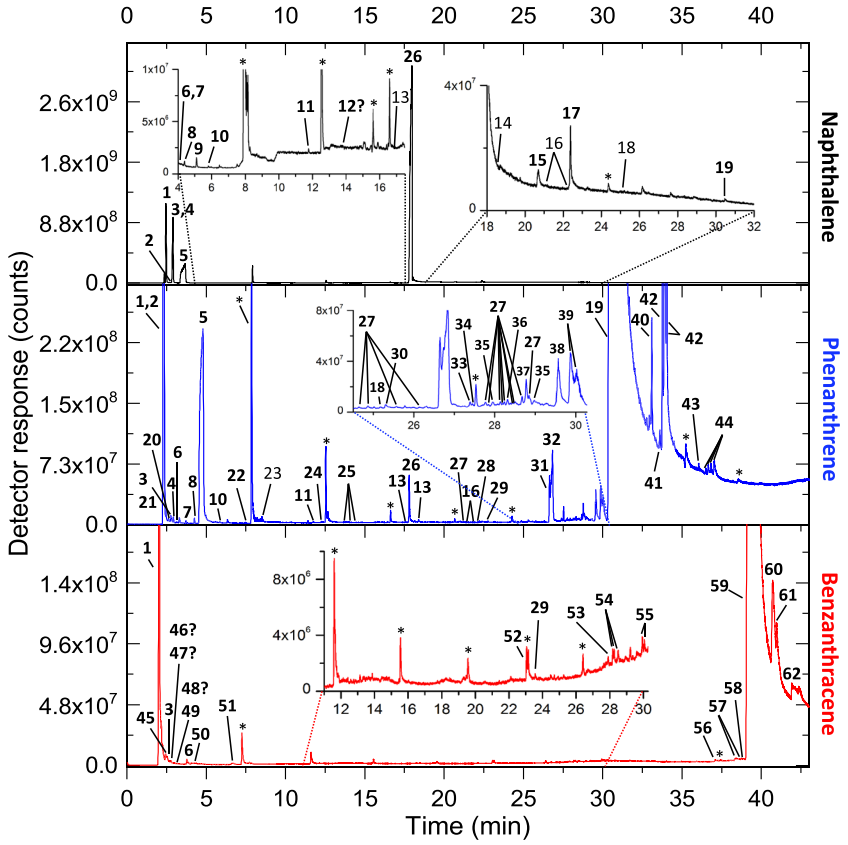



**Figure 4.** Gas chromatograms recorded after the pyrolysis of each PAH diluted at 0.5 wt% in the fused silica and mixed with 1 wt% of calcium perchlorate: naphthalene (black), phenanthrene (blue), and benzanthracene (red). The mixtures were pyrolyzed using a SAM-like pyrolysis ramp temperature corresponding to a 35 °C/min rate. The identification and structures of the compounds can be found in the supporting information Table S3. (*) Compounds related to column bleeding and (?) compound identification not confirmed. The compounds that are not represented in bold were found only by EIC.

higher relative abundances in glutamic acid. These compounds would then not be useful to retrieve the parent amino acid present in a Mars sample. However, the size of the chloroalkanes detected in a sample could give clue on the size of the amino acid present. Chloroethane is detected only in alanine and could be a discriminator for this amino acid if not detected in presence of other amino acids or compounds not targeted in this study. In glutamic acid only, two chlorinated N-bearing compounds are detected: chloroacetonitrile and dichloroacetonitrile, the first one in low abundance. These compounds seem to be characteristic of the chlorination of the nitrile pyrolysis fragments of glutamic acid, and because they are not detected with the other amino acids, it could help us retrieve glutamic acid as initially present in a sample before pyrolysis. It also has to be considered that these compounds can be formed by the reaction of calcium perchlorate with other amino acids or N-containing compounds not targeted in this study. However, since they are not produced in presence of alanine and glycine, alanine and glycine are unlikely precursors of those chloronitriles.

### 3.2.2. Influence of Calcium Perchlorate on PAHs in Presence of Silica

The chromatograms obtained after pyrolysis of naphthalene, phenanthrene, and benzanthracene in presence of silica appear in Figure 4 and Table S3.

#### 3.2.2.1. Influence of Calcium Perchlorate on Naphthalene

Naphthalene is still detected after its pyrolysis in presence of calcium perchlorate. It sublimes at low temperatures (80–150 °C with almost no sublimation tail), before the thermal decomposition of calcium perchlorate begins. A large amount of naphthalene is observed in the chromatogram and the number of products of reaction is limited showing its high thermal stability. This observation is interesting as if present in a sample collected on Mars; we could detect naphthalene. Nevertheless, several decomposition products are detected:

$CO_2$, HCl (detectable because the MS scanning started at m/z 35), some aromatic hydrocarbons of lighter molecular weight than naphthalene, O-bearing molecules, and chlorinated aromatic and aliphatic hydrocarbons. The other molecules detected are chlorinated and oxidized, indicating that the majority of the decomposition products of naphthalene reacted with calcium perchlorate during pyrolysis.

The oxidized compounds formed in presence of calcium perchlorate are acetone, phthalic acid anhydride, and diethyl phthalate. Those last are often detected in the analysis and without a preference for one molecule or another so they likely come from contamination from cleaning the tools used for the experiments (acetone) and the plastic containers used to store the chemicals (phthalic acid anhydride and diethyl phthalate).

Chlorinated aromatic compounds were detected by EIC such as a trichlorobenzene isomer, two tetrachlorobenzene isomers, and pentachlorobenzene. Both chloronaphthalene isomers were detected in the TIC. We also detected chloroalkanes bearing one to four chlorine atoms: chlo-, dichlo-, trichlo-, and tetrachloromethane. Branched chloroalkanes were detected: 1, 2-dichloro-2-methyl-propane, 1, 2, 3-trichloro-2-methyl-propane, and 1-chloro-2-ethyl-hexane or their respective isomers.

Despite the low sublimation temperature of naphthalene, chlorinated and oxidized molecules are produced consistent with oxidation and chlorination reactions between the inorganic species released by calcium perchlorate ($O_2$, HCl, and $Cl_2$) and naphthalene and its pyrolysis fragments. The formation of chloroalkanes, directly related to the chlorination of the alkanes decomposition fragments of naphthalene, confirms this statement. Some of these chloroalkanes were also detected while pyrolyzing amino acids with calcium perchlorate and then are not specific to naphthalene. More chlorinated compounds are formed in comparison to oxidized molecules indicating that naphthalene is more sensitive to chlorination.

#### 3.2.2.2. Influence of Calcium Perchlorate on Phenanthrene

Phenanthrene is still detected after its pyrolysis with calcium perchlorate but not in the same extent as naphthalene. It is thermally stable but sublimes at higher temperatures compared to naphthalene (80–230 °C with a small sublimation tail), closer to the temperature of decomposition of calcium perchlorate. Phenanthrene should be detectable after its thermal extraction by pyrolysis from a Martian sample composed of calcium perchlorate.

Pyrolysis of phenanthrene produced 15 aliphatic and 21 aromatic compounds. Some aromatics come from the thermal decomposition of phenanthrene: benzene, naphthalene, phenalene, biphenyl, benzazulene, and alkanes. Because they have very similar MS, we were not able to identify those compounds (27 and 29 in Figure 4) in the chromatogram without the aid of retention times. Here we focused on the identification of the chemical family rather than the specific compounds.

Regarding oxidized compounds, ketones are detected including acenaphthenone, anthraquinone, and pyridinol such the identification was not confirmed. However, this N-bearing compound is coming from contaminations. Acenaphthenone and anthraquinone are characteristics of the oxidation of phrenanthrene and its pyrolysis fragments.

An equivalent number of aromatic and aliphatic chlorinated molecules was detected (~10). Among the aromatics, chlorobenzene was highlighted in the TIC, the three dichlorobenzene, two trichlorobenzene, and two tetrachlorobenzene isomers were detected as well as pentachlorobenzene. The three chloroanthracene and/or chlorophenanthrene isomers and four isomers of the dichloroanthracene and/or dichlorophenanthrene. There is also the potential detection of phenoxy-benzyl-chloride, but the identification cannot be strictly confirmed only from the National Standard Institute of Technology mass spectrum. The aliphatic organo-chlorinated molecules include chloromethane, chloroethane (identified by EIC), dichloromethane, trichloromethane, and tetrachloromethane. Chlorodecane and tetrachlorodecane were also detected and led to the search of the $C_1$–$C_9$ chloroalkanes by EIC and highlighted these chlorohydrocarbons at consistent retention times compared to the $C_1$–$C_4$ identified by MS and retention times. Aliphatic chlorinated molecules also detected after pyrolysis of naphthalene/calcium perchlorate were detected: 1, 2-dichloro-2-methyl-propane and 1, 2, 3-trichloro-2-methyl-propane.

The formation of chlorinated, oxidized, and one potential oxychlorinated compounds is consistent with the action of chlorination and oxidation of perchlorate on phenanthrene and its pyrolysis fragments. As for naphthalene, calcium perchlorate has a stronger chlorination impact on phenanthrene compared to oxidation with fewer oxidized compounds detected compared to the number of chlorinated compounds.

#### 3.2.2.3. Influence of Calcium Perchlorate on Benzanthracene

Benzanthracene is detected after pyrolysis and would be detectable after thermal extraction from a Mars sample. Compared to naphthalene and phenanthrene, benzanthracene produced fewer products most of which were aromatic. Benzene, 9-ethyl-7H-benzoanthracene, naphthacene, long-chain alkanes, phenyl-bearing long chain alkane isomers, and few alkenes are detected and come from the thermal decomposition of benzanthracene.

More oxidized compounds are detected compared to chlorinated and they are mostly aromatic. The ketones aromatics detected: benzofluorene-11-one and benzanthracene-7,12-dione or isomer indicate a direct oxidation action on benzanthracene itself. Phenyl-dibenzofuran isomers, methyl-propanal, 2,4-dimethyl-3-pentanone or isomer (also detected in glycine), 5,12-naphthacenequinone or isomer, 2,6-tert-butyl-p-benzoquinone, and metoxy-pentane/pentene (identification not strictly confirmed) are reaction products from pyrolysis between the $O_2$ released and the thermal decomposition fragments of benzanthracene.

Only two chlorinated molecules, including one potential oxychlorinated were detected: the aromatic 3-chloro-1-(1-indenylidene)-1H-indene and dichloropropanol. They are coming from reactions between the pyrolysis products of benzanthracene and the inorganics released by calcium perchlorate during pyrolysis. No chlorinated molecules specific to benzanthracene (e.g., chlorobenzanthracene) were detected.

The oxidized and chlorinated compounds detected are consistent with the oxidation/chlorination action of $O_2$, HCl, and $Cl_2$ released from calcium perchlorate during the SAM-like pyrolysis. Benzanthracene is more sensitive to oxidation compared to chlorination, as shown by the respective number of oxidized and chlorinated compounds detected. Part of this result could be explained by the starting release temperature of $O_2$ (~350 °C), slightly earlier than HCl/$Cl_2$ (~400 °C) when a portion of benzanthracene is still being released as shown by its small sublimation tail (Figure 2). All the $O_2$ from calcium perchlorate will then be available during the release of benzanthracene to oxidize its pyrolysis fragments and the molecule itself. The fewer number of chlorinated compounds produced compared to naphthalene and phenanthrene can be due to the higher temperature release of HCl/$Cl_2$ compared to $O_2$ and to the higher thermal stability of benzanthracene due to its size (four aromatic carbon rings). It then decomposed in fewer compounds when heated and consequently released less compounds for calcium perchlorate to oxidizing and chlorinating.

#### 3.2.2.4. Discussion: Influence of Calcium Perchlorate on PAHs

All three PAHs studied are thermally and chemically stable after SAM-like pyrolysis in presence of calcium perchlorate. Even if a portion reacts with calcium perchlorate to form oxidized, chlorinated, and oxychlorine compounds, their stability should allow their detection and identification in a Mars solid sample containing calcium perchlorate, if they were present. Their decomposition products, except for a few compounds for each PAH, are not specific to the thermal degradation of the parent molecule but are characteristic of the thermal degradation of PAHs. Aliphatic hydrocarbons (long-chain straight and branched alkanes) are also detected after the pyrolysis of amino acids and are likely related to the thermal degradation of organics in general, and if detected on Mars, it would not be sufficient to identify the PAH parent molecule in a sample. During pyrolysis, molecular bonds are broken, either by the thermal effect or by the action of calcium perchlorate, which could explain the formation of those aliphatics. This thermal effect was also observed in a previous study during the pyrolysis of coals which decomposed in short and long-chains alkanes (Bonfanti et al., 1997). However and despite the high purity of the organic compounds (≥99.5%), we do not exclude the possibility that a fraction of the alkanes detected are impurities from the substrate. Aromatic compounds, characteristic of the thermal degradation of the PAH, are detected in laboratory, and if detected on Mars, it would only give clues on the chemical family present.

The detection of chlorobenzene and numerous aliphatic chlorinated (e.g., chloroalkanes) is a characteristic of the chlorination of the pyrolysis products of PAH (mostly aromatic hydrocarbons) and alkanes. Their presence in a Mars solid sample will then not be sufficient to retrieve the parent molecule present in the sample before the pyrolysis. Some chlorinated and oxidized compounds are characteristic of the PAH and result directly from the action of calcium perchlorate on each specific one. The two chloronaphthalene isomers are specific to naphthalene, anthraquinone, chloro- and dichloro-phenanthrene, or anthracene isomers are specific to phenanthrene. We note that those last compounds could also come from the oxidation/chlorination of phenanthrene's isomer (anthracene) and that it will be difficult to discriminate one parent molecule from the other in a Martian sample. Benzofluorene-11-one and benzanthracene-dione are specific to benzanthracene.

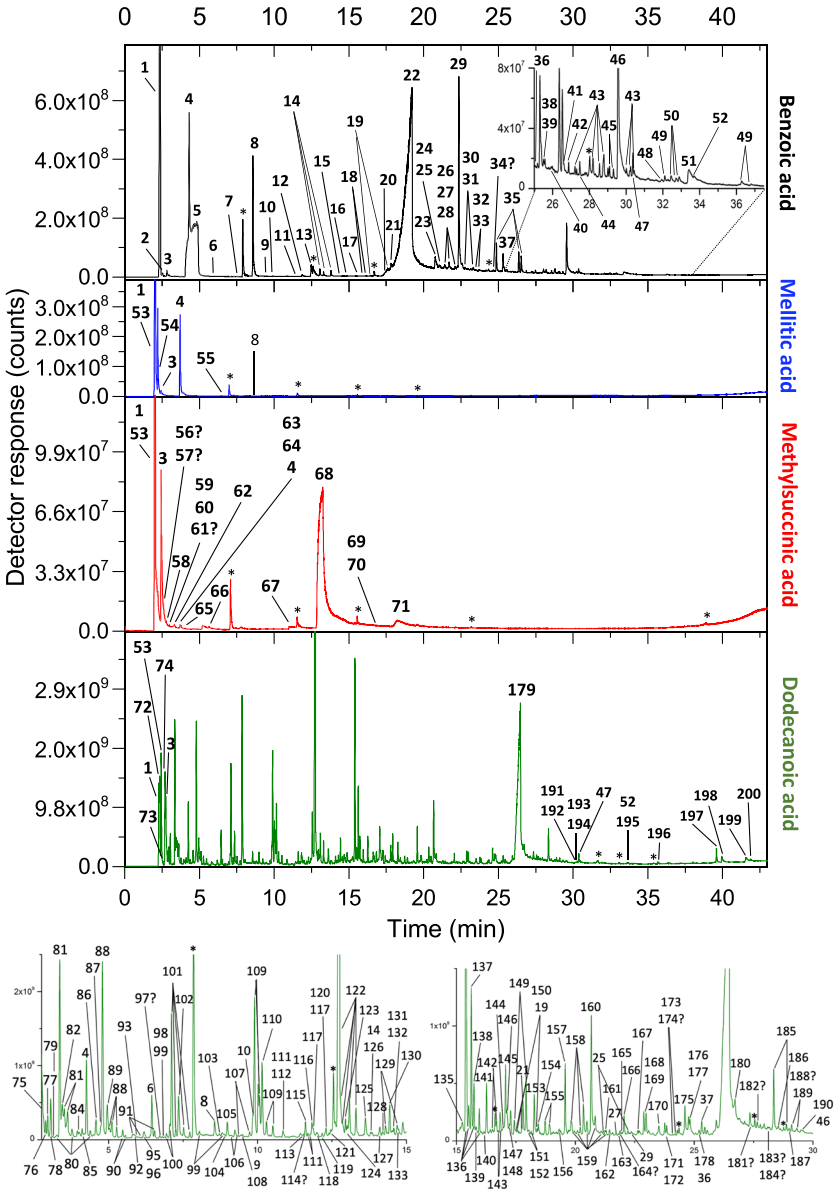



**Figure 5.** Gas chromatograms recorded after the pyrolysis of each carboxylic acid diluted at 0.5 wt% in the fused silica and mixed with 1 wt% of calcium perchlorate: benzoic acid (black), mellitic acid (blue), methylsuccinic acid (red), and dodecanoic acid (green). The mixtures were pyrolyzed using a SAM-like pyrolysis ramp temperature corresponding to a 35 °C/min rate. The identification and structures of the compounds can be found in the supporting information Table S4. (*) Compounds from column bleeding and (?) compound identification not confirmed

All those modified chlorinated and oxidized molecules, if they were detected in a Martian sample, could help confirm and support the presence and identification of those three PAHs after their pyrolysis in presence of calcium perchlorate.

In conclusion, detecting PAH in the SAM-flight chromatograms, added to their equivalent chlorinated or oxidized molecule, indicates their direct chlorination by $HCl/Cl_2$ released from calcium perchlorate and will help retrieve the parent PAH in a Martian sample. The branched chlorinated compound groups detected in both naphthalene and phenanthrene pyrolysis seem to be specific to those two PAHs and indicate the chlorination of the pyrolysis fragments of naphthalene and phenanthrene in presence of calcium perchlorate. Their detection in a Martian sample could give clue on the nature of the chemical family present in the sample (PAH) as well as the size of the PAH (two and/or three cycles), as those compounds were not detected after pyrolysis of benzanthracene.

#### 3.2.3. Influence of Calcium Perchlorate on Carboxylic Acids in Presence of Silica

Benzoic acid, mellitic acid, methylsuccinic acid, and dodecanoic acid were pyrolyzed in presence of calcium perchlorate and silica (Figure 5 and Table S4). For clarity regarding the number of compounds detected after pyrolysis of the dodecanoic acid, two regions were extracted from the chromatograms and presented separately.

##### 3.2.3.1. Influence of Calcium Perchlorate on Benzoic Acid

Benzoic acid is still detected after pyrolysis showing its thermal stability. Plus, it starts subliming from 80 °C, that is, well below the temperature of decomposition of calcium perchlorate. Its decomposition products included aromatic hydrocarbons and a few aliphatic compounds: monomethylated and polymethylated alkanes such as 4-methyl-tetradecane, trimethyl-dodecane, and 2-methyl-6-propyl-dodecane (or isomers of those compounds). Those nonchlorinated compounds indicate that calcium perchlorate is not reacting entirely with the thermal decomposition fragments during pyrolysis.

As observed after pyrolysis of the PAHs, most of the molecules detected are chlorinated. They include chlorobenzene, three dichlorobenzene isomers, three chlorobiphenyl isomers, and five dichlorobiphenyl isomers. Chloromethane, chloroethane, dichlo-, trichlo-, and tetrachloromethane were also detected but found by EIC. The detection of benzoic acid methyl ester indicates a rearrangement of the molecule and a reaction with the methyl groups available, potentially helped by the oxidation power of calcium perchlorate. The nature of the compounds reveals mostly chlorination of the compounds resulting from the thermal decomposition of benzoic acid.

##### 3.2.3.2. Influence of Calcium Perchlorate on Mellitic Acid

Mellitic acid is not detected after pyrolysis, even in absence of calcium perchlorate (Millan et al., 2017). This is mainly due to its strong polarity and poor affinity with the stationary phase of the column. The few compounds detected, $CO_2$, acetone, benzene, one butene isomer, ethanol, and 2,4-dimethyl-3-pentanone (detected in glycine and benzanthracene), are mostly coming from its thermal decomposition.

Only chlorobenzene and at least one dichlorobenzene isomer and one trichlorobenzene isomer were found by EIC showing they are produced in a very low abundance. Mellitic acid did not induce the formation of many chlorinated organics.

In conclusion, mellitic acid is not thermally stable probably because of its high oxidation degree that makes it prone to easily break down during pyrolysis. Even though it is not the main influencing factor, we note that it sublimes at a maximum of 420 °C (Figure 2), which is the same temperature as calcium perchlorate (Figure 1), representing an easy target molecule for calcium perchlorate to attack and/or destroy which could also influence its chemical stability.

##### 3.2.3.3. Influence of Calcium Perchlorate on Methylsuccinic Acid

Methylsuccinic acid and methylsuccinic anhydride (formed after water removal) are both detected after SAM-like pyrolysis of methylsuccinic acid. As for benzoic acid, this should be mostly due to its thermal stability and temperature of sublimation, which is lower that the range of temperatures that calcium perchlorate decomposes. Even if present at low concentration, both broad peaks (68 and 71 for the methylsuccinic anhydride and methylsuccinic acid, respectively, on Figure 5) show the saturation of the stationary phase and that they are release in high abundance.

Among the 19 compounds detected after pyrolysis 85% are aliphatic and decomposition products. Aliphatic alkenes are abundant and are characteristics of the thermal decomposition of aliphatic carboxylic acids such as butene, methyl-propene, and hexadiene. Cyclopentadiene is the unique aromatic alkene detected and is probably a reaction and/or recombination product of aliphatic alkenes at high temperature. The other few compounds detected are methyl-furandione, dodecane, decanal, acetic acid and possibly methylsuccinic dimethyl-ester, and benzoic acid ester. They are consistent with the nature of the thermal decomposition products from linear carboxylic acids (Millan et al., 2017; Moldoveanu, 2009) and are then mostly decomposition products of methylsuccinic acid.

Few chlorinated and oxychlorinated compounds are detected including chlorohydroxypropanoic acid, dichloroacteldehyde, dichloropropanoic acid, and tetrachloromethane. Using EIC, we also detected chlorobenzene and two dichlorobenzene isomers. Regarding their nature and number, these compounds would mostly be the results of chlorination and oxychlorination reactions from calcium perchlorate on the decomposition products of methylsuccinic acid, which is still being detected in high abundance.

To conclude, the detection of methylsuccinic acid in SAM-like pyrolysis indicates that it is thermally stable during a slow-pyrolysis and would be detectable in a Martian sample if present. This can be explained by the thermal decomposition temperature of methylsuccinic acid, which does not overlap with the thermal decomposition temperature of calcium perchlorate. A few O-bearing and chlorinated molecules are detected after pyrolysis and show the thermal and/or chemical decomposition of the methylsuccinic acid during pyrolysis.

#### 3.2.3.4. Influence of Calcium Perchlorate on Dodecanoic Acid

Dodecanoic acid is detected after pyrolyzis with calcium perchlorate as shown by its broad peak saturating the stationary phase at 26.4 min in the chromatogram. Dodecanoic acid is then thermally stable, and we note that it sublimes at temperatures lower (90–220 °C) compared to calcium perchlorate.

About 40% of the number of compounds detected are aliphatic and correspond to thermal degradation products of the aliphatic chain of dodecanoic acid. They are alkenes characteristic of the thermal decomposition of aliphatic carboxylic acids (Moldoveanu, 2009). A few aromatic alkenes were detected and are certainly produced in the oven from cyclizations and aromatizations of aliphatic alkenes at high pyrolysis temperatures. When a linear alkene is detected, all its configuration isomers (e.g., cis- and trans-) are present in the chromatogram. The numerous aliphatic alkenes detected indicate that they are not all affected by oxidation nor chlorination from the inorganic species released by calcium perchlorate.

On the 126 compounds detected, 33 are O-bearing organics and eight are chlorinated. This means only a fraction of the gases released from the thermal decomposition of dodecanoic acid reacts with calcium perchlorate to form the (oxy)chlorinated molecules. The nature of the compounds detected varies with heterocycles aromatics and aliphatic ketones (e.g., octanone, decanone, and undecanone). Those O-bearing organics result mostly from the thermal decomposition of dodecanoic acid and from cyclizations and aromatizations happening in the oven during pyrolysis (Millan et al., 2017; Moldoveanu, 2009).

Chlorinated aromatics are detected such as chlorobenzene, dichlorobenzene isomers, trichlorobenzene, tetrachlorobenzene, 3-chloro-1-(1-indenylidene)-1H-indene, 1, 2-bis-(4-chlorobiphenyl)-1, 2-ethandiol, and 2,6-dichloro-4-methyl-phenol (or isomers). These compounds are consistent with an action of chlorination of calcium perchlorate on dodecanoic acid and its pyrolyzates released during the SAM-like pyrolysis.

In summary, the detection of dodecanoic acid in SAM-like pyrolysis indicates its sublimation and would allow its detection in a Martian sample if present. It is thermally stable and is released at lower temperature compared to calcium perchlorate, limiting its influence. However, some pyrolyzates are impacted by calcium perchlorate, as shown by the formation (oxy) chlorinated compounds. Even in presence of calcium perchlorate, the thermal decomposition of dodecanoic acid led to the formation of many aliphatic alkenes, characteristic of the pyrolysis of linear carboxylic acids as observed after pyrolysis of methylsuccinic acid (Moldoveanu, 2009) showing they are not all influenced by perchlorate.

#### 3.2.3.5. Discussion: Influence of Calcium Perchlorate on Carboxylic Acids

Benzoic acid, methylsuccinic acid, and dodecanoic acid are all still detected after SAM-like pyrolysis in presence of calcium perchlorate and would be detected if present in such concentration (0.5 wt%) in a Martian sample. They are thermally stable and their release temperature, all below 300 °C and the release temperature of calcium perchlorate (>400 °C), probably limits its influence. However, all the carboxylic acids studied are favorable to the formation of aromatic chlorohydrocarbons such as the dichlorobenzene and trichlorobenzene isomers as well as aliphatic chlorohydrocarbons. Calcium perchlorate reacts preferentially with the compounds released from the thermal decomposition of the carboxylic acids as shown by the numerous (oxy)chlorinated molecules detected. Only few chlorinated and in very low abundance (found by EIC) are detected after the pyrolysis of mellitic acid. It shows that chlorine attacks preferentially the carbon system and has less effect on a molecule with a full steric hindrance. Mellitic acid is then unlikely the major contributor of the chlorinated compounds formed during SAM-like pyrolysis, and it would not be identifiable through specific secondary molecules.

Aliphatic compounds (alkanes and alkenes) are detected after SAM-like pyrolysis of methylsuccinic and dodecanoic acids, and if detected in a sample, it could be indicators of the presence of an aliphatic carboxylic acid.

The thermal extraction of most carboxylic acids in SAM-like pyrolysis is favorable for their detection, even in presence of calcium perchlorate. This is likely related to their thermal stability, their decomposition temperature (below the decomposition temperature of calcium perchlorate), and their high concentration in our

analog samples. They would then be detectable in a Martian sample, even after interacting with calcium perchlorate, in a concentration twice as high compared to the concentration in organics. The influence of calcium perchlorate is more important in terms of chlorination of the carboxylic acids and the gases from their thermal decomposition. Even if many (oxy) chlorinated compounds are formed, calcium perchlorate does not degrade all the pyrolyzates characteristics of the parent molecules and only react with a fraction of them. The carboxylic acids are easily detectable at the concentration chosen for this study when using a SAM-like pyrolysis. However, most of the chlorinated compounds detected are not characteristic of the parent molecule pyrolyzed. Only a few chlorinated compounds (e.g., chlorobiphenyl detected only with benzoic acid) are characteristic of the chemical family pyrolyzed and of the structure of the parent molecule (aromatic).

## 4. Thermal and Chemical Stability of the Organics and Identification of the Parent Molecule

Among the organics studied, we evaluated the most chemically and thermally stable during pyrolysis and under the influence of calcium perchlorate. Amino acids, as expected due to their polarity and low thermal stability, are not detected after pyrolysis and require prior chemistry derivatization method (Buch et al., 2009). However, the detection of characteristic pyrolysis fragment from their thermal decomposition (e.g., diketopiperazine of alanine) could help identify and/or give hints on their potential presence on Mars. Glycine would be difficult to identify since it does not decompose in specific pyrolyzates. The amino acids targeted are slightly influenced by calcium perchlorate. Glutamic acid has the highest reaction rate of all the amino acids tested as shown by the production of nitrogen-bearing aliphatics (cyanogenchloride, chloroacetonitrile, and dichloroacetonitrile). Traces of chlorobenzene, dichlobenzene, and trichlorobenzene are detected along with chloromethane, dichlomethane, trichlomethane, and tetrachloromethane for mostly all the amino acids, with again a preference for glutamic acid. This is likely due to the presence of a supplementary carboxyl group in glutamic acid compared to alanine and glycine, increasing its reactivity potential.

The PAHs tested were not entirely thermally or chemically degraded when pyrolyzed and could be detectable in a Martian sample containing twice as much of calcium perchlorate. PAHs have a high chemical and thermal stability comparatively to the other molecules studied. It would be interesting to study the chemical stability of the PAHs in presence of a higher concentration of perchlorates and see from which concentration PAHs react entirely. The chlorination/oxidation behavior of PAHs under the influence of calcium perchlorate mostly depends on their structure. Phenanthrene was the most reactive since it produced the highest number of chlorohydrocarbons followed by naphthalene and benzanthracene. The few numbers of (oxy) chlorinated molecules detected after pyrolysis of naphthalene and benzanthracene could be explained by their release temperatures compared to the release temperatures of $O_2$, HCl, and $Cl_2$ from calcium perchlorate. Fewer compounds resulting from the thermal decomposition of benzanthracene shows its high thermal stability, certainly due to its heavier molecular weight than the other PAHs studies. The fact it decomposed in fewer pyrolysis fragments compared to naphthalene and phenanthrene could also explain the small number of chlorinated compounds detected. Chlorinated/oxidized versions of the parent molecule indicate that they were directly attacked by $O_2$, HCl/$Cl_2$ during pyrolysis without being entirely degraded.

The stability of the carboxylic acids depends on their nature. Benzoic acid is the most thermally stable among the four carboxylic acids tested. Its saturation in the chromatogram indicates that it was not chemically degraded either and that it could be detectable in a Martian sample, even in a hypothetical low concentration. However, benzoic acid is the less chemically stable of all and it is the most reactive to chlorination as shown by its high number of chlorohydrocarbons produced, followed by the dodecanoic and methylsuccinic acids.

Mellitic acid was not detected after pyrolysis which is certainly due to its high polarity and low affinity with the stationary phase and would require prior derivatization. It decomposed in a few nonchlorinated compounds, indicating its thermal decomposition rather than chemical decomposition. Mellitic acid produced chlorohydrocarbons in a very low abundance. Due to its oxidation degree and steric hindrance, mellitic acid is entirely combusted into $CO_2$ during pyrolysis leaving benzene as the only decomposition product that does not seem to strongly react. Both aliphatic carboxylic acids were detected after pyrolysis mostly stable and were then thermally stable. Methylsuccinic anhydride was also detected and would facilitate the

**Table 4**

*Summary of the Chemical Families and Organic Molecules (Including Chlorinated and Oxidized Molecules) Detected in the Laboratory Chromatograms and That Are Specific to the Parent Chemical Families and/or the Parent Organic Molecules Pyrolyzed With Calcium Perchlorates*

| Chemical Family | Amino acids | | | Polycyclic Aromatic Hydrocarbons | | | Carboxylic acids | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Molecule | Alanine | Glycine | Glutamic acid | Naphthalene | Phenanthrene | Benzanthracene | Benzoic acid | Mellitic acid | Methylsuccinic acid | Dodecanoic acid |
| Parent Molecule detected | - | - | - | X | X | X | X | - | X | X |
| Non-chlorinated molecule related **only** to the parent molecule | 3,6-dimethylpiperazine-2,5-dione | - | 1H-pyrrole-2,5-dione | - | - | - | - | - | Methylsuccinic acid anhydride | - |
| Main chemical families of pyrolyzates | Aliphatic and aromatic N-bearing Aliphatic alkenes and some alkanes | | | Aliphatic and aromatic (<$C_{10}$) hydrocarbons (HC) | | | Aromatic HC *and* methylalkanes | Benzene only | Aliphatic alkenes | |
| Chlorinated *and/or* oxidized chemical family related to the parent chemical family or parent molecule | Chloroalkanes | | | Aromatic chlorohydrocarbons | | | Aromatic chlorohydrocarbons | Chlorobenzene only (in low abundance) | Aliphatic and aromatic chlorohydrocarbons | |
| | | | | | Ketones aromatics | | | | | |
| | | | | Aliphatic chlorohydrocarbons | | | | | | |
| | - | - | Chloronitriles | | | | | | | |
| Chlorinated *and/or* oxidized molecule related **only** to the parent molecule | - | - | - | Dichloro- and trichloromethylpropane | | Benzofluorenone Benzanthracendione | Chlo-, dichlo- & trichlobiphenyl Chlo-, dichlo- and trichlorophenol | - | - | - |
| | | | | 2x Chloronaphthalene isomers | 3x Chlorophenanthrene/ Chloroanthracene isomers 4x Dichlorophenanthrene/Dichloroanthracene isomers | | | | | |

identification of methylsuccinic acid if present in a Martian sample. They thermally decomposed in unsaturated hydrocarbons (alkenes) and reacted to form chlorinated molecules.

The degradation and evolution of the organic molecules as well as the chlorination and oxidation processes are influenced by several parameters: the nature of the compound itself, its size/number of carbons, the number of hydrogen atoms available to be substituted by oxygen and/or the chlorine species and its structure (aromatic or aliphatic), and their thermal stability and their reactivity potential. The releasing temperature of the molecules compared to the release temperature of calcium perchlorate also plays a role in its degradation by combustion in $CO_2$ and by oxidizing the organics. Oxidation and chlorination are probably competing and depending on the nature of the molecule, one of this process will be favored (e.g., benzanthracene). In conclusion, despite their reaction with calcium perchlorate, PAHs and carboxylic acids would be detectable on Mars since most parent molecules were not thermally nor chemically degraded. In addition, the detection of characteristic pyrolyzates (chlorinated/oxidized or not) would allow a double identification and help confirm their presence on Mars (Table 4). Figures 6 and 7 summarize the pyrolysis chemical families and compounds detected in our laboratory experiments and their precursors.

## 5. The Precursors of the Chlorohydrocarbons Detected by SAM on Mars

One of the main objectives of this work was to know if the pyrolysis of organic molecules from different chemical families, in presence of calcium perchlorate, would help us identify the nature of the organic precursors of the chlorohydrocarbons detected at Mars' subsurface with SAM. Are the chlorohydrocarbons detected on Mars coming from reactions between calcium perchlorate and the organic molecules targeted for this study? To answer this question, the nature of the chlorohydrocarbons detected by SAM was listed

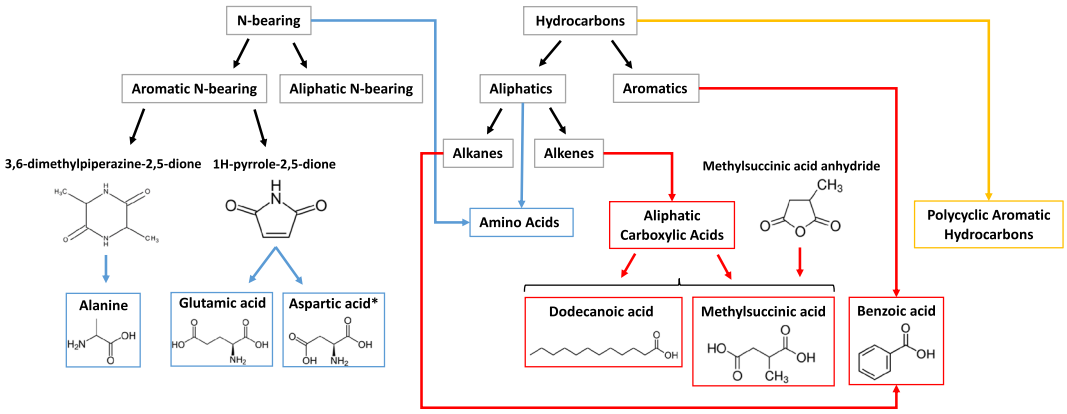



**Figure 6.** Chemical families and compounds detected after pyrolysis of the molecules targeted in this study and their parent chemical families and/or molecules retrieved from our results. The amino acids are in blue, the carboxylic acids in red, and the polycyclic aromatic hydrocarbons in yellow.

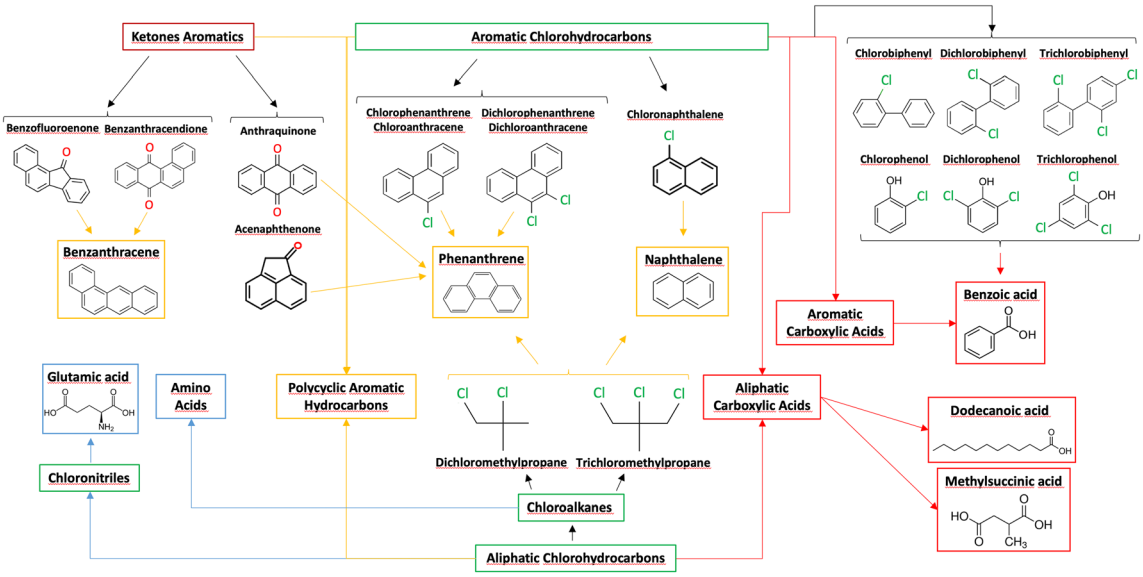



**Figure 7.** Chlorinated and oxygen-bearing chemical families and compounds detected after pyrolysis of the molecules targeted in this study and their parent chemical families and/or molecules retrieved from our results. The chlorinated compounds are in green. The O-bearing were considered only for the PAHs and are represented in red. The amino acids, carboxylic acids, and PAHs are represented in blue, red, and yellow, respectively.

in Table 5 and is compared to those detected in laboratory if/when they were detected. Figures 8 and 9 show the chemical families and/or compounds that according to our study, could be precursors of the Martian and supposedly terrestrial carbon detected with the SAM instrument.

Chlorobenzene was detected in the CB sample (Freissinet et al., 2015). It would come from reactions between the chlorinated gaseous species released from the perchlorates and chlorates in Mars' soils and the organic matter indigenous to the CB sample. From these results, molecules with high molecular weights and/or with an aromatic structure such the phenanthrene, benzoic acid, and dodecanoic acid have higher reaction rates with calcium perchlorate. However, chlorobenzene is often found by EIC, in a very low abundance, in the blanks, and in the chromatograms of pure organic molecules. It seems to be one of the most stable chlorohydrocarbons formed during pyrolysis, and it indicates that chlorine easily reacts with an intermediary organic molecule resulting from the thermal decomposition of the organics. This intermediary molecule could be benzene, which is formed after pyrolysis of all the organics regardless of their nature. Nevertheless, it does not explain the amount of chlorobenzene formed by this process (Miller et al., 2016). Since it is detected in each analysis, chlorobenzene could be a universal tracer of organic matter, but its detection on Mars does not allow the identification of its precursors. From this work, it is unlikely that the Martian chlorobenzene is coming from reaction between amino acids or PAH and calcium perchlorate. Carboxylic acids, especially benzoic acid and dodecanoic acid, are favorable to its production in abundance and will be the most likely precursors. This result has been confirmed by laboratory experiments that were performed on the SAM testbed replica (located at NASA Goddard Space Flight Center) with benzoic acid and another type of perchlorates: magnesium perchlorate (Mg-PCL). Benzoic acid and magnesium perchlorate were spiked on a Cumberland Analog solid sample made of minerals similar to the mineral present in the CB sample. Results showed the production of chlorobenzene in a similar abundance to the chlorobenzene detected in CB and support the results of our study (Freissinet et al., 2019).

At least two of the three dichlorobenzene isomers were detected in the CB mudstone (Szopa et al., 2019). Regarding these results and as observed for chlorobenzene, the dichlorobenzene isomers are formed after the pyrolysis of all the organics with calcium perchlorate but in traces amount for the amino acids, naphthalene, mellitic acid, and methylsuccinic acid. They are produced in a higher amount during the pyrolysis of phenanthrene, benzoic acid, and dodecanoic acid. Those molecules are then most likely precursors of the dichlorobenzene detected by SAM, which is consistent with the detection of chlorobenzene. When the dichlorobenzene isomers are detected, the tribenzene, tetrachlorobenzene, and pentachlorobenzene isomers are usually also detected. These compounds have not been detected on Mars with SAM so far. To be

**Table 5**
*Table Summarizing the Nature of the Chlorinated Organics Detected on Mars and in Laboratory to Help Identify Their Potential Precursors*

| Chlorinated organics | | SAM | Laboratory | | |
|---|---|---|---|---|---|
| | | | AA | PAH | CA |
| Martian Carbon | chlorobenzene | X | (X) | (P) | BA, DA |
| | dichlorobenzene | X | (X) | P | BA, DA |
| | dichloroethane | X | | | |
| | dichloropropane | X | | | |
| | dichlorobutane | X | | | |
| | trichloromethylpropane | X | | N, P | |
| Terrestrial Carbon | chloromethane | X | A, (Gly) Glu | (N), P | |
| | dichloromethane | X | (A), (Gly), Glu | N, P | |
| | trichloromethane | X | (A), Glu | N, P | |
| Detected Only in Laboratory Experiments | trichlorobenzene | | (X) | (N), P | BA, DA |
| | tetrachlorobenzene | | | N, P | BA, DA |
| | pentachlorobenzene | | A | (N), P | BA |
| | chloronaphthalene | | | N | |
| | chloroanthracene/chlorophenanthrene | | | P | |
| | chloroindenylidene indene | | | B | DA |
| | dichloroanthracene | | | P | |
| | chlorobiphenyl | | | | BA |
| | dichlorobiphenyl | | | | BA |
| | trichlorobiphenyl | | | | BA |
| | chlorophenylethene | | | | BA |
| | chlorobenzaldehyde | | | | BA |
| | dichlorophenol | | | | BA |
| | trichlorophenol | | | | BA |
| | tetrachlorophenol | | | | BA |
| | chlorobenzenediol | | | | BA |
| | chlorobenzoic acid | | | | BA |
| | chlorophenylethanediol | | | | DA |
| | dichloromethylphenol | | | | DA |
| | cyanogen-chloride (CNCl) | | Glu | P | |
| | chloroacetonitrile | | (Glu) | | |
| | dichloroacetonitrile | | Glu | P[a] | |
| | chloroethane | | Ala | (P) | DA |
| | tetrachloromethane | | (A), Glu | N, P, B | MSA |
| | dichloromethylpropane | | | N, P | |
| | chloroethylhexane | | | N | |
| | chlorodecane | | | P | |
| | chlorotetradecane | | | P | |
| | dichloropropanol | | | B? | DA |
| | dichloroacetaldehyde | | | | MSA |
| | chlorohydroxybutyric acid or methylbutanoic acid | | | P | |
| | chlorohydroxypropanoic acid | | | | MSA |
| | chlorobenzenedicarboxylic acid | | | | BA |
| | tetrachloroethene | | | P | |

*Note*. A: alanine, Gly: glycine, Glu: Glutamic acid, N: naphthalene, P: phenanthrene, B: benzanthracene, BA: benzoic acid, MA: mellitic acid, MSA: methylsuccinic acid, DA: dodecanoic acid. The molecules indicated in parenthesis are chlorohydrocarbons that were found only after extracting the SIM from the chromatogram and that were not detected in the TIC.
[a]Chlorohydrocarbons from contaminations.

produced, it is likely that they need a higher amount of organics that the one present in the samples collected by Curiosity (>300 ppb) (Freissinet et al., 2015). Their nondetection on Mars could also be explained by too long retention times to be detected within the time of analysis of a SAM-GC run or by other technical constraints such as the scanning rate of the SAM MS (Millan et al., 2016).

Chloromethane, dichloromethane, and trichloromethane were detected in several Martian samples (Glavin et al., 2013). Their formation was interpreted as reactions between the oxychlorines present in the samples and organic matter from the SAM instrument background such as the N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide:dimethylformamide (MTBSTFA:DMF) known to be present in the SMS since the

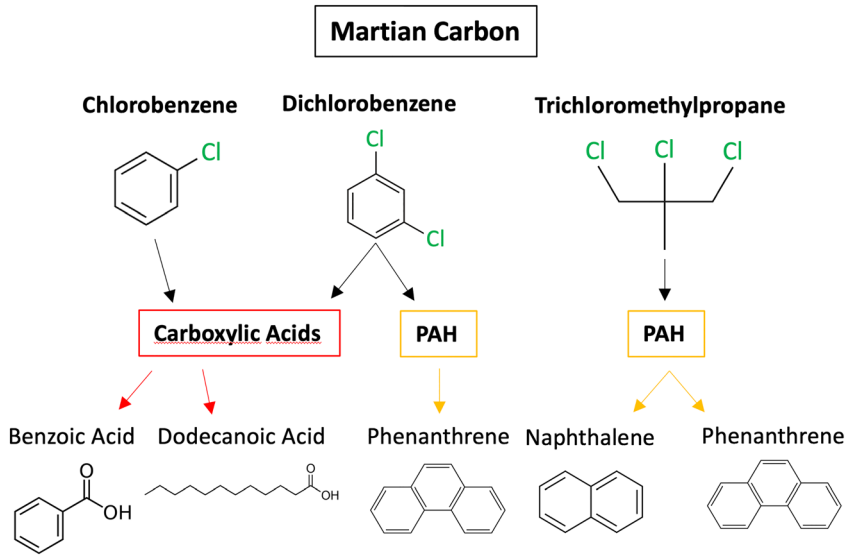



**Figure 8.** Potential precursors of the chlorohydrocarbons detected by the SAM instrument and known to be originated from Martian carbon.

beginning of the mission. Those experiments showed the production of these chlorohydrocarbons during the pyrolysis of amino acids and PAHs in presence of calcium perchlorate. Chloromethane is mostly produced with alanine, glutamic acid, and phenanthrene. Dichloromethane and trichloromethane are mostly produced in presence of glutamic acid, naphthalene, and phenanthrene. Amino acids and PAHs could then be precursors of the chloroalkanes detected at Mars' surface and contribute to the signal of the chloroalkanes detected in the flight chromatograms, by reactions with the calcium perchlorate present in the samples. This work also showed the formation of tetrachloromethane in presence of those molecules, added to benzanthracene and methylsuccinic acid. This could be related to the kinetic of reaction and that this chlorohydrocarbon might need heavier molecules and/or higher sublimation temperature and a long contact with the species from calcium perchlorate to be produced. Tetrachloromethane was not detected on Mars, so benzanthracene and methylsuccinic acid are unlikely the precursors of the chloroalkanes detected on Mars. Chloroalkanes from 1 (chloromethane) to 11 (chloroundecane) carbon atoms were detected, as well as

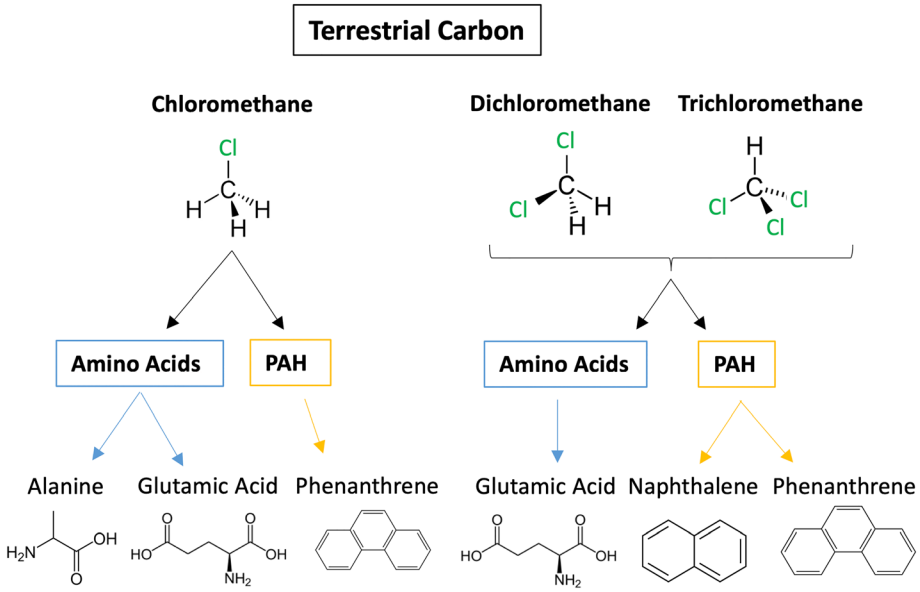



**Figure 9.** Other potential precursors of the chlorohydrocarbons detected by the SAM instrument and known to be originated from terrestrial carbon contaminations.

chlorodecane and chlorotetradecane, after pyrolysis of dodecanoic acid and phenanthrene respectively with calcium perchlorate. If those chloroalkanes were detected in future Martian samples, their number of carbons could give hints on the number of carbons of the parent molecule present in the sample.

In the CB sample, dichloroethane, dichloropropane, dichlorobutane, and trichloromethylpropane were detected. As chlorobenzene, they would come from reactions between the perchlorates/chlorates present at Mars' surface and organic molecules indigenous to Mars. From those molecules, only trichloromethylpropane was detected after pyrolysis of naphthalene and phenanthrene, along with dichloromethylpropane (not detected on Mars). Naphthalene and phenanthrene could be possible precursors of the trichloromethylpropane detected on Mars; however, it should likely be accompanied by dichloromethylpropane and the chlorinated versions of those two parent molecules, chloronaphthalene and chlorophenanthrene, which were not detected. Understanding the formation processes of molecules bearing methyl group are mandatory to confirm their formation only from reactions between PAH and calcium perchlorate.

Some chlorohydrocarbons (e.g., chloroethane) were detected only in our laboratory experiments, and they are produced after pyrolysis of several molecules from all the chemical families studied. If detected on Mars, they would then not be sufficient to retrieve the parent molecule originally present in the sample. Other chlorohydrocarbons are sometimes produced only after the pyrolysis of a specific chemical family or a specific molecule. For example, tetrachloroethene is formed only from the pyrolysis of phenanthrene/calcium perchlorate. Chlo-, dichlo-, trichlorobiphenyl, dichlo-, trichlo-, and tetrachlorophenol are formed only after the pyrolysis of benzoic acid/calcium perchlorate. The detection of a combination of all these chlorohydrocarbons in a Martian sample could then strongly suggest the presence of benzoic acid. Chloroacetonitrile and dichloroacetonitrile are produced only after the pyrolysis of glutamic acid/calcium perchlorate and if detected on Mars that could suggest the presence of glutamic acid. Some chlorohydrocarbons are even very specific to the parent molecule. For example, chlorobenzoic acid is detected only after the pyrolysis of benzoic acid. The chloronaphthalene isomers, chlorophenanthrene, and dichlorophenanthrene (or anthracene) are detected only after the pyrolysis of calcium perchlorate with naphthalene and phenanthrene, respectively. These compounds are produced from direct reactions between the oxychlorine gases released by calcium perchlorate and the parent molecule itself. Even if the parent molecule is not detected, the detection of the chlorinated and/or oxychlorinated version of the parent molecule as in those laboratory experiments would help detect and identify the precursor of the molecule present in the sample or eventually the chemical family from which the parent molecule is from.

Thus, the precursors of the chlorohydrocarbons detected on Mars could be molecules from the three chemical families studied. However, from the trends observed, it appears more likely that the aromatic chlorohydrocarbons (chlorobenzene and dichlorobenzene) are coming from carboxylic acids. The aliphatic chloroalkanes (chloromethane, dichloromethane, and trichloromethane) seem most likely to originate from the heaviest amino acids and the two lightest PAH targeted.

## 6. Conclusion and Perspectives

The objectives of this work were to study the stability and evolution of organic molecules coming from three chemical families in presence of calcium perchlorate to (1) know if parent molecules would be detectable and identifiable after pyrolysis, by the detection of the parent molecule itself or their pyrolysis products, (2) understand the influence of calcium perchlorate in terms of degradation/evolution of the molecules, and (3) help determine the nature of the organic precursors of the chlorohydrocarbons detected at Mars' surface.

Calcium perchlorate significantly influences organic molecules during SAM-like pyrolysis. The nature of the chemical family from which the parent molecule comes, its structure, and the physicochemical properties related to the molecule influences stability in terms of degradation and evolution into oxidized and chlorinated molecules. The parent molecule is impacted, as well as the nature and number of pyrolysis products from its thermal decomposition. The molecules react with gaseous species ($O_2$, HCl, and $Cl_2$) released during pyrolysis through chlorination, oxidation, and oxychlorination processes.

The pyrolysis experiments performed here on organic molecules from different chemical families in presence of calcium perchlorate highlight that thermal and chemical stabilities depend on the nature of the molecule in question, the size, the structure, and the decomposition temperature. Molecules with aromatic structures, with the

exception of mellitic acid, are the most stable after pyrolysis and detectable despite the presence of calcium perchlorate. As expected, we observed that organics mostly decomposed into molecules characteristic of their structure and the chemical family they belong to. Some were detectable at high concentrations in a Martian sample (e.g., 0.5 wt%), even in the presence of twice of high calcium perchlorate (1 wt%). Considering the saturation of the peak corresponding to the parent molecules in the chromatograms, it is likely that these molecules also would have been detectable at lower concentrations. Testing the concentrations at which these three chemical families are entirely consumed by calcium perchlorate would be a fascinating area for future study. Even if the aliphatic amino acids and carboxylic acids are affected by calcium perchlorate in terms chlorination, both chemical families should be detectable in a Martian sample. Some amino acids, not directly detectable by pyrolysis-GCMS due to their polarity, nevertheless, produced pyrolysis fragments specific to their thermal decomposition, a fact that could aid in their identification if they were detected in a Martian sample. However, the presence of mellitic acid, which decomposes to organic molecules that could come from many organics, would likely be impossible to infer on Mars.

This study underscores that calcium perchlorate does not degrade entirely the parent molecules and their pyrolysates. Pyrolysis products are sometimes specific of the chemical family pyrolyzed and the parent molecules, which is also the case for the molecules that went through chlorination processes by the gases released from the calcium perchlorate. This indicates that chlorine species attack directly the parent molecule and its pyrolysis products. By chlorinating the parent molecule and its pyrolysates, calcium perchlorate may even help identify the nature of the chemical family or the molecule itself present in a sample.

We found that calcium perchlorate reacts with organics to form many chlorohydrocarbons. Some of those detected on Mars may have formed from reactions in the SAM pyrolysis oven between unknown organic molecules and the chlorinated gaseous species released by the perchlorates and chlorates present at Mars' surface. Our results highlight that these organics could come from the chemical families targeted in this study. Chlorobenzene and dichlorobenzene are mostly produced from reactions between calcium perchlorate and benzoic acid or dodecanoic acid. A fraction of the chlorobenzene detected on Mars could then come from reactions between oxychlorines and those two carboxylic acids present in the Martian samples collected by Curiosity. $Cl_1$–$Cl_3$ chloromethanes were detected by *Curiosity* and are known to be coming from SAM's background (MTBSTFA/DMF) and the oxychlorinated minerals present in the samples. $Cl_1$–$Cl_4$ chloromethanes were detected in our laboratory experiments with amino acids and PAHs mixed with calcium perchlorate. Thus, a fraction of the chloromethanes detected on Mars could come from molecules of these chemical families present on Mars and reacting with oxychlorines.

Independent of the presence of calcium perchlorate, the chemical reactions occurring during pyrolysis are complex and depend on many parameters. To better identify the organics at Mars' surface with this extraction technique, it is necessary to build a database containing the retention times of the parent molecules and their pyrolysis fragments. The database will aid in the search for peaks in the flight chromatograms and their subsequent identification. The necessary experiments should be performed in SAM-like conditions, with GC columns identical to those used on flight like it has been done in the past for molecules suspected and expected to be present on Mars (Millan et al., 2016). As MTBSTFA is present in SAM's SMS, it is also important to reproduce these experiments in presence of MTBSTFA to see if we can still detect parent molecules, and how MTBSTFA influences the nature of chlorohydrocarbons formed during pyrolysis.

To better approximate conditions on Mars, other types of oxychlorines and organics, including mixtures, should be taken into consideration. Our study did not consider the complete mineralogy of the samples collected on Mars in Gale Crater. The deliberate choice of excluding iron oxides and sulfates known to be present on the Martian surface allowed to study exclusively the influence of calcium perchlorate on the organics targeted. Further experiments, however, should include these minerals and other lithologies of relevance to Gale Crater as well as the Mars 2020 and ExoMars 2022 landing sites. For example, studying the impact of the solid matrix and confirming those results using the synthetic CB analog sample (Freissinet et al., 2019) instead of fused silica would be particularly interesting, as previous studies have shown both the catalyzing and protecting effects of iron oxides and sulfates, respectively, on the pyrolysis of organics in presence of oxychlorine minerals.

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## References

Adande, G., Ouni, F., Thissen, R., Szopa, C., Dutuit, O., Cernogora, G., Laprévote, O., 2007. Chemical analysis of Titan's aerosol analogues (tholins) by high resolution mass spectrometry, European Planetary Sciences Conference 2, Potsdam (Ger.).

Altwegg, K., Balsiger, H., Bar-Nun, A., Berthelier, J. -J., Bieler, A., Bochsler, P., et al. (2016). Prebiotic chemicals—Amino acid and phosphorus—In the coma of comet 67P/Churyumov-Gerasimenko. *Science Advances*, *2*(5), e1600285. https://doi.org/10.1126/sciadv.1600285

Archer, P. D., Franz, H. B., Sutter, B., Arevalo, R. D., Coll, P., Eigenbrode, J. L., et al. (2014). Abundances and implications of volatile-bearing species from evolved gas analysis of the Rocknest aeolian deposit, Gale Crater, Mars. *Journal of Geophysical Research: Planets*, *119*, 237–254. https://doi.org/10.1002/2013JE004493

Benner, S. A., Devine, K. G., Matveeva, L. N., & Powell, D. H. (2000). The missing organic molecules on Mars. *Proceedings of the National Academy of Science of the USA*, *97*(6), 2425–2430. https://doi.org/10.1073/pnas.040539497

Biemann, K., Oro, J., Toulmin, P., Orgel, L. E., Nier, A. O., Anderson, D. M., et al. (1976). Search for organic and volatile inorganic-compounds in 2 surface samples from CHRYSE-PLANITIA region of Mars. *Science*, *194*(4260), 72–76. https://doi.org/10.1126/science.194.4260.72

Biemann, K., Oro, J., Toulmin, P., Orgel, L. E., Nier, A. O., Anderson, D. M., et al. (1977). The search for organic substances and inorganic volatile compounds in the surface of Mars. *Journal of Geophysical Research*, *82*(28), 4641–4658. https://doi.org/10.1029/JS082i028p04641

Bonfanti, L., Comellas, L., Lliberia, J. L., Vallhonrat-Matalonga, R., Pich-Santacana, M., & Lopez-Pinol, D. (1997). Production of n-alkanes and polycyclic aromatic hydrocarbons in coal pyrolysis. *Journal of Anlaytical and Applied Pyrolysis*, *44*(1), 89–99. https://doi.org/10.1016/S0165-2370(97)00074-0

Buch, A., Belmahdi, I., Szopa, C., Freissinet, C., Glavin, D. P., Millan, M., et al. (2019). Role of the Tenax® adsorbent in the interpretation of the EGA and GC-MS analyses performed with the Sample Analysis at Mars in Gale Crater. *Journal of Geophysical Research: Planets*, *124*, 2819–2851. https://doi.org/10.1029/2019JE005973

Buch, A., Glavin, D. P., Sternberg, R., Szopa, C., Rodier, C., Navarro-González, R., et al. (2006). A new extraction technique for in situ analyses of amino and carboxylic acids on Mars by gas chromatography mass spectrometry. *Planetary and Space Science*, *54*(15), 1592–1599. https://doi.org/10.1016/j.pss.2006.05.041

Buch, A., Sternberg, R., Szopa, C., Freissinet, C., Garnier, C., Bekri, E. J., et al. (2009). Development of a gas chromatography compatible sample processing system (SPS) for the in-situ analysis of refractory organic matter in Martian soil: Preliminary results. *Advances in Space Research*, *43*(1), 143–151. https://doi.org/10.1016/j.asr.2008.05.001

Cull, S. C., Arvidson, R. E., Catalano, J. G., Ming, D. W., Morris, R. V., Mellon, M. T., & Lemmon, M. (2010). Concentrated perchlorate at the Mars Phoenix landing site: Evidence for thin film liquid water on Mars. *Geophysical Research Letters*, *37*, L22203. https://doi.org/10.1029/2010GL045269

Dow, C. C. H. -A., 2003. Guide to Properties. Forms, storage and handling, the Dow Chemical Company.

Eigenbrode, J. L., Summons, R. E., Steele, A., Freissinet, C., Millan, M., Navarro-González, R., et al. (2018). Organic matter preserved in 3-billion-year-old mudstones at Gale crater, Mars. *Science*, *360*(6393), 1096–1101. https://doi.org/10.1126/science.aas9185

Elsenousy, A., Hanley, J., & Chevrier, V. F. (2015). Effect of evaporation and freezing on the salt paragenesis and habitability of brines at the Phoenix landing site. *Earth and Planetary Science Letters*, *421*, 39–46. https://doi.org/10.1016/j.epsl.2015.03.047

Flynn, G. J., Keller, L. P., Wirick, S., & Jacobsen, C. (2008). Organic matter in interplanetary dust particles. In S. Kwok, & S. Sandford (Eds.), *Iau: Organic Matter in Space*, (pp. 267–275). Cambridge: Cambridge Univ Press.

Francois, P., Szopa, C., Buch, A., Coll, P., McAdam, A. C., Mahaffy, P. R., et al. (2016). Magnesium sulfate as a key mineral for the detection of organic molecules on Mars using pyrolysis. *Journal of Geophysical Research: Planets*, *121*, 61–74. https://doi.org/10.1002/2015JE004884

Freissinet, C., Glavin, D. P., Mahaffy, P. R., Miller, K. E., Eigenbrode, J. L., Summons, R. E., et al. (2015). Organic molecules in the Sheepbed Mudstone, Gale Crater, Mars. *Journal of Geophysical Research: Planets*, *120*, 495–514. https://doi.org/10.1002/2014JE004737

Freissinet, C., Graham, H., Knudson, C. A., Lewis, J. M., Lasue, J., McAdam, A., et al. (2019. New insights from the Cumberland analog investigation: Benzoic acid as the preferred precursor for chlorobenzene detected on Mars, 2019 Astrobiology Science Conference. AGU.

Glavin, D. P., Bada, J. L., Brinton, K. L. F., & McDonald, G. D. (1999). Amino acids in the Martian meteorite Nakhla. *Proceedings of the National Academy of Sciences of the United States of America*, *96*(16), 8835–8838. https://doi.org/10.1073/pnas.96.16.8835

Glavin, D. P., Freissinet, C., Miller, K. E., Eigenbrode, J. L., Brunner, A. E., Buch, A., et al. (2013). Evidence for perchlorates and the origin of chlorinated hydrocarbons detected by SAM at the Rocknest aeolian deposit in Gale Crater. *Journal of Geophysical Research: Planets*, *118*, 1–18. https://doi.org/10.1002/jgre.20144

Glavin, D. P., Matrajt, G., & Bada, J. L. (2004). Re-examination of amino acids in Antarctic micrometeorites. In M. P. Bernstein, M. Kress, & R. NavarroGonzalez (Eds.), *Space Life Sciences: Steps toward Origin(S) of Life*, (pp. 106–113). Kidlington: Pergamon-Elsevier Science Ltd.

Guzman, M., McKay, C. P., Quinn, R. C., Szopa, C., Davila, A. F., Navarro-González, R., & Freissinet, C. (2018). Identification of chlorobenzene in the Viking gas chromatograph-mass spectrometer data sets: Reanalysis of Viking Mission data consistent with aromatic organic compounds on Mars. *Journal of Geophysical Research: Planets*, *123*, 1674–1683. https://doi.org/10.1029/2018JE005544

Hecht, M. H., Kounaves, S. P., Quinn, R. C., West, S. J., Young, S. M. M., Ming, D. W., et al. (2009). Detection of perchlorate and the soluble chemistry of Martian soil at the Phoenix Lander site. *Science*, *325*(5936), 64–67. https://doi.org/10.1126/science.1172466

Klein, H. P. (1998). The search for life on Mars: What we learned from Viking. *Journal of Geophysical Research*, *103*, 28,463–28,466. https://doi.org/10.1029/98JE01722

Leshin, L. A., Mahaffy, P. R., Webster, C. R., Cabane, M., Coll, P., Conrad, P. G., et al. (2013). Volatile, isotope, and organic analysis of Martian fines with the Mars curiosity rover. *Science*, *341*, 9.

Martins, Z. (2011). Organic chemistry of carbonaceous meteorites. *Elements*, *7*(1), 35–40. https://doi.org/10.2113/gselements.7.1.35

Migdał-Mikuli, A., & Hetmańczyk, J. (2008). Thermal behavior of $[Ca(H2O)_4](ClO_4)_2$ and $[Ca(NH_3)_6](ClO_4)_2$. *Journal of Thermal Analysis and Calorimetry*, *91*(2), 529–534. https://doi.org/10.1007/s10973-007-8511-z

Millan, M., Szopa, C., Buch, A., Belmahdi, I., Glavin, D. P., Freissinet, C., et al. (2017. Influence of oxychlorine phases during the pyrolysis of organic compounds and the quest of organics on Mars with the SAM instrument, astrobiology science conference 2017. Lunar and planetary institute, Houston, p. abstract #3423.

Millan, M., Szopa, C., Buch, A., Coll, P., Glavin, D. P., Freissinet, C., et al. (2016). In situ analysis of Martian regolith with the SAM experiment during the first mars year of the MSL mission: Identification of organic molecules by gas chromatography from laboratory measurements. *Planetary and Space Science*, *129*, 88–102. https://doi.org/10.1016/j.pss.2016.06.007

Miller, K. E., Eigenbrode, J. L., Freissinet, C., Glavin, D. P., Kotrc, B., Francois, P., & Summons, R. E. (2016). Potential precursor compounds for chlorohydrocarbons detected in Gale Crater, Mars, by the SAM instrument suite on the curiosity rover. *Journal of Geophysical Research: Planets*, *121*, 296–308. https://doi.org/10.1002/2015JE004939

Miller, K. E., Kotrc, B., Summons, R. E., Belmahdi, I., Buch, A., Eigenbrode, J. L., et al. (2015). Evaluation of the Tenax trap in the sample analysis at Mars instrument suite on the curiosity rover as a potential hydrocarbon source for chlorinated organics detected in Gale crater. *Journal of Geophysical Research: Planets*, *120*, 1446–1459. https://doi.org/10.1002/2015JE004825

Ming, D. W., Archer, P. D., Glavin, D. P., Eigenbrode, J. L., Franz, H. B., Sutter, B., et al. (2014). Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale Crater, Mars. *Science*, *343*.

Mißbach, H., Steininger, H., Thiel, V., & Goetz, W. (2019). Investigating the effect of perchlorate on flight-like gas chromatography–mass spectrometry as performed by MOMA on board the ExoMars 2020 rover. *Astrobiology*, *19*(11), 1339–1352. https://doi.org/10.1089/ast.2018.1997

Moldoveanu, S. C. (1998). *Analytical pyrolysis of natural organic polymers*. New York: Elsevier.

Moldoveanu, S. C. (2009). *Pyrolysis of organic molecules: Applications to health and environmental issues*. New York: Elsevier.

Navarro-Gonzalez, R., Vargas, E., de la Rosa, J., Raga, A. C., & McKay, C. P. (2010). Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars. *Journal of Geophysical Research*, *115*, E12010. https://doi.org/10.1029/2010JE003599

Poch, O., Noblet, A., Stalport, F., Correia, J. J., Grand, N., Szopa, C., & Coll, P. (2013). Chemical evolution of organic molecules under Mars-like UV radiation conditions simulated in the laboratory with the "Mars organic molecule irradiation and evolution" (MOMIE) setup. *Planetary and Space Science*, *85*, 188–197. https://doi.org/10.1016/j.pss.2013.06.013

Schulten, H. R., & Leinweber, P. (1993). Pyrolysis-field ionization mass-spectrometry of agricultural soils and humic substances—Effect of cropping systems and influence of the mineral matrix. *Plant and Soil*, *151*(1), 77–90. https://doi.org/10.1007/BF00010788

Sephton, M. A. (2012). Pyrolysis and mass spectrometry studies of meteoritic organic matter. *Mass Spectrometry Reviews*, *31*(5), 560–569. https://doi.org/10.1002/mas.20354

Steele, A., McCubbin, F. M., Fries, M., Kater, L., Boctor, N. Z., Fogel, M. L., et al. (2012). A reduced organic carbon component in Martian basalts. *Science*, *337*(6091), 212–215. https://doi.org/10.1126/science.1220715

Steininger, H., Goesmann, F., & Goetz, W. (2012). Influence of magnesium perchlorate on the pyrolysis of organic compounds in Mars analogue soils. *Planetary and Space Science*, *71*(1), 9–17. https://doi.org/10.1016/j.pss.2012.06.015

Sutter, B., McAdam, A., Rampe, E., Ming, D., Mahaffy, P., Navarro-Gonzalez, R., et al. (2016. Evolved gas analyses of sedimentary materials in Gale Crater, Mars: Results of the curiosity rover's Sample Analysis at Mars (SAM) Instrument from Yellowknife Bay to the Stimson Formation.

Sutter, B., Quinn, R., Archer, P., Glavin, D., Glotch, T., Kounaves, S., et al. (2016. Measurements of oxychlorine species on Mars.

Szopa, C., Freissinet, C., Glavin, D. P., Millan, M., Buch, A., Franz, H. B., et al. (2019. First detections of dichlorobenzene isomers and trichloromethylpropane from organic matter indigenous to Mars Mudstone in Gale Crater, Mars: Results from the sample analysis at Mars instrument onboard the curiosity rover. Astrobiology.