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RESEARCH ARTICLE

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Key Points:

- Magnesium sulfate leads to oxidation of organic molecules during pyrolysis
- Trapped organics are protected from oxidation from perchlorate decomposition

Supporting Information:

- Figures S1 and S2 and Tables S1-S7

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Magnesium sulfate as a key mineral for the detection of organic molecules on Mars using pyrolysis

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Abstract Pyrolysis of soil or rock samples is the preferred preparation technique used on Mars to search for organic molecules up today. During pyrolysis, oxichlorines present in the soil of Mars release oxidant species that alter the organic molecules potentially contained in the samples collected by the space probes. This process can explain the difficulty experienced by in situ exploration probes to detect organic materials in Mars soil samples until recently. Within a few months, the Curiosity rover should reach and analyze for the first time soils rich in sulfates which could induce a different behavior of the organics during the pyrolysis compared with the types of soils analyzed up today. For this reason, we systematically studied the pyrolysis of organic molecules trapped in magnesium sulfate, in the presence or absence of calcium perchlorate. Our results show that organics trapped in magnesium sulfate can undergo some oxidation and sulfuration during the pyrolysis. But these sulfates are also shown to protect organics trapped inside the crystal lattice and/or present in fluid inclusions from the oxidation induced by the decomposition of calcium perchlorate and probably other oxychlorine phases currently detected on Mars. Trapped organics may also be protected from degradation processes induced by other minerals present in the sample, at least until these organics are released from the pyrolyzed sulfate mineral (~700°C in our experiment). Hence, we suggest magnesium sulfate as one of the minerals to target in priority for the search of organic molecules by the Curiosity and ExoMars 2018 rovers.

1. Introduction

The search for organic molecules is a main objective of the landed space missions that have been exploring Mars over the last 30 years and a primary goal of the Mars Exploration Program Analysis Group 2015. The first definitive detection of Martian organic matter was recently achieved by the Sample Analysis at Mars (SAM) experiment on board the Curiosity rover. SAM-detected chlorobenzene and C₂ to C₄ dichloroalkanes produced from indigenous organic matter during the pyrolysis of a sample of mudstone collected at the Sheepbed site in Gale Crater [Freissinet *et al.*, 2015]. The presence of refractory-reduced carbon was also suggested at the Rocknest aeolian deposit at Gale Crater [Eigenbrode *et al.*, 2014]. However, both the low level and diversity of organics detected with in situ measurements are surprising because it is recognized that micro-meteorites, meteorites, and comets (exogenous sources) have delivered organic compounds to the Mars surface throughout its history [Benner *et al.*, 2000; Bland and Smith, 2000; Flynn, 1996] and numerous organics have been detected in Martian meteorites [Callahan *et al.*, 2013; Steele *et al.*, 2012]. Furthermore, environmental conditions on Mars may have been favorable to an abiotic synthesis of organic molecules (indigenous sources) [Heinrich *et al.*, 2007; Steele *et al.*, 2012] that would increase their concentration in the Mars' regolith.

There are different ways to interpret the low abundance and diversity of the organic molecules detected at the Mars surface by space probes. The main ones are that organic molecules may be destroyed under the environmental conditions (oxidation, cosmic ray, UV, and others) [Benner *et al.*, 2000; Oro and Holzer, 1979; Pavlov *et al.*, 2012; Poch, 2013] of the Mars surface, and/or that analytical and/or sample processing biases can limit the detection of organics present in the collected samples [Klein, 1977; Ming *et al.*, 2009, 2014; Navarro-Gonzalez *et al.*, 2006].

When considering the second argument, it can be noticed that pyrolysis was used for all the soil samples analyzed by the Viking [Biemann *et al.*, 1977] and Phoenix [Boynton *et al.*, 2009; Hoffman *et al.*, 2008] probes that did not detect indigenous organics above the instrumental detection limit. Pyrolysis is also used in the SAM experiment of the Mars Science Laboratory (MSL) mission [Mahaffy *et al.*, 2012] and is planned for the ExoMars 2018 mission. Pyrolysis (pyro: heat and lysis: break down) consists of heating samples to vaporize volatile compounds and break down refractory ones into smaller volatile molecules. During pyrolysis the sample temperature can typically reach 600 to 1000°C, and minerals can have an influence on the thermal extraction of the molecules. A well-known example for Mars comes from the presence of perchlorate salts in the soil, which are thermally decomposed to release molecular oxygen and chlorine-bearing volatile compounds such as HCl. These species lead to the oxidation and chlorination of organics during the pyrolysis [Glavin *et al.*, 2013; Ming *et al.*, 2009; Navarro-Gonzalez *et al.*, 2010; Steininger *et al.*, 2012; Sephton *et al.*, 2014]. The perchlorates were first detected in northern Martian soils during the Phoenix mission [Hecht *et al.*, 2009], and more recently in Gale Crater by SAM [Glavin *et al.*, 2013; Leshin *et al.*, 2013; Ming *et al.*, 2014]. It was also possibly detected in the Martian meteorite EETA79001 [Kounaves *et al.*, 2014]. The detection of carbon dioxide correlated with the release of dioxygen when pyrolyzing samples from northern soils (Phoenix), as well as samples from an aeolian bed form and a mudstone in Gale Crater (MSL), can tentatively be attributed to the oxidation of organic matter by dioxygen released from the thermal decomposition of perchlorates [Leshin *et al.*, 2013; Ming *et al.*, 2009, 2014]. Navarro-Gonzalez *et al.* [2010] observed a similar behavior when studying the pyrolysis of an Atacama Desert soil sample, an analog of Mars soil, in the presence of 1 wt% perchlorate under Viking-like pyrolysis conditions. They also observed the formation of chloromethane and dichloromethane that were detected with the gas chromatography mass spectrometry (GC-MS) experiment on board the Viking landers but attributed to contaminants brought by the experiment itself [Biemann *et al.*, 1976]. Based on these observations, they reinterpreted the Viking results as a possible detection of Martian organic carbon. Chloromethane and dichloromethane were also detected by the SAM experiment at Gale Crater. However, those compounds were interpreted as reaction products between Martian perchlorate and organic terrestrial contamination [Glavin *et al.*, 2013; Leshin *et al.*, 2013; Ming *et al.*, 2014].

In the same way as perchlorates, other minerals present in the Mars soil can lead to the production of dioxygen which can oxidize organics during the pyrolysis. In particular, this is the case for sulfates. Lewis *et al.* [2015] demonstrated that iron sulfate leads to the combustion of organic matter into carbon dioxide during the pyrolysis. The oxidation of organics during the pyrolysis of iron sulfate, as well as potentially of other sulfates-bearing samples, can be a major issue as sulfates are targeted minerals for the search for organic molecules on Mars. Indeed, during their crystallization, sulfates may trap organics as fluid inclusions and/or inside the crystal lattice, resulting in the protection of organics from the harsh Mars surface environmental conditions [Aubrey *et al.*, 2006; Bowden and Parnell, 2007]. Furthermore, sulfates are minerals widespread at the Mars' surface, especially magnesium and iron sulfates [Gaillard *et al.*, 2013].

The SAM experiment of the MSL mission is specifically devoted to search for organic compounds in the soil and atmosphere of Mars [Mahaffy *et al.*, 2012]. SAM consists of a gas chromatograph (GC) and a quadrupole mass spectrometer (QMS) both coupled with a pyrolysis setup (pyr). SAM works in two modes: pyr-GC-QMS and direct pyr-QMS, this latter being also called evolved gas analysis (EGA). The SAM experiment will have the opportunity to analyze magnesium sulfate-bearing layers observed from the orbit at the base of Mount Sharp in Gale Crater. The most abundant sulfate detected in this layer is kieserite (monohydrated magnesium sulfate) [Milliken *et al.*, 2010; Thomson *et al.*, 2011]. It may contain oxychlorine phases such as calcium perchlorates which have been detected in all the samples analyzed, to date, by the SAM experiment at Gale Crater. They are now assumed to be widespread at the Mars' surface and subsurface at concentrations in the 0.07 to 1.3 wt% [e.g., Glavin *et al.*, 2013; Leshin *et al.*, 2013; Ming *et al.*, 2014].

In this work, we study the influence of magnesium sulfate on the pyrolysis of *o*-phthalic acid under SAM-like pyrolysis conditions, in the presence or absence of perchlorate. Phthalic acid has been selected as it may be formed and accumulated at the Mars' surface by oxidation processes of organic material [Benner *et al.*, 2000]. Furthermore, phthalic acid is a potential precursor of the chlorobenzene detected by the SAM experiment to the Sheepbed mudstone at Gale Crater [Miller *et al.*, 2013]. Kieserite and calcium perchlorate were selected to simulate the material present in the magnesium sulfate layer at the base of the Mount Sharp. This work is of primary interest to (1) determine the best mineralogical environment for the detection of organic matter

when using pyrolysis as the extraction method and (2) help for the identification of the original organic molecules and minerals present in the samples analyzed by the SAM experiment, as the interaction between organics and minerals during the pyrolysis can result in the release of secondary organic and inorganic volatiles.

2. Experimental

2.1. Chemicals

Magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), phthalic acid, and calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$) were purchased from Sigma-Aldrich and Alfa Aesar and were of the highest purity available (>98%, 99.9%, and 99%, respectively). The fused silica was purchased from H. P. Technical Ceramic and had a purity of 99.5%. During the preparation of the samples, distilled water was used as a solvent.

2.2. Samples

A list of analyzed samples is presented in Table 1. We analyzed a sample of phthalic acid ($\text{C}_6\text{H}_4(\text{COOH})_2$) trapped in kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) mixed with calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$). This analogue is compared to mixtures and pure samples of phthalic acid, magnesium sulfate, and calcium perchlorate with the aim to discriminate the influence of each constituent on the analysis and to characterize the interactions between them. The amounts of kieserite and calcium perchlorate used in the ternary mixture sample were chosen from our current knowledge about the mineralogy of the magnesium sulfate layers at the base of Mount Sharp. The amount of calcium perchlorate was chosen to be 0.5 wt % (compared to magnesium sulfate) to be consistent with perchlorate abundances deduced from analyses done with the SAM experiment in Gale Crater [Glavin *et al.*, 2013; Ming *et al.*, 2014], as well as by Phoenix in polar regions soils [Hecht *et al.*, 2009]. A relatively high concentration of phthalic acid was used (1 wt %, without considering the fused silica) to enable the effects of pyrolysis on the organic molecule to be readily detectable. The mass ratio between organics and minerals in ternary and binary mixture samples are identical.

For phthalic acid and calcium perchlorate samples, those molecules were adsorbed on a substrate, fused silica, which does not influence the pyrolysis process [Schulten and Leinweber, 1993] and which is thermally inert over the temperature range studied. Before using it, the fused silica was heated to 850°C for 2 days in order to remove any organic contamination. Then phthalic acid or calcium perchlorate was adsorbed on the fused silica using aqueous solutions and then evaporating the solvent. For the samples containing magnesium sulfate, phthalic acid and magnesium sulfate were coprecipitated in distilled water to favor the trapping of the organic molecules in the crystal lattice and/or in fluid inclusions, as it could have happened on Mars [Aubrey *et al.*, 2006]. The pure magnesium sulfate sample was prepared in the same way. From X-ray diffraction analyses (XRD), the magnesium sulfate obtained after its precipitation was polyhydrated (from $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, Figures S1 and S2 in the supporting information). Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) was formed by dehydration of polyhydrated magnesium sulfate by heating the samples containing magnesium sulfate at 180°C prior to the pyrolysis (the temperature of formation of kieserite was experimentally determined). Thermogravimetric and thermal differential analyses (TG-TDA) confirmed the formation of kieserite by heating at 180°C prior to pyrolysis. Indeed, mass loss and thermal effects (endothermic in this case) observed during pyrolysis of the samples after the thermal treatment at 180°C are consistent with kieserite dehydration for binary and ternary mixtures containing calcium perchlorate. Calcium perchlorate adsorbed on fused silica was added to pure phthalic acid and kieserite samples and to phthalic acid-bearing kieserite samples. All the samples were crushed and homogenized in an agate mortar mill. The samples were sieved to keep the particle size fraction <150 μm because SAM analyzes this fraction of Martian samples delivered by the robotic arm of Curiosity. For TG-TDA analyses, pure phthalic acid and kieserite samples, and phthalic acid mixed with calcium perchlorate samples were prepared without fused silica in order to increase their instrumental signal (their responses were close to the detection limit of the instrument using samples containing fused silica).

2.3. Analytical Methods

2.3.1. Pyrolysis Gas Chromatographic and Evolved Gas Analysis Experiments

Pyr-GC-MS and EGA experiments were performed with a CDS analytical pyroprobe 5150 connected by a transfer line set at 250°C to a Thermo Scientific Trace GC-ISO. The pyrolysis was set as close as possible to

Table 1. Description of the Analyzed Samples

Description (ID)	Phthalic Acid (wt %)		Calcium Perchlorate (wt %)		Kieserite (wt %)		Fused Silica (wt %)	
	GC-MS EGA ^a	TG-TDA ^a	GC-MS EGA ^a	TG-TDA ^a	GC-MS EGA ^a	TG-TDA ^a	GC-MS EGA ^a	TG-TDA ^a
Fused silica (substrate)	0.00	0.00	0.00	0.00	0.00	0.00	100	100
Phthalic acid (PA)	1.00	100	0.00	0.00	0.00	0.00	99.0	0.00
Ca perchlorate (CAP)	0.00	0.00	0.50	100	0.00	0.00	99.5	0.00
Kieserite (MGS)	0.00	0.00	0.00	0.00	100	100	0.00	0.00
MGS + PA (MGS-PA)	1.00	1.00	0.00	0.00	99.0	99.0	0.00	0.00
CAP + PA (PA-CAP)	0.50	66.66	0.25	33.33	0.00	0.00	99.25	0.00
MGS + CAP (MGS-CAP)	0.00	0.00	0.25	0.25	50.0	50.0	49.75	49.75
MGS + PA + CAP (MGS-PA-CAP)	0.50	0.50	0.25	0.25	50.0	50.0	49.25	49.25

^aGC-MS: gas chromatography coupled to mass spectrometry; EGA: evolved gas analysis; and TG-TDA: thermogravimetry coupled to thermal differential analysis.

the SAM experiment pyrolysis conditions (Table 2). Our experiment does not include a pressure sensor inside the pyrolysis. However, based on the instrument configuration and on similar experiments realized with a pressure sensor, the helium pressure inside the pyrolysis is estimated to be closed to 1.5 bars.

2.3.1.1. Pyrolysis Gas Chromatographic Mass Spectrometry Experiment

During the pyr-GC-MS experiments, most of the gases evolving from the samples were trapped on a cold trap (glass beads cooled down to -30°C). The compounds not trapped because of their too low boiling point, were simultaneously analyzed by GC-MS. Then the trap was heated from -30 to 250°C at $600^{\circ}\text{C}/\text{min}$ rate to quickly release the trapped compounds for their analysis by GC-MS. Helium was used as the carrier gas at a $1.1\text{ mL}/\text{min}$ constant flow rate in the column and a $15\text{ mL}/\text{min}$ split flow rate. A ZB-5HT capillary column (30 m length, 0.25 mm internal diameter, and $0.25\text{ }\mu\text{m}$ film thickness) was used for the separation of the compounds. It was initially heated at 30°C for 5 min and then heated at a $10^{\circ}\text{C}/\text{min}$ up to 250°C . The quadrupole mass analyzer was operated in the full scan mode from $m/z = 25$ to 535 using electron impact ionization at 70 eV energy. The temperatures of the transfer line and of the ionization chamber were maintained at 300°C and 250°C , respectively.

2.3.1.2. Evolved Gas Analysis Experiment

For the EGA experiments, the GC injector temperature was set to 250°C with a $14\text{ mL}/\text{min}$ split flow rate. A deactivated column (10 m length, 0.25 mm internal diameter) heated at 250°C with a $2.1\text{ mL}/\text{min}$ helium flow rate was used. The MS analytical conditions were the same as for the GC-MS analyses except for the mass range scanned that was set to 10 to $535\text{ }m/z$.

2.3.2. Thermogravimetric and Thermal Differential Analyses

TG-TDA analyses were performed with a SETARAM TGA 92. The total mass of sample analyzed was in the 10 to 30 mg range. The samples were heated from 40 to 850°C at a $35^{\circ}\text{C}/\text{min}$ heating rate, as for the SAM experiment pyrolysis [Mahaffy *et al.*, 2012]. The sample heating was done under an inert atmosphere of helium flowing at $20\text{ mL}/\text{min}$. Baseline calibration were also done using the same conditions. Before the start of the temperature program, the samples were maintained a few minutes at 40°C to wait for the stabilization of the oven temperature.

2.3.3. X-Ray Diffraction (XRD) Analyses

The XRD experiments were carried out on a Panalytical Empyrean diffractometer operated at 45 kV and 40 mA at 1.5435 \AA wavelength acquired from 5 to 70° by 0.0013° steps, 180 s per step.

Table 2. Comparison of the Pyrolysis Conditions Used in the Laboratory and the SAM Experiment

	Laboratory	SAM Experiment ^a
Initial temperature ($^{\circ}\text{C}$)	40	≈ 30
Final temperature ($^{\circ}\text{C}$)	850	850–860
Temperature ramp ($^{\circ}\text{C}/\text{min}$)	35	35
Carrier gas	helium	helium
Helium flow (mL/min)	21	$\approx 0,4$
Helium pressure (mbar)	≈ 1500	25

^aMahaffy *et al.* [2012].

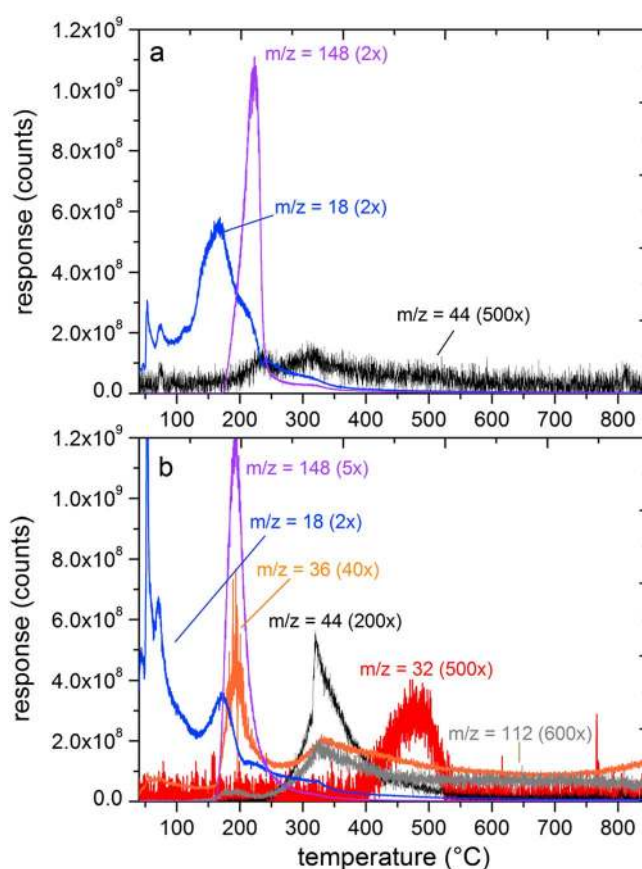


Figure 1. Thermally evolved gas analyses of (a) phthalic acid and (b) phthalic acid and calcium perchlorate mixture under SAM-like pyrolysis conditions. Compounds presenting the same profile were represented by only one m/z ratio for more clarity. Compounds: $m/z = 18$: water; $m/z = 44$: carbon dioxide; $m/z = 148$: phthalic anhydride, $m/z = 36$: hydrochloric acid, $m/z = 32$: dioxygen; and $m/z = 112$: chlorobenzene, dichlorobenzene, and trichlorobenzene. In Figure 1b, the peak at 200°C of $m/z = 36$ corresponds to phthalic anhydride and not hydrochloric acid.

3. Results and Discussions

3.1. Pyrolysis of Phthalic Acid

Figure 1a shows the thermograms of the gases released by phthalic acid alone under SAM-like pyrolysis conditions (Table 2). The thermal decomposition of phthalic acid occurs at temperature around 240°C. That results in a mass loss of $96.5 \pm 3.4\%$ correlated with an endothermic peak observed in TG-TDA data (Table S1) and to the release of phthalic anhydride, H_2O , and CO_2 , thus suggesting dehydration and decarboxylation of phthalic acid. The water released from 40 to 170°C has been attributed to free water adsorbed on fused silica, based on pyrolysis of pure fused silica. Phthalic anhydride, H_2O and CO_2 compounds also present a peak of detection around 310°C without any mass loss. Therefore, it can be assumed that those molecules probably come from the thermal degradation of phthalic acid present in the gaseous phase at this temperature.

3.2. Pyrolysis of Calcium Perchlorate

The thermal evolution of calcium perchlorate occurs in six steps, including dehydration and thermal decomposition, presented in Table S2, as previously observed by Migdal-Mikuli and Hetmańczyk [2008].

The dehydration of calcium perchlorate takes place in two steps determined by a major H_2O release observed at 158°C and a minor one at 299°C. At those temperatures, a H_2O release (Figure 2a) associated with a mass loss and endothermic behavior (Table S2) is observed. A H_2O release is also observed at 83°C (Figure 2a), but it is not correlated to a sample mass loss (Table S2). During TG-TDA analyses, this water was probably lost

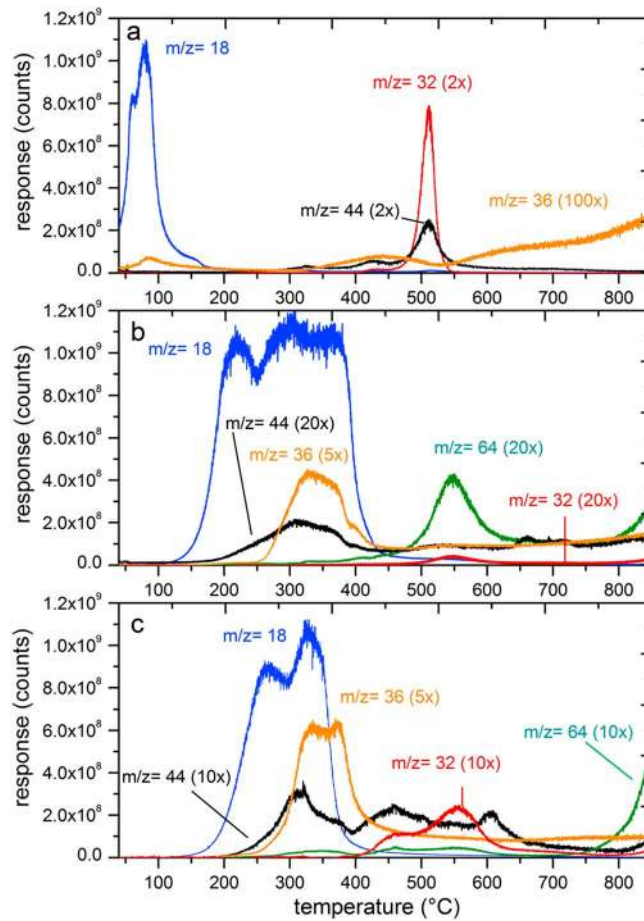
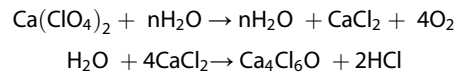


Figure 2. Thermally evolved gas analyses of (a) calcium perchlorate, (b) kieserite, and (c) kieserite and calcium perchlorate mixture under SAM-like pyrolysis conditions. Compounds: $m/z = 18$: water; $m/z = 32$: dioxygen; $m/z = 36$: hydrochloric acid; $m/z = 44$: carbon dioxide; and $m/z = 64$: sulfur dioxide.

during the step of stabilization of the temperature prior to the analyses (see section 2.2), and it can be identified as adsorbed water.

Under our pyrolysis conditions, calcium perchlorate is thermally decomposed mainly at temperatures around 500°C leading to the release of gaseous O₂ and HCl as stable end products (Figure 2a). This decomposition can be described by the following reactions [Glavin *et al.*, 2013]:



From 300 to 570°C, the O₂ release is associated with HCl, and it presents maxima at 350 ± 25, 430 ± 30, and 530 ± 31°C. Major releases observed at 430 and 530°C are consistent with temperatures of thermal decomposition of calcium perchlorate (Table S2), whereas the minor release observed at 350°C is more consistent with a thermal decomposition of calcium chlorate (Ca(ClO₃)₂) [Uehara *et al.*, 1978]. HCl evolved from 40 to 850°C (Figure 2a). HCl observed from 40 to 300°C was attributed to contamination from a previous experiment as it was also detected in this range of temperature in the blanks done before the analyses of samples of calcium perchlorate. From 570 to 850°C, HCl comes from the reaction of CaCl₂ with H₂O.

CO₂ attributed to organic contamination was also detected. As no organic molecule was detected by pyr-GC-MS analysis, this contamination is probably minor and it does not change our conclusions. However, the possibility that the contamination corresponds to the presence of refractory organic molecules that are not detectable by GC-MS cannot be excluded.

Table 3. List of Compounds Generated by Pure Phthalic acid (PA) and Phthalic Acid With Calcium Perchlorate (PA-CAP) and/or Kieserite (MGS-PA; MGS-PA-CAP)^a

Nature	Identified Compound	PA	MGS-PA	PA-CAP	MGS-PA-CAP
Inorganic	CO ₂	x	x	x	x
	H ₂ O	x	x	x	x
	SO ₂		x		x
	O ₂		x	x	x
	HCl			x	x
Carboxylic acid	phthalic acid monoethyl ester		x		x
Aromatic heterocycle (O) and ketone	phthalic anhydride	x	x	x	x
	benzofuran		x		x
	benzophenone		x		x
	9H-fluoren-9-one		x		x
	2-furfuraldehyde or isomer		x		x
Chlorinated compounds	chlorobenzene			x	x
	dichlorobenzene			x	x
	trichlorobenzene			x	x
	chlorophenol				x
Alcohol	phenol		x		x
Aromatic hydrocarbon	benzene		x		x
	1-ethyl-2-methylbenzene or isomers		x		
Linear hydrocarbon	6-methyloctene		x		x
	2-methyl-2-octene		x		x
	2-nonene and isomers		x		x
Sulfur compounds	2-benzothiophene		x		x
	hexathiane		x		x
	octathiocane		x		x
	3H-1,2-benzodithiol-3-one		x		x
	diphenyl sulfide		x		
	naphtho[2,3-b]thiophene		x		x

^aCompounds identified through GC-MS analyses.

3.3. Pyrolysis of Phthalic Acid Mixed With Calcium Perchlorate

Figure 1b shows the gases released when pyrolyzing phthalic acid mixed with calcium perchlorate under SAM-like pyrolysis conditions. From 150 to 250°C, phthalic acid is partially thermally decomposed. A $55.3 \pm 3.7\%$ mass loss is measured. It is correlated with an endothermic peak (Table S3), and the release of phthalic anhydride, H₂O, and CO₂ centered around 210°C. The mass loss also includes the first step of calcium perchlorate dehydration (Table S3).

From 250 to about 400°C, O₂ and HCl evolving from the Ca perchlorate oxidize and chlorinate phthalic acid and/or its pyrolysis by-product (Table 3). CO₂, H₂O, HCl, phthalic anhydride, and chlorinated hydrocarbons (chlorobenzene, dichlorobenzene, and trichlorobenzene) are detected with a maximum release observed around 320°C. These releases are correlated to a $10.5 \pm 1\%$ mass loss, to an exothermic peak (Table S3) as well as to O₂ and HCl availability in the pure calcium perchlorate sample (see section 3.2). The mass loss includes the second step of calcium perchlorate dehydration and the correlated endothermic reaction is probably hidden by the exothermic peak due to the oxidation of phthalic acid (Tables S2 and S3).

From 40 to 150°C and from 450 to 850°C, the gases released and TG-TDA measurements data are quite comparable to what it was observed for calcium perchlorate (CAP) sample, except for the peak of CO₂ observed at 500°C in CAP which is not clearly seen in phthalic acid mixed with calcium perchlorate (PA-CAP) although CO₂ is present at this temperature (Figures 1b and 2a and Tables S2 and S3).

3.4. Pyrolysis of Kieserite (MGS)

From 40 to 850°C, the gases released from kieserite are H₂O, SO₂, O₂, HCl, and CO₂ (Figure 2b).

From 70 to 650°C, magnesium sulfate is dehydrated. The water evolved in this temperature range with peaks centered at 218 ± 12 , 294 ± 22 , 360 ± 23 , and 540 ± 30 °C. From 70 to 450°C, a $13.5 \pm 3.9\%$ total mass loss is measured and it is correlated with an endothermic behavior (Table S4). This is consistent with the dehydration of kieserite. The observation of water below 180°C (the temperature samples were heated at in order to

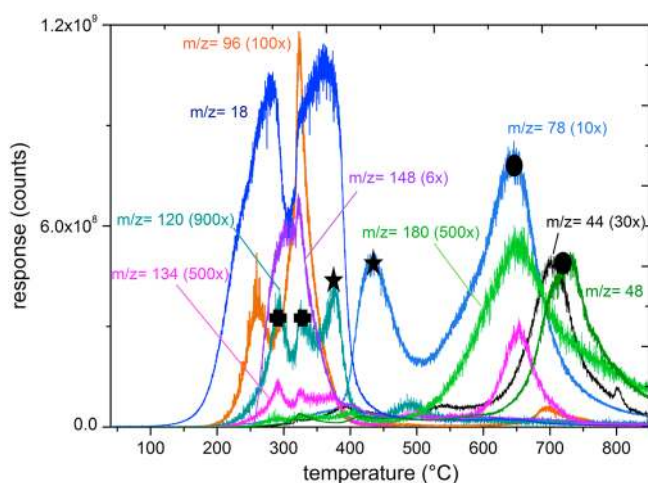
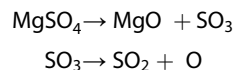


Figure 3. Thermally evolved gas analyses of the phthalic acid-bearing kieserite under SAM-like pyrolysis conditions. Peaks marked by the same symbol (star, circle, or cross) present similar temperature considering error bars (60°C for circles, 35°C for stars, and 27°C for crosses). Compounds presenting the same profile were represented by only one m/z ratio for more clarity. The SO_2 was plot with $m/z = 48$ since $m/z = 64$ was also present in the mass spectra of other compounds released (e.g., octathiocane). Compounds: $m/z = 18$: water; $m/z = 44$: carbon dioxide; $m/z = 48$: sulfur dioxide; $m/z = 78$: benzene; $m/z = 96$: 2-furaldehyde or isomer, and phenol; $m/z = 120$: 1-ethyl-2-methylbenzene or isomer; $m/z = 134$: 2-benzothiophene and benzofuran; $m/z = 148$: phthalic acid monoethyl ester, phthalic anhydride, 6-methyloctene, 2-methyl-2-octene, and 2-nonene and isomer; and $m/z = 180$: hexathiane, 3H-1,2-benzodithiol-3-one, diphenyl sulfide, benzophenone, 9H-fluorèn-9-one, naphtho[2,3-b]thiophène, and octathiocane.

generate the kieserite from polyhydrated Mg sulfate prior these analyses, see section 2.3) suggests that the kieserite is at least partially rehydrated because this mineral is highly hygroscopic [Grevel and Majzlan, 2009]. This rehydration explains the observation of three peaks of water rather than one for the dehydration of kieserite [Emons *et al.*, 1990]. However, the total mass loss observed ($13.5 \pm 3.9\%$) is consistent with the theoretical mass loss for the kieserite dehydration (13%). Therefore, the sample is mainly composed of kieserite. The small peak of water centered at 540°C probably corresponds to the dehydration of hemihydrate magnesium sulfate ($\text{MgSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) [Emons *et al.*, 1990].

From 150 to 850°C, decomposition of magnesium sulfate is observed. SO_2 and O_2 are detected in this temperature range with a maximum observed at $539 \pm 32^\circ\text{C}$ and a high temperature peak starting at 800°C. The thermal decomposition of magnesium sulfate leads to the production of SO_2 and O_2 , and it can be described by the following reactions [Lau *et al.*, 1977]:



In the absence of a reducing agent, this decomposition occurs around 1000°C [Scheidema and Taskinen, 2011] and we observe it starting from 800 to 850°C (maximum temperature of the experiment) in our experiment. SO_2 and O_2 released below 800°C are correlated to H_2O . It can be deduced that they probably come from a minor decomposition of magnesium sulfate induced by its dehydration.

CO_2 evolved from 150 to 850°C with a maximum observed at $325 \pm 33^\circ\text{C}$. According to the XRD analyses and to commercial information, the sample of kieserite used in our experiments does not contain any mineral suitable to generate CO_2 . Therefore, it was attributed to occluded CO_2 as it was previously observed for kaolinite [Heide and Földvari, 2006], partial oxidation of organics, such as high molecular weight organics, in the presence of the atomic oxygen, O_2 and/or the significant amount of H_2O evolved at these temperatures, and/or thermal decomposition of inorganic contaminants (such as carbonates) not detected by XRD analyses because they are present at abundances below the XRD detection limit or are poorly crystalline. As no organic molecule was detected by pyr-GC-MS analyses, this contamination is probably minor and does not influence our conclusions. However, the possibility that the contamination corresponds to refractory organics which are not detectable by GC-MS cannot be excluded. HCl was detected with a maximum centered at about

350°C. HCl cannot be generated from magnesium sulfate, and it was attributed to a contamination of the instrument from the previous run.

3.5. Pyrolysis of Phthalic Acid-Bearing Kieserite (MGS-PA)

Gases released by the pyrolysis of phthalic acid-bearing kieserite are presented in Figure 3. From 100 to 450°C, the kieserite is dehydrated, as observed for MGS. The water released in this temperature range matches with a total mass loss of $13.7 \pm 0.7\%$ and an endothermic behavior, as observed for MGS (Table S5).

From 150 to 500°C, a fraction of phthalic acid trapped inside the crystal lattice and/or as fluid inclusions inside magnesium sulfate is released and oxidized. The gases released in this temperature range are CO_2 , SO_2 , and organic compounds, including phthalic anhydride and sulfur-bearing compounds, with peaks observed around 290, 320, 385, and 495°C, as well as H_2O at 290 and 385°C. The formation of phthalic anhydride and CO_2 occurs at a higher temperature (at least 46°C) than for PA (see Figures 1a and 3, purple lines). The peaks initiation temperatures attributed to phthalic acid related compounds and to SO_2 due to magnesium sulfate decomposition are correlated. Furthermore, the detection of mainly the same organic compounds from 100 to 500°C suggests a common source: the release of trapped phthalic acid. A possible stabilization of phthalic acid by adsorption on magnesium sulfate cannot be excluded. The organic compounds detected in this temperature range include molecules not observed from PA sample, such as benzene, linear alkenes, and sulfur-bearing compounds. This may be due to the oxidation and sulfidation of phthalic acid by the atomic oxygen, O_2 , SO_3 , and/or SO_2 coming from the minor decomposition of the magnesium sulfate (see section 3.4).

From 500 to 850°C, a mass loss of $2.0 \pm 0.3\%$ at about 700°C, not observed for MGS or PA, is correlated to an endothermic behavior (Table S5) and to the release of SO_2 , CO_2 , and organics, including sulfur-bearing compounds with two peaks at 650 and 720°C. In the presence of a reducing agent, magnesium sulfate is reduced at about 750°C [Scheidema and Taskinen, 2011]:



In the experiments discussed here, the reducing agent corresponds to trapped phthalic acid as suggested by the results on the 150–500°C temperature range on this experiment. Another reducing agent, in addition to trapped phthalic acid, could be the magnesium phthalate. Magnesium phthalate may be generated during our sample preparation (see section 2.3) and be oxidized on this temperature range leading to the generation of benzene and CO_2 [Sun et al., 2000; Zhan et al., 2005].

Magnesium sulfate influences the phthalic acid chemical reactivity during the pyrolysis by leading to the formation of linear and aromatic hydrocarbons, alcohol, and sulfur-bearing compounds which are not observed when pyrolyzing PA alone (Table 3 and Figure 4). This different chemical reactivity can be mainly attributed to the oxidation and sulfidation of phthalic acid and/or its by-products by the reduction of magnesium sulfate and by atomic oxygen, O_2 , SO_3 , and/or SO_2 generated by magnesium sulfate minor decomposition (see section 3.4).

3.6. Pyrolysis of Kieserite Mixed With Calcium Perchlorate (MGS-CAP)

The thermal evolution of MGS-CAP is mainly similar to the sum of those observed for MGS and CAP. From 100 to 450°C, the kieserite is dehydrated leading to the release of water, a total mass loss of $13.9 \pm 4.8\%$ and to an endothermic behavior (Table S6), as observed for MGS. The CO_2 , HCl, O_2 , and SO_2 profiles are mainly similar to the sum of those observed for MGS and CAP (Figure 2c). Minor differences are the peak of CO_2 at 600°C not observed in MGS or CAP and the water release centered at 80°C in the calcium perchlorate (Figure 2a) which is not observed here because of the thermal treatment applied to this sample before its pyrolysis (see section 2.2). The thermal behavior due to calcium perchlorate is also not observed during TG-TDA analysis of MGS-CAP (Table S6). This is because of the small amount of perchlorate in the MGS-CAP sample, which resulted in perchlorate related mass loss and thermal effects being below the detection limit of the instrument.

3.7. Pyrolysis of Phthalic Acid-Bearing Kieserite Mixed With Calcium Perchlorate (MGS-PA-CAP)

Figure 5 shows the gases released from the phthalic acid-bearing kieserite and calcium perchlorate when it is pyrolyzed under SAM-like pyrolysis conditions.

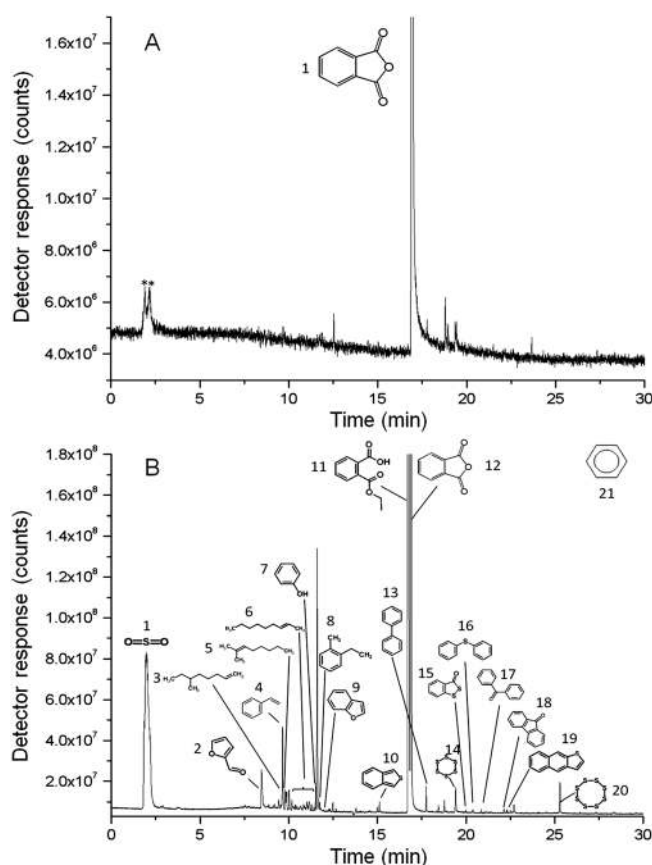


Figure 4. Gas chromatograms recorded during pyrolysis of (a) phthalic acid and (b) phthalic acid-bearing kieserite. Carrier gas: He. Column temperature program: 30°C hold 5 min to 250°C (10°C/min). Detector: QMS. Star = not identified compounds also detected in blanks. (a) 1 = phthalic anhydride. (b) 1 = SO₂, 2 = 2-furfuraldehyde or isomer, 3 = 6-methyloctene, 4 = styrene, 5 = 2-methyl-2-octene, 2-nonene, and isomers, 7 = phenol, 8 = 1-ethyl-2-methylbenzene or isomers, 9 = benzofuran, 10 = 2-benzothiothiophene, 11 = phthalic acid monoethyl ester, 12 = anhydride phthalic, 13 = biphenyl, 14 = hexathiane, 15 = 3H-1,2-benzodithiol-3-one, 16 = diphenyl sulfide, 17 = benzophenone, 18 = 9H-fluoren-9-one, 19 = naphtho[2,3-b]thiophene, 20 = octathiocane, and 21 = benzene. Styrene and biphenyl were also detected in blanks and are therefore attributed to contamination of the instrument. However, their formation from the sample cannot be excluded. Benzene was detected during the first step of GC-MS analyses.

From 100 to 450°C, the kieserite and calcium perchlorate are dehydrated resulting in the H₂O release in this temperature range which matches with a mass loss of 14.5 ± 1.1% and to an endothermic behavior (Table S7).

From 150 to 450°C, similar chemical processes as those indicated for the MGS-PA and PA-CAP samples are observed: oxidation, sulfidation, and chlorination of phthalic acid progressively released from magnesium sulfate. This is explained by atomic oxygen, O₂, SO₂, SO₃, and HCl produced by the decomposition of perchlorate and magnesium sulfate. In this temperature range, H₂O, CO₂, HCl, and organic compounds, including sulfur- and chlorine-bearing compounds, are released with maxima observed around 290, 320, and 380°C. The compounds detected are similar to those observed for MGS-CAP, MGS-PA, and PA-CAP samples at the same temperatures, except chlorophenol detected only for this sample. Chlorophenol might come from the chlorination of phenol detected in MGS-PA sample. For PA-CAP sample, the chlorination of phthalic acid begins around 250°C, temperature at which HCl is available from Ca perchlorate decomposition. In this sample, the chlorination begins at 150°C and is correlated with the release of HCl as observed for MGS-CAP. The presence of HCl at temperatures below 250°C is attributed to a contamination of the instrument. Without this contamination, the chlorination of phthalic acid in the MGS-PA-CAP sample is expected to begin at 250°C.

From 450 to 550°C, phthalic acid released from magnesium sulfate and/or its by-products are likely undergoing oxidation, chlorination, and sulfidation due to gases released during thermal decomposition of calcium perchlorate and partial decomposition of magnesium sulfate. In this temperature range, organic compounds,

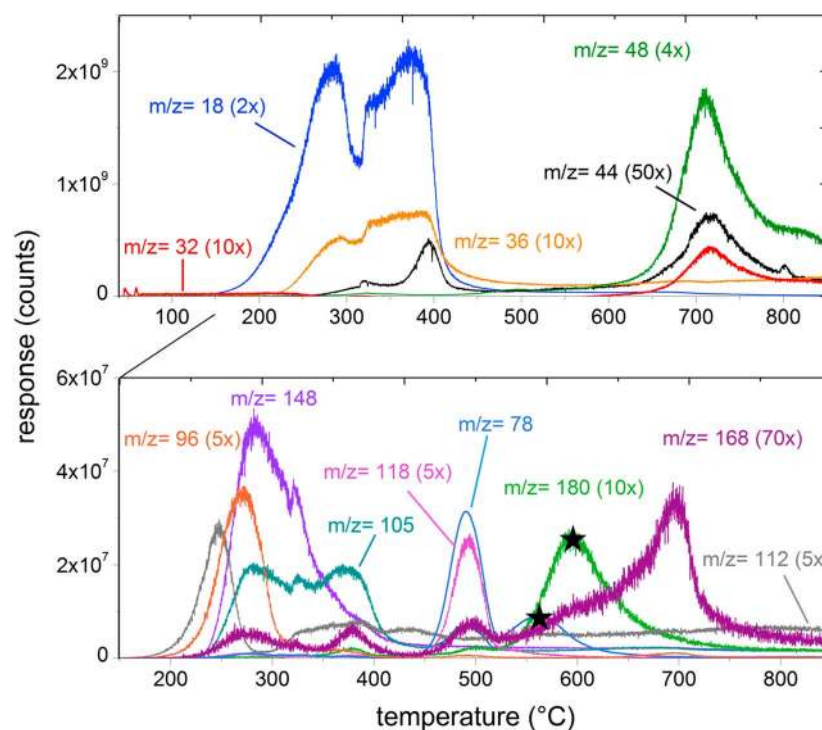


Figure 5. Thermally evolved gas analyses of the phthalic acid-bearing kieserite and calcium perchlorate mixture under SAM-like pyrolysis conditions. Compounds presenting the same profile were represented by only one m/z ratio for more clarity. Peaks marked by star present similar temperature considering error bar (30°C). The SO_2 was plot with $m/z = 48$ as $m/z = 64$ was also present in the mass spectra of other compounds released (e.g., octathiocane). Compounds: $m/z = 18$: water; $m/z = 32$: dioxygen; $m/z = 36$: hydrochloric acid; $m/z = 44$: carbon dioxide; $m/z = 48$: sulfur dioxide; $m/z = 78$: benzene; $m/z = 96$: 2-furfuraldehyde or isomer, phenol, chlorophenol, and octathiocane; $m/z = 105$: benzophenone; $m/z = 112$: chlorobenzene and dichlorobenzene; $m/z = 118$: 6-methyloctene, 2-methyl-2-octene, 2-nonene and isomers, benzofuran, and hexathiane; $m/z = 148$: phthalic acid monoethyl ester and phthalic anhydride; $m/z = 168$: 2-benzothiophene, naphtho[2,3-b] thiophene, 3H-1,2-benzodithiol-3-one, and trichlorobenzene; and $m/z = 180$: 9H-fluoren-9-one.

including sulfur- and chlorine-bearing species are observed around 495°C , as well as HCl and SO_2 but without a clear maximum. Those molecules are not detected at this temperature in MGS-CAP, PA-CAP, and MGS-PA samples, with the exception of SO_2 , HCl, and linear alkene. At about 495°C , O_2 released from the thermal decomposition of calcium perchlorate should be detected as in the MGS-CAP and PA-CAP samples (Figures 1b and 2c, red lines). HCl detection suggests that this decomposition occurs; therefore, O_2 might be consumed.

From 550 to 850°C , the magnesium sulfate is reduced by phthalic acid and potentially magnesium phthalate and their by-products are partially chlorinated by HCl available at this temperature, as observed for MGS-CAP and PA-CAP samples. In this temperature range, SO_2 , CO_2 , HCl, and organic molecules, including chlorine- and sulfur-bearing compounds, are detected with maxima observed around 600 and 700°C . These releases are correlated to a mass loss of $2.1 \pm 0.0\%$ and to an endothermic peak (Table S7). These features and the compounds released were also observed in the MGS-PA sample except for the release of HCl, benzofuran, diphenyl sulfide, and chlorine-bearing compounds. The formation of benzofuran and diphenyl sulfide is probably inhibited by chlorination reactions. As the calcium perchlorate is already completely thermally decomposed, the organics released in this higher temperature range are not submitted to oxidation induced by dioxygen released from calcium perchlorate.

The mixture of magnesium sulfate and calcium perchlorate does not seem to have a strong influence on the chemical reactivity of the phthalic acid. Indeed, the stable end products observed for MGS-PA-CAP mainly correspond to the addition of those obtained for MGS-AP and PA-CAP samples. The few exceptions might be explained by a higher oxidation rate due to the combination of oxidation from calcium perchlorate and magnesium sulfate (Table 3). However, the mixture of magnesium sulfate and calcium perchlorate does affect

the temperature range at which the chemical reactions occur and the related volatiles are released. The oxidation and chlorination occurring in the MGS-PA-CAP sample occurs over a broader temperature range than for the PA-CAP sample because when the PA is contained within the kieserite, that trapped PA is available for interaction after release during high temperature decomposition of the sulfate.

3.8. The Case of Alanine

In addition to the experiments presented here for the phthalic acid, we also investigated alanine in interaction with kieserite in presence or absence of calcium perchlorate. The results we obtained were quite similar to those for phthalic acid in terms of chemical processes and their indicated temperature ranges. We therefore chose not to present them in the manuscript.

3.9. Overall Discussions

Lewis et al. [2015] suggested that ferric sulfates may be a complication for the detection of organic matter using a thermal treatment, as they generate oxidative species during their thermal decomposition occurring in the temperature range commonly used for these analyses on Mars (<1000°C). In the same way, the authors suggested that other sulfates which are thermally decomposed in this temperature range may also be an issue for the detection of organic compounds (e.g., aluminum sulfate). Therefore, calcium and magnesium sulfates which are thermally decomposed above 1000°C [*Lau et al.*, 1977; *West and Sutton*, 1954] were not expected to result in the oxidation of organic molecules. This work demonstrates that magnesium sulfate contributes to the degradation of organics during the pyrolysis by oxidation below 1000°C. This oxidation is not associated with the thermal decomposition of magnesium but to its reduction at above 700°C and to its minor decomposition apparently related to its dehydration. In the same way, calcium sulfate may be reduced in the presence of carbon-bearing molecules from 750 to 850°C depending of their impurity content [*Kuusik et al.*, 1985]. Therefore, not only the thermal decomposition temperature but also the reduction temperature of sulfates have to be taken into consideration to estimate if they may undergo oxidation of organic matter during thermal treatment used on Mars.

For a process such as oxidation, the number of organics by-products detected decreases with the concentration of organic molecules initially present in the sample. At low levels, organic compounds may be entirely transformed into inorganic by-products (e.g., mainly CO₂), or be present below an instrument's detection limit [*Iniguez et al.*, 2009; *Navarro-Gonzalez et al.*, 2006; *Steininger et al.*, 2012]. The total amount of organic carbon at the Mars surface is expected to be at a trace level. It is estimated to be ~60 ppm based on estimation done from the current meteoritic and micrometeoritic influx under the hypothesis that these were constant over the time and that exogenous carbon was mixed into a 100 m thick layer of Martian regolith [*Anders*, 1989; *Flynn*, 1996]. Therefore, magnesium sulfate, like perchlorates, may represent an issue for organic matter detection using pyrolysis as the sample extraction method. However, the amount of organic compounds potentially trapped inside magnesium sulfate may be enough to allow the detection of organics pyrolysis by-products despite oxidation processes. For example, during the crystallization of magnesium sulfate of Gale Crater (3.5–3.8 Ga) [*Cabrol et al.*, 1999], environmental conditions could be favorable to abiotic synthesis of organic molecules in addition to exogenous sources. Those organic compounds may be trapped inside magnesium sulfate and preserved over time [*Bowden and Parnell*, 2007].

On Mars, magnesium sulfate could be mixed with others minerals which also favor the decomposition of organic molecules during pyrolysis, such as perchlorates and iron oxides [*Iniguez et al.*, 2009; *Navarro-Gonzalez et al.*, 2006; *Schulten and Leinweber*, 1993]. In the analog samples we studied, trapped organic molecules are completely released at 700°C under SAM-like pyrolysis conditions. Calcium perchlorate is already thermally decomposed at this temperature, and, therefore, organic compounds released at 700°C are protected against oxidation induced by calcium perchlorate. There is strong evidence of the presence of magnesium, and probably calcium and iron, perchlorates on Mars' surface [*Glavin et al.*, 2013; *Hecht et al.*, 2009; *Ming et al.*, 2014]. Under SAM-like pyrolysis conditions these are thermally decomposed below 600°C [*Ming et al.*, 2014]. If magnesium sulfate does not substantially influence their thermal decomposition temperature, as observed for calcium perchlorate in this study, trapped organics released at 700°C are protected from oxidation due to all perchlorates currently detected on Mars. By extension, trapped organics inside magnesium sulfate should be protected from other minerals influence at least until their release temperature (700°C in our pyrolysis conditions). Therefore, potentially trapped organic compounds inside

magnesium sulfate may be detectable using pyrolysis as an extraction method. In the same way, this conclusion could be applied to other sulfates which are reduced at a high temperature, typically above 600°C considering perchlorates currently detected on Mars, such as calcium sulfate [Kusik *et al.*, 1985].

4. Conclusion

Our data show that magnesium sulfate has a strong influence on the chemical processes occurring during the pyrolysis of organic matter, mainly leading to its oxidation and sulfuration. This influences the nature of the pyrolysis products, as well as their temperature of release compared to pure organic matter and pure magnesium sulfate pyrolysis. Our data are helpful to interpret SAM experiment results, providing information to help identify potential precursors of organic molecules as well as magnesium sulfate in analyzed samples. A detection of SO₂ from magnesium sulfate correlated with a CO₂ release at about 700°C may suggest the oxidation of organic molecules at this temperature, even if no organic product is detected. We also demonstrated that magnesium sulfate protects organic matter from oxidation due to calcium perchlorate during pyrolysis. This is due to the complete release of organic molecules trapped in the magnesium sulfate at a higher temperature than the one at which the calcium perchlorate thermal decomposition occurs. This protective effect may apply to all perchlorates currently detected at the Mars' surface, as well as to other minerals at least until organic molecules complete release. Therefore, using pyrolysis as an extraction method may allow the detection of potentially trapped organic compounds inside magnesium sulfate on Mars even in the presence of perchlorates or other minerals in the sample that could result in decomposition of any free sample organics during pyrolysis. We suggest that magnesium sulfate should be targeted as a priority mineral environment in which to conduct the search for organics on Mars by the MSL and ExoMars space missions.

Acknowledgments

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