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RESEARCH ARTICLE

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Key Points:

- SAM-like pyrolysis of Cl salts forms chlorobenzene, benzoic, and phthalic acid
- Chlorobenzene from Tenax and Cl salt volatiles reacting correlates with HCl
- On Mars, chlorobenzene does not correlate with HCl, so could be sample derived

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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

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Abstract The Sample Analysis at Mars (SAM) instrument suite aboard Curiosity has detected chlorinated organic compounds in Martian sediment samples. The chlorine in these molecules is thought to derive from oxychlorine salts in Martian sediments, but the carbon source remains under investigation. To constrain possible carbon sources, we investigated how the composition and concentration of oxychlorine phases in solid samples affect organic molecules released from the Tenax traps on board SAM. We created Mars analogue soils by spiking olivine sand with calcium perchlorate, magnesium perchlorate, or ferric iron chloride and analyzed the volatiles generated during pyrolysis–gas chromatography–mass spectrometry using commercial instruments operated under SAM-like conditions, with and without a Tenax trap. Benzoic acid, phthalic anhydride, high molecular weight aromatics, and chlorobenzenes are produced from the trap in response to volatiles released during Cl salt pyrolysis. Changes in composition or concentration of oxychlorine phases between samples could thus potentially produce an increase in chlorobenzene, as observed between samples from Rocknest and Cumberland. However, in our experiments benzoic acid, phthalic anhydride, and chlorobenzenes increase in proportion with the amount of HCl sent to the trap, while in Cumberland samples the chlorobenzene increase showed no corresponding increase in HCl. Based on our experiments, the Tenax trap is a possible source of the traces of chlorobenzene observed at Rocknest, John Klein, and Confidence Hills. The order-of-magnitude higher chlorobenzene abundances observed at Cumberland cannot be attributed to the Tenax trap. Furthermore, we found no evidence of significant trap degradation after hundreds of experiments with Cl salt-containing analogue soils.

1. Introduction

The Mars Science Laboratory (MSL) rover, Curiosity, which landed on Mars on 6 August 2012, found evidence for an ancient lake bed at Yellowknife Bay in Gale Crater that could have supported life for hundreds to tens of thousands of years or longer [Grotzinger *et al.*, 2013]. If life was once present in this ancient lakebed, indigenous organic compounds should be preserved in the sediment, in addition to exogenous organics delivered to the surface of Mars through meteorite and interplanetary dust infall [Flynn, 1996]. However, the presence of oxychlorine phases (e.g., chlorate and perchlorate salts) in the Martian soil [Hecht *et al.*, 2009; Glavin *et al.*, 2013] limits our ability to detect and identify organic compounds that may be present. Perchlorate salts are strongly oxidizing and facilitate the combustion of organic compounds when heated to elevated (>150°C) temperatures such as those used to thermally desorb or pyrolyze organic matter from solid samples in experiments conducted by the Mars surface exploration missions Viking, Phoenix, and MSL. The pyrolysis of oxychlorine phases in the presence of organic compounds, however, also results in the formation of low quantities of chlorinated organic compounds, resulting from a competition between combustion and oxidative chlorination of the organic molecules [Navarro-Gonzalez *et al.*, 2010; Steininger *et al.*, 2012; Glavin *et al.*, 2013; Keppler *et al.*, 2014; Freissinet *et al.*, 2015].

The Sample Analysis at Mars (SAM) instrument suite aboard the Curiosity rover, which includes a pyrolysis–gas chromatograph–mass spectrometer (py-GC-MS) system, has detected a suite of chlorinated organic compounds (Table 1) during pyrolysis at temperatures corresponding to the sample release of O₂ and HCl [Leshin *et al.*, 2013;

Table 1. Chlorinated Compounds and Their Possible Sources From SAM Sample Sites

Chlorinated Compounds	Possible Sources	Sample Sites
Chloromethane	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
Dichloromethane	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
Trichloromethane	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a
Tetrachloromethane	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a
Chloromethylpropene	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
<i>Tert</i> -butyldimethylchlorosilane	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
Chlorocyanogen	MTBSTFA/DMF ^{b,c}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
1,2-dichloroethane	Indigenous aliphatic compounds ^a	Cumberland ^a
1,2-dichloropropane	Indigenous aliphatic compounds ^a	Cumberland ^a
1,2-dichlorobutane	Indigenous aliphatic compounds ^a	Cumberland ^a
Chlorobenzene	Tenax TA ^{a,e}	Rocknest ^{b,c} , John Klein ^d , Cumberland ^a , Confidence Hills ^a
	Indigenous functionalized aromatic compounds ^a	Cumberland ^a

^aFreissinet et al. [2015].

^bGlavin et al. [2013].

^cLeshin et al. [2013].

^dMing et al. [2013].

^eThis study.

Glavin et al., 2013; Ming et al., 2013]. This simultaneous occurrence of chlorinated organic compounds and evolved O₂ and HCl likely results from the thermal decomposition of oxychlorine compounds reacting with either Martian organic compounds or terrestrial carbon present in the SAM instrument suite. Comparing the temperature of O₂ release with laboratory analyses of various oxychlorine phases did not provide an exact match to any particular perchlorate or chlorate species, but calcium perchlorate was deemed the closest match for the oxychlorine species in Rocknest [Leshin et al., 2013], and magnesium perchlorate and iron perchlorate are possibilities for the oxychlorine compounds at John Klein and Cumberland (see Glavin et al. [2013] and Ming et al. [2013] for a detailed explanation).

The source of carbon for these chlorinated hydrocarbons has been under intense investigation. Laboratory analogue experiments show that many of the chlorinated hydrocarbons detected by SAM can be generated through reactions between known terrestrially derived or “background” organics present in SAM and thermal degradation products of calcium perchlorate [Leshin et al., 2013; Ming et al., 2013; Glavin et al., 2013; Freissinet et al., 2015]. For example, chloromethanes and chloromethylpropene are the main chlorinated products of *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) pyrolyzed in the presence of perchlorate. MTBSTFA is a derivatization reagent present in SAM as part of a wet chemistry experiment (Table 1). Although none of the wet chemistry cups were punctured on SAM, the presence of MTBSTFA vapor in the sample manipulation system has been confirmed and is believed to result from a leak in at least one cup [Leshin et al., 2013; Glavin et al., 2013; Ming et al., 2013; Freissinet et al., 2015]. Additionally, Tenax TA, a porous 2,6-diphenyl-*p*-phenylene oxide polymer adsorbent in the Tenax trap (cryogenic hydrocarbon trap) used to collect and concentrate organics during SAM pyrolysis prior to GC-MS analyses, can be a source of trace amounts of chlorobenzene identified in the SAM solid samples (Table 1) [Glavin et al., 2013; Ming et al., 2013], as well as analogue laboratory experiments conducted on Earth [Freissinet et al., 2015].

In drilled samples from the Cumberland mudstone, however, not all chlorinated hydrocarbons detected by SAM can be explained through chlorination of background organics [Freissinet et al., 2015]. In the Cumberland mudstone samples, the abundance of chlorobenzene is an order of magnitude higher than in previous samples and subsequent samples. Additionally, three dichlorinated alkanes—dichloroethane, dichloropropane, and dichlorobutane—were detected by GC-MS after pyrolysis of the Cumberland samples but were not observed in any other solid samples or blanks (Table 1) [Freissinet et al., 2015]. Moreover, these

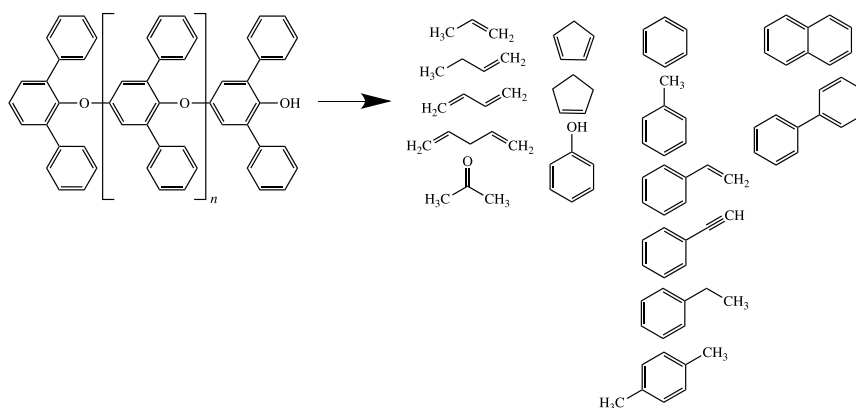


Figure 1. Tenax TA poly(2,6-diphenyl-*p*-phenylene oxide) and Tenax TA decomposition products observed in SAM data [Freissinet *et al.*, 2015].

dichlorinated alkanes have not been observed in laboratory experiments where MTBSTFA was pyrolyzed in the presence of a 1 wt % mixture of calcium perchlorate in fused silica [Freissinet *et al.*, 2015]. The order-of-magnitude increase in chlorobenzene observed in the Cumberland analyses is also difficult to attribute to changes in the composition or abundance of background organics, which remained stable from run to run [Freissinet *et al.*, 2015].

Here we provide a further constraint on the carbon sources for the organic compounds detected in SAM by investigating how the composition and abundance of oxychlorine species in samples might affect the distribution and abundance of organic molecules released from the Tenax trap. Essential to the SAM GC-MS analysis system, the Tenax trap is a cryogenic hydrocarbon trap composed of 0.49 g of 0.38 mm silica beads, 0.079 g of Tenax TA, and 0.11 g of Carbosieve G and is designed to concentrate volatile organics at 5°C prior to their transfer to the GC column by heating the trap to 300°C for several minutes under He flow [Mahaffy *et al.*, 2012]. Upon excessive heating, the Tenax TA polymer is known to degrade and release aromatic organic compounds, some of which could be detected in SAM (Figure 1) [Freissinet *et al.*, 2015]. Potentially caustic volatiles (e.g., Cl_2 , HCl, and O_2) released from oxychlorine minerals may also react with the Tenax trap materials during the pyrolysis-GC cut when volatiles released from the sample are collected on the Tenax trap (approximately 1.4–21 min) or during the ~300°C heating of the Tenax trap when volatiles are sent to the GC. The presence of corrosive volatiles such as O_2 , Cl_2 , and HCl released from perchlorates or other volatile products (e.g., SO_2 , H_2SO_3 , and NO) released from the sample could potentially degrade the Tenax trap materials, especially the Tenax TA, causing increased organics to be released and decreasing the overall effectiveness of the trap. Accordingly, our focus in this study was on the Tenax trap as a potential source of background organics.

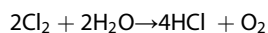
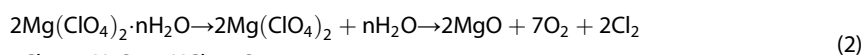
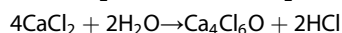
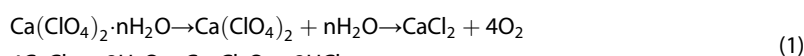
2. Methods

In this study, we evaluated the relationship between the reactive volatiles formed during the pyrolysis of Ca perchlorate ($\text{Ca}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$), Mg perchlorate ($\text{Mg}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$), and Fe chloride ($\text{FeCl}_3 \cdot n\text{H}_2\text{O}$) and the volatiles released from the Tenax trap. Ca and Mg perchlorates are representative of the types of oxychlorine phases detected in the Rocknest, John Klein, and Cumberland samples, as they thermally decompose to form Cl species (CaCl_2 and Cl_2 , respectively) and O_2 (equations (1) and (2)). Additionally, background water and water released from the samples are available for reactions with the thermally evolved Cl species resulting in the formation of HCl (equations (1) and (2)). Assuming all of the CaCl_2 and Cl_2 react with the excess of water in our experiments, Mg perchlorate should produce approximately 4X as much HCl as an equal amount of Ca perchlorate. The Fe chloride, on the other hand, thermally decomposes to Fe_2O_3 and approximately 6X as much HCl as Ca perchlorate but does not release O_2 (equation (3)). The analysis of these Cl salts allows us to better understand the impact that the oxidative volatiles, HCl and O_2 , have on the degradation of the Tenax trap.

Table 2. A Comparison of SAM Flight Model and SAM-Like Laboratory GC-MS Methods^a

Instrument	SAM Flight Model	Laboratory GC-MS
<i>Pyrolysis oven and transfer line</i>		
Initial (°C)	~45–320	50
Final (°C)	~870–960	750
Ramp rate (°C min ^{−1})	35	35
He pressure (mbar)	25	1013
He flow rate (mL min ^{−1})	~0.8 ^b	35
Valve oven (°C)		300
Transfer line (°C)	135	300
<i>Pyrolysis-GC-MS temperature cut</i>		
Initial (°C)	~92–420	50
Final (°C)	~275–960	750
<i>Tenax (cryogenic hydrocarbon) trap–glass beads/Tenax TA/Carbosieve G</i>		
Initial (°C)	5	−10
Final (°C)	300	300
Desorption time (min)	4	5
<i>Injection trap–Tenax GR (70% Tenax TA, 30% graphite)</i>		
Desorption (°C)	300	none
<i>Gas chromatograph (GC)</i>		
Column type	MXT-CLP	Rtx-CLP
He flow rate (mL min ^{−1})	~0.4 ^b	1.5
Split flow (to MS or GC)	~250:1 ^b (MS)	10:1 (GC)
Initial (°C)	~35–50	35
Hold (min)	4	5
Ramp rate (°C min ^{−1})	10	10
Final (°C)	220	300
Final hold (min)	3	8.5
<i>Mass spectrometer (MS)</i>		
Scan range (m/z)	2–535	10–535

^aModified from Glavin *et al.* [2013].

^bValues based on a model of the SAM gas processing system which considered the Martian ambient pressure, the SAM helium pressure regulator setting, the thermal state of the pipes and manifolds, and SAM valve states to compute time-accurate values for pressure and flow rates within the SAM instrument. The uncertainties in the modeled values are approximately ±15%.


2.1. Design of SAM-Like Experiments

In order to simulate the reactions occurring in the SAM Tenax trap that might result in the formation of chlorinated hydrocarbons, we conducted analogue experiments using commercial instruments operated under “SAM-like” conditions. While many aspects of these analogue experiments were similar to the SAM operating conditions, such as pyrolysis and GC temperature programs, Tenax trap materials, and GC column dimensions and composition, other conditions such as pyrolysis pressures and helium flow rates were different (as summarized in Table 2).

Probably the most impactful differences between our analogue experiments and SAM analyses were the temperatures of the valve oven and transfer lines (which are equivalent to the gas processing system (GPS) in SAM), the He pressure and flow rate, and the absence of an injection trap. Due to power restrictions, the GPS on SAM is held at 135°C. However, since we were interested to see all pyrolysis products in our experiments, and a temperature of 135°C might preclude higher molecular weight compounds from

reaching the MS, we held all sample gas lines (valve oven and transfer line) at 300°C. Being able to detect all pyrolysis products affords detection of compounds that might accumulate in the GPS. While not directly seen in the SAM data, these compounds would still be available to react with oxychlorine decomposition products and could therefore be a source of carbon for the generation of chlorinated hydrocarbons. Additionally, a higher gas line temperature in these laboratory experiments may affect the relative abundance of the oxychlorine decomposition products that are introduced onto the Tenax trap after pyrolysis. Perhaps the most significant example of this, as it pertains to our study, is that the reaction of Cl_2 with H_2O shifts more toward the production of HCl and O_2 at higher temperatures [Nanda and Ulrichson, 1988]. This would affect the potential degradation of the Tenax trap materials, as HCl is less reactive than Cl_2 . However, the high abundance of H_2O background in SAM analyses ($\approx 47 \mu\text{mol}$ from CB samples) relative to the calculated maximum Cl_2 produced during the pyrolysis of CB samples ($7.2 \mu\text{mol}$) suggests that all available Cl_2 likely reacts with an excess of H_2O to form HCl prior to reaching the Tenax trap [Freissinet *et al.*, 2015]. This greatly diminishes the impact that differences between our gas line temperature and the SAM GPS temperature has on the degradation of the Tenax trap. Lastly, keeping the gas lines at 300°C in our experiments limits carryover between sample runs; this is particularly important since we conduct many more experiments in the laboratory compared to SAM on Mars.

Another important difference between these analogue experiments and the SAM analyses is the He pressure and flow rate. Helium pressure during SAM pyrolysis is ~ 25 mbar (close to Mars atmospheric pressure), whereas He pressure for the analogue experiments was 1013 mbar (Earth atmospheric pressure). Due to the differences in pressure, the rate of chemical reactions occurring in SAM should be slower than the rate of reactions occurring during pyrolysis in the laboratory experiments. However, it is not evident that the kinetics of these reactions would markedly alter the relative abundances and distribution of the pyrolysis products.

He flow rate, on the other hand, which is $\sim 0.8 \text{ mL min}^{-1}$ in SAM and $\sim 35 \text{ mL min}^{-1}$ in our experiments, has a significant impact on the amount of time corrosive gases could be in contact with organics. The slower He flow rate on SAM means that volatiles released during pyrolysis would take longer to reach the Tenax trap, thereby allowing more time for reactions to occur in the pyrolysis oven and GPS. Nanda and Ulrichson [1988] also found that increasing the flow rate of H_2O results in a corresponding increase in the rate of reaction between Cl_2 and H_2O to form HCl . Therefore, Cl_2 may remain in the pyrolysis oven and GPS for a longer period of time, before being converted to HCl , than in our experiments. Additionally, volatiles adsorbed on the Tenax trap would have more time to interact with trap materials during the 4 min desorption time when the Tenax trap is heated to 300°C to release the volatiles. However, it is unclear how or if differences in He flow rate would affect the relative abundance of these products.

Lastly, on SAM, volatiles released from the Tenax trap are collected on an injection trap composed of Tenax GR (a mixture of Tenax TA and 30% graphite) and flash heated to $\sim 350^\circ\text{C}$ prior to GC-MS analyses [Mahaffy *et al.*, 2012]. This differs from our analogue experiments in that volatiles desorbed from the SAM-like Tenax trap are carried directly to the GC column prior to GC-MS analysis.

2.1.1. Sample Preparation

A simple Mars analogue soil was created for this study by spiking olivine sand with aqueous solutions of calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$; Sigma-Aldrich, 99% purity), magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$; Sigma-Aldrich, 99% purity), or ferric chloride (FeCl_3 ; Sigma-Aldrich, 97% purity). The olivine sand, acquired from the NASA Goddard Space Flight Center (GSFC), was acid washed in 6 N HCl to remove plasticizers and neutralized with H_2O before being powdered in a stainless steel mill with a ceramic puck. The olivine powder was then sieved to $125 \mu\text{m}$, approximately the same grain size as the powder delivered to SAM ($< 150 \mu\text{m}$). It was then fired at 550°C for 5 h to remove any remaining organics. Approximately 5 mg of the prepared olivine sand was added to a CDS quartz sample tube packed with a quartz filler rod and a plug of quartz wool. The sample tubes and filler rods were cleaned by sequential sonication in dichloromethane, methanol, and hexane followed by firing at 850°C for 10 h. The quartz wool was fired at 450°C for 10 h prior to use. The olivine-containing sample tubes were then individually spiked with $5 \mu\text{L}$ of a 0.1%, 1%, or 10% chlorine salt solution (5, 50, and $500 \mu\text{g}$ chlorine salt per sample, respectively) and allowed to dry in a fume hood overnight. Once dry, the samples were loaded into a pyroprobe autosampler for pyrolysis followed by GC-MS analysis; each sample was bracketed by two blanks consisting of CDS quartz tubes packed with a filler rod and quartz wool plug.

2.1.2. Analytical Methods

Laboratory pyrolysis experiments were performed using a CDS Analytical 5250 T pyroprobe equipped with a liquid N₂-cooled cryogenic Tenax trap. For SAM-like sample analyses, the pyrolysis chamber was programmed to hold at 50°C for 40 s and then heat to 750°C at 35°C min⁻¹, where it was then held for 40 s under a constant He flow rate of 35 mL min⁻¹ at 1013 mbar. The final pyrolysis temperature, 750°C, is lower than the pyrolysis temperatures attained in SAM experiments (~870–960°C [Freissinet *et al.*, 2015]), but the Cl salts should completely decompose by this temperature [Acheson and Jacobs, 1970; Devlin and Herley, 1986; Bruck *et al.*, 2014]. The evolved volatiles were concentrated on a 0.635 cm stainless steel Tenax trap consisting of an equal volume of glass beads, Tenax TA, and Carbosieve G, the same composition as the Tenax trap on SAM. The trap was held at -10°C under ~35 mL min⁻¹ He flow during pyrolysis, after which the products were desorbed by heating to 300°C for 5 min under reversed He flow. The desorbed volatiles were then carried in the He stream to the GC-MS for separation and detection.

Direct-pyrolysis-GC-MS experiments, where the Tenax trap was bypassed, were also conducted. The pyrolysis chamber for these experiments was programmed to hold at 50°C for 40 s and then heated to 750°C at 100°C min⁻¹, and the resulting products carried in a stream of He (~35 mL min⁻¹) directly to the GC. The pyroprobe valve oven and transfer line were held at 300°C throughout all analyses.

GC-MS analysis of the volatiles released during pyrolysis was conducted using an Agilent 6890 N GC coupled to a Micromass Autospec-Ultima MS. The GC was equipped with a Restek Rtx-CLP column (length 30 m, internal diameter 0.25 mm, and film thickness 0.25 μm), equivalent to the GC-5 (channel 5) used on SAM, and was operated in split mode with a 10:1 split and 1.5 mL min⁻¹ He flow rate. The GC oven was held at 35°C for 2 min and then heated to 300°C at 10°C min⁻¹ where it was held for 8.5 min. The MS was operated in electron impact mode at 70 eV and ions scanned over a range of *m/z* 10–535 or 49–535, depending on the experiment. Changes in CO₂ (*m/z* 44 and 45), O₂ (*m/z* 34 and 32), HCl (*m/z* 36 and 38), and Cl₂ (*m/z* 70, 72, and 74) were monitored, as were extracted ions for chloromethanes (*m/z* 49, 50, 83, and 117), chlorinated alkanes (*m/z* 55), chlorobenzenes (*m/z* 112, 114, 146, 180, 216, 250, and 284), phthalic anhydride (*m/z* 148), and benzoic acid (*m/z* 122).

In evaluating the abundances of products in our experiments, we assumed no change in the sensitivity of the mass spectrometer during each experiment. For example, all of the Ca perchlorate, Mg perchlorate, and Fe chloride samples were analyzed within a 24 h time period, during which mass spectrometer tuning showed no changes in analytical sensitivity. A direct comparison of product abundances between these experiments and Ca perchlorate pyrolysis experiments conducted with and without the Tenax trap, however, is more complex, as these experiments were conducted at different times and therefore may be prone to slight instrumental drift.

2.2. Solvent Extraction of Chlorine Salts

In order to exclude the possibility that organic contaminants in our reagents (particularly from plasticizers) were affecting our results, we tested solvent extracts of each of the salts used in the experiments. We dissolved 1 g of each salt in 2 mL of solvent-washed water and extracted this solution in 1 mL dichloromethane at room temperature, along with a water rinse blank. We evaporated the extracts to dryness under a stream of pure N₂ and redissolved them in 100 μL pentane. Adding 500 ng pregnane diacetate (Sigma-Aldrich, 99% purity) as an internal standard and 500 ng aiC₂₂ (Ultra Scientific, 99% purity) as an injection standard, we then analyzed these samples by GC-MS on the instrumentation described above, using an Agilent DB-5MS column (60 m × 0.25 mm × 0.25 μm) on the GC with the mass spectrometer scanning all ions from *m/z* 49–535.

3. Results

3.1. SAM-Like Experiments

3.1.1. Ca Perchlorate, Mg Perchlorate, and Fe Chloride Experiments

While no Cl₂, chloromethanes, or other chlorinated alkanes were detected in any of the pyrolysis-GC-MS experiments, CO₂, O₂, HCl, benzene, toluene, benzoic acid, phthalic anhydride, unidentified high molecular weight aromatic compounds (referred to as A1 and A2), and chlorobenzenes ranging from chlorobenzene to hexachlorobenzene were identified (Figure 2). For each Cl salt analyzed, the number and concentration of chlorobenzenes increased with increasing Cl salt concentration. Additionally, with the exception of benzene and

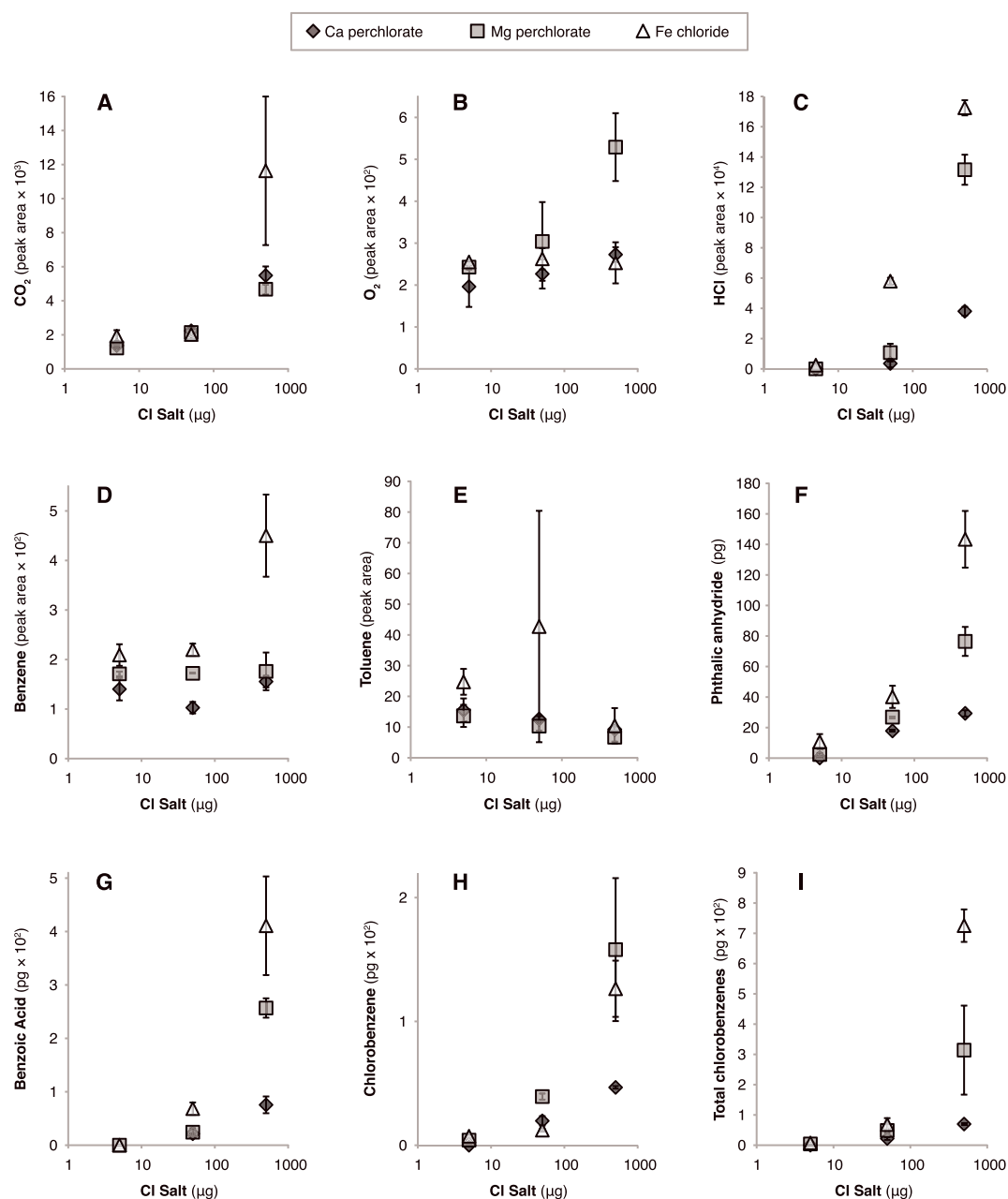


Figure 2. Compounds detected in SAM-like pyrolysis-GC-MS experiments with three different concentrations of three different Cl salts on olivine sand: (a) carbon dioxide, (b) diatomic oxygen, (c) hydrogen chloride, (d) benzene, (e) toluene, (f) phthalic anhydride, (g) benzoic acid, (h) chlorobenzene, and (i) the sum of all chlorobenzenes (i.e., chlorobenzene and dichlorobenzene, through hexachlorobenzene). The error bars indicate the standard error of three replicates (1σ).

toluene, the abundance of each compound increased with increasing Cl salt concentration, while the amount of each compound detected varied with the species of Cl salt analyzed. For example, the abundance of CO₂, HCl, benzoic acid, phthalic anhydride, and total chlorobenzenes were the highest in the Fe chloride experiments and the lowest in the Ca-perchlorate experiments (Figure 2). Oxygen, chlorobenzene, and the high molecular weight aromatics (Figure 3), on the other hand, were most abundant in the Mg-perchlorate experiments.

3.1.2. Trap Versus No Trap Experiments

In order to differentiate between organic compounds originating in the Tenax trap and those originating from other instrumental sources or sample impurities, we conducted several pyrolysis-GC-MS experiments

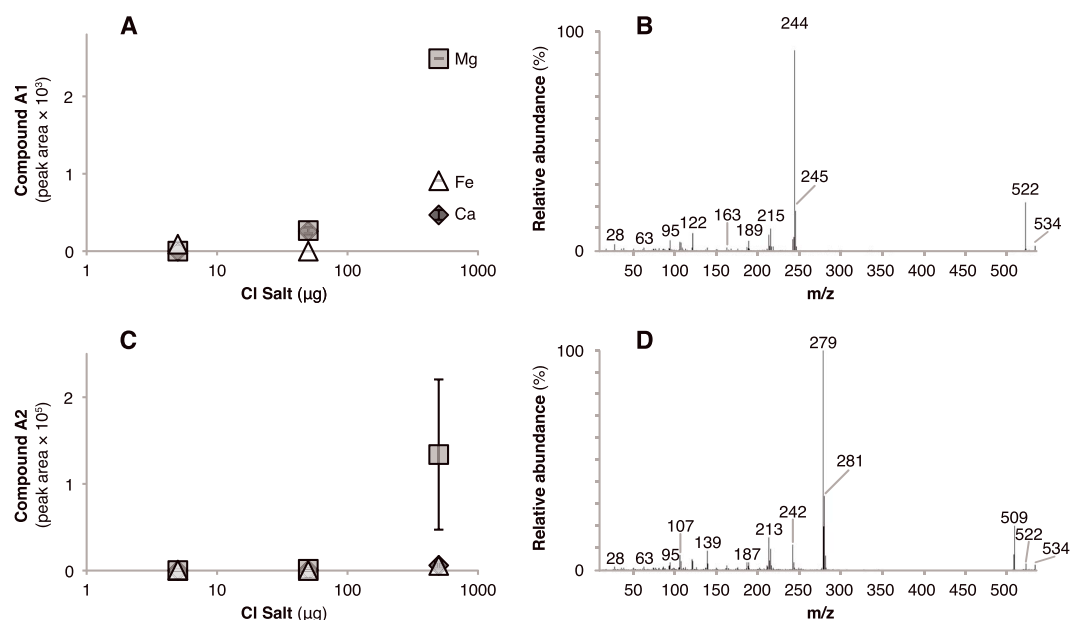


Figure 3. High molecular weight aromatic compounds detected in SAM-like pyrolysis-GC-MS experiments with three different concentrations of three different Cl salts on olivine sand. (a and b) The compounds are identified by their mass spectra and (c and d) increase with increasing Cl salt concentration. The symbols are the same as in Figure 2. The error bars indicate the standard error of three replicates (1σ).

that bypassed the Tenax trap. Quartz wool blanks, olivine sand blanks, and 1 wt % Ca perchlorate (50 μ g) on olivine sand were pyrolyzed with and without the Tenax trap. In this case, the mass spectrometer was programmed to scan ions m/z 49–535 in order to improve the measurement precision that was otherwise compromised by the high abundance of low molecular weight gases, primarily H_2O , CO_2 , and HCl . The pyrolysis and GC temperature programs were, however, the same as in the Cl salt experiments employing the trap. Benzene, toluene, chlorobenzene, benzoic acid, phthalic anhydride, and the high molecular weight aromatics (A1 and A2) identified in the Cl salt experiments were monitored (Figure 4). Again, all compound abundances were greater with the trap than without the trap. Benzene and toluene, however, showed no significant variation between samples. One of the unidentified high molecular weight aromatic compounds (A1) was present in the quartz wool and olivine blanks as well as the Ca perchlorate samples but only when the Tenax trap was employed. The other unidentified high molecular weight aromatic compound (A2) was present in the Ca perchlorate samples but also only when the Tenax trap was used. Chlorobenzene and phthalic anhydride, on the other hand, were present in the Ca perchlorate samples, both with and without the Tenax trap, but absent in the quartz wool blanks. However, the Ca perchlorate experiments with the trap produced 5 times more chlorobenzene and 8 times more phthalic anhydride than the experiments without the Tenax trap. A trace amount of chlorobenzene was also observed in the olivine blank when the Tenax trap was employed.

3.2. Additional Experiments

3.2.1. Cl Salt Extracts

Conventional GC-MS analyses of solvent extracts of the Cl salts used in these experiments revealed that the Ca and Mg perchlorates did not contain organic compounds above the 5 pmol detection limit. No phthalic acid, benzoic acid, chlorobenzene, dichlorobenzene, trichlorobenzene, or tetrachlorobenzene were detected in the ferric chloride extract, either; however, traces of pentachlorobenzene and hexachlorobenzene were detected, as were the higher molecular weight chlorinated aromatics trichloroethenyl-pentachlorobenzene and decachlorobiphenyl. While these impurities ought to be kept in mind when interpreting the ferric chloride results, it is important to note that we used between 3 and 5 orders of magnitude more Cl salt in the solvent extractions as compared to the pyrolysis experiments, and we are confident that contamination would not have affected our results.

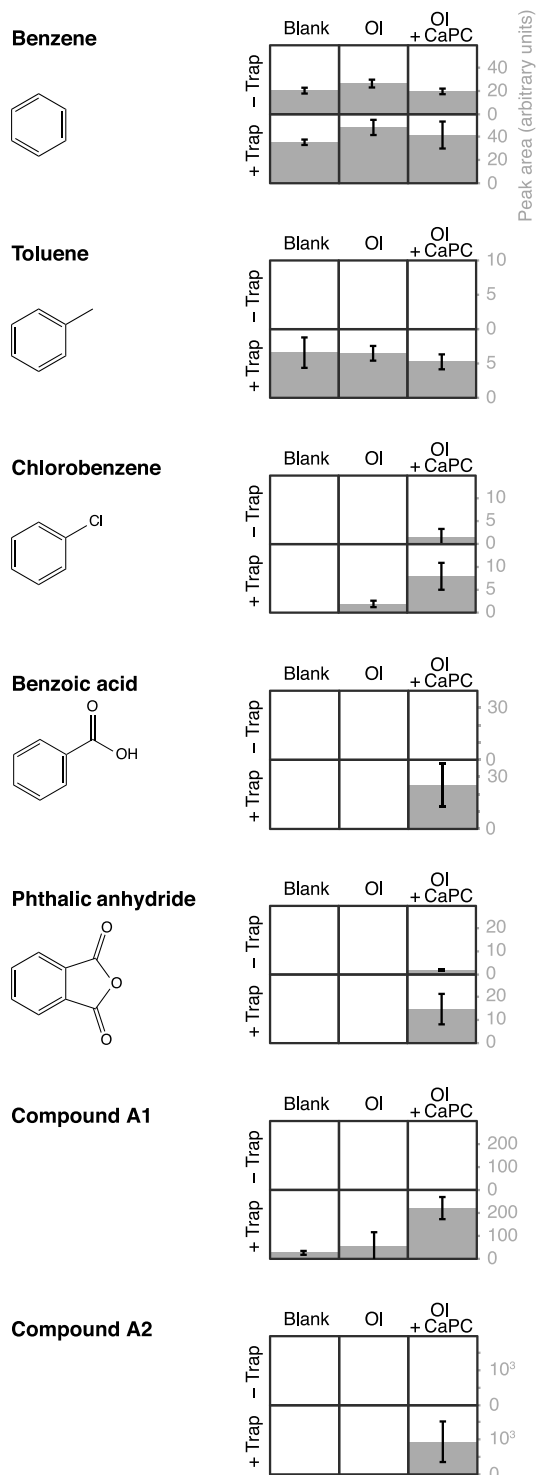


Figure 4. Trap/no-trap experiments, m/z scan range 49–535. For each compound, the abundance detected in six experiments are shown: (top row) experiments carried out bypassing the Tenax trap (“–Trap”), (bottom row) experiments carried out with the Tenax trap (“+Trap”), (left column) experiments with a quartz wool blank only (“Blank”), (middle column) experiments with olivine sand on quartz wool only (“OI”), and (right column) experiments with 50 μg calcium perchlorate on olivine sand and quartz wool (“OI + CaPC”). The six abundances for each compound are plotted to the same scale of peak area in arbitrary units. The error bars indicate the standard error of three replicates (1σ).

4. Discussion

Understanding how the Tenax trap reacts to potentially corrosive volatiles released during the pyrolysis of various Cl salts is essential to evaluate the sources of organics observed in the SAM data. Several compounds, including benzene, toluene, and at least some of the chlorobenzene observed in the SAM pyrolysis-GC-MS data from scoop and drill samples collected in Gale Crater, are thought to derive from the Tenax trap [Glavin *et al.*, 2013; Leshin *et al.*, 2013; Ming *et al.*, 2013; Freissinet *et al.*, 2015]. However, Freissinet *et al.* [2015] make a compelling argument for the presence of Martian organics based on the dichlorinated alkanes and the order-of-magnitude increase in chlorobenzene observed in the Cumberland drill fines compared to the Rocknest scoop fines, procedural blanks, and a subsequent analysis of a drill sample analyzed at Confidence Hills. The results presented here shed more light on how the composition and concentration of oxychlorine minerals in Martian surface materials may affect the composition and relative abundance of organic compounds observed in the SAM data.

4.1. Generation of Corrosive Volatiles (Cl_2 , HCl, and O_2)

Thermal decomposition of the Cl salts included in this study produces several reactive volatiles, mainly Cl_2 , HCl, and O_2 (equations (1)–(3)). While the thermal decomposition of Ca and Mg perchlorates do not directly generate HCl, the detection of increasing amounts of HCl with increasing perchlorate concentration confirms our hypothesis that secondary reactions between the evolved Cl species and H_2O occur to produce HCl. The relative amount of HCl generated by each Cl salt is also in keeping with what we expected; Fe chloride produced the greatest amount of HCl, followed by Mg perchlorate and then Ca perchlorate.

The relative amount of O_2 generated by each Cl salt, however, was not what we expected (Figure 2). Based on the stoichiometry of equations (1) and (2), we expected the O_2 generated from Ca and Mg perchlorates to be roughly equivalent and to increase with increasing perchlorate concentration. The O_2 detected in Fe chloride experiments, on the other hand, should only be O_2 from instrument background and should not increase with increasing Fe chloride concentration. However, the O_2 produced from Mg perchlorate significantly increases with increasing Mg perchlorate concentration, whereas the O_2 from the Ca perchlorate increases only slightly and remains within error of the O_2 detected in the Fe chloride experiments. One possible explanation for this observation is that much of the O_2 generated during the thermal decomposition of the Ca and Mg perchlorates is consumed, possibly through combustion of trace organics in the pyrolysis chamber, gas lines, or Tenax trap. The O_2 detected in the Mg perchlorate experiments possibly reflects secondary generation of O_2 through the reaction of thermally derived Cl_2 with H_2O . Based on our current data we cannot determine if this secondary generation of O_2 occurs prior to material reaching the Tenax trap. However, given the excess of H_2O in our experiments, which is derived from the hygroscopic nature of the samples as well as instrumental background, it is likely that all of the Cl_2 generated from the Mg perchlorate reacted with H_2O to form HCl and O_2 prior to reaching the Tenax trap.

4.2. Sources of Background Organic Compounds

The SAM-like pyrolysis-GC-MS experiments of three Cl salts (Ca perchlorate, Mg perchlorate, and Fe chloride) produced a variety of organic compounds. No organics were added to the samples prior to analysis; therefore, the resulting organics must either be contaminants in the sample materials themselves (e.g., the Cl salts, olivine sand, or quartz wool) or they must originate from within our analytical system (e.g., the Tenax trap, valves, or stainless steel tubing). SAM-like pyrolysis-GC-MS analyses of the sample tube materials (sample tube, filler rod, quartz wool, and olivine sand) did not produce any organic compounds above background levels. Benzene and toluene were identified whenever the Tenax trap was employed, and when the Tenax trap was bypassed, the abundances of these aromatic compounds dropped significantly (Figure 4). Furthermore, unlike the other organic compounds identified in the Cl salt experiments, benzene and toluene did not increase as the concentrations of Ca and Mg perchlorates were increased (Figure 2). Therefore, these compounds likely originate from the trap but are not affected by the volatiles produced during the pyrolysis of perchlorates.

Similarly, the unidentified high molecular weight aromatics (compounds A1 and A2) were only observed when the Tenax trap was used, indicating that they originate from the Tenax trap itself (Figure 4). However, unlike benzene and toluene, these compound abundances increased with increasing Cl salt concentration with the highest amount produced in the Mg perchlorate experiments (Figure 3). The

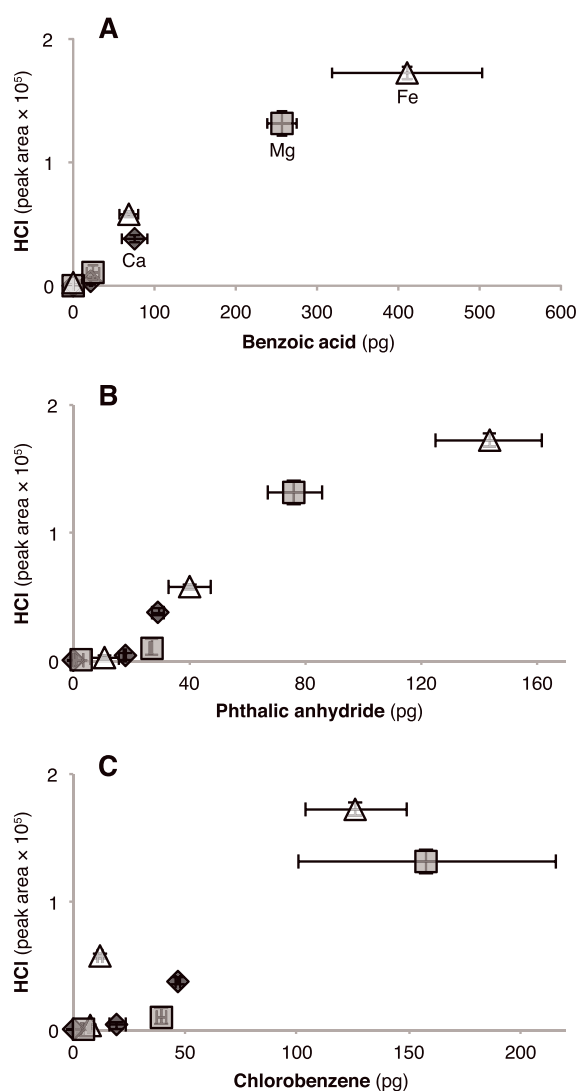


Figure 5. Crossplots of (a) benzoic acid, (b) phthalic anhydride, and (c) chlorobenzene against hydrogen chloride abundances detected in various Cl salt experiments on olivine sand. The symbols are the same as in Figure 2 (Fe = ferric iron chloride, Mg = magnesium perchlorate, and Ca = calcium perchlorate). The error bars indicate the standard error of three replicates (1σ).

predominance of the high molecular weight aromatics from the Mg perchlorate may correspond to the high O_2 release from this Cl salt. Therefore, while these high molecular weight aromatic compounds are produced with each use of the Tenax trap, their abundance appears to be enhanced by the corrosive volatiles released during the pyrolysis of oxychlorine minerals.

Additionally, the SAM-like pyrolysis of the Cl salts with and without the Tenax trap produced trace amounts of phthalic anhydride and chlorobenzene. Solvent extracts of the Cl salts, which were analyzed via conventional GC-MS analysis, show that these compounds are not contaminants within the Cl salts themselves. Therefore, the trace amounts of phthalic anhydride and chlorobenzene observed when the Tenax trap is bypassed must come from reactions between Cl salt decomposition products with other background components within our pyroprobe system. A likely explanation is that there was a buildup of organic residues from previous analyses that only becomes evident when a corrosive volatile, such as HCl, is passed through the system. Despite this anomaly, the relative abundances of phthalic anhydride and chlorobenzene are significantly higher when the Tenax trap is employed than when it is bypassed, indicating that these compounds are primarily derived from reactions between Cl salt pyrolysis products and the Tenax trap components.

Based on our experiments, the primary compounds formed from the interaction of Tenax trap materials and Cl salt degradation products are benzoic acid, phthalic anhydride, high molecular weight aromatics, and chlorobenzenes. The benzoic acid, phthalic anhydride, and high molecular weight aromatics likely form in traces via degradation of the Tenax TA polymer in the trap. These compounds are readily rationalized as oxidation products of the poly (2,6-diphenylphenylene oxide) adsorbent material. The chlorobenzenes could either form from the thermal decomposition of the Tenax TA polymer and subsequent chlorination of the products or indirectly through chlorination of the benzoic acid or, possibly, phthalic anhydride [Miller *et al.*, 2013; K. E. Miller *et al.*, Possible precursor compounds for chlorohydrocarbons detected in SAM, manuscript in preparation] formed from oxidation of Tenax TA. An important observation stemming from these experiments is that the abundance of Tenax TA degradation products are directly related to the amount of Cl produced from the decomposing salt, as indicated by the crossplots of HCl abundance versus product abundance where HCl is a proxy for the amount of Cl produced by the sample (Figure 5). Therefore, it is possible that changes in the concentration of oxychlorine phases, or a variation in the oxychlorine species in a sample analyzed by SAM, could alter the amount of HCl entering the Tenax trap, thereby resulting in changes

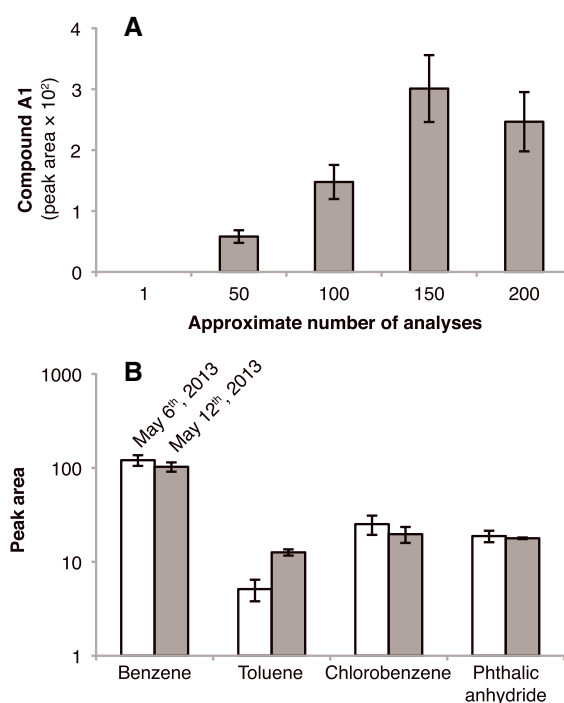


Figure 6. (a) The average abundance, in arbitrary units, of a high molecular weight aromatic compound, compound A1, in three quartz wool blanks from every ~50 analyses and (b) abundances of benzene, toluene, chlorobenzene, and phthalic anhydride, in arbitrary units, detected in repeated analyses of Ca perchlorate (50 μ g) separated by more than 80 analyses of various concentrations of Cl salts. The error bars indicate the standard error of three replicates (1σ).

likely to be seen in SAM data due to their long retention time (~24 to 26 min) under the typical experimental conditions, the lower He flow, and the lower final GC column temperature used in SAM GC-MS analyses (Table 2). The abundances of these compounds gradually increased in our experiments over the lifetime of the Tenax trap, as seen in Figure 6a, which displays the average abundance of compound A1 from quartz wool blanks from every ~50 analyses. A possible explanation is that these compounds are accumulating in the system, perhaps within the trap. After ~150 analyses, however, the average abundance of the aromatic compound A1 stabilizes, possibly indicating a natural limit to Tenax trap degradation. The abundances of benzene and toluene, however, did not increase through the duration of our experiments, which involved more than 200 analyses. Additionally, repeated analyses of Ca perchlorate (50 μ g) separated by more than 80 analyses of various concentrations of Cl salts displayed no significant difference in the abundances of benzene, toluene, chlorobenzene, and phthalic anhydride (Figure 6b). This indicates that the Tenax trap in SAM is relatively stable in the face of repeated exposure to the corrosive pyrolysis products of chloride and oxychlorine salts. Furthermore, the stability of chlorobenzene abundance in the face of increasing high molecular weight aromatics with time and trap use indicates that these high molecular weight aromatics are not involved in the formation of chlorobenzene.

In addition, we observed a strong correlation between the amount of hydrochloric acid produced through the pyrolysis of these salts and the abundances of chlorobenzene, benzoic acid, and phthalic anhydride in the laboratory experiments (Figure 5). Thus, the magnitude of the chlorobenzene signal observed in pyrolysis products of the Cumberland mudstone samples, compared to other samples analyzed so far, cannot be attributed to the Tenax trap. This is because results from SAM do not follow the same trends that are observed in our experiments. In addition, ions corresponding to chlorobenzene (m/z 112 and 114) were detected in the SAM evolved gas analysis (EGA) mode that directly monitors gases released by the Cumberland sample during pyrolysis; this chlorobenzene cannot be attributed to reaction products from the SAM Tenax trap [Freissinet *et al.*, 2015]. Moreover, if the chlorobenzene released from the Cumberland

in the abundances of chlorobenzenes, benzoic acid, and phthalic anhydride. However, we also note that the temperature range over which volatiles were collected on the Tenax trap in SAM experiments varied between experiments [see Freissinet *et al.*, 2015]. SAM experimental conditions were adjusted during the mission to address a number of different questions, and therefore, we do not expect that the concentration or type of oxychlorine species in the sample would always reflect the amount of HCl and other volatiles actually sent to the trap.

4.3. Implications for the Interpretation of SAM Results

The analogue experiments reported here yield a number of observations that are significant for the interpretation of data acquired by the SAM instrument on Curiosity during landed operations. First, traces of benzene and toluene are always observed as products when using the Tenax trap. High molecular weight aromatics are also present whenever the trap is used, but these compounds are not

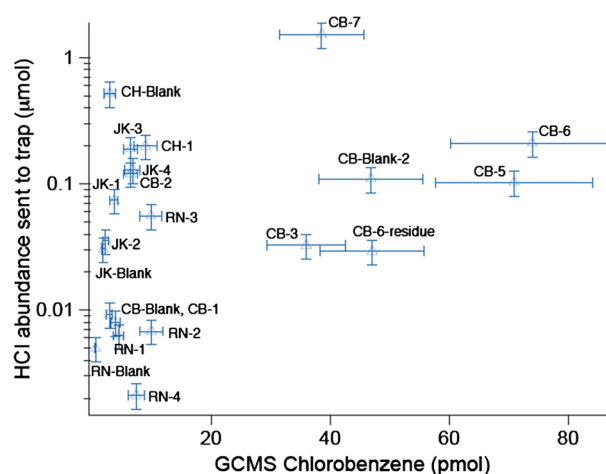


Figure 7. HCl sent to the Tenax trap versus chlorobenzene [Freissinet *et al.*, 2015].

samples during pyrolysis was the result of a shift in the concentration or composition of oxychlorine salts in these samples, a corresponding increase in the yield of HCl would be expected. However, there was no correlation between the amounts of chlorobenzene detected by GC-MS and the amounts of HCl sent to the Tenax trap in the Cumberland analyses (Figure 7) [Freissinet *et al.*, 2015].

A third, and not insignificant, observation that can be drawn from these analog experiments is that we only observed aromatic compounds in the pyrolysates, which are consistent with the chemical structure of the Tenax TA polymer. Dichloroethane, dichloropropane, and dichlorobutane were not detected in our experiments. Thus, the dichlorinated aliphatic molecules detected by SAM in the Cumberland mudstone could not be products of the Tenax trap on board SAM and likely require an additional carbon source.

5. Conclusions

The Tenax trap, a vital component of the SAM pyrolysis-GC-MS system operating on Mars, is a possible source of low levels of chlorobenzene observed in the Rocknest analyses as previously suggested by Glavin *et al.* [2013]. However, it cannot account for the order-of-magnitude increase in chlorobenzene observed in the Cumberland samples in both EGA and GC-MS modes. Based on our laboratory experiments, benzoic acid, phthalic anhydride, high molecular weight aromatics, and chlorobenzene are produced from the trap in response to volatiles released during the pyrolysis of various Cl salts. It is therefore possible that an increase in the concentration of oxychlorine salts could produce an increase in the chlorobenzene observed on Mars by GC-MS. However, in our experiments, the benzoic acid, phthalic anhydride, and chlorobenzenes produced increase in proportion to the amount of HCl sent to the Tenax trap. This is in contrast to the increase in chlorobenzene observed in the Cumberland samples, which was not accompanied by a corresponding increase in HCl.

Additionally, we found no evidence of significant trap degradation after conducting hundreds of laboratory experiments using Mars analogue soils with added Cl salts. While the high molecular weight aromatics, which are degradation products of the Tenax TA, did increase gradually with trap use, the other trap-related compounds remained stable. SAM results also suggest very little degradation after repeated exposures to volatiles released from samples collected at Rocknest, Yellowknife Bay, Windjana, and Confidence Hills [Freissinet *et al.*, 2015].

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