ORIGIN OF CHLOROBENZENE DETECTED BY THE CURIOSITY ROVER IN YELLOWKNIFE BAY: EVIDENCE FOR MARTIAN ORGANICS IN THE SHEEPBED MUDSTONE?

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Introduction: The Sample Analysis at Mars (SAM) instrument on the Curiosity rover is designed to determine the inventory of organic and inorganic volatiles thermally evolved from solid samples using a combination of evolved gas analysis (EGA), gas chromatography mass spectrometry (GCMS), and tunable laser spectroscopy [1]. The first solid samples analyzed by SAM, a scoop of windblown dust and sand at Rocknest (RN), revealed chlorinated hydrocarbons derived primarily from reactions between a martian oxychlorine phase (e.g. perchlorate) and terrestrial carbon from *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) vapor present in the SAM instrument background [2]. Chlorobenzene (CBZ) was also identified by SAM GCMS at RN at trace levels (~0.007 nmol) and was attributed to the reaction of chlorine with the Tenax polymers used in the hydrocarbon traps [2]. After the RN analyses, Curiosity traveled to Yellowknife Bay and drilled two separate holes designated John Klein (JK) and Cumberland (CB). Analyses of JK and CB by both SAM and the CheMin x-ray diffraction instrument revealed a mudstone consisting of ~20 wt% smectite clays [3,4], which on Earth are known to aid the concentration and preservation of organic matter. In addition, higher abundances and a more diverse suite of chlorinated hydrocarbons in CB compared to RN suggests that martian or meteoritic organic sources may be preserved in the mudstone [3].

Here we discuss the SAM EGA and GCMS measurements of volatiles released from the Sheepbed mudstone. We focus primarily on the elevated CBZ detections at CB and laboratory analog experiments conducted to help determine if CBZ is derived from primarily terrestrial, martian, or a combination of sources.

Sample Processing and SAM Protocol: The JK and CB drilled samples collected by Curiosity's solid sample acquisition and handling system called CHIMRA was sieved to <150 μm, portioned (<76 mm³), and single or triple portion aliquots were delivered to individual SAM cups. Prior to and following the analyses of the mudstone, a procedural blank run using an empty quartz cup was carried out to character-ize the background of the SAM instrument. The cup and sample were sealed inside the pyrolysis oven and heated to ~850°C at a rate of 35°C/min under He carrier gas flow (~25 mbar, 0.8 sccm). For some runs, a sample preheating was employed prior to pyrolysis to reduce the MTBSTFA background. A small fraction of the gas released from the cup (~1:800 split) was measured by direct EGA. The larger fraction of evolved gas was directed to a cooled (~5°C) hydrocarbon trap (Silica beads/Tenax TA/Carbosieve G) over a specified oven temperature range (i.e., the GC cut). The trap was subsequently heated to a temperature of ~300°C for 4 min under He flow and the volatiles released were sent to the Tenax GR injection trap on the GC column (MXT-CLP, 30 m length, 0.25 mm I.D.). Trapped compounds were separated on the GC column set at an initial temperature of 30°C followed by ramp heating to 190°C at 10°C/min. Eluting compounds, including CBZ, were detected by the QMS and identified by their relative retention time compared to standards and mass spectrum compared to NIST spectra. The methods used for determining compound abundances are described in detail elsewhere [2,3].

Results: CBZ was identified at RN, JK, and CB (Fig. 1, right; Table 1). Trace levels (0.003 to 0.007 nmol) of CBZ were measured in different GC cuts of the RN1, JK3, CB blank 1, CB1 and CB2 runs (Table 1). These trace CBZ detections are likely the result of reactions between HCl, O_2, and the Tenax polymers used in the traps (Table 1). The low CBZ levels in the JK3 triple portion analysis may be a result of CBZ loss from the sample during the ~20 min boil-off to ~323°C and venting of the evolved gases prior to the GC cut. Order of magnitude higher CBZ levels (~0.04 to 0.07 nmol or ~90 to 180 parts-per-billion assuming a 45 mg single portion sample mass) were measured in the 229-350°C GC cuts of CB3, CB5, and CB6 runs (Table 1). The CB6 triple portion run had ~2 to 3 times more CBZ than the CB3 and CB5 single portion runs (based on the EGA-corrected values in Table 1). In the CB5 EGA, several masses not attributed to residual MTBSTFA products were detected in the ~200-350°C

range (Fig. 1, left), including *m/z* 112 and 114 peaks at a 3:1 ratio that can be attributed to CBZ. In comparison, only a weak signal for *m/z* 112 was observed in the 200-350°C range in the RN and blank EGA runs.
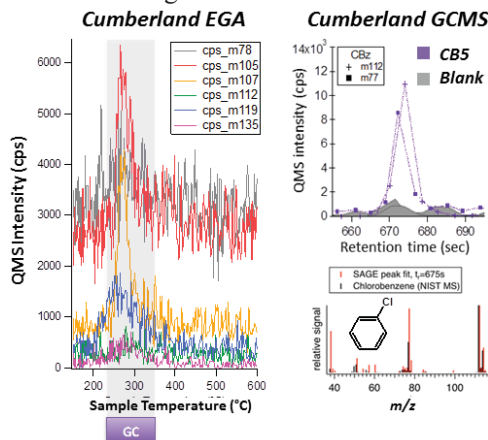

Figure 1. LEFT: SAM EGA analysis showing masses corresponding to possible martian hydrocarbon fragments released from CB5 as a function of sample temperature and the temperature cut indicated by the purple bar sent to the GC. **RIGHT:** CBZ was identified by both retention time and comparison of the mass spectrum to the NIST library and was present well above CB blank levels.

Origin(s) of Chlorobenzene: There are four possible explanations for the presence of CBZ detected by SAM in the CB3-6 runs that were considered: (1) reaction of martian oxidants (e.g. Cl and O_2 from oxychlorine compounds, NO, etc. [3]) with the Tenax polymers during hydrocarbon trap heatings, (2) reaction of martian oxidants with known terrestrial organics in SAM (e.g. MTBSTFA) during pyrolysis, (3) reaction of martian oxidants with martian organics during pyrolysis, and (4) thermal desorption of CBZ directly from the samples. Since CBZ was not identified above the 0.001 nmol level in the first SAM GCMS blank run at RN (Table 1), CBZ itself is not a significant contaminant in the SAM instrument. Based on lab pyrolysis experiments using a SAM-like hydrocarbon trap exposed to O_2 and HCl released from Ca- and Mg-perchlorates, small amounts of CBZ can be produced from Tenax TA [2]. This reaction probably accounts for the low levels of CBZ observed at RN and in blanks. So far, we have no evidence from SAM or laboratory analog experiments that CBZ is formed from MTBSTFA and DMF when heated in the presence of Ca- and Mg-perchlorates. Three observations point toward a *possible* martian organic contribution to the CBZ detected at CB. (1) Elevated abundances of CBZ were detected in the <350°C GC cut CB single and triple portion runs. (2) EGA data shows masses, possibly aromatic in nature, that are not attributed to MTBSTFA products and may be reactants in CBZ formation, and (3) lab studies demonstrate that CBZ formation by reactions between Tenax TA and per-

chlorate volatiles does not increase as a function of time or overall trap degradation (Table 1). Research continues to understand the effects of HCl, O_2, and other potential oxidants on Tenax degradation and CBZ production. Lab experiments conducted under SAM-like conditions have shown that benzenecarboxylic acids, such as benzoic acid, phthalic acid, and mellitic acid will produce chlorobenzenes when heated in the presence of perchlorates [5,6]. It is also possible that magnetite present in CB [4] catalyzed CBZ formation during pyrolysis from reactions between aromatics, HCl, and water vapor. Benzene-carboxylates derived from the UV-induced oxidation of meteoritic or martian aromatic hydrocarbons could contribute up to 500 parts-per-million organic carbon in the martian surface regolith [7,8]. Although the origin of CBZ and its molecular precursor(s) remain unclear, metastable oxidized aromatic hydrocarbons of martian or meteoritic origins are good candidate precursors for CBZ detected in the Sheepbed mudstone.

Table 1. Comparison of the chlorobenzene (CBZ) abundances determined by GC, EGA-corrected CBZ abundances, and amounts of O_2 and HCl in the GC-cuts for selected SAM sample analyses.

Sample	GC Cut	CBZ (nmol)	O_2 (nmol)[b]	HCl (nmol)[b]
RN Blank	146-533°C	< 0.001	ND	4 ± 1
RN1	146-533°C	0.004 ± 0.002	2,970 ± 182	6 ± 1
JK3 (triple)	323-643°C	0.007 ± 0.002	1,300 ± 80	190 ± 42
CB Blank1	445-548°C	0.004 ± 0.001	ND	8 ± 2
CB1	445-548°C	0.003 ± 0.001	10.7 ± 0.7	9 ± 2
CB2	574-797°C	0.007 ± 0.002	8.9 ± 0.5	120 ± 27
CB3	229-350°C	0.036 ± 0.013 (0.14 ± 0.05)[†]	7,250 ± 444	33 ± 7
CB5	229-350°C	0.071 ± 0.026 (0.24 ± 0.09)[†]	8,200 ± 502	103 ± 23
CB6 (triple)	229-350°C	0.074 ± 0.027 (0.50 ± 0.15)[†]	15,200 ± 928	210 ± 47
CB6 (residue)	229-350°C	0.047 ± 0.017	ND	29 ± 7
CB7 (triple)	496-797°C	0.039 ± 0.014	104 ± 6	1,530 ± 342
CB Blank2	496-797°C	0.047 ± 0.017	ND	110 ± 25

[a]SAM cup/sample temperature estimate indicating temperature range where volatiles were collected on the hydrocarbon trap for GCMS analysis. [b]O_2 and HCl abundances are the amounts sent to the hydrocarbon trap based on EGA data. [†]GCMS abundances corrected for the fraction of CBZ sent to the hydrocarbon trap based on the EGA *m/z* 112 signal and GC temperature cut used. ND = not determined due to low signal. CB4 used for a different experiment.

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