

MARTIAN CHLOROBENZENE IDENTIFIED BY CURIOSITY IN YELLOWKNIFE BAY: EVIDENCE FOR THE PRESERVATION OF ORGANICS IN A MUDSTONE ON MARS. D. Glavin¹, C. Freissinet¹, P. Mahaffy¹, K. Miller², J. Eigenbrode¹, R. Summons², M. Martin¹, H. Franz¹, A. Steele³, D. Archer⁴, S. Atreya⁵, W. Brinckerhoff¹, A. Brunner², A. Buch⁶, M. Cabane⁷, P. Coll⁸, P. Conrad¹, D. Des Marais⁹, J. Dworkin¹, A. Fairén^{10,15}, P. François⁸, J. Grotzinger¹¹, S. Kashyap¹², C. Malespin¹, A. McAdam¹, D. Ming¹³, R. Navarro-González¹⁴, A. Pavlov¹, S. Squyres¹⁵, J. Stern¹, D. Sumner¹⁶, B. Sutter⁴, C. Szopa⁷, and the MSL Science Team. ¹NASA GSFC, Greenbelt, MD 20771 (daniel.p.glavin@nasa.gov), ²MIT, Cambridge, MA 02139, ³CIW, Washington, DC 20015, ⁴Jacobs, NASA JSC, Houston TX 77058, ⁵University of Michigan, Ann Arbor, MI 48109, ⁶Ecole Centrale Paris, 92295 Chatenay-Malabry, France, ⁷LATMOS, UPMC, Univ. Versailles Saint-Quentin & CNRS, 75005 Paris, France, ⁸LISA, Univ. Paris-Est Créteil, Univ. Denis Diderot & CNRS, 94000 Créteil, France, ⁹NASA ARC, Moffett Field, CA 94035, ¹⁰Centro de Astrobiología, INTA-CSIC, 28850 Madrid, Spain, ¹¹Caltech, Pasadena, CA 91125, ¹²University of Massachusetts, Amherst MA 01003, ¹³NASA JSC, Houston TX 77058, ¹⁴UNAM, México, D.F. 04510, Mexico, ¹⁵Cornell University, Ithaca, NY 14853, ¹⁶U. C. Davis, CA 95616.

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 sample analyzed by SAM at the Rocknest (RN) aeolian deposit revealed chlorohydrocarbons 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]. No conclusive evidence for martian chlorohydrocarbons in the RN sand was found [2]. After RN, Curiosity traveled to Yellowknife Bay and drilled two holes separated by 2.75 m 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 (called Sheepbed) consisting of ~20 wt% smectite clays [3], which on Earth are known to aid the concentration and preservation of organic matter.

Last year at LPSC we reported elevated abundances of chlorobenzene (CBZ) and a more diverse suite of chlorinated hydrocarbons including dichloroalkanes in CB compared to RN, suggesting that martian or meteoritic organic compounds may be preserved in the mudstone [4]. Here we present SAM data from additional analyses of the CB sample and of Confidence Hills (CH), another drill sample collected at the base of Mt. Sharp. This new SAM data along with supporting laboratory analog experiments indicate that most of the chlorobenzene detected in CB is derived from martian organic matter preserved in the mudstone [5].

Sample Processing: The JK, CB, and CH drilled samples collected by Curiosity's solid sample acquisition and handling system called CHIMRA were sieved to <150 μm and single or triple portion aliquots were delivered to individual SAM cups for EGA and pyrolysis GCMS analysis. Prior to and following the analyses of the samples, multiple blank runs using empty quartz cups were carried out to characterize the back-

ground of the SAM instrument. The SAM experimental details and the methods used for determining the abundances of CBZ are described in detail elsewhere [2]. A separate SAM wet chemistry experiment that was optimized for MTBSTFA vapor derivatization was also carried out to further investigate the nature of the organic matter in CB [6].

Results: With the exception of the first SAM blank run on Mars, CBZ was identified at RN, JK, CB, and CH. Trace levels (3 to 8 pmol) of CBZ were measured in different GC cuts of the RN-1, JK-3, CB Blank-1, CB-1 and CB-2 runs (Table 1). The CBZ detections in these runs were attributed to reactions between HCl, O₂ and the Tenax polymers used in the hydrocarbon traps and constrain the maximum SAM instrument background contribution to CBZ. In contrast, much higher CBZ levels ranging from 90-180 pmol (~150-300 parts-per-billion by weight) were measured by direct EGA and in the EGA-corrected, low temperature GC cuts of CB-3, CB-5, and CB-6 (Table 1).

In the CB-6 triple portion EGA, several high mass fragments not attributed to MTBSTFA reaction products were detected in the ~200-350°C range (Fig. 1), including m/z 112 and 114 at the ~3:1 ratio expected for CBZ. Due to the SAM gas flow design, direct EGA detection of CBZ masses released from CB cannot be the products of reactions on the trap. In addition, a reheat of the CB-6 residue showed no evidence for m/z 112 or 114 in the EGA data (Fig. 1). CBZ was identified by both GC retention time and its mass spectrum in the low temperature gases released from CB. After the CB-6 reheat, the CBZ level measured by GCMS was reduced to ~39 pmol, but remained at an elevated level over the previous CBZ background levels measured at RN. The CBZ levels then returned to the original ~3 to 9 pmol background levels in the CH blank and CH-1 drill sample runs that followed an O₂ combustion experiment of CB. The combustion experiment may have reduced the CBZ background in SAM (Table 1). Therefore, it is possible that carry-over of martian CBZ or CBZ precursors from prior CB runs contributed to the elevated CBZ backgrounds observed

in the CB-6 residue, CB-7 triple portion and CB Blank-2 runs (Table 1). A subsequent derivatization experiment on a triple portion CB sample (CB-9) that had been stored inside SAM released a total of ~160 pmol CBZ after two heatings (Table 1), consistent with the elevated CBZ levels observed previously at CB.

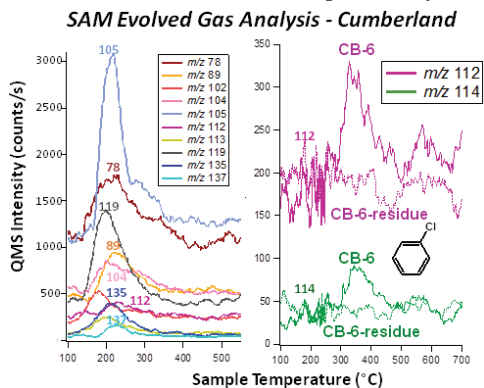


Figure 1. LEFT: SAM EGA showing masses corresponding to possible martian hydrocarbon fragments released from CB-5 as a function of sample temperature. RIGHT: Masses 112 and 114 corresponding to CBZ were released from the CB-6 triple portion during pyrolysis, but not in a second heating of the sample residue.

Origin(s) of Chlorobenzene: Since we observed no correlations between the abundance of MTBSTFA products measured in SAM and the levels of CBZ detected by EGA and GCMS, we focused on the two most probable explanations for the elevated CBZ levels observed at CB: (1) reaction of martian oxidants (e.g. HCl, Cl₂, and O₂ from oxychlorine compounds, NO, and SO₂ released from the sample) with the Tenax polymers during hydrocarbon trap heatings, and (2) reaction of martian oxidants with martian organics during pyrolysis. Based on lab pyrolysis experiments using a SAM-like hydrocarbon trap exposed to O₂ and HCl released from Ca- and Mg-perchlorates, small amounts of CBZ can be produced from Tenax TA [2]. However, lab studies also show that CBZ formation by reactions between Tenax TA and perchlorate volatiles does not increase as a function of time. Nor do we observe overall trap degradation with repeated exposure to perchlorate pyrolysis products [7]. In addition, no correlations between the total amount of HCl, O₂, SO₂, and NO sent to the trap during pyrolysis and the abundance of CBZ measured by GCMS were found.

Since Tenax, MTBSTFA and other instrument background sources can be ruled out as the primary source of the aromatic hydrocarbon fragments detected during EGA analyses of CB (Fig. 1) as well as most of the CBZ identified in the GCMS analyses, we conclude that these organics originate from the mudstone itself, either as martian (hydrothermal, igneous, atmospheric or biological) or exogenous carbon (meteoritic, cometary or from interplanetary dust particles – IDPs). Organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and kerogen-like compounds de-

livered to Mars by meteorites, comets and IDPs may undergo successive oxidation reactions to eventually form metastable benzenecarboxylates, including phthalic and mellitic acids that could accumulate in the martian regolith [8]. Although the origin of CBZ and its precursor(s) remain unclear, metastable oxidized aromatics of martian or meteoritic origin are candidates for the CBZ detected in the mudstone.

Conclusions: The discovery of CBZ in the martian surface means that organics survived a significant high-energy radiation exposure and the presence of oxidants: the occurrence of perchlorate does not fully inhibit the detection of organics by pyrolysis EGA and GCMS, despite being a strong oxidant when heated. Actually, of all analyzed samples, CB has the highest amount of oxychlorine species [9], confirming that the production and detection of chlorohydrocarbons is possible when samples containing organics are heated in the presence of perchlorate. Future SAM measurements on Mt. Sharp may shed additional light on the nature and origin of organic matter in Gale Crater.

Table 1. Details of the SAM pyrolysis experiments and comparison of the absolute and EGA-corrected chlorobenzene abundances determined by GCMS in selected runs.

Sample (mass) [†]	Analysis on Mars (Sol)	Pyrolysis Temp.	GC Trap Temp. Cut [‡]	Chlorobenzene (x 10 ⁻¹² mol)
RN Blank	86/88	~45-875°C	~92-479 °C	< 1
RN-1 (50 ± 8 mg)	93	~45-875°C	~92-479 °C	8 ± 1
JK-3 (135 ± 31 mg)	224	~320-881°C	~326-581°C	7 ± 1
CB Blank-1	277	~45-875°C	~380-495°C	4 ± 1
CB-1 (45 ± 18 mg)	282/283	~45-875°C	~380-495°C	3 ± 1
CB-2 (45 ± 18 mg)	286	~45-875°C	~524-794°C	6 ± 1
CB-3 (45 ± 18 mg)	290	~45-875°C	~157-275°C	36 ± 7 (120 ± 23) ^{††}
CB-5 (45 ± 18 mg)	368	~45-875°C	~157-275°C	71 ± 13 (90 ± 17) ^{††}
CB-6 (135 ± 31 mg)	382	~250-870°C	~272-320°C	74 ± 14 (180 ± 32) ^{††}
CB-6 (residue)	394	~250-870°C	~272-320°C	47 ± 9
CB-7 (135 ± 31 mg)	408	~250-870°C	~420-784°C	39 ± 7
CB Blank-2	421	~250-870°C	~420-784°C	47 ± 9
CB-8 (135 ± 31 mg)	555-558	O ₂ Combustion Experiment		
CH Blank	770	~45-960°C	~210-960°C	3 ± 1
CH-1 (45 ± 18 mg)	773	~45-960°C	~210-960°C	9 ± 2
CB-9 Derivatization (135 ± 31 mg)	821	~45-250°C	~45-125°C	32 ± 6 [§]
	823	~45-900°C	~250-900°C	129 ± 24 [§]

[†]Estimated mass of sample heated. [‡]SAM cup/sample temperature estimate indicating temperature range where volatiles were collected on the hydrocarbon trap for GCMS analysis. ^{††}GCMS abundances corrected for the instrument background and the fraction of CBZ sent to the hydrocarbon trap based on the EGA m/z 112 signal and GC trap temperature cut used. CB-4 was used for a different noble gas experiment. [§]Preliminary CBZ abundance estimate.

References: [1] Mahaffy, P. et al. (2012) *Space Sci. Res.*, 170, 401-478. [2] Glavin, D. et al. (2013) *JGR*, 118, 1955-1973. [3] Vaniman, D. et al. (2013) *Science*, 343, 1243480. [4] Glavin, D. et al. (2014) *45th LPSC*, #1157. [5] Freissinet, C. et al. (2015) *JGR*, in review. [6] Freissinet, C. et al. (2015) *46th LPSC*, this meeting. [7] Miller, K. et al. (2013) *46th AGU*, #1785. [8] Benner, S. et al. (2000) *PNAS*, 97, 2425-2430. [9] Archer, D. et al. (2015) *46th LPSC*, this meeting.