NEW INSIGHTS FROM THE CUMBLERLAND ANALOG INVESTIGATION: BENZOIC ACID AS THE PREFERRED PRECURSOR FOR CHLOROBENZENE DETECTED ON MARS. C. Freissinet[1], H. V. Graham[2], C. A. Knudson[2], J. Lewis[2], J. Lasue[3], A. C. McAdam[2], C. Szopa[1], S. Teinturier[2], M. Millan[2], S. Andrejkovicova[4], A. Buch[5], C. A. Malespin[2] and P. R. Mahaffy[2].
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Introduction: The Mars Science Laboratory (MSL) Curiosity rover carries a suite of instruments which provide complementary geochemical and mineralogical data to investigate the possibility of habitable conditions throughout martian history [1]. The Cumberland (CB) drill sample from the Sheepbed mudstone in Gale Crater was analyzed by MSL instruments between sols 282-408 [2, 3] and the first evidence for an indigenous martian organic molecule, chlorobenzene, was made by the Sample Analysis at Mars (SAM [4]) instrument during pyrolysis gas chromatography-mass spectrometry (pyr-GCMS - [2]). A mineralogical analog of the Cumberland sample was created in the laboratory to aid in the understanding of the organic decomposition of precursor molecule(s) that led to the detection of chlorobenzene.

Cumberland analog: The Cumberland Analog (CBA) is based on mineral abundances determined by the Chemistry and Mineralogy (CheMin) instrument onboard MSL, that employs X-Ray Diffraction (XRD) for identification and relative abundance of crystalline minerals. The CBA mixture includes fourteen minerals that were individually characterized by XRD and GCMS. These analyses were also used to account for any trace mineral and organic components. CBA includes several key components such as a fine-grained palagonite material to represent the unknown X-ray amorphous portion of the sample, and griffithite, a close terrestrial analog to the Fe-smectite found in the Cumberland drill sample [5, 6].

CBA was characterized by SAM-like evolved gas analysis (EGA), ChemCam-like near-infrared and Laser Induced Breakdown Spectroscopy (LIBS) [7], and thermogravimetry-EGA.

SAM Testbed (TB) experiment: The SAM TB is a duplicate of the Flight Model currently onboard the Curiosity rover in Gale Crater, Mars. It is placed in a Mars chamber, designed to test the instruments in Mars-like conditions, providing high fidelity boundary conditions with interfaces developed to recreate how the instruments are mounted in the spacecraft [8].

Two CBA samples, of 19.16 and 9.7 mg, were each spiked with 0.5 wt% of benzoic acid, and magnesium perchlorate (1 wt% and 2 wt%, respectively). Mg-perchlorate was chosen as being the most likely form of oxychlorine present at CB [9]. A following control experiment consisted of organics-free fused silica spiked with 2 wt% Mg-perchlorate. Blank runs were performed before each sample run to assure no contamination came from the apparatus. The TB EGA and GCMS runs on CBA were performed under similar experimental conditions than during SAM analyses of CB on Mars.

The TB chromatogram displayed the presence of chlorobenzene in both CBA experiments, confirmed by both GC retention time and identification *via* MS. The quantification of chlorobenzene on CBA runs, 23 ± 4 and 28 ± 5 pmol respectively, is comparable with the abundance of chlorobenzene detected at CB on Mars, between 27 ± 5 and 31 ± 6 pmol (Freissinet et al. 2015). The blank GCMS runs did not show any sign of chlorobenzene, while the control GCMS run with perchlorate only fell under the expected background level of chlorobenzene (2 ± 0.4 pmol). We also tentatively detected dichlorobenzene, at a retention time compatible with that of laboratory experiments. Dichlorobenzene isomers were observed at CB [10].

The results presented in this paper show that in the closest SAM py-GCMS conditions we could reach in laboratory, *e.g.* using a home-made CB analog sample and the SAM testbed, we were able to form chlorobenzene from benzoic acid and Mg-perchlorates, in abundances similar to those detected on Mars. The case for benzoic acid as a potential precursor for the chlorobenzene detected in the martian regolith (Freissinet *et al*. 2015) is strengthened with this new supporting laboratory data from the Cumberland analog.

References:

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