THE CHARACTERIZATION AND DEVELOPMENT OF A MINERALOGICAL ANALOG OF THE MSL CUMBERLAND DRILL SAMPLE FOR ORGANIC MOLECULE IDENTIFICATION IN SAM-LIKE EXPERIMENTS.

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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 Crate 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 [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 lead to the detection of chlorobenzene.

Although both the carbon and chlorine are of martian origin, it is thought that the chlorobenzene detected on Mars is the result of a reaction between organic precursor(s) and an oxychlorine phase (likely Mg perchlorate [5]), inside the SAM ovens, during the pyrolysis step. Laboratory experiments demonstrate that benzoic acid is a good candidate for a possible precursor of chlorobenzene, as the carboxylic acid functional group would readily substitute for Cl during SAM-like pyrolysis in the presence of Mg perchlorate, forming chlorobenzene. To investigate benzoic acid as a precursor of chlorobenzene in SAM-like conditions, we ran pyrolysis of the CB analog sample on the SAM tested, a high-fidelity mockup of the SAM flight instrument, available at NASA Goddard Space Flight Center.

Analog Preparation: The Cumberland analog (CBA) was created using the minerals and mineral abundances of the Cumberland drill sample as determined by the CheMin instrument [3]. Some minor phases were substituted or combined (e.g. anhydrite was used in place of the minor amount of bassanite and augite was used in place of pigeonite) (Figure 1). Three separate mixtures were created; all three contain the same crystalline minerals but the amorphous component and the clay mineral vary. Results here are from the first mixture, where the amorphous component is a Hawaiian palagonite (HWML101) and the clay mineral is an Fe-smectite, Griffith saponite, collected from Griffith Park in Los Angeles, California. This particular Fe-smectite was used because it is structurally very similar to the trioctahedral clay mineral identified by CheMin [3, 6].

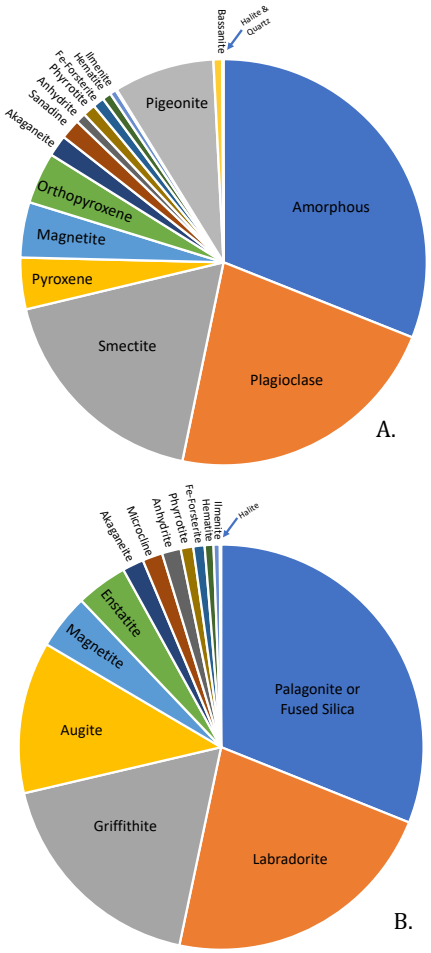

Figure 1. The minerals and their abundances of the Cumberland (CB) sample analyzed on Mars (A) [3, 8], and the laboratory-made Cumberland analog (CBA) (B).

Mineral Characterization. Each crystalline mineral, as well as the palagonite and the griffith saponite

were characterized using X-Ray Diffraction (XRD) and SAM-like Evolved Gas Analysis (EGA) and Gas Chromatograph Mass Spectrometry (GCMS). XRD analyses were carried out on a Bruker D8 Discover Diffractometer (Cu-Kα radiation (λ = 1.54059 Å)). EGA was performed on a Setaram LabSys Evo calorimeter/thermogravimeter coupled to a Pfeiffer OmniStar Quadrupole Mass Spectrometer (QMS) set up to operate under SAM-like conditions. GCMS analyzes were carried out on a CDS Analytical Pyroprobe 5000 coupled to an Agilent Trace Ultra GCMS and Thermo ISQ LT single QMS. XRD analyses allowed for the purity of the components to be characterized, and the EGA and GCMS analyses provided background data for the decomposition of any trace minerals and organic compounds present in the analog components (*e.g.* cyclic hydrocarbons, sulfur compounds).

All of the components were individually crushed and sieved to < 150 μm and then mixed by mortar and pestle to create a homogeneous sample. This sample was divided into equal portions which were used for different SAM-like and MSL-like analyses on various instruments. Here, we will focus on the experiments and the results of the samples analyzed on the SAM Testbed at NASA Goddard Space Flight Center.

SAM-like Experiments: The SAM Testbed is set up to operate at Mars conditions and is an exact replica of the SAM instrument onboard the Curiosity rover [7]. To confirm that benzoic acid could be a precursor of chlorobenzene, the analog was spiked with 0.5 wt. % benzoic acid and 2 wt. % Mg perchlorate. The sample was run on the SAM Testbed using similar conditions (*e.g.* temperature ramp rate, temperature range sampled to the GC trap during heating) to those which were used for the analysis of the martian Cumberland sample on Mars in which the discovery of martian chlorobenzenes was made [2].

Results: The SAM Testbed results showed the presence of chlorobenzene in the CBA run, at a level similar to the chlorobenzene detection in Cumberland on Mars (~28 pmol) [2]. A subsequent Testbed blank run of inert fused silica spiked with 2 wt. % Mg perchlorate, was run to dismiss the possibility of chlorobenzene formation from the testbed itself in the presence of HCl, and displayed a background chlorobenzene level of only ~2 pmol. This exciting result strongly supports the idea that benzoic acid, or a similarly structured organic molecule, as the most likely organic precursor of the chlorobenzene detected on Mars.

Additional MSL-like Analyses: While the main purpose for the production of this analog was to understand organic evolution using SAM-like instruments on a Mars analog material, sample was sent to other MSL instrument teams (*e.g.* ChemCam, CheMin) for analysis on those testbed or flight spare instruments as well [8, 9]. A portion of the CBA will also be analyzed using a Mars 2020 SuperCam model for comparison to MSL ChemCam results. Additional portions of CBA mixtures are available as a resource to the wider science community in support of MSL data interpretation.

References: [1] Grotzinger J. P. et al. (2012) *Space Science Reviews, 170, 1–4, 5–56.* [2] Freissinet C. et al. (2015) *JGR: Planets, 120,* 495–514. [3] Vaniman D. T. et al. (2014) *Science, 343*. [4] Mahaffy P. R. et al. (2012) *Space Science Reviews, 170, 401-478.* [5] Sutter B. et al. (2017) *JGR: Planets, 122, doi:10.1002/2016JE005225.* [6] Treiman, A. H. et al. (2014) *American Mineralogist, 99, 2234–2250.* [7] Malespin, C. A. (2017) *AGU 2017, Abstract #273817.* [8] Stern J. C. (2018) *AGU 2018, Abstract #423222.* [9] Lasue, J. *(Submitted 2019) LPSC L.*