

**ORGANIC MATTER HETEROGENEITY IN THE MARY ANNING/ GROKEN DRILL SITE, GALE CRATER, MARS.** A.J. Williams<sup>1</sup>, N. L. Lanza<sup>2</sup>, M. Millan<sup>3,4</sup>, A. McAdam<sup>4</sup>, C.H. House<sup>5</sup>, J.M.T. Lewis<sup>4,6,7</sup>, E. Rampe<sup>8</sup>, W.W. Fischer<sup>9</sup>, A.M. Ollila<sup>2</sup>, M. Thorpe<sup>8</sup>, P. Mahaffy<sup>4</sup>. <sup>1</sup>University of Florida ([amywilliams1@ufl.edu](mailto:amywilliams1@ufl.edu)), <sup>2</sup>Los Alamos National Laboratory, <sup>3</sup>Georgetown University, <sup>4</sup>NASA Goddard Space Flight Center, <sup>5</sup>Pennsylvania State University, <sup>6</sup>Howard University, <sup>7</sup>Center for Research and Exploration in Space Science and Technology, <sup>8</sup>NASA Johnson Space Center, <sup>9</sup>California Institute of Technology.

**Introduction:** The Mars Curiosity rover is ascending Mt. Sharp, in Gale crater, exploring stratigraphic packages of rocks for evidence of habitability and searching for organic compounds using the Sample Analysis at Mars (SAM) instrument suite. SAM can perform direct sample pyrolysis and gas chromatography mass spectrometry (GC-MS) analyses. SAM also has the capability of performing wet chemistry experiments, either by *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) derivatization or tetramethylammonium hydroxide (TMAH) thermochemolysis. Coupled with wet chemistry experiments, the GC-MS is capable of detecting carboxylic acids, aromatic molecules, and other hydrocarbons. If present, these molecules may be bound into large macromolecules (e.g., biomolecules or kerogen) as they are on Earth.

In July 2020, the Curiosity rover encountered a region of bedrock that contained an abundance of layered concretion-like features and unusual Mn- and P-rich chemistries (Fig.1) in Glen Torridon (GT), a phyllosilicate-rich lacustrine mudstone deposit [1]. The Mary Anning/ Groken sampling location, in the Knockfarril Hill member (KHm), was carefully selected at a distance as a site for analysis for the SAM instrument to perform one of its two TMAH wet chemistry experiments [2].

Regions of high Mn abundance have previously been observed in Gale crater (e.g., [4-6]). However, no sample of high Mn material up to this time had been delivered to either the CheMin or SAM instruments due to the challenge of sampling features such as thin fracture fills and small regions containing concretions with the drill. Based on the overall high Mn abundance throughout the bedrock, the unusual density of dark, often Mn-rich concretion-like features [7], and exciting preliminary TMAH results from the nearby Mary Anning target [2], the team pursued a drill campaign to attempt delivery of the unusual high Mn phase to CheMin [3,8] and SAM. Of particular interest was to determine the mineralogy and redox state of Mn, both of which have important implications for environmental conditions [e.g., 5, 9]. Here we describe organics results from the SAM instrument on the Groken target and a comparison with the adjacent Mary Anning target, only *ca.* 61 cm away.

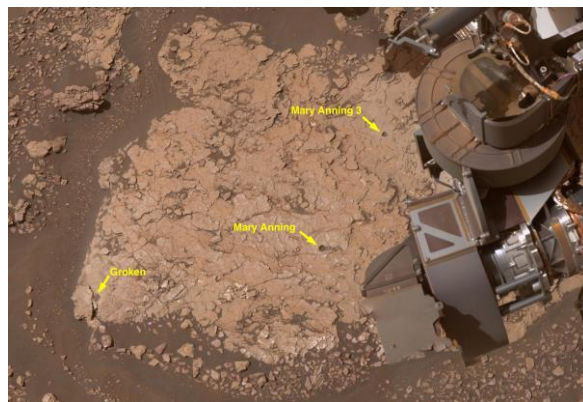


Figure 1. Mary Anning and Groken targets. Credit NASA/JPL-Caltech/MSSS

**Methods:** As evolved gas analysis (EGA), GC-MS, and both TMAH and MTBSTFA wet chemistry experiments were performed by the SAM instrument at the Mary Anning (MA) target, but only EGA and GC-MS performed at the Groken (GR) target, this work will report solely on a comparison of the EGA and GC-MS data. At MA, a split column GC1-GC4 analysis was performed. It was concluded after this analysis that a clog had occurred in the GC4 channel, rendering no useable data from the GC4 column. The GC1 column performed as expected. At GR, a split column GC1-GC2 analysis was performed. For both targets, temperature cuts of 1) 257-548°C and 2) 693-832°C were sent to the SAM hydrocarbon trap to capture organics; 1) related to evolved CO<sub>2</sub> and CO, and SO<sub>2</sub> from sulfates, and 2) related to evolved CO at high temperature and to avoid interference with evolved S.

**Results:** At MA, S-bearing molecules are present and include SO<sub>2</sub>, H<sub>2</sub>S, COS, and CS<sub>2</sub>. S-bearing organics include dithiapentane, dithiolane, and trithiane [10]. Other possible S-bearing phases include thiophene and dimethylsulfide, but they along with masses consistent with chloromethane, dichloromethane, and chlorobenzene are difficult to confirm with GC1 data.

Due to a leak in one of the MTBSTFA cups prior to landing, MTBSTFA vapor has been reacting within the SAM system for years, generating several standard byproducts, including monosilylated (MSW) and bisilylated water (BSW), silylated phenol, silylated boric acid, and TFMA (2,2,2-trifluoro-*N*-methylacetamide), which were all detected in the MA analysis. After the MA analysis, the SAM instrument

performed two wet chemistry experiments which added a significant new background to the SAM system [2].

At GR, there was no detection of native organics, including the S-organics detected at MA. Benzonitrile is detected but was also detected in MA3 (the MTBSTFA experiment at MA), and therefore may be carryover of a reaction product of the Mary Anning wet chemistry experiment.

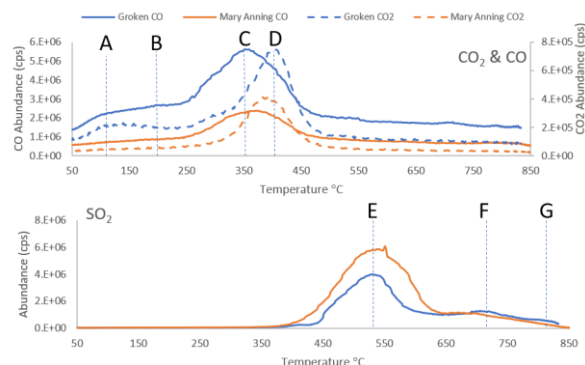


Figure 2. EGA of CO<sub>2</sub>, CO, and SO<sub>2</sub>, for Groken and Mary Anning.

**Discussion:** Within the small distance between the Mary Anning and Groken drill targets, the mineralogy is consistent except for one notable exception. CheMin [3,8] X-ray diffraction patterns show the presence of a 9.22 Å phase consistent with either a Mn<sup>2+</sup>-bearing phosphate within the jahnsite-whiteite group, or a mixed-layer phyllosilicate (e.g., talc-serpentine), that may be part of the dark nodules present in the Groken target. Other minerals detected at Groken and MA include additional clay minerals, feldspar, pyroxene, and Ca-sulfates. APXS geochemical data also demonstrate enrichments in Mn, P, Ca, and S at GR [11].

EGA reveals some key differences and similarities between the two targets (Fig. 2). The major CO<sub>2</sub> peak (line C) is likely related to a carbonate phase in both targets, whereas the lower temperature CO<sub>2</sub> peaks (lines A and B) in GR are attributed to residual wet chemistry byproducts. Wet chemistry byproducts are elevated in GR compared to other Glen Torridon samples. In most SAM EGA runs, CO (line D) will coevolve with CO<sub>2</sub> and this is taken to indicate that some of the CO<sub>2</sub> likely results from sources such as oxidized organics (e.g., oxalate salts) because oxidized organics can evolve CO<sub>2</sub> and CO together while carbonates generally do not evolve CO. There is an offset in CO<sub>2</sub> vs CO evolution in GR and MA. This indicates that some of the CO<sub>2</sub> is likely from carbonate. CO and CO<sub>2</sub> co-evolve in most other Glen Torridon samples.

The primary SO<sub>2</sub> peak (line E) is consistent between GR and MA, and with other Glen Torridon samples, and

is likely attributed to a sulfate phase. Higher temperature SO<sub>2</sub> releases (lines F and G) are also likely attributed to sulfate-bearing phases and are not seen in the MA sample. Groken has a unique high temperature HCl release (not shown) which may be attributed to a chloride-bearing salt (e.g., NaCl, MnCl, etc). A lack of significant O<sub>2</sub> evolution indicates that neither Mn<sup>3+/4+</sup> oxides nor oxychlorine phases are present [12].

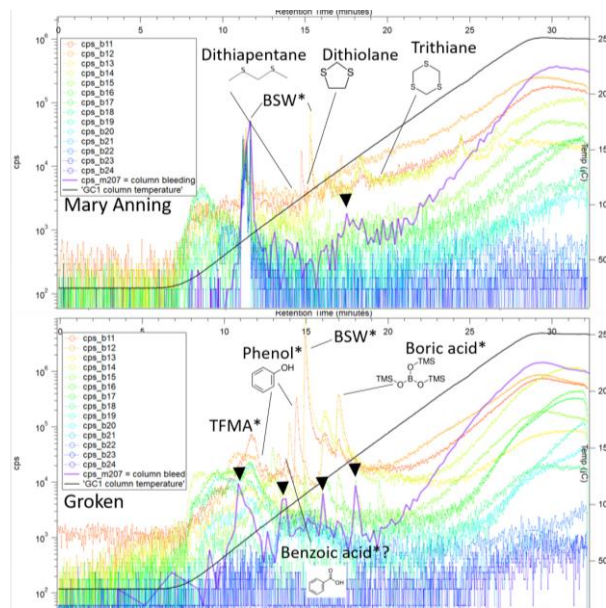


Figure 3. Comparison of GC1 from Mary Anning and Groken. Triangles indicate column bleeding.

High molecular weight (HMW) molecules (up to  $m/z=537$ ) are present in both MA and GR (Fig. 3), in GC1 and GC2, suggesting the presence of large and complex molecules. The S-bearing organics present in MA are not detected in GR. This may be due to an absence of the molecules or to the much higher background in GR obfuscating the signal.

HMW molecules have been observed to be preserved in biogenically produced Mn-oxides on Earth [13]. Additional benchtop experiments will work to elucidate the presence of any additional native molecules in the GR sample that may explain the dearth of S-bearing molecules.

**References:** [1] Fox, V.K. et al. (this meeting). [2] Williams, A., et al. (this meeting). [3] Thorpe, M. et al. (this meeting). [4] Lanza, N.L. et al. (2014). GRL 41(16), 5755-5763. [5] Lanza, N.L. et al., (2016). GRL 43(14), 7398-7407. [6] Lamm, S.N. et al. (2018). 49th LPSC, no. 2903. [7] Gasda, P.J. et al. (this meeting). [8] Treiman, A.H. et al. (this meeting). [9] Johnson, J.E. et al. (2016). GCA 173, 210-231. [10] Millan, M. et al. (this meeting). [11] Berger, J. et al. (this meeting). [12] Clark, J.V. et al. (this meeting). [13] Estes, E.R. et al. (2016). Geobiology, 1-15.