Organics on Mars: What we've learned at Gale crater.

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Introduction: One of the major contributions of the Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) rover, Curiosity, has been the *in situ* confirmation of the presence of C1-C11 organic compounds and macromolecules on the surface of Mars. Up until the MSL mission, organics had been detected in Martian meteorites [e.g., 1,2], and were suggested by reinterpretation of Viking data [3]. The SAM organics measurements are complemented by geochemical and geological environmental context and included details regarding molecular- and isotopic-compositions and abundances.

MSL landed at Bradbury landing, Gale crater, on August 5, 2012, and celebrated its 10th Anniversary on Mars in August 2022. Here we detail and discuss the body of measurements detecting and characterizing organic molecules in Gale crater materials, and their significance in the context of habitability and life detection goals of MSL and other missions.

Methods: SAM can perform in three main operational modes designed to characterize carbon in different ways [4]. Evolved gas analysis coupled with mass spectrometry (EGA-MS) pyrolyzes a sample using ramped heating. Volatile organic molecules are identified by their mass spectra. Their evolution temperatures indicate the refractory nature of organic matter in samples, with smaller, simpler molecules evolving below 500°C and fragments of macromolecules or mineral-bound organics evolving between 500° and ~900°C. SAM also performs pyrolysis coupled with gas chromatography-MS (Py-GC-MS) to extract and separate complex mixtures of organic molecules enabling identification of organics by mass spectra and retention time. As part of the Py-GC-MS experiment, SAM includes the option to either derivatize organics with N-methyl-N-tert-butyl-dimethylsilyl-trifluoroacetamide (MTBSTFA) or hydrolyze and methylate them with tetramethyl-ammonium hydroxide TMAH (i.e., thermochemolysis) [4]. These wet chemistry procedures were optimized for detection of different classes of organic molecules relevant to biochemistry that are not detectable by Py-GC-MS alone (e.g., amino acids and fatty acid lipids). Finally, SAM can perform a stepped combustion experiment to drive oxidation of reduced carbon to CO_2, enabling measurement of bulk organic carbon abundance and carbon isotopic composition ($\delta^{13}C$) using the tunable laser spectrometer (TLS).

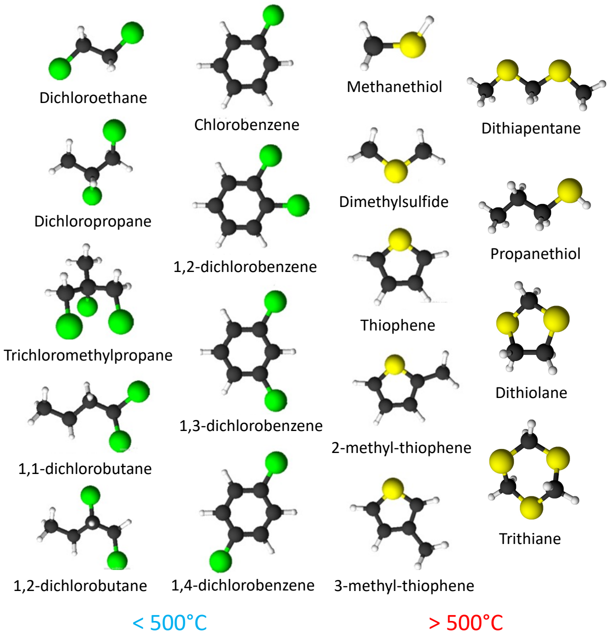

Figure 1. Chlorine and Sulfur-bearing molecules detected in SAM pyrolysis-GC-MS experiments at low and high pyrolysis temperature.

Results: To date, SAM has reported detections of N, S, O, and Cl-bearing organics including both aliphatic and aromatic molecules (Figure 1; [5,6,7,8,9]). Some of these molecules originate from the decomposition of the wet chemistry reagents [e.g., 9]. However, other compounds including a variety of S-bearing organics extracted at high temperature are highly likely to be indigenous to Mars [5,6,7,8,9]

SAM experiments have also provided information about the abundance and isotopic composition of organics. In many samples, a broad CO_2 peak observed between 200-500°C coupled with evidence of oxychlorine species suggest combustion of reduced organics [e.g, 11]. While some reduced organics evolved at these lower temperatures are derived from instrument sources, isotope mass balance was used to estimate that at least 430 ppm organic C comes from the sample itself [12]. At temperatures above 550°C, Gale crater mudstones evolved at least 273 ppm of organic C in the form of CO_2 and CO during a closed oven combustion experiment [12]. Finally, $\delta^{13}C$ values of CO_2 evolved during both oxychlorine induced combustion [13] and intentional stepped combustion [12] are consistent with meteoritic and igneous organic materials and can be used to discriminate between organic and inorganic sources of carbon.

Discussion: The SAM organics detections confirm the presence of organic molecules on the surface of Mars. Beyond this, the SAM detections offer several new insights with respect to how we think about organics on Mars. (1) Despite exposure to ionizing radiation most likely for 10's of millions of years [14], complex organic molecules, either stabilized by sulfurization or occlusion in minerals, are still present. (2) Organics can be detected in the presence of oxychlorine species. Oxychlorine-induced combustion may provide more energy to release recalcitrant organics from mineral-bound phases than pyrolysis alone. Despite conversion of reduced organics to CO_2, the $\delta^{13}C$ value of that CO_2 strongly points to the presence of organic carbon. (3) The combination of EGA-MS data [5, 9], GC-MS data [6, 7, 8, 9], and $\delta^{13}C$ values of CO_2 and CH_4 evolved below ~500°C [12, 13, 15] support the presence of labile or unbound organics on Mars. Confirming the presence of this low temperature Martian organic phase in Mars meteorites has been confounded by terrestrial contamination [e.g., 16]. Laboratory analyses of simple organic acids [13, 17, 18] provide indirect evidence for a labile source of carbon present either as (radiolytic) decomposition products of larger organic molecules or as products of photocatalysis. This finding supports the notion of active cycling of carbon on Mars. (4) Finally, the refractory carbon detected in Gale crater sediments during high temperature pyrolysis and combustion are consistent in composition [9] and abundance [12] with the macromolecular carbon [MMC] found in Martian meteorites [e.g., 2], Further, this MMC has $\delta^{13}C$ values consistent with both meteoritic and igneous Martian sources. Its detection in Gale crater sediments as well as a diverse range of Martian meteorites suggest this component could be ubiquitous on Mars.

Implications for Jezero Crater and Sample Return. Direct comparisons between Gale crater data acquired by SAM/MSL and the SHERLOC Raman/UV spectrometer measurements at Jezero crater are complicated by the differences inherent in the different techniques. However, SAM data have broad implications for what one might expect to find in another past habitable environment on Mars with similar features (deltas, clays). Compositionally similar organics (aromatics) have been detected at Jezero [19], furthering the notion of a global organic signature present due to meteoritic infall or atmospheric/radiative processing of such infall. However, detection of significantly different suites of organics at Jezero could indicate a localized source of organic chemistry.

SAM EGA data support a relationship between organics and minerals, and Perseverance data reveal additional information on these relationships. SHERLOC data show an association between aromatic organics and aqueous minerals, suggesting aqueous alteration of igneous materials may also play a role in the processing of organics on Mars [19].

Conclusion: The SAM has detected aromatic and aliphatic organics in a broad range of sediment types. Both SAM/MSL and SHERLOC/Perseverance datasets can be used to target choices of samples for sample return. SAM abundances, if representative of global abundances, can be extrapolated to help assess sample amounts required for further molecular and isotopic analyses of organics in returned samples. The analyses of returned samples using analytical techniques similar to those used on Perseverance and Curiosity could enable a direct comparison of the composition of organics in Jezero crater and Gale crater materials.

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