ORGANIC CARBON CONCENTRATIONS IN 3-BILLION-YEAR-OLD LACUSTRINE MUDSTONES OF MARS.

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Introduction: Understanding the inventory of carbon on Mars is relevant to the question of whether Mars was ever habitable. While the Mars atmosphere represents a large reservoir of carbon, *in situ* pyrolysis performed on Mars and meteorite analyses indicate that another significant reservoir of carbon is the rocks themselves. Complex organic carbon was discovered in 3.5 Ga mudstones sampled at Cumberland (CB) in the Yellowknife Bay Formation in Gale Crater by the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) [1] using a thermal decomposition technique called evolved gas analysis (EGA). Other simple organics have also been detected in these same CB materials [2]. Low temperature co-evolution of CO and CO_2 ($\sim 200°C – 500°C$) has been detected in many samples from Gale Crater where SAM EGA has been performed, and potential sources include combustion of terrestrial organics from SAM, as well as combustion and/or decarboxylation of either indigenous martian or exogenous organic carbon [3,4].

SAM performed an experiment designed to combust refractory organic carbon to CO_2 to obtain carbon abundance and carbon isotopic composition ($\delta^{13}C$). This experiment is similar to laboratory stepped combustion of meteorites [5,6]. These results represent the first quantification of bulk refractory carbon in Mars surface materials.

Methods: The SAM Combustion experiment used the SAM quadrupole mass spectrometer (QMS) and the SAM tunable laser spectrometer (TLS), which measures abundance and isotopic composition of CO_2. Combustion was performed in a closed oven in the presence of oxygen, which was either sourced from oxychlorine in the sample or added to the cup as O_2 gas prior to the experiment using an onboard reservoir tank. Unlike pyrolysis, where gases evolved are continuously monitored using the QMS, gases produced during closed oven combustion were only released into the SAM manifold and analyzed by QMS and TLS once the heating step is finished.

The SAM combustion experiment was conducted in a four-step process to isolate combustible materials below and above ~550ºC (Table 1). Combustion below

Table 1. Combustion experiment steps and rationale.

Step	Details	Comments
1	Heat cup to 550°C and hold for 25 min, QMS/ TLS analysis, Return cup to SMS	Used oxychlorine native to the Mars soil as the oxidant instead of added O_2. 24-30 μmol O_2 estimated.
2	Return cup to oven, add O_2 (~3.7 μmol) and heat to 550°C, hold 25 min, QMS/TLS analysis	Designed to measure contamination from on board sources of carbon
3	Add O_2 (~3.7 μmol), heat to 860°C, hold 25 min, QMS/TLS analysis	Designed to access refractory carbon
4	Add O_2 (~3.7 μmol), heat to 860°C, hold 25 min, QMS/TLS analysis	Designed to access refractory carbon that was not combusted in Step 3

550ºC is known have carbon contributions from the decomposition of MTBSTFA, a reagent SAM carries for an experiment to derivatize organic matter that was identified in the background of blank and sample runs [7] that may adsorb to the sample while the cup is in the Sample Manipulation System (SMS). The experiment was designed so that differences between Step 1 and Step 2 as well as between Combustion and EGA experiments could reveal information regarding bulk martian carbon abundance. Combustion above 550ºC targeted refractory organic matter.

Results: CO_2 abundances were measured by both TLS and QMS for steps 2-4, allowing for cross-instrument validation of this data (Fig. 1). The amount of volatile material evolved in Step 1 exceeded the safety limits set for the QMS, which shut itself down during analysis to prevent damage to the instrument. This allowed us to only collect TLS data for Step 1. TLS and QMS data were within error for CO_2 abundances.

QMS data for steps 2-4 allowed quantification of several additional oxidized and reduced species. SO_2 was the most abundant species after CO_2 and H_2O, with the equivalent of 0.16% SO_3 evolved in Step 3. O_2 was
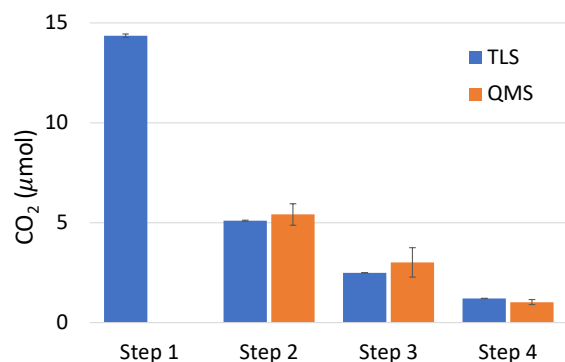
Figure 1. Abundance of CO_2 and H_2O evolved during SAM Combustion Experiment.

Figure 2. Comparison of $\delta^{13}C$ of CO_2 (‰, V-PDB) produced during combustion above and below 550 °C with known carbon reservoirs [8,10,11,12].

present in steps 2-4 at nanomolar abundance, although in step 3 all O_2 can be attributed to sulfate decomposition, suggesting all oxygen was used in this step. We note a rise in CO during step 4, suggesting partial oxidation of a refractory phase. Trace OCS (carbonyl sulfide or COS) was present at pmol abundances in steps 2 and 3. CH_4 was present in steps 2-3 and saturated below 550°C. HCl also saturated in step 2. H_2 saturated in Step 4, consistent with observations from CB pyrolysis [3], but present at nmol abundances in steps 2 and 3. Trace amounts of H_2S, C_2H_6, and HCN were also present in steps 2-4.

Discussion: Over the entire temperature range of the experiment, the combustion run produced twice as much carbon in the form of CO_2 (1543 ± 41 μg C/g) as pyrolysis runs (~667-827 μg C/g, [4]). Low temperature (<500°C) combustion was responsible for most of this carbon. While we know that MTBSTFA-derived carbon accounts for some portion of the CO_2 evolved below 550°C, the stable isotope compositions (Figure 2) indicate the presence of at least one other carbon component from a ^{13}C enriched reservoir of carbon. In addition, we note the presence of CH_4 in all steps, suggesting incomplete combustion of reduced carbon.

More CO_2 was evolved above 550°C in closed oven combustion experiments than during pyrolysis of the same sample, indicating that this experiment was successful in releasing mineral-bound and refractory carbon in this temperature range. Our results above 550ºC suggest up to 260 μg C/g of refractory organic carbon may be present in 3.5 Ga mudstones in Gale Crater, depending on the contributions from carbonates, which can be constrained by SAM pyrolysis analysis.

Other than eliminating instrument carbon as the sole source of CO_2 evolved during the combustion experiment, $\delta^{13}C$ values place limited constraints on the carbon sources in these experiments. SAM EGA pyrolysis experiments of 13 samples demonstrated that
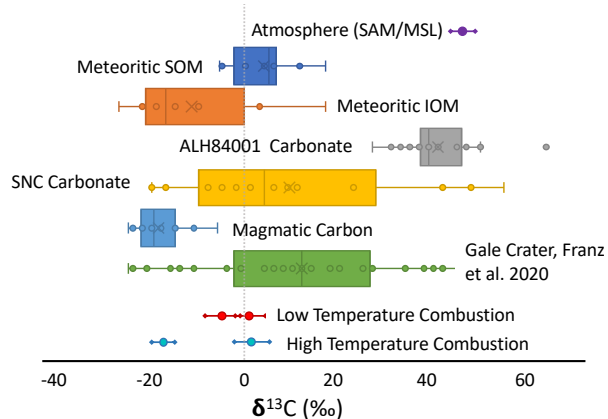
CO_2 evolved below 550 ºC had a broad range of $\delta^{13}C$ (-25 ± 20‰ to 56 ± 11‰ PDB) representing multiple carbon sources [8]. In addition to the previously discussed instrument carbon source, carbon evolved as CO_2 during the combustion experiment could come from oxidation or decarboxylation of Martian organics or exogenous carbon [1,2,3,4,8,9]. Minor carbonate components may be present, even below 550°C, as carbonate decrepitation occurs over a broad temperature range (400° – 700°C) in stepped combustion of meteorites [6].

Measured $\delta^{13}C$ values are bulk values, and likely incorporate both ^{13}C-enriched and ^{13}C-depleted carbon sources. For this reason, measured $\delta^{13}C$ values do not entirely rule out the potential for some portion of this organic carbon to be present as a remnant of ancient biological processes in lake waters or sediments.

Conclusions: SAM combustion of the Cumberland sample produced more CO_2 than EGA alone. The results of the SAM combustion experiment are consistent with the identification of complex refractory organic carbon in Cumberland fines [1]. Our combustion results above 550ºC suggest significantly more organic carbon than previously reported may be present in 3.5 Ga mudstones in Gale Crater.

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