THE COMBUSTION EXPERIMENT ON THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE ON THE CURIOSITY ROVER.

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Introduction: The combustion experiment on the Sample Analysis at Mars (SAM) suite on Curiosity will heat a sample of Mars regolith in the presence of oxygen and measure composition of the evolved gases using quadrupole mass spectrometry (QMS) and tunable laser spectrometry (TLS) [1]. QMS will enable detection of combustion products such as CO, CO_2, NO, and other oxidized species, while TLS will enable precise measurements of the abundance and carbon isotopic composition ($\delta^{13}C$) of the evolved CO_2 and hydrogen isotopic composition (δD) of H_2O. SAM will perform a two-step combustion to isolate combustible materials below ~550º C and above ~550º C.

The combustion experiment on SAM, if properly designed and executed, has the potential to answer multiple questions regarding the origins of volatiles seen thus far in SAM evolved gas analysis (EGA) on Mars. Constraints imposed by SAM and MSL time and power resources, as well as SAM consumables (oxygen gas), will limit the number of SAM combustion experiments, so it is imperative to design an experiment targeting the most pressing science questions. Low temperature combustion experiments will primarily target the quantification of carbon (and nitrogen) contributed by SAM wet chemistry reagants MTBSTFA (N-Methyl-N-tert-butyldimethylsilyltrifluoroacetamide) and DMF (Dimethylformamide), which have been identified in the background of blank and sample runs [2] and may adsorb to the sample while the cup is in the Sample Manipulation System (SMS). In addition, differences between the sample and "blank" may yield information regarding abundance and $\delta^{13}C$ of bulk (both organic and inorganic) martian carbon. High temperature combustion experiments primarily aim to detect refractory organic matter, if present in Cumberland fines, as well as address the question of quantification and δD value of water evolution associated with hydroxyl hydrogen in clay minerals [3,4,5].

Laboratory Validation: To optimize and characterize combustion of complex organic molecules in rock matrices, combustion experiments simulating those to be performed on SAM were conducted at NASA Goddard on a combustion breadboard and on the SAM testbed. A well-characterized kerogen material was heated at 35º C/min to temperatures of 550º C and/or 950º C in the presence of oxygen in a SAM-like oven on a laboratory breadboard (or SAM testbed) and held for 25 minutes. These temperatures, the number of steps, and the time of the temperature hold were chosen based on power and time constraints imposed by SAM and MSL/Curiosity operations. At the end of combustion breadboard experiments, the valve isolating the oven was opened and gas flowed via capillary into a commercial mass spectrometer (Hiden Analytical, Inc.) for measurement of CO_2, O_2, H_2O, CO, NO, and organic fragments associated with decomposition of the kerogen. In some experiments, evolved gas was captured and analyzed via a gas-bench coupled to an isotope ratio mass spectrometer (IRMS) for $\delta^{13}C$. Values obtained using a) this method on the combustion breadboard and b) using the SAM testbed QMS and TLS were compared to bulk and total organic carbon (TOC) abundance and $\delta^{13}C$ values for this kerogen standard using commercial flash combustion elemental analysis (EA)-IRMS. In addition, EGA with 30 mb O_2 carrier gas was performed on a commercial laboratory instrument in order to determine evolution temperatures of combusted organics (Fig. 1).

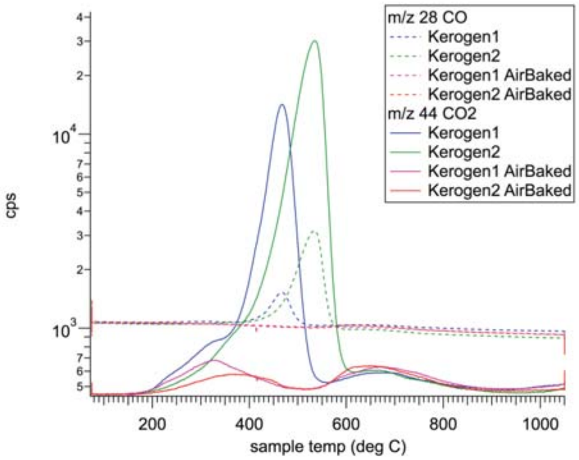

Figure 1. EGA analysis of kerogen using commercial EGA system with O_2 carrier gas at 30 mb at 35ºC/min.

Preliminary Results: Fig. 1 shows results of EGA heating the kerogen standard in the presence of oxygen. This experiment was run to determine which temperatures were characteristic for the combustion of different reservoirs of carbon (e.g. more refractory vs. less refractory to oxidation). Choice of 550º C as the first temperature step in our two step combustion experiment was in part based on the fact that most of the CO_2 from kerogen has evolved by 550-600º C, leaving only a refractory, high temperature component that will be combusted during the second temperature step at 950º C.

This lower temperature combustion step, when performed on Mars, will represent multiple carbon sources that may be difficult to deconvolve. In addition to any possible indigenous martian carbon, we expect a small contribution of CO_2 from combustion of SAM wet chemistry reagants MTBSTFA and DMF. Preliminary calculations estimating CO_2 evolved by the most abundant MTSBSTFA-related products, mono- and bi-silylated water derivatives, suggest that the upper limit for the relative amount of CO_2 represented by combustion of MTBSTFA-related products is ~ 3% of the total CO_2 evolved during John Klein and Cumberland EGA experiments [4]. CO_2 evolved during decomposition of carbonates is also likely to be present at temperatures below ~550º C, particularly when perchlorates are present, as evidenced by EGA experiments performed at Rocknest [6].

Combustion Breadboard Experiments: Experiments were run using the kerogen standard on the combustion breadboard as described above. Kerogen samples were mixed with fused silica to yield 1% carbon and 30 mg of sample was weighed into a quartz boat to be inserted into the GSFC-built combustion oven. Experiments performed included single step combustion at 950º C, two-step combustion at 550º C and then 950º C, and re-combusting already combusted samples at both temperatures to determine whether all material has been combusted. Acetanalide, a standard of known %C and $\delta^{13}C$, was run to calibrate instrument response and determine the amount of carbon combusted during kerogen runs.

Repeated combustion experiments using the kerogen sample resulted in 50-60% yield of combustion. CO_2 evolved during the 550º C temperature step accounted for ~91.5% of the total evolved CO_2, with the remaining ~8.5% evolved at the 950º C temperature step. $\delta^{13}C$ values of gases evolved at the low temperature step were within 2‰ of $\delta^{13}C$ values obtained for kerogen using EA-IRMS, suggesting that carbon isotopes do not undergo considerable fractionation when combustion yields are at least 50%.

Discussion: Based on the separate science questions addressed by low and high temperature combustion experiments coupled with the limited amount of oxygen available for combustion experiments, our current plan for the first combustion experiment on Mars is as follows: *Step 1: Ramp and hold at 550º C on a fresh sample without O_2 addition.* Previous runs on Cumberland samples show that the O_2 evolved from soil oxidants during EGA is well in excess of what we would add from our O_2 tank. Gases evolved in this experiment will include any indigenous organics, any carbonate, and any MTBSTFA derived carbon. *Step 2: Re-expose cup to SMS, ramp and hold combustion at 550º C in the presence of added O_2.* This run will serve as a blank for the previous run. The hold at 550º C will combust any MTBSTFA adsorbed to the sample during SMS exposure. Quantification of CO_2 using QMS and TLS (and NO using QMS) from this run will help constrain the amount of MTBSTFA contributed C and N to a sample, and possibly help deconvolve sources of C. *Step 3: Ramp to 950º C and hold in the presence of added O_2.* The hold at 950º C will address the question of whether there is a high temperature source of organic carbon at Cumberland. In addition, EGA experiments in Cumberland show water and H_2 [4,6] evolved between 550º C and 950º C. These gases will be sent to the TLS for H_2O quantification and δD measurement, helping validate these measurements from SAM EGA runs at Cumberland. *Step 4: Ramp to 950ºC again and hold in the presence of added O_2.* This will serve as a blank for the previous run.

Conclusion: The first combustion experiment on Mars will be performed on a triple portion sample of Cumberland drill fines that was delivered into a SAM sample cup prior to leaving the Cumberland drill site in the Sheepbed Member at Yellowknife Bay. This sample has been well characterized through multiple SAM EGA analyses [3]. The combustion experiment, as detailed above, will enable quantification of MTBSTFA/DMF - derived carbon (and nitrogen), and possibly aid in deconvolution of this carbon source from indigenous sources. In addition, the high temperature step of the experiment will probe for refractory organic matter as well as enable conversion of H_2 to H_2O for confirmatory high temperature D/H measurements.

References: [1] Mahaffy, P.R. et al. (2012) *Space Sci. Rev. 170*(1-4), 401-478 [2] Glavin, D.P. et al., (2013) JGR Planets, 10 1955-1973 [3] Ming, D.W. et al. (2013) *Science* 342 [4] Vaniman, D.T. et al., (2013) *Science, 342* [5] Mahaffy, P.R. et al. (2014) LPS XLV [6] Leshin, L.A. et al. (2013) *Science*, *341*(6153)