

THE COMBUSTION EXPERIMENT ON THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE ON THE CURIOSITY ROVER. J. C. Stern¹, C. A. Malespin^{1,2}, J. Eigenbrode¹, H. V. Graham³, P. D. Archer, Jr.⁴, A. Brunner¹, C. Freissinet³, H. B. Franz^{1,5}, J. Fuentes⁶, D.P. Glavin¹, P. R. Mahaffy¹, A. C. McAdam¹, D. W. Ming⁴, P. B. Niles⁴, A. Steele⁷ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.C.Stern@nasa.gov ²Goddard Earth Science Technology and Research, Universities Space Research Association, Columbia, MD, ³NASA Postdoctoral Program, NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, ⁴NASA Johnson Space Center, Houston, TX 77058, ⁵University of Maryland, Baltimore County, Baltimore, MD 21228 ⁶University of Maryland, College Park, MD 20742, ⁷Carnegie Institution of Washington, Washington, DC 20015

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, CO₂, NO, and other oxidized species, while TLS will enable precision measurements of the abundance and carbon isotopic composition ($\delta^{13}\text{C}$) of the evolved CO₂ and hydrogen isotopic composition (δD) of H₂O. SAM will perform a two-step combustion to isolate combustible materials below ~550° C and above ~550° C.

Combustion Experiment Plan and Rationale: Our current plan for the first combustion experiment on Mars is as follows:

1) *Ramp and hold at 550° C on a fresh sample (Cumberland, already in cup) without O₂ addition.* Previous runs on Cumberland samples show that the O₂ evolved from soil oxidants during EGA is well in excess of what we would add from our O₂ tank. Gases evolved in this experiment will include any indigenous organics, any carbonate, and any MTBSTFA derived carbon. 2) *Re-expose cup to SMS, add ramp and hold combustion at 550° C in the presence of added O₂.* This run will serve as a blank for the previous run. The hold at 550° C will combust any MTSBTFA adsorbed to the sample after SMS exposure. Quantification of CO₂ using QMS and TLS (and NO using QMS) from this run will help put constraints of the amount of MTBSTFA contributed C and N to a sample, and possibly help deconvolve sources of C.

3) *Ramp to 950° C and hold in the presence of added O₂.* The hold at 950° 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 H₂ [4,6] evolved between 550° C and 950° C. These gases will be sent to the TLS for quantification and δD measurement, helping validate these measurements from SAM EGA runs at Cumberland.

4) *Ramp to 950° C again and hold in the presence of added O₂.* This will serve as a blank for the previous run.

Materials/Methods: 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 35° C/min to temperatures of 550° C or 950° 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 oven was opened and gas flowed via capillary into a commercial mass spectrometer (Hiden Analytical, Inc.) for measurement of CO₂, O₂, H₂O, 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 $\delta^{13}\text{C}$. 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 $\delta^{13}\text{C}$ values for this kerogen standard using commercial flash combustion elemental analysis (EA)-IRMS. In addition, commercial EGA with O₂ carrier gas was performed in order to determine evolution temperatures of combusted organics (Fig. 1).

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 pools of carbon (e.g. more refractory vs. less refractory). Choice of 550° C as the first temperature step in our two step combustion experiment was in part based on the fact that most of the CO₂ from kerogen has evolved by 550-600° C, leaving only a refractory, high temperature component that will be combusted during the second temperature step at 950° 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

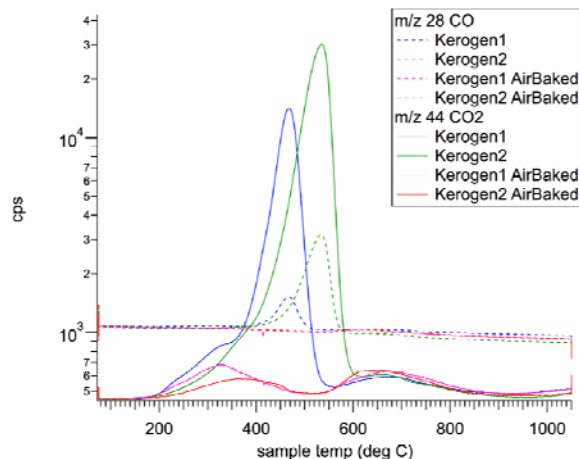


Figure 1. EGA analysis of kerogen using commercial EGA system with O₂ carrier gas at 30 mb at 35°C/min.

expect a small contribution of CO₂ from combustion of SAM wet chemistry reagents MTBSTFA (N-Methyl-N-tert-butyldimethylsilyltrifluoroacetamide) and DMF (Dimethylformamide), which have been identified in the background of blank and sample runs [2,3]. Preliminary calculations estimating CO₂ evolved by the most abundant MTBSTFA-related products, mono- and bi-silylated water, suggest an upper limit for the relative amount of CO₂ represented by combustion of MTBSTFA-related products is ~ 3% of the total CO₂ evolved during John Klein and Cumberland EGA experiments [4]. CO₂ evolved during decomposition of carbonates is also likely to be present at temperatures below ~550° C, particularly when perchlorates are present, as evidenced by EGA experiments performed at Rocknest [5].

Combustion Breadboard Experiments: Experiments were run using the kerogen standard on the combustion breadboard as described in the Materials/Methods section. 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 950° C, two-step combustion at 550° C and 950° C, and re-combusting already combusted samples at both temperatures to determine whether all material has been combusted. Acetaldehyde, a standard of known %C and $\delta^{13}\text{C}$, 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. CO₂ evolved during the 550° C temperature step accounted for ~91.5% of the total evolved CO₂, with the

remaining ~8.5% evolved at the 950° C temperature step. $\delta^{13}\text{C}$ values of gases evolved at the low temperature step were within 2‰ of $\delta^{13}\text{C}$ values obtained for kerogen using EA-IRMS, suggesting that carbon isotopes do not undergo considerable fractionation when combustion yields are at least 50%.

Discussion: 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 EGA analyses 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 MTBSTFA adsorbed to the sample while the cup is in the SMS. In addition, differences between the sample and “blank” may yield information regarding abundance and $\delta^{13}\text{C}$ of bulk (both organic and inorganic) martian carbon. High temperature combustion experiments will primarily target the question of whether high temperature organic carbon is present at Cumberland, as well as address the question of quantification and δD composition of high temperature water evolution associated with hydroxyl hydrogen in clay minerals thought to be present at Cumberland [6].

References: [1] Mahaffy et al. (2012) *Space Sci. Rev.* 170(1-4), 401-478 [2] Freissinet et al. (2013) LPS XLIV [3] Buch et al. (2013) LPS XLIV [4] Ming, D. W., et al. (2013) *Science* 342 [5] Leshin et al. (2013) *Science*, 341(6153) [6] Mahaffy et al. (2014) LPS XLV