THE COMBUSTION EXPERIMENT ON THE SAMPLE ANALYSIS AT MARS (SAM) INSTRUMENT SUITE ON THE CURIOSITY ROVER. J. C. Stern\textsuperscript{1}, C. A. Malespin\textsuperscript{1,2}, J. Eigenbrode\textsuperscript{3}, H. V. Graham\textsuperscript{4}, P. D. Archer, Jr.\textsuperscript{4}, A. Brunner\textsuperscript{1}, C. Freissinet\textsuperscript{1}, H. B. Franz\textsuperscript{1,5}, J. Fuentes\textsuperscript{6}, D.P. Glavin\textsuperscript{1}, P. R. Mahaffy\textsuperscript{1}, A. C. McAdam\textsuperscript{1}, D. W. Ming\textsuperscript{4}, P. B. Niles\textsuperscript{4}, A. Steele\textsuperscript{1} and the MSL Science Team. \textsuperscript{1}NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.C.Stern@nasa.gov \textsuperscript{2}Goddard Earth Science Technology and Research, Universites Space Research Association, Columbia, MD, \textsuperscript{3}NASA Postdoctoral Program, NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, \textsuperscript{4}NASA Johnson Space Center, Houston, TX 77058, \textsuperscript{5}University of Maryland, Baltimore County, Baltimore, MD 21228 \textsuperscript{6}University of Maryland, College Park, MD 20742, \textsuperscript{7}Carnegie 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) \cite{1}. QMS will enable detection of combustion products such as CO, CO\textsubscript{2}, NO, and other oxidized species, while TLS will enable precision measurements of the abundance and carbon isotopic composition ($\delta^{13}$C) of the evolved CO\textsubscript{2} and hydrogen isotopic composition ($\delta$D) of H\textsubscript{2}O. SAM will perform a two-step combustion to isolate combustible materials below ~550º C and above ~550º C.

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

1) Ramp and hold at 550º C on a fresh sample (Cumberland, already in cup) without O\textsubscript{2} addition. Previous runs on Cumberland samples show that the O\textsubscript{2} evolved from soil oxidants during EGA is well in excess of what we would add from our O\textsubscript{2} 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 550º C in the presence of added O\textsubscript{2}. This run will serve as a blank for the previous run. The hold at 550º C will combust any MTSBTFA adsorbed to the sample after SMS exposure. Quantification of CO\textsubscript{2} 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 950º C and hold in the presence of added O\textsubscript{2}. The high temperature component that will be combusted has evolved by 550-600º C, leaving only a refractory, high temperature source of organic carbon at Cumberland. In addition, EGA experiments in Cumberland show water and H\textsubscript{2} [4,6] evolved between 550º C and 950º C. These gases will be sent to the TLS for quantification and $\delta$D measurement, helping validate these measurements from SAM EGA runs at Cumberland. 4) Ramp to 950ºC again and hold in the presence of added O\textsubscript{2}. 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 ºC/min to temperatures of 550º C 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 oven was opened and gas flowed via capillary into a commercial mass spectrometer (Hiden Analytical, Inc.) for measurement of CO\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, 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, commercial EGA with O\textsubscript{2} 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 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\textsubscript{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 CO₂ from combustion of SAM wet chemistry reagents MTBSTFA (N-Methyl-N-tert-butylidemethylsilyltrifluoroacetamide) 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 ~550º 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 950º C, two-step combustion at 550º C and 950º C, and re-combusting already combusted samples are both temperatures to determine whether all material has been combusted. Acetanalide, a standard of known %C and δ¹³C, 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 550º C temperature step accounted for ~91.5% of the total evolved CO₂, with the remaining ~8.5% evolved at the 950º C temperature step. δ¹³C values of gases evolved at the low temperature step were within 2‰ of δ¹³C 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 δ¹³C 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:**

[3] Buch et al. (2013) LPS XLIV