SEARCHING FOR REDUCED CARBON ON THE SURFACE OF MARS: THE SAM COMBUSTION EXPERIMENT. J.C. Stern[1], C.A. Malespin[1,2], P.R. Mahaffy[1], C.R. Webster[3], J.L. Eigenbrode[1], P.D. Archer, Jr.[4,5], A.E. Brunner[1,6], C. Freissinet[1,7], H.B. Franz[1,8], D.P. Glavin[1], H.V. Graham[1,7], A.C. McAdam[1], D.W. Ming[5], R. Navarro-González[9], P.B. Niles[5], A. Steele[10], B. Sutter[4,5], M.G. Trainer[1], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.C.Stern@nasa.gov [2]Goddard Earth Science Technology and Research, Universities Space Research Association, Columbia, MD, [3]Jet Propulsion Laboratory, Pasadena, CA 91109 [4]Jacobs, Houston,TX 77058, [5]NASA Johnson Space Center, Houston, TX 77058, [6]CRESST, U. Maryland, College Park, MD 20740, [7]NASA Postdoctoral Program, NASA Goddard Space Flight Center, Greenbelt, MD 20771, [8]University of Maryland, Baltimore County, Baltimore, MD 21228, [9]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [10]Carnegie Institution of Washington, Washington, DC 20015

Introduction: The search for reduced carbon has been a major focus of past and present missions to Mars. Thermal evolved gas analysis was used by the Viking and Phoenix landers and is currently in use by the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) to characterize volatiles evolved from solid samples, including those associated with reduced organic species. SAM has the additional capability to perform a combustion experiment, in which a sample of Mars regolith is heated in the presence of oxygen and the composition of the evolved gases is measured using quadrupole mass spectrometry (QMS) and tunable laser spectrometry (TLS) [1].

Organics detection on the Martian surface has been complicated by oxidation and destruction during heating by soil oxidants [2], including oxychlorine compounds, and terrestrial organics in the SAM background contributed by one of the SAM wet chemistry reagents MTBSTFA (N-Methyl-N-tert-butyldimethylsilyl-trifluoroacetamide) [3,4]. Thermal Evolved Gas Analysis (TEGA) results from Phoenix show a mid temperature CO_2 release between 400°C – 680°C speculated to be carbonate, CO_2 adsorbed to grains, or combustion of organics by soil oxidants [5]. Low temperature CO_2 evolutions (~200°C – 400°C) were also present at all three sites in Gale Crater where SAM Evolved Gas Analysis (EGA) was performed, and potential sources include combustion of terrestrial organics from SAM, as well as combustion and/or decarboxylation either indigenous martian or exogenous organic carbon [4,6].

By performing an experiment to intentionally combust all reduced materials in the sample, we hope to compare the bulk abundance of CO_2 and other oxidized species evolved by combustion to that evolved during an EGA experiment to estimate how much CO_2 could be contributed by reduced carbon sources. In addition, C, O, and H isotopic compositions of CO_2 and H_2O measured by TLS can contribute information regarding the potential sources of these volatiles.

Methods: The SAM combustion experiment was designed as a two-step combustion to isolate combustible materials below ~550ºC and above ~550ºC. Low temperature combustion experiments target the quantification of carbon (and nitrogen) contributed by MTBSTFA which has been identified in the background of blank and sample runs [7] 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. The low temperature step will also allow measurements of the δD value of adsorbed water in the sample, which is evolved below 550ºC (Fig. 1), and should be representative of the atmospheric water reservoir. High temperature combustion experiments primarily aim to detect refractory organic matter, if present at Cumberland, as well as address the question of quantification and δD value of water and H_2 evolution associated with hydroxyl hydrogen in clay minerals as shown in Figure 1 [8,9].

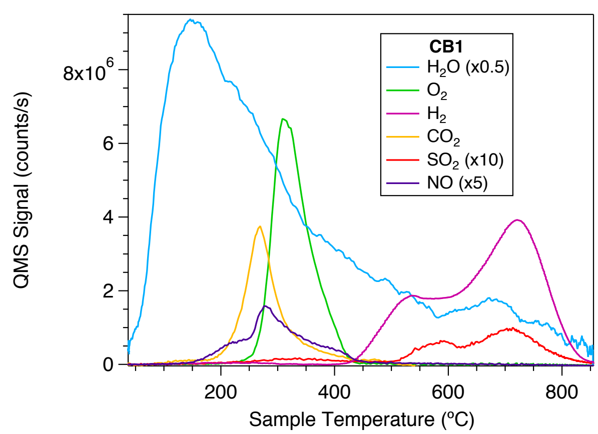

Figure 1. Major volatiles evolved during Cumberland EGA analysis. O_2 from soil oxidants evolves <550°C and is used as the O_2 source for step 1 of the combustion experiment. CO_2 and H_2O captured <550ºC are sent to the TLS for isotopic analysis. In step 3, H_2 from clay dehydroyxlation >550ºC is combusted to H_2O to get a total high temperature water δD. value. SO_2 is also evolved >550ºC from sulfate decomposition.

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, the first combustion experiment on Mars was performed as follows: *Step 1: Ramp and hold at 550ºC on a fresh sample without O_2 addition.* Previous runs show that the O_2 evolved from soil oxidants during EGA of the Cumberland drill sample is well in excess of what we would add from our O_2 tank (Fig. 1). CO_2 evolved in this experiment includes that from oxidation of any indigenous organics, any carbonate, and any MTBSTFA derived carbon. *Step 2: Re-expose cup to SMS, ramp and hold combustion at 550ºC in the presence of added O_2.* This run serves as a blank for the previous run. The hold at 550º C combusts any MTBSTFA adsorbed to the sample during SMS exposure. Quantification of CO_2 using QMS and TLS (and other volatiles such as NO using QMS) from this run can help constrain the amount of MTBSTFA contributed C and N to a sample, and possibly help deconvolve sources of C. *Step 3: Ramp to 950ºC and hold in the presence of added O_2.* The hold at 950ºC addresses the question of whether there is a high temperature source of reduced carbon in the sample. In addition, EGA experiments at Cumberland show water and H_2 [6,9] evolved between 550º C and 950º C due to dehydoxylation of clays (Fig. 1). These gases are sent to the TLS for H_2O quantification and δD measurement. *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.

Results: At the time of submission, one combustion experiment on Mars has been performed on a triple portion sample of Cumberland drill fines delivered into a SAM sample cup containing a previously pyrolyzed single portion sample prior to leaving the Cumberland drill site in the Sheepbed Member at Yellowknife Bay. These deposits are inferred to be ancient fluvio-lacustrine deposits and their mineralogy and volatile content suggests an ancient habitable environment at this location on Mars [10], as well as the possibility of indigenous organic carbon preserved in this mudstone [6].

Data analysis is still underway, but the initial results indicate that the combustion experiment was successful in producing CO_2 and H_2O in each step of the experiment in sufficient abundance to obtain TLS measurements of C, O, and H isotopes. In particular, this method allowed separate isotopic measurements of the low temperature and high temperature water components of the sample [11].

QMS data was not obtained in the low temperature (<550ºC) step of the experiment due to the large amounts of volatiles produced. However, TLS data indicate that more CO_2 was produced at this temperature using the combustion experiment than traditional EGA analyses of Cumberland fines, suggesting the presence of reduced carbon in the sample. Determination of how much of this carbon is attributable to terrestrial background is currently underway. Some reduced species were also present in step 2, the low temperature "blank." Volatiles produced at high temperature (>550ºC) include CO_2, H_2O and SO_2.

Discussion: The first combustion experiment on Mars was successful in producing useful data for comparison to traditional EGA of the same samples. Some factors complicating the interpretation of results include the possibility of incomplete combustion, either due to insufficient oxygen or simply the refractory nature of the materials in the sample. The presence of some reduced species along with significant amounts of CO_2 in step 2, the low temperature "blank," suggest combustion/CO_2 evolution may have been incomplete during step 1. To mitigate this for future experiments, we will reduce the number of portions delivered to SAM.

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