

**DETECTION OF REDUCED ORGANIC CARBON IN GALE CRATER SEDIMENTS: RESULTS FROM THE SAM COMBUSTION EXPERIMENT.** J.C. Stern<sup>1</sup>, C.A. Malespin<sup>1</sup>, J.L. Eigenbrode<sup>1</sup>, H.B. Franz<sup>1</sup>, C.R. Webster<sup>2</sup>, P.D. Archer<sup>3,4</sup>, B. Sutter<sup>3,4</sup>, R. Navarro-Gonzalez<sup>5</sup>, and P.R. Mahaffy<sup>1</sup>. <sup>1</sup>NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.C.Stern@nasa.gov, <sup>2</sup>Jet Propulsion Laboratory, Pasadena, CA 91109 <sup>3</sup>Jacobs, Houston, TX 77058, <sup>4</sup>NASA Johnson Space Center, Houston, TX 77058, <sup>5</sup>Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico

**Introduction:** The search for organic carbon has been a major focus of past and present missions to Mars. 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<sub>2</sub> (~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].

To target reduced organic carbon, SAM performed a combustion experiment in which a sample of 3.5 Ga mudstone at Cumberland was step-heated in the presence of oxygen and the composition of the evolved gases was measured using quadrupole mass spectrometry (QMS) and tunable laser spectrometry (TLS). By performing an experiment to intentionally combust all reduced materials in the sample, we can compare the bulk abundance of CO<sub>2</sub> and other oxidized species evolved by combustion to that evolved during an EGA experiment to estimate how much additional CO<sub>2</sub> could be contributed by reduced carbon sources. In addition, C and H isotopic compositions of CO<sub>2</sub> and H<sub>2</sub>O measured by TLS can contribute information regarding the potential sources of these volatiles.

**Methods:** The SAM combustion experiment was conducted in a two-step process to isolate combustible materials below and above ~550°C. Combustion below 550°C targeted the quantification of carbon contributed by MTBSTFA, a reagent SAM carries for an experiment to derivatize organic matter that was identified in the background of blank and sample runs [5] and may adsorb to the sample while the cup is in the Sample Manipulation System (SMS). In addition, differences between the sample and “blank” yields information regarding abundance and δ<sup>13</sup>C of bulk (both organic and inorganic) martian carbon. The low temperature step measures the δD value of adsorbed water in the sample, which is evolved below 550°C, and should be representative of the atmospheric water reservoir. Combustion above 550°C targeted mostly refractory organic matter, if present at Cumberland, as well as abundance

and δD value of water associated with hydroxyl hydrogen in clay minerals, detected by CheMin and SAM [6].

The first combustion experiment on Mars was performed as follows: *Step 1: Ramp and hold at 550°C on a fresh sample without O<sub>2</sub> addition.* O<sub>2</sub> evolved from soil oxidants during earlier EGA of the Cumberland drill sample [3] exceeded what would be added from our on-board O<sub>2</sub> tank. CO<sub>2</sub> evolved in this step includes that from oxidation of any indigenous organics, any carbonate, and any MTBSTFA derived carbon. *Step 2: Repose sample to SMS, ramp and hold combustion at 550°C in the presence of added O<sub>2</sub>.* This run served as a blank for the previous run. The hold at 550°C combusted any MTBSTFA adsorbed to the sample during SMS exposure. Quantification of CO<sub>2</sub> using QMS and TLS from this step constrained the amount of MTBSTFA contributed C to the sample, and possibly help deconvolve sources of C. *Step 3: Ramp to 860°C and hold in the presence of added O<sub>2</sub>.* The hold at 860°C (maximum SAM oven temperature) combusted reduced carbon in the sample and targeted hydroxyl groups of clays for δD analysis by TLS [e.g., 6]. *Step 4: Ramp to 950°C again and hold in the presence of added O<sub>2</sub>.* This served as a blank for the previous run.

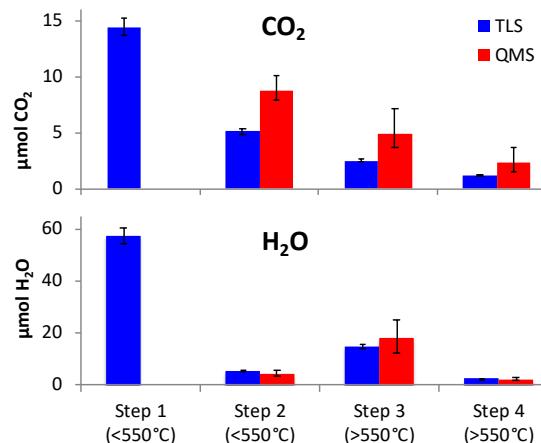


Figure 1. Abundance of CO<sub>2</sub> and H<sub>2</sub>O evolved during combustion. No QMS data is available for step 1 due to the instrument shutting itself down due to the high pressures of gas evolved.

**Results:** CO<sub>2</sub> and H<sub>2</sub>O were evolved in all 4 steps of the combustion experiment (Fig. 1). QMS data was not obtained in step 1 due to the large amounts of volatiles produced, which caused the QMS to shut down to

protect the filament. However, TLS data indicate that this step produced approximately 14  $\mu\text{mol}$   $\text{CO}_2$  and 58  $\mu\text{mol}$   $\text{H}_2\text{O}$ . Significant  $\text{CO}_2$  was also evolved in step 2, the low temperature “blank.” In the high temperature ( $>550^\circ\text{C}$ ) steps (3 and 4), lesser amounts of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were produced than below  $550^\circ\text{C}$ , while significant  $\text{HCl}$ ,  $\text{SO}_2$ , and  $\text{CO}$  were produced in step 3.

**Discussion:** TLS and QMS data indicate that more  $\text{CO}_2$  was produced using the combustion experiment than traditional EGA analyses of Cumberland fines, and in fact show that more  $\text{CO}_2$  was evolved during combustion than in any other sample analyzed thus far in Gale Crater (Fig. 2). We calculate total abundances of  $1284 \pm 302$  ppm reduced carbon in the fraction evolving  $\text{CO}_2$  below  $550^\circ\text{C}$  and  $222 \pm 52$  ppm in the fraction evolving  $\text{CO}_2$  above  $550^\circ\text{C}$ .

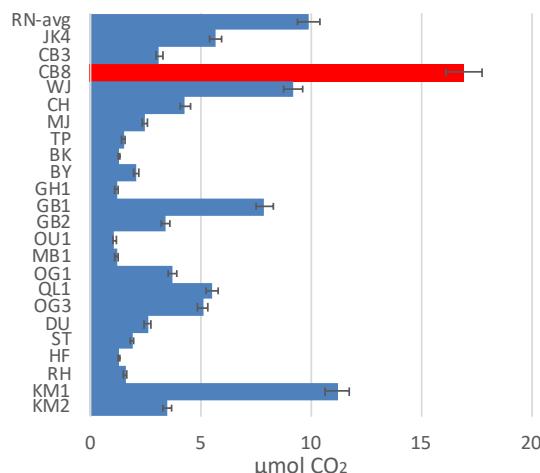


Figure 2. CB8 Steps 1 and 3 combined produced more  $\text{CO}_2$  than any other sample analyzed thus far.

$\text{CO}_2$  produced in step 1 is a combination of combustion and decarboxylation of martian carbon, thermal decomposition of any carbonate, and instrument derived MTBSTFA. The TLS derived  $\delta^{13}\text{C}$  value for step 1 was  $-1.1 \pm 4.2\text{\textperthousand}$ , which is significantly different than the value of MTBSTFA ( $-35.5\text{\textperthousand}$ ), suggesting the presence of martian carbon.  $\text{CO}_2$  produced in step 2 could either be due to incomplete combustion in step 1, or it could represent combustion of MTBSTFA adsorbed onto the fines when the sample was returned to the SMS. If step 2 is treated as a blank for step 1, 9.32  $\mu\text{mol}$  of  $\text{CO}_2$  remains after the subtraction of step 2  $\text{CO}_2$ , corresponding to  $828 \pm 195$  ppm carbon.

$\text{CO}_2$  evolved in step 3 above  $550^\circ\text{C}$  should primarily represent martian carbon and not byproducts of MTBSTFA, which predominantly evolve below  $550^\circ\text{C}$  and would have been removed during step 2, which was performed immediately before step 3. Approximately 4  $\mu\text{mol}$  of  $\text{CO}_2$  in step 3 based on QMS. In addition,

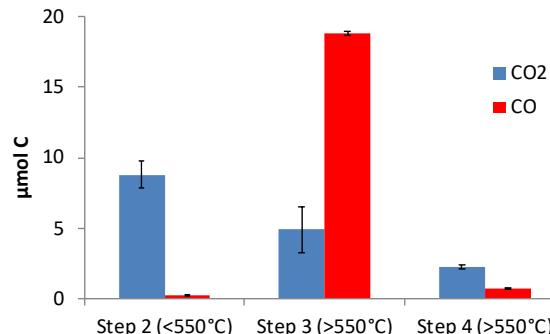


Figure 3. Abundance of  $\text{CO}_2$  and  $\text{CO}$  derived from QMS data. More abundant  $\text{CO}$  than  $\text{CO}_2$  in step 3 suggests incomplete combustion of refractory organic carbon.

approximately 19  $\mu\text{mol}$  of  $\text{CO}$  was evolved in step 3 (Fig. 3), suggesting partial combustion of organic material. Step 3 also had more residual oxygen present than steps 2 and 4, further suggesting that combustion was kinetically inhibited. This is not surprising, as complete combustion of refractory organic matter is difficult to achieve at temperatures of  $860^\circ\text{C}$ , even in the presence of catalyzing materials such as  $\text{Fe}_2\text{O}_3$  present in the sample [7]. The  $\delta^{13}\text{C}$  value for step 3 was  $-25.9 \pm 3.1\text{\textperthousand}$ , which is consistent with values reported for magmatic and macromolecular carbon in Mars meteorites [8, 9].

TLS and QMS derived  $\delta\text{D}$  compositions from this experiment have been published elsewhere [6].  $\delta^{18}\text{O}$  data for both  $\text{H}_2\text{O}$  and  $\text{CO}_2$  was strongly affected by the isotopic composition of the  $\text{O}_2$  provided by the on-board tank in steps 2-4 and by oxychlorine and other soil oxidants in step 1.

**Conclusions:** SAM combustion of the Cumberland sample produced more  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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  $550^\circ\text{C}$  suggest significantly more organic carbon than previously reported may be present in 3.5 Ga mudstones in Gale Crater.

- References:** [1] Eigenbrode, J.L. et al. (2018) *Science*, 360(6393). [2] Freissinet, C. et al. (2015) *JGR Planets*, 120(3). [3] Ming, D.W. et al. (2013) *Science* 342 [4] Sutter, B., et al. (2017) *JGR Planets* 122(12). [5] Glavin, D.P. et al., (2013) *JGR Planets*, 10 1955-1973 [6] Mahaffy, P.R. et al. (2014) *Science* 347(6220) [7] Vaniman, D.T. et al. (2014) *Science* 343(6169) [8] Grady, M.M. et al. (2004) *Int. J. Astrobiol.* 3, 117. [9] Steele, A. et al. (2012) *Science*, 337(6091)