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CARBON ISOTOPIC COMPOSITION OF CO₂ EVOLVED DURING PERCHLORATE-INDUCED REACTIONS IN MARS ANALOG MATERIALS: INTERPRETING SAM/MSL ROCKNEST DATA. J. C. Stern¹, A. C. McAdam¹, P. D. Archer, Jr.², H. Bower^{1,3}, A. Buch⁴, J. Eigenbrode¹, C. Freissinet¹, H. B. Franz^{1,3}, D. Glavin¹, J. H. Jones², P. R. Mahaffy¹, D. W. Ming², P. B. Niles², A. Steele⁵, B. Sutter⁶ and the MSL Science Team. ¹NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.C.Stern@nasa.gov ²NASA Johnson Space Center, Houston, TX 77058 ³University of Maryland, Baltimore County, Baltimore, MD 21228 ⁴Ecole Centrale Paris, LGPM, Grande voie des vignes, 92295 Châtenay-Malabry, France ⁵Carnegie Institution of Washington, Washington, DC 20015 ⁶Jacobs/ESCG Houston, TX 77058

Introduction: The Sample Analysis at Mars (SAM) Instrument Suite on the Mars Science Laboratory (MSL) Rover Curiosity made its first solid sample evolved gas analysis of unconsolidated material at aeolian bedform Rocknest in Gale Crater. The magnitude of O₂ evolved in each run as well as the chlorinated hydrocarbons detected by SAM gas chromatograph/mass spectrometer (GCMS) [1] suggest a chlorinated oxidant such as perchlorate in Rocknest materials [2]. Perchlorate induced combustion of organics present in the sample would contribute to the CO₂ volatile inventory, possibly overlapping with CO₂ from inorganic sources. The resulting carbon and oxygen isotopic composition of CO₂ sent to the Tunable Laser Spectrometer (TLS) for analysis would represent mixed sources. This work was undertaken to better understand a) how well the carbon isotopic composition ($\delta^{13}\text{C}$) of CO₂ from partially combusted products represents their source and b) how the $\delta^{13}\text{C}$ of combusted products can be deconvolved from other carbon sources such as thermal decomposition of carbonate.

Materials/Methods: SAM received a portion of Rocknest material [3] sieved to <150 μm for Evolved Gas Analysis (EGA). Samples were heated from 35° to ~835° C in a stream of He at 1.5 sccm at a ramp rate of 35° C/min under a 30 mb pressure of He in the SAM pyrolysis oven. Evolved gas was continuously sampled by the quadrupole mass spectrometer (QMS) on SAM, and a portion of gas evolved over a pre-determined temperature range was sent to the TLS for isotopic analysis of evolved CO₂ and H₂O.

A SAM-like EGA system consisting of an in-house pyrocell coupled to a commercial Hiden Mass Spectrometer fitted with a gas manifold to collect CO₂ evolved during pyrolysis has been established at GSFC and used successfully in conjunction with commercial Cavity Ringdown Spectroscopy (Picarro) to measure $\delta^{13}\text{C}$ of CO₂ evolved from carbonate-bearing Mars analog materials [4]. For perchlorate EGA-MS experiments, samples consisted of simple organic compounds dried down onto fused silica and Mars analog samples representing a range of % carbon. Samples were heated both with and without 1 wt% Mg-perchlorate and volatile releases were monitored by the Hiden mass spectrometer. Once CO₂ evolution vs.

temperature curves were established for each sample, gas collection using the manifold system was timed for collection of bulk CO₂ and CO₂ evolved over selected temperature ranges to model the SAM-EGA-TLS experiment. $\delta^{13}\text{C}$ of evolved CO₂ was measured by injection into a Thermo Trace Ultra GC with Carboxen 1006 GC column coupled to a Thermo Scientific Delta V Plus isotope ratio mass spectrometer (IRMS). $\delta^{13}\text{C}$ of all solid samples was measured using conventional laboratory combustion Elemental Analysis (EA) coupled to IRMS.

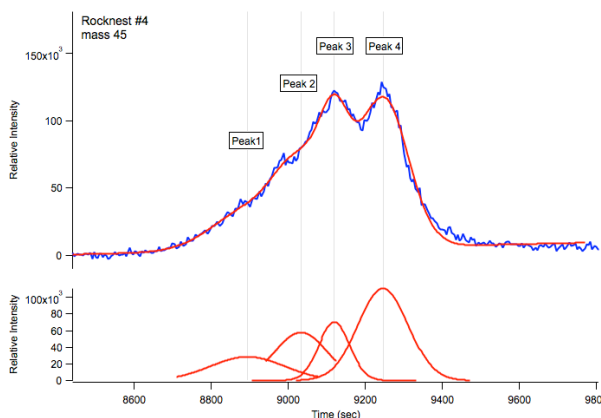


Figure 1. Rocknest #4 mass 45 trace suggesting 4 peaks for CO₂. Data in blue, fitted peaks in red.

Preliminary Results: Four analyses of Rocknest material, preceded by a blank, showed generally consistent results with respect to evolution of volatile species H₂O, CO₂, SO₂, and O₂ [5]. Rocknest material released CO₂ from ~200° C to ~600° C. All four runs are generally consistent, with four CO₂ peaks as suggested by Gaussian peak fitting routine (Figure 1). Contributions of individual sources to each release are currently being studied and suggest a combination of adsorbed CO₂, combustion of organics, and carbonate decomposition [6]. Preliminary $\delta^{13}\text{C}$ calculated from QMS data show similar values for Peaks 3 and 4, suggesting they may have similar carbon sources [5]. Analysis of TLS data is currently in progress.

Because fragments consistent with SAM wet chemistry reagents MTBSTFA (N-Methyl-N-tert-butyltrimethylsilyltrifluoroacetamide) and DMF (Dimethylformamide) have been identified in the background of blank and Rocknest runs [7,8], we expect a

small contribution of CO₂ from combustion of these organics. Preliminary calculations estimating CO₂ evolved by the most abundant MTSBSTFA-related products, mono- and bi-silylated water [8], suggest 260-420 nmol CO₂ could come from the combustion of these compounds. The total CO₂ molar abundance during EGA of Rocknest samples is approximately 10 μmol [3]. Accordingly, an upper limit for the relative amount of CO₂ represented by combustion of MTBSTFA-related products is ~ 4% of the total CO₂ evolved during Rocknest EGA experiments [2,8].

One interesting benefit of the presence of perchlorate in Martian soils is the resulting perchlorate-induced combustion of reduced carbon during pyrolysis. CO₂ from combustion of reduced carbon can be sent to the TLS for δ¹³C analysis. In this way, the δ¹³C composition of any combustible organic carbon on Mars could be measured. SAM carried a small volume of oxygen to Mars to perform a combustion experiment with the objective of obtaining δ¹³C composition of any reduced carbon species found; however, perchlorate may provide an additional boost in the combustion of more refractory carbon, and, if ubiquitous in Mars surface materials, provides a non-consumable source of oxygen for combustion.

Perchlorate-induced combustion experiments

Laboratory experiments using SAM-like techniques help us understand the effects of perchlorate on combustion of organics and the δ¹³C of the CO₂ evolved by this process. Preliminary data from samples run on the SAM-like Hiden system show significant differences between CO₂ evolution in the presence and absence of perchlorate. Figure 2 shows CO₂ evolution during heating of Green River Shale alone and with 1 wt% Mg-perchlorate. In Hiden EGA experiments without perchlorate, there appears to be minimal oxidation of organic carbon, and the main CO₂ peak evolution between 525° C to 725° C is consistent with thermal decomposition of carbonate minerals known to be present in the sample. In the experiment with 1% perchlorate, CO₂ is evolved in a broad peak between 200-500 °C. This may be due to a combination of factors. CO₂ evolution from carbonate may occur at lower temperatures via dissolution by HCl produced during decomposition of Mg-perchlorate [9]. However, organic fragments in Green River Shale also show changes in their thermal decomposition profile in the presence of perchlorate. Figure 3 suggests that there is some combustion of organics, as well as an earlier onset temperature (~100° C lower) for their evolution. Most likely, a combination of combusted organics and carbonate dissolution are responsible for the CO₂ evolution in this experiment.

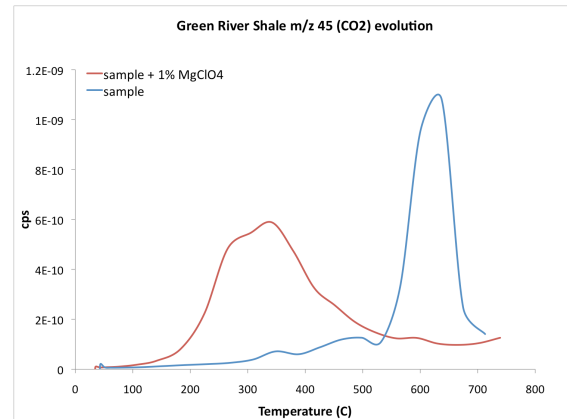


Figure 2. CO₂ evolution from Green River Shale in the presence (red) and absence (blue) of 1% Mg perchlorate.

Green River Shale, while not a perfect Mars analog in terms of concentration of organic carbon, is used as a model for samples with two distinct carbon components, carbonate and kerogen [10]. These two components have distinct isotopic compositions, with carbonate δ¹³C ~ 9‰ and kerogen δ¹³C ~ -28‰ [10 and this work]. Because these two contributions have δ¹³C almost 40‰ apart from one another, this sample is well suited to examine the effects described above on isotopic composition of CO₂ evolved in the presence of perchlorates. Ongoing work is underway to characterize the effects of oxidants proposed at Rocknest, notably Ca-perchlorate [2], on the δ¹³C of CO₂ evolved during EGA of multi-component analog samples.

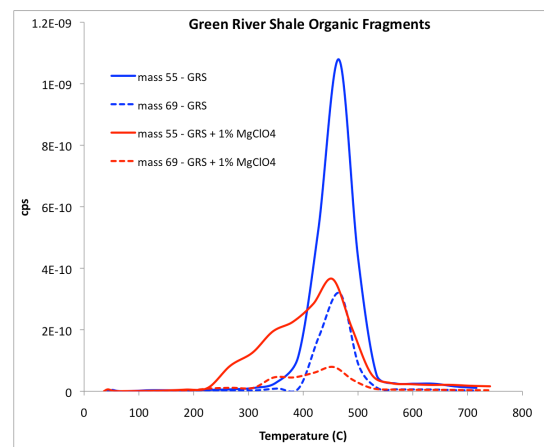


Figure 3. Major organic fragments evolved during pyrolysis of Green River Shale, with and without 1% Mg Perchlorate.

References: [1] Glavin et al. (2013) LPS XLIV [2] Sutter et al. (2013a) LPS XLIV [3] Archer et al. (2013) LPS XLIV [4] Stern et al. (2012) *Icarus*. [5] Franz et al. (2013) LPS XLIV. [6] Sutter et al. (2013b) LPS XLIV [7] Freissinet et al. (2013) LPS XLIV [8] Buch et al. (2013) LPS XLIV [9] Cannon et al. (2012) GRL 39, L13203. [10] I. Gilmour and C. T. Pillinger (1985) *Organic Geochemistry* (8) 6.