

ASSESSING MARS PYROLYSIS DATA FOR THE PRESENCE OF ORGANIC SALTS J. M. T. Lewis^{1,2,3}, J. L. Eigenbrode², G. M. Wong⁴, A. C. McAdam², P. D. Archer⁵, B. Sutter⁵, M. Millan⁶, R. H. Williams^{2,3,7}, M. Guzman⁸, A. Das⁹, E. B. Rampe¹⁰, C. N. Achilles^{2,11}, H. B. Franz², S. Andrejkovicova¹², C. A. Knudson^{2,3,7}, and P. R. Mahaffy², ¹Department of Physics and Astronomy, Howard University, Washington, D.C. (james.m.lewis@nasa.gov), ²NASA Goddard Space Flight Center, Greenbelt, MD, ³Center for Research and Exploration in Space Science and Technology, Greenbelt, MD, ⁴Department of Geosciences, The Pennsylvania State University, PA, ⁵Jacobs, NASA Johnson Space Center, ⁶Department of Biology, Georgetown University, Washington, D.C., ⁷Center for Research and Exploration in Space Science and Technology, University of Maryland, College Park, MD, ⁸LATMOS/IPSL, UVSQ Université Paris-Saclay, Sorbonne Université, CNRS, Guyancourt, France, ⁹International Space University, Strasbourg, France, ¹⁰NASA Johnson Space Center, Houston, TX, ¹¹Universities Space Research Association, Columbia, MD, ¹²Geosciences Department, GEOBIOTEC unit, Aveiro University, Aveiro, Portugal.

Introduction: The Sample Analysis at Mars (SAM) instrument suite on board the Mars Science Laboratory (MSL) Curiosity rover has examined the volatile chemistry of multiple Martian samples from Gale crater [1-4]. A diverse array of organic products in SAM pyrolysis data have indicated that organic matter is preserved in Martian sediments, but the parent molecules of these products remain unknown [5-7]. The degradation of organic matter on the Martian surface by radiation, oxidation, or volcanism may have led to the accumulation of metastable organic salts, such as oxalates and acetates [8-11]. If organic salts are widespread on Mars, they could play an important role in Martian carbon cycling and habitability and their composition and distribution could inform about the less altered organic record at depth.

Organic salts hosted in complex natural samples are challenging to investigate via pyrolysis as species such as oxalates and acetates produce simple pyrolysis products that can be contributed by many other phases and instrument backgrounds [12]. Additionally, the thermal decomposition of organic salts can be impacted by the presence of O₂ and catalysts in pyrolysis ovens [13]. Metal oxalates typically decompose to form either (a) the metal carbonate and CO, (b) the metal oxide, CO, and CO₂, or (c) the metal and CO₂ [12,13]. Metal acetate pyrolysis is typically associated with the evolution of CO₂, acetone, and acetic acid and the formation of carbonate or oxide residues [12,13].

CO₂ and CO are ubiquitous in SAM data and organic salts have previously been suggested as potential sources [2-4,14,15]. Other possible CO₂ and CO contributors include adsorbed CO₂, the thermal decomposition of carbonates, the oxidation of organic matter, and the release of organic compounds trapped within minerals [2]. In this work, we performed SAM-like analyses of oxalates and acetates as pure standards and in Mars-relevant synthetic mixtures. We compared our laboratory data with SAM flight data, in order to examine whether SAM results are consistent with the potential presence of organic salts in Gale crater.

Materials and Methods Iron, calcium, and magnesium oxalates and acetates were examined by SAM-like evolved gas analysis (EGA) experiments using a Frontier Laboratories 3030D multi-shot pyrolyzer connected to an Agilent 5975T low thermal mass gas chromatograph/ mass spectrometer. The samples were heated to 850°C at a ramp rate of 35°C/min. In addition to examining the pure standards, the organic salts were dispersed in an amorphous fused silica matrix and subsamples of each silica mixture were pyrolyzed in the presence of Ca or Mg perchlorate. A range of calcite masses were pyrolyzed in order to construct a CO₂ calibration curve and enable quantification of the CO₂ releases from the organic salt experiments.

Results: The oxalate standards evolved sharp CO₂ peaks over a wide temperature range during SAM-like EGA (Fig. 1). The majority of the oxalate CO₂ peaks were accompanied by strong CO releases, while the acetates produced CO₂ peaks that were associated with an array of organic products dominated by acetone and acetic acid. Dispersal within silica was found to alter the relative abundances of the organic salt pyrolysis products and appeared to impede the standard thermal decomposition of organic salts that form carbonate residues.

Perchlorates shifted Fe oxalate CO₂ peaks to lower temperatures and scrubbed the CO releases. The Ca and Mg oxalate CO₂ and CO peaks did not shift but the CO peak intensity decreased. Perchlorates greatly strengthened the CO₂ releases from acetates at the expense of acetone and acetic acid. Many of the acetate-perchlorate mixtures evolved chloromethane. When acetate concentrations were elevated relative to perchlorates, chloroacetone was observed. We also discovered that mixing Ca or Mg perchlorate with Fe-bearing organic salts shifted the perchlorate O₂ peaks to lower temperatures.

When perchlorates were absent or at low concentrations, oxalates produced $\sim 11 \pm 1.5$ $\mu\text{mol CO}_2/\text{mg}$ of oxalate and acetates $\sim 8 \pm 1.5$ $\mu\text{mol CO}_2/\text{mg}$ of acetate. When perchlorate concentrations were

elevated, oxalates produced $\sim 16 \pm 2 \mu\text{mol CO}_2/\text{mg}$ of oxalate and acetates $\sim 13 \pm 2 \mu\text{mol CO}_2/\text{mg}$ of acetate.

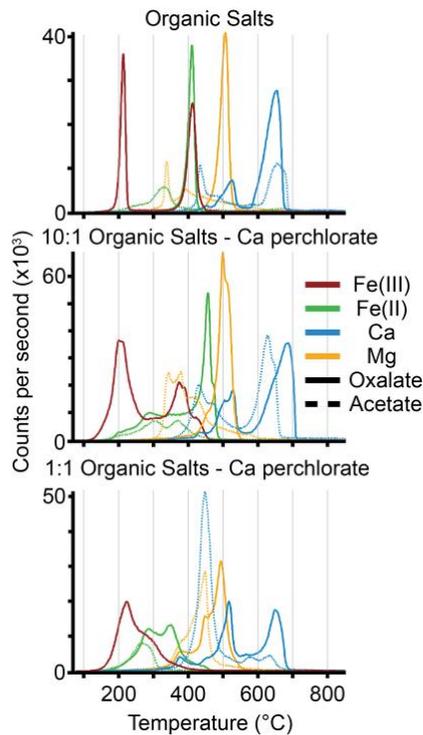


Figure 1. CO₂ evolutions detected during SAM-like EGA of a range of organic salts, 10:1 organic-salt-Ca-perchlorate mixtures, and 1:1 organic-salt-Ca-perchlorate mixtures.

Discussion: Organic-salt-perchlorate mixtures produced CO₂ peaks that were similar to many of the CO₂ releases evolved by Martian samples during SAM EGA. The best fits between laboratory and SAM data included SAM targets from modern eolian deposits and sedimentary rocks with evidence for low-temperature alteration, such as veining and alteration halos. The eolian materials produced complex CO₂ profiles that were consistent with our mixtures of Fe, Ca, and Mg oxalates and acetates with perchlorates. The first two drill samples analyzed by the rover were the John Klein (JK) and Cumberland (CB) targets acquired from the Sheepbed mudstone [2]. The major CO₂ and CO peaks evolved at $\sim 260\text{--}270^\circ\text{C}$ by both JK and CB were similar to those of our Fe(II)-acetate-perchlorate mixtures. JK produced additional CO₂ shoulders, with no associated CO peaks, that fit well with our Fe-oxalate-perchlorate data. The JK drill hole was found to be more heavily veined than the CB drill hole [2]. If organic salts were the dominant contributors of CO₂ in JK and CB it suggests the alteration experienced by JK may have generated additional organic salts.

Many recent SAM analyses have lacked O₂ peaks indicative of oxychlorine phases [13]. If organic salts

were present in these samples, oxalate CO₂ peaks would be expected to be accompanied by prominent CO releases and acetate CO₂ peaks by acetone and acetic acid. Drill samples from the Vera Rubin Ridge (VRR) produced CO₂ releases that were extremely similar to our Fe(II) acetate data [14]. However, the lack of acetone and acetic acid in VRR data challenged an acetate explanation. Several samples from the clay-bearing Glen Torridon region produced CO₂ and CO profiles similar to those of our Fe(II) oxalate experiments but often at significantly lower temperatures. The numerous fits between SAM data and our Fe(II)-bearing organic salt data are not necessarily inconsistent with Martian samples that were deposited under oxidizing conditions, as Fe(III) oxalate has been shown to decompose to Fe(II) oxalate under gamma radiation [15].

Comparing our quantitative laboratory data with the abundances of CO₂ evolved by SAM samples enabled upper limits for organic salt concentrations to be calculated. While most SAM samples had low upper limits, a few targets, including the eolian materials and JK, had upper limits on the order of 0.5-1.5 wt.%.

The shift of the perchlorate O₂ peaks to lower temperatures in the presence of Fe-bearing organic salts in our experiments produced O₂ profiles that fit well with many SAM O₂ releases. Our acetate-perchlorate mixtures produced low-temperature chloromethane evolutions similar to those seen in SAM samples such as the Rocknest eolian deposit. We did not identify chloroacetone in our analyses of Mars pyrolysis data.

Conclusions: The numerous fits between SAM data and our laboratory data support hypotheses that organic salts could be widespread phases in Gale crater. The most compelling fits occurred for perchlorate-bearing modern eolian samples and sedimentary rocks with evidence for low-temperature alteration.

References: [1] Leshin L. et al. (2013) *Science*, 341. [2] Sutter B. et al. (2017) *JGR: Planets*, 122. [3] Stern J. C. et al. (2018) *GRL*, 45. [4] Franz H. B. et al. (2020) *Nature Astronomy*, 4. [5] Freissinet C. et al. (2015) *JGR: Planets*, 120. [6] Eigenbrode J. L. et al. (2018) *Science*, 360. [7] Szopa C. et al. (2020) *Astrobiology*, 20. [8] Hofmann and Bernasconi (1998) *Chemical Geology*, 149. [9] Benner S. A. et al. (2000) *PNAS*, 97. [10] Applin D. M. et al. (2015) *EPSL*, 420. [11] Fox A. C. et al. (2019) *JGR: Planets*, 124. [12] Galwey A. K. & Brown M. E. (1999) *Elsevier* [13] Bamford C. H. and Tipper C. F. H. (1980) *Elsevier* [14] Eigenbrode J. L. et al. (2014) *LPSC XLV* [15] Ming D. W. et al. (2014) *Science*, 343. [16] Archer P. D. et al. (2018) *AGU Fall Meeting* [17] McAdam A. C. et al. (2020) *JGR: Planets*, 125. [18] Saito N. et al. (1965) *Bulletin of the Chemical Society of Japan*.