

THE SEARCH FOR ORGANIC MINERALS ON MARS. J. M. T. Lewis^{1,2,3}, J. L. Eigenbrode², G. M. Wong⁴, A. C. McAdam², M. Millan^{2,5}, R. H. Williams^{1,2,6}, M. Guzman⁷, E. B. Rampe⁸, C. N. Achilles^{2,9}, H. B. Franz², B. Sutter⁸, P. D. Archer⁸, S. Andrejkovicova¹⁰, C. A. Knudson^{1,2,6}, M. Craddock¹¹, and P. R. Mahaffy², ¹Department of Physics and Astronomy, Howard University, Washington D.C. (james.m.lewis@nasa.gov), ²NASA GSFC, Greenbelt, MD, ³Center for Research and Exploration in Space Science and Technology, NASA GSFC, Greenbelt, MD, ⁴Department of Geosciences, Pennsylvania State University, University Park, PA, ⁵Georgetown University, Washington D.C., ⁶University of Maryland College Park, College Park, MD, ⁷LATMOS, Guyancourt, France, ⁸NASA JSC, Houston, TX, ⁹USRA, Columbia, MD, ¹⁰Geosciences Department, Aveiro University, Portugal, ¹¹Virginia Polytechnic Institute and State University, Blacksburg, VA.

Introduction: The surface of Mars is exposed to high levels of ionizing radiation, which can decompose indigenous and exogenous organic compounds and generate powerful oxidants via the radiolysis of water [1-3]. In such an environment, much of the organic matter on the Martian surface may have been transformed into metastable carboxylate salts, such as oxalates and acetates [4,5].

On Earth, oxalates are the most common type of organic mineral and can be formed by biological processes, thermal degradation, and radiolysis [6,7]. They are found in settings such as carbonate concretions, marine and lake sediments, and hydrothermal veins [6]. Ca, Mg, and Fe oxalates have low solubilities and therefore resist physical and chemical degradation [6]. Oxalates persist in environments challenging to life, where oxalotrophic processes cannot operate [7]. It is therefore reasonable to assume that organic minerals could be an important component of the present-day Martian carbon cycle.

Understanding the organic chemistry of Mars. Multiple missions have been sent to the Martian surface to hunt for organic compounds [8-10]. These probes have primarily made use of a technique called pyrolysis, where Martian materials are heated to high temperatures in an attempt to extract organic fragments [8-10]. CO₂ has been a ubiquitous product of such experiments (Fig. 1) [11]. The potential sources of this CO₂ include magmatic carbon, carbonates, and organic matter [11]. Organic matter can generate CO₂ via oxidation or the decarboxylation of carboxylic acids or carboxylates [12,13].

The thermal decomposition products of oxalates are simply CO₂ and CO, so their presence on the Martian surface cannot be ruled out by existing pyrolysis data [4]. Acetates evolve acetone and acetic acid in addition to CO₂ and CO. Organic-detection experiments on Mars have identified simple organic molecules, such as chloromethanes, chlorobenzene, and thiophenes, but no indigenous acetone or acetic acid have been observed [14,15]. For this reason, acetates were ruled out as a potential phase at the Martian surface localities investigated so far [4].

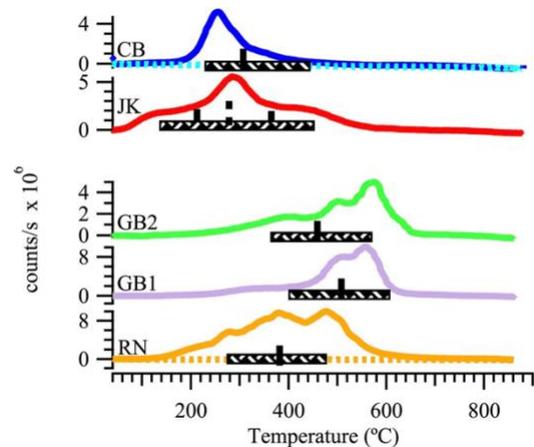


Figure 1. CO₂ evolved during pyrolysis of the eolian materials Rocknest (RN) and Gobabeb (GB), and the drilled samples John Klein (JK) and Cumberland (CB) by the Sample Analysis at Mars (SAM) instrument suite. The cross-hatched bars indicate the range of O₂ evolutions in each sample (Sutter et al., 2017).

Minerals can have a significant impact on how organic matter behaves during pyrolysis [16,17]. Salts that thermally decompose to release O₂, such as perchlorates and sulfates, are known to be widespread on Mars [16,17]. Perchlorates are particularly problematic because they evolve Cl (in addition to O₂) and produce chlorides, which can chlorinate organic molecules [16].

In this work, we assess whether organic minerals are a plausible explanation for any of the CO₂ evolved by Martian samples during pyrolysis. We examine the decomposition of pure organic salts, how organic salts behave when present as a trace phase in a matrix, and how oxalates and acetates respond to the presence of perchlorates during pyrolysis.

Materials and Methods: A range of oxalate and acetate standards were analyzed by a Frontier Labs 3030D multi-shot pyrolyser connected to an Agilent 5975 mass spectrometer. The samples were subjected to pyrolysis conditions similar to those used by the Sample Analysis at Mars (SAM) instrument suite on board Curiosity rover [10]. The organic salts were heated at a

rate of 35°C/min up to 850°C, with the evolved gases swept by a helium flow to the mass analyzer.

The organic salts were pyrolyzed as pure samples, as trace phases in an inert fused silica matrix, and in the presence of different perchlorate salts. Ca, Mg and Fe(III) perchlorates were used as they are Mars-relevant and evolve O₂ and Cl/HCl at a range of different temperatures.

Results: The oxalates and acetates studied in this work produced a diverse set of CO₂ peaks over a wide temperature range during SAM-like pyrolysis (Table 1).

Table 1. CO₂ peaks detected during the pyrolysis of organic salts

Organic Salt	CO ₂ peaks (°C)
Fe(III) oxalate	200, 400
Fe(II) oxalate	418
Ca oxalate	535, 730
Mg oxalate	518
Fe(II) acetate	300
Ca acetate	450, 730
Mg acetate	400

Fe(III) oxalate began to evolve CO₂ from ~160°C and Fe(II) acetate from ~195°C. The CaCO₃ intermediates generated during the decomposition of Ca oxalate and Ca acetate evolved CO₂ up to ~750°C. The majority of oxalate CO₂ peaks were accompanied by strong CO releases. Acetate CO₂ evolutions co-occurred with strong peaks for acetone, and minor peaks for acetic acid and CO.

Pyrolysis in fused silica. Dispersing the organic salts in an inert fused silica matrix generally caused minor peak shifts during SAM-like pyrolysis. For example, the CO₂ peak produced by pure Fe(III) oxalate at 400°C shifted to 410°C, while the CO₂ peak evolved by Ca-oxalate-derived CaCO₃ shifted 80°C lower. For acetates, the acetone peak weakened in fused silica, while the acetic acid profiles were largely unchanged.

The impact of perchlorates. The different organic salts examined in this project exhibited a range of responses when pyrolyzed in the presence of perchlorates. Iron oxalates were particularly sensitive to O₂, both Fe(III) and Fe(II) oxalate formed a single broad CO₂ peak at ~220°C rather than evolving sharp distinct CO₂ peaks at 400°C. CO was not evolved by the iron oxalate-perchlorate mixtures. Ca and Mg oxalate were less impacted by perchlorates, the CO₂ and CO peaks observed between 500-550°C did not shift significantly, however the CaCO₃ CO₂ peak did weaken. The CO peaks also weakened but remained detectable.

Perchlorates generally caused the CO₂ and CO releases from acetates to strengthen and shift to slightly lower temperatures. Fe(II) acetate no longer produced detectable acetone or acetic acid. Ca and Mg acetate showed a significant weakening of their acetone and acetic acid evolutions but peaks were still observed. Chloromethane was produced by all of the acetate-perchlorate mixtures.

Implications: The majority of SAM CO₂ and CO peaks could be explained by different combinations of oxalates, acetates, and perchlorates. Iron-oxalate-perchlorate mixtures would be expected to produce low-temperature CO₂ with no associated CO, while samples containing iron acetates and perchlorates could produce low-temperature CO₂, CO and chloromethane peaks, with the acetone and acetic acid scrubbed by the perchlorate.

In the absence of perchlorates, the CO releases from oxalates would be expected to strengthen and the acetone and acetic acid evolved by acetates could become detectable. However, the acetone peak would likely remain weak if the acetate was present as a trace phase in a matrix, making it challenging to differentiate from instrument backgrounds [15].

The eolian samples analyzed by SAM have all evolved CO₂ peaks at ~500°C (Fig. 1) [11]. Mg and Ca oxalates evolve CO₂ at around the same temperature and have demonstrated a remarkable resistance to peak shifting when diluted in a matrix or mixed with perchlorates. Martian dust may therefore contain a Mg and/or Ca oxalate component. Further pyrolysis experiments of eolian materials should be conducted, along with studies by X-ray diffraction and remote sensing [18].

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