

ANALYZING THE ORGANIC CHEMISTRY OF HESPERIAN MARS. J. M. T. Lewis^{1,2,3}, J. L. Eigenbrode², X. Li^{2,3,4}, D. Bower^{2,3,5}, G. M. Wong⁶, A. C. McAdam², M. Millan^{2,7}, S. T. Wieman^{2,3,4}, J. Stern², R. V. Morris⁸, R. H. Williams^{2,3,5}, C. A. Knudson^{2,3,5}, C. Achilles^{2,9}, C. Freissinet¹⁰, and S Andrejkovicova¹¹, 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, ⁴University of Maryland, Baltimore County, Baltimore, MD, ⁵University of Maryland College Park, College Park, MD, ⁶Department of Geosciences, Pennsylvania State University, University Park, PA, ⁷Georgetown University, Washington D.C., ⁸NASA JSC, Houston, TX, ⁹USRA, Columbia, MD, ¹⁰LATMOS, Guyancourt, France, ¹¹Geosciences Department, Aveiro University, Portugal.

Introduction: Ancient Noachian terrains on Mars preserve evidence of significant aqueous activity, including bodies of water that would have been habitable to terrestrial life [1,2]. The transition from these relatively Earth-like conditions to the desiccated deserts of the Amazonian was marked by a period dominated by acidic alteration, known as the Hesperian [3]. These environmental changes were triggered by thinning of the Martian atmosphere, which caused erupting lavas to degas significant amounts of sulfur volatiles [4]. The resulting sulfur-dominated, low-pH conditions were conducive to the widespread formation of the iron sulfate mineral jarosite [5]. In our efforts to understand if molecular evidence of ancient life is preserved on Mars, there is a clear need to understand how low-pH fluids and jarosite would have interacted with the Noachian and Hesperian organic records.

Jarosite-group minerals have the general formula $A(\text{Fe}^{3+})_3(\text{SO}_4)_2(\text{OH})_6$, where the A site can be occupied by ions such as K, Na, and H_3O [6]. Jarosite is a useful environmental indicator because it only forms in acidic aqueous conditions, but it remains stable for geological timescales only in extremely arid environments [5]. K-bearing jarosite is the most thermodynamically stable form, and if present in sufficient abundance it can be used for K-Ar age dating [5,7].

Jarosite was identified on the surface of Mars by the MER-B rover Opportunity as a major phase in the Burn's formation [8]. Mars Reconnaissance Orbiter has detected jarosite spectral signatures in locations such as Melas Chasma and Noctis Labyrinthus [9,10]. The Chemistry and Mineralogy (CheMin) instrument on board the Mars Science Laboratory (MSL) rover Curiosity has identified jarosite in multiple drilled samples in its study site of Gale crater using X-ray diffraction (XRD) [11]. K-Ar dating of jarosite in MSL's Mojave-2 drill sample by the Sample Analysis at Mars (SAM) instrument suite gave a relatively young age of 2.12 Ga [12].

Past and present organic-detection experiments on Mars have primarily made use of thermal extraction in combination with mass spectrometry [13-15]. Future endeavors will employ laser desorption/ionization mass spectrometry (LDI-MS) and Raman spectroscopy

[16,17]. Previous research has focused on how the O_2 released by jarosite during thermal decomposition may complicate our ability to detect Martian organic matter [18]. However, MSL's Mojave-2 sample, which contained several weight percent jarosite, evolved a number of different organic fragments during pyrolysis by SAM [19].

Minerals that decompose at high-temperatures during SAM-like pyrolysis, such as sulfates, may be releasing organic fragments that were trapped within their crystal structures [20]. Such behavior has been demonstrated in the laboratory by Mg sulfate and phthalic acid mixtures [21]. In this work we investigate if synthetic jarosite can also trap phthalic acid and release its fragments upon thermal decomposition.

Material and methods: K and Na jarosites were synthesized in glass vials within a sealed Parr acid-digestion vessel at 110°C using a method adapted from that of Basciano & Peterson (2008) [6]. Once successful synthesis procedures were established, phthalic acid was added to the starting reagents at a concentration of 3 wt.%, in order to examine how organic matter would interact with jarosite during its crystallization. The precipitated jarosite and jarosite-organic mixtures were rinsed in DI water and dried at room temperature. Each sample was then homogenized in a pestle and mortar.

The jarosite powders were first analyzed by XRD and Fourier Transform Infrared Spectroscopy (FTIR). Subsamples were pyrolyzed by SAM-like Evolved Gas Analysis (EGA) using a ramp rate of 35°C/min. LDI-MS was carried out on a Bruker autospeed MALDI-TOF (Matrix Assisted Laser Desorption/Ionization-Time-of-Flight) mass spectrometer. Surfaces were ablated with a 355 nm laser at a frequency of up to 1000 Hz. Analyses were conducted in both positive and negative mode.

Results: XRD and FTIR identified the precipitates as K and Na jarosite. In previous benchtop synthesis experiments in a glass beaker, powders were formed that were also identified as jarosite by XRD and FTIR. However, when these materials were analyzed by EGA they dehydrated at temperatures much lower than expected for jarosite. The jarosite produced by the new synthesis method with the Parr pressure vessel also

produced a low-temperature water peak but a far stronger water peak was observed at the temperature expected for jarosite dehydration (Fig. 1). A significant SO₂ peak was evolved by jarosite decomposition, with the onset starting at ~500°C and peaking at 700°C.

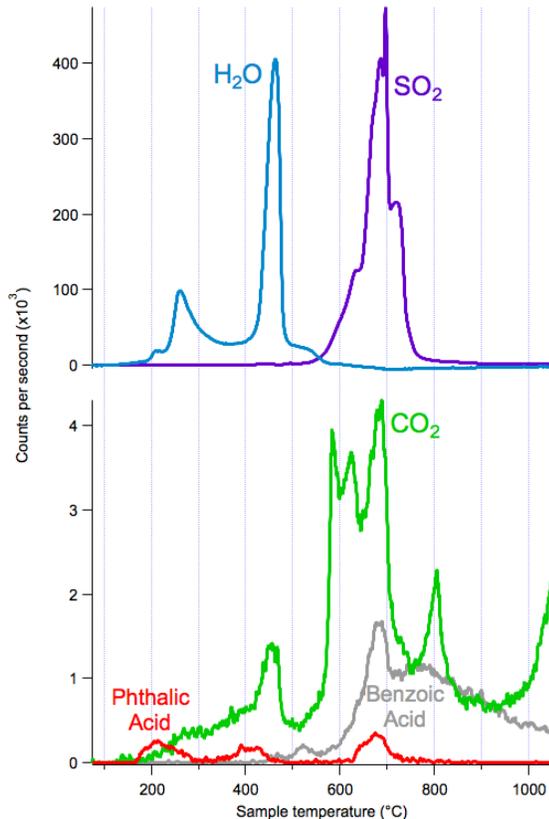


Figure 1. Evolved volatiles versus temperature during SAM-like EGA of synthetic K jarosite with 3 wt.% phthalic acid.

Three evolutions of the base peak of phthalic acid (m/z 104) were seen. The first occurred at the same temperature at which phthalic acid decomposes on its own. The second occurred with major CO₂ and H₂O peaks and a minor SO₂ release. This suggests some of the phthalic acid may have been adsorbed onto the surface of the sulfate and was liberated as the jarosite dehydrated. The strongest organic release occurred with the major SO₂ peak from the decomposing jarosite. A peak for phthalic acid was seen but benzoic acid (m/z 105) evolved a much stronger peak at the same temperature. A benzene release was also detected. These observations suggest phthalic acid was incorporated into jarosite during its crystallization but it partially decomposed to benzoic acid and benzene through loss of carboxylic acid groups, either during the jarosite synthesis reaction or pyrolysis.

LDI-MS was unable to detect phthalic acid, benzoic acid or benzene in the jarosite-phthalic acid mixture in either positive or negative mode. It is likely that some of the phthalic acid may have been lost during rinsing of the precipitate and the organic concentration could be below 3 wt.%. Total carbon analyses of the sample are planned in order to confirm this.

Ca perchlorate was added to the jarosite-phthalic-acid mixture to examine if incorporation into an iron sulfate can offer protection from oxidation during pyrolysis. Very few organic fragments were detected indicating that unlike Mg sulfate, which decomposes at higher temperatures, jarosite is not particularly effective at sheltering organics from oxidation.

Implications: Like Mg sulfate, jarosite can incorporate phthalic acid during its crystallization and release organic fragments upon decomposition of the sulfate during pyrolysis. However, some decomposition of the phthalic acid occurred prior to release and oxidation of the jarosite-bound organics took place when perchlorates were present.

The jarosite deposits encountered by MSL so far appear to have been relatively young, rather than Hesperian in age [12]. MSL is currently driving towards sulfate-rich sediments and perchlorates have been absent in many recent MSL drill samples [22,23]. If older jarosite enrichments are encountered and perchlorate concentrations remain low, organic fragments trapped within jarosite may be liberated during SAM pyrolysis from ~600°C.

References: [1] Ehlmann B. L. et al. (2011) *Nature*, 479, 53-60. [2] Grotzinger J. P. et al. (2014) *Science*, 343. [3] Bibring J. P. et al. (2006). *Science*, 132, 400-404. [4] Gaillard F. et al. (2013) *Space Sci. Rev.*, 174, 251-300 [5] Stoffregen R. E. et al. (2000) *Rev. Min. Geo.*, 40, 453-479. [6] Basciano L. C. & Peterson R. C. (2008) *American Min.*, 93, 853-862. [7] Dutrizac J. E. & Jambor J. L. (2000) *Rev. Min. Geo.*, 40, 405-452. [8] Squyres S. W. et al. (2004) *Science*, 306, 1709-1714. [9] Milliken R. E. et al. (2008) *Geology*, 36, 847-850. [10] Weitz C. M. et al. (2011) *Icarus*, 205, 73-102. [11] Rampe E. B. et al. (2017) *EPSL*, 471, 172-185. [12] Martin P. E. et al. (2017) *JGR:Planets*, 122. [13] Biemann K. et al. (1977) *JGR*, 82, 4641-4658. [14] Guinn J. R. et al. (2008) *JGR:Planets*, 113. [15] Mahaffy P. R. et al. (2012) *Space Sci Rev*, 170, 401-478. [16] Vago J. L. et al. (2018) *Hab. Life Mars*, 309-347. [17] Williford K. H. et al. (2018) *Hab. Life Mars*, 275-308. [18] Lewis J. M. T. et al. (2015) *Astrobiology*, 15, 247-258. [19] Eigenbrode J. L. et al. (2018) *Science*, 360, 1096-1101. [20] Sutter B. et al. (2017) *JGR:Planets*, 122. [21] Francois P. et al. (2015) *JGR: Planets*, 121.