The Preservation and Detection of Lipids in Mars-Relevant Sulfates and Chlorides. J. M. T. Lewis[1,2], J. L. Eigenbrode[1], A. C. McAdam[1], A. A. Pavlov[1], X. Li[1,3], D. M. Bower[1,4], J. C. Stern[1], M. Millan[5], and C. Freissinet[6]
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Introduction: In terrestrial sediments the majority of life's molecular fossils are derived from cell membrane lipids such as oils, fats and waxes [1-3]. As lipids are essential for life on Earth it is reasonable to assume that martian life, if it ever existed, would also have employed lipids for structural integrity and as a barrier from the external environment [1-4]. The fatty acids used by terrestrial organisms are predominantly polymers of acetate and have even carbon numbers, with some of the most important being myristic acid (C14), palmitic acid (C16) and stearic acid (C18) [1-3]. In our search for life elsewhere in the Solar System, fatty acid distributions with an even-over-odd predominance are a molecular biosignature of great interest [1-3].

All of the organic detection experiments we have sent to Mars so far have used thermal extraction to attempt to liberate organic fragments from martian samples [5-7]. These experiments include ovens on board each Viking Lander, the Phoenix Lander's Thermal and Evolved Gas Analyzer (TEGA) and the Sample Analysis at Mars (SAM) instrument suite currently operating on the Mars Science Laboratory Curiosity rover [5-7]. The martian organics detected by these instruments include sulfurized and chlorinated species of unknown origin [8,9]. Exploring the interactions that can occur between organic matter and sulfur and chlorine phases, both in situ and within instrument ovens, is therefore of great importance in our attempts to decipher what the parent compounds of these detected species might be.

In this work, we investigate the roles that sulfur and chlorine phases might play in the preservation of fatty acids and our ability to detect them. Recent laboratory studies by Francois et al., (2016) have shown that magnesium sulfate can trap phthalic acid and release its pyrolysis fragments upon decomposition of the sulfate at high temperatures [10]. Our project aims to examine whether fatty acids such as myristic, palmitic and stearic acid can be incorporated into magnesium sulfates, iron sulfates and chlorides.

In addition to laboratory pyrolysis experiments, the ability of laser desorption-mass spectrometry (LD-MS) and Raman spectroscopy to examine mineral-hosted fatty acids will be studied. These techniques will be part of the science payloads of the upcoming ExoMars and Mars 2020 missions and are likely to also be utilized on future spacecraft in development [11-13].

Materials and Methods: Myristic acid was mixed with different Mars-relevant synthetic standards as they precipitated out of aqueous solution. The standards include magnesium sulfate, halite and jarosite. Each mixture was characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), optical microscopy and Scanning Electron Microscopy (SEM). Subsamples were analyzed on a commercial Evolved Gas Analysis (EGA) system with a SAM-like temperature ramp. In EGA samples are heated and the evolved gases are swept to a mass spectrometer by a helium carrier gas and detected by their mass-to-charge ratio.

LD-MS analyses were performed on a Bruker autospeed MALDI-TOF (Matrix Assisted Laser Desorption/Ionization-Time-of-Flight) mass spectrometer with a 355 nm laser ablating the surfaces of powdered samples at a frequency of up to 1000 Hz. The instrument features both positive and negative modes.

Spot scans of the samples were done using a WITec Alpha 300 confocal imaging Raman microscope with a 532 nm excitation source with 30-40 s acquisition times and 5-10 accumulations under low power (1-3 µW at the sample), as monitored with a power meter.

Initial Results: EGA of a magnesium sulfate-myristic acid mixture produced two distinct releases of fatty acid fragments (Fig. 1).

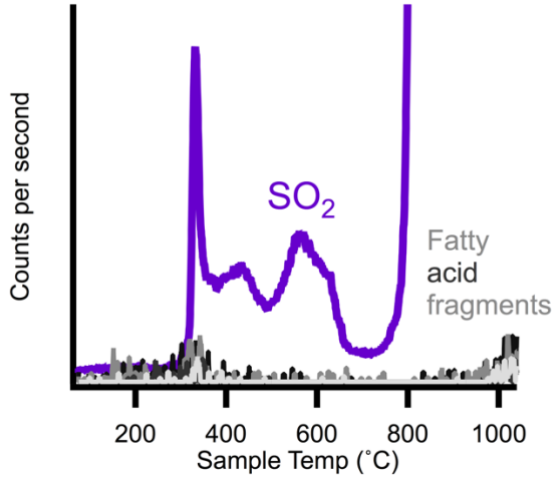

Figure 1. EGA plots for SO_2 (purple) and fatty acid fragments (grays) released by a myristic acid-magnesium sulfate mixture.

The first organic release occurred at the same temperature at which myristic acid decomposes on its own, but was accompanied by a small SO_2 peak, suggesting some of the fatty acid was adsorbed onto the surface of the sulfate. The second release occurred as the magnesium sulfate began to decompose around 800 ºC, indicating that incorporation of myristic acid into the sulfate had occurred during precipitation.

LD-MS, FTIR, and Raman spectroscopy were also able to detect fatty acid signatures in the myristic acid-magnesium sulfate mixture, further supporting the conclusion that the fatty acid was both incorporated and adsorbed onto the sulfate (Fig. 2).

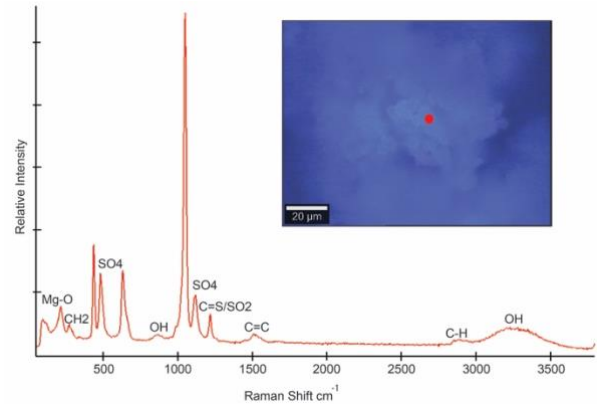

Figure 2. Raman spectrum of magnesium sulfate with adsorbed fatty acid.

The LD-MS experiments were performed without a MALDI matrix so negative mode was more efficient for detecting the de-protonated fatty acid parent ions (Fig. 3). LD-MS in current mission instruments, such as the Mars Organic Molecule Analyzer (MOMA) on the ExoMars rover, include positive mode only [14] but future flight LD-MS instruments may be capable of both positive and negative modes.

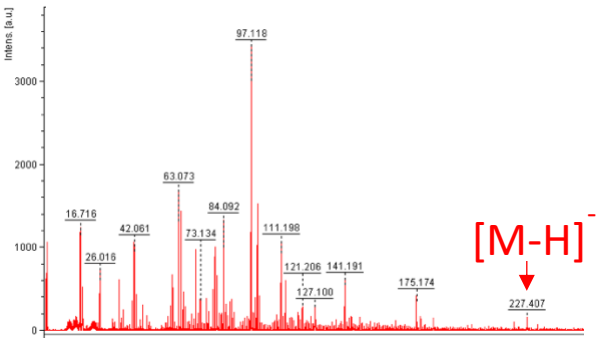

Figure 3. Mass spectrum acquired in negative mode LD-MS for magnesium sulfate with adsorbed fatty acid. The de-protonated parent ion of myristic acid is highlighted.

Ongoing and Future Work: We have successfully demonstrated that magnesium sulfate can incorporate myristic acid during its precipitation. As we develop our understanding of how myristic acid is incorporated into jarosite and halite, longer chain fatty acids will also be investigated, up to Lignoceric acid (C24). The eventual goal is to incorporate mixtures of fatty acids into minerals and examine whether a mineral-incorporated even-over-odd fatty acid distribution can be distinguished from an abiotic signal using flight-like methods.

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