Preservation of Biosignatures in Icelandic Hot Spring Deposits Spanning Acidic to Circumneutral Conditions

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Introduction: Organic biosignatures are key targets in the search for extraterrestrial life because they indicate processes unique to living oganisms (Des Marais et al., 2003, MEPAG, 2015, Singh et al., 2022). Mars is a prime candidate for life detection due to evidence of past liquid water, habitable conditions, preobiotic organics, and available energy sources (Grotzinger et al., 2014, Westall et al., 2015, Wordsworth 2016). Although no life is known to exist on Mars today, biosignatures from extinct life may be preserved in the rock record. Terrestrial analogs, such as iron-rich silica sinter from Icelandic hydrothermal systems, demonstrate how rapid silica precipitation can preserve molecular and physical biosignatures (Sanchez-Garcia et al., 2017, Kaur et al., 2011, and Campbell et al., 2015). This study evaluates GC-MS pyrolysis techniques to determine which methods most effectively detect preserved organic biosignatures under space-flight like conditions

Sample Location: Two Icelandic hydrothermal sites were sampled. Kerlingarfjöll (N64°38.728' W19°17.344'), a central volcano in the West Volcanic Zone, yielded seven acidic samples (pH 3.43–4.05) from Ca/Mg–sulfate–dominated waters. The second site near Helgrindur (Lýsuskarð/Lysuhóll) on the Snæfellsnes Peninsula (N64°50.651' W23°13.281') produced three circumneutral samples (pH 6.85–7.01) from Na/K–bicarbonate–dominated waters.

Methods: Thermochemolysis was used to combine heating and derivatization for GC-MS analysis (Boulesteix et al., 2023). Lipids were extracted using the Bligh and Dyer method and derivatized prior to analysis, while on-line thermochemolysis was performed directly within the GC-MS. For thermochemolysis, powdered samples were mixed 1:1 with reagent and loaded into pyro-cups; neat flash pyrolysis used 5–7 mg of powdered sample. Nonadecanoic acid methyl ester (nC19:0) or naphthalene-D8 served as internal standards. Pyrolysis was conducted using a Frontier Pyrolyzer 3030D coupled to either an Agilent 7890A–5975C inertXL or Thermo Fisher TSQ800 GC-MS with a 30 m Restek MXT-5 column. Analyses were run with a 280 °C interface, helium carrier gas at 1 mL min^{-1}, split flows of 20–50 mL min^{-1}, and an m/z range of 40–500, with compound identification via the NIST library.

Results: Bligh and Dyer extractions recovered both fatty acid methyl esters (FAMEs) and hydrocarbons from acidic and neutral fractions. Acidic extracts were dominated by mid-chain saturated FAMEs (C12:0–C18:0) and alkanes (C16–C23), forming a consistent molecular core, while short- and long-chain compounds occurred less frequently. Neutral extracts exhibited greater molecular diversity, with FAMEs extending to C26:0 and hydrocarbons to C33, including a broader range of unsaturated and branched species. Thermochemolysis with TMAH at 500 °C liberated abundant FAMEs (C8:0–C18:0) from both fractions, with acidic samples showing more continuous saturated distributions and neutral samples displaying greater variability. In contrast, TMSH flash pyrolysis at 400 °C produced limited lipid diversity, yielding only a narrow suite of saturated FAMEs (C14:0–C18:0) in neutral samples and none in acidic samples. SAM-like pyrolysis conditions recovered a similarly restricted subset of short- to mid-chain hydrocarbons and FAMEs, highlighting strong methodological controls on lipid detectability. Together, these results demonstrate that solvent extraction and high-temperature thermochemolysis recover broader and more diverse lipid inventories than lower-temperature or SAM-analog pyrolysis approaches. Figure 1 shows the distribution of FAMES in the neutral faction of samples analyzed with TMAH flash pyrolysis at 500˚C.

Discussion: The combined results indicate that lipid molecular diversity is intrinsic to the samples but is differentially revealed depending on analytical approach. Methods that access a broader fraction of the preserved organic inventory consistently recover mid-chain saturated fatty acids and alkanes, suggesting these compounds represent a stable and resilient molecular signature under conditions relevant to Mars. In contrast, short-chain, branched, and long-chain lipids appear less frequently, consistent with increased susceptibility to degradation or reduced preservation potential in oxidizing or radiation-exposed environments. These patterns imply that mid-chain saturated lipids are more likely to persist and remain detectable over geological timescales on Mars. Together, the results support the targeting of robust lipid classes when assessing organic preservation and biosignature potential in Martian analog settings.

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Figure 1

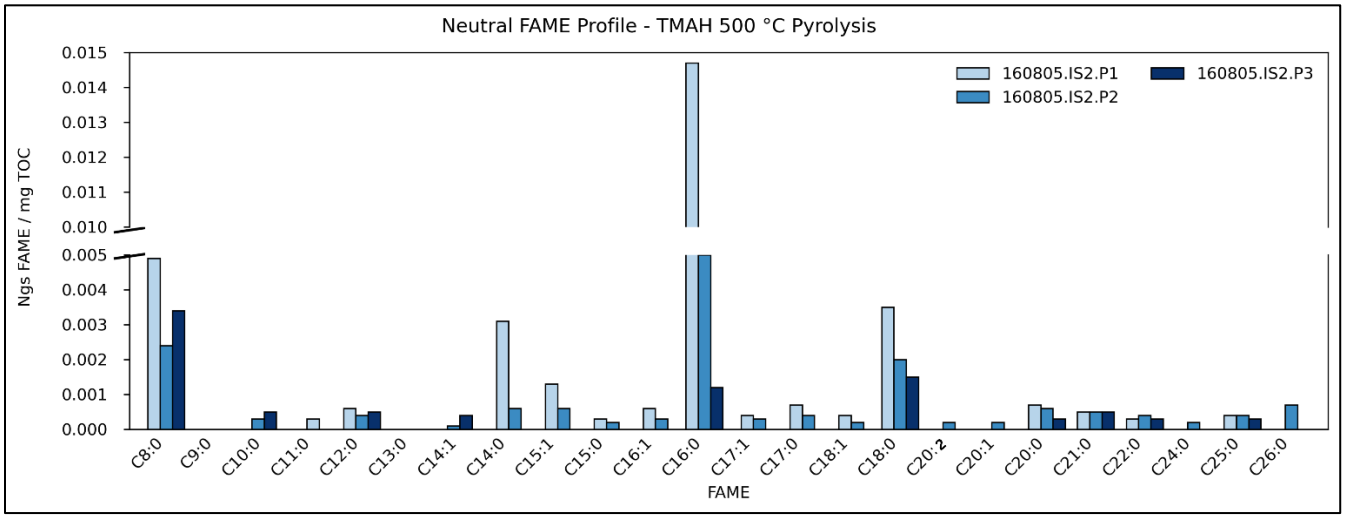

Figure 1: Shows the abundance and unique FAMES of the neutral sample set analyzed with TMAH pyrolysis at 500˚C.