

MOLECULAR BIOSIGNATURE PRESERVATION POTENTIAL IN SUBSURFACE MARTIAN BRINES.

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Introduction: The presence of chloride and sulfate minerals indicate that acidic saline lakes may have been found on ancient Mars [1,2]. On Earth, sediment samples from acid brine lakes have been considered an excellent Martian analogue and shown promising abundances of lipids [3]. Such environments may be able to preserve microorganisms and organic compounds through entombment and fluid inclusions, even over geologic time scales [4]. In general, organic matter analyzed from a geologic environment can fall into three categories: abiotic compounds that are not associated with biological organisms, biogenic compounds produced by biological organisms, and thermogenic compounds derived from the thermal decomposition of biologically generated compounds undergoing diagenetic processes [5]. The report of the Mars 2020 Science Definition Team [6] states that “the scientific significance of any potential sign of past life comes not only from the probability of life having produced it, but also from the improbability of non-biological processes producing it.” Therefore, it is critical that biosignatures used to evidence past or present life on Mars are not only biogenic or thermogenic, but discernable from abiotic compounds despite significant diagenetic or fluid alteration processes.

Near the end of the Martian Noachian period, salt-saturated solutions became prevalent in groundwater environments and the surface hydrological environment subsisted. During this transition, brine solutions may have presented a barrier to habitability [8] as well as biosignature preservation. Thus, it is necessary to understand how molecular biosignatures are preserved, degraded, and transformed in such environments. In this study, we aim to provide a fuller understanding of preservation potential by considering several variables, including pressure, temperature, the mineral matrix environment, and fluid chemistry. This research expands previous anhydrous work [7] to investigate the influence of lower pressure regimes, especially in a dynamic fluid/brine environment.

Experimental Methods: Using batch reaction vessels (Fig.1) at the University of Edinburgh, experiments were conducted under various pressure-temperature regimes to simulate subsurface rock-brine reactions.



Fig. 1. Batch reaction vessels capable of 15 MPa pressure and up to 80 °C for a wide variety of rock and fluid types, as well as fluid sampling for further analysis.

The temperature and pressure conditions relevant to the Martian crust are shown in Fig. 2. An endolithic and organic-rich natural calcite deposited from a CO₂-rich hot spring served as the starting material [7]. Three fluids were studied near the Noachian gradient and magmatism regions with different acidities, salinities, and fluid compositions based on previous studies [9]. These included pure H₂O, a NaCl brine, and an acidic brine of NaCl, MgCl₂, and KCl.

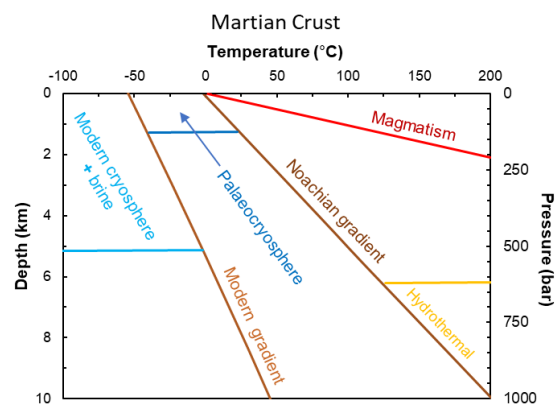


Fig. 2. Schematic showing pressure-temperature regimes in the modern and ancient Martian crust [10]. The Noachian gradient is of particular interest as higher temperatures increase thermal degradation products.

Organic Analysis: Biosignatures were analyzed by GC-MS and LC-MS, while ICP-MS, XRD, and Raman were used for additional sample characterization. Following the experiments, detectable biosignatures were generally below limits of detection on the GC-MS and LC-MS was used instead as it affords far greater sensitivity. For GC-MS, compound identification is possible by the comparison of mass spectra to reference databases, however, the identification of molecules detected in untargeted analysis by LC-MS remains a major impediment. Therefore, both analysis methods were employed. Comparisons of both the retention times and the mass spectra before and following the experiments reveal how the overall organic profile and specific biosignatures respond to temperature, pressure, and experimental duration. Although the identification of preserved compounds in high abundance can be relatively straightforward, the identification of minute quantities of degradation or newly synthesized products remains a challenge.

Results and Discussion: Results from brine experiments were compared to previous work on dry artificial thermal maturation experiments conducted at ambient pressure and atmosphere conditions as well as results from piston cylinder experiments at high-pressure and high-temperature conditions [7]. The use of the same starting material for these different experimental protocols allows for a direct comparison between results. An example of principal component analysis (PCA) for the anhydrous experiments is shown in Fig. 3, where the starting material signature is distinct from various degraded signatures as determined by mass spectra and retention times.

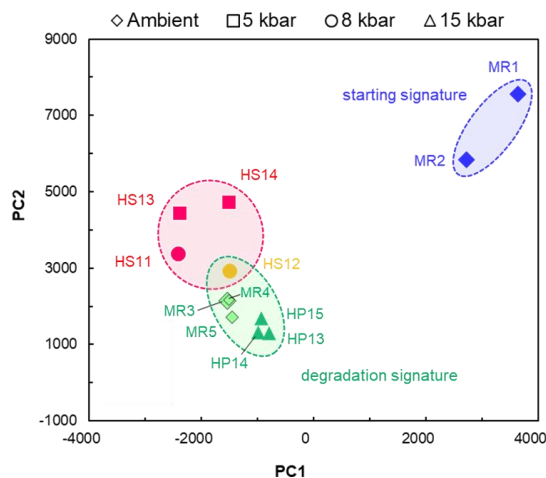


Fig. 3. PCA analysis of the GC-MS data from high pressure experiments demonstrates clear degradation signatures at high pressures.

Thus, under various subsurface regimes, the preservation potential of various molecular biosignatures can be estimated. In fluid conditions, the biosignatures behaved dramatically differently compared to nominally anhydrous environments, even under similar pressure and temperature environments. Fig. 4 shows the preservation of several compounds following an acidic brine experiment.

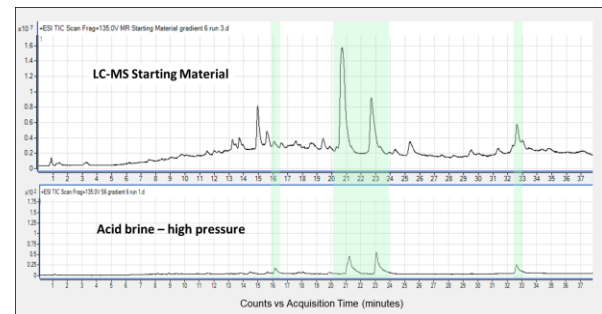


Fig. 4. LC-MS chromatograms comparing the starting material (top) to a sample treated in the batch reaction vessel in an acidic salt solution (bottom). Highlighted green peaks suggest preserved organic compounds.

Many compounds were highly mobile in the experimental fluids even when the structural integrity of the rock sample was maintained. A number of new compounds were also identified within the fluid, which likely represent degradation products and compounds produced through acid catalysis, hydrolysis or salt-organic reactions.

Additionally, the analytical chemistry protocols used for sample analysis were challenging for the detection of biosignatures at very low concentrations or with low analyte response. These results have implications for optimizing the analysis of Martian sediments for the detection of molecular biosignatures, both by rovers sent to Mars and for returned samples.

References: [1] Fukushi et al. K. (2019) *Nat. Commun.* 10: 4896. [2] Thomas N. H. et al. (2019) *Geophys. Res. Lett.* 46: 10754-10763. [3] Johnson S. S. et al. (2020) *Astrobiology* 20:167-178. [4] Gaboyer F. et al. (2017) *Sci. Rep.* 7, 8775. [5] McCollom T. M. and Seewald J. S. (2007) *Chem. Rev.* 107: 382-401. [6] Mustard J. F. et al. (2013) *MEPAG Report*, http://mepag.jpl.nasa.gov/reports/MEP/Mars_2020_SDT_Report_Final.pdf. [7] Bravenec A. D. et al. (2020) *LPS LI*, Abstract #1847. [8] Fox-Powell G. M. et al. (2016) *Astrobiology* 16:427-42. [9] Tosca et al. N. J. (2011) *J. Geophys. Res.* 116: E05004. [10] Michalski J. R. et al. (2013) *Nat. Geosci.* 6:133-138.