Detecting a Novel Biosignature Using Modern Spaceflight Technology. P.C. Gant[1], A.J. Williams[1], M.A.M. Floyd[2], D. Emerson[3], [1]University of Florida (pgant@ufl.edu), [2]Peatland Technologies, LLC, [3]Bigelow Laboratory for Ocean Sciences

Introduction: When searching for life on other planets, an organic biological signature is a key finding because it gives evidence to activity that is only possible by a living organism. Searching for habitable environments and signs of past or present life are key components of space exploration. Mars is an attractive target for the search for life because it is known from mission science that it once hosted habitable environments [1]. While there are no indications of life existing currently on Mars, there may be evidence of extinct life preserved in the Martian rock record. Biosignatures are defined as the chemical and/or morphologic remains of life preserved in rocks, sediments, and minerals [2]. The chemical remains can be organic, elemental, isotopic, or mineralogic.

Pterins: A Novel Metabolic Biosignature: Previous studies have identified organic molecules from the near surface of Mars, such as chlorobenzene in the Bagnold dune field at Gale Crater [3] and thiophens in the lacustrine mudstones at Gale Crater [4]. Here, we discuss the potential for a new class of metabolic biosignatures: pterins (Fig 1). Pterins are a part of the pteridines family, containing a nitrogen heterocycle with an amino group at position 2 and a keto group at position 4 [5]. Pterins are found in all domains of life, are widely conserved, and play an important part in metabolism [6].

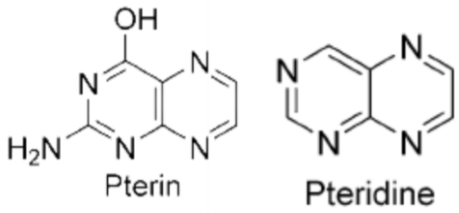

FIG 1. *Pterin and Pteridine structures. Adapted from* [7].

Floyd et al. [8] discovered a putative pterin signal using on-line (coupled directly with the GC-MS instead of off-line, which take place in a vial prior to the GC-MS step) thermochemolysis and GC-MS. Floyd et al. [8] tested both biological and geological samples and identified a small molecular weight (SMW) doublet signal in every sample that was known to contain iron oxidizing bacteria. Floyd et al. [8] identified a small molecular weight organic molecule that has double peaks when methylated with trimethylsulfonium hydroxide (TMSH) using thermal desorption GC-MS. Fig 2 is a representative chromatogram that shows preliminary data of the pterin signal found in a sample that has Mn and Fe coatings found in the Upper Florida Aquifer when derivatized with TMSH.

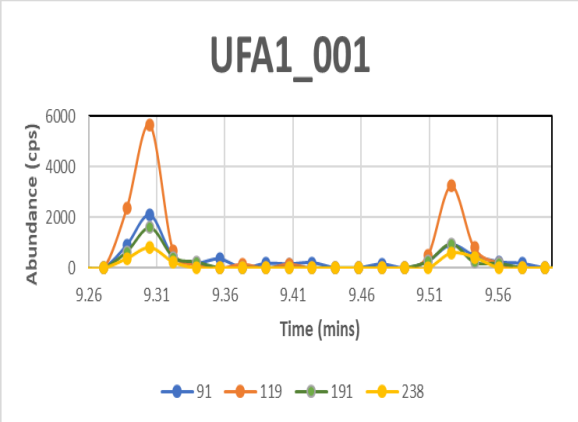

FIG 2. *Figure 2 shows a chromatograph of a sample generated by TMSH derivatization at 450˚C. Selected ions representing the pterin-bearing molecule are shown as individual colored lines on the graph.*

The pterin signal was not found when using tetramethylammonium hydroxide (TMAH) but there is evidence to suggest that the signal is silylated with N-tert-butyldimethylsilyl-N-methyltrifluoroacetamide (MTBSTFA).

Methods: This work seeks to determine the limits of detection and limits of quantitation of the biomarker with TMSH thermochemolysis and the detectability of the biomarker with MTSBSTFA derivatization. A subset of samples was created using preliminary data that has already been collected to place the samples in one of two categories, either high or low relative signal, with high being identified as the pterin signal is present and has the highest abundance (counts per second) and low being defined as the pterin signal is present but it has a low abundance. Additionally, a pterin 6-COOH standard will be analyzed as well. Each of the samples in this subset will be derivatized with TMSH and MTBSTFA, analyzed in triplicate, and then the limit of the blank (LOB), LOD, and LOQ will be calculated using the following three equations:

1. LOB = mean blank + 1.645(Std Dev blank)
2. LOD = LOB + 1.645(Std Dev low concentration sample)
3. LOQ ≥ LOD, where the critical value = 20%

Future Implications: Knowing where to look for biosignatures will influence landing site recommendations for future Mars missions, sample site investigations, and ultimately give key insight into extant life on Mars. Current spaceflight technologies are equipped with an GC-MS instrument that uses both TMAH and MTBSTFA. Neither the SAM instrument aboard the Mars Curiosity Rover nor the MOMA instrument aboard the ExoMars Rover are equipped with TMSH. Designing future missions with TMSH will open a new class of biosignatures to search for in the hunt to find microbial life on other worlds. Additionally, determining the biomarker detection availability with MTBSTFA opens previously collected data for re-interpretation and the potential for finding life on Mars.

References: [1] Grotzinger J. P. et al. (2014) *Science*, 343. [2] Westall F. et al. (2021) *Int. Journal Astrobiology*, 20.6. [3] Freissinet C. et al. (2015) *JGR*, 120.3, 495-514. [4] Eigenbrode J. L. et al. (2018) *Science*, 360, 1096-1101. [5] Basu P. and Burgmayer S. J. N. (2011*), Coordination chemistry reviews*, 255.9 – 10, 1016 – 1038. [6] Feirer N. and Fuqua C. (2017), *Pteridines*, 28.1, 23 – 36. [7] Marin – Yaseli M. R. et al. (2015), *Chemistry – A European Journal*, 21.39, 13531 – 13534. [8] Floyd M. A. M. (2019), *Astrobiology*, 19.1, 40 – 52.