Survivability of Prebiotic Molecules on Lunar Soils. J. L. McLain[1], L.H. Yeo[1,2], H.L. McLain[1,3], and D. Simkus[1,3]
[1]NASA Goddard Space Flight Center, [2]NASA NPP Fellow, and [3]Catholic University of America.
jason.l.mclain@nasa.gov

Introduction: One of the biggest curiosities from the Apollo-era was the discovery of small amounts of prebiotic molecules like amino acids and hydrocarbons on lunar dust samples. This study aims to constrain the origin of these organic molecules by simulating the lunar environment and, making use of recent advances in organic molecule detection technology, measuring their survivability on lunar regolith. These experiments are designed to mimic the conditions on the lunar surface and determine the lifetime and/or evolution of prebiotic molecules in that environment. This work is supported by the Lunar Environment And Dynamics for Exploration Research (LEADER) Institute along with NASA GSFC Analytical Astrobiology Lab (AAL).

Lunar soil samples are baked and irradiated under vacuum to chemically re-activate them. Their surfaces are then precision-dosed with prebiotic molecules before being exposed to radiation and vacuum conditions mimicking the lunar environment. AAL will quantify the concentrations of aliphatic amines in the samples and procedural blanks by ultrahigh performance liquid chromatography with UV fluorescence using a Waters ACQUITY H Class Plus UHPLC, and triple quadrupole mass spectrometry detection using a Waters Xevo TQ-S Micro triple quadrupole. The amino acid derivatization and subsequent LC-FD/QqQ-MS analysis used for this study was modeled after the amino acid method used by [1].

Discussion: This work addresses 3 overarching Artemis III Science plan objectives, namely: (1) Understanding planetary processes (2) Understanding the character and origin of lunar polar volatiles (3) Interpreting the impact history of the Earth-Moon system

One of the most stunning findings from the Apollo era was the discovery of organic compounds in lunar soil samples. Compounds like amino acids, urea, and hydrocarbons were detected by numerous studies in concentrations of up to 70 parts per billion [2–7]. Contemporaneously, an examination of the Murchison meteorite produced evidence of extraterrestrial amino acids, and hydrocarbons [8]. Today, it is widely accepted that active organic chemistry is prolific throughout the solar system. However, the historical presence and evolution of organic material on the Moon remains an area of open study. Organic compounds could have been delivered to the Moon in large quantities by meteoric and cometary bombardment, especially during the late heavy bombardment 4 billion years ago [9–10]. These bodies have been known to contain significant quantities of organic material [11, 12]. Further, rocks ejected from the Earth itself, where prebiotic matter was likely abundant, could be embedded and preserved on the Moon. Recent models suggest some amount of volatile retention is possible [14, 15]. This is of incredible significance as the preservation on the Moon of biotic or pre-biotic organic molecules contemporaneous to the development of life on Earth would provide an invaluable historical record that has been lost on Earth [16].

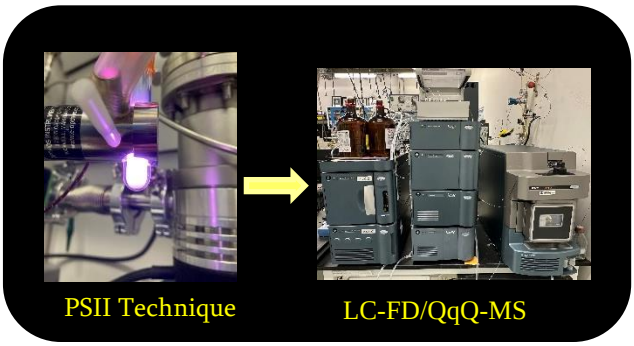

Figure 1. Pictures of the experimental vacuum manifold during an active H_2 plasma afterglow and the Waters ACQUITY/Xevo.

Experimental Procedure: The scope of this work will focus on three objectives: reactivation of lunar soils, exposure calibration standards for amino acids, and method development with the AAL, as listed below.

1. Reactivate Lunar Sample in Plasma Source Ion Implantation (PSII) Apparatus
2. Expose to prebiotic molecules
3. AAL work-up method development for detection

For Step 1, to simulate the environmental conditions on the lunar surface, we reactivate the sample surface with PSII prior to exposure prebiotic molecules. Starting with <100 mg of loose-grain lunar sample in a test tube, we begin with desiccating the lunar samples via heating in high vacuum. Curated lunar regolith samples available for this investigation compliments a recent study to determine the origin of amino acids in lunar samples by Elsila et al., Geochimica et Cosmochimica Acta 172 (2016)

Our PSII technique employs a RF discharge H_2 plasma electrically coupled through the glass test tube to an electrode. Hydrogen ions are driven into the soil

by an +/-8 keV in-house optocoupler circuit that we have nicknamed, Acceletron. The Acceletron is pulsed from ground potential to negative high voltage at ~1 kHz to replenish the plasma sheath above the sample surface with hydrogen ions. The degree to which this approach is effective will be measured for the first time. Previous attempts at reactivation include simple grinding as an analog to micrometeorite crushing [17], as well as UV irradiation on lunar simulant that resulted in a time-dependent increase in chemical reactivity.

For Step 2, the soil is exposed in vacuum to a specified amount of an amino acid vapor, e.g., alanine. This step also involves the creation of a blank (sample procedure without organics), a control (sample with specified amount of exposure) and the actual experiment (lunar sample plus irradiation).

For Step 3, the solid samples are taken to the AAL where they are derivatized with the AccQ·Tag protocol for analysis (1). The amino acids are detected and quantified in the standards, blanks, controls, and samples using LC-FD/QqQ-MS. Separation of amino acids is accomplished by injecting 1 µL of the AccQ•Tag derivatized sample onto an Acquity AccQ•Tag Ultra C18, 150 x 2.1 mm column (1.7 µm particle size) and detecting the analytes with fluorescence detection and Xevo TQ-S Micro Triple Quadrupole Multiple Reaction Monitoring mass spectrometry.

Figure 2 shows that the dosing of alanine works for this study and can be detected but more work is needed to make sure that this method is quantifiable and can be used to measure differences in attachment to the lunar surface vs. degradation.

The work-up includes concentrating the organic residues and standardizing the exposure to the detector calibrations by performing each test on the blank, control and the actual experiment.

Conclusion: We plan to present our up-to-date experimental data and on our method development, including reaction products and chemistry. Future studies will be directed at quantifying possibly peptide bond formation as a function of irradiation and lunar soil mineralogy.

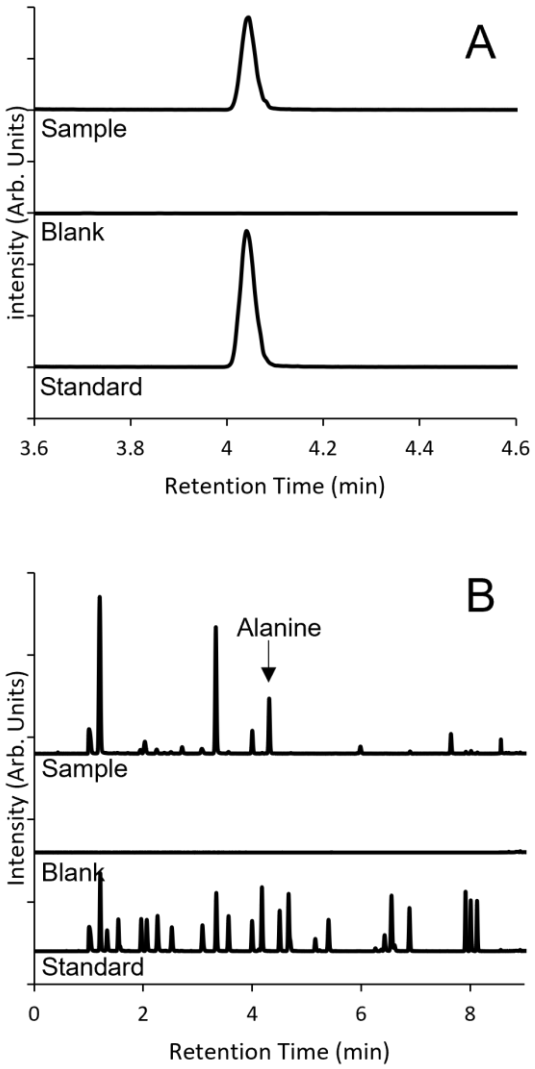

Figure 2. Positive electrospray, LC-FD/QqQ-MS chromatograms of dosed alanine derivatized amino acids on JSC-1A, procedural blank, compared to commercially available standards (all traces are on the same intensity scale). Figure 2A is the multiple reaction monitoring QqQ MS trace for derivatized alanine of 260.1 > 171.1. Figure 2B is the fluorescence trace for derivatized amino acids.

References: 1. A. A. Pavlov, et.al., Astrobio. 2022. 2. P. Hare, et al., Geochim Cosmochim. Acta 1970. 3. B. Nagy, et al., Science 167, 770–773 1970. 4. K. Harada, et al., Science 173, 433–435 1971. 5. B. Nagy, et al., Nature 232, 94–98 1971. 6. C. W. Gehrke, et al., Space Life Sci. 3, 197). 7. V. E. Modzeleski, et al., Nat. Phys. Sci. 242, 1973. 8. K. Kvenvolden, et al., Nature 228, 923–926 1970. 9. C. F. Chyba, et al., Science 249, 366–373 1990.

10. C. Chyba and C. Sagan, Nature 355, 1992.
11. P. Ehrenfreund, Annual Review A&A 38, 2000.
12. M. A. Sephton, Natural Product Rep. 19, 2002.
13. J. M. McDermott, et al., Proc. of the National Academy of Sciences 112, 2015.
14. L. Ong, et al., Icarus 207, 578–589, 2010.
15. B. D. Stewart, et al., Icarus 215, 1–16, 2011.
16. R. Matthewman, Astrobiology 16, 900–912, 2016.
17. W. T. Wallace, et al., Meteo. & Planet. Sci. 2009.