TRACE LEVELS OF VOLATILE ORGANIC COMPOUNDS AND CYANIDE IN THE APOLLO 73002 CORE SAMPLE.

J. E. Elsila[1,*], J. C. Aponte[1,2,3], J. P. Dworkin[1], D. P. Glavin[1], H. L. McLain[1,2,3], D. N. Simkus[1,2,3], and the ANGSA Science Team. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [2]Department of Physics, Catholic University of America, Washington, DC 20064, [3]Center for Research and Exploration in Space Science and Technology, NASA/GSFC, Greenbelt, MD 20771 *Email: Jamie.Elsila@nasa.gov

Introduction: Analyses of the organic content of lunar samples began soon after the initial return of Apollo regolith samples and has continued through the present day [1-6]. Amino acids were an early priority because of their significance to life on Earth, with multiple reported studies of amino acid content and distribution [1-5]. More recent work determined that detected amino acids were likely a combination of terrestrial contamination and meteoritic or cometary infall to the lunar surface [6]. In addition, a majority of the amino acids studied appeared to derive from precursor molecules that reacted to form amino acids during laboratory procedures including hot-water extraction and acid hydrolysis. The identity of these precursor molecules remained unknown but could include hydrogen cyanide (HCN) and volatile organic species such as amines, carboxylic acids, aldehydes and/or ketones [7-9].

It is unknown if these volatile organic compounds could be subject to loss under typical curation conditions at room temperature under nitrogen gas purge during the decades-long storage of Apollo samples. The special samples available through the Apollo Next Generation Sample Analysis (ANGSA) program [10] provide an opportunity to both search for potential volatile precursors and examine whether curation under different conditions (*e.g.*, vacuum sealed or freezing temperatures) may help preserve these volatile organics.

In this study, we have examined the first of the ANGSA samples made available for study, the 73002 core. This sample is from the top half of a double drive tube collected by Apollo 17 astronauts. The bottom portion (73001) was sealed under vacuum on the moon and will be opened in 2022. The top portion (73002) was not vacuum sealed, but the closed drive tube was curated under standard conditions until its opening in 2019 [10]. We have analyzed three samples from different depths within the drive tube for the presence of amino acids and their potential volatile precursors, including HCN, aldehydes, ketones, amines, and monocarboxylic acids. Future work will compare these results with samples from the 73001 core for additional depth and curation comparisons.

Methods: Three samples, each ~2 g, were taken from the Apollo 73002 core as indicated in Figure 1. The core was extruded from the drive tube in November 2019 and was dissected in three passes; each pass removed depths of ~1 cm in intervals of 0.5 cm along the length of the tube [11]. Sample 73002,1 was removed from the bottom few centimeters of the tube within 24 hours of extruding the sample in November 2019. Samples 73002,2009 and 73002,2027 were removed from intervals 5-7 and 18-20, respectively, during the third pass in May 2021 (delayed due to the ongoing global pandemic). All samples were unsieved. Corresponding contamination control coupons of ashed aluminum foil (~3 cm x 3 cm) that had been placed in the processing glovebox at the same time as the core were removed at the same time as each sample. Samples and witness foils were shipped in separate cleaned stainless-steel containers form the curation facility at NASA Johnson Space Center (JSC) to NASA Goddard Space Flight Center (GSFC); empty stainless-steel containers were also sent as additional contamination witness material.

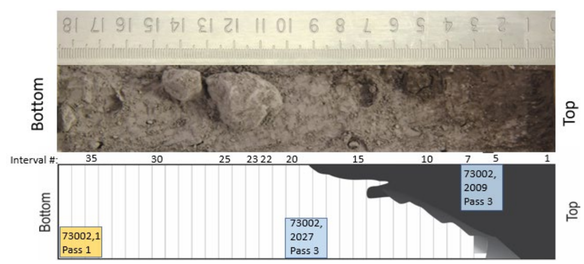

Figure 1. Location of three analyzed samples, representing various depths in the 73002 core: close to the lunar surface ("top", right side of photo), ~9 cm in depth (middle), and ~18 cm in depth ("bottom", left side of photo). See [11] for processing details.

At GSFC, samples and witness foils were processed in two batches, one in November 2019 and the other in May 2021. Each batch included two additional control samples: 1) a procedural blank, and 2) a pre-baked (500 °C, 24 hours) 2 g portion of JSC-1 lunar simulant [12] that was shaken inside the cleaned empty stainless-steel container sent from JSC. Each sample was sealed in an ampoule with ultra-pure water and heated at 100 °C for 24 hours. After extraction, each sample was then split into multiple portions, each designated for a specific organic analysis (Figure 2). Sample splitting and the methods for analysis have been described elsewhere [13].

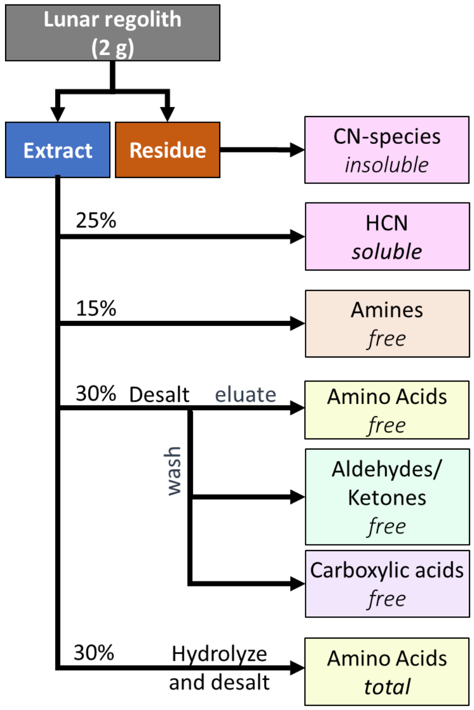

Figure 2. Hot-water extracts of each sample and control were split into multiple aliquots to allow analysis of multiple compound classes.

Discussion: Very low abundances of organic compounds were observed in all samples. Quantitation was difficult for many organic compounds due to observations of low concentrations of the same species in the witness materials.

Although no soluble cyanide species were observed in the hot-water extracts from the three lunar samples, insoluble cyanide-containing species were present in the extracted residues. The insoluble CN-species showed a correlation with sample depth, with concentrations in the order 73002,2009 (top of core) > 73002,2027 (middle of core) > 73002,1 (bottom of core). Both the detection of CN-species and the correlation with depth are consistent with previous analyses of Apollo lunar regolith samples [14]. This depth correlation could indicate that the CN-species are delivered exogenously and that the delivery rate is faster than any potential destruction processes, or could potentially indicate a correlation with mineralogy depth profile.

Trace levels of both free and total (released upon acid hydrolysis) amino acids were observed at the picogram-to-nanogram per gram (pptr-ppb) level. There is evidence of potential contamination observed in low levels of amino acids on witness materials and in excesses of the L-enantiomers in proteinogenic amino acids; however, the overall concentrations are low and indicate only minor contamination.

Although a few aldehydes and ketones, including formaldehyde and acetone, were detected at very low concentrations, similar concentrations were observed on the witness foils, indicating potential contamination sources. Further work is necessary to understand if any of these compounds are indigenous to the samples.

Methylamine was observed in the lunar samples, but as with the aldehydes and ketones, low levels of methylamine on the witness materials complicate the quantitation or determination of the origin of this compound. Ethylamine was also present on the witness foils at levels similar to those observed in the lunar regolith.

Dicarboxylic acids, including oxalic and succinic acids, were detected in the lunar samples but not present in witness materials. These compounds have not been previously reported from lunar regolith analyses.

These initial results from the Apollo 73002 core sample must be compared with future analyses from the 73001 sample to further understand depth profiles and the effect of curation on these volatile organics. However, the low abundances currently observed suggest that the standard curation processes are effective in minimizing terrestrial organic contamination of lunar samples. These results may be relevant not only to future lunar sample collection, but also to future human missions to Mars, indicating the ability for astronauts to collect martian sample cores cleanly enough to allow analysis of amino acids and other chemical biosignatures. In addition, this type of organic-poor lunar material may be able to play a role in future planetary protection experiments carried out with lunar astronauts during Artemis missions by serving as a natural blank sample.

References:

[1] Fox S. W. et al. (1973) *Proc. Fourth Lunar Sci. Conf.; Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2,* 2241-2248. [2] Fox S. W. et al. (1976) *Geochim. Cosmochim. Acta*, 40, 1069-1071. [3] Hare P. E. et al. (1970) *Proc. Apollo 11 Lunar Sci. Conf.; Geochim. Cosmochim. Acta, Suppl. 4, Vol. 2*, 1799-1803. [4] Harada K. et al. (1971) *Science*, 173, 433-435. [5] Nagy B. et al. (1971) *Nature*, 232, 94-98. [6] Elsila J. E. et al. (2016) *Geochim. Cosmochim. Acta*, 172, 357-369. [7] Yuasa S. et al. (1984*) J. Mol. Evol.*, 20, 52-58. [8] Biemann K. (1972) *Space Life Sci*., 3, 469-473. [9] Fox S. W. et al. (1972) *Space Life Sci*., 3, 425-431. [10] McCubbin F. M. et al. (2021) *LPSC LII*, Abstract #1541. [11] Gross J. et al.,(2021) *LPSC LII*, Abstract #2684. [12] McKay D. S. et al.,(1993) *LPSC XXIV,* Abstract #1483. [13] Elsila J. E. et al. (2020), *LPSC LI*, Abstract #1039. [14] Holland P. T. et al. (1972) *Proceedings of the Lunar Science Conference*, 2, 2131-2147.