ORGANIC COMPOUNDS AND CYANIDE IN THE APOLLO 17 SPECIALLY CURATED ANGSA SAMPLES. J. E. Elsila[1,*], J. C. Aponte[1], 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 Chemistry, Catholic University of America, Washington, DC 20064, [3]Center for Research and Exploration in Space Science and Technology, NASA/GSFC, Greenbelt, MD 20771, USA. *Email: Jamie.Elsila@nasa.gov

Introduction: Beginning in the Apollo era, studies of returned lunar samples have included efforts to understand their organic content [1-6]. Amino acids were a focus of many early studies because of the significance of these compounds to life on Earth; several studies reported amino acid contents and their molecular identities, but without a clear consensus on their origin [1-5]. More recent analyses concluded that some of the amino acids detected in returned lunar regolith samples likely resulted from terrestrial contamination, while others may have been delivered by meteoritic or cometary infall to the lunar surface [6]. The majority of the detected amino acids were produced upon hydrolysis of the lunar samples, suggesting their formation during laboratory analysis from the reaction of precursor molecules. Such precursors could include cyanides (CN^-) and organic species such as amines, carboxylic acids, and aldehydes[7-9].

These potential precursors include small, volatile molecules whose preservation in returned samples may be affected by the curation conditions under which the samples are stored, including temperature and exposure to atmospheric gases. The range of specially curated samples made available through the Apollo Next Generation Sample Analysis (ANGSA) program [10] allows the opportunity to examine these effects through the analysis of both frozen and vacuum-sealed samples and their comparison with samples curated under room temperature with exposure to nitrogen purge. Identifying and measuring the abundance and molecular distribution of amino acids and their potential precursors in these samples can answer science questions about the organic inventory on the lunar surface as well as provide guidance on the best way to preserve such compounds in the curation of future returned samples.

Our current study examined the content of amino acids and potential volatile precursors in 12 samples made available through ANGSA. These include samples from different depths within both halves of a double drive tube collected by Apollo 17 astronauts. The top half (73002) was curated under standard conditions until being opened in 2019 [10], while the bottom half (73001) was sealed under vacuum on the Moon and opened in 2022. We also analyzed frozen and non-frozen portions from three different Apollo 17 lunar sites (sunlit, partially shadowed, and completely shadowed). Figure 1 illustrates the locations and curation conditions of the samples in our study.

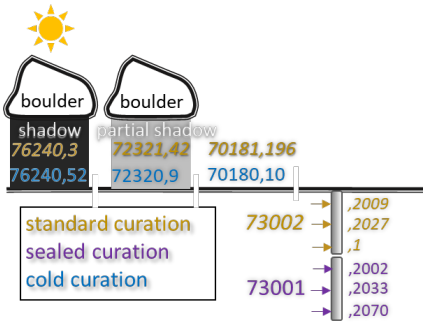

Figure 1. The 12 samples analyzed in this project include a range of surface illumination environments and core depths, as well as curation conditions including frozen and sealed vacuum storage.

Methods: Unsieved lunar samples were provided by the curation team at NASA Johnson Space Center (JSC). Corresponding aluminum foil contamination control coupons that were baked at 500 °C overnight and subsequently exposed to the same processing environment as the lunar samples were also provided. Samples and witness foils were shipped in separate cleaned stainless-steel containers from JSC to NASA Goddard Space Flight Center (GSFC); empty stainless-steel containers were also sent as additional contamination witness material. The frozen samples were sent in a cold shipping container, remained frozen throughout transit, and were placed in a –20 °C freezer upon arrival at GSFC.

At GSFC, samples and witness foils were processed in batches: 73002 samples in November 2019 and May 2021, 73001 in April 2022, and the frozen and standard-curation surface samples (76240, 72320/1, and 70180/1) in July 2022. Each batch also included two additional control samples: 1) a procedural blank, and 2) a pre-baked 2 g portion of JSC-1 lunar simulant [11] 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 split into multiple portions, each designated for a specific organic analysis as shown in Figure 2. Sample splitting and the methods for analysis have been described elsewhere [12].

Results and Discussion: Overall, low abundances of organic compounds were observed in most of the lunar samples analyzed in this study. Substantially higher abundances of many compounds were observed in the

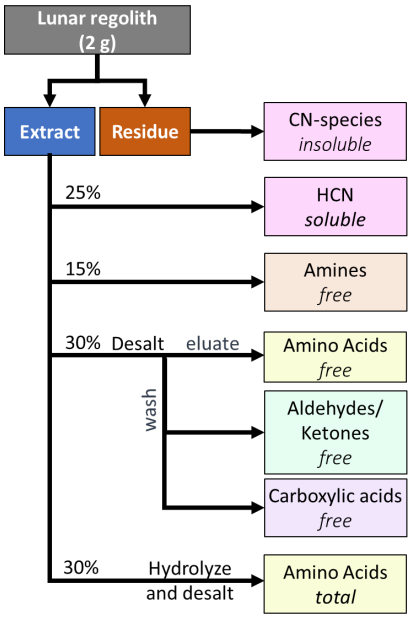

Figure 2. Hot-water extracts of each sample and control were split into aliquots to allow the targeted analysis of multiple compound classes.

shadowed sample curated at room temperature compared to all other samples. Quantitation was difficult for many organic compounds due to low concentrations of analytes in the samples. However, some qualitative trends were observed, as well as identification of some compounds not previously reported in lunar samples.

Amino acids: Amino acid abundances were low (pmol/g) compared to previous lunar analyses.

Cyanides: Insoluble cyanide species were observed with decreasing abundance correlating with increasing depth in the 73002 core. No insoluble cyanide was detected in the 73001 core. Insoluble cyanide was also observed in many of the surface samples, with no clear correlation between illumination or curation conditions.

Amines: Methylamine and ethylamine were observed in multiple samples. Low levels of these compounds were also present on some witness materials, complicating the quantitation and determination of the origin of these compounds.

Carboxylic acids: Formic acid and acetic acid were observed in samples from the 73001 core, decreasing with depth. They were also observed in the shadowed sample curated at room temperature. We believe this is the first report of these compounds in lunar samples

Aldehydes: We identified formaldehyde and acetaldehyde in low concentrations in all six surface samples, as well as in the 73001 core samples. To the best of our knowledge, this is the first report of these compounds in lunar samples. There was no observable correlation of abundance with core depth.

Sample variability: Although the low abundances led to difficulties in quantifying trends for most organic compounds, the correlation of decreasing abundances with increasing depth seen in insoluble cyanides and carboxylic acids suggests the importance of exogenous delivery of organics to the lunar surface. No obvious trends were observed with illumination conditions. The high abundances seen in the shadowed, room temperature sample (but not in its counterpart frozen sample) suggests heterogeneity perhaps from micrometeorite delivery.

Curation effects: The presence of aldehydes and acids in the sealed 73001 core but not the unsealed 73002 suggests that sealed curation may better preserve volatile species. However, we did not see a similar preservation effect when comparing frozen curation with room-temperature curation.

In addition, the low organic abundances 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.

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