ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN THE APOLLO NEXT GENERATION SAMPLE ANALYSIS (ANGSA) 73002 CORE SAMPLE. J. E. Elsila[1], J. C. Aponte[1,2], J. P. Dworkin[1], D. P. Glavin[1], H. L. McLain[1,2], D. N. Simkus[1,3], 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]NASA Postdoctoral Program, Universities Space Research Association, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771. Email: Jamie.Elsila@nasa.gov

Introduction: Understanding the organic content of lunar regolith was an early priority upon the return of Apollo samples, with amino acids being of special interest because of their importance to life on Earth and their astrobiological relevance. Many initial studies focused on the detection of amino acids in these samples and attempts to determine the origin of those compounds [1-5]. Although no consensus on the origin of the amino acids was reached in those early studies, more recent work determined that the detected amino acids originated from both terrestrial contamination and meteoritic or cometary infall to the lunar surface [6]. A majority of the amino acids in the Apollo samples studied originated from precursor molecules, either indigenous to the lunar samples or contaminants, that reacted during the water extraction and acid hydrolysis process for analysis in the laboratory, but the identities of the amino acid precursors still remain poorly understood. Such precursors could include hydrogen cyanide (HCN) and other volatile organic compounds such as amines, carboxylic acids, or aldehydes and ketones [7-9]. The identities of these compounds, as well as the effects of years of curation on their abundances in lunar regolith samples stored at ambient temperature under nitrogen gas purge, are not clear.

The specially curated samples available through the Apollo Next Generation Sample Analysis (ANGSA) program provide a unique opportunity to use state-of-the-art analytical techniques to examine previously unstudied lunar materials. The ANGSA samples include three types of samples: 1) samples stored frozen since <1 month after Earth arrival; 2) samples stored under helium; and 3) a double drive tube collected by Apollo 17 astronauts, with the bottom portion of the drive tube sealed under vacuum on the Moon and never opened. In contrast to the typically curated Apollo samples that have been kept for decades at room temperature under flowing nitrogen purge that may have significantly reduced the abundance of volatiles, the vacuum-sealed and frozen samples may have enhanced preservation of these volatiles.

Our initial investigation examines amino acids and their potential volatile precursors, including hydrogen cyanide (HCN), aldehydes, ketones, amines, and monocarboxylic acids, in a sample from the top portion of the Apollo 17 double drive tube. These results will aid in understanding the lunar abundances of these molecules and will also be compared to future analyses of other drive tube and frozen ANGSA samples.

Methods: A 2.0 g sample was taken from the lower part of the Apollo 73002 drive tube sample within 24 hours of extruding the sample [10]. This sample was sealed in a cleaned stainless steel container and sent from the curation facility at NASA Johnson Space Center to NASA Goddard Space Flight Center. Contamination control witness material, in the form of a ~3 cm x 3 cm aluminum foil piece that had been cleaned and placed in the processing glovebox to witness the processing environment was also removed from the glovebox and sent in a separate container.

At NASA Goddard, the 73002 sample and witness foil were subjected to hot-water extraction, as were two additional control samples: 1) a procedural blank, and 2) a 2 g portion of JSC-1 lunar simulant that had been baked at 500 °C for 24 hours. The JSC-1 lunar simulant was placed inside a cleaned stainless steel sample container sent from JSC for 24 hours as a control for contamination transfer from the container.

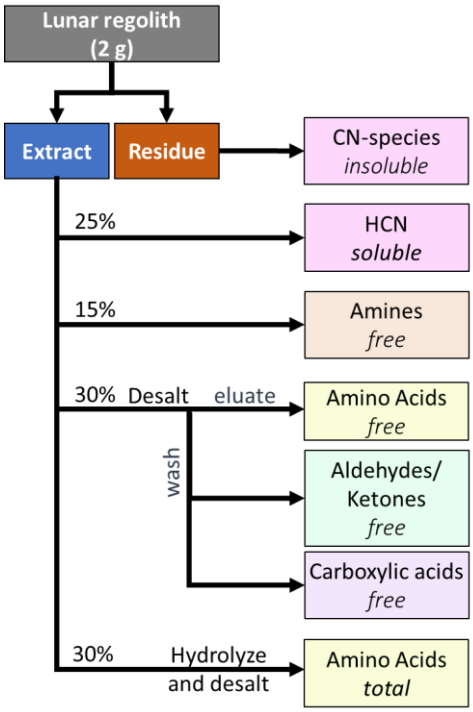

Figure 1. Hot-water extracts of each sample and control were split into multiple aliquots to allow analysis of multiple compound classes.

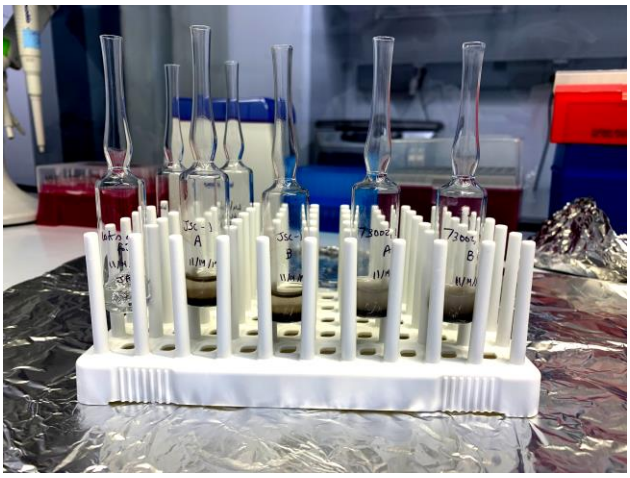

Figure 2. Sample aliquots were placed in glass ampoules with ultrapure water; ampoules were then sealed and heated to extract compounds of interest.

Extraction consisted of sealing samples in ampoules with ultrapure water and heating at 100 °C for 24 hours (Figure 2). After extraction, each sample was split into multiple portions, as shown in Figure 1. One portion was taken for analysis of soluble HCN, and a second for amine analysis. Another portion was desalted through cation exchange [11], with the eluate analyzed for free amino acid content. The wash from this desalted portion was split to allow analysis of monocarboxylic acids, aldehydes, and ketones. A final portion was subjected to acid-vapor hydrolysis [11] to liberate bound amino acids; after desalting, the eluate was analyzed for total amino acid content. Finally, the extracted residue was kept for analysis of insoluble cyanide-containing species.

Methods for analysis have been described elsewhere. Briefly, amino acid analysis was carried out by ultrahigh performance liquid chromatography coupled with fluorescence detection and mass spectrometry (LC-FD/MS) after *o*-phthaldialdehyde/*N*-acetyl-L-cysteine derivatization [12]. Amines were also analyzed with UHPLC-FD/MS after AccQ•Tag derivatization [13]. Aldehydes and ketones were derivatized using *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) and analyzed by gas chromatography-mass spectrometry (GC-MS) [14]. Monocarboxylic acids were derivatized with 2-pentanol and analyzed by GC-MS [15]. Both soluble and insoluble HCN were analyzed by microdistillation followed by derivatization with naphthalene-2,3-dicarboxaldehyde (NDA) and glycine and detection with LC-FD/MS [16].

Discussion: Analyses are ongoing and results will be presented. The compound class distributions and abundances will be used to address both science and curation questions, as shown in Table 1. In order to fully address these questions, the results from sample 73002 will be compared with future analyses of samples taken from different depths within the two portions of the Apollo 17 drive tube, including the sealed bottom half (73001). In addition, the ANGSA frozen samples will be analyzed and compared against portions of the same soils that were stored under standard curation conditions.

The science questions focus on the identity and abundances of amino acids and related volatile organic species, enabling us to understand their prevalence and distribution in lunar soils and to interpret the origin of the amino acids detected in prior lunar analyses. The answers to our curation questions may inform and influence curation practices for future returned samples from the Moon, Mars, asteroids, comets, and other solar system bodies.

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