DISTRIBUTION OF AMINO ACIDS IN LUNAR REGOLITH. J. E. Elsila1, M.P. Callahan1, D.P. Glavin1, J.P. Dworkin1, S.K. Noble1, and E.K. Gibson, Jr.2, 1NASA Goddard Space Flight Center, Greenbelt, MD 20771, 2ARES, NASA/Johnson Space Center, Mail Code KA, Houston, TX 77058. Email: Jamie.Elsila@nasa.gov

Introduction: One of the most eagerly studied questions upon initial return of lunar samples was whether significant amounts of organic compounds, including amino acids, were present. Analyses during the 1970s produced only tentative and inconclusive identifications of indigenous amino acids (e.g. [1],[2]). Those analyses were hampered by analytical difficulties including relative insensitivity to certain compounds, the inability to separate chiral enantiomers, and the lack of compound-specific isotopic measurements, which made it impossible to determine whether the detected amino acids were indigenous to the lunar samples or the results of contamination. Numerous advances have been made in instrumentation and methodology for amino acid characterization in extra-terrestrial samples in the intervening years, yet the origin of amino acids in lunar regolith samples has been revisited only once for a single lunar sample [3] and remains unclear.

Here, we present initial data from the analyses of amino acid abundances in 12 lunar regolith samples. We discuss these abundances in the context of four potential amino acid sources: (1) terrestrial biological contamination; (2) contamination from lunar module (LM) exhaust; (3) derivation from solar wind-implanted precursors; and (4) exogenous delivery from meteorites.

Analytical techniques and samples: We analyzed 12 lunar regolith samples (Table 1). Five samples were allocated from the pristine lunar collection at NASA Johnson Space Center (JSC), while the remaining seven had previously been allocated to Dr. Everett Gibson and had resided in his laboratory for many years. The samples spanned a range of maturities as measured by Is/FeO ratio [4] and included two samples from Apollo 17 that were collected to test exposure to the lunar module exhaust. Three regoliths had been previously analyzed for amino acid content.

Regolith samples were analyzed using previously published methods [5]. Portions (masses ranged from ~250 to 800 mg) of the lunar regolith powders were extracted in ultrapure water. Half of each extract was hydrolyzed with HCl acid vapor to release or create amino acids from precursors. Both the unhydrolyzed and hydrolyzed extracts were then desalted with cation-exchange resin. Amino acid abundances and distributions were analyzed via ultrahigh-performance liquid chromatography with fluorescence detection and time-of-flight mass spectrometry following derivatization with o-phthalaldehyd/N-acetyl-L-cysteine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Is/FeO ratio (maturity)</th>
<th>Amino acid analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>61221</td>
<td>9.2, immature</td>
<td>This study</td>
</tr>
<tr>
<td>73131a</td>
<td>16, immature</td>
<td>This study</td>
</tr>
<tr>
<td>73241a</td>
<td>18, immature</td>
<td>This study</td>
</tr>
<tr>
<td>78501</td>
<td>36, submature</td>
<td>This study</td>
</tr>
<tr>
<td>73141</td>
<td>48, submature</td>
<td>This study</td>
</tr>
<tr>
<td>70011ab</td>
<td>54, submature</td>
<td>This study, [6],[7]</td>
</tr>
<tr>
<td>76501</td>
<td>58, submature</td>
<td>This study</td>
</tr>
<tr>
<td>15271</td>
<td>63, mature</td>
<td>This study</td>
</tr>
<tr>
<td>15261</td>
<td>77, mature</td>
<td>This study</td>
</tr>
<tr>
<td>72501ac</td>
<td>81, mature</td>
<td>This study, [6],[7]</td>
</tr>
<tr>
<td>78421a</td>
<td>92, mature</td>
<td>This study, [3]</td>
</tr>
<tr>
<td>69961</td>
<td>92, mature</td>
<td>This study</td>
</tr>
</tbody>
</table>

aNew (pristine) allocation
bCollected beneath LM as an exhaust-exposed sample
cCollected 6.5 km from LM as LM exhaust control

Results and Discussion: Amino acid abundances and curation effects: Amino acids were detected in all 12 regolith samples, with total concentrations ranging from 0.3 to 139 parts-per-billion (ppb) in the unhydrolyzed extracts and 105 to 1910 ppb for the hydrolyzed extracts. There were distinct differences between the new allocations from the JSC curation facility and those samples that had been stored outside of the curation facility in a separate laboratory. The laboratory-stored samples contained higher concentrations of the amino acids γ-amino-n-butyric acid (γ-ABA) and ε-amino-n-caproic acid (ε-ACA) compared to the curated samples. The hydrolyzed extracts from the laboratory samples also contained roughly racemic mixtures of D-serine and L-serine (D/L ~ 1), while those of the JSC-curated samples contained more L-serine (D/L = 0.04 to 0.25). These differences may reflect contamination of the laboratory-stored samples during the past >35 years. The source of the contamination remains unknown, although ε-ACA is a monomer released upon hydrolysis of Nylon-6, commonly found in the storage bags used for curation [8]. In the remainder of this abstract, we focus on the data from the five JSC-curated samples (70011, 72501, 73131, 73241, and 78421).

Amino acid distributions: Amino acids detected in the hydrolyzed extracts of all five curated samples were glycine, β-alanine, D- and L-alanine, α-aminoisobutyric acid (AIB), and ε-ACA. In addition, several other amino acids were detected in one or more samples, including D- and L-β-amino-n-butyric acid, α-amino-n-...
butyric acid (enantiomers not separated), γ-ABA, D-
and L-aspartic acid, glutamic acid (enantiomers not
separated), D- and L-serine, L-threonine, and L-valine.
The detection of AIB as typical because it is a common
meteoritic amino acid that is rare in the terrestrial bio-
sphere; it is often used to argue for the indigenous na-
ture of amino acids in carbonaceous chondrites. A
tentative identification of AIB was previously made in
sample 78421 [3] with a concentration of ≤0.3 ppb, but
this is the first confirmed detection in a lunar sample.
We detected AIB with concentrations of 0.7 to 1.6 ppb
in the hydrolyzed extracts. Another amino acid that is
rare in the terrestrial biosphere but common in carbo-
naceous chondrites is isovaline [9]; we did not detect
isovaline in any of the lunar samples.

**Hydrolyzed vs. unhydrolyzed samples:** In these five
regolith samples, we observe a marked increase in
amino acid abundance upon hydrolysis, with the per-
centage of free amino acids (detected in the unhydr-
yzed extract) ranging from 0.05% to 43% (Table 2). In
carbonaceous chondrites, this value is typically in the
30% to 60% range [e.g., 10]. The large increase upon
acid hydrolysis in certain samples suggests creation or
liberation of amino acids from a precursor. This pre-
cursor could be a protein from terrestrial biological
contamination, and the predominance of L- over D-
enantiomers in several proteinogenic amino acids sug-
gests that this is a likely possibility. However, such a
range in the percentage of free amino acids among
samples that have been curated under the same con-
tions and protocols in the same facility suggests that
other precursors may also be present. Alternatively,
the amino acids could be formed by hydrolysis of hy-
drogen cyanide (HCN) polymer. HCN could be im-
planted in the regolith by the solar wind (see below for
further discussion) and polymerized during hot-water
extraction [11]. HCN was also one of the primary vol-
atiles in the LM exhaust [12]; the LM-exposed (70011)
and the LM-control (72501) samples, however, had
similar free and hydrolyzed amino acid abundances,
with the smallest increases in abundances upon hydro-
ysis of the samples in our study (see Table 2). This
argues against HCN from the LM exhaust as a precur-
sor to the amino acids released upon hydrolysis.

**Correlation with sample maturity:** We compared
amino acid abundance to sample maturity, as measured
by I/FeO ratio [4]. Soil maturity correlates with sur-
face exposure and, hence, exposure to solar wind; there-
fore, correlation between amino acid abundance and
maturity would suggest a solar-wind-implanted
origin of amino acid precursors. Intriguingly, opposite
trends emerged for the hydrolyzed and unhydrolyzed
samples. In the unhydrolyzed extracts, the least mature
samples analyzed contained the lowest levels of amino

<table>
<thead>
<tr>
<th>Sample</th>
<th>I/FeO</th>
<th>Free (ppb)</th>
<th>Total (ppb)</th>
<th>% Free</th>
</tr>
</thead>
<tbody>
<tr>
<td>73131</td>
<td>16</td>
<td>5.1</td>
<td>494.0</td>
<td>1.0%</td>
</tr>
<tr>
<td>73241</td>
<td>18</td>
<td>0.3</td>
<td>651.2</td>
<td>0.05%</td>
</tr>
<tr>
<td>70011</td>
<td>54</td>
<td>33.8</td>
<td>106.4</td>
<td>32%</td>
</tr>
<tr>
<td>72501</td>
<td>81</td>
<td>42.7</td>
<td>105.3</td>
<td>43%</td>
</tr>
<tr>
<td>78421</td>
<td>92</td>
<td>12.0</td>
<td>157.6</td>
<td>7.6%</td>
</tr>
</tbody>
</table>

**Future directions:** We have confirmed and expan-
ed on earlier detections of amino acids in lunar rego-
liths. However, the origin of these amino acids re-
 mains undetermined. Compound-specific isotopic
measurements should help distinguish between poten-
tial sources of these compounds, as the isotopic signa-
tures of biological contamination, solar wind precu-
sors, and meteoritic infall should be distinct. The need
for such measurements was acknowledged in previous
analyses [3]; instrumental capabilities did not then ex-
ist, but have since been developed. Planned future
isotopic measurements, combined with the data on
amino acid abundances and distributions in this initial
study, should help to answer the decades-old questions
about the presence and origin of lunar amino acids.

**References:**