The chemical evolution in open space: An experimental approach

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dust is the flesh of time
J. Brodsky

silicate dust (olivine, pyroxene) is common in many astrophysical settings circumstellar, interstellar, and interplanetary environments

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the main place of interstellar chemistry –
icy mantles on interstellar dust particles
# Energy Fluxes in the Interstellar Medium

<table>
<thead>
<tr>
<th>Environment</th>
<th>Ion Processing</th>
<th>Photon Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux, 1 MeV p⁺ (eV cm⁻² s⁻¹)</td>
<td>Energy absorbed (eV cm⁻² s⁻¹)</td>
</tr>
<tr>
<td>Diffuse ISM (10⁵–10⁷)†</td>
<td>1 × 10⁷</td>
<td>1.2 × 10⁴</td>
</tr>
<tr>
<td>Dense cloud (10⁵–10⁷)†</td>
<td>1 × 10⁶</td>
<td>1.2 × 10³</td>
</tr>
<tr>
<td>Protoplanetary nebula (10⁵–10⁷)§</td>
<td>1 × 10⁶</td>
<td>1.2 × 10³</td>
</tr>
<tr>
<td>Oort cloud (4.6 × 10⁹)</td>
<td>φ(E)**</td>
<td>**</td>
</tr>
<tr>
<td>Laboratory (4.6 × 10⁻⁴)††</td>
<td>8 × 10¹⁶</td>
<td>2 × 10¹⁵</td>
</tr>
</tbody>
</table>

Colangeli et al., 2005
radiation environment affecting the surface of the solar system bodies
solar radiation

45% - IR
47% - visible
7% - UV

1.371 kW/m² - the solar constant at 1AU
Extraterrestrial matter is broadly divisible into three groups by size:

- large impactors (comets and large asteroids),
- meteorites,
- interplanetary dust particles.

The total flux of extraterrestrial material to the surface of the early earth is estimated as being between $2 \times 10^{20}$ kg (Marty and Yokochi, 2006) and $5 \times 10^{22}$ kg (Owen 1998).
CARBON IN METEORITES

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic matter</td>
<td>2.0</td>
</tr>
<tr>
<td>carbonate</td>
<td>0.2</td>
</tr>
<tr>
<td>diamonds</td>
<td>0.04</td>
</tr>
<tr>
<td>graphite</td>
<td>0.005</td>
</tr>
<tr>
<td>silicon carbide</td>
<td>0.009</td>
</tr>
</tbody>
</table>
carbonaceous chondrites

Murchison (CM)  Orgueil (CI)  Allende (CV3)
amino acids in meteorites

from 883 ppb (Tagish Lake) up to 12270 ppb (Murchison)

- 78 amino acids (including 7 ones from peptides and 11 ones from earth biosphere;
- length of carbon chains from 2 to 9 atoms;
- there are all possible isomers, the branched ones are predominate;
- $\alpha$-amino acids more spread ($\alpha>\gamma>\beta$)
- concentration diminish along with chain increasing;
- all amino acids display $\sigma$D values that are much higher than those of terrestrial compounds

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## some interesting amino acids from CCs

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycine</td>
<td>α-amino-(n)-butyric acid (ABA)</td>
</tr>
<tr>
<td>alanine</td>
<td>β-aminoisobutyric acid (AIB)</td>
</tr>
<tr>
<td>glutamic acid</td>
<td>norvaline</td>
</tr>
<tr>
<td>valine</td>
<td>pipecolic acid</td>
</tr>
<tr>
<td>proline</td>
<td>isovaline</td>
</tr>
<tr>
<td>aspartic acid</td>
<td>(N)-methylalanine</td>
</tr>
<tr>
<td>leucine</td>
<td>β-amino-(n)-butyric acid</td>
</tr>
<tr>
<td></td>
<td>(N)-methylglycine (sarcosine)</td>
</tr>
<tr>
<td></td>
<td>β-alanine</td>
</tr>
<tr>
<td></td>
<td>(N)-ethylglycine</td>
</tr>
<tr>
<td></td>
<td>α-aminoisobutyric acid (2-methylalanine)</td>
</tr>
<tr>
<td></td>
<td>γ-amino-(n)-butyric acid</td>
</tr>
</tbody>
</table>
in our experiments the solid mixtures of amino acids were exposed to different energy sources available in open space:

- vacuum ultraviolet photons (VUV);
- ultraviolet photons (UV);
- protons;
- space exposure

It was important to test experimentally how far the process of chemical evolution could take place on the surface of space bodies under action of energy sources available at that period and evaluate a possible role of mineral components in such processes.
**Character of Amino Acid**

Zwitterion at solid phase. (pH vary in aqueous solution.)

- Vapor pressure is very low.
- Stable existence at solid phase in space.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Resonance</th>
<th>Quantum efficiency $\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5 (146 nm)</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>0.0060±0.0004</td>
</tr>
<tr>
<td>400</td>
<td>N pre-edge</td>
<td>0.12±0.02</td>
</tr>
<tr>
<td>407</td>
<td>N 1s $\rightarrow \sigma^*$</td>
<td>0.015±0.003</td>
</tr>
<tr>
<td>413</td>
<td>N ionization</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>530</td>
<td>O pre-edge</td>
<td>0.07±0.08</td>
</tr>
<tr>
<td>533</td>
<td>O 1s $\rightarrow \pi^*$</td>
<td>--</td>
</tr>
<tr>
<td>539</td>
<td>O 1s $\rightarrow \sigma_1^*$</td>
<td>0.020±0.001</td>
</tr>
<tr>
<td>860</td>
<td>--</td>
<td>0.032±0.015</td>
</tr>
</tbody>
</table>

**Structural formula**

Gly→(Gly)$_2$ Kanako (2005)
abiogenic synthesis of oligopeptides

Irradiation of VUV

- Light source: Kr₂ lamp
- Irradiated energy: 8.5 eV (145 nm)
- Light intensity: $6.9 \times 10^{15}$ (photons/sec·cm²)

Excited $\pi \rightarrow \pi^*$
- Resonance of COO⁻

Absorption spectra

- Gly
- (Gly)$_2$

Gly-Phe-Gly

Glycine

Phenylalanine

Gly-Phe-Gly

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**abiogenic synthesis of Trp-Trp under action of different energy sources**

<table>
<thead>
<tr>
<th>energy source</th>
<th>dose</th>
<th>yield (%)</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>p⁺</td>
<td>$5.0 \times 10^{11}$ p⁺/cm²</td>
<td>2.43</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>VUV</td>
<td>$3.8 \times 10^{3}$ J/m²</td>
<td>1.87</td>
<td>$6.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>γ(Cs¹³⁷)</td>
<td>$3.0 \times 10^{9}$ J/g</td>
<td>0.41</td>
<td>$3.8 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

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minerals

olivine \( (\text{Mg}_x\text{Fe}_{1-x})_2\text{SiO}_4 \)

pyroxene \( (\text{Mg}_x\text{Fe}_{1-x})\text{SiO}_3 \)

\( \text{SiO}_2 \)
yields of oligopeptides

VUV (145 nm), dose $2.1 \times 10^5$ J/m$^2$

VUV Gly+Phe

- without mineral
- Olivine
- Pyroxene
abiogenic synthesis of Gly-Gly

VUV
Gly+Phe

**Graph:**
- Y-axis: Gly-Gly yield (%)
- X-axis: Irradiation time (hrs)
- Curves 1, 2, 3:
  - 1: control
  - 2: olivine
  - 3: pyroxene

**Bar Chart:**
- Colors: blue (cont), red (oliv), green (pyr)
- Values: 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3
total yields of oligopeptides

VUV
Gly+Phe

- control
- olivine
- pyroxene

irradiation time (hrs)

yield (%)
abiogenic synthesis of Phe-Gly-Gly

VUV
Gly+Phe

yield (%)

Phe-Gly-Gly

1 - control
2 - olivine
3 - pyroxene
4 - SiO$_2$

irradiation time (hrs)

SiO$_2$

Pyr

Oliv

0 0.5 1

%
• in all cases solid films were obtained from similar basic solution of 10 µM Gly and Trp amino acids;
• flight data were calculated as a result of 115-days long exposure on the outside core of MIR space station;
• heating at the temperatures exceeding 60°C triggered formation of dipeptides;
• presence of minerals promoted higher yield.
synthesis of oligopeptides in presence of lunar soil

Gly+Trp → Gly-Trp

VUV | lunar soil | free
UV  | lunar soil | free
space | lunar soil | free

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survival of the initial amino acids

- Gly
- Trp

lunar soil
free

%
formation of biomolecules in presence of extraterrestrial minerals

- Lunar soil
- Merchison
- Allende

S’AMP amount in presence of mineral
S’AMP - absence of mineral

Gly-Gly amount in presence of mineral
Gly-Gly amount in the absence of mineral
BION-M hardware
the mineral matrices could acted as:

- matrices for concentration of organics;
- catalysts for abiogenic reactions (including polymerization);
- shield for initial and newly synthesized compounds from harsh radiation environments.
so, we can propose that a large reservoir of complex organic molecules was synthesized in the warm, inner Solar nebula via reaction on the surface of silicate and oxide dust grains.

and these materials could be delivered by different vesicles to the primordial Earth.
sources of organic compounds on prebiotic Earth

extraterrestrial matter

comets

interplanetary dust

asteroids

meteorites

planetary abiogenic synthesis

volcanic synthesis

Miller-Uri synthesis