Prebiotic chemistry

Studies on the origin of life

- Fields of research related to the studies of the origin of life
  - Prebiotic chemistry (synthesis of precursors of biomolecules)
  - Emergence of replicative and metabolic functions
  - Characterization of the first living organisms

- Two types of approaches are used:
  - "bottom-up"
    - trying to build up complex biological molecules in laboratory, starting from non biological constituents
  - "top-down"
    - trying to cast light on the characteristics of the least evolved forms of life, proceeding "backwards" in evolution

Synthesis of biological precursors

- Prebiotic chemistry: study of the stages of chemical evolution that precede the origin of life
- Search for plausible chemical pathways of synthesis of the molecular building blocks of biological macromolecules
  - One of the goals of prebiotic chemistry is to understand which organic molecules are the most likely to initiate these chemical pathways
- Possible scenarios for the synthesis of prebiotic material:
  - In space
  - On Earth
- Both scenarios are taken in consideration in studies of the origin of life

Prebiotic chemistry in space

- The primitive Earth is likely to have been enriched by organic material delivered by meteorites of asteroidal and cometary origin
  - complex organic material delivered from space may have played a role in prebiotic chemistry
  - the synthesis of organic molecules may have taken place in the molecular cloud from which the protosolar nebula originated
  - additional chemical processing must have taken place during the stages of planetary formation, during the delivery on Earth, and on the Earth’s surface
- Indirect evidence supporting the delivery of complex organics in the past is found from the study of meteorites recently arrived on Earth and of space observations of comets
Prebiotic chemistry in space
From molecular clouds to planetary formation

Herbst & van Dishoeck 2009

Prebiotic material delivered on Earth by meteorites

- Meteorites are representative of the epoch of planetary formation
  - Some of the meteorites collected on Earth show evidence of relatively complex organic material
- One of the most interesting cases is the Murchison meteorite (Australia, 1969) where evidence have been found of aminoacids and nucleobasis.
  The non-terrestrial origin of these organic compounds is confirmed by several tests:
    - Out of the 74 aminoacids found, only 11 are protein aminoacids
    - The aminoacids appear in a near racemic mixtures (both L- and D- types), at variance with protein aminoacids

A slight excess of the L enantiomer has been found, the same enantiomer of biological aminoacids

Prebiotic material delivered on Earth by comets

- Also comets may have delivered organic material on the primitive Earth
  - the early flux of comets was likely to be higher in the early stages of evolution of the Solar System
  - analysis of present-day comets that still preserve their original composition can be used to trace the history of organic material in comets
  - several studies confirm that comets do possess organic material
  - fresh and detailed evidence has been provided by the Rosetta mission

ESA Rosetta mission to comet 67 P/C-G
Rosetta mission: organics in comet 67 P/C-G

- D/H higher than in terrestrial oceans

D/H ~5.3 \(10^{-4}\) in \(H_2O\)

Altwegg et al., Science, 2015

- In situ mass spectrometry of cometary volatiles: discovered a large number of organics, many of them for the first time in a comet

<table>
<thead>
<tr>
<th>Organics</th>
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<tbody>
<tr>
<td>Ammonia, Methylamine, Ethylamine</td>
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<tr>
<td>Benzene, Toluene, Xylene, Benzoic acid, Naphthalene</td>
</tr>
<tr>
<td>Methane, Ethane, Propane, Butane, Pentane, Hexane, Heptane</td>
</tr>
<tr>
<td>Methanol, Ethanol, Propanol, Butanol, Pentanol</td>
</tr>
<tr>
<td>Acetylene, HCN, CH3CN, Formaldehyde</td>
</tr>
<tr>
<td>Hydrogensulfide, Carbonylsulfide, Sulfur dioxide, Carbon disulfide, Thioformaldehyde</td>
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<tr>
<td>Glycine</td>
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Delivery of water on Earth

- In the context of the standard model of accretion of terrestrial planets, the Earth accreted from a swarm of planetesimals and planetary embryos
- Therefore, Earth’s water is likely to have been derived from their planetesimal precursors and their chondritic building blocks
- Specifically, the most likely sources of Earth’s volatiles could have been the outer asteroid belt, the giant planet regions, and the Kuiper belt
- (Morbidelli et al. 2000)
- Gases in the solar nebula were probably not an important source of volatiles
- the extreme solar wind associated with the T-Tauri phase of stellar evolution is likely to have blown the solar gas away

Testing the origin of Earth’s water

- The possibility that water has been delivered on Earth by impacts of minor bodies (asteroids and comets) is tested with studies of the isotopic ratio D/H
- The oceanic D/H ratio is compared with measurements performed in meteorites and comets
- So far, asteroids appear to be favoured, but the experimental evidence may change with future studies of comets

Prebiotic chemistry in the primitive Earth

The physico/chemical conditions of the early Earth set the reference frame for studying which chemical pathways may have lead to the origin of life

Properties of the Earth at the epoch of the origin of life

We briefly mention two aspects of the physico-chemical conditions relevant to the origin of life:

Early atmospheric composition of the Earth
- Early climate of the Earth
- Origin of Earth’s oceans
The early atmosphere of the Earth

• The primary atmosphere of the Earth must have been lost
  – This is deduced from the low abundances of rare gases ($^{20}$Ne, $^{36}$Ar, $^{84}$Kr) in the present-day atmosphere, compared to the cosmic abundances of the same elements

• Different hypothesis have been advanced on the composition of the secondary atmosphere of the primitive Earth
  – Old models
    Slow formation of the Earth, with interior cold and rich of volatiles
    Volatiles from the interior are gradually heated and released to the atmosphere
    These volcanic emissions produce a “reducing” atmosphere (rich of hydrogen), with a high content of $\text{H}_2$, $\text{CH}_4$, and $\text{NH}_3$
  – Present models
    Fast formation of the Earth (10-100 million years)
    Because of the impacts with accreting planetesimals, the interior is hot and does not have volatiles
    By the end of the accretion process, the atmosphere is “weakly reducing”, being dominated by $\text{CO}_2$, $\text{N}_2$ with traces of CO and $\text{H}_2$

The early climate of the Earth:
the “Faint Young Sun paradox”

• The standard model of evolution of the Sun indicates that the solar luminosity at the epoch of the origin of life was about 25% fainter than today

• With a lower level of insolation, models of Earth climate indicate that the Earth should have been completely frozen
  – Assuming an intensity of the greenhouse effect similar to the present-day one

• We know that this was not the case, since there are evidences of liquid water at the same epoch of Earth’s history

• This contradiction is known as the “faint young Sun paradox”

Possible solutions of the “Faint Young Sun paradox”

• Most commonly adopted explanation:
  – Larger efficiency of the greenhouse effect
  – Atmosphere rich in $\text{CO}_2$ and/or $\text{CH}_4$
  However, this solutions faces some limitations since the possible amount of $\text{CO}_2$ is limited by geochemical constraints

– Outflow of internal heating
  The internal heat in the primitive Earth must have been much larger than at the present time
  However, once the crust of the planet is solidified, the internal heating is trapped inside and does not provide a significant heating of the surface

– Larger value of atmospheric pressure
  Tested with climate models: an atmosphere with 3 bars of $\text{N}_2$ would help in solving the problem, in combination with a modest increase of $\text{CO}_2$
Laboratory studies of prebiotic chemistry

- Laboratory experiments are a fundamental tool for studies of prebiotic chemistry
- They aim at reproducing the physico-chemical conditions existing in space (e.g. ionizing radiation fields) or in the primitive Earth
  - The first, historical, experiment of prebiotic chemistry on Earth was performed by Urey & Miller in 1953

The Urey-Miller experiment

- In the original version, the authors adopted a "reducing" atmosphere, considered to be representative of the early Earth’s atmosphere at the time of the original experiment
  - The adoption of a "reducing" atmosphere gives a high yield of aminoacids
- Recent versions of the Urey-Miller experiment adopt a "weakly reducing" atmosphere, in agreement with the current expectations for the early Earth’s atmosphere
  - The experiment is still able to produce aminoacids, albeit with a much lower efficiency

The aminoacids found in laboratory experiments of prebiotic chemistry are α-aminoacids, i.e. the same type found in the proteins of terrestrial life

α-aminoacido β-aminoacido γ-aminoacido
Developments of prebiotic chemistry in laboratory

- After the formation of amino acids, experiments of prebiotic chemistry aimed at producing the bases of nucleic acids
  - The first successful experiments, performed by Joan Oró, managed to produce adenine, in addition to amino acids, using hydrogen cyanide (HCN) as a precursor
  - Later on, also guanine was produced, always starting from HCN
  - However, the formation of pyrimidines (uracil, thymine and cytosine) from the same chemical pathways was not possible
  - In addition, the nucleic bases produced were highly unstable, posing a problem for the viability of subsequent prebiotic steps

Prebiotic chemistry with formamide

- Formamide (HCONH₂) can be produced by the reaction of water and hydrogen cyanide (HCN)
  - The prebiotic potential of formamide is remarkable
    - Formamide produces all four nucleic acid bases and other biological molecules when warmed in the presence of naturally occurring minerals, such as montmorillonite
  - Formamide gives rise to cycles of production, degradation and reformation of nucleic acid bases
    - This cyclic behaviour solves the problem of the instability of nucleic bases, since they can be constantly reformed, becoming available when needed for subsequent steps of prebiotic chemistry
Prebiotic chemistry with formamide

- Formamide is involved in chemiomimetic processes
- According to Eschenmoser (1992), a chemiomimetic process is a biological process that mimics a prebiotic reaction
- Present-day biological processes may represent a sophisticated version of naturally occurring prebiotic processes

Hydrogen bonds properties of formamide

Hydrogen bonding is essential in terrestrial biochemistry and probably in any form of biochemistry

Formamide has an excellent capability of hydrogen bonding:
- Three acceptors (the lone pairs of electrons)
- Three donors (the hydrogen atoms)