Prebiotic chemistry

Planets and Astrobiology (2018-2019)
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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

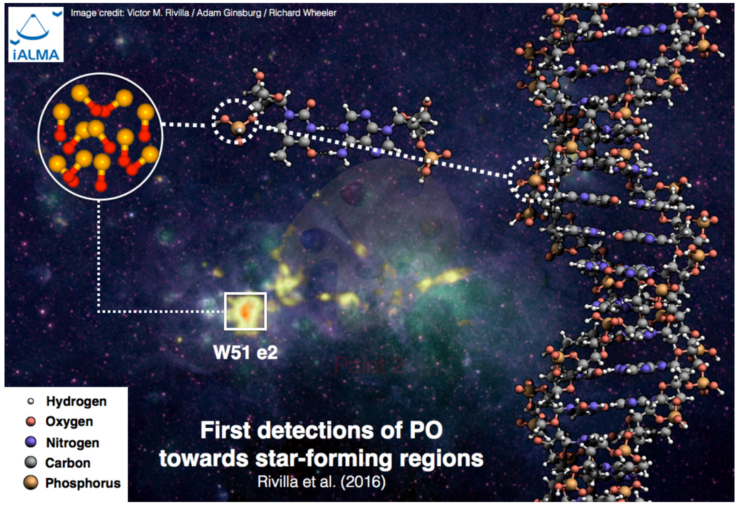
Synthesis of biological precursors

- 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

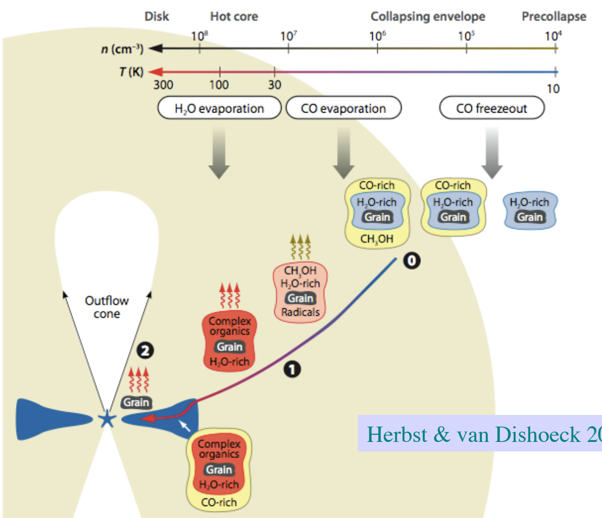
- The primitive Earth is likely to have been enriched by organic material delivered by meteorites of asteroidal and cometary origin
  - complex organic material delivered from space may have played a role in prebiotic chemistry
  - the synthesis of organic molecules may have taken place in the molecular 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 molecular clouds



Prebiotic chemistry in space

From molecular clouds to protoplanetary disks



Herbst & van Dishoeck 2009

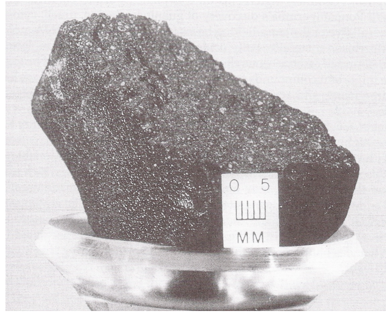
Prebiotic material delivered on Earth by meteorites

- 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 organics 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

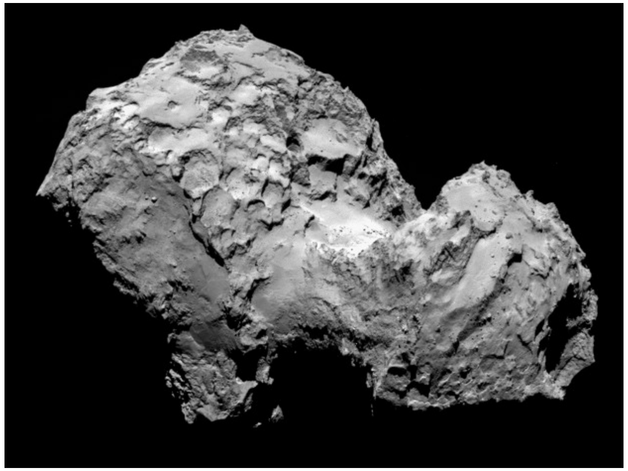


A slight eccess of the L enantiomer has been found, the same enantiomer of biological aminoacids

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

Ammonia Methylamine, Ethylamine
Benzene, Toluene, Xylene, Benzoic acid, Naphthalene
Methane, Ethane, Propane, Butane, Pentane, Hexane, Heptane
Methanol, Ethanol, Propanol, Butanol, Pentanol
Acetylene, HCN, CH3CN, Formaldehyde
Hydrogensulfide, Carbonylsulfide, Sulfur dioxyde, Carbon disulfide, Thioformaldehyde
Glycine

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 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

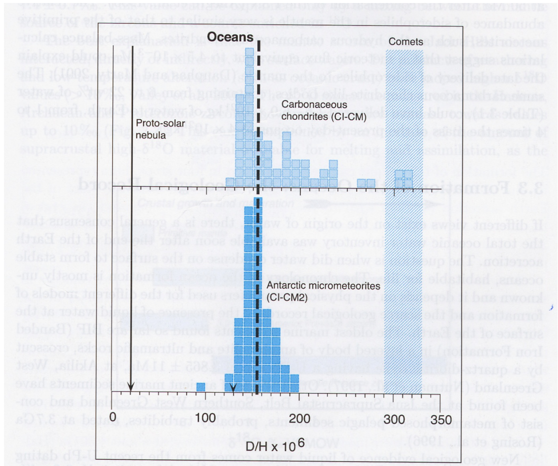


Fig. 3.2. Frequency distribution of the D/H ratios measured in carbonaceous chondrites and Antarctic micrometeorites compared to values for the PSN, Earth oceans and comets. Data: Déloule et al., 1991; Engrand et al., 1999; Maurette et al., 2000; Robert et al. 2000

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 H_2, CH_4, and NH_3
  - Present models

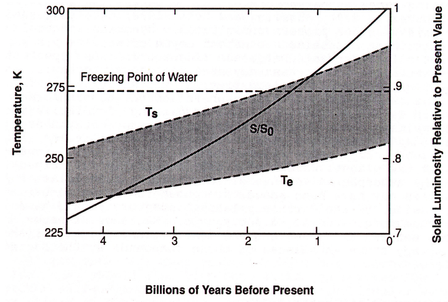
    Fast formation of the Earth (10-100 millon years)

    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 CO_2 e N_2 with traces of CO and 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"



Te – Effective temperature of the Earth
Ts – Mean surface temperature of the Earth
The shaded region indicates the greenhouse effect

Possible solutions of the "Faint Young Sun paradox"

- Most commonly adopted explanation:
  - Larger efficiency of the greenhouse effect in the primitive Earth
- Specific scenarios:
  - Atmosphere rich in CO_2 and/or CH_4

    However, this solutions is problematic because the possible amount of CO_2 is limited by geochemical constraints
  - Creation of N_2O, a strong greenhouse gas, in the upper atmosphere by energetic protons generated by the strong activity of the young Sun (Airapetian 2018)

    Subsequent decline of solar activity would be compensated by the rise of solar luminosity

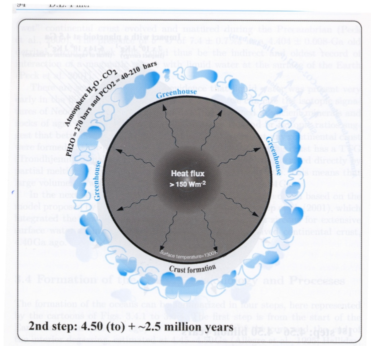


Fig. 3.4.2. Ibid

Possible solutions of the “Faint Young Sun paradox”

– Outflow of internal heating

The internal heat in the primitive Earth must have been much larger than at the present time

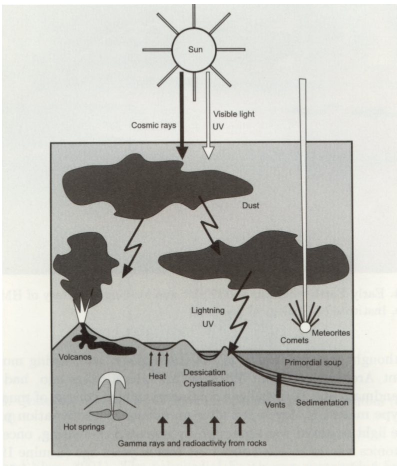
However, once the crust of the planet is solidified, the internal heating is trapped inside and does not provide a significant heating of the surface

– Larger value of atmospheric pressure

Tested with climate models: an atmosphere with 3 bars of N_2 would help in solving the problem, in combination with a modest increase of CO_2

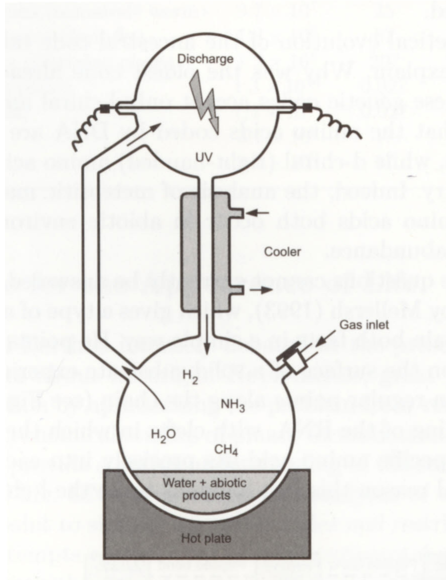
Laboratory studies of prebiotic chemistry

- 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



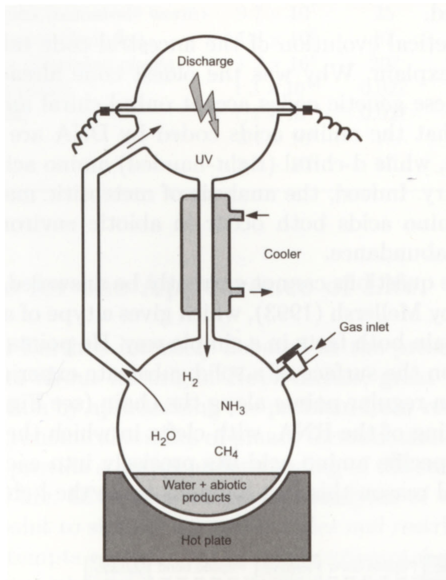
The Urey-Miller experiment

- The Urey-Miller experiment proved that aminoacids can spontaneously form in simulated conditions of the early Earth (electric discharges, oceans) starting from very simple molecules (H_2, H_2O, CH_4, NH_3)

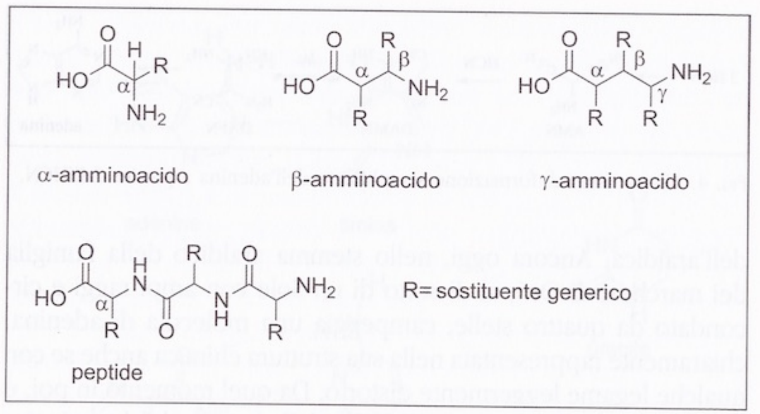


The Urey-Miller experiment

- 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



Developments of prebiotic chemistry in laboratory

- After the formation of aminoacids, experiments of prebiotic chemistry aimed at producing the bases of nucleic acids
  - The first succesful experiments, performed by Joan Oró, managed to produce adenine, in addition to amino acids, using hydrogen cyanide (HCN) as a precursor

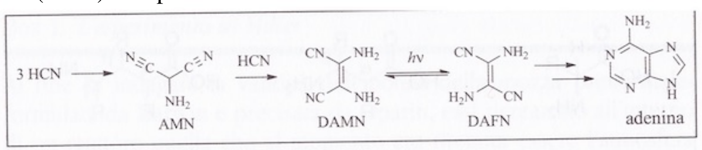


FIG. 4. Meccanismo di formazione semplificato dell'adenina a partire dall'HCN.

  - Later on, also guanine was produced, always starting from HCN
  - However, the formation of pyrimidines (uracil, thymin and cytosin) 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

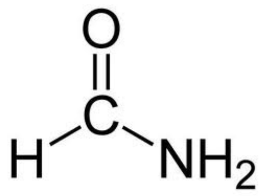
Formamide ($HCONH_2$) can be produced by the reaction of water and hydrogen cyanide (HCN)

In laboratory experiments of prebiotic chemistry formamide presents several advantages compared to HCN

The concentration of HCN is difficult because HCN is in gaseous form at ambient temperature and pressure

Formamide, instead, has a boiling point of 210ºC, higher than the water boiling point

Therefore, formamide can be easily become concentrated through the evaporation of water



Formamide has been found in the interstellar medium

Prebiotic chemistry with formamide

- 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 (a mineral)

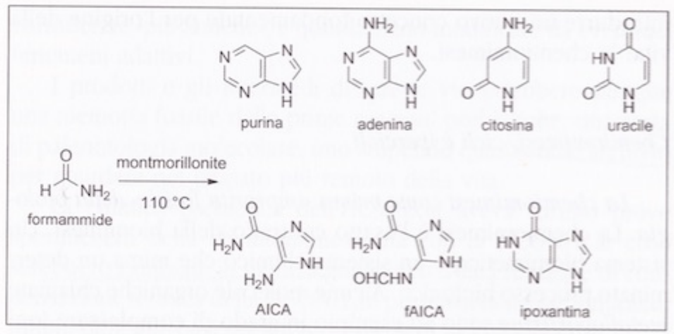


FIG. 9. Sintesi delle basi nucleiche e di loro intermedi dalla formammide in presenza di montmorilloniti.

Prebiotic chemistry with formamide

- 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

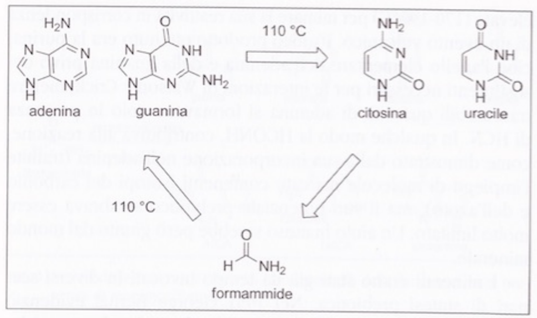
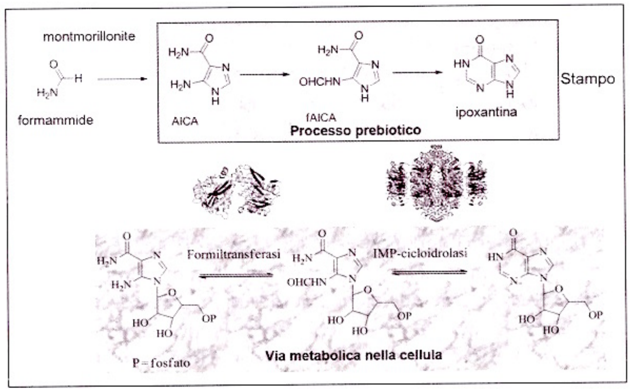


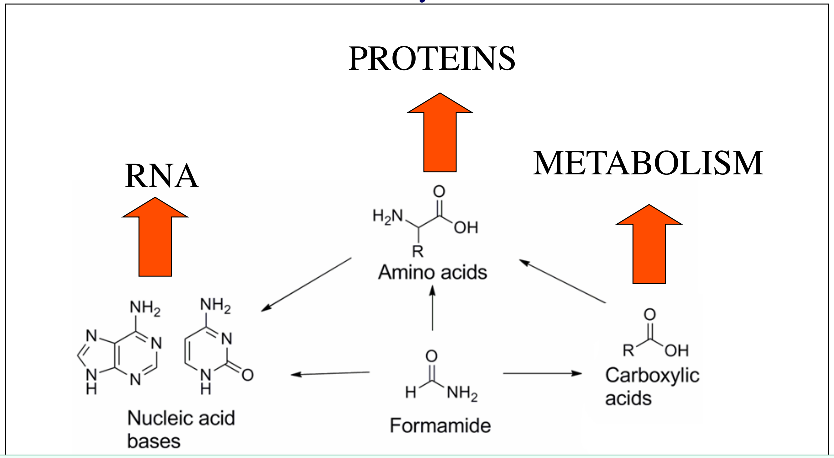
FIG. 8. Ciclo di degradazione e sintesi delle basi nucleiche a partire dalla formammide.

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



Prebiotic chemistry with formamide



Formamide is potentially involved in all relevant steps of prebiotic chemistry. Succesful experiments exist for most steps of prebiotic chemistry. However, experiments in a "single pot" are able to perform only one, or a few, steps at a time.

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)