Astrobiology
Lecture 9

Prebiotic chemistry

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Origin of life

- The origin of life is a central topic of astrobiology
  - To predict if life can originate in remote astronomical environments we need to understand which conditions led to the origin of life on Earth
  - The habitability of an environment does not guarantee the presence of life because the requirements for the origin of life could be different (presumably tighter) than the requiremens of habitability
- The scientific approach
  - The origin of life is assumed to be the result of as a <u>sequence of spontaneous processes that leads to the formation of the first living cells starting from non-biological chemical compounds</u>
- Abiogenesis
  - The transition from the abiotic world to life is called <u>*abiogenesis*</u> or <u>*biopoiesis*</u> ("the making of life")

Studies on the origin of life

- Two approaches:
  - “bottom-up”

    trying to reconstruct the emergence of biological molecules and the first cells starting from non biological constituents
  - “top-down”

    trying to reconstruct the early stages of biological evolution from the characteristics of the least evolved organism

- Main fields of research in the ”bottom-up” approach
  - Prebiotic chemistry (synthesis of precursors of biomolecules)

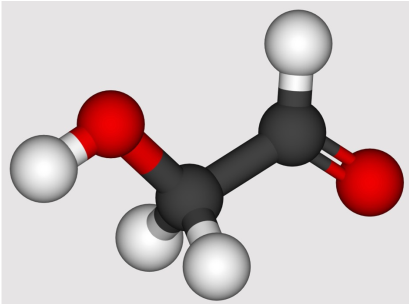
    Origin of homochirality
  - Emergence of genetic molecules
  - Emergence of catalytic molecules
  - Emergence of cell compartments

Prebiotic chemistry

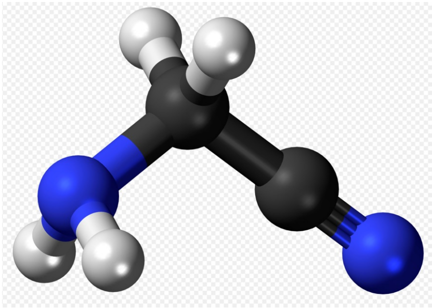
- Search for plausible chemical pathways of synthesis of the molecular building blocks of biological macromolecules
  - One of the goals of prebiotic chemistry is to understand which organic molecules are the most likely to initiate these chemical pathways
- Possible scenarios for the synthesis of prebiotic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

Molecular clouds

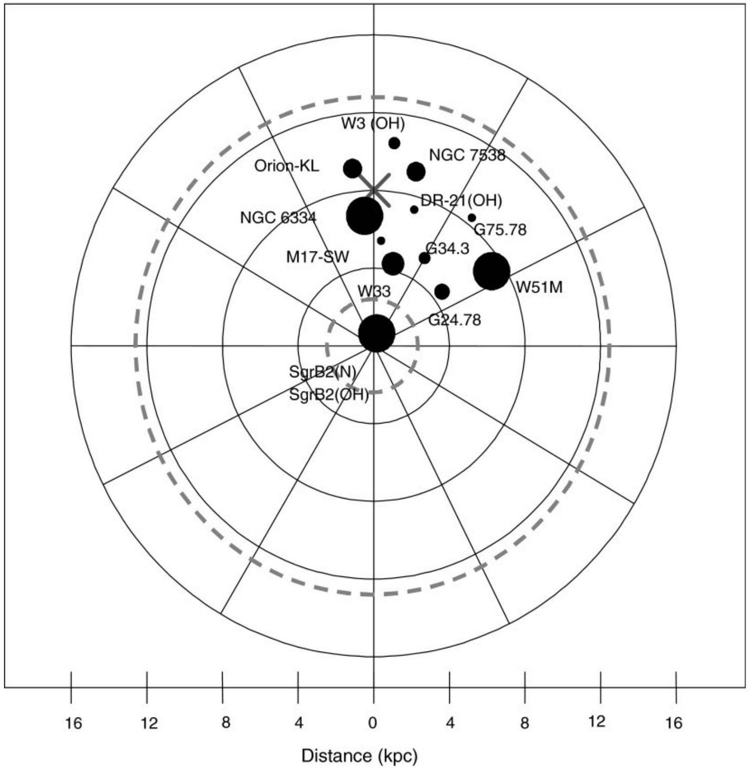
- Organic molecules are commonly found in dense molecular clouds, which are the cradles of stellar and planetary formation
- Observations of molecular clouds performed with mm and sub-mm radiotelescopes, like ALMA (ESO, Chile), are detecting more and more molecules of prebiotic interest
  - Examples:
  - glycolaldehyde (the simplest sugar)

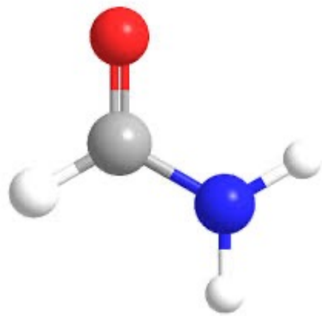


  - aminoacetonitrile (a possible precursor of glycine)

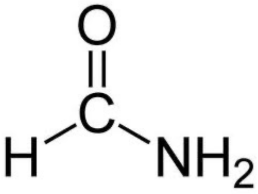


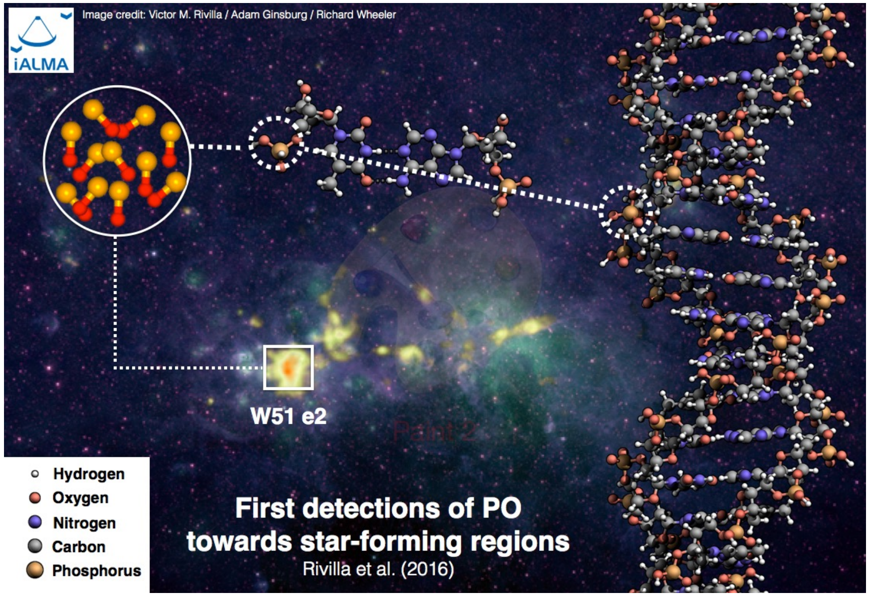
Prebiotic chemistry in molecular clouds





Formamide





Phosphate groups

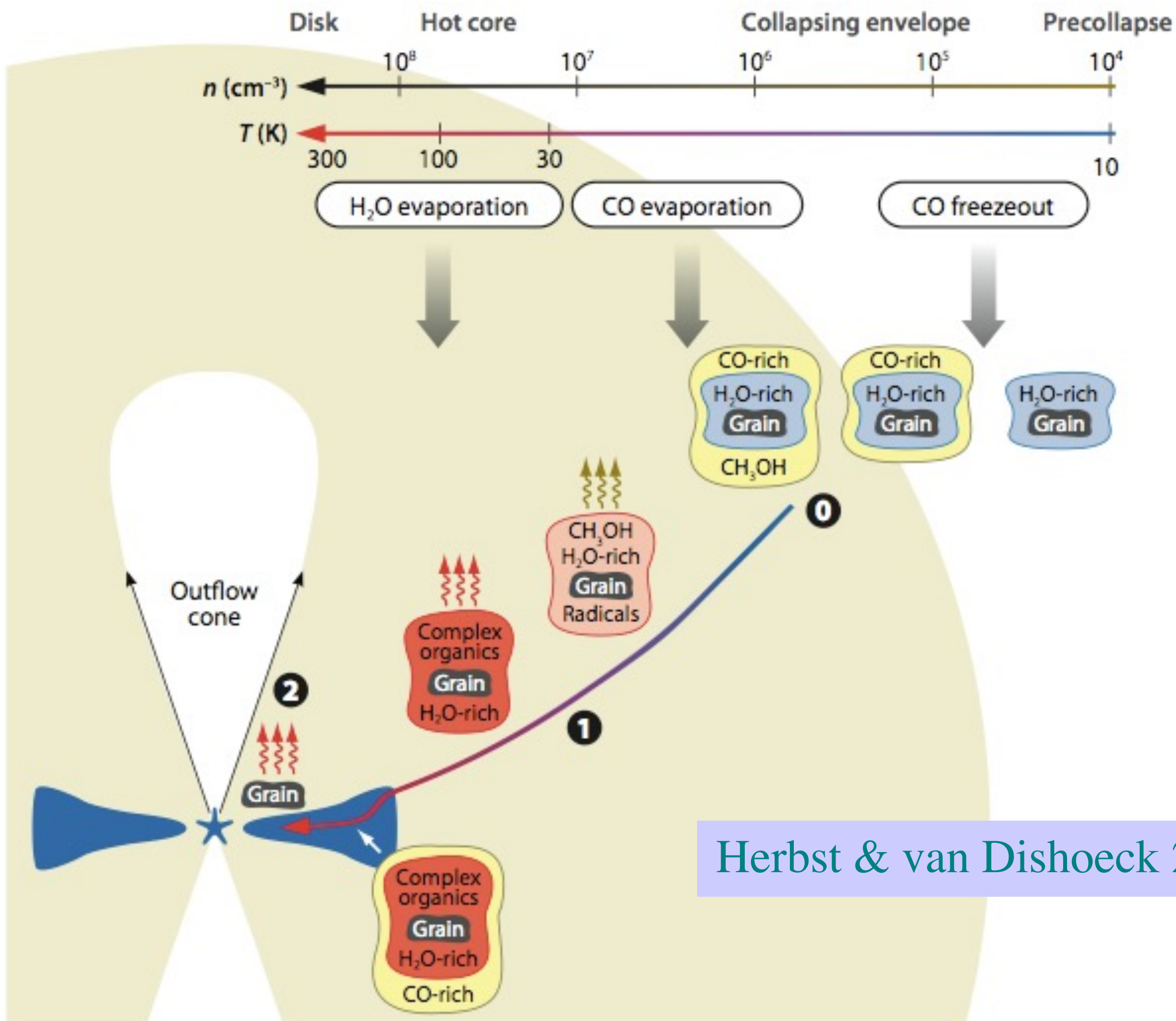
Molecular clouds

- Issues with the interpretation
  - Understanding the formation of organic molecules in low-density, harsh interstellar conditions requires theoretical and laboratory studies
    - Databases of molecular transitions need to be expanded
    - Theoretical interpretation requires a quantum-chemistry approach
    - Including interstellar dust as a catalyst of molecular formation

- Origin of water
  - Based on our current knowledge of molecular clouds, we believe that the synthesis of <u>terrestrial water and of some prebiotic molecules</u> may have taken place in the molecular cloud from which the protosolar nebula originated 4.5 Gyr ago

Protoplanetary disks

Additional processing of the prebiotic material synthesized in molecular clouds must have taken place during the stages of planetary formation



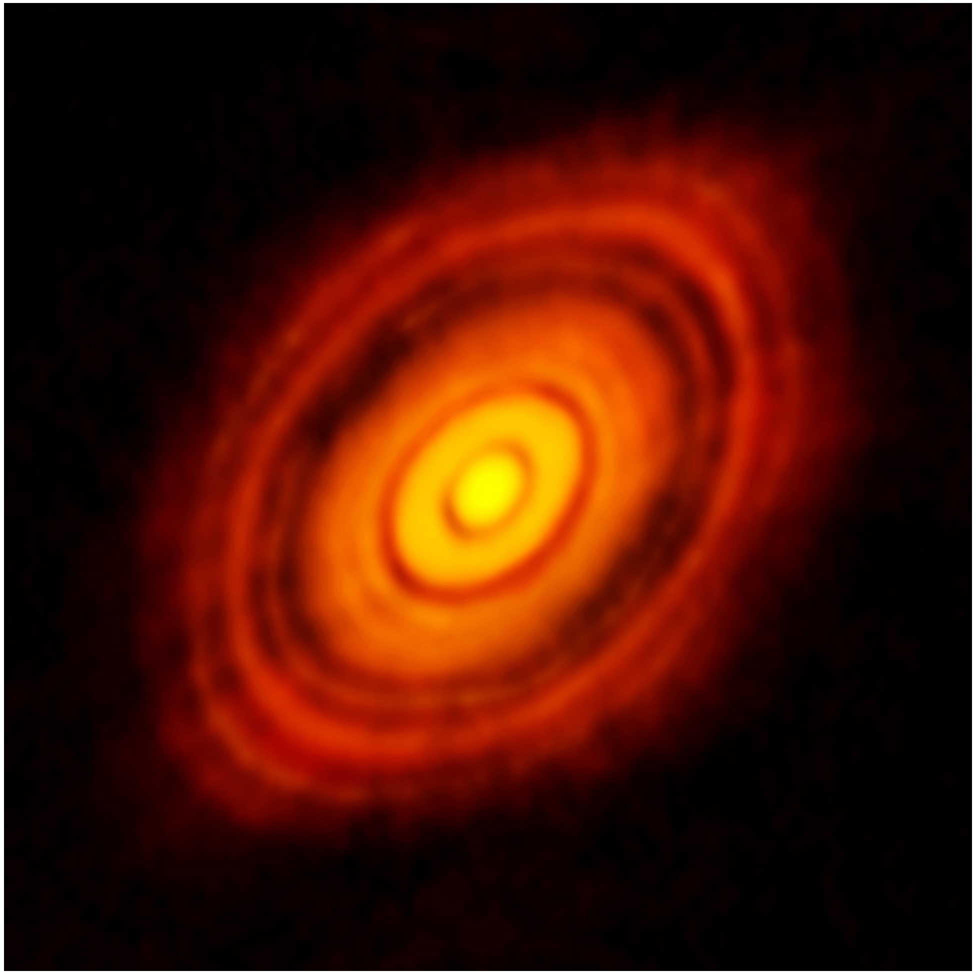
Herbst & van Dishoeck 2009

Protoplanetary disks

- Thanks to the high-resolution observations of ALMA, today we are in the position to cast light on the processes taking place in protoplanetary disks

- In particular, planetary formation and production of molecules of astrobiological interest

- This will help us in reconstructing the chemical processing of prebiotic material that must have taken place in the protosolar nebula



Delivery of prebiotic material on planets

- During the stages of formation of extrasolar planetary systems, minor bodies may deliver organic material and water on planets

- The study of meteorites recently arrived on Earth and of space observations of asteroids/comets shows that indeed complex organics and water can be delivered from space to Earth

- The primitive Earth is likely to have been enriched by organic material delivered by meteorites of asteroidal and cometary origin

  The early flux of comets was likely to be higher in the early stages of evolution of the Solar System

Material delivered on Earth by comets

- Comets may have delivered material on the primitive Earth
  - analysis of present-day comets that still preserve their original composition can be used to trace the history of material in comets
  - several studies confirm that comets do possess volatiles and organic material
  - data from the Rosetta mission to comet 67P have revealed in detail the richness of organic material in comets

Rosetta mission: organics in comet 67 P (C-G)

- In situ mass spectrometry of cometary volatiles:

  large number of organics, many of them for the first time in a comet (bold characters below)

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

- As in other comets, cometary D/H is higher than in terrestrial oceans

D/H ~5.3 10^{-4} in H_2O
Altwegg et al., Science, 2015

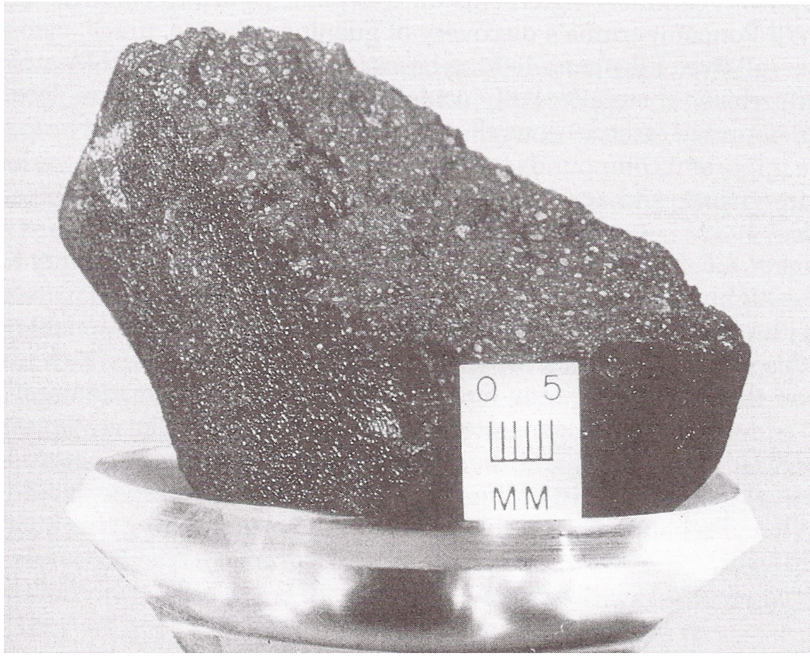
Prebiotic material delivered on Earth by meteorites

- One of the most interesting cases is the Murchison meteorite (Australia, 1969)
- Evidence have been found of aminoacids and nucleobases

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

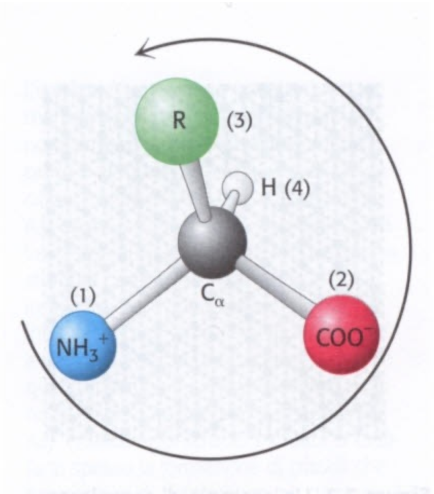


A slight eccess of the L enantiomer has been found, the same enantiomer of biological aminoacids

Origin of the homochirality of biological molecules

- Understanding the origin of homochirality may cast light on the early stages of prebiotic chemistry

- One possible scenario is that a slight enantiomeric eccess was produced by some prebiotic process
  - At a later stage, the enantiomeric eccess would have been amplified up to the point of attaining homochirality



On the origin of the enantiomeric eccess

- The hypothesis of an enantiomeric eccess of astronomical origin is taken into consideration

- A possible physical mechanism:
  - Circularly polarized interstellar radiation field

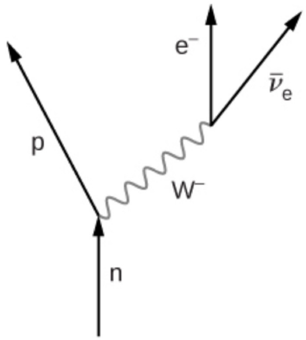
    might affect the early prebiotic chemical reactions in interstellar space, leading to a small enantiomeric eccess

    However, the predicted effect is extremely small

    The chiral excess could be either left- or right-handed

    The L-type excess of terrestrial amino acids would be accidental

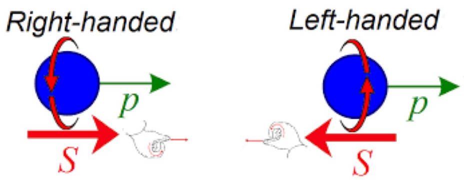
On the origin of the enantiomeric eccess



- Other potential physical mechanisms
  - Beta decays of unstable radionuclides (e.g., ^{40}K)

$$ {}^{40}_{19}\mathrm{K} \rightarrow [{}^{40}_{20}\mathrm{Ca}]^{+} + \beta^{-} + \overline{\nu}_e $$

  - Due to parity violation of the weak nuclear force, the emitted beta particle is "chiral": its spin is always antiparallel to its direction of motion



  - Very small effect predicted also in this case, but with an L-type enantiomeric eccess for amino acids

  - Potassium, together with its unstable isotope ^{40}K, was likely to be present in all stages of terrestrial prebiotic chemistry

Vladilo, G. On the Role of 40K in the Origin of Terrestrial Life. *Life* 2022, 12, 1620

Prebiotic chemistry: laboratory studies

- Laboratory experiments
  - Searching for plausible chemical pathways that may lead to the spontaneous assemblage of basic prebiotic constituents, such as amino acids or nucleosides
  - Simulating the physical conditions and chemical ingredients that are expected to be present in:

    Minor bodies of the Solar System (e.g., comets or asteroids)

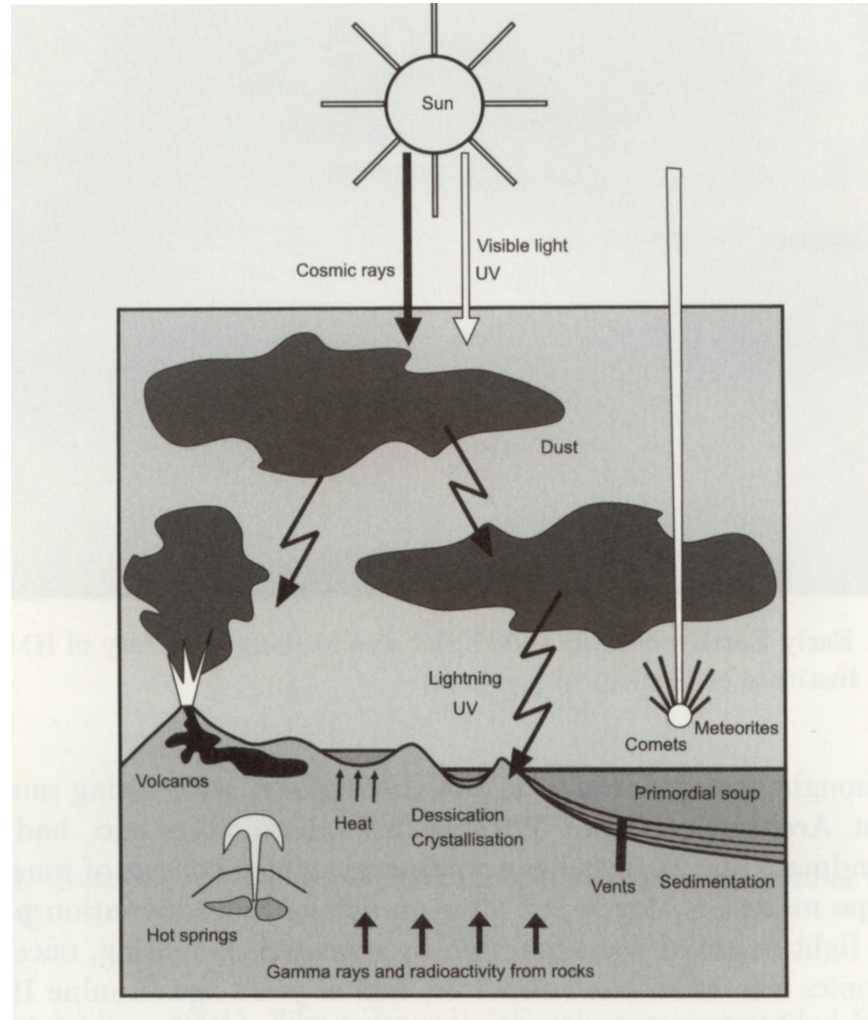
    The primitive Earth

- Plausible chemical pathways
  - The reactants should expected to be present in the environment that is simulated
  - The physical and chemical conditions are simulated to the best of our knowledge
  - The products of the chemical reactions should be stable

Simulations of physical conditions

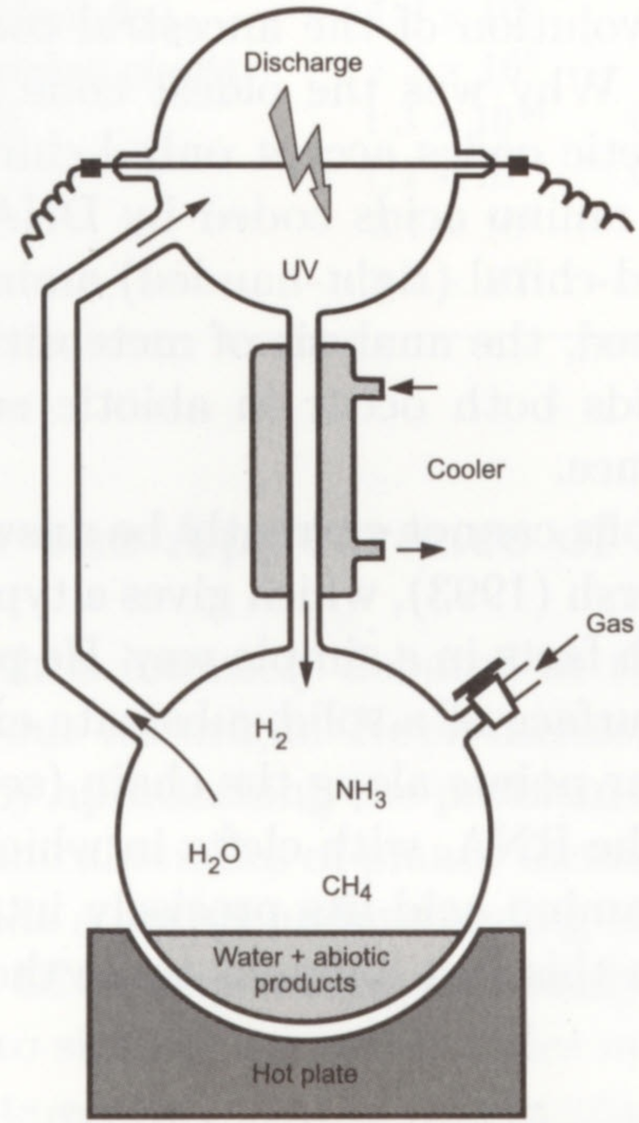
- Comets or asteroids
  - Fluxes of ionizing particles need to be generated
  - The targets are made of different types of material that is found in meteorites

- Primitive Earth
  - The physical conditions and atmospheric composition of the Earth in the Archean era are simulated
  - The first, 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 reducing power of the early earth atmosphere was probably overestimated
- 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



Early investigations of prebiotic chemistry

- 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

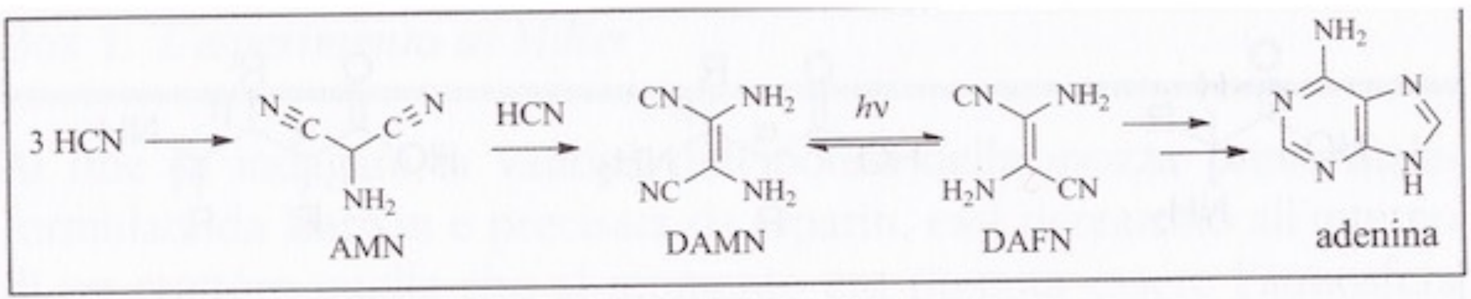


Fig. 4. Meccanismo di formazione semplificato dell'adenina a partire dall'HCN.

  - 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

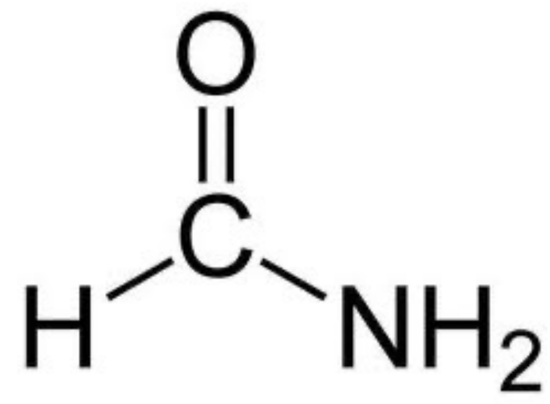
Prebiotic chemistry with formamide

Formamide ($HCONH_2$) is ubiquitous in the Universe

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

From the point of view of prebiotic chemistry formamide presents several advantages compared to HCN

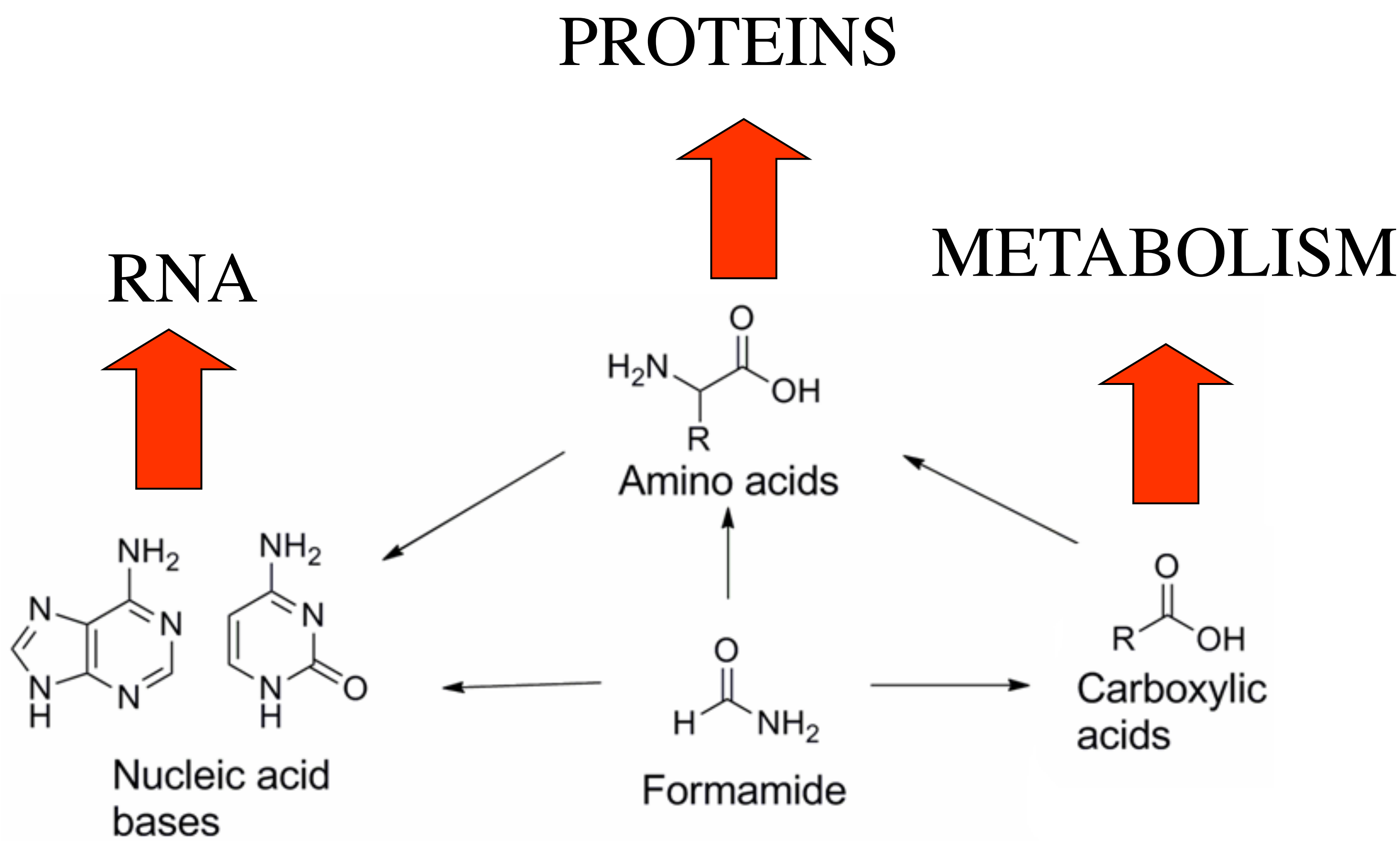
- Boiling point of 210^{o}C, higher than the water boiling point
- Therefore, it can be easily become concentrated through the evaporation of water
- The concentration of HCN is difficult because HCN is in gaseous form at ambient temperature and pressure



Formamide has a remarkable capability of forming a network of hydrogen bonds:

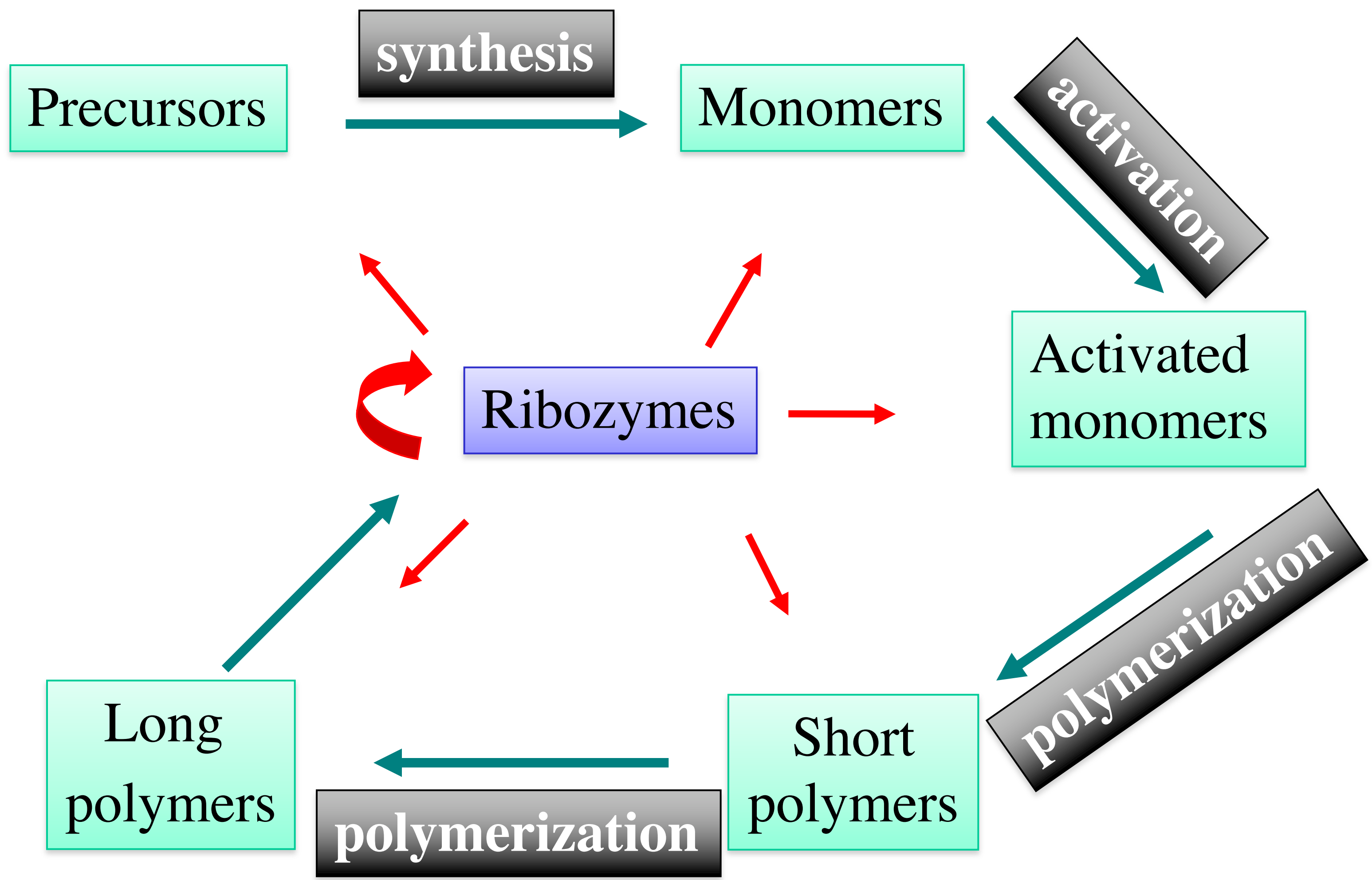
3 donors and ~3 acceptors, even better than water

Prebiotic chemistry with formamide



Formamide is potentially involved in all relevant steps of prebiotic chemistry.
Succesful experiments exist for most steps of prebiotic chemistry.

Steps of prebiotic chemistry leading to the emergence of biopolymers



Laboratory studies show that each step of this hypothetical prebiotic pathway requires its own specific physico-chemical conditions

Origin of life not possible "in a single pot"