# Astrobiology
## Lecture 9

## Prebiotic chemistry

Trieste University, Academic Year 2021-2022
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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 (probably tighter) than the requiremens of habitability
- The scientific approach
  - The origin of life is assumed to be the result of as a sequence of spontaneous processes that leads to the formation of the first living cells starting from non-biological chemical compounds
- Abiogenesis
  - The transition from the abiotic world to life is called *abiogenesis*

# Studies on the origin of life

- Two approaches:
  - "bottom-up"

    trying to reconstruct the emergence of biological molecules starting from non biological constituents
  - "top-down"

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

- Fields of research in the "bottom-up" approach
  - Prebiotic chemistry (synthesis of precursors of biomolecules)

    Origin of homochirality
  - Emergence of replicative and metabolic functions

# 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

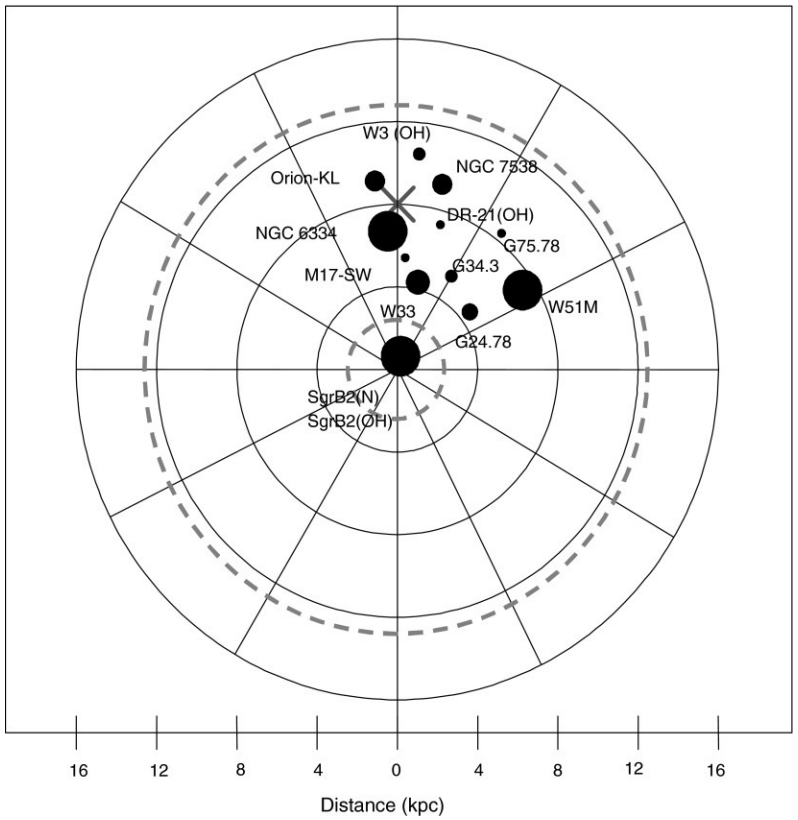
- Early synthesis of prebiotic constituents probably took place in the molecular cloud from which the protosolar nebula originated 4.5 Gyr ago

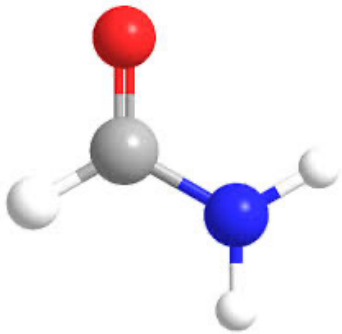
- We can find evidence of this type of processes in present-day molecular clouds that we can now investigate with mm and sub-mm radiotelescopes, like ALMA (ESO, Chile)

- The number of prebiotic precursors found in molecular clouds is increasing over the years

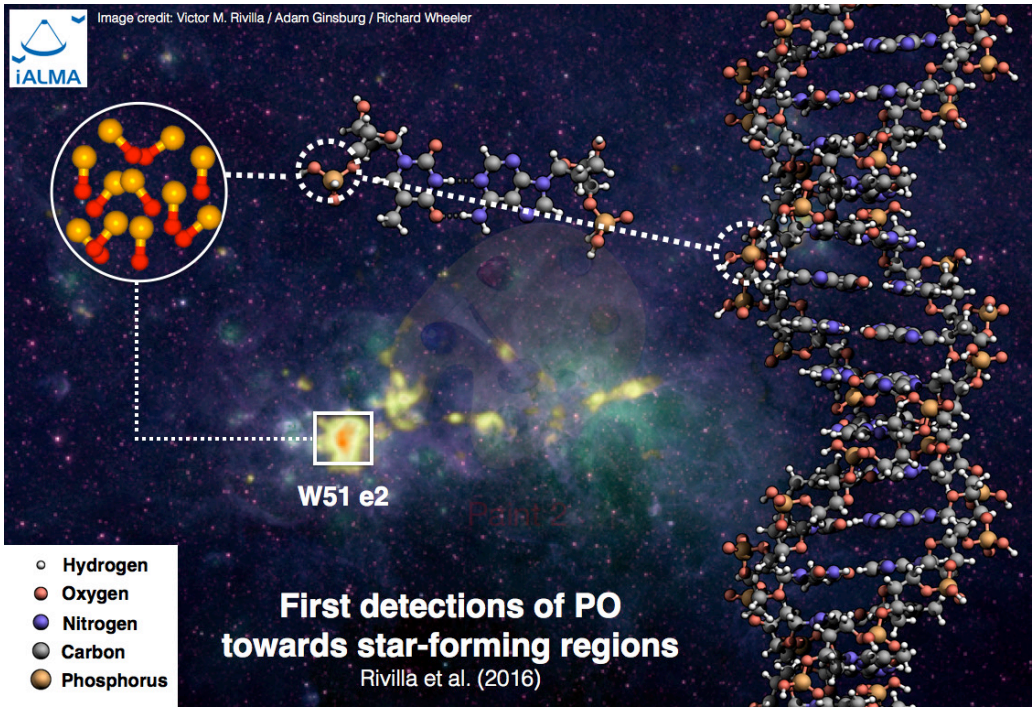
- The interpretation of how organic molecules can form in harsch interstellar conditions requires theoretical and laboratory investigations
  - Databases of molecular transitions need to be expanded
  - Theoretical studies require a quantum-chemistry approach

# Prebiotic chemistry in molecular clouds



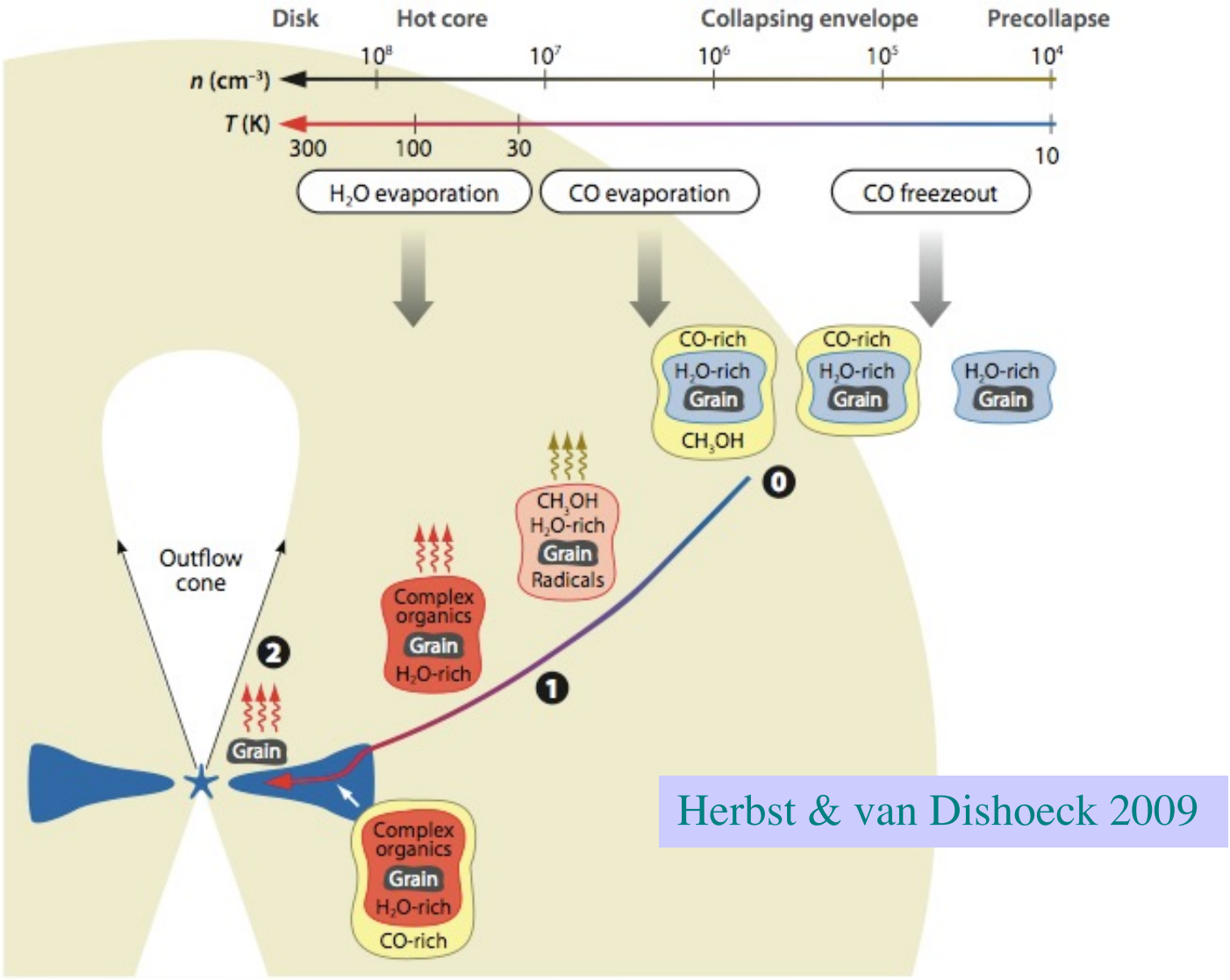



**Formamide**



# Protoplanetary disks

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



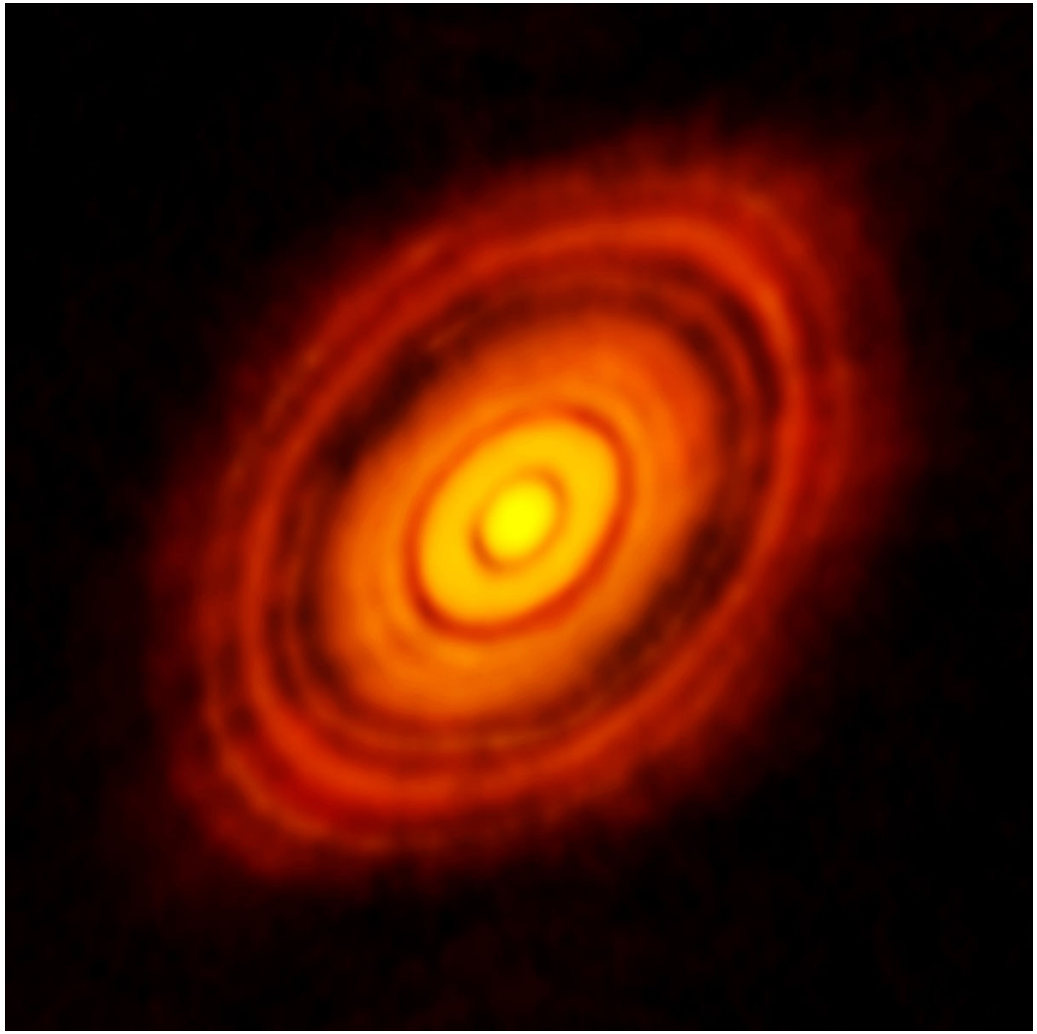

Herbst & van Dishoeck 2009

# Protoplanetary disks

- Reconstructing the chemical processing of prebiotic material in the protosolar nebula is not an easy task

- Today we are in the position to directly study this type of processes in protoplanetary disks observed at high spatial resolution with ALMA

- These observations are casting light on planetary formation and on the production of molecules of astrobiological interest (e.g. water) in protoplanetarty disks



# Delivery of prebiotic material on planets

- The primitive Earth is likely to have been enriched by organic material delivered by meteorites of asteroidal and cometary origin
- 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
- We expect similar processes to take place at the present time at the early stages of evolution of planetary systems

# Material delivered on Earth by comets

- Comets may have delivered 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 material in comets

  – several studies confirm that comets do possess volatiles and organic material

  – data from the Rosetta mission suggests that
    - comets did deliver xenon on the Earth, but only a small fraction of water
    - comets do have complex organic material

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

- Confirms that cometary D/H is 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**

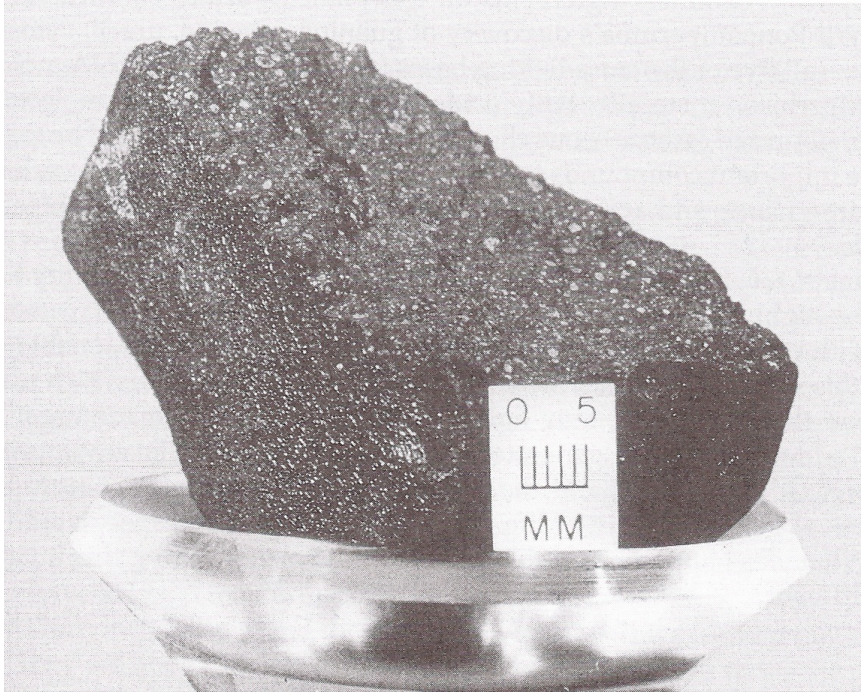
# Prebiotic material delivered on Earth by meteorites

- 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

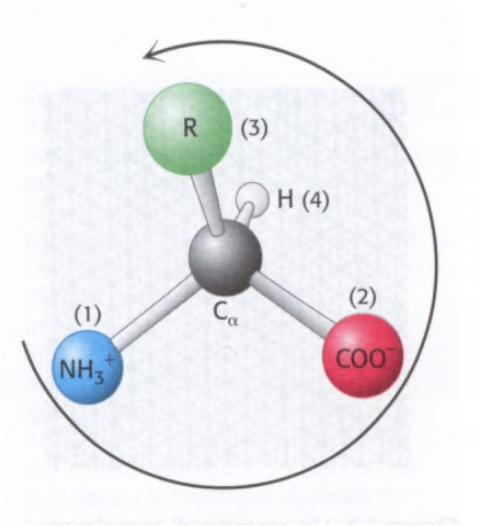



A slight eccess of the L enantiomer has been found, the same enantiomer of biological aminoacids

# Origin of the homochirality of biological molecules

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

- The general idea 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



# The hypothesis of an interstellar origin of a prebiotic enantiomeric eccess

- The hypothesis of an enantiomeric eccess of astronomical origin is taken into consideration
  - Motivated by the discovery of the weak enantiomeric eccesses in the Murchison meteorite

- A possible scenario:
  - A circularly polarized interstellar radiation field may have affected the early prebiotic chemical reactions in interstellar space, leading to a small eccess of molecules with one type of symmetry

- Laboratory tests can be perfomed using circularly polarized light produced in synchrotron experiments

# Prebiotic chemistry: laboratory studies

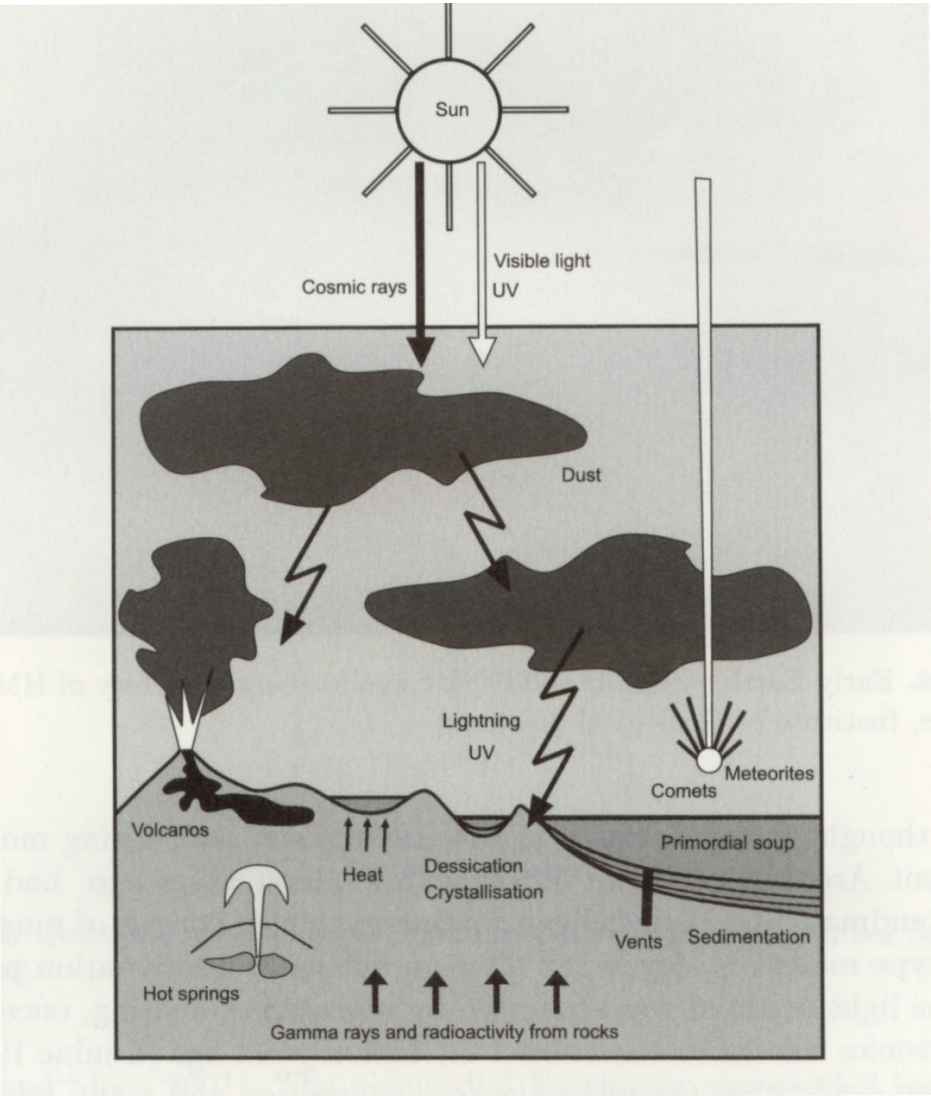
- Laboratory experiments
  - Searching for plausible chemical pathways that may lead to the spontaneous assemblage of basic prebiotic constituents, such as amino acids or nucleosides
  - Simulating the physical conditions and chemical ingredients that are expected to be present in:

    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 products of the chemical reactions should be stable

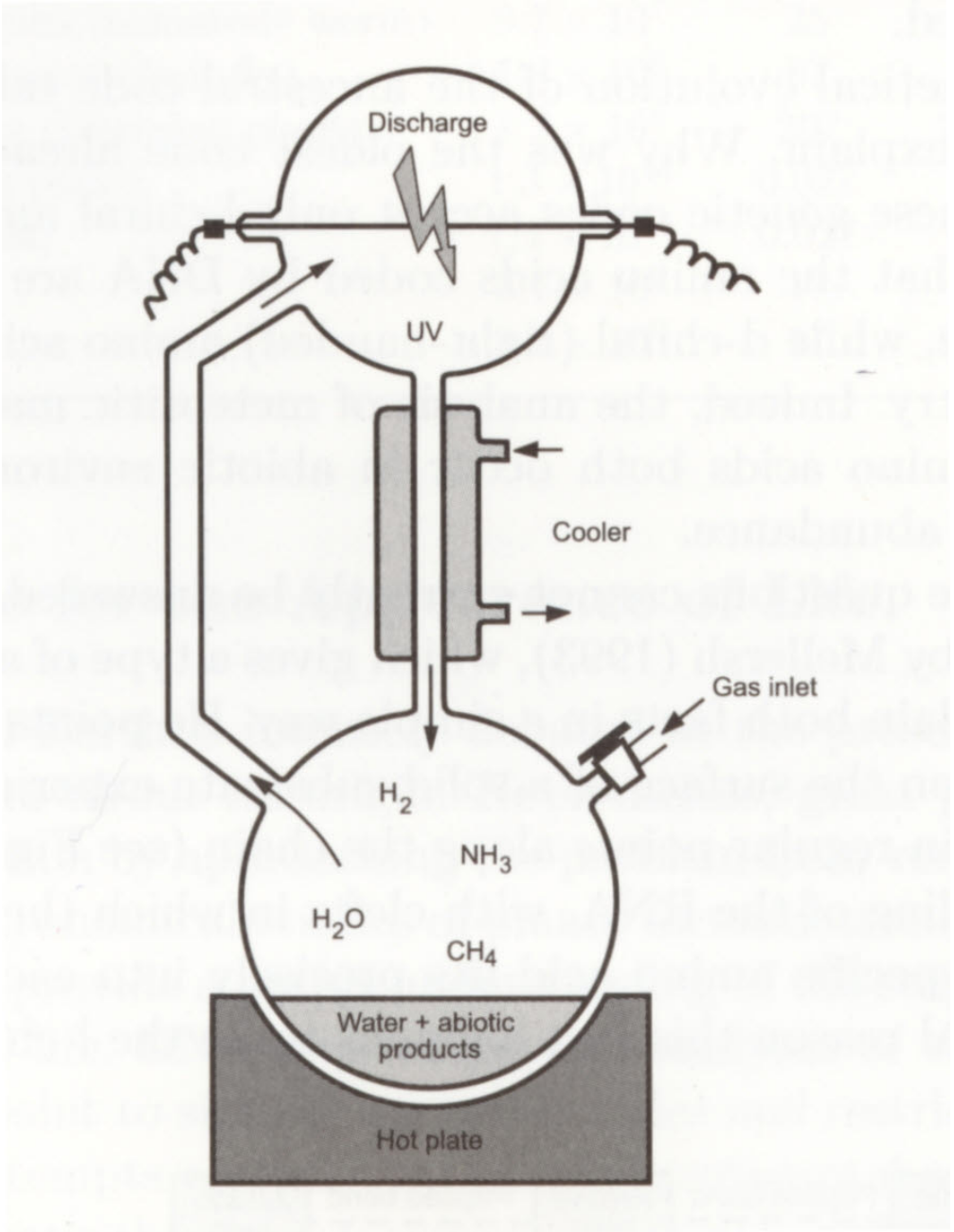
- Comets or asteroids
  - Fluxes of ionizing particles need to be generated
  - The targets are made of different types of material that is found in meteorites

- 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

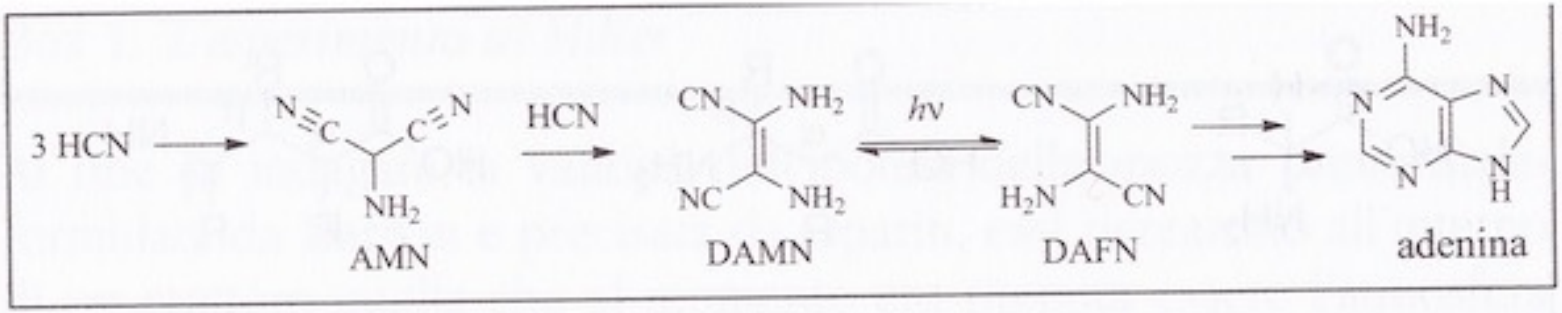



FIG. 4. Meccanismo di formazione semplificato dell'adenina a partire dall'HCN.

  - 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

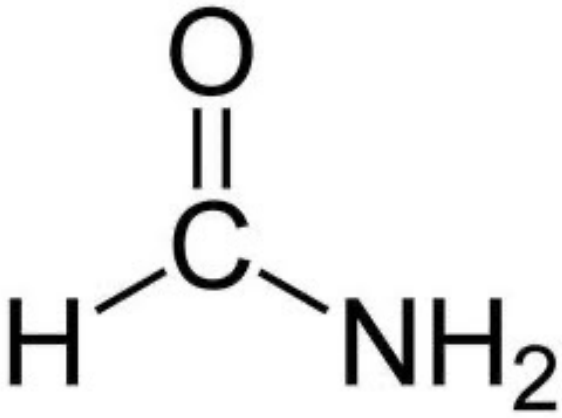
# Prebiotic chemistry with formamide

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

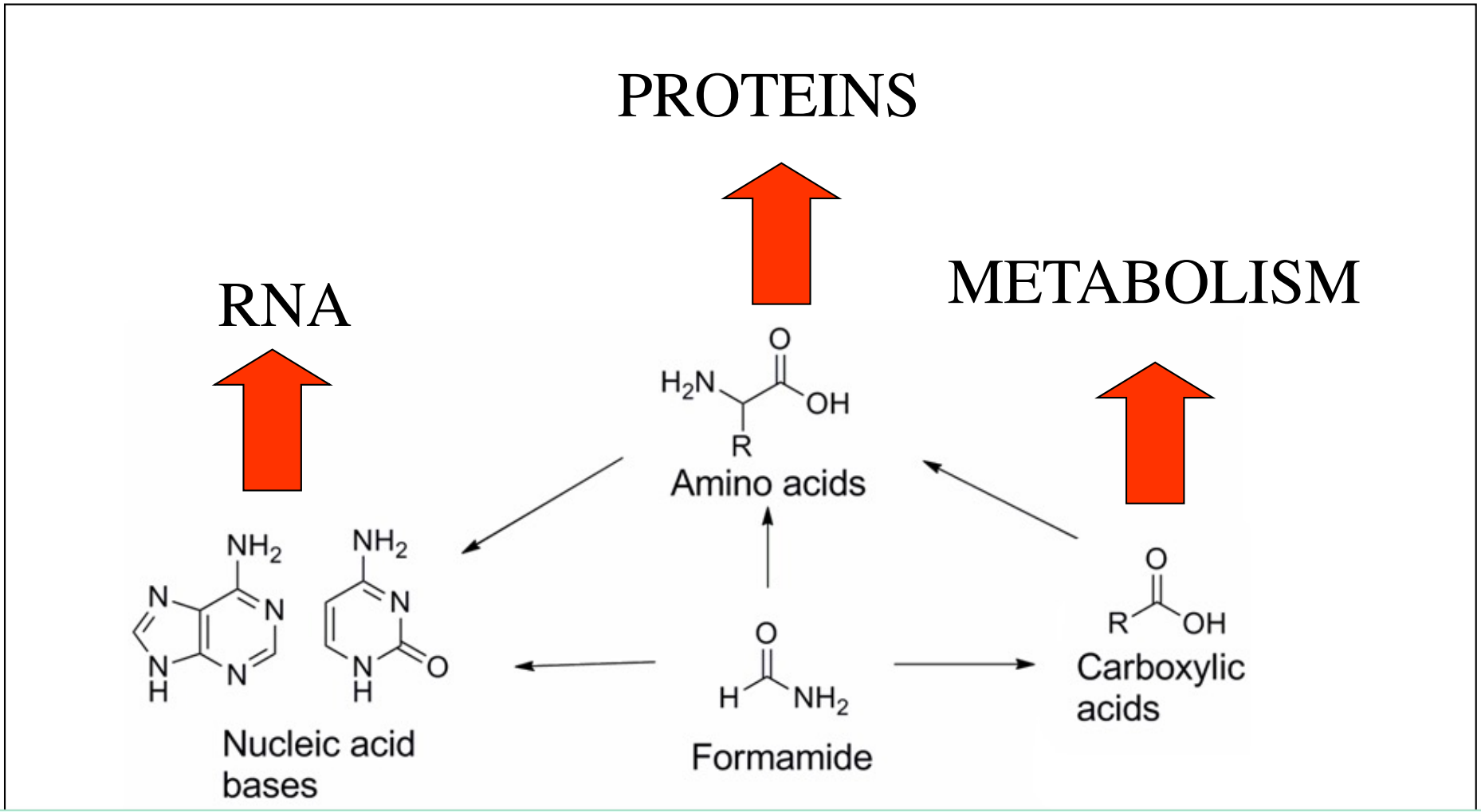
- Boiling point of 210°C, higher than the water boiling point
- Therefore, it can be easily become concentrated through the evaporation of water
- The concentration of HCN is difficult because HCN is in gaseous form at ambient temperature and pressure




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. However, experiments in a "single pot" are able to perform only one, or a few, steps at a time.

Steps of prebiotic chemistry leading to the emergence of biopolymers

The ambient physico-chemical requirements may change in different steps