# Prebiotic chemistry

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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)

    Origin of homochirality
  - Emergence of replicative and metabolic functions
  - Search for the least evolved 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

# Prebiotic chemistry

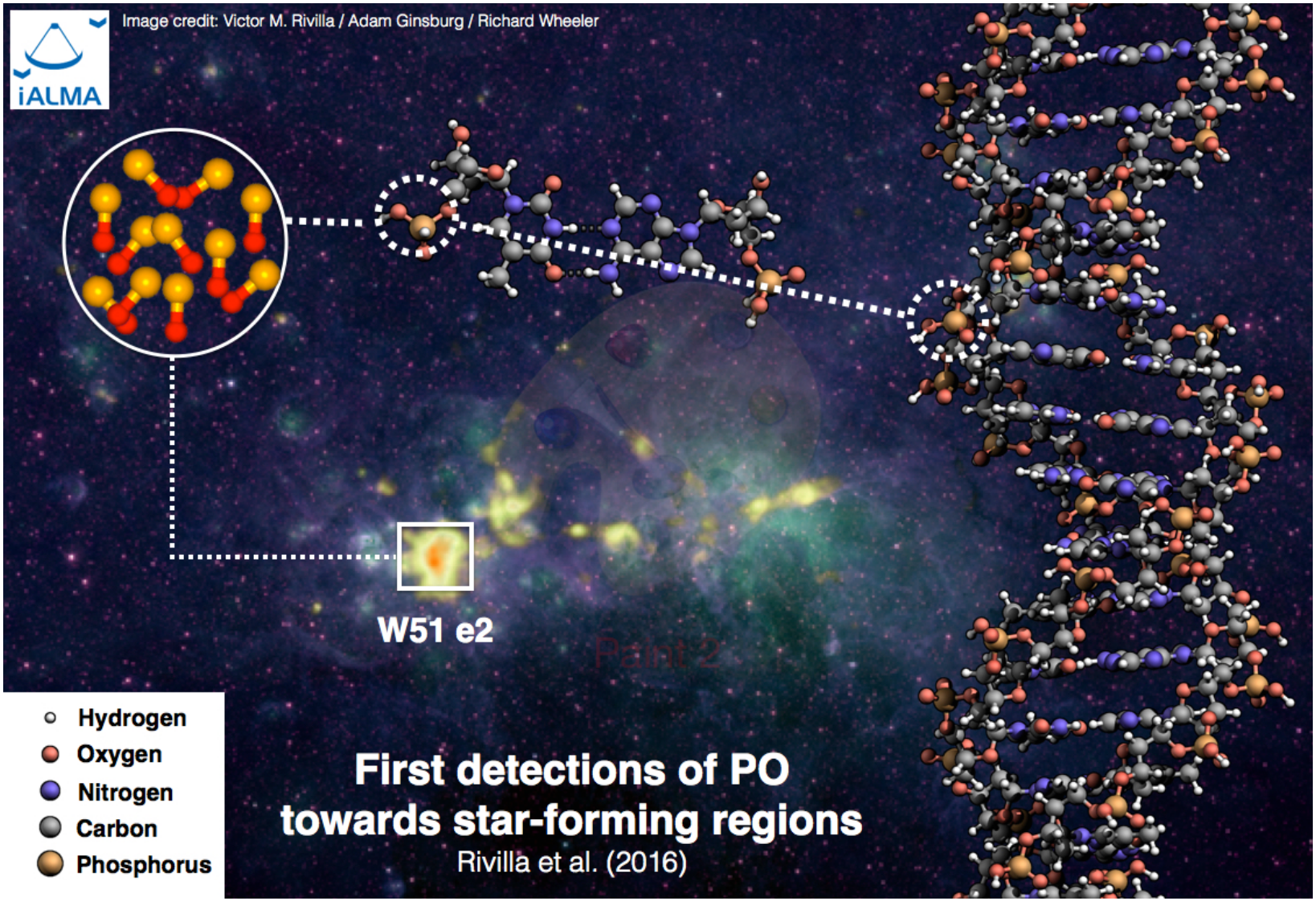
- Search for plausible chemical pathways of synthesis of the molecular building blocks of biological macromolecules
  - One of the goals of prebiotic chemistry is to understand which organic molecules are the most likely to initiate these chemical pathways
- Possible scenarios for the synthesis of prebiotic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

# 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

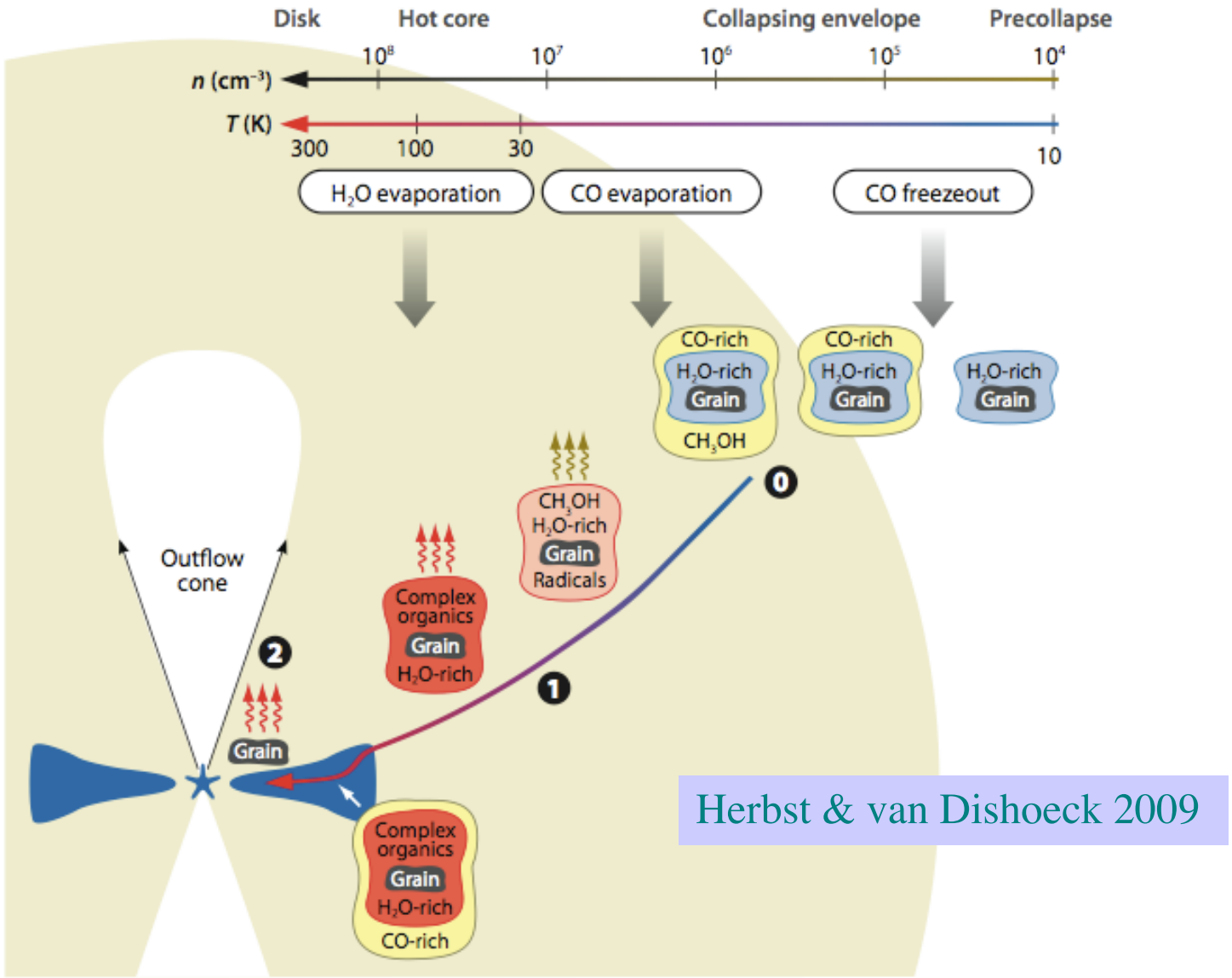
- Indirect evidence supporting the delivery of complex organics in the past is found from the study of meteorites recently arrived on Earth and of space observations of comets

# Prebiotic chemistry in molecular clouds



# Prebiotic chemistry in space

## From molecular clouds to protoplanetary disks




Herbst & van Dishoeck 2009

# Material delivered on Earth by comets

- Also 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**

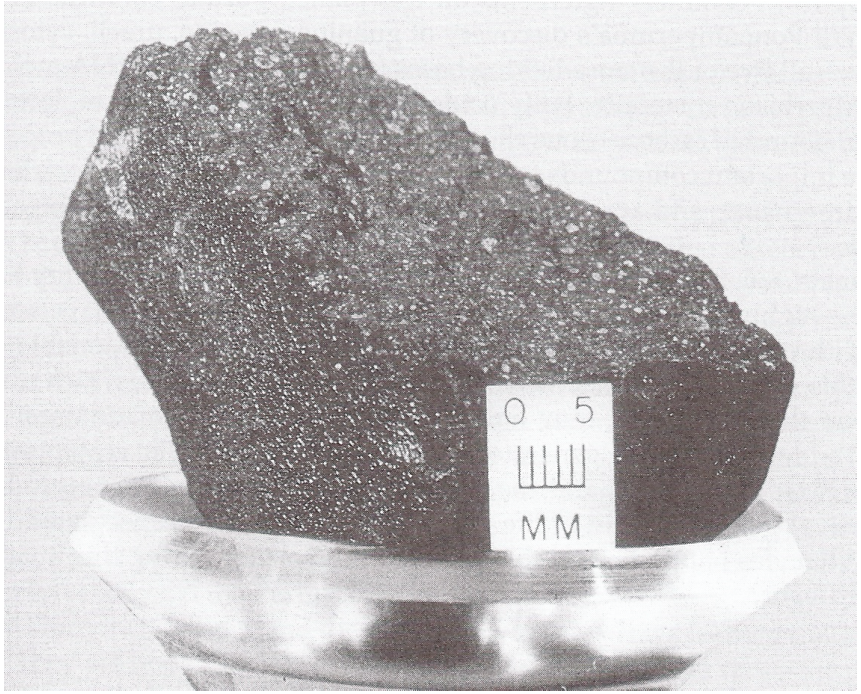
# Prebiotic material delivered on Earth by meteorites

- 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

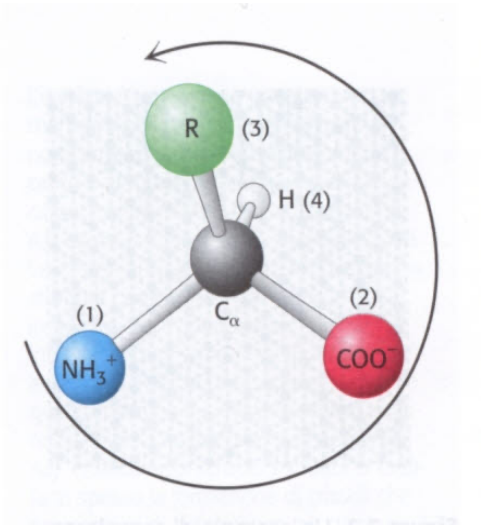



A slight eccess of the L enantiomer has been found, the same enantiomer of biological aminoacids

# 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

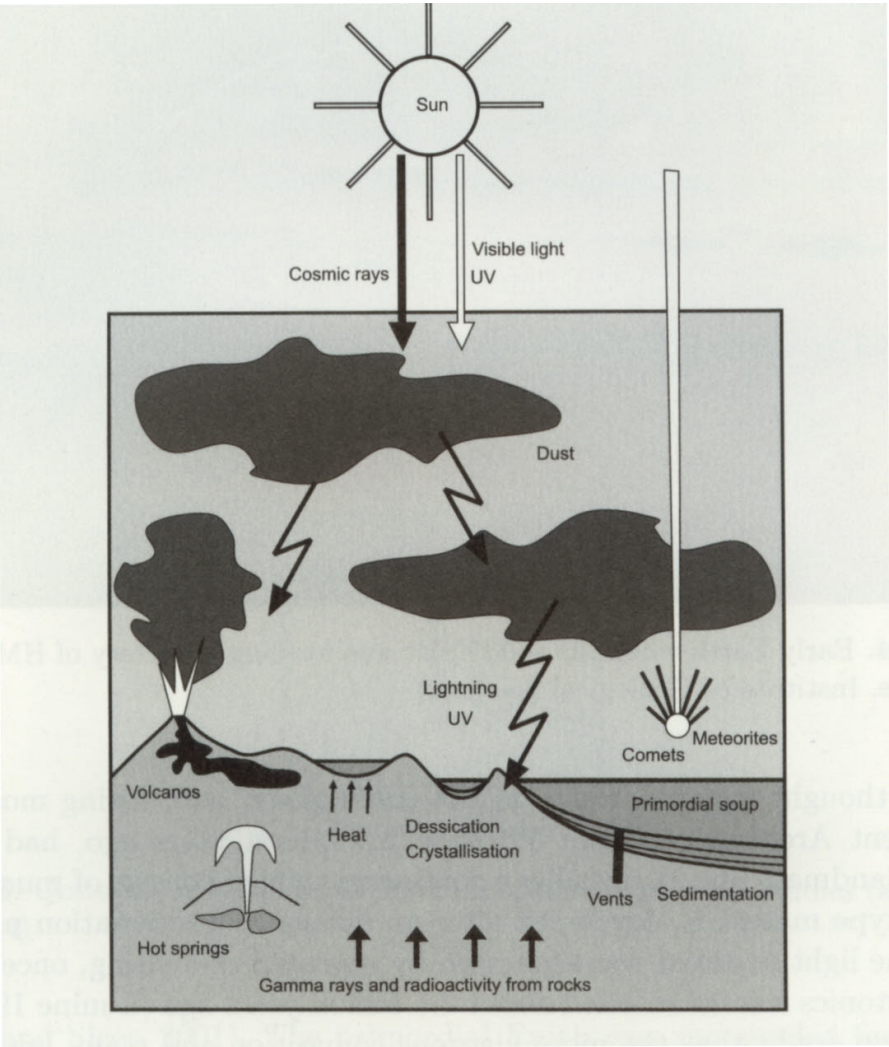
- The hypothesis of an enantiomeric eccess of astronomical origin is taken into consideration
  - Motivated by the discovery of the weak enantiomeric eccesses in the Murchison meteorite

- 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

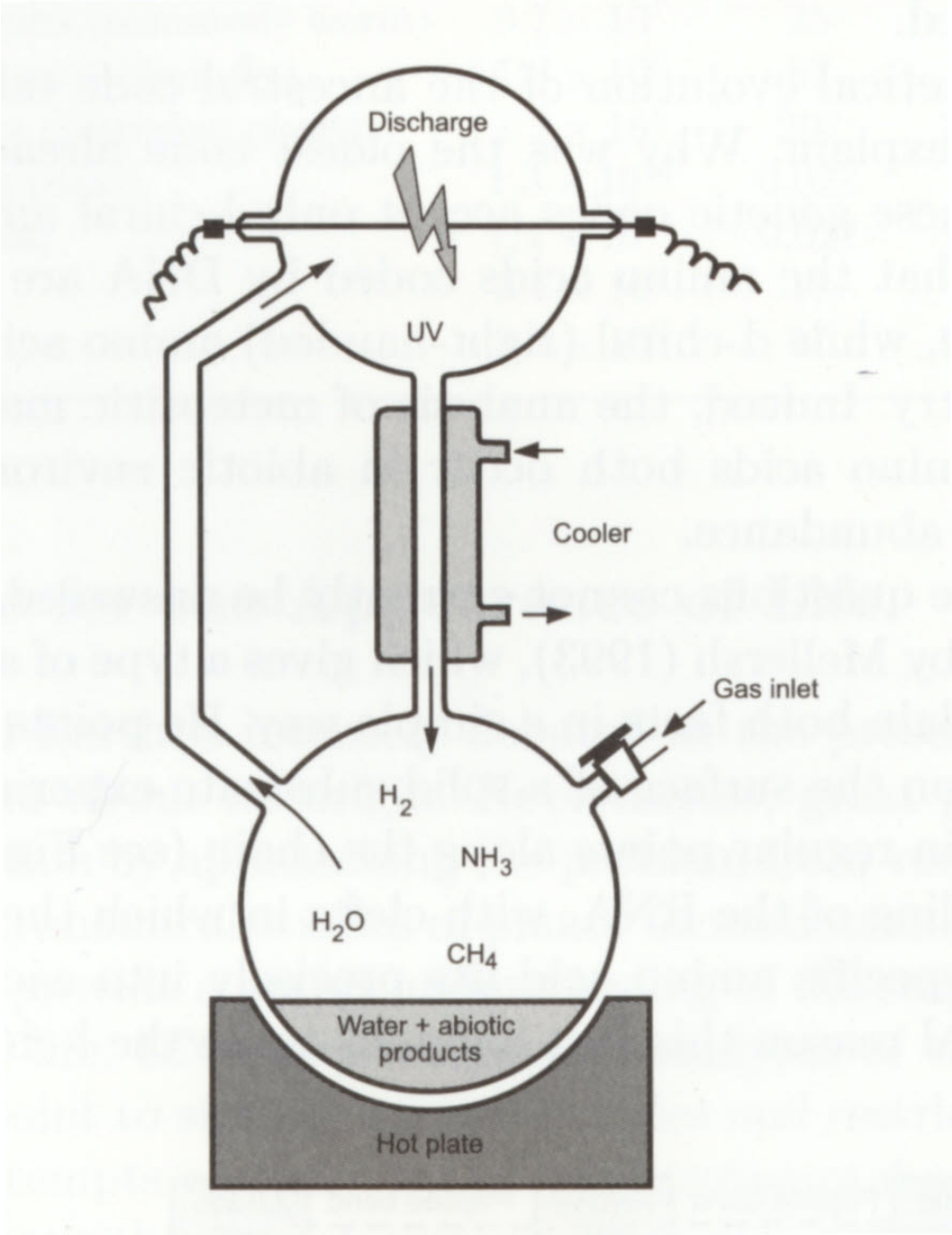
# Laboratory studies of prebiotic chemistry

- Laboratory experiments are a fundamental tool for studies of prebiotic chemistry
- They aim at reproducing the physico-chemical conditions conducive to prebiotic chemistry in space and 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 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 developments 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

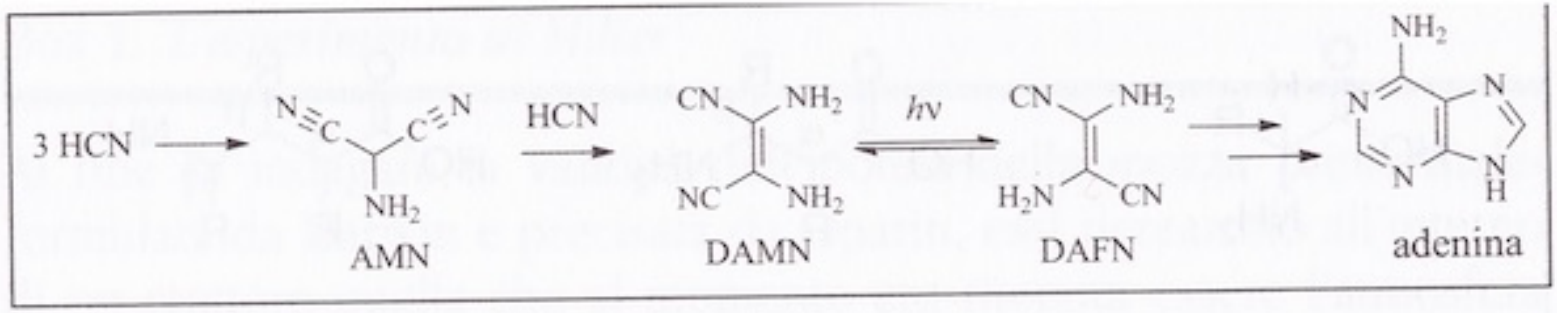



FIG. 4. Meccanismo di formazione semplificato dell'adenina a partire dall'HCN.

  - 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

Interstellar observations show that formamide ($HCONH_2$) is ubiquitous in the Universe

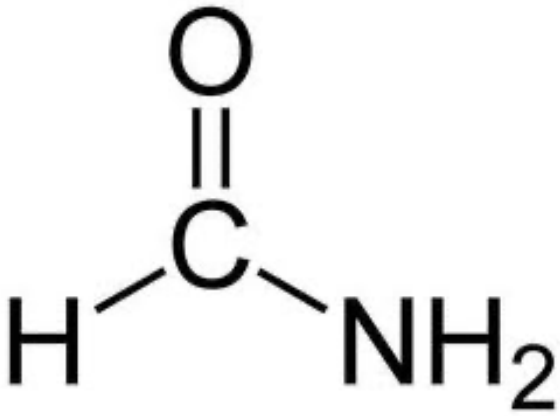
Formamide can be produced by the reaction of water and hydrogen cyanide (HCN)

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

Formamide has a boiling point of 210°C, higher than the water boiling point

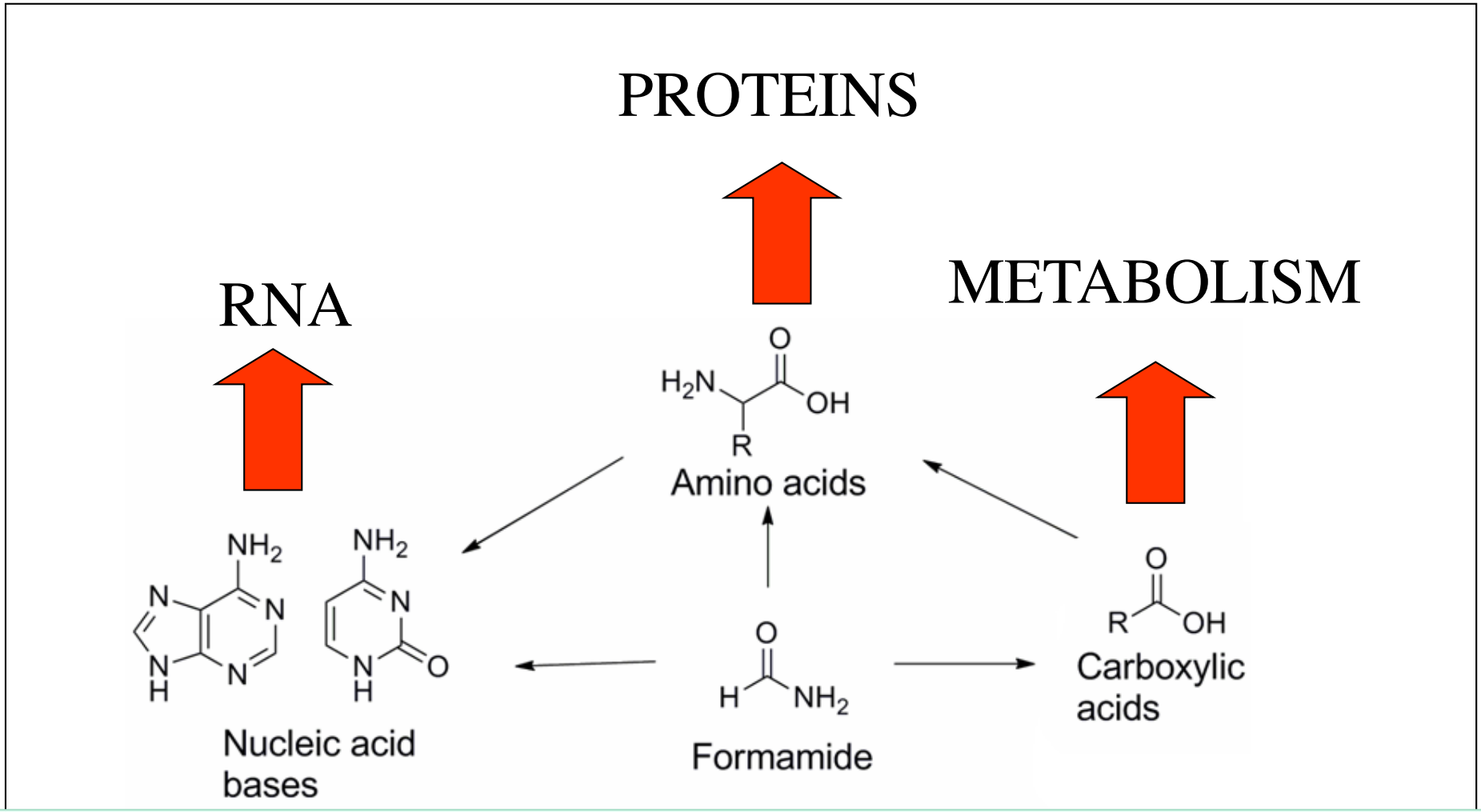
Therefore, formamide can be easily become concentrated through the evaporation of water

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, perhaps 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 biopolymers

The ambient physico-chemical requirements may change in different steps