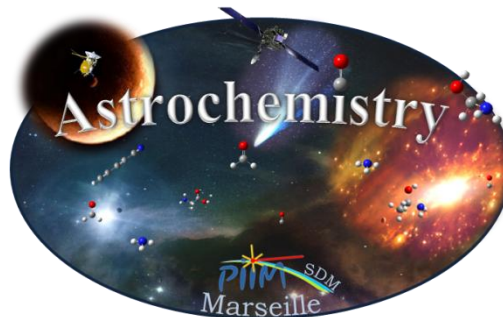


Habitability: Chemist point of view

Grégoire DANGER

Groupe Astrochimie, Equipe Spectrométries et Dynamique Moléculaire
Laboratoire Physique des Interactions Ioniques et Moléculaires
UMR-CNRS 7345, Centre Saint-Jérôme, case 252
Université d'Aix-Marseille, 13397, Marseille, France
gregoire.danger@univ-amu.fr
<http://piim.univ-amu.fr/SDM-Astrochimie>





Early Earth

The background image is a full-page photograph of a coastal scene at dusk or dawn. The sky is filled with dense, textured clouds in shades of orange, red, and pink, with a bright white glow on the horizon where the sun is setting or rising. The sea is calm, reflecting the colors of the sky. In the foreground, numerous dark, wet, and jagged rocks are scattered across the lower half of the frame, some partially submerged in the shallow water.

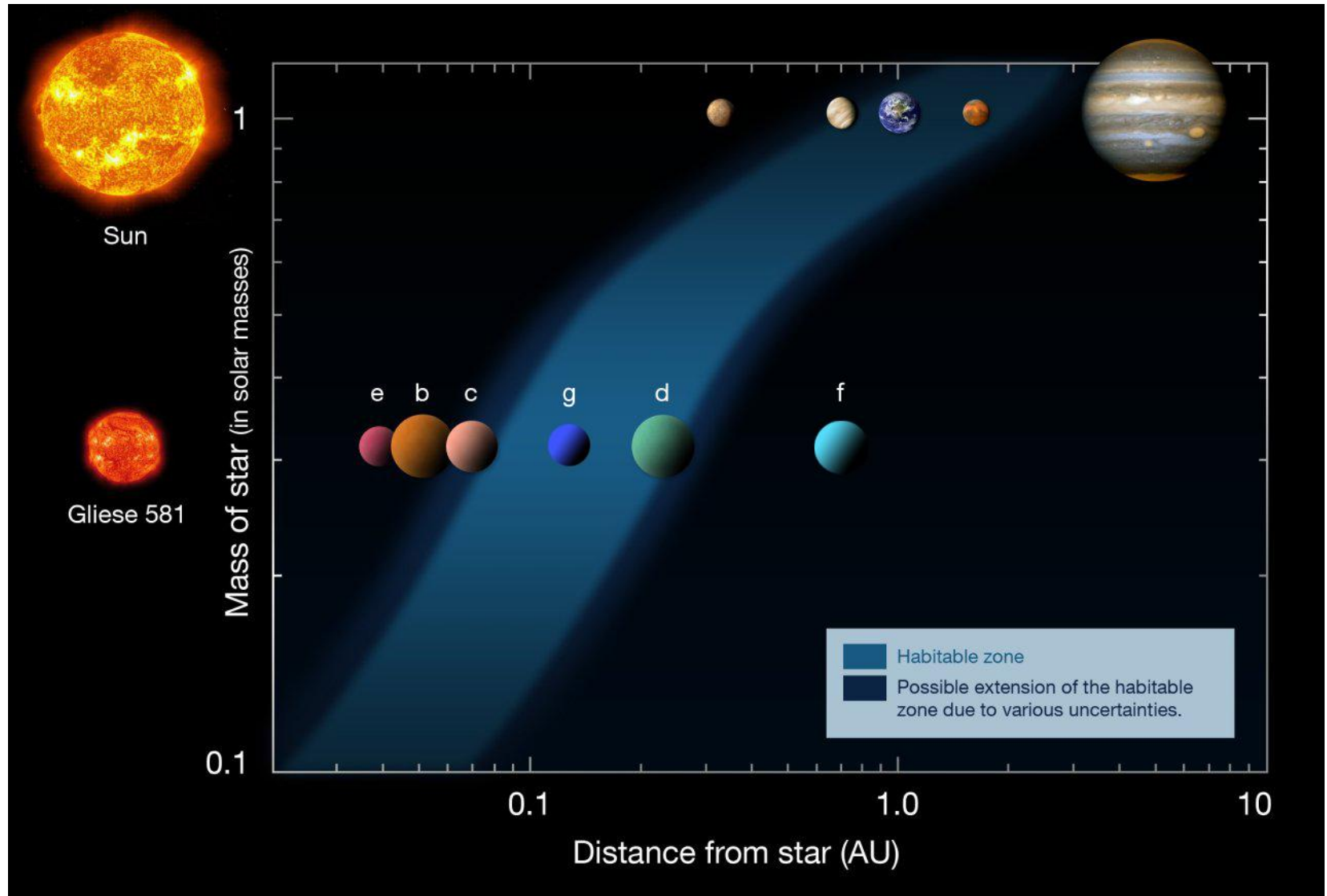
What conditions for the emergence of biochemical systems on Earth?

Wet environments

- **Liquid water a major constituent of living organisms**

Wet environments

- Liquid water a major constituent of living organisms



Wet environments

- Liquid water a major constituent of living organisms

- Importance of liquid water in biochemical reactions

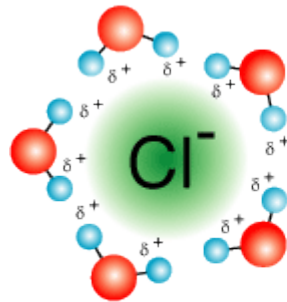
- ✓ Facilitate molecular diffusion from different environments

- ✓ Liquid state over a large range of temperature (up to 100 °C at 1 atm)

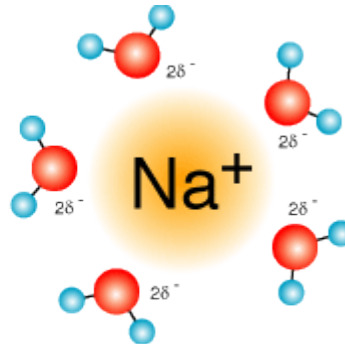
	melting point	liquid state	boiling point
CH₄ methane	91 K	Δ 21 K	112 K
NH₃ ammonia	195 K	Δ 44 K	239 K
H₂O water	273 K	Δ 100 K	373 K

Wet environments

- Liquid water a major constituent of living organisms
- Importance of liquid water in biochemical reactions
 - ✓ Facilitate molecular diffusion from different environments
 - ✓ Liquid state over a large range of temperature (up to 100 °C at 1 atm)
 - ✓ High polarity allowing to dissolve ions and polar molecules



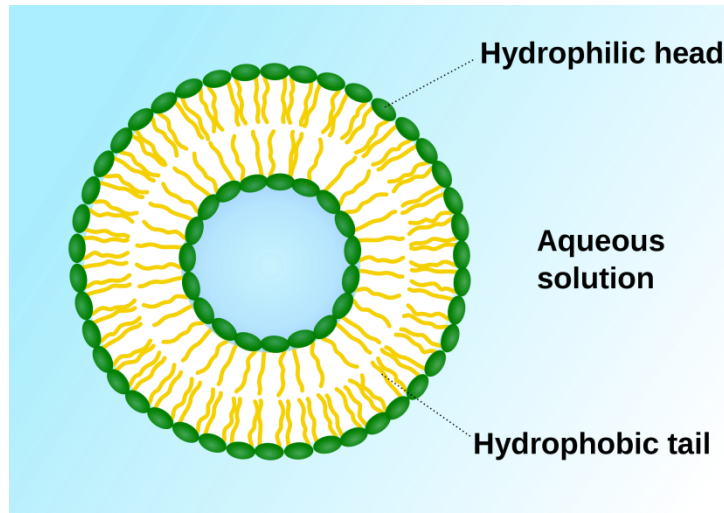
Slightly positive hydrogen are attracted to chlorine anions



Slightly negative oxygen are attracted to sodium cations

Wet environments

- **Liquid water a major constituent of living organisms**
- **Importance of liquid water in biochemical reactions**
 - ✓ Facilitate molecular diffusion from different environments
 - ✓ Liquid state over a large range of temperature (up to 100 °C at 1 atm)
 - ✓ High polarity allowing to dissolve ions and polar molecules
 - ✓ Hydrogen bond network facilitating proton exchanges
 - ✓ Induce hydrophobic interaction



Liquid Water

Early Earth



Liquid Water

Early Earth

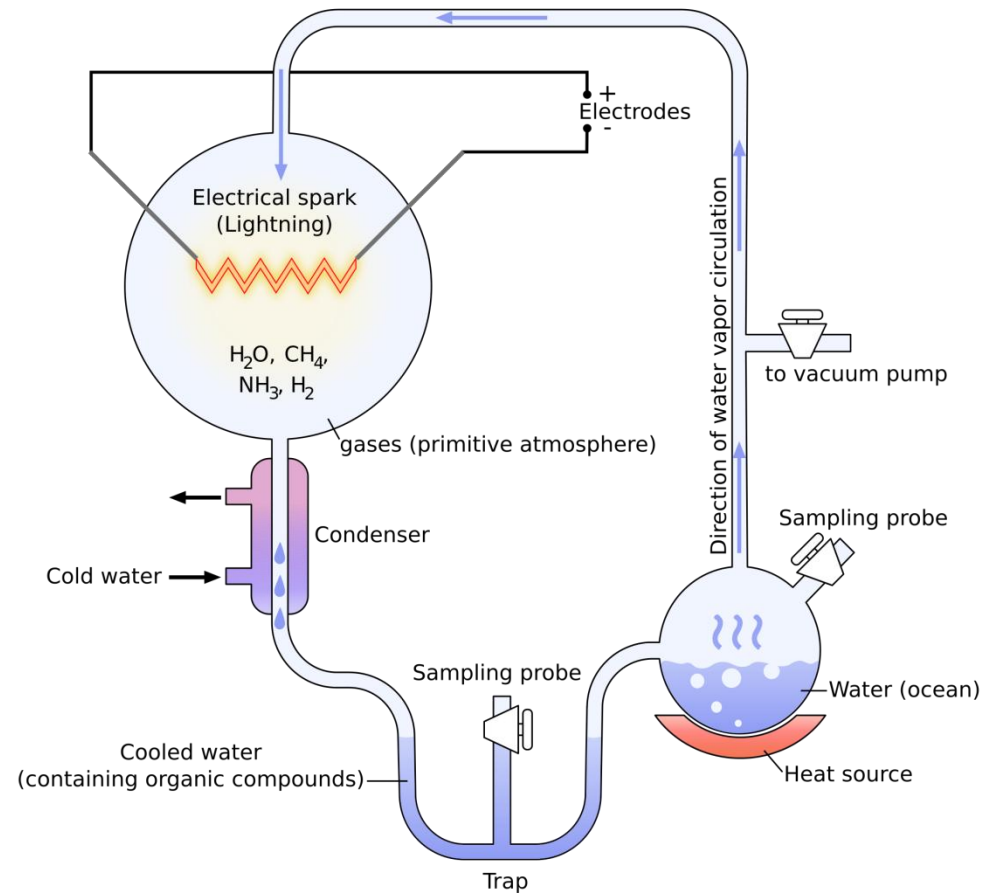
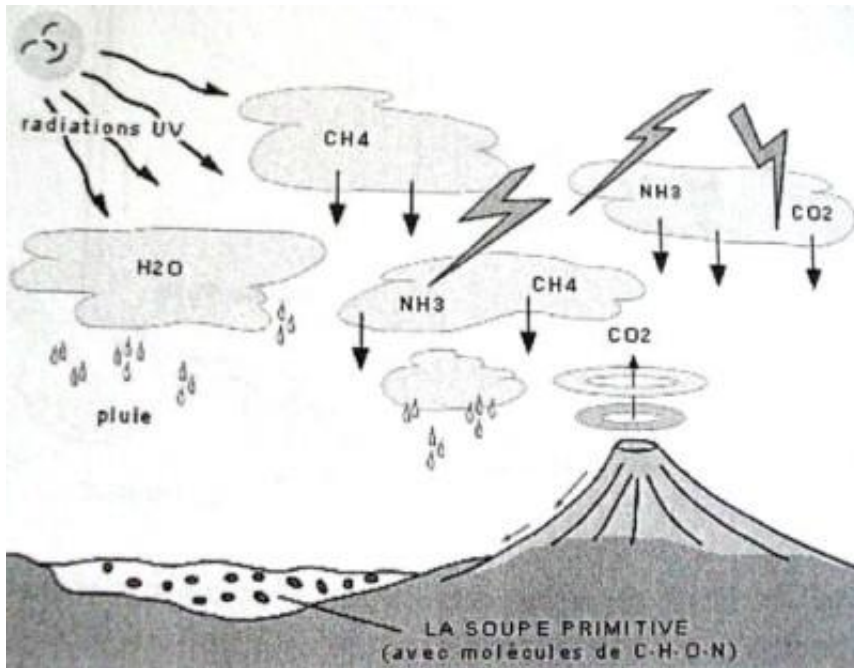
small molecules
(*i.e.* ammonia, CO₂, methane)



building blocks

Endogenous origin of organic matter

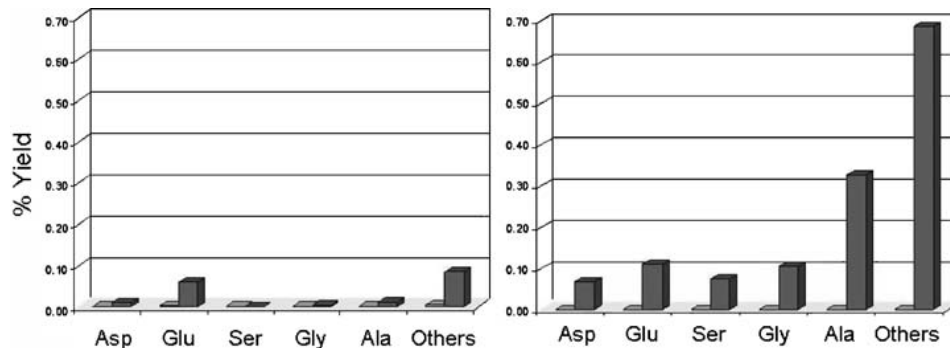
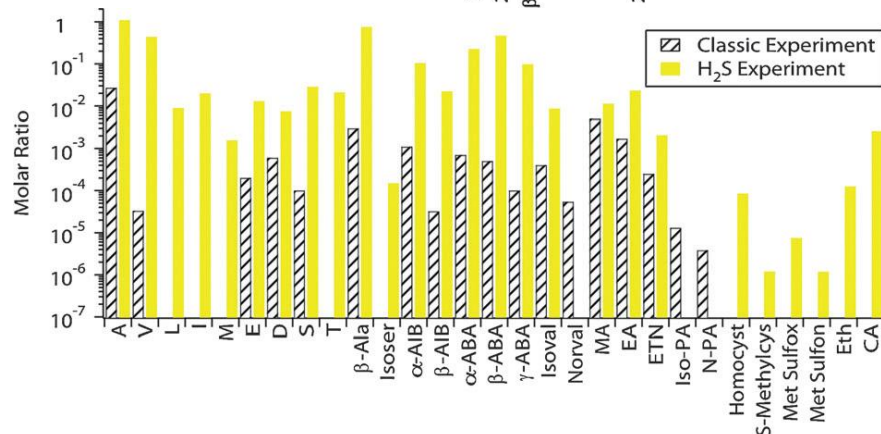
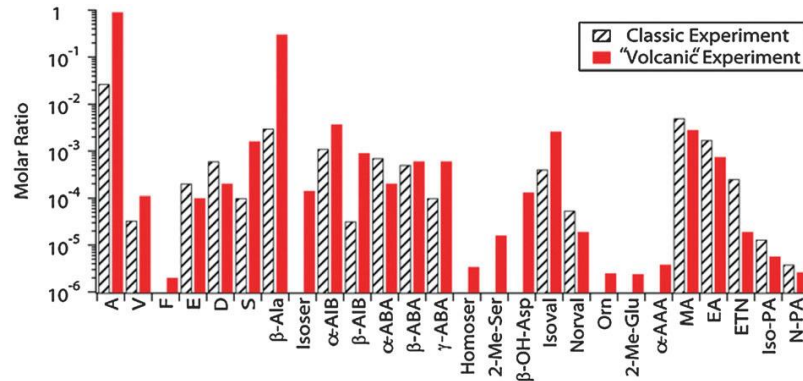
● The Miller's experiment: organic synthesis in the primitive Earth atmosphere



Endogenous origin of organic matter

The Miller's experiment: organic synthesis in the primitive Earth atmosphere

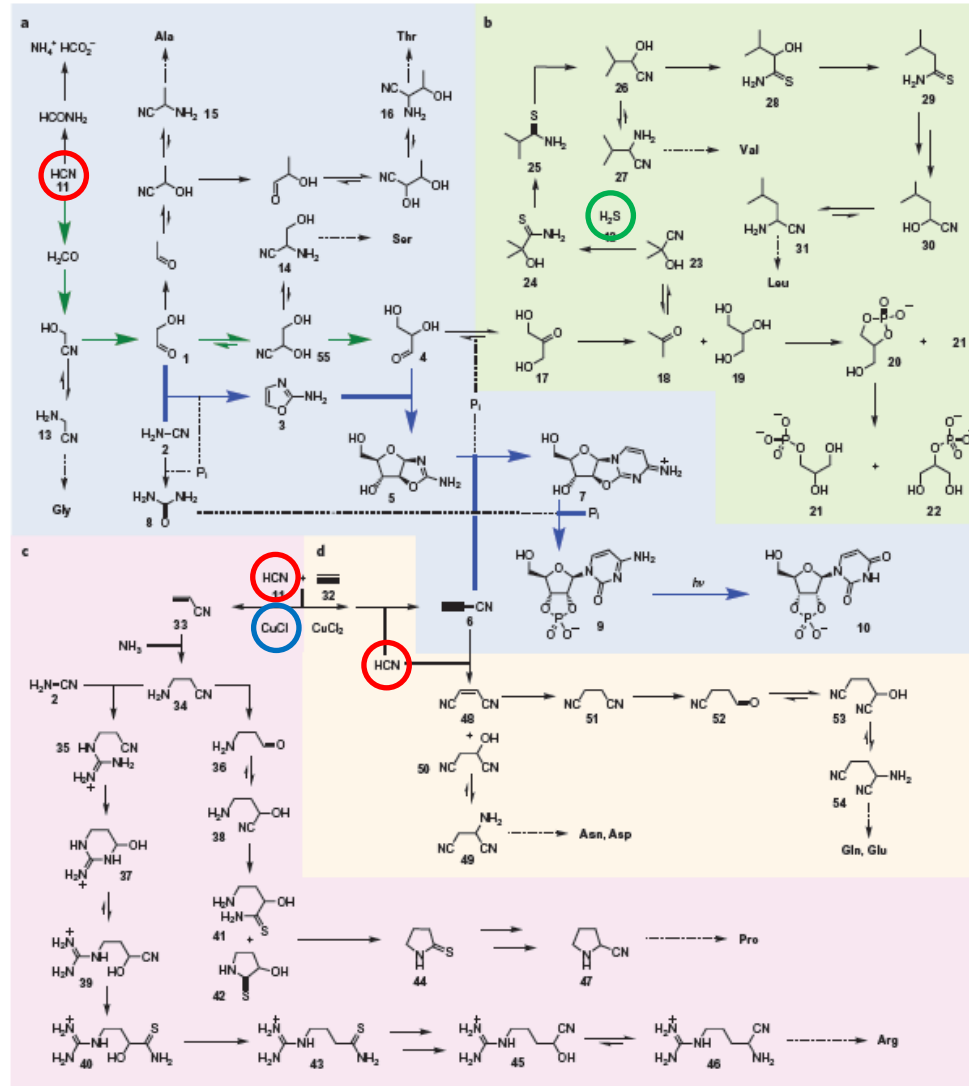
Amino acid formation



Endogenous origin of organic matter

The Sutherland's experiment: All you need

From HCN, H₂S, Cu and UV light (254 nm)

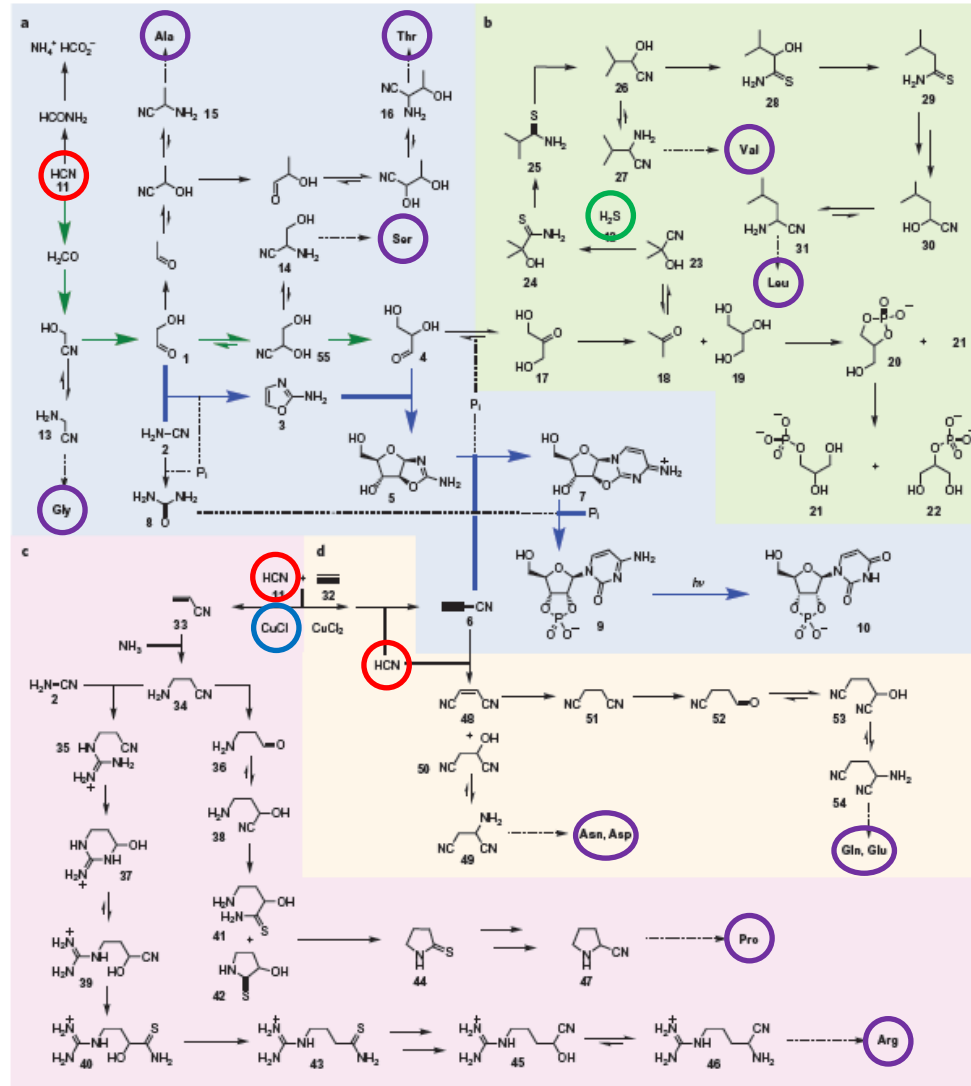


Endogenous origin of organic matter

The Sutherland's experiment: All you need

From HCN, H₂S, Cu and UV light (254 nm)

✓ Amino acids



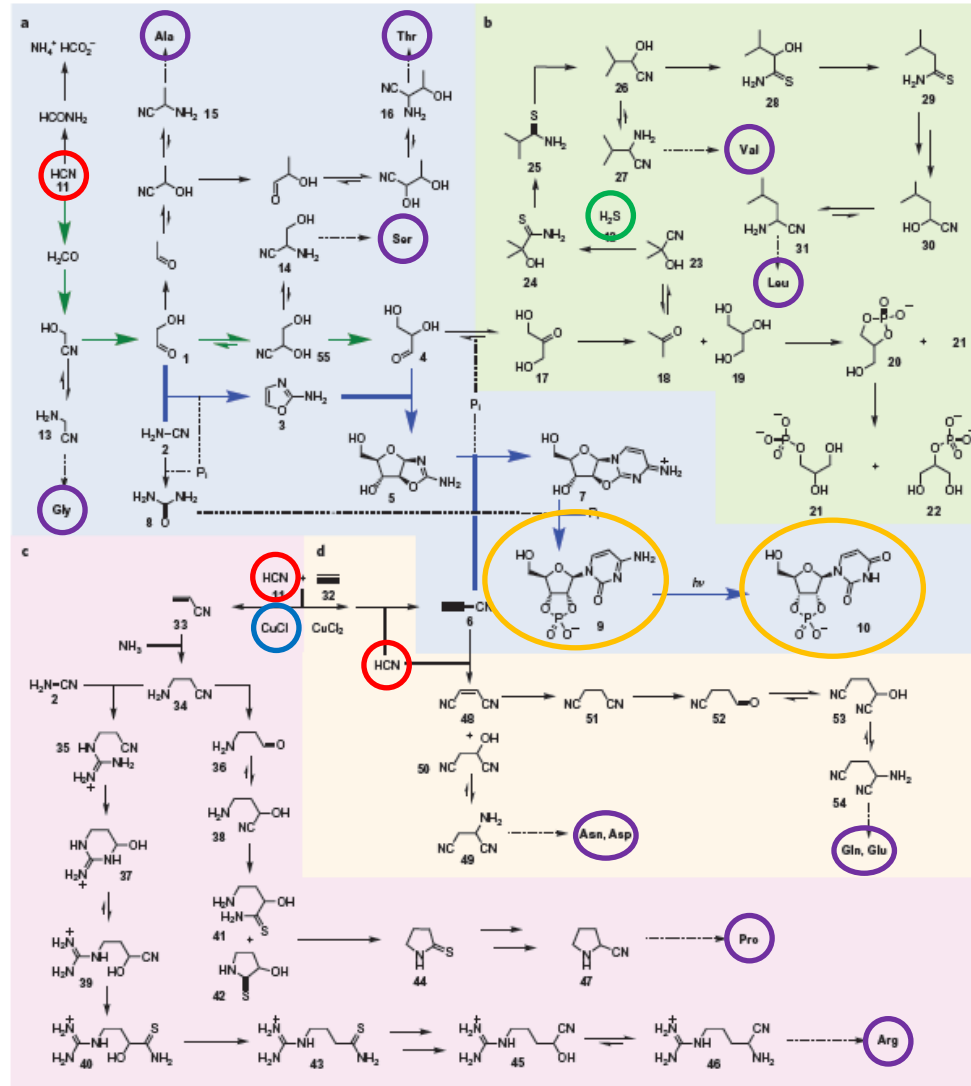
Endogenous origin of organic matter

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✓ Amino acids

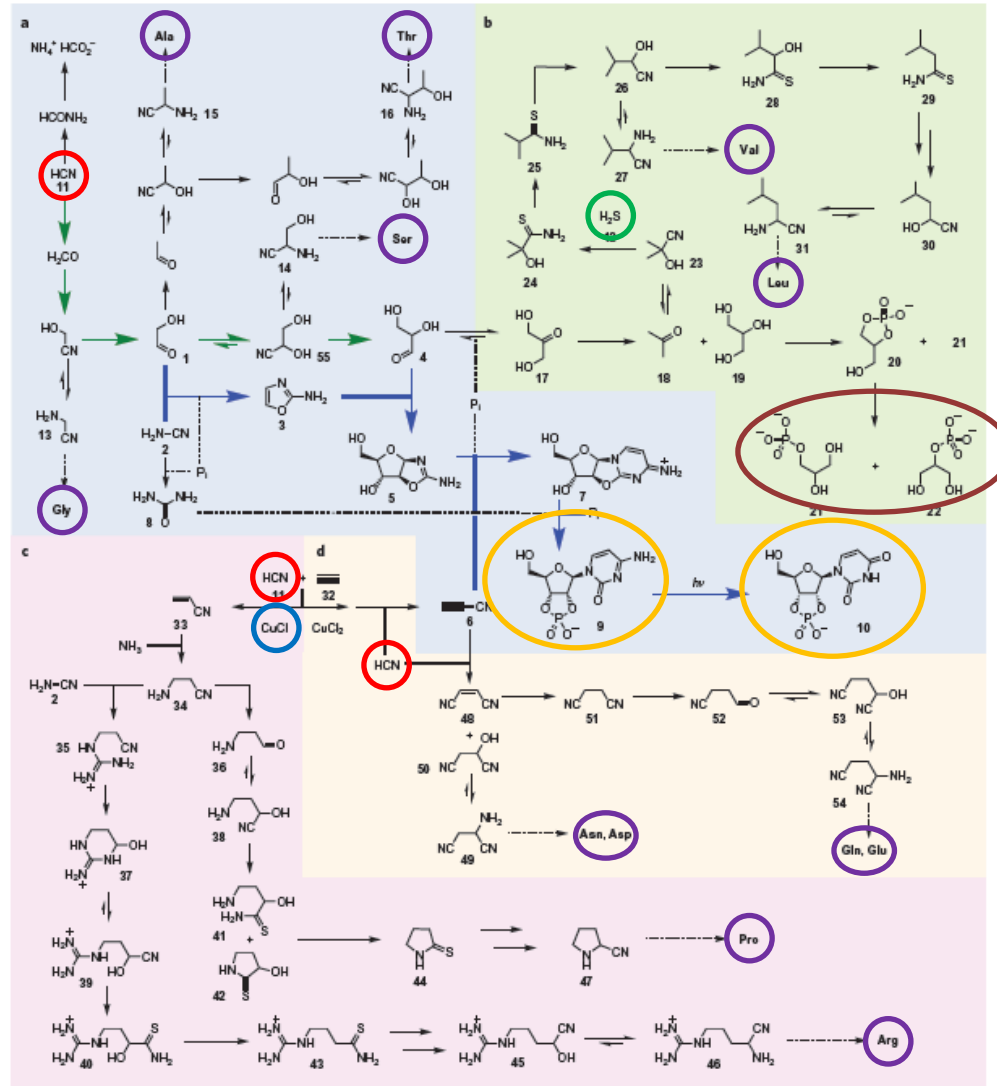
✓ Nucleotides



Endogenous origin of organic matter

The Sutherland's experiment: All you need

From HCN, H₂S, Cu and UV light (254 nm)



✓ Amino acids

✓ Nucleotides

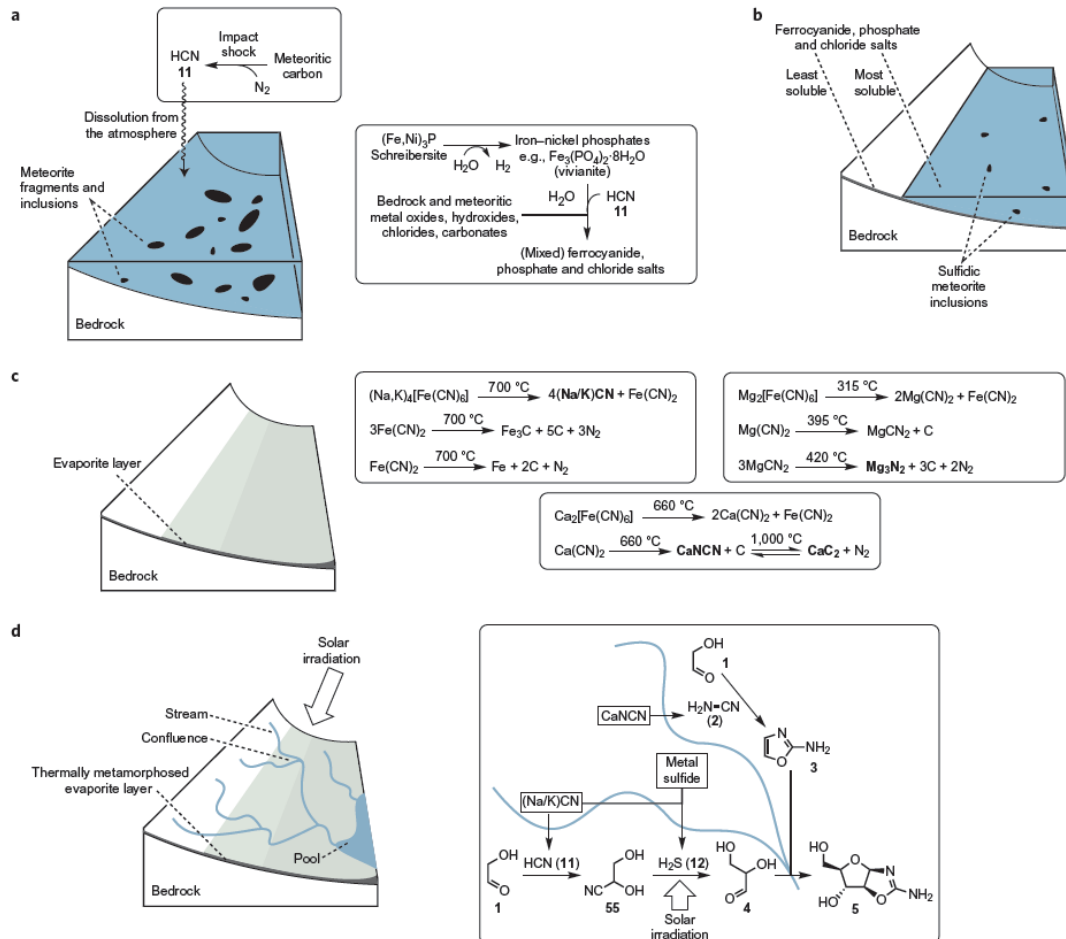
✓ Phospholipid precursors

Endogenous origin of organic matter

● The Sutherland's experiment: All you need

From HCN, H₂S, Cu and UV light (254 nm)

Chemistry in a post-impact scenario



Exogenous source of organic matter

➡ chondrite carbonaceous meteorites:



Carbonaceous matter

75-95% of insoluble organic molecules

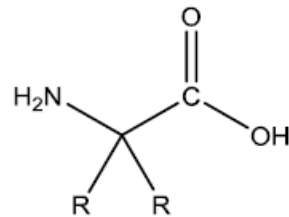
5-25% of soluble organic matter

Targeted analyzes of the soluble organic matter in chondritic meteorites

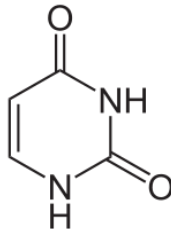
■ Soluble Organic Matter (SOM)



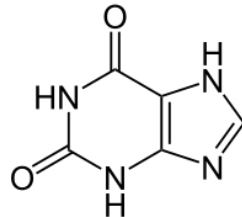
Chemical treatment: extraction (H_2O , 100 °C; hydrolysis HCl 6M) et derivatization



Amino acids



Nucleobases : uracile



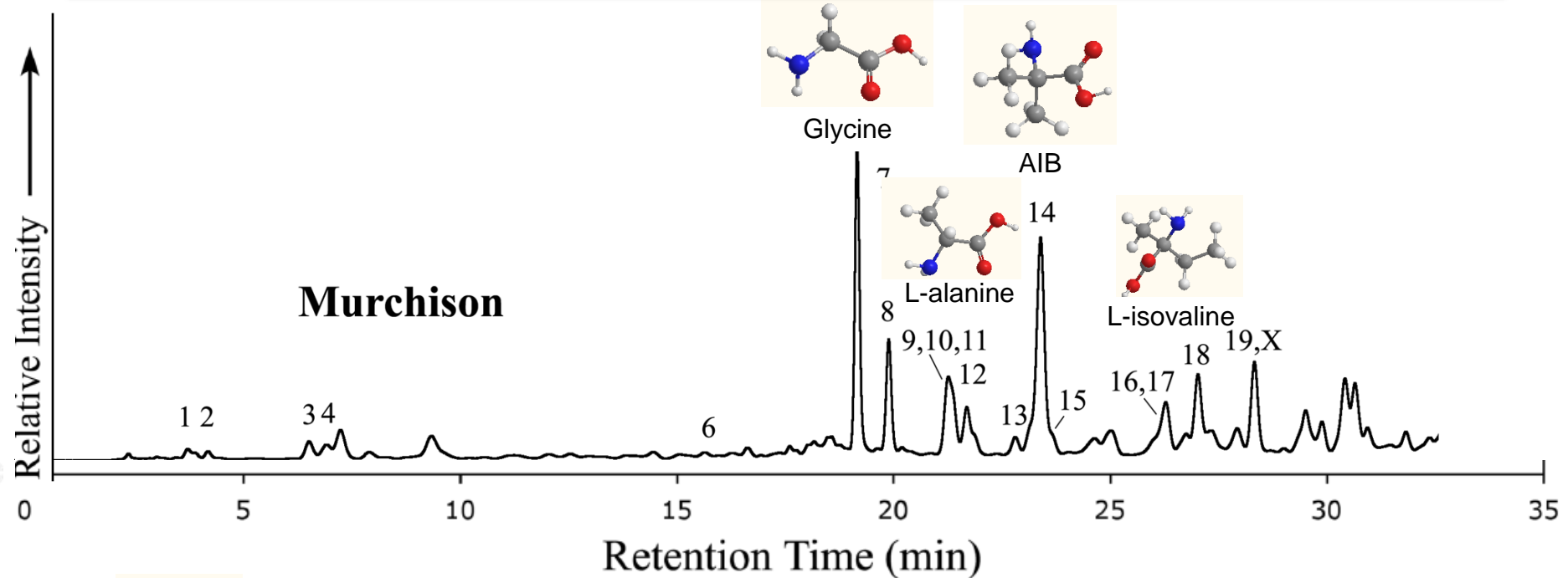
xanthine

More than 500 structures identified

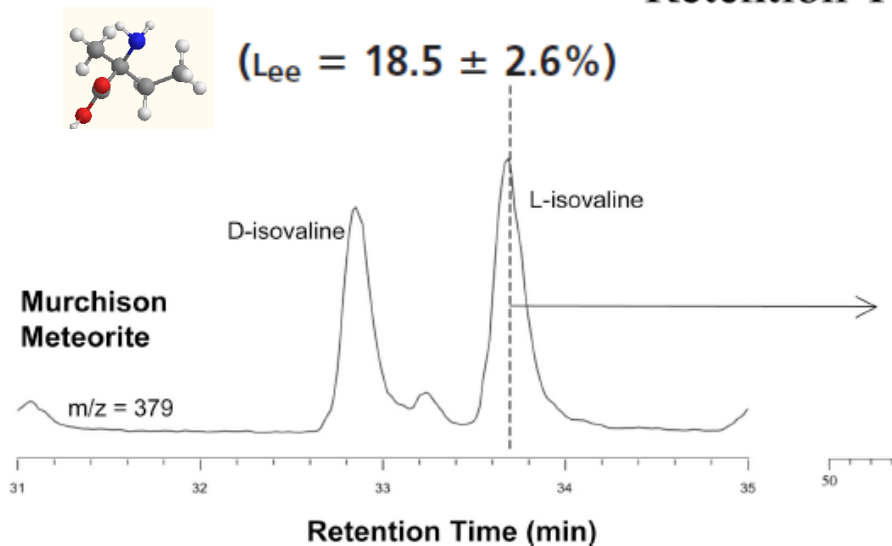
Insoluble Organic Matter (IOM)	Abundance
Macromolecular material ($\text{C}_{100}\text{H}_{70}\text{N}_3\text{O}_{12}\text{S}_2$)	70-99% total organic C
Soluble Organic Matter (SOM)	Concentration (ppm)
Carboxylic acids	>300
Polar hydrocarbons	<120
Sulfonic acids	67
Amino acids (83 named)	60
Dicarboxyimides	>50
Aliphatic hydrocarbons	>35
Dicarboxylic acids	>30
Polyols	30
Aromatic hydrocarbons	15-28
Hydroxy acids	15
Amines	13
Pyridine carboxylic acids	>7
N-heterocycles	7
Phosphonic acids	2
Purines and pyrimidines	1

Pizzarello et al., *Meteorites and the Early Solar System II*, 2006, 625-651

Targeted analyzes of the soluble organic matter in chondritic meteorites



Glavin et al., *Meteor. Planet. Sci.*, **41** (2006) 889-902

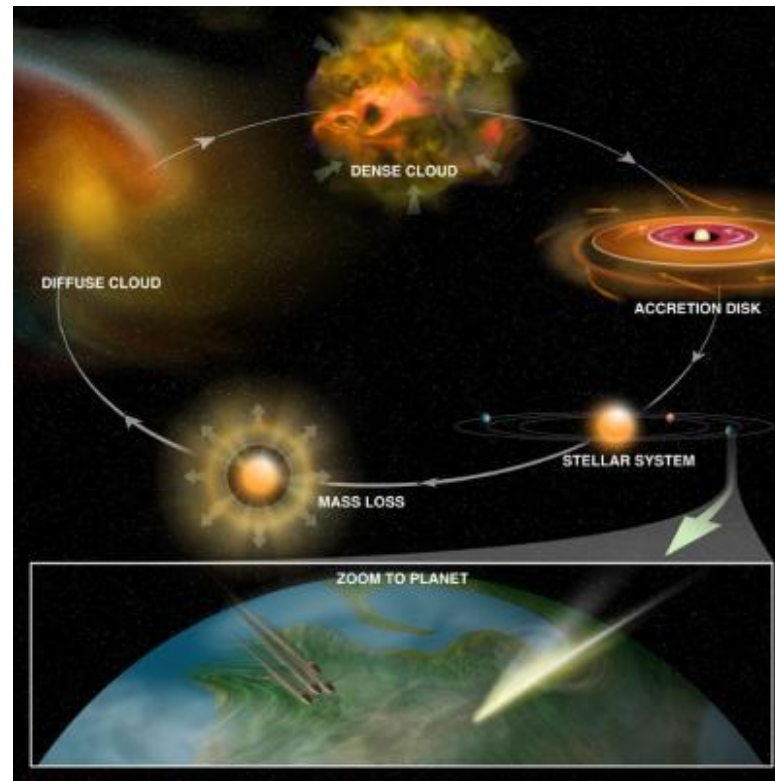


Enantiomeric excess on amino acids



Link between extraterrestrial organic matter and the emergence of homochirality on Earth?

Evolution of interstellar icy grains toward the formation of complex organic molecules in interplanetary objects



- ✓ A rich and universal reservoir of organic molecules
- ✓ Can seed planets with organic molecules via interplanetary bodies
- ✓ May be one of the most important source of organic matter for starting chemical evolutions toward life

Liquid Water

Early Earth

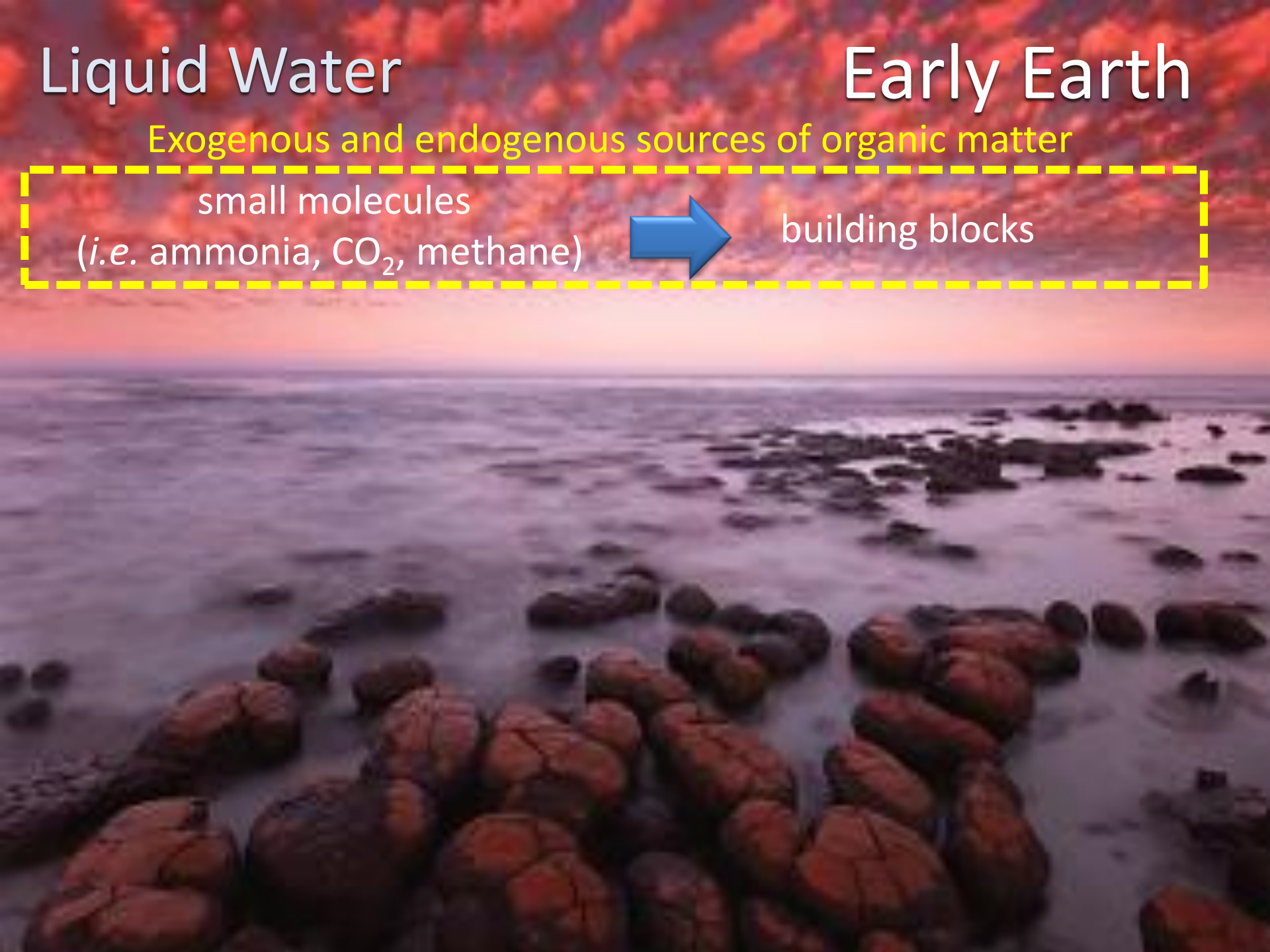
Exogenous and endogenous sources of organic matter

small molecules

(*i.e.* ammonia, CO₂, methane)



building blocks



Liquid Water

Early Earth

Exogenous and endogenous sources of organic matter

small molecules
(*i.e.* ammonia, CO₂, methane)



building blocks



macromolecule
(polymers)



Self-organization

A search for the origin of life

Origin of life

Prebiotic chemistry

Biochemistry

Prebiotic chemistry: How form complex structures in molecular terms or chemical networks.

A search for the origin of life

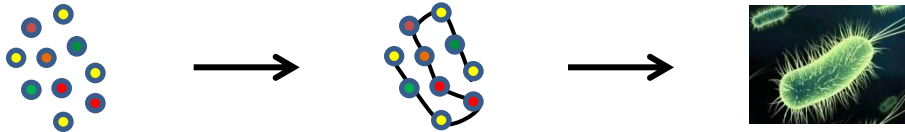
Origin of life

Prebiotic chemistry

Biochemistry

Prebiotic chemistry: How form complex structures in molecular terms or chemical networks.

1- Building blocks from extraterrestrial and planetary reservoir.



A search for the origin of life

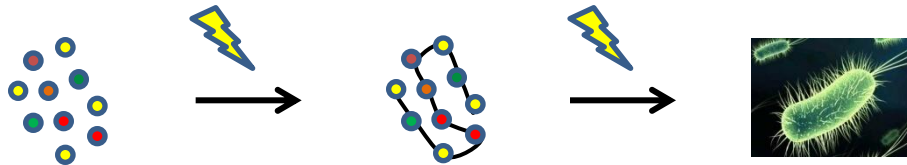
Origin of life

Prebiotic chemistry

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Prebiotic chemistry: How form complex structures in molecular terms or chemical networks.

1- Building blocks from extraterrestrial and planetary reservoir.



2- Energy

A search for the origin of life

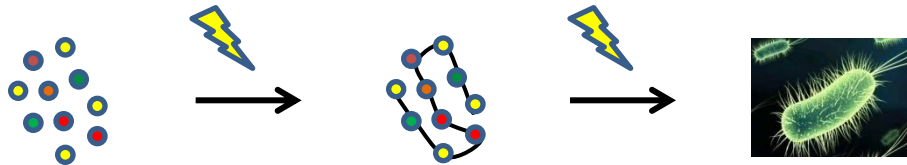
Origin of life

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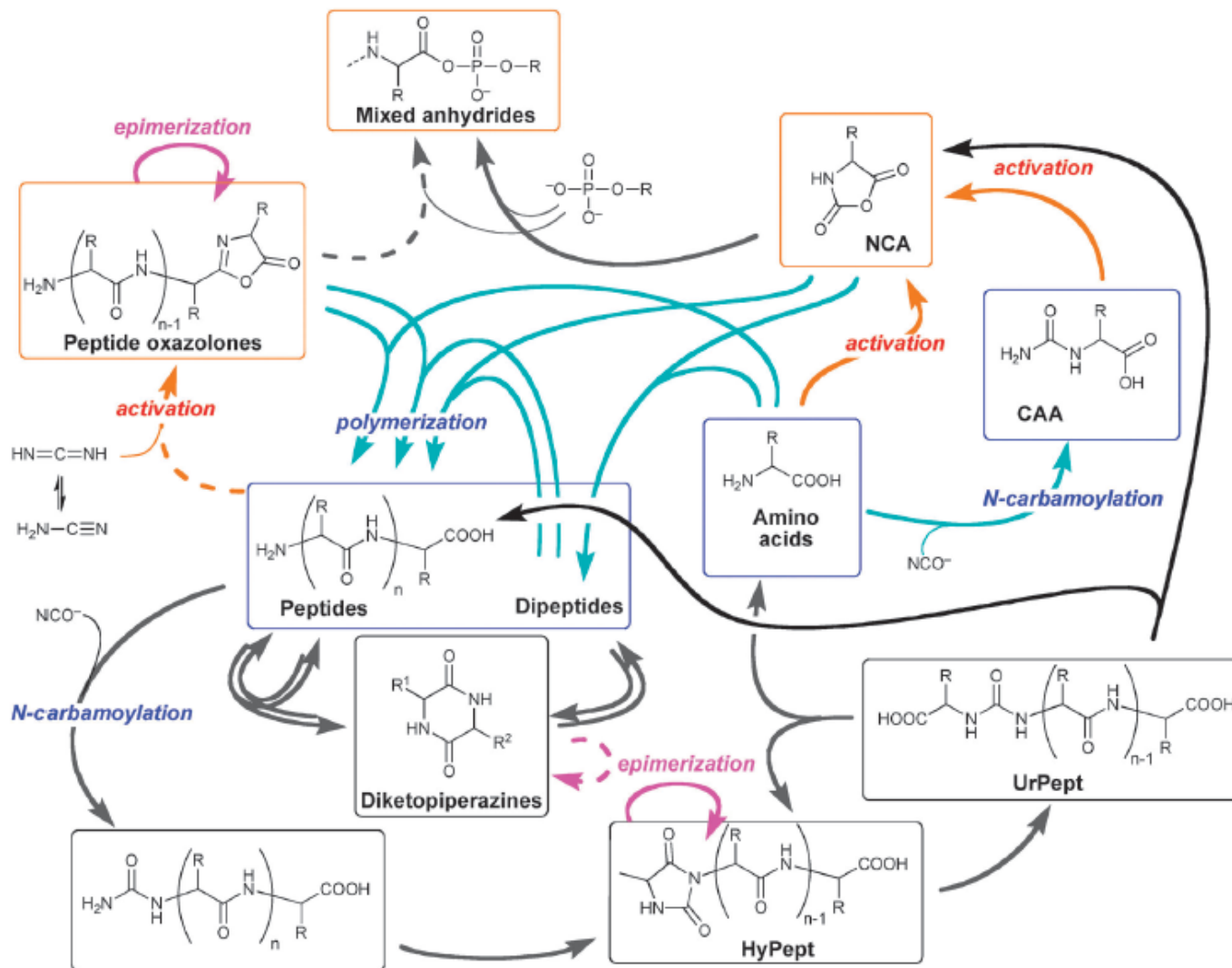
1- Building blocks from extraterrestrial and planetary reservoir.



2- Energy

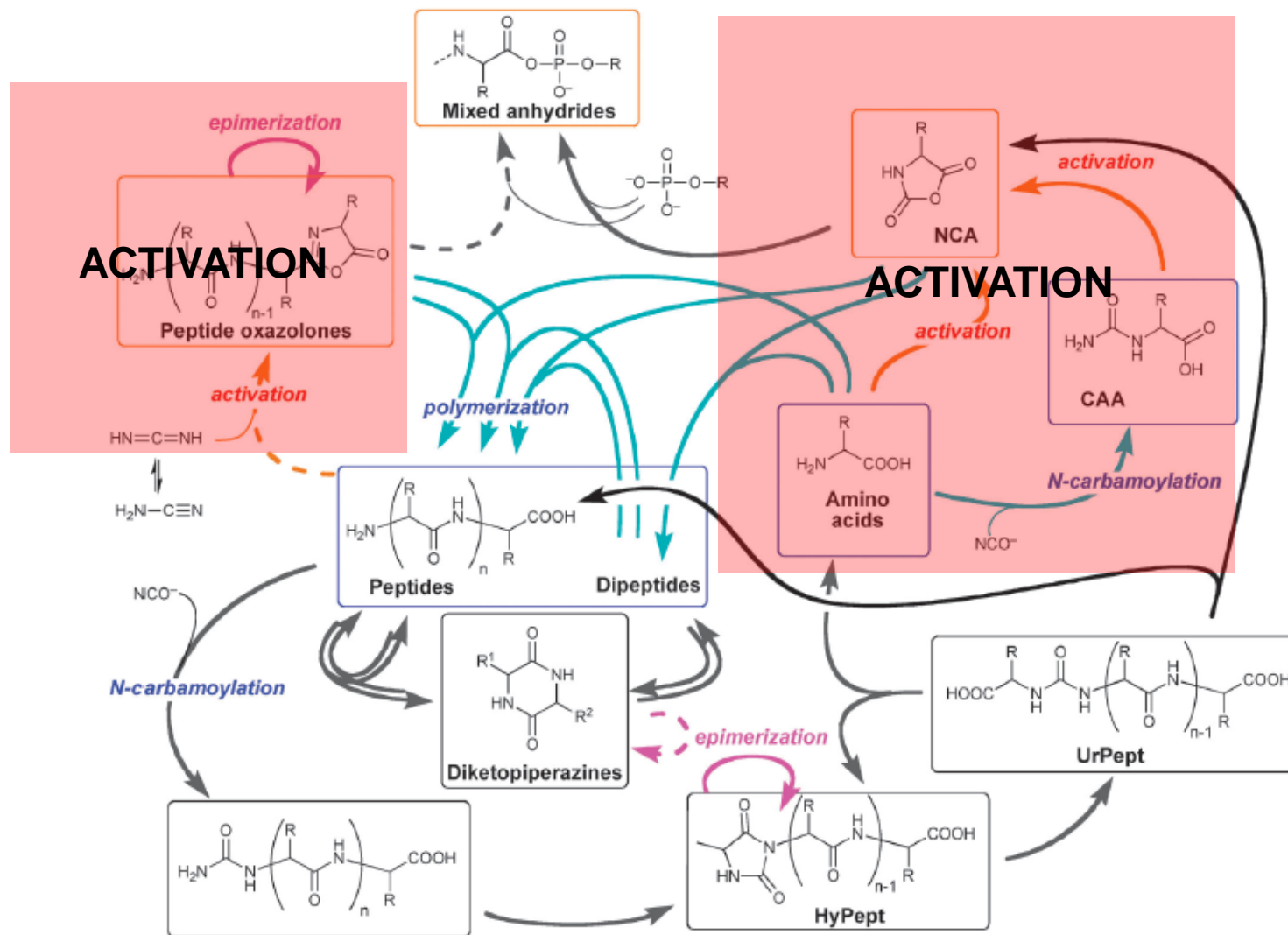
3- Self-organization of organic matter

Formation of proteins



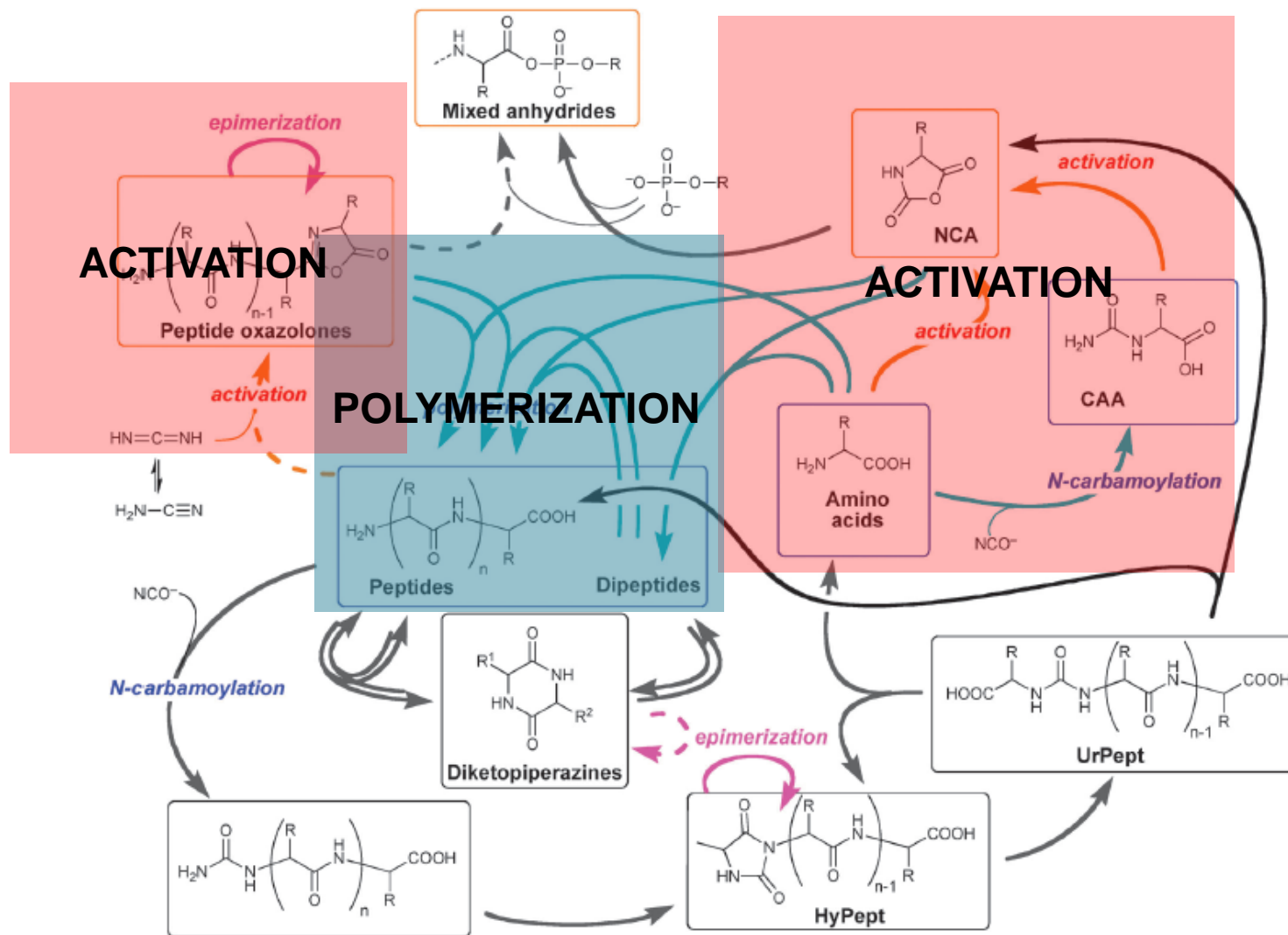
Scheme 13 Overall view of selected pathways identified from experiments or presumed from the analysis of the literature, which could constitute the systems chemistry of α -amino acids and peptides in prebiotic aqueous environments at values of pH close to neutrality. The network is based on the reactivity of four cyclic intermediates, namely NCAs, 5(4*H*)-oxazolones, hydantoins, and diketopiperazines, which are involved in reaction loops and introduce possibilities of racemization/epimerization. The high reactivity of NCAs and 5(4*H*)-oxazolones gives rise to possibilities of connection with nucleotide chemistry.

Formation of proteins



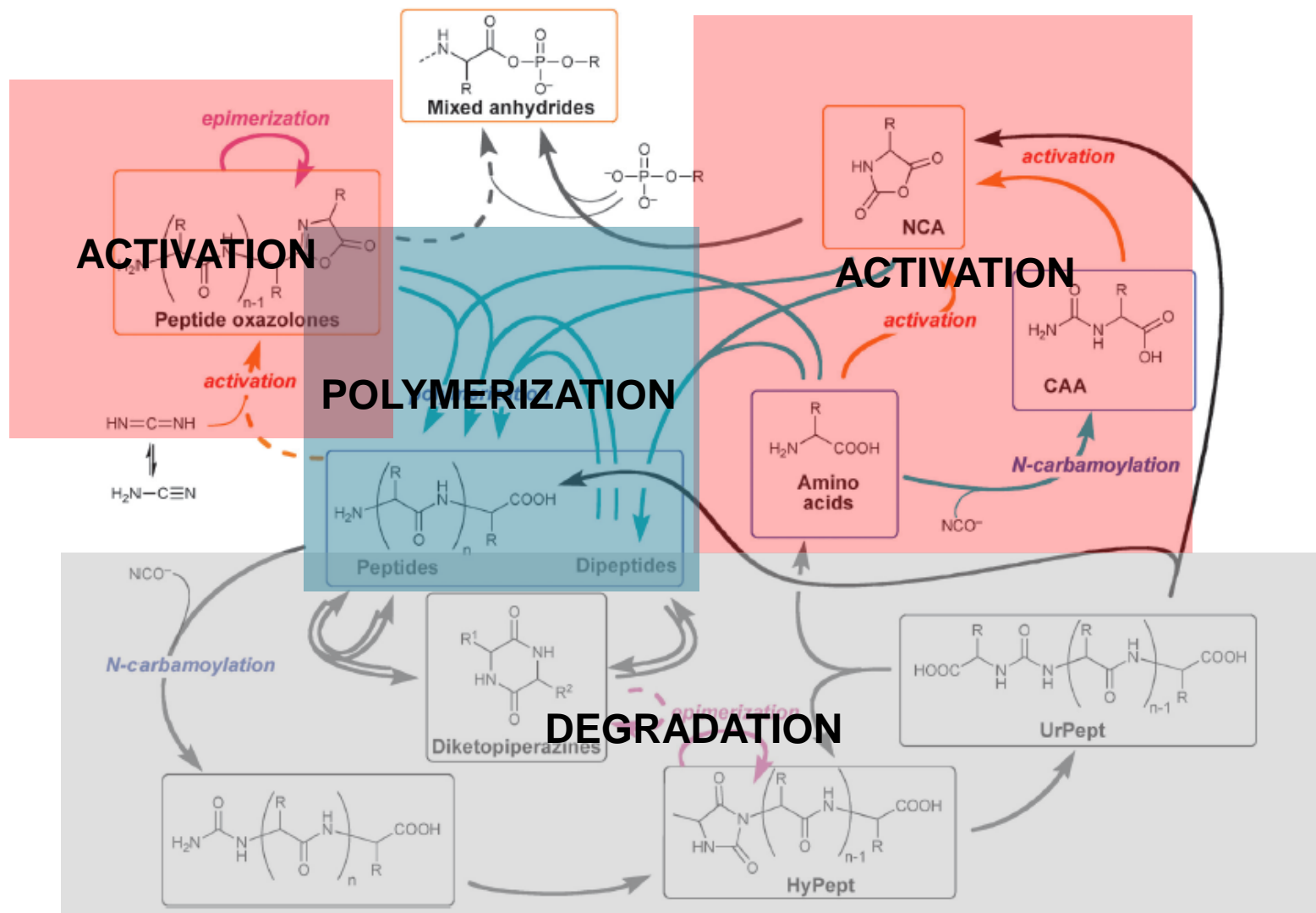
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Liquid Water

Early Earth

Exogenous and endogenous sources of organic matter

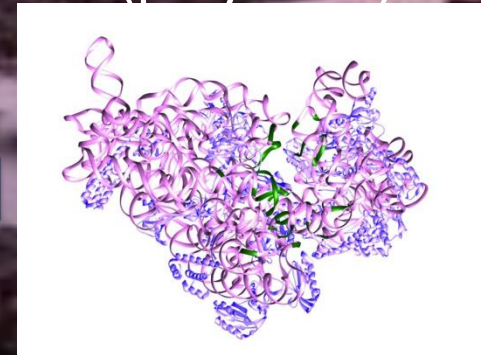
small molecules
(i.e. ammonia, CO₂, methane)



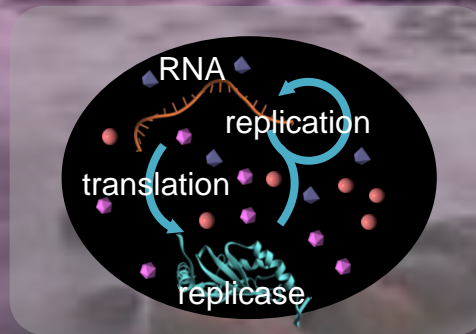
building blocks



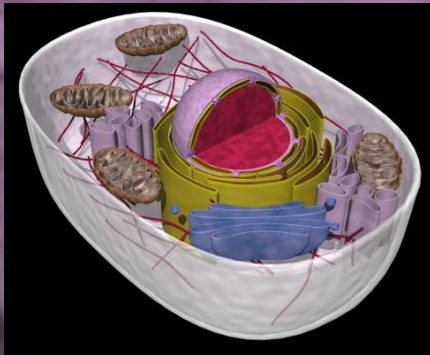
macromolecule
(polymers)



primitive cell



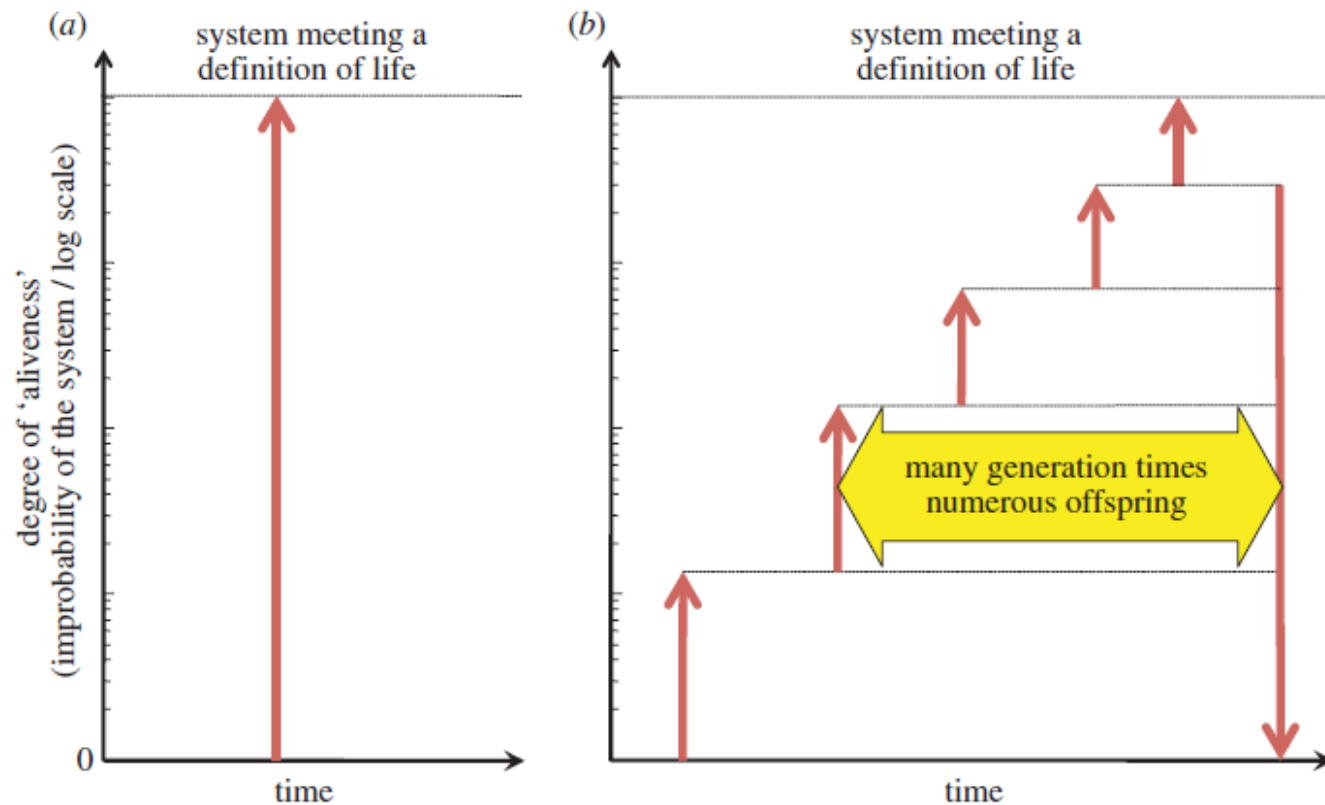
Living cell



Evolution toward biochemical systems

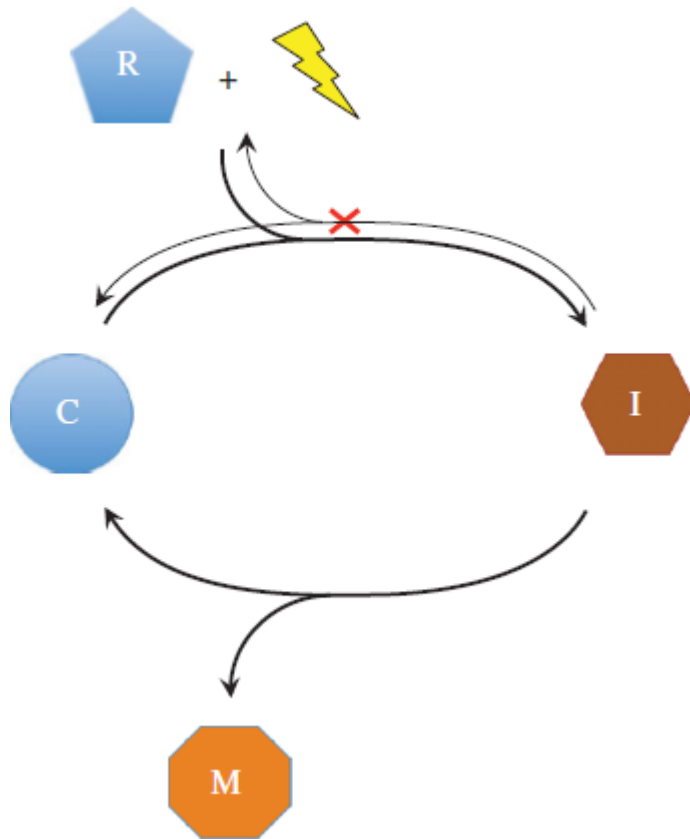
Self-organization
Energy

Replicators for chemical evolution



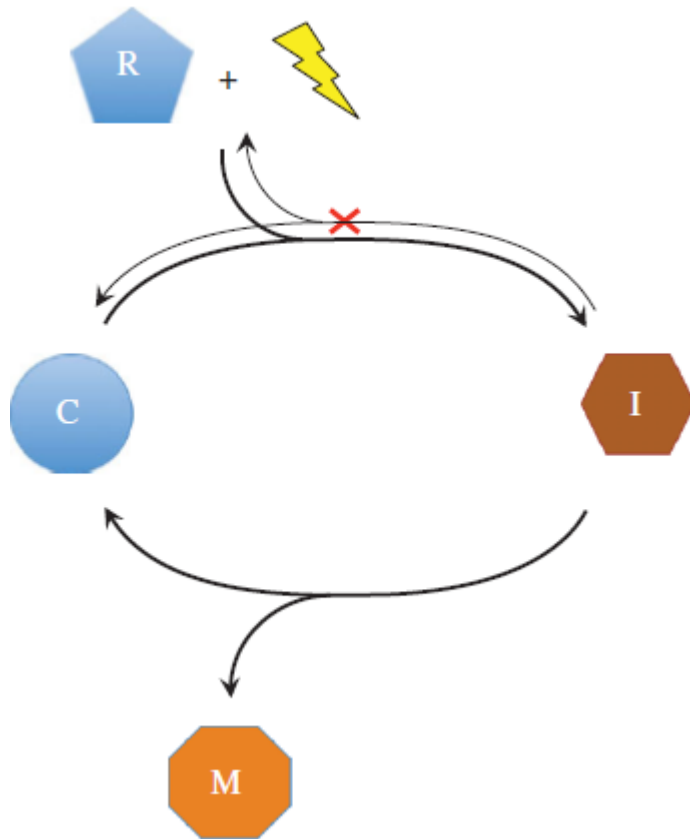
Scheme 1. The emergence of life considered as a transition to a highly improbable system. (a) Abrupt transition induced by a highly improbable random event in contradiction with the 2nd Law; (b) Stepwise process in which intermediate steps (there is in principle no limitation to the number of steps) allow further evolution towards greater degrees of organization on the basis of entities that are capable of reproducing themselves and, therefore, that exhibit a significant persistence before reverting to the unorganized state (right arrow). The choice of a logarithmic scale of improbability for characterizing 'aliveness' as the ordinate is purely arbitrary, but in line with the characterization of the emergence of life as an event of low probability.

Emergence of replicative systems

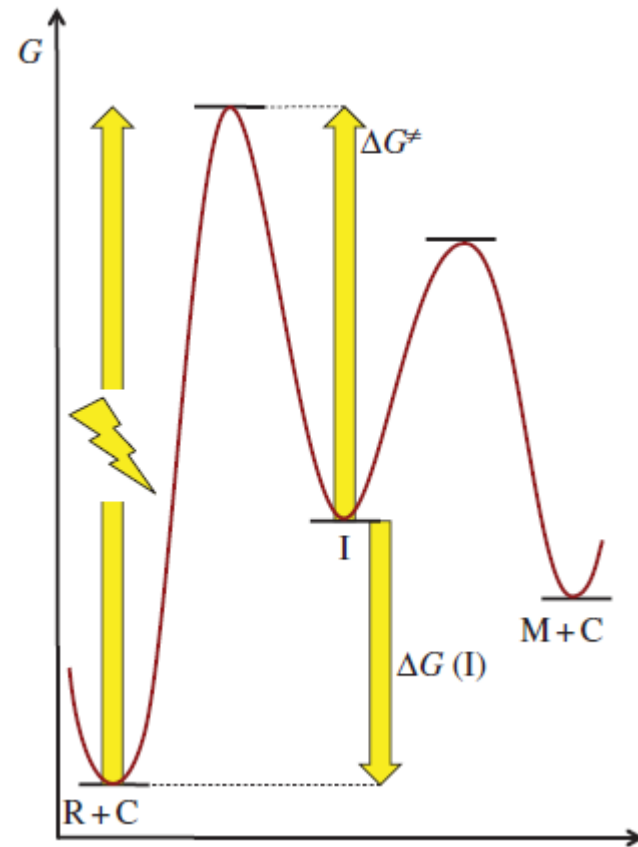


Autocatalytic systems

Emergence of replicative systems

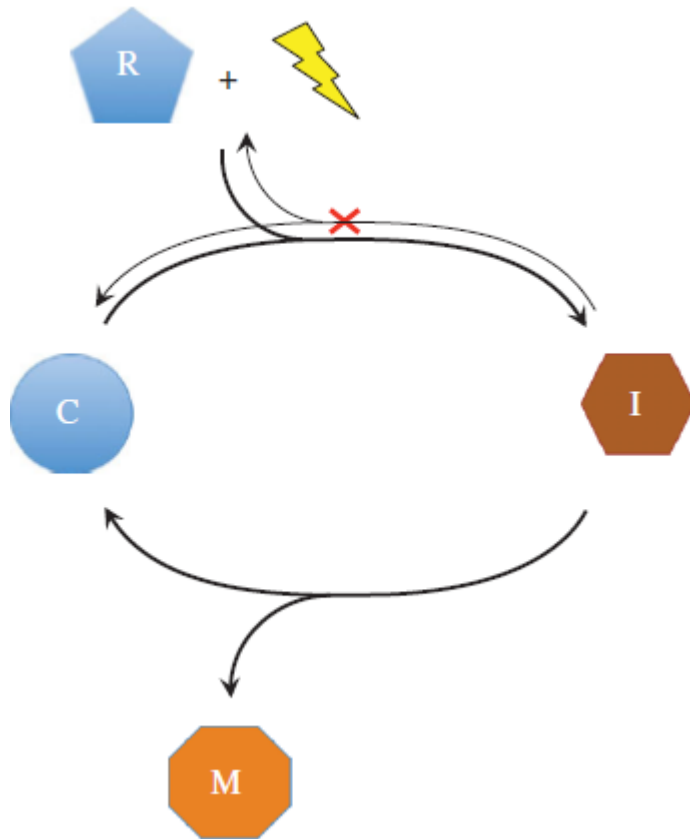


Autocatalytic systems

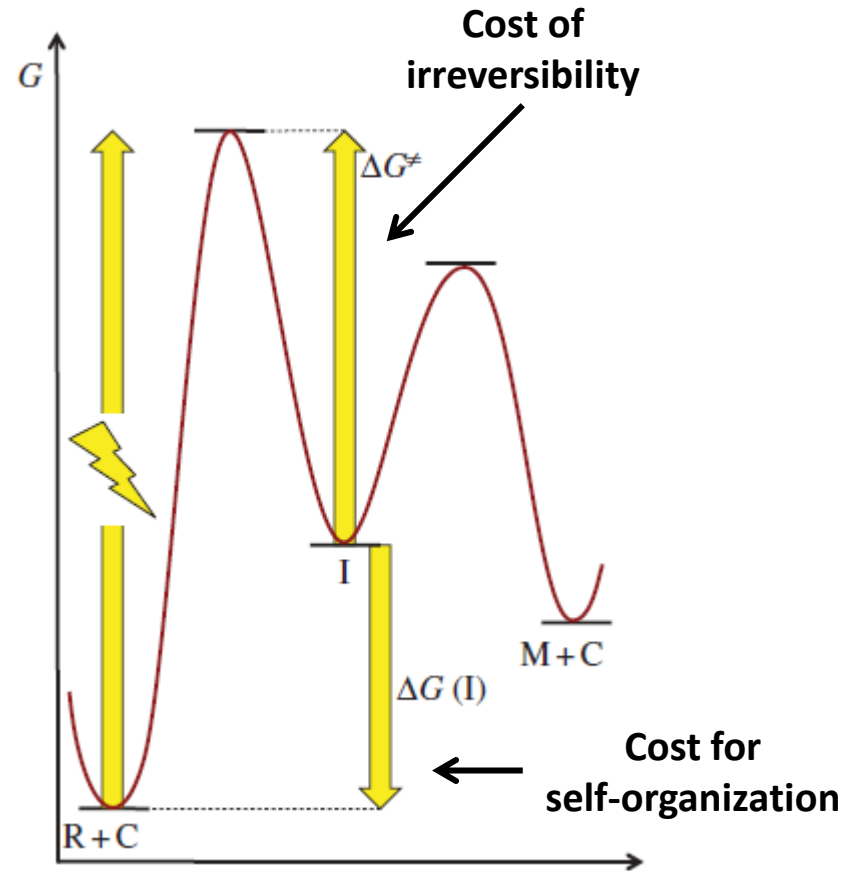


**Irreversibility
Kinetic stability**

Emergence of replicative systems



Autocatalytic systems



Irreversibility
Kinetic stability

Liquid Water

Early Earth

Exogenous and endogenous sources of organic matter

small molecules
(i.e. ammonia, CO₂, methane)



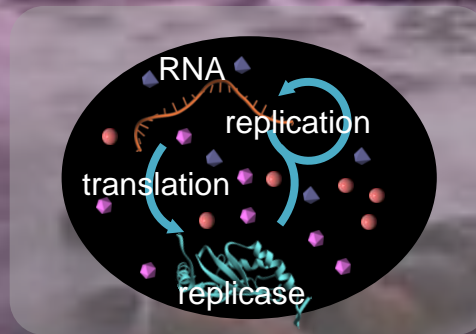
building blocks



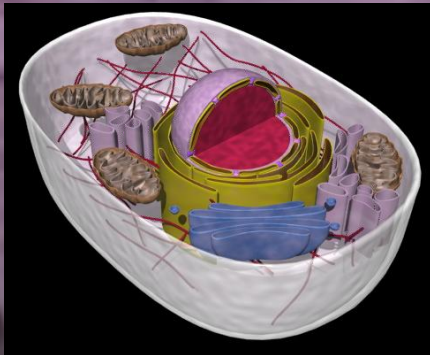
macromolecule
(polymers)



primitive cell



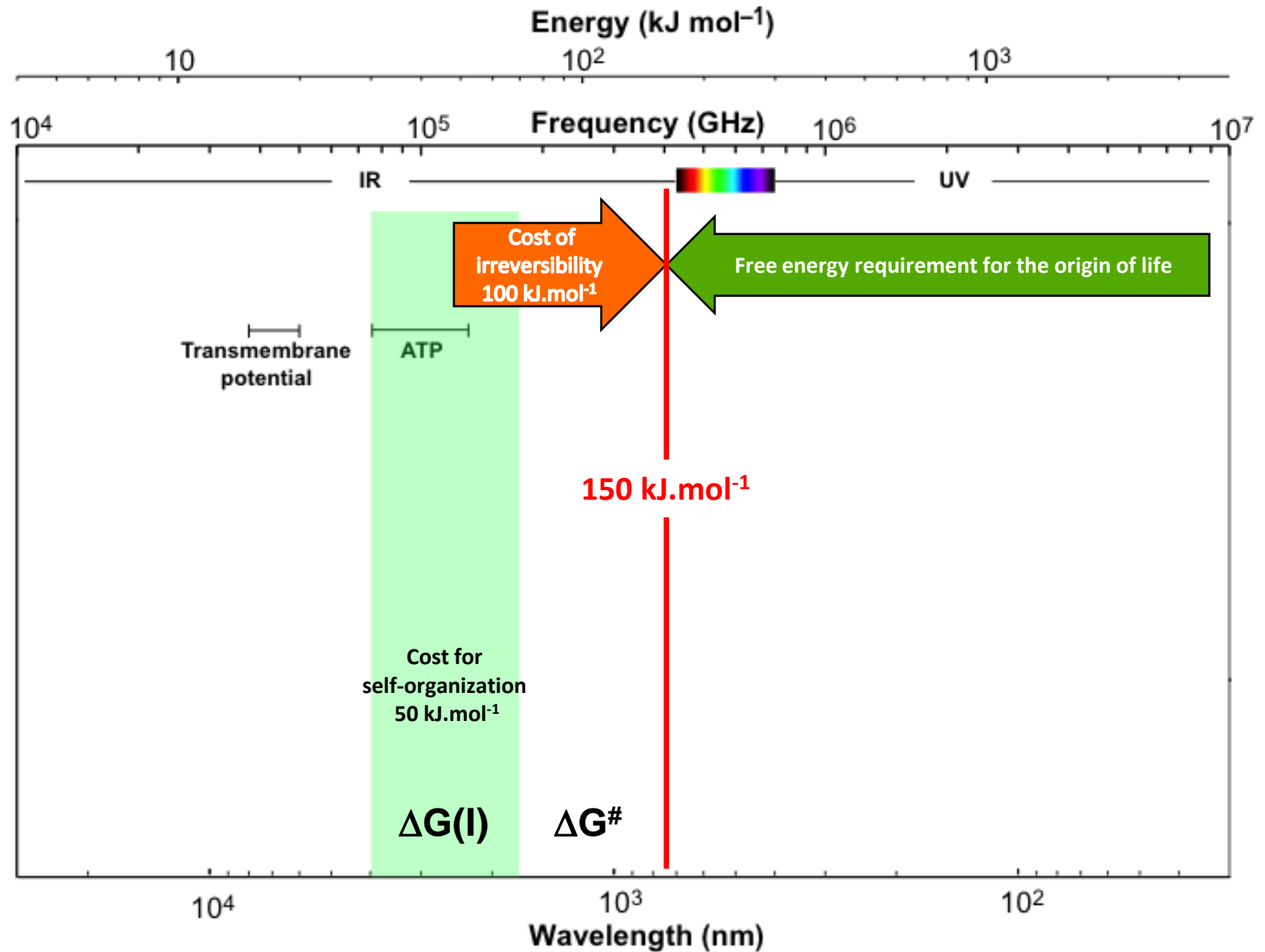
Living cell



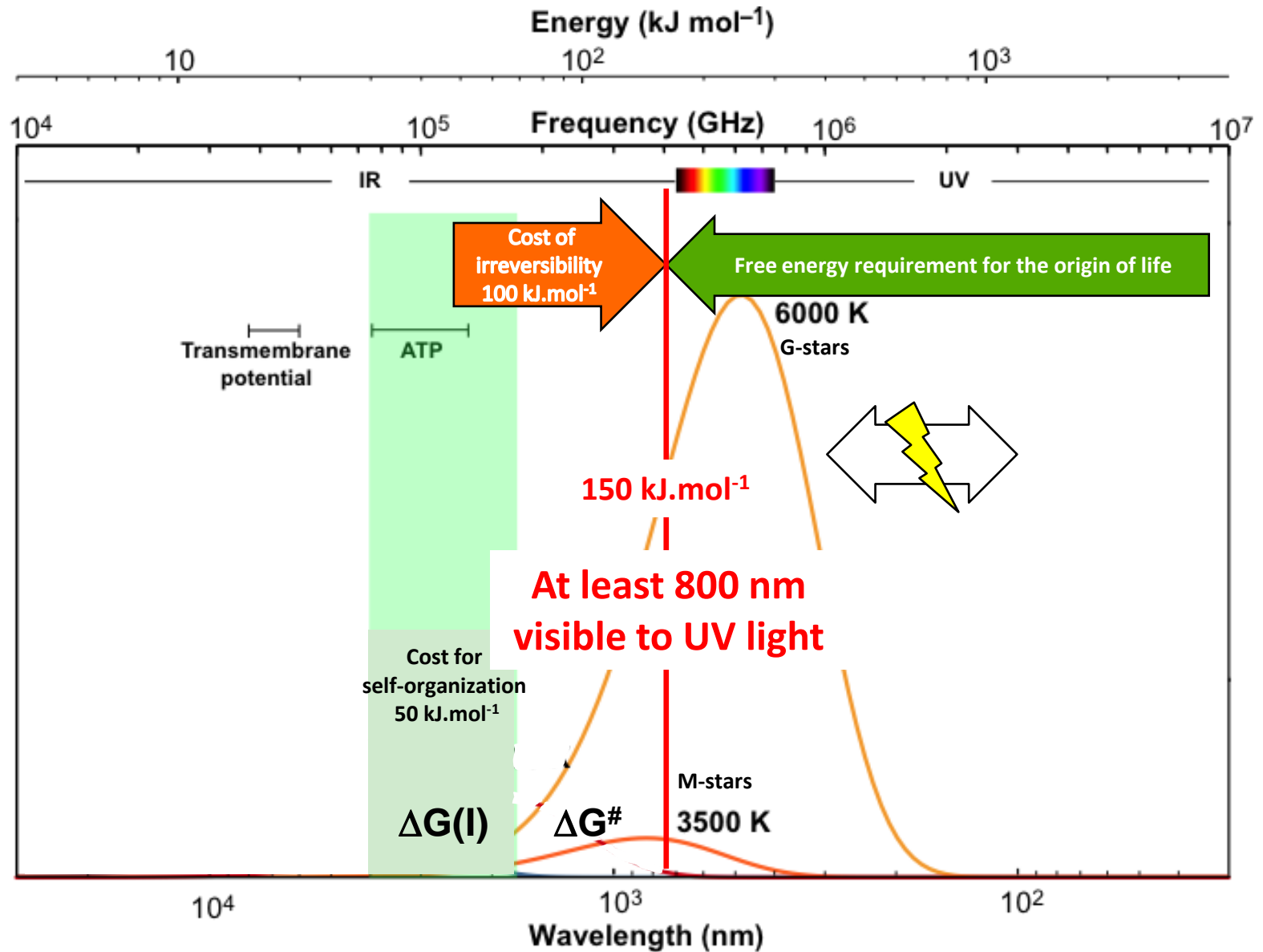
Emergence of replicators
Autocatalysis and Energy
Evolution and Selectivity

Self-organization
Energy

Impact on Habitability



Impact on Habitability



What do we need?

- ✓ **Liquid water**
- ✓ **Source of organic matter**
 - Exogenous – “Universal”**
 - Endogenous – “Specific”**
- ✓ **Energy for self-organization**
- ✓ **Autocatalysis and irreversibility for chemical evolution**

What do we need?

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In which environment?

- ✓ **Hydrothermal vent?**
- ✓ **Volcano environments?**
- ✓ **If it needs UV-visible light (<800 nm) for the self-organization and the cost of irreversibility:**
 - ⇒ **Environment where surface liquid water is available**

How can we constrain the habitability concept?

- ✓ Liquid water
- ✓ Source of organic matter
Exogenous – “Universal”
- ✓ Energy for self-organization
- ✓ Autocatalysis and irreversibility for chemical evolution

Experiment this scenario in a simulated primitive Earth environment

- ✓ Is it possible to experimentally demonstrate that replicators can emerge from an aqueous environment in which organic matter is associated to a sufficient source of energy?
- ✓ Constrain the range of environmental conditions in which replicators could emerge

Liquid Water

Early Earth

Exogenous and endogenous sources of organic matter

small molecules
(i.e. ammonia, CO₂, methane)



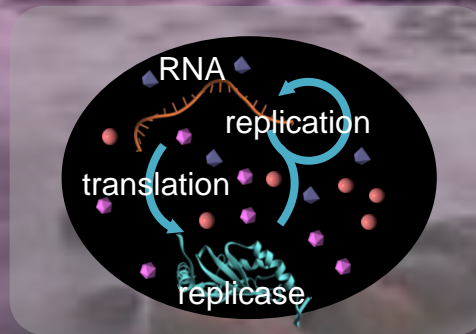
building blocks



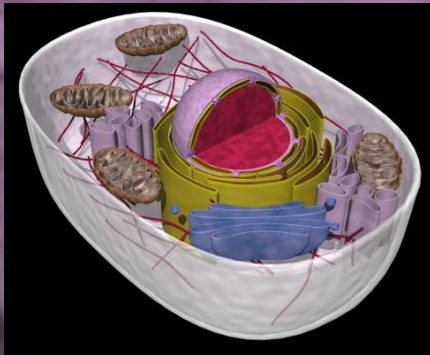
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Living cell



Emergence of replicators
Autocatalysis and Energy
Evolution and Selectivity

Self-organization
Energy