

Exobiology and Mars

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OUTLINES

Exobiology

Some historical aspect

Current exobiology

The terrestrial example

Life on Earth

The origin(s) of Life on Earth

A Mars Example?

Did we already find it?

What to search for?

How to search for?

The PP aspects and future prospects

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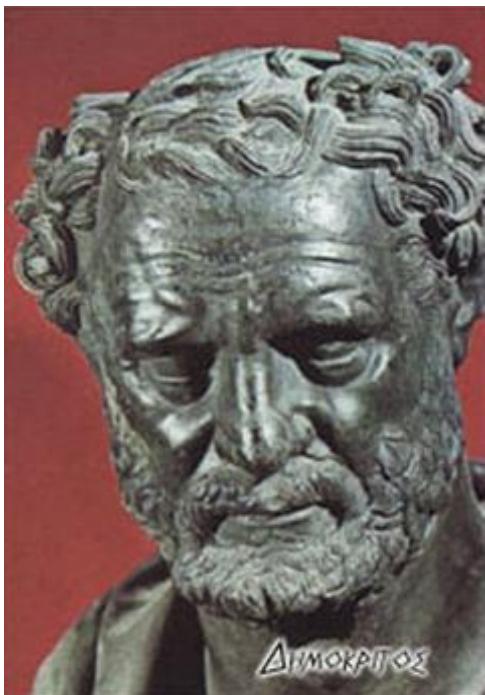
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Did we already find it?

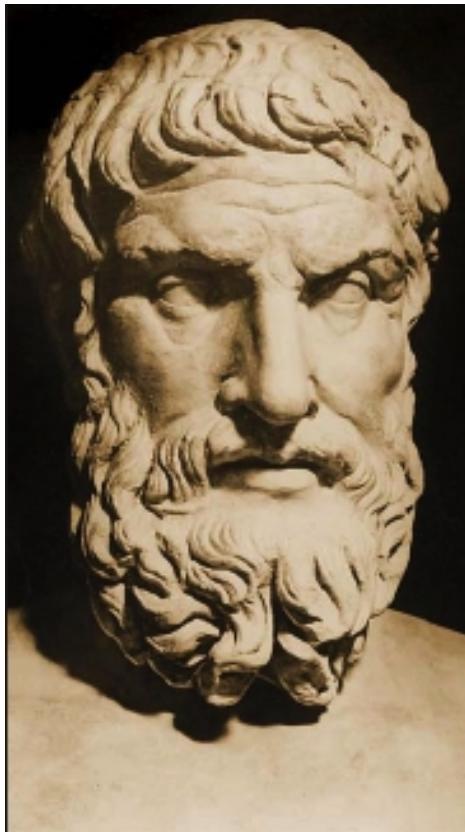
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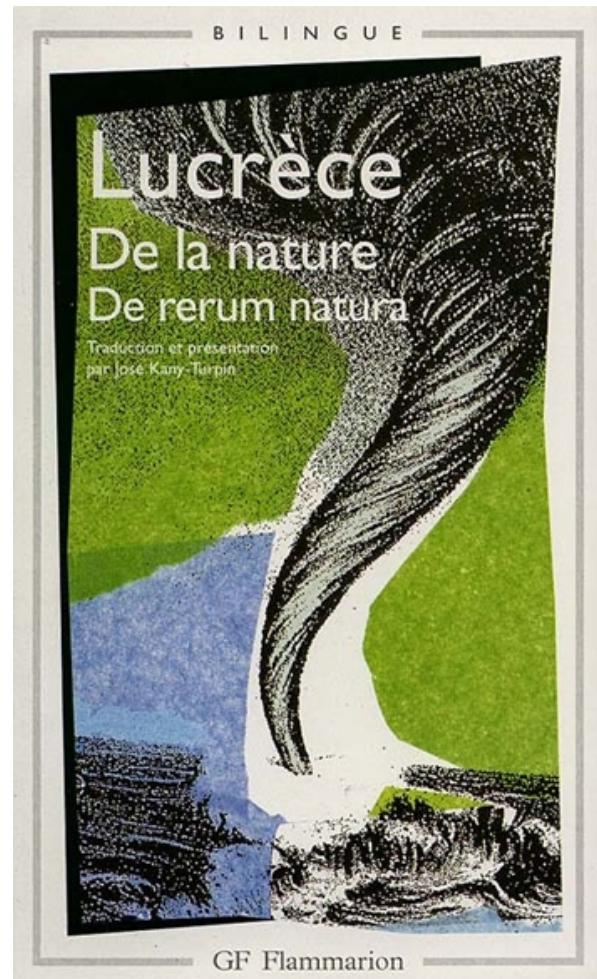
The PP aspects and future prospects



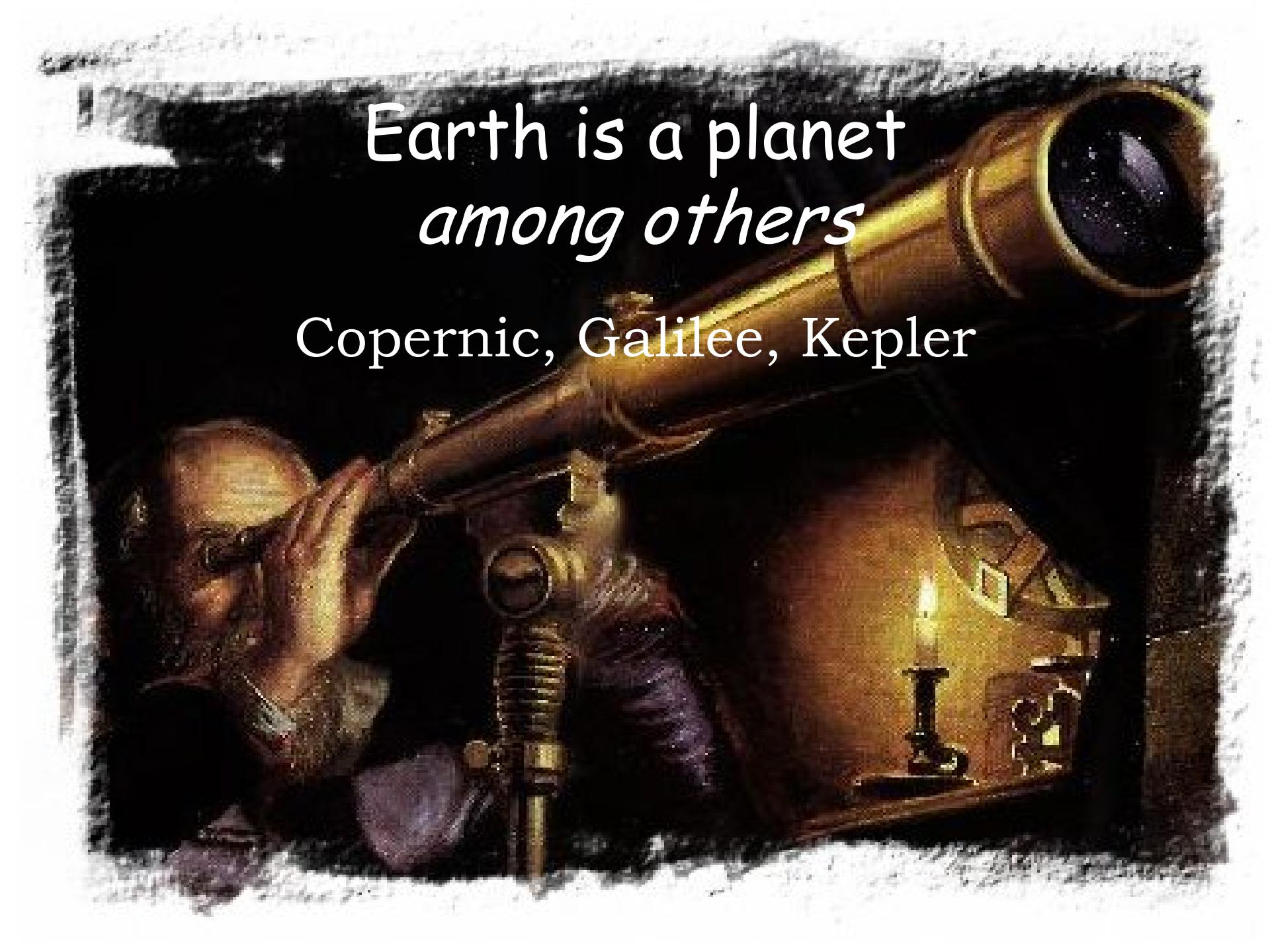
Democrate



Epicure



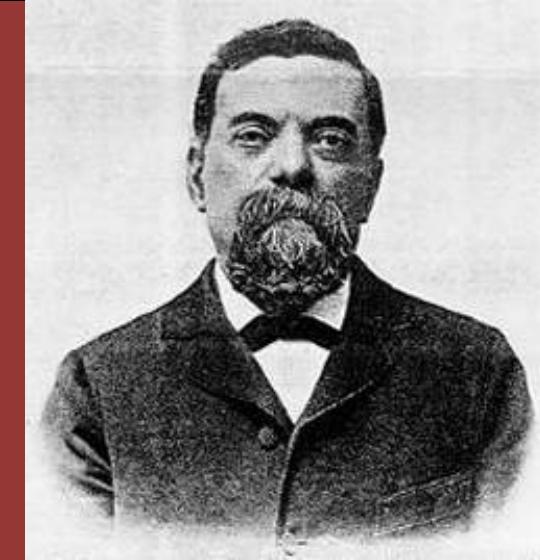
Lucrece



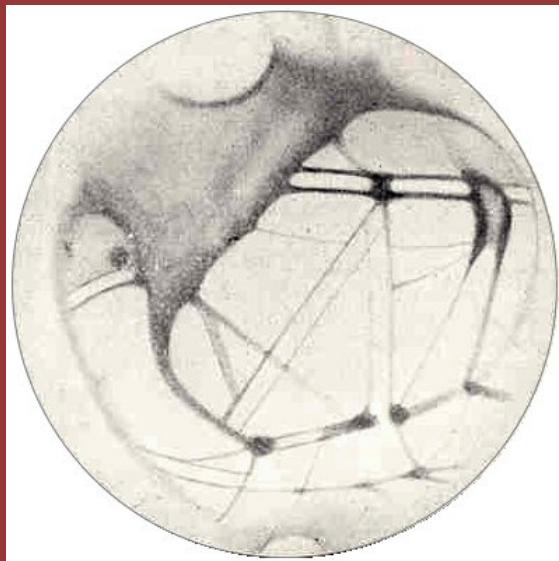
Earth is a planet
among others

Copernic, Galilee, Kepler

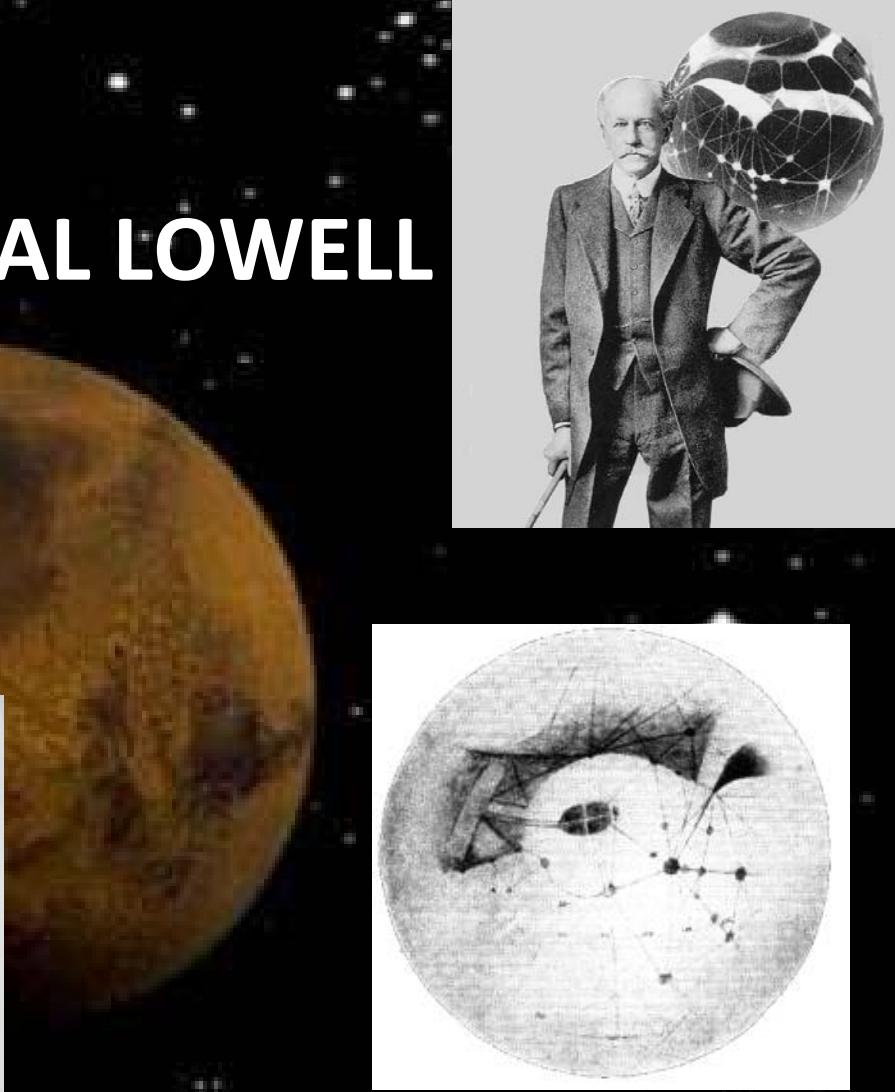
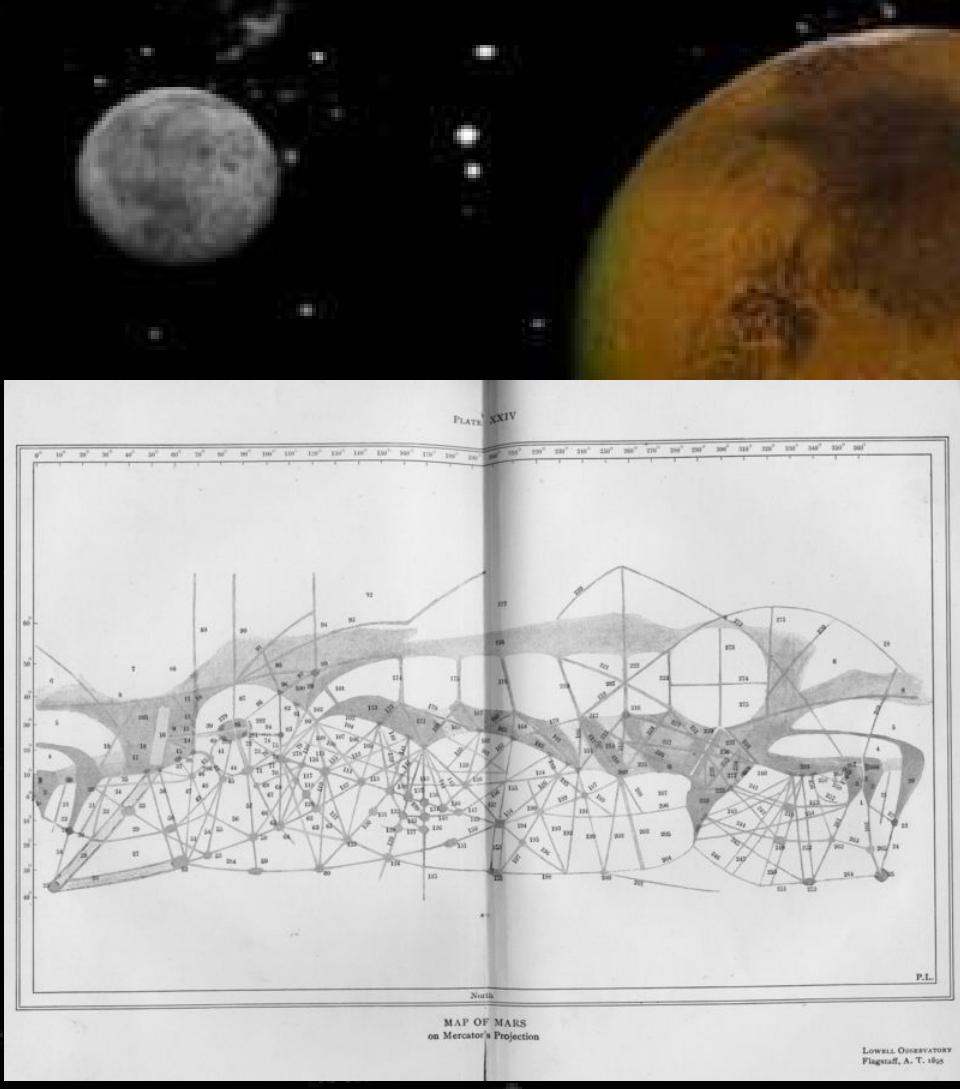
THE MYTH OF MARTIAN CANALS



- 1877 : Schiaparelli's observations

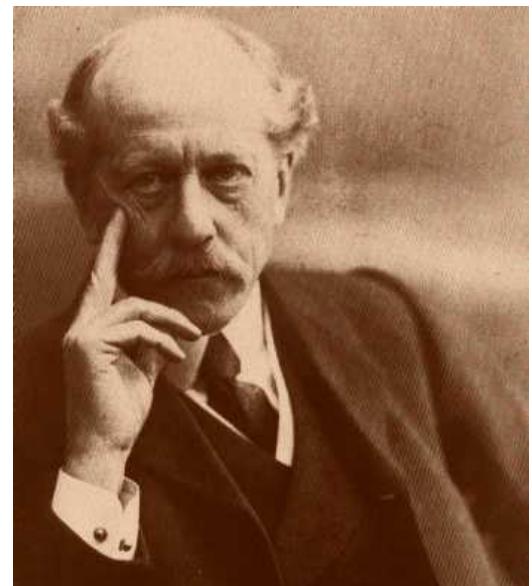
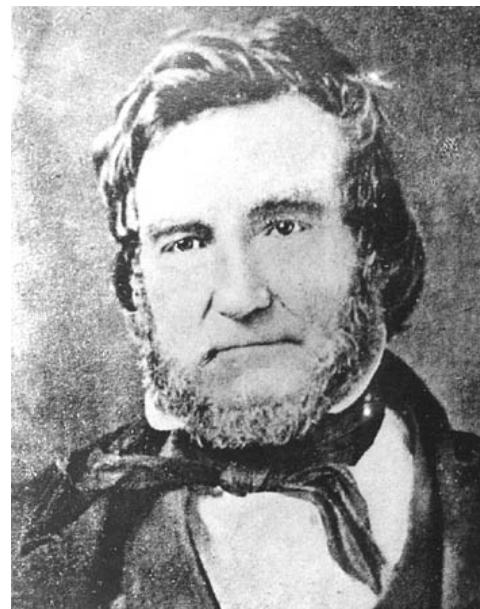
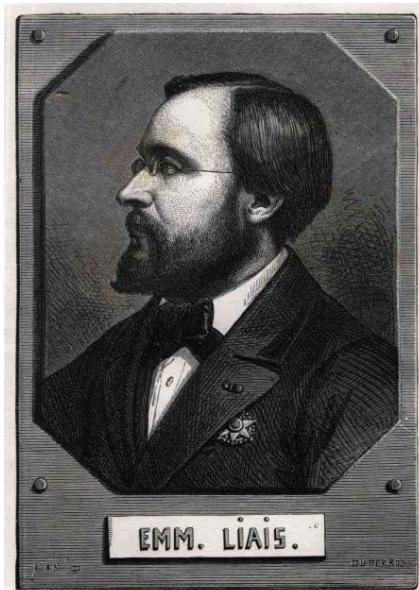


MARS SEEN BY PERCIVAL LOWELL



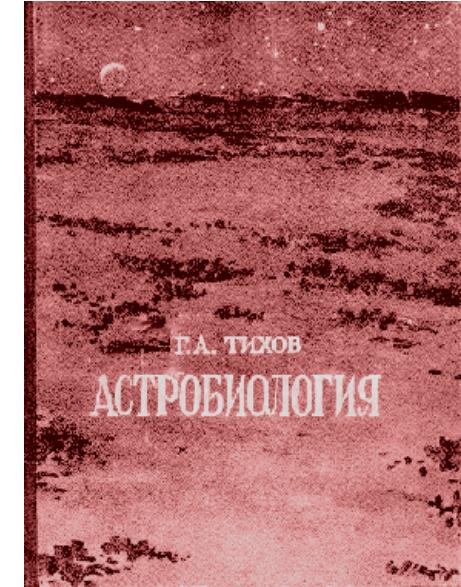
THE HYPOTHESIS OF MARTIAN VEGETATION

Emmanuel Liais, William Pickering, Percival Lowell,
etc...



TIKHOV' ASTROBOTANY

Spectroscopy for detecting
Martian vegetation



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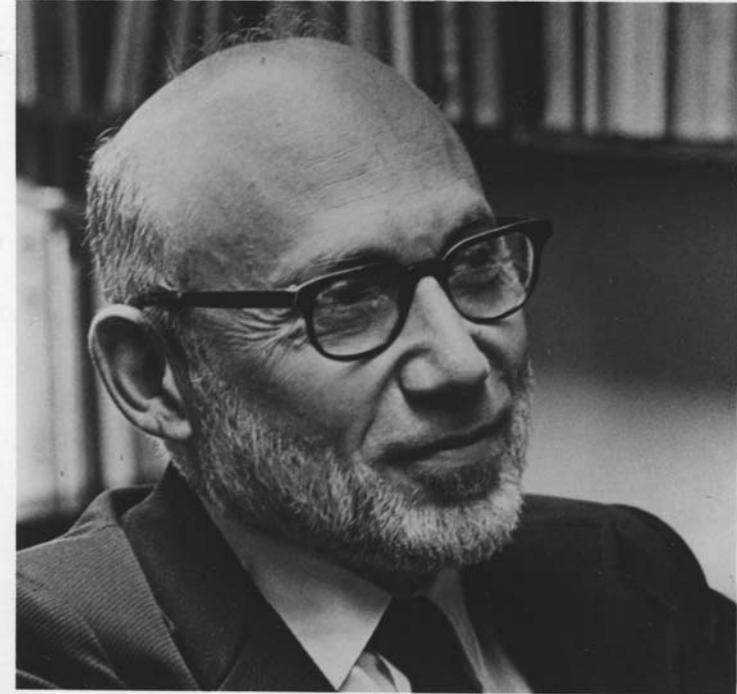
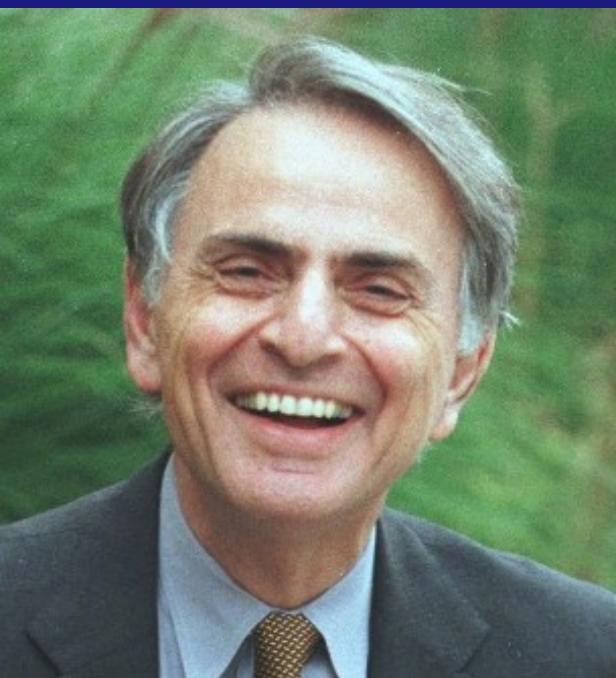
The PP aspects and future prospects

Apollo: systematic scientific approaches





**Josua Lederberg, microbiologist,
Nobel laureate in Medicin 1958 :
introduce the word « Exobiology »**



**Carl Sagan, astrophysicist one of the
great promoters of Exobiology**

**Exobiology : Initialy search for and study of
extraterrestrial life (life beyond the Earth)**

EXOBIOLOGY - Life in the universe

= Astrobiology

= Bioastronomy

= Cosmobiology

Study of life in the universe

its origins

its distribution

its evolution

including its destiny

the associated structures et processus

A highly pluridisciplinary field with many approaches

- SETI (Search for ExtraTerrestrial Intelligence)
- Search for life – past or present – on extraterrestrial objects in the solar system (by remote sensing and in situ techniques)
- Search for signatures of life beyond the solar system (by remote sensing techniques so far ...)
- Study of extraterrestrial organic matter
- Study of the origin, properties and evolution of life on Earth

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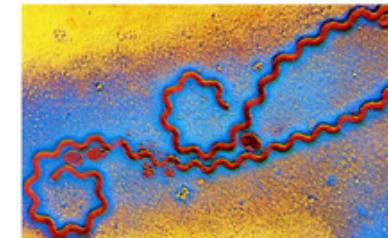
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THE DIVERSITY OF LIFE



TOTAL NUMBERS OF KNOWN SPECIES

Bacteria ~ 10,000

Archaea ~ 5000

Fungi ~ 101,000

Plants ~ 260,000

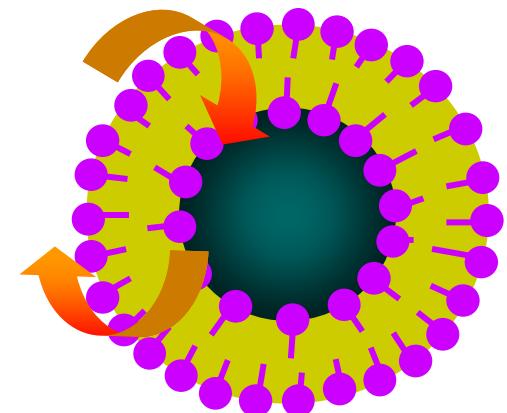
Animals ~ 1,200,000

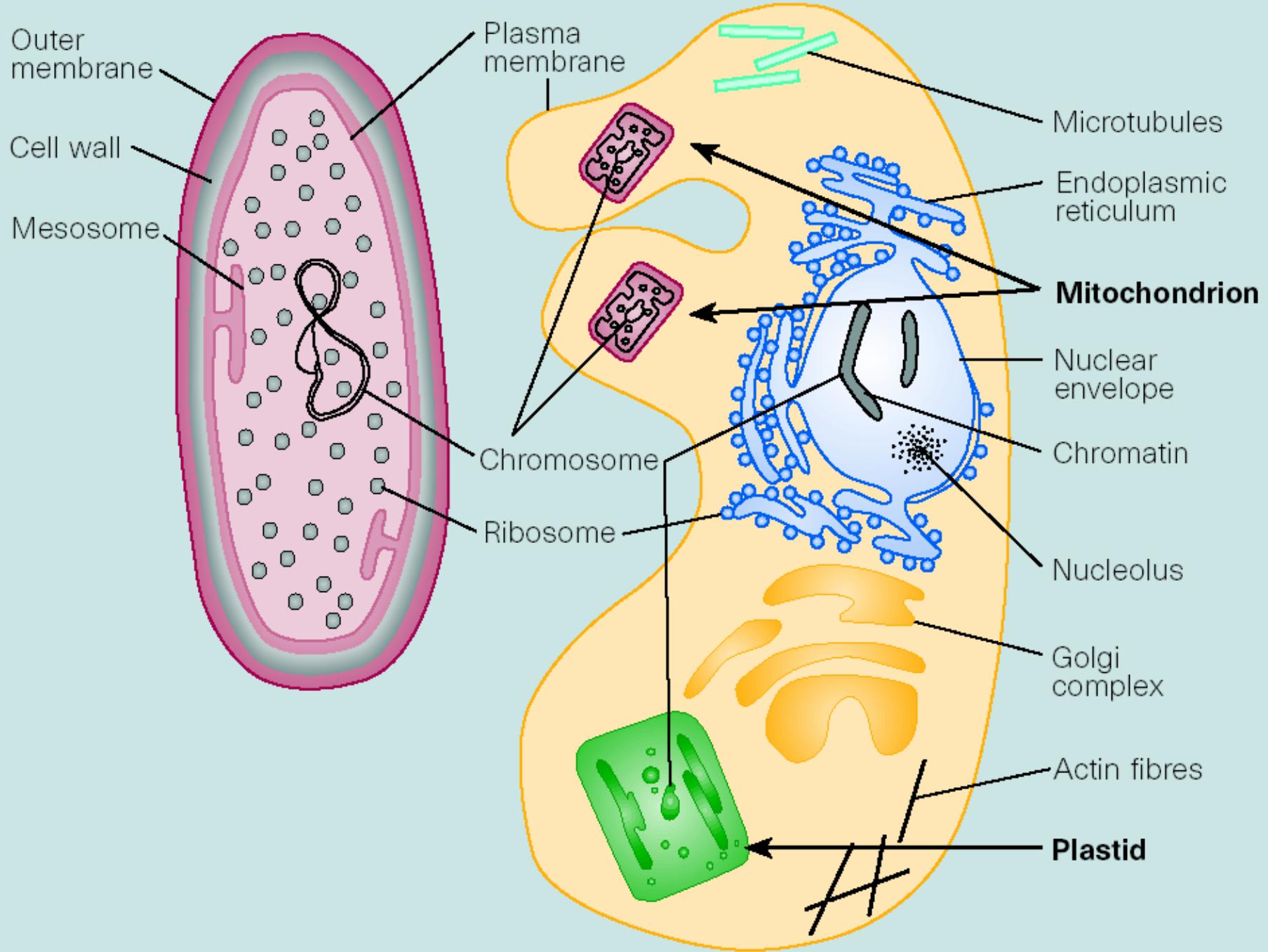
TOTAL ~ 1.6 million



But the unity of Life

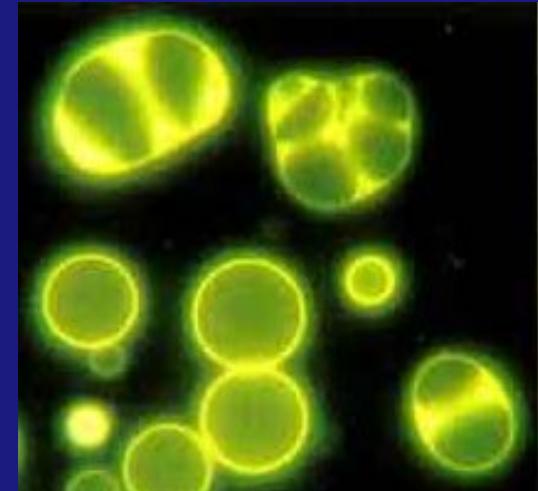
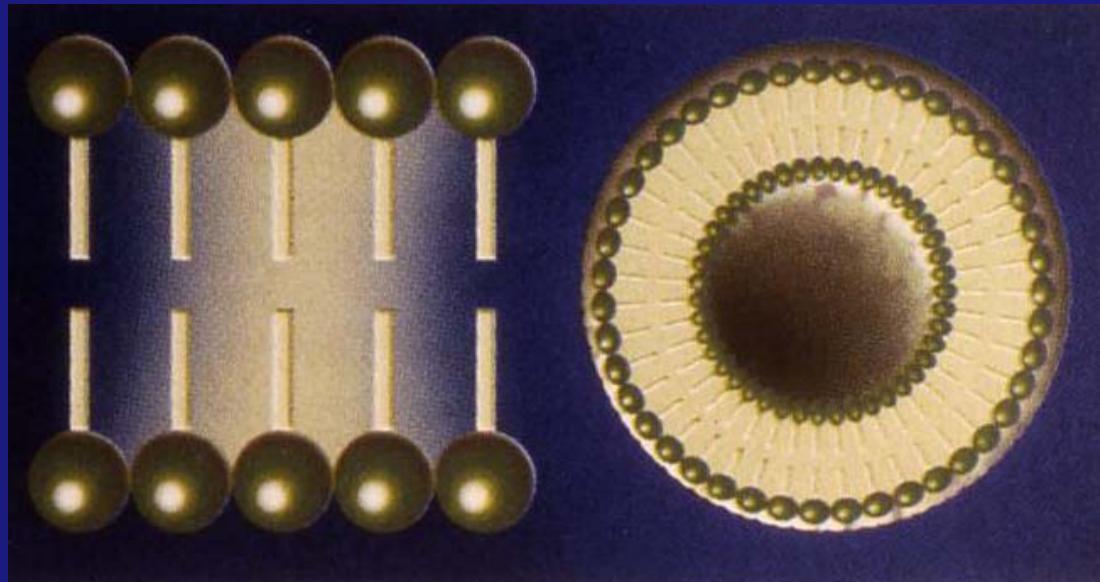
- Life is a chemical system, self-maintained and capable of Darwinian evolution (NASA)
- 2 main characteristics: auto-replication and evolution
- ***Minimal life***: a system delimited by a semi-permeable membrane formed by the system itself, able of self-maintenance and producing its own constituting elements by transformation of exogeneous nutriments and energy through its own processes of production (P. L. Luisi)



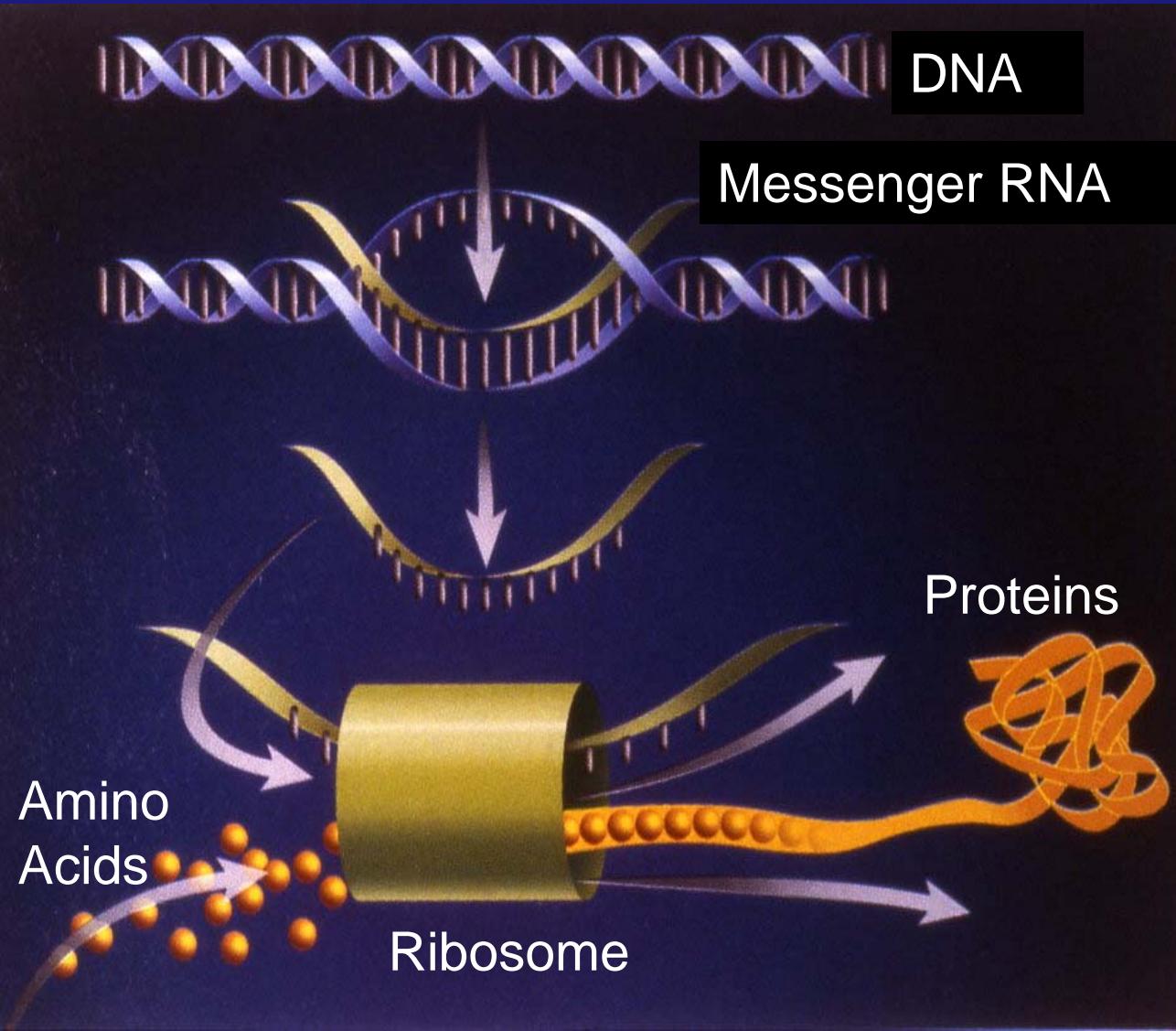


A membrane

- Long organic chain molecules - *amphiphiles* thanks to a polar head with an apolar tail insoluble in water
- Structures capable of forming vesicles.



The cell factory: DNA/RNA and proteins

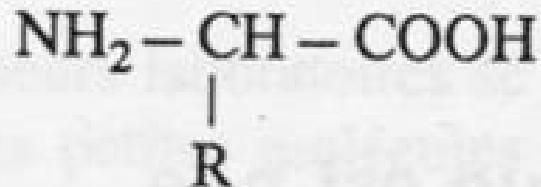


DNA: complex macromolecule => information carrier + replication and evolution capability

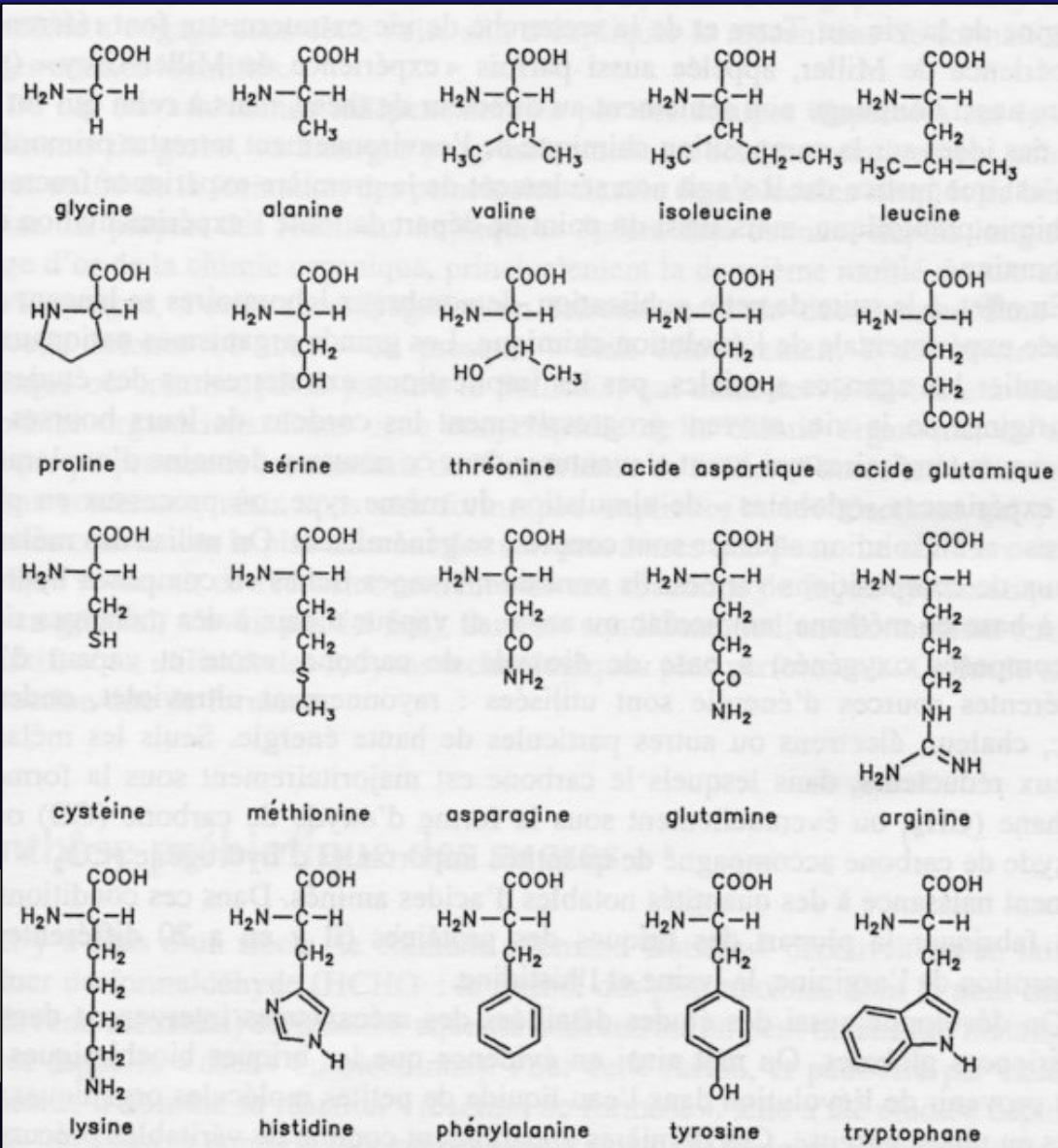
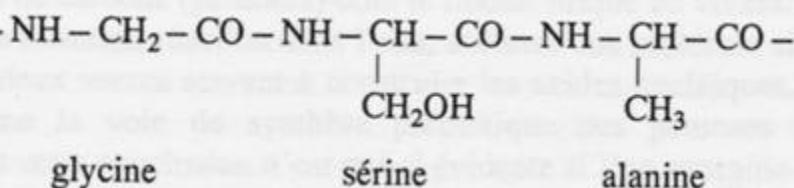
Proteins: complex macromolecule => structural role + catalyst

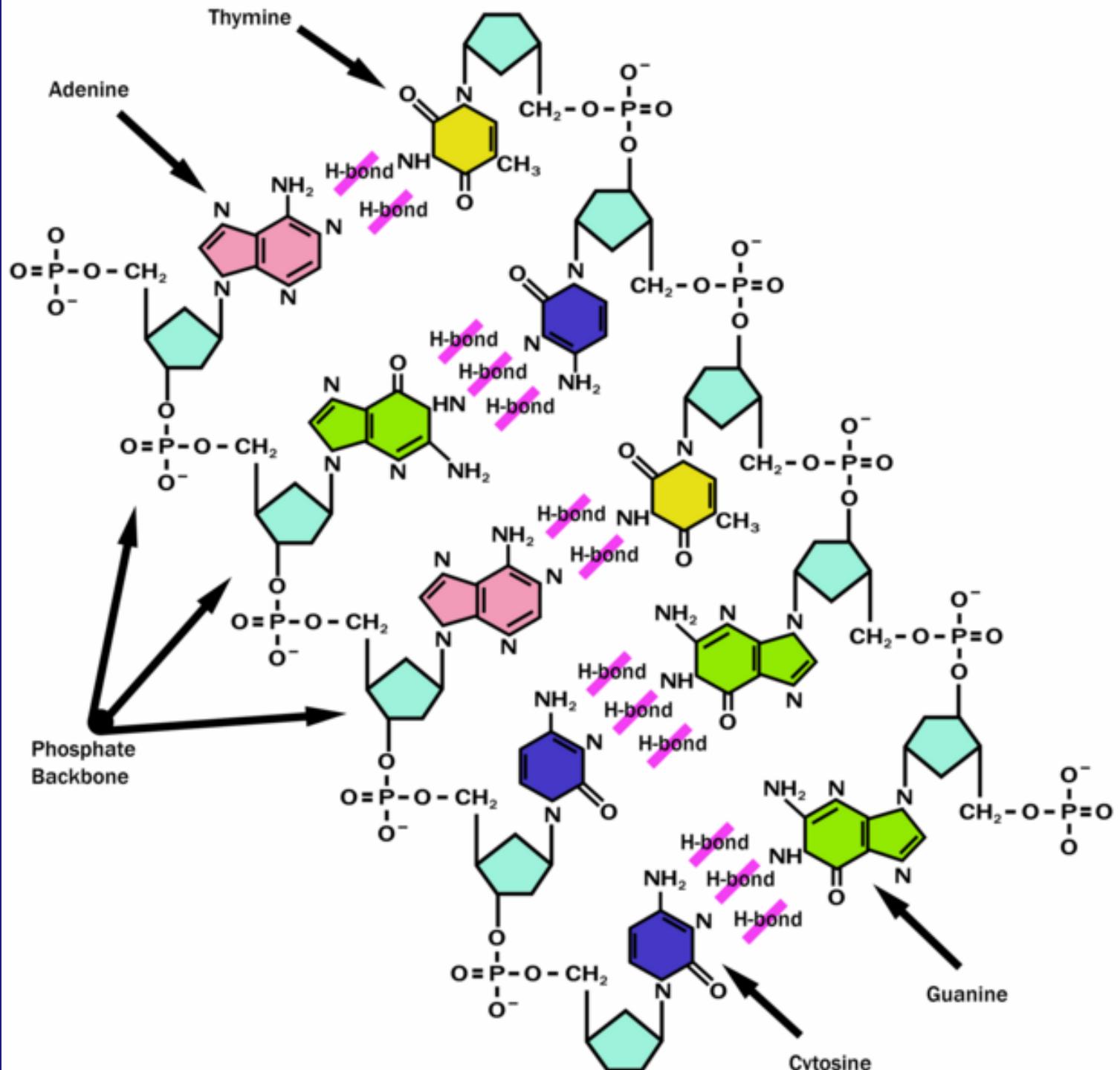
Ribosomes made of proteins and RNA

Building blocks of proteins : amino acids



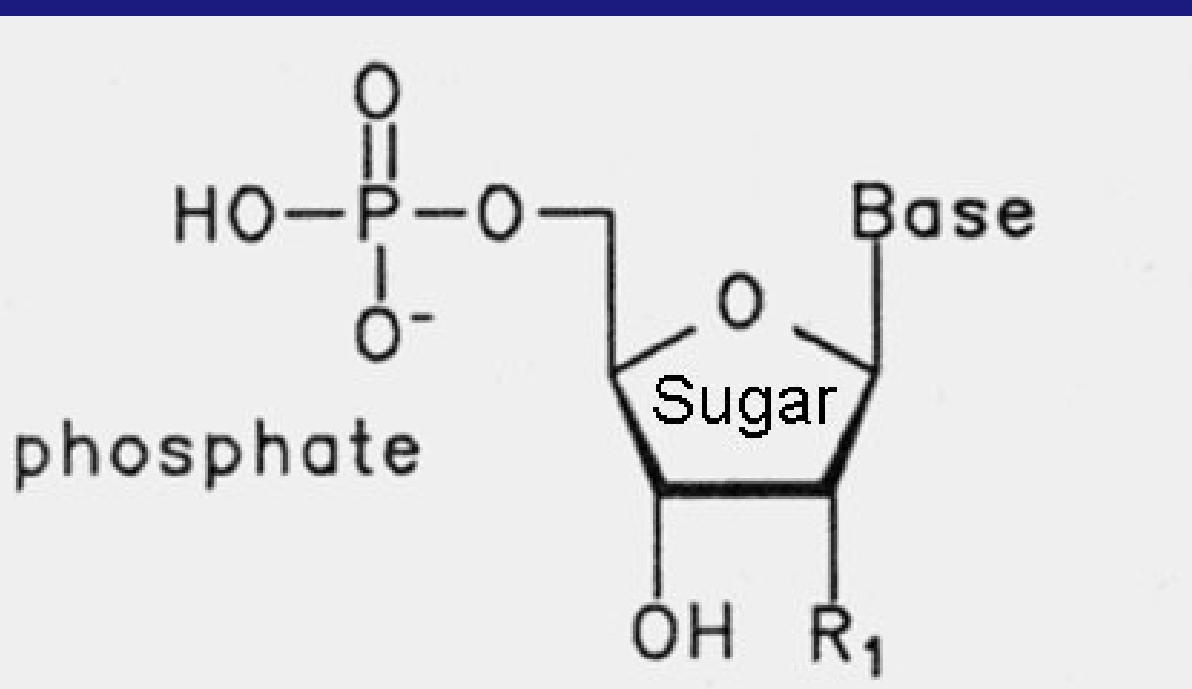
Only 20 different
α-amino acids





In DNA or RNA only 4 different « bases »

=> A vocabulary with only 4 « letters »

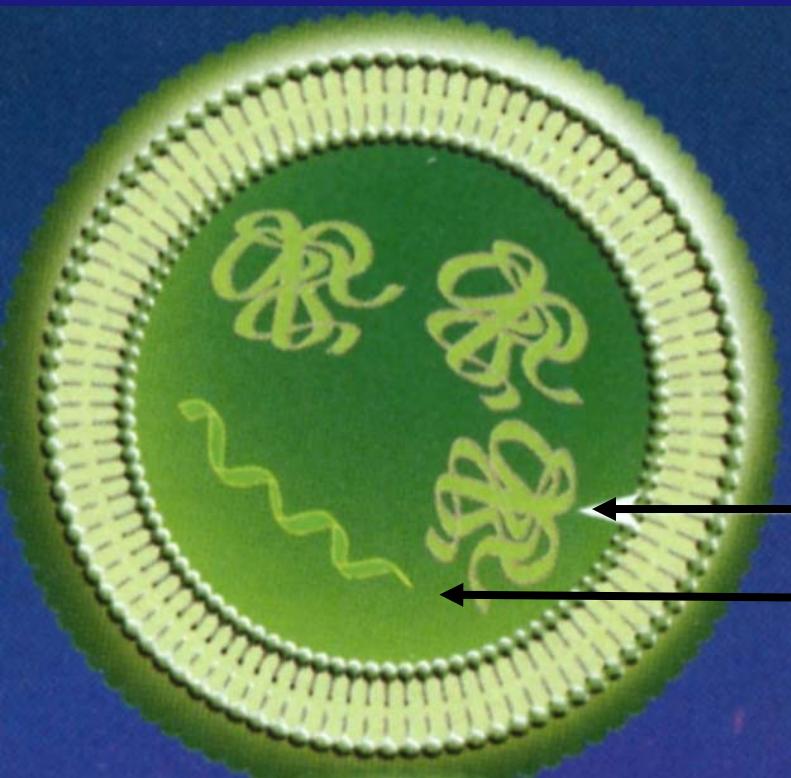


This « letter » in
the « word »
DNA or RNA is
named
« Nucleotide »

$\text{R}_1 = \text{H}$: desoxyribose (DNA)

$\text{R}_1 = \text{OH}$: ribose (RNA)

An RNA world without protein and a simplified cell machinery ?

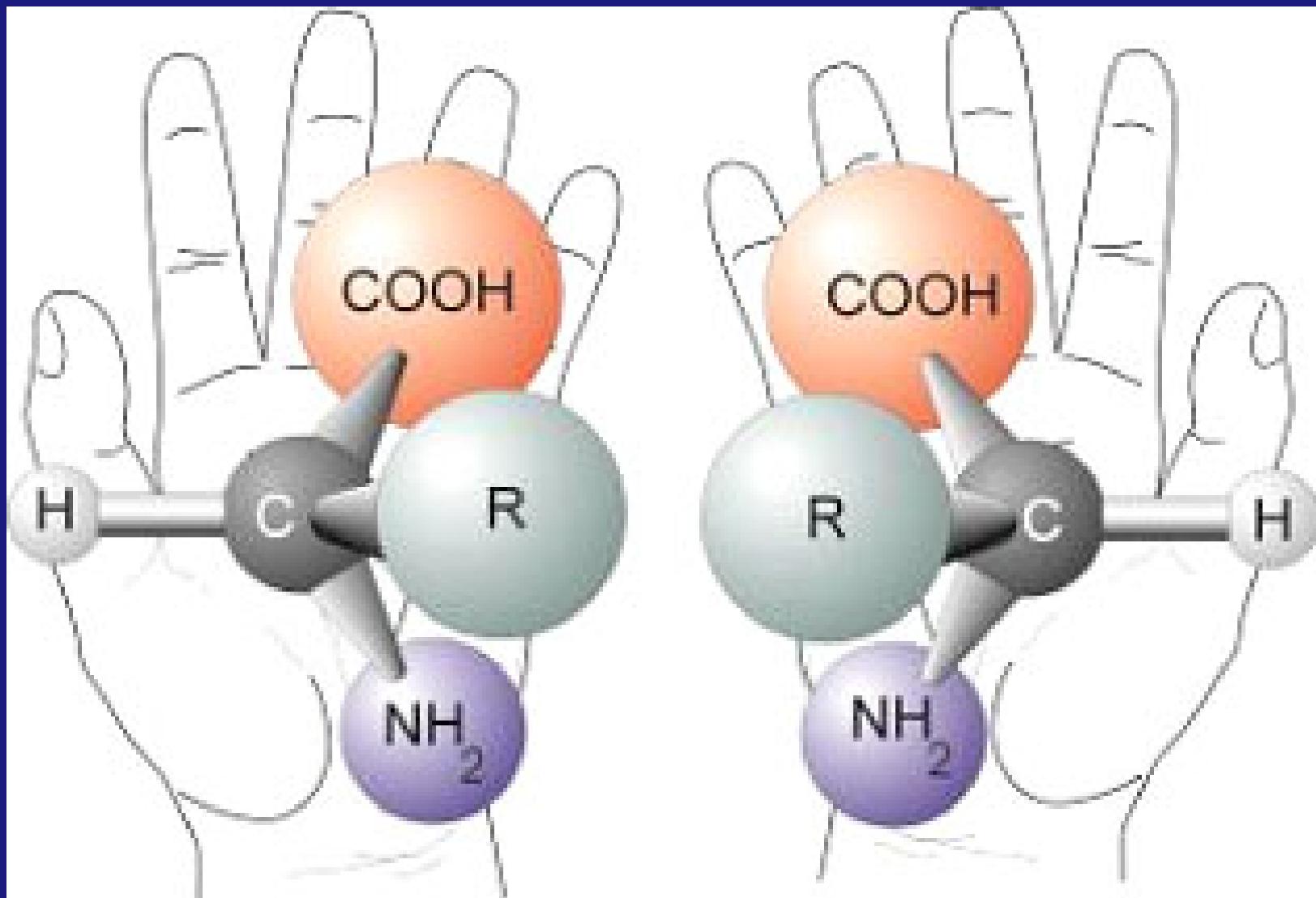


A few decades ago, catalytic properties of RNA have been discovered => RNA could be its own catalyst of its replication

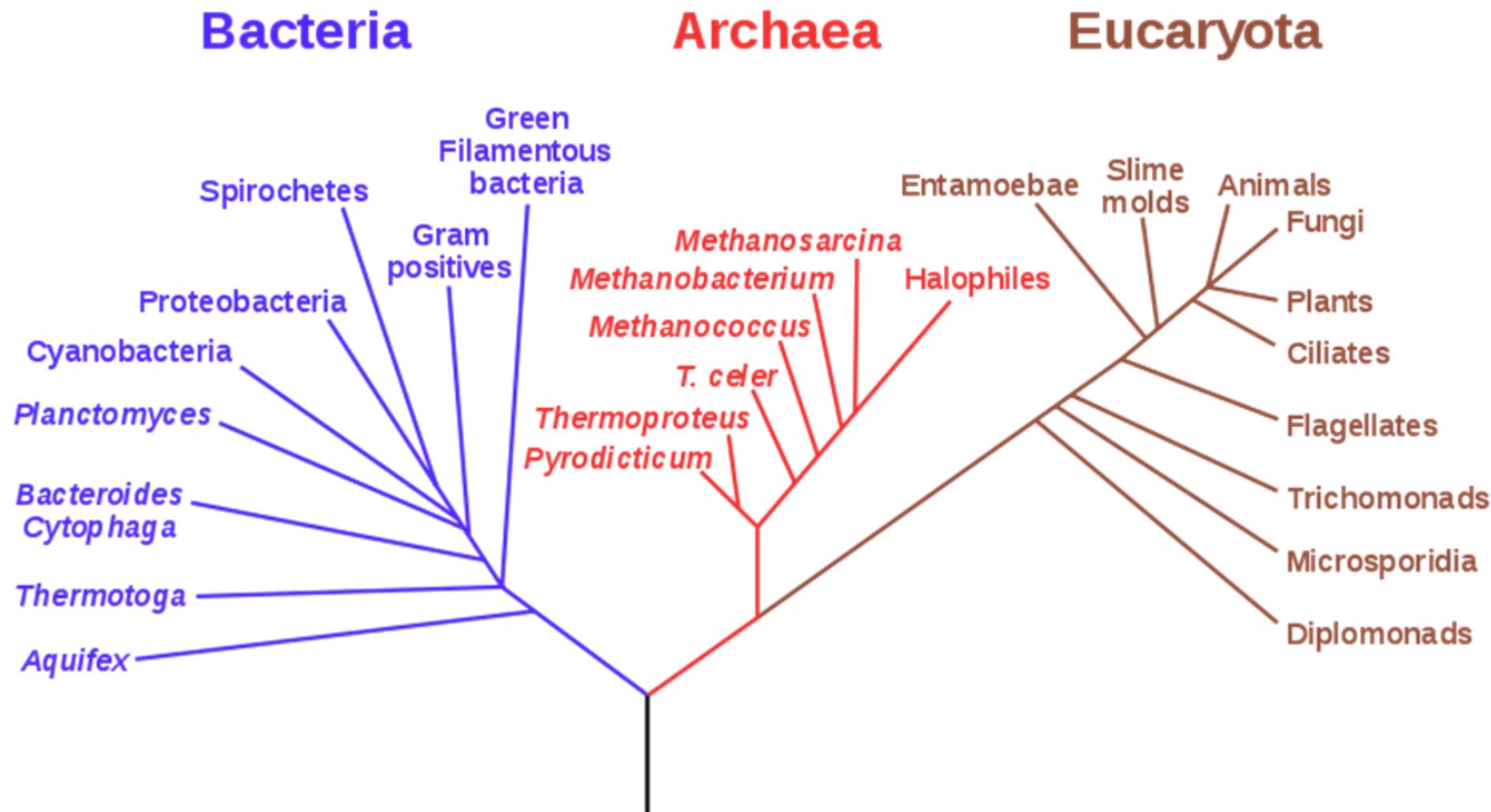
Catalytic RNA

Information RNA

Chirality: property of many biological molecules



Phylogenetic Tree of Life



LUCA: Last Universal Common Ancestor

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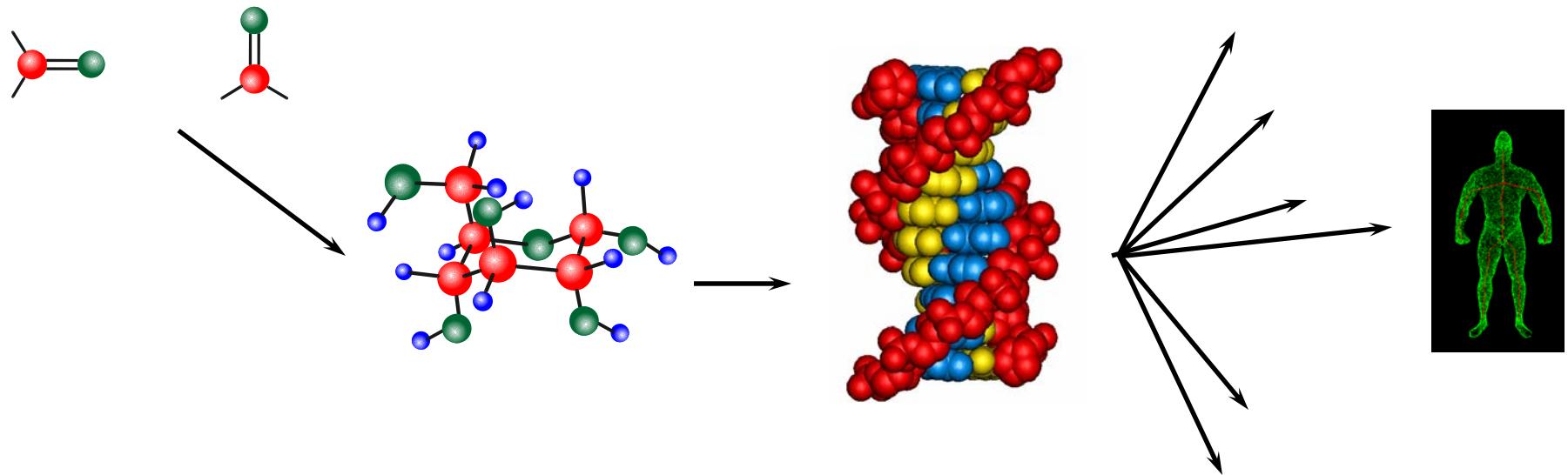
Until mid-19th : Spontaneous generation

End 19th – early 20th : Panspermia

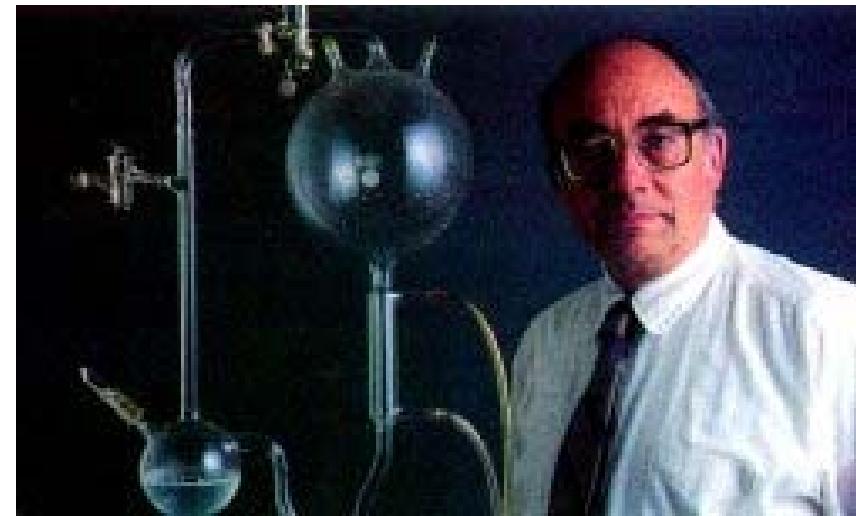
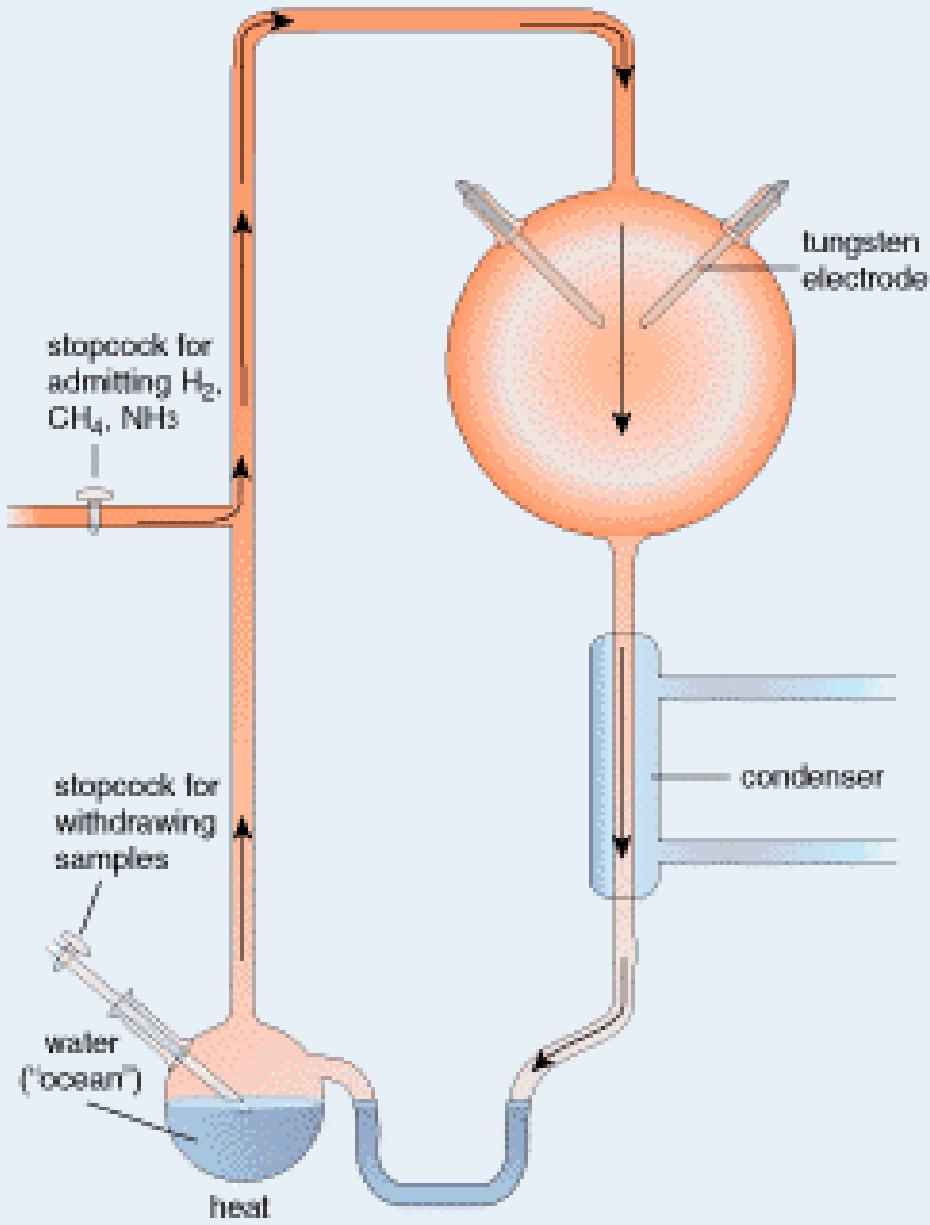
Since 1924+: Chemical evolution (Oparin 1924; Haldane 1929)

A long spontaneous (thermodynamically speaking) evolution of organics from simple molecules to complex organics including macromolecules capable of self-replication, preceding the biological evolution

Organic matter + Liquid water + Energy



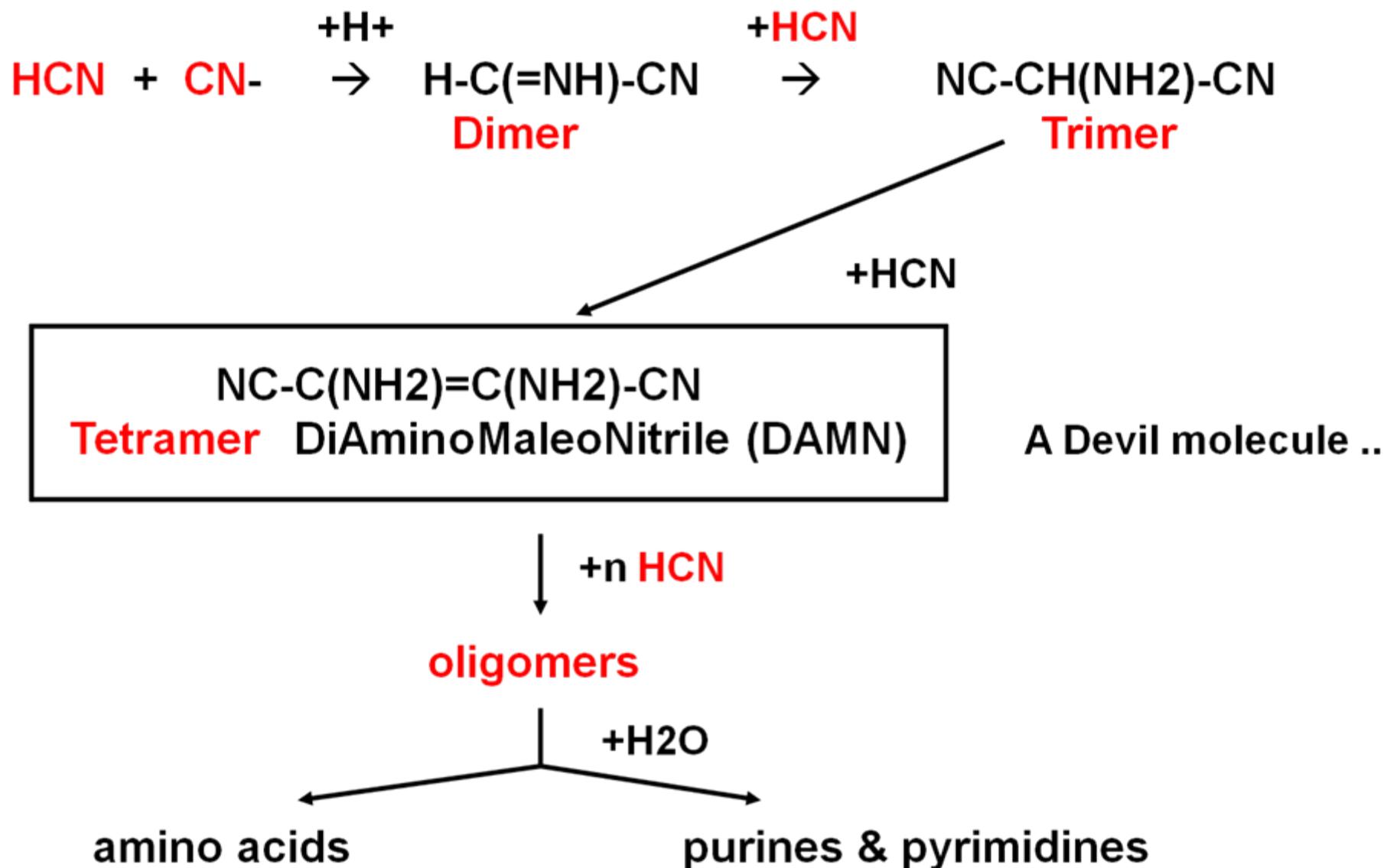
The Miller/Urey experiment



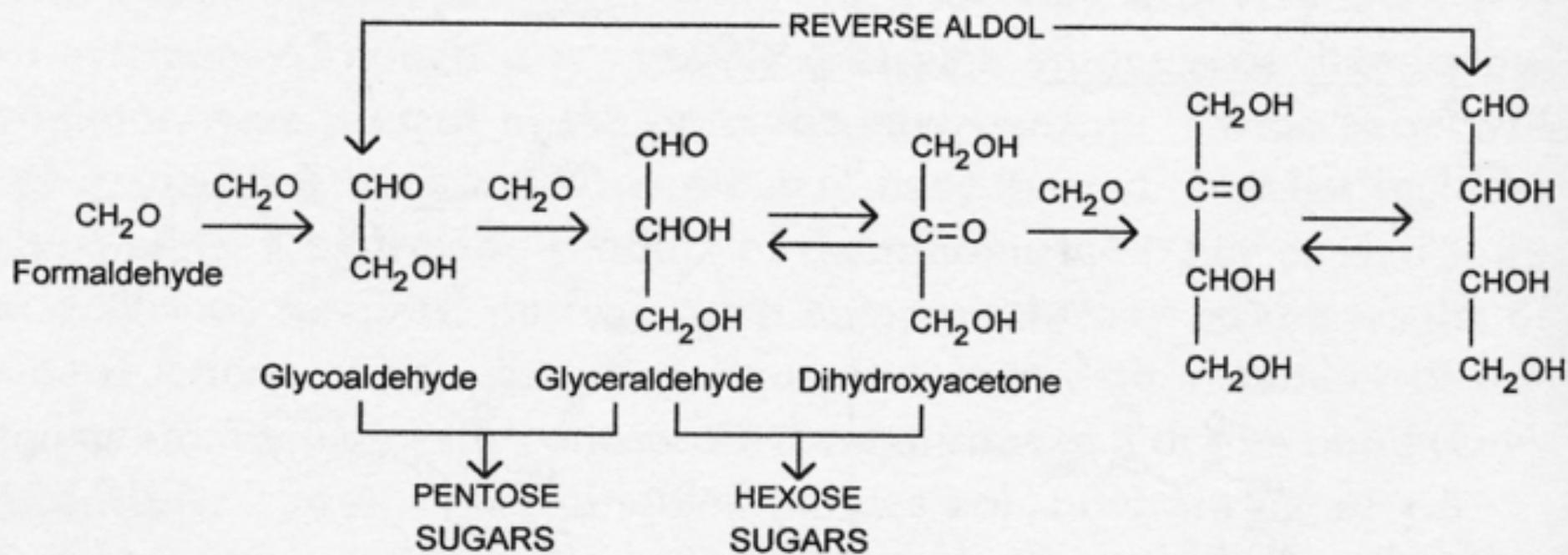
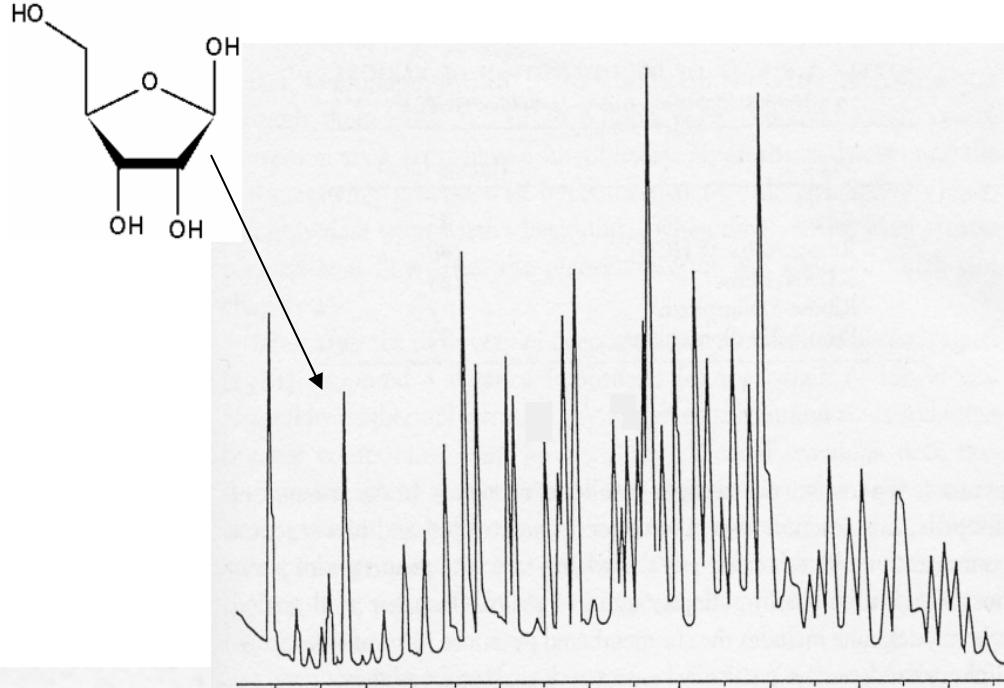
Production of a large range of organic compounds including amino acids (racemic mixture)

SL Miller Science 117,528 (1953)

Prebiotic chemistry of HCN



Formose reaction :
Formaldehyde solution
+ catalyst such as
 $\text{Ca}(\text{OH})_2$, CaCO_3 ,
or clay minerals



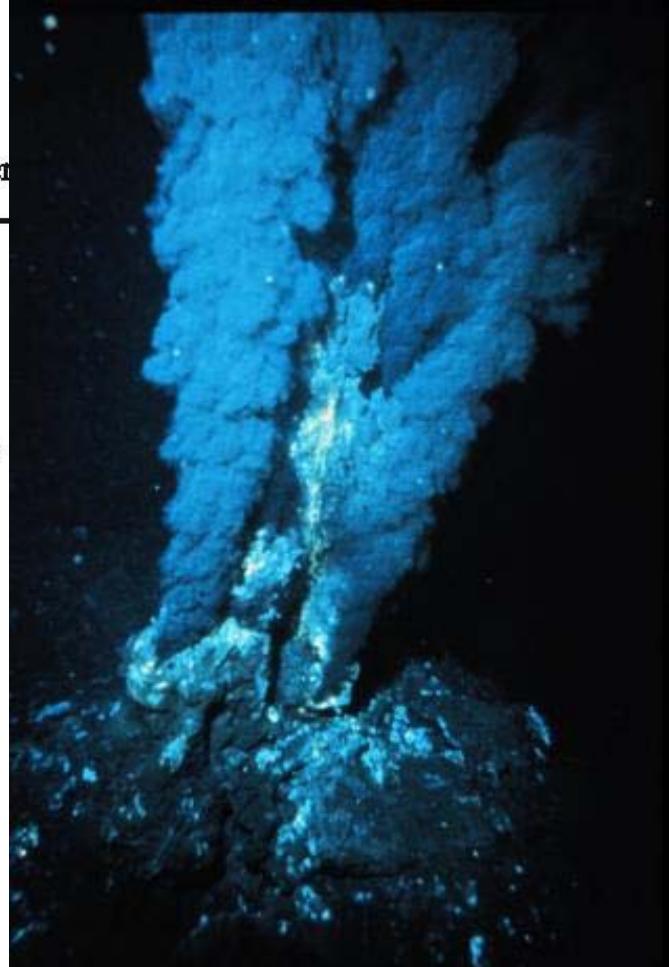
Thermodynamic Potential for the Abiotic Synthesis of Adenine, Cytosine, Guanine, Thymine, Uracil, Ribose, and Deoxyribose in Hydrothermal Systems

Douglas E. LaRowe · Pierre Regnier

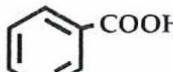
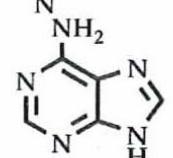
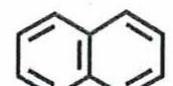
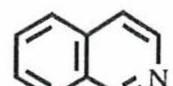
Received: 6 March 2008 / Accepted: 16 April 2008 /

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Abstract The thermodynamic potential for the abiotic synthesis of the five common nucleobases (adenine, cytosine, guanine, thymine, and uracil) and two monosaccharides (ribose and deoxyribose) from formaldehyde and hydrogen cyanide has been quantified under temperature, pressure, and bulk composition conditions that are representative of hydrothermal systems. The activities of the precursor molecules (formaldehyde and hydrogen cyanide) required to evaluate the thermodynamics of biomolecule synthesis were computed using the concentrations of aqueous N₂, CO, CO₂ and H₂ reported in the modern Rainbow hydrothermal system. The concentrations of precursor molecules that can be synthesized are strongly dependent on temperature with larger concentrations prevailing at lower temperatures. Similarly, the thermodynamic drive to synthesize nucleobases, ribose and deoxyribose varies considerably as a function of temperature; all of the biomolecules

Compound	Typical Molecule and Structure	Typical Molecule
Carboxylic acids	$\text{H}_3\text{C}-\text{COOH}$	Acetic acid
Amino acids	$\text{H}_3\text{C}-\overset{\text{NH}_2}{\underset{\text{H}_3\text{C}}{\text{CH}}}-\text{COOH}$	Alanine
Hydroxy acids	$\text{H}_3\text{C}-\overset{\text{OH}}{\underset{\text{H}_3\text{C}}{\text{CH}}}-\text{COOH}$	Lactic acid
Ketoacids	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{\text{H}_3\text{C}}{\text{C}}}-\text{COOH}$	Pyruvic acid
Dicarboxylic acids	$\text{OOC}-(\text{CH}_2)_2-\text{COOH}$	Succinic acid
Sugar alcohols and acids	$\text{H}_2\text{C}-\overset{\text{OH}}{\underset{\text{OH}}{\text{CH}}}-\text{COOH}$	Glyceric acid
Alcohols, aldehydes and ketones	$\text{H}_3\text{C}-\text{CH}_2\text{OH}$	Ethanol
Amines and amides	$\text{H}_3\text{C}-\text{CH}_2\text{NH}_2$	Ethyl amine
Pyridine carboxylic acids		Nicotinic acid
Purines and pyrimidines		Adenine
Hydrocarbons:		
Alyphatic	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$	Propane
Aromatic		Naphthalene
Polar		Isoquinoline

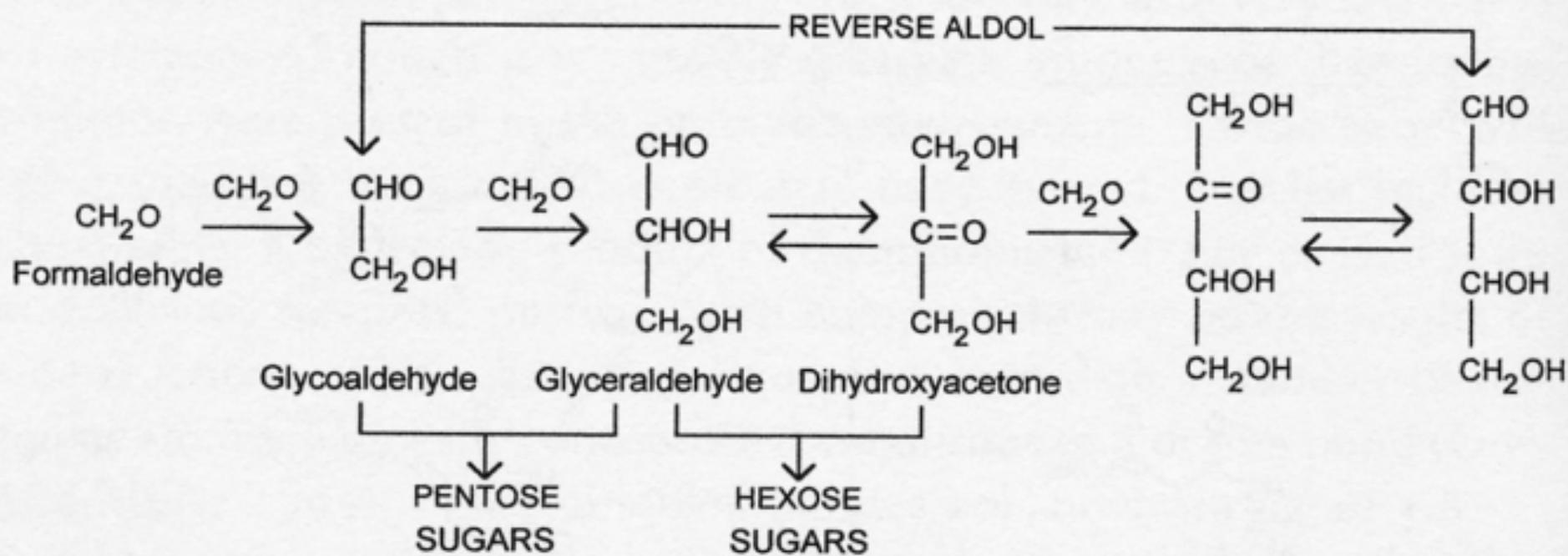
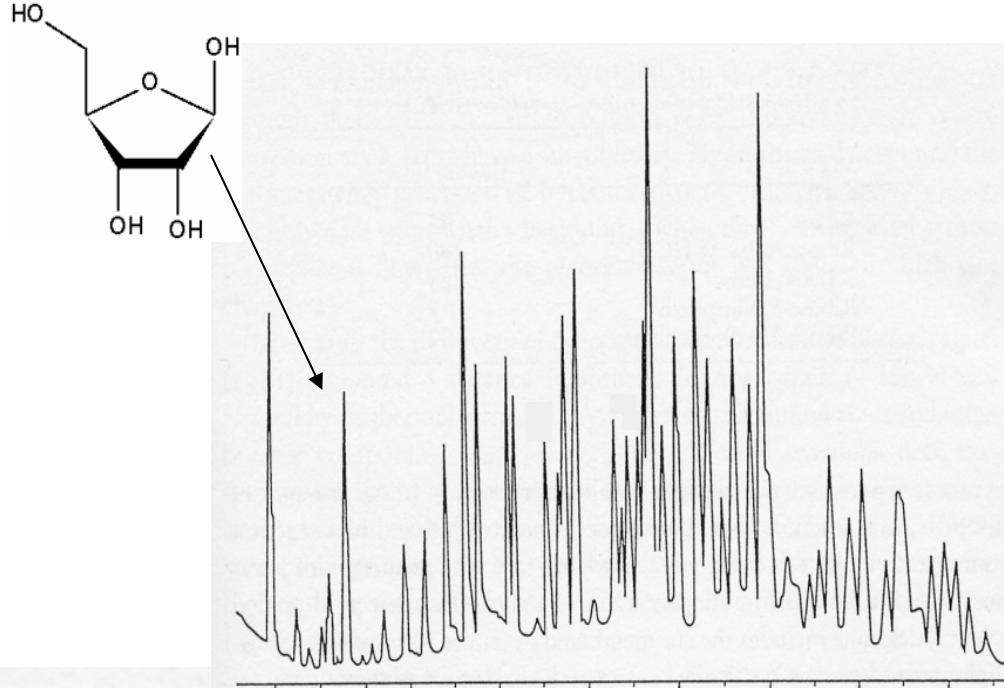
Organic matter in carbonaceous chondrites

soluble compounds

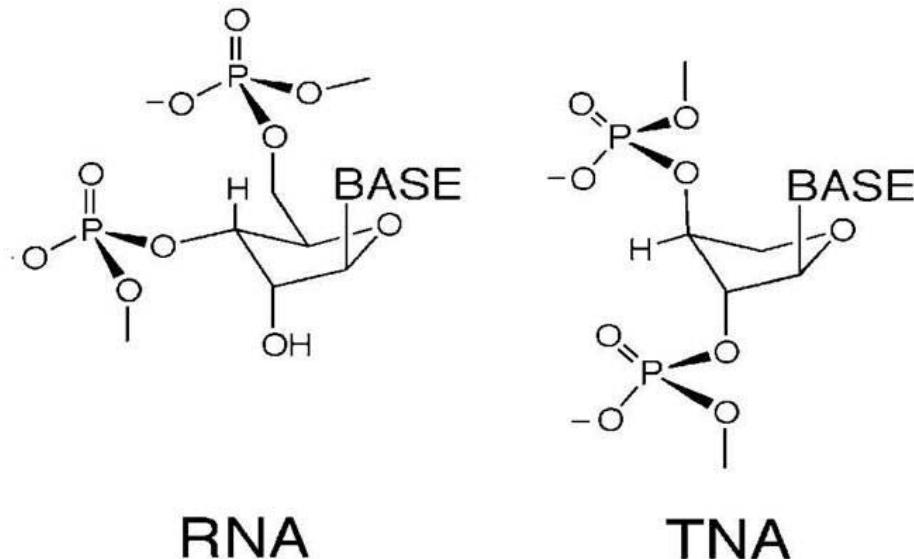
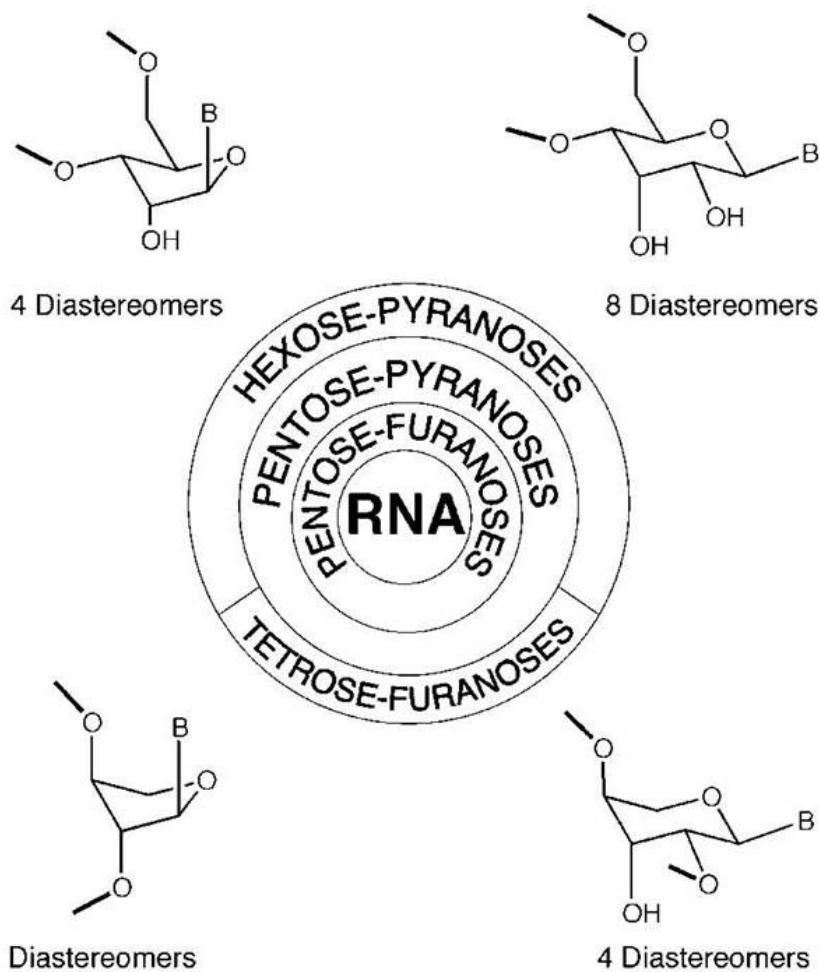
An example : Murchison



Formose reaction :
Formaldehyde solution
+ catalyst such as
 $\text{Ca}(\text{OH})_2$, CaCO_3 ,
or clay minerals

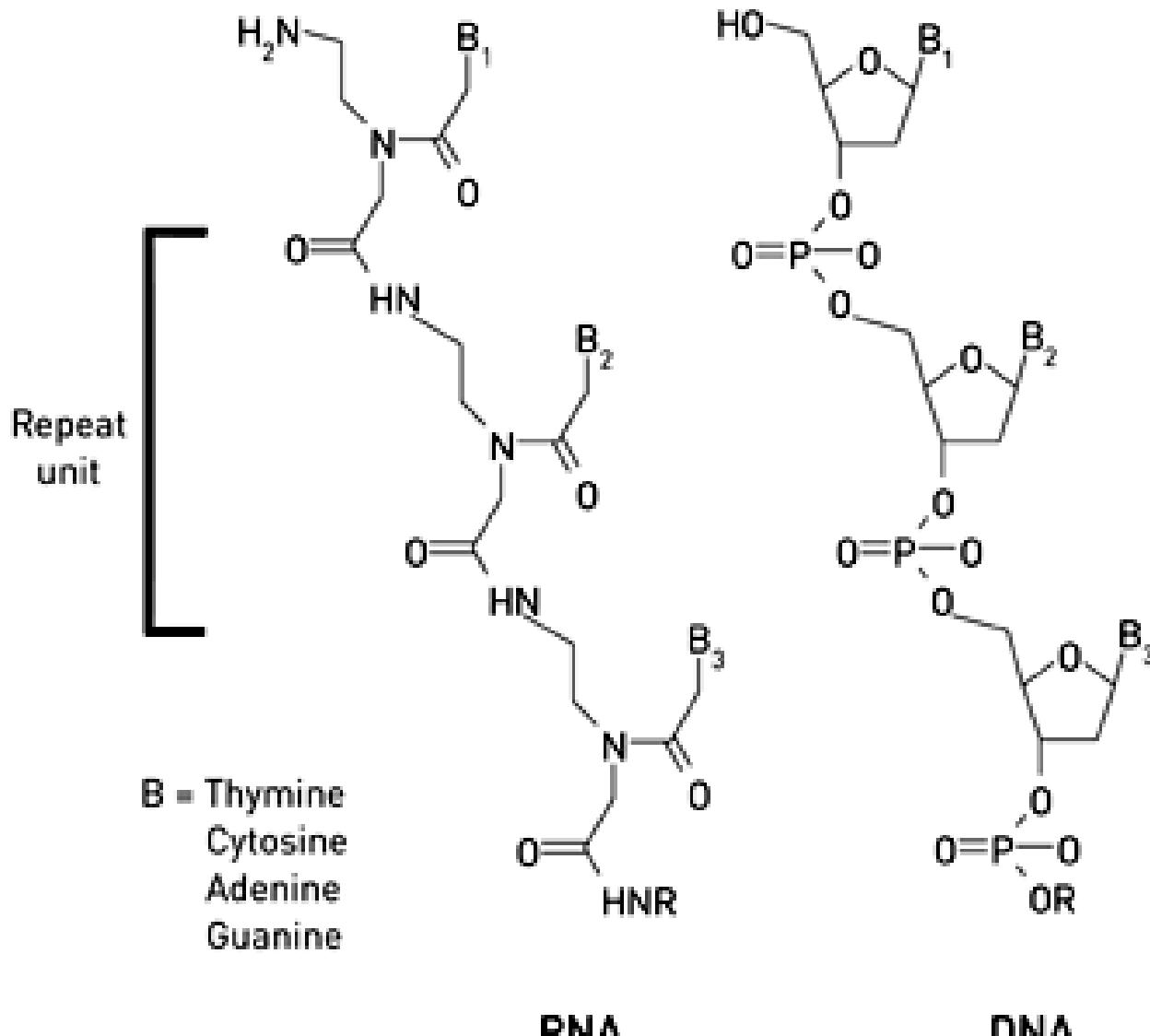


A TNA world?



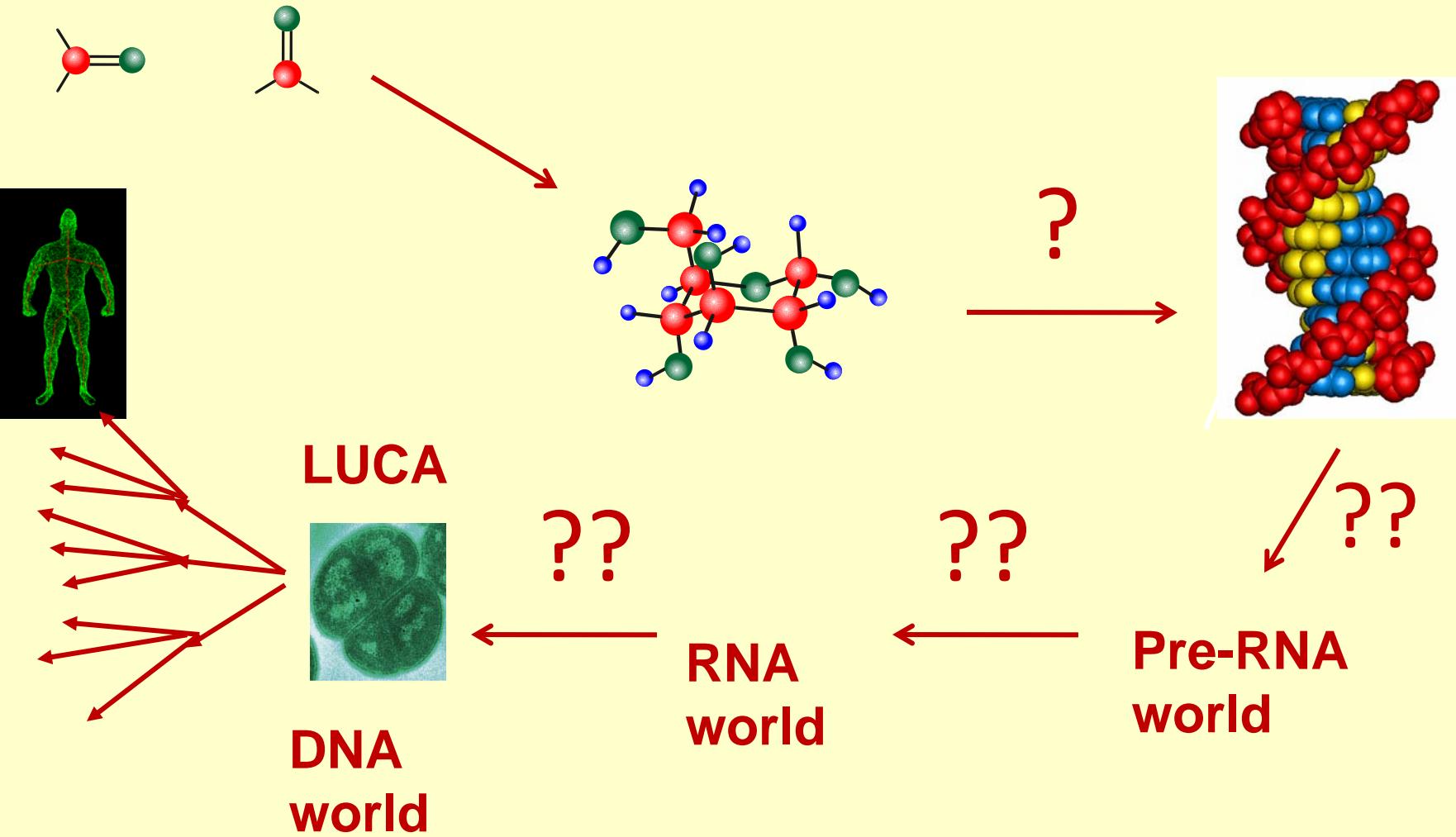
The TNA-Family of nucleic acid systems: properties and prospects - A Eschenmoser, OLEB 34, 277-306 (2004)

A PNA world?



DNA/RNA chimera first invented by PE Nielsen et al., Science 254, 1497 (1991)

Carbonaceous matter + liquid water + Energy

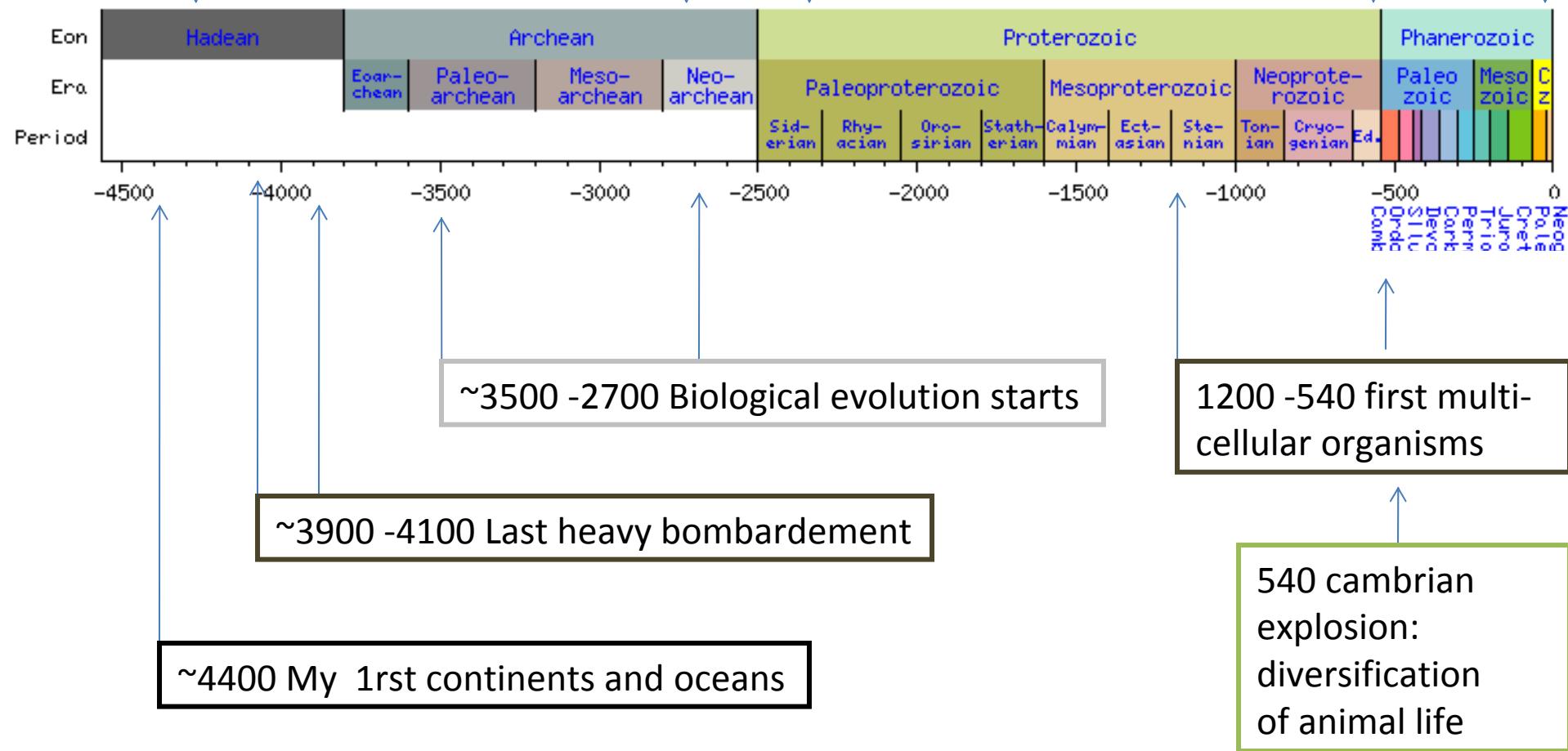


~2400: O₂ rising in oceans and atmosphere

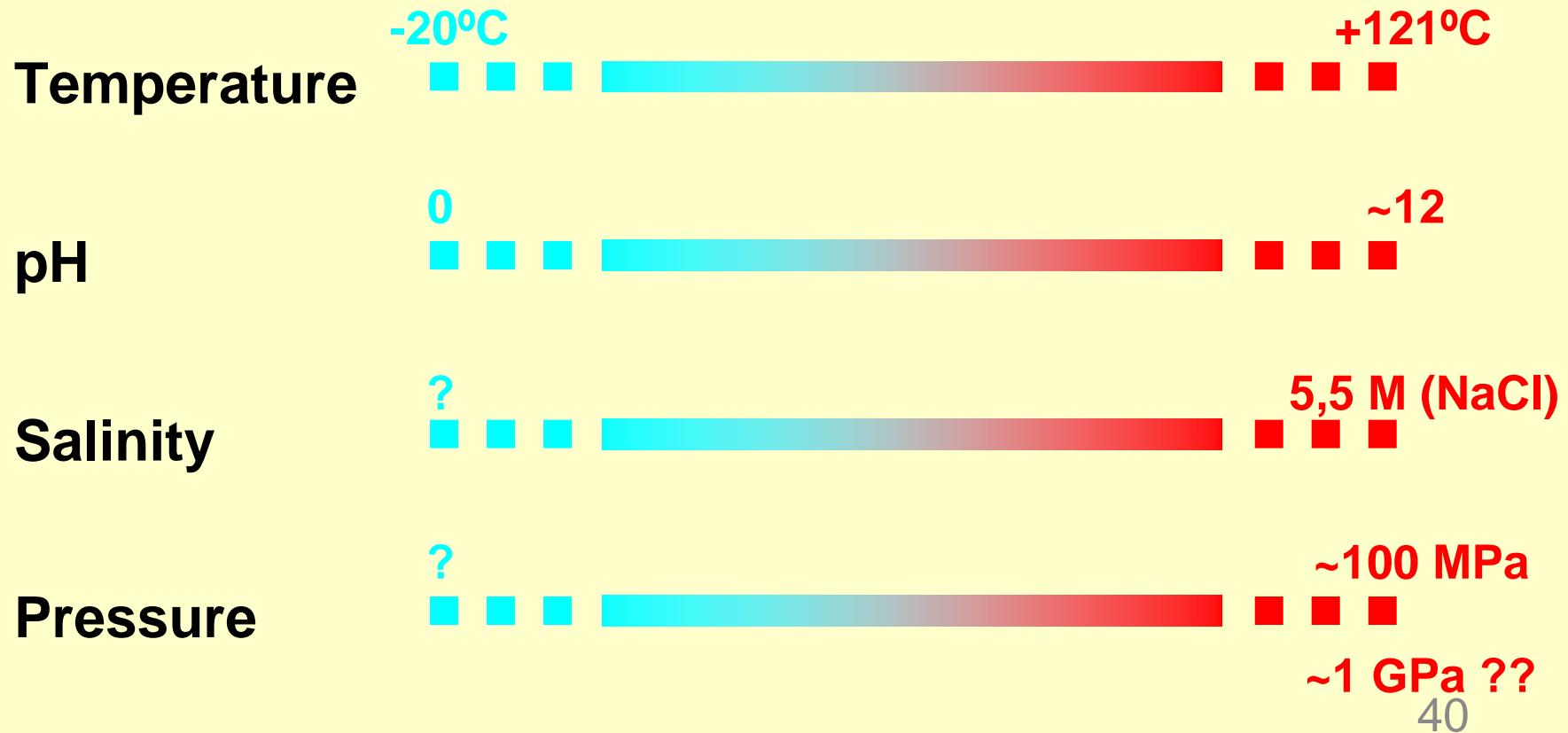
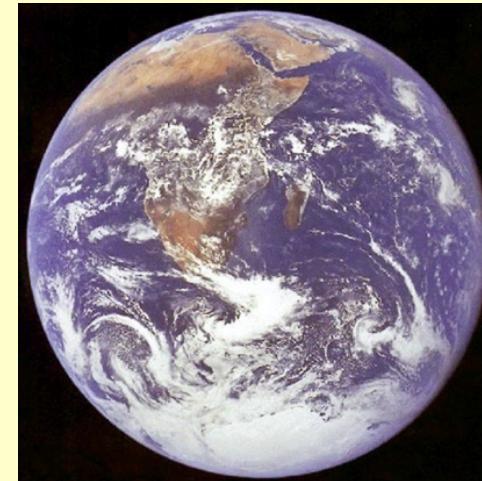
540-0 :explosion of macroscopic life

4300 -2700: From pre-biotic chemistry to life

540 cambrian explosion
Diversification of animal life



Extremophiles and limits for terrestrial life



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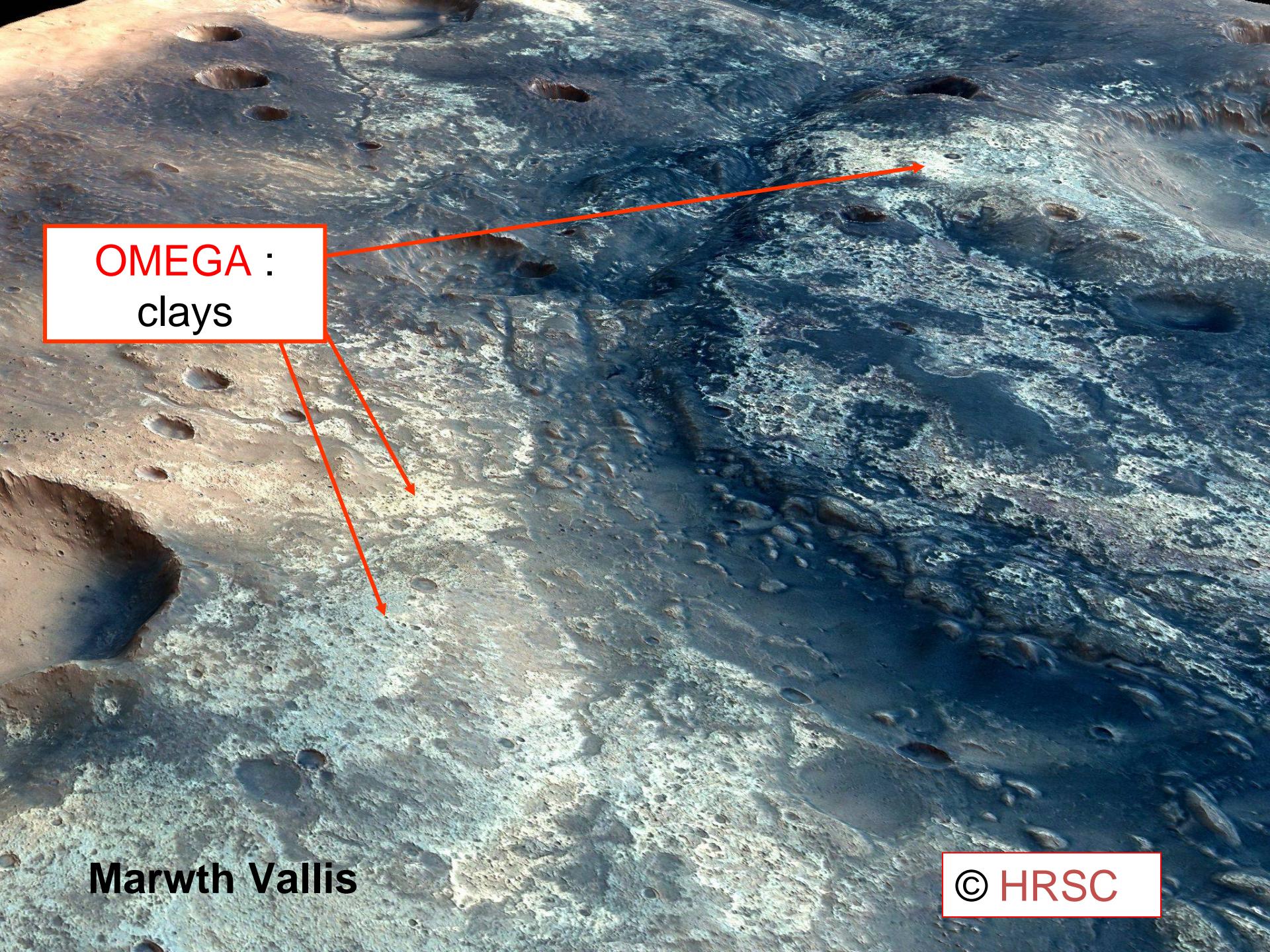
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OMEGA :
clays

Marwath Vallis

© HRSC



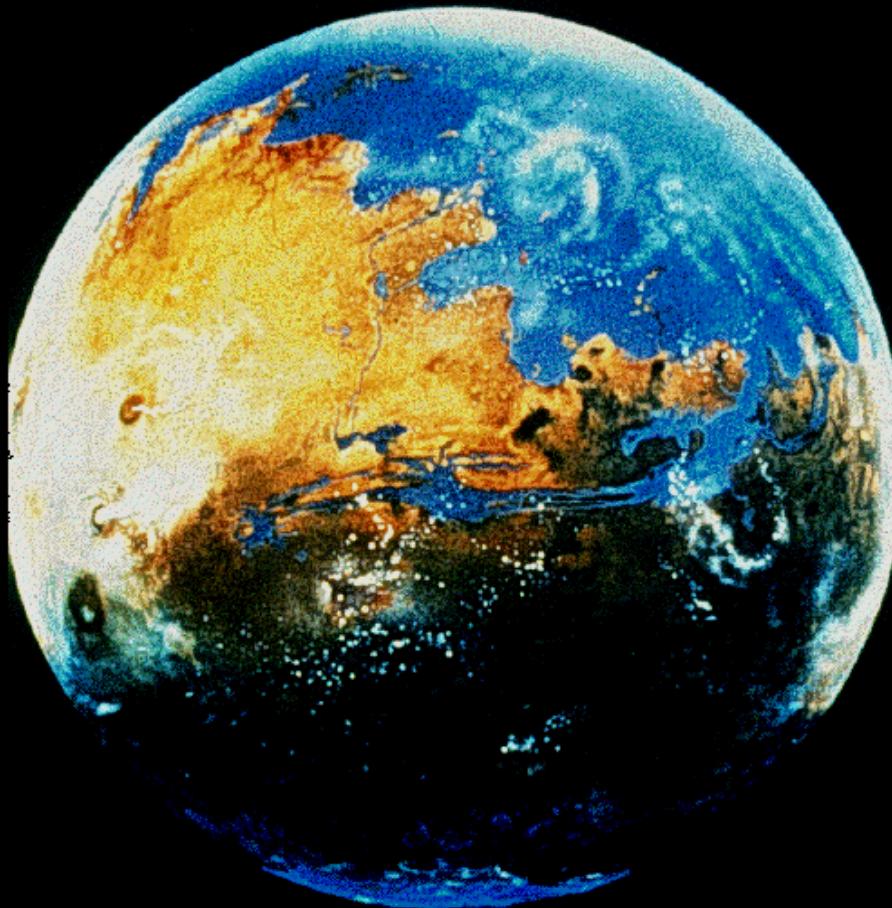
Liquid water



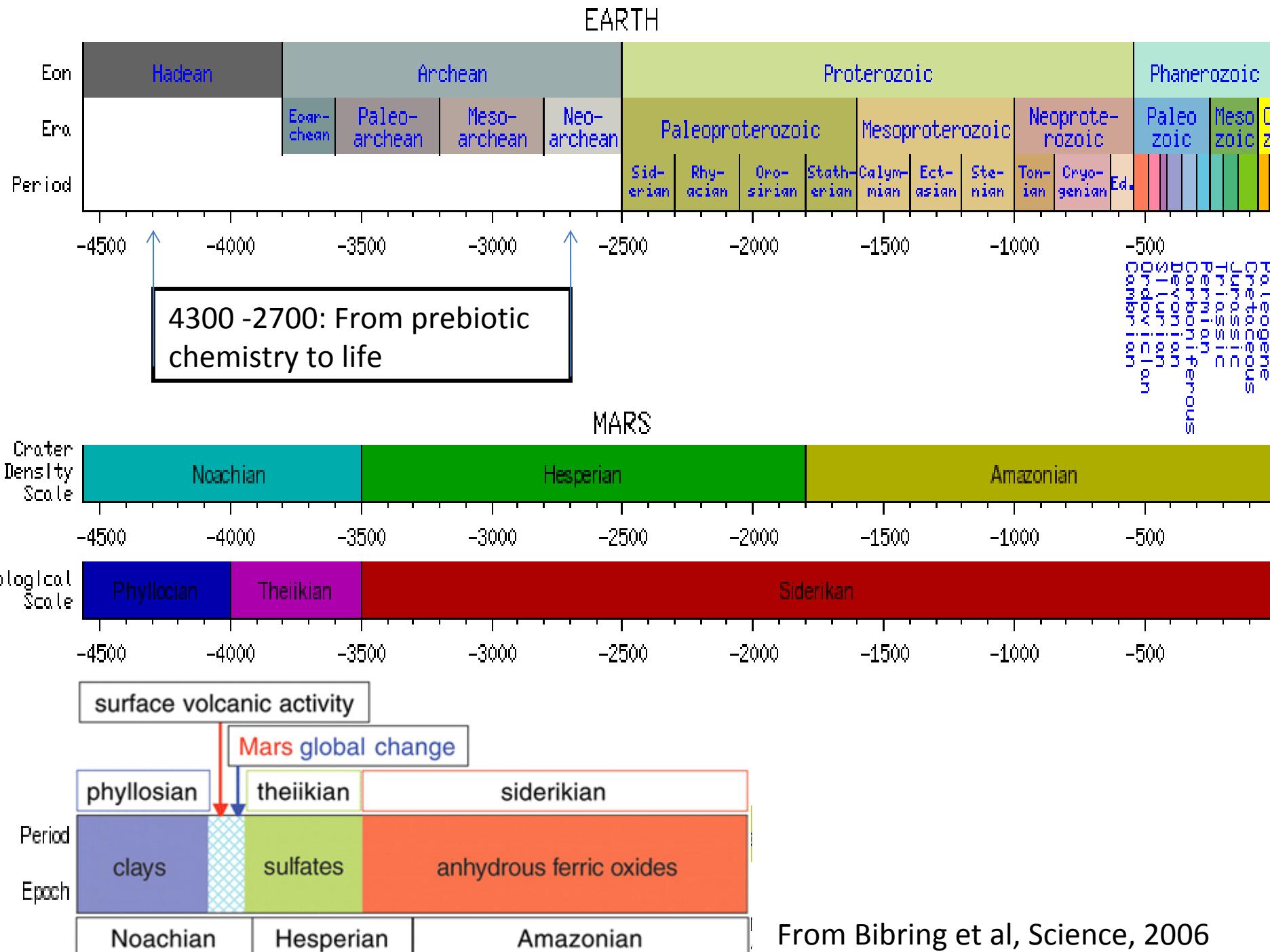
Organics



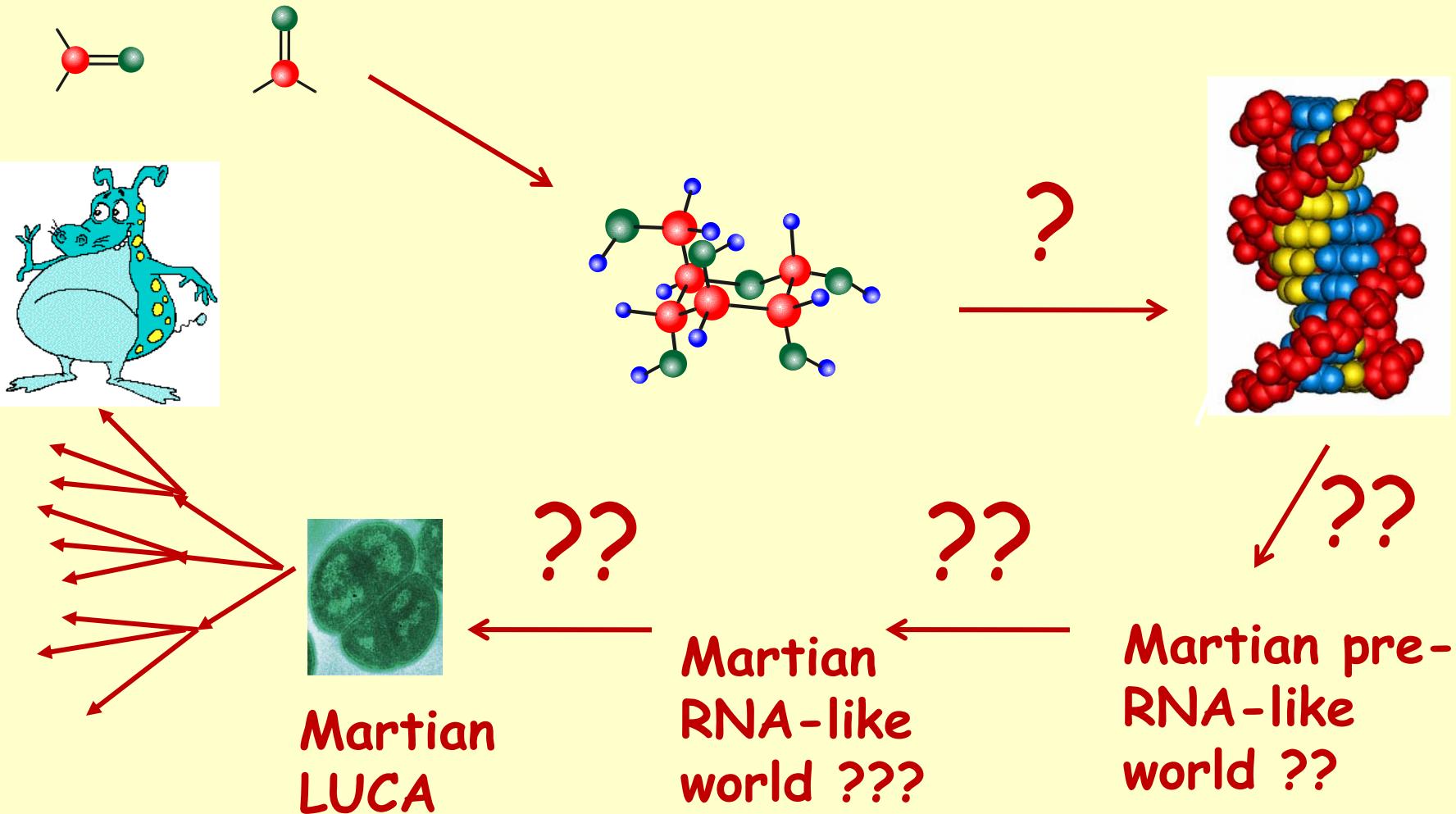
Energy

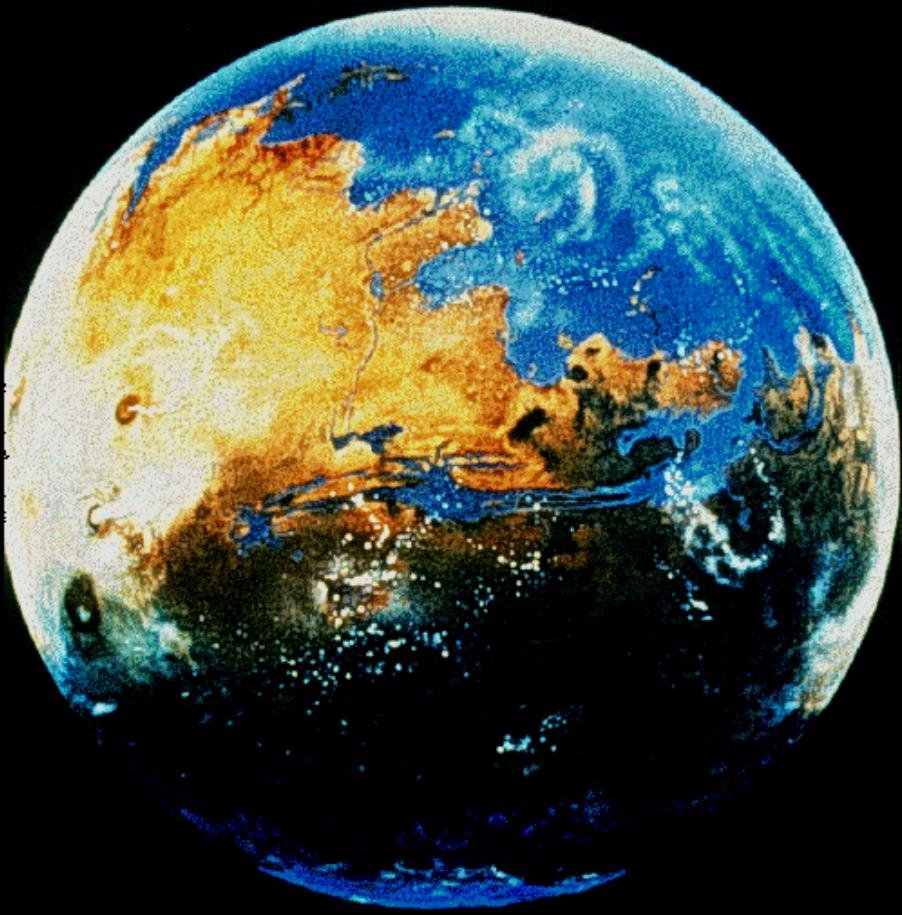


Early Mars

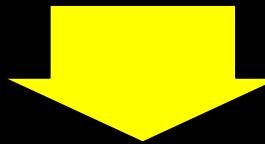


Carbonaceous matter + liquid water + Energy



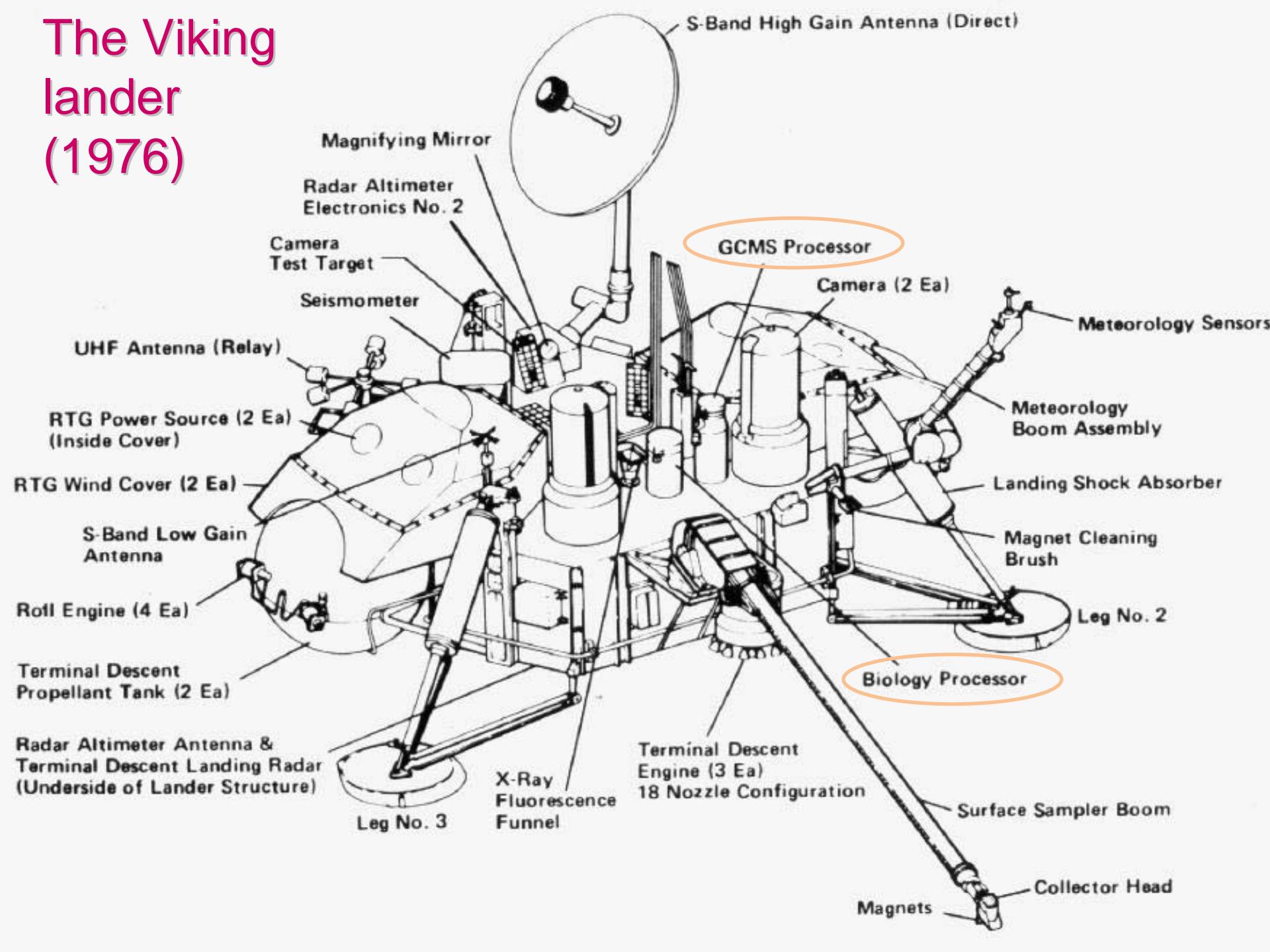


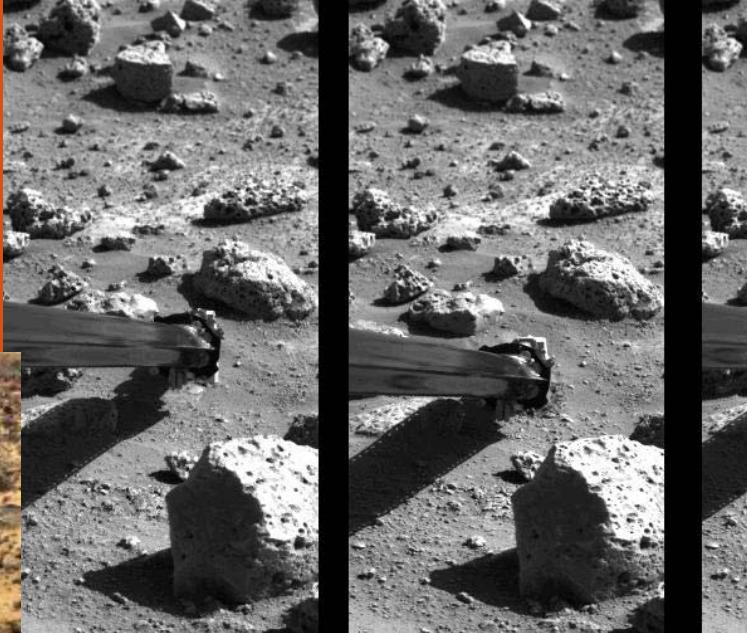
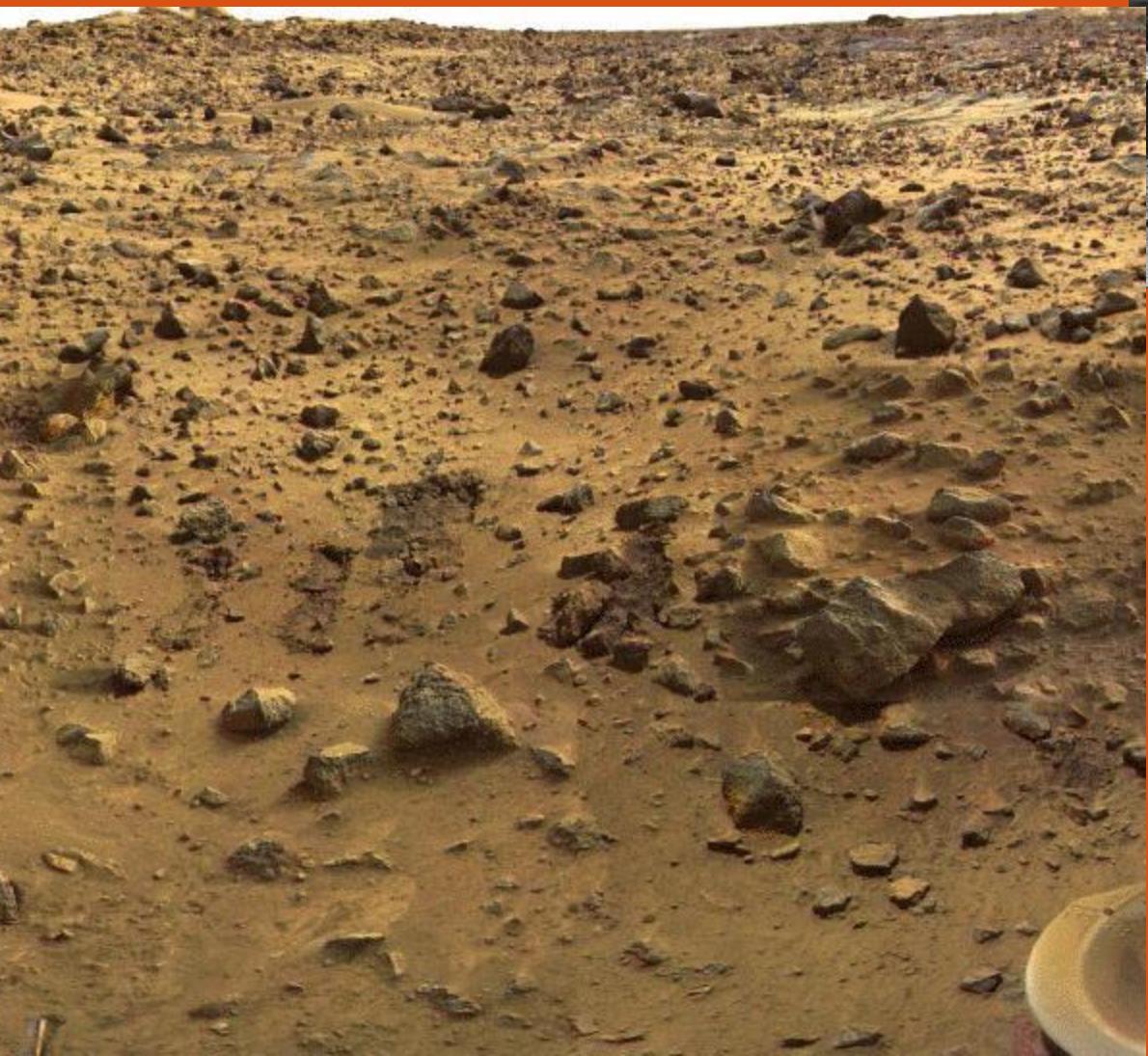
- A primitive Mars and an early evolution similar to that of the Earth
- But no big impact of tectonics or climate on the evolution of Mars up to now

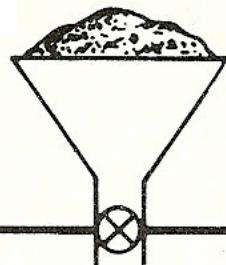


If life emerged on early Mars, and even if it disappeared, there may still be traces of a past life, and even of a prebiotic environment, easier to find than in the Earth case.

The Viking lander (1976)







Soil sample

Duplicate to control analysis

Carbon
dioxide
labeled
 $(^{14}\text{CO}_2)$

Light
source

Sample

Pyrolysis

Column

Detector
for C^{14}

Labeled
nutrient
medium

Sample

Detector
for C^{14}

Unlabeled
nutrient
medium

Unlabeled
 $\text{He}/\text{Kr}/\text{CO}_2$

Sample

Gas
chromatograph

Detector
for $\text{H}_2/\text{N}_2/\text{O}_2/\text{CH}_4/\text{CO}_2$

Pyrolytic Release

Labelled Release

Gas exchange

Experiment	Response for sample	Response for heat-sterilized control
Testing terrestrial life		
PR	Carbon detected	None
GEX	O ₂ or CO ₂ emitted	None
LR	Labelled gas emitted	None
Mars sample in absence of Martian life		
PR	None	None
GEX	None	None
LR	None	None
Actual Viking results with Martian samples		
PR	Carbon detected	Carbon detected
GEX	O ₂ emitted	O ₂ emitted
LR	Labelled gas emitted	None

Viking GC-MS did not detect any Martian organic molecule in the soil, although the instrument worked perfectly as designed (Biemann et al., Sciences 194, 72 (1976); J. G. R. 30 4641 (1977)

Organics too refractory to be released at the temperatures achieved or oxidized during the TV step by the iron present in the soil (Navarro et al, PNAS 103 (44), 16089-16094 (2006); Benner et al. PNAS 97, 2425 (2000).

Table 1. Expected Metastable Products from Organic Substances in the Murchison meteorite^{5,6}

Substance	Concentration (parts per million)	Metastable Products
Acid insoluble kerogen	14500	Benzene carboxylic acids
Aliphatic hydrocarbons	12–35	Acetate
Aromatic hydrocarbons	15–28	Benzene carboxylic acids
Monocarboxylic acids	≈330	Acetate/oxalate
2-Hydroxycarboxylic acids	14.6	Acetate/carbonate
Alcohols (primary)	11	Acetate
Aldehydes	11	Acetate
Ketones	16	Acetate, benzene carboxylic acids
Amines	10.7	Acetate
Urea	25	Carbonate
Heterocycles	12	Carbonate, other products

Past Martian life in SNC ALH84001 ?

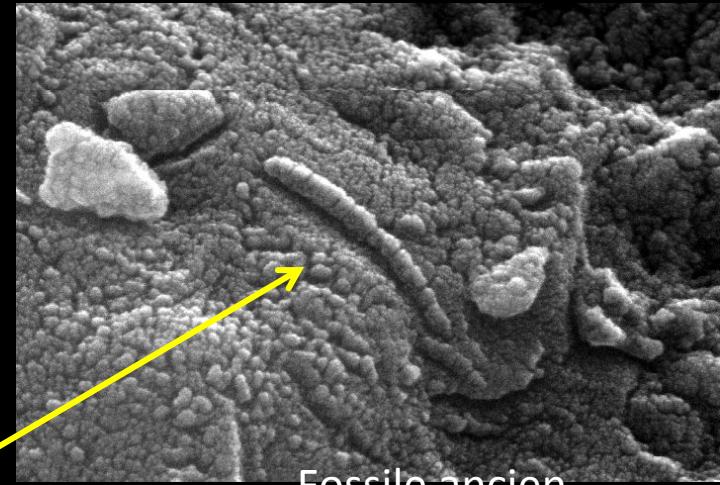


McKay *et al. Science* 273, 924 (1996)

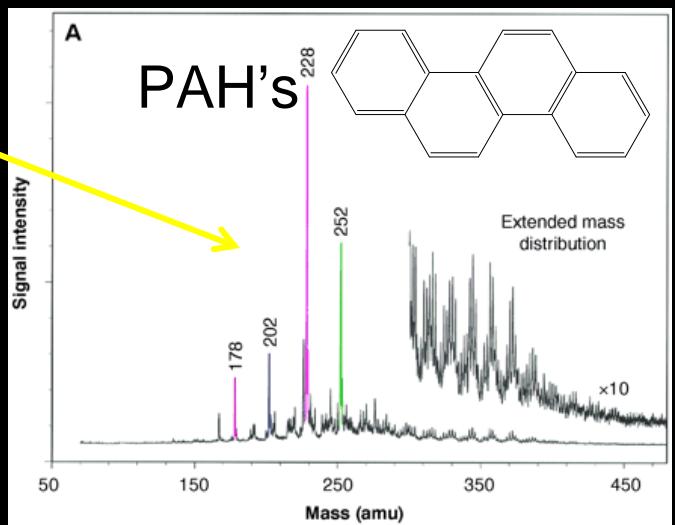
Globules
of amber
Carbonate



Martian organics
or terrestrial
contamination ?



Fossile ancien



WE HAVE SOME CIRCUMSTANTIAL EVIDENCE THAT MIGHT POINT, IN A TENTATIVE WAY, TO THE SLIGHT POSSIBILITY THAT MAYBE 3 BILLION YEARS AGO THERE'S A CHANCE THAT THERE COULD HAVE BEEN :AHEM! LIFE ON MARS

DID YOU HEAR THAT?!?
LIFE ON MARS!

WAA HOO!

THE UNIVERSE IS INHABITED!

WE'RE NOT ALONE!

A NEW ERA DAWNS!



LET'S HOPE LIFE ON MARS IS MORE INTELLIGENT THAN LIFE ON EARTH.



Available online at www.sciencedirect.com



ScienceDirect

Geochimica et Cosmochimica Acta 73 (2009) 6631–6677

**Geochimica et
Cosmochimica
Acta**

www.elsevier.com/locate/gca

Origins of magnetite nanocrystals in Martian meteorite ALH84001

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.... We suggest that the majority of ALH84001 magnetites has an allochthonous origin and was added to the carbonate system from an outside source. This origin does not exclude the possibility that a fraction is consistent with formation by biogenic processes, as proposed in previous studies.

Exobiology

Some historical aspect

Current exobiology

The terrestrial example

Life on Earth

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A Mars Example?

Did we already find it?

What to search for?

How to search for?

The PP aspects and future prospects

Signatures of extant Life

At the level of a cell or of an ecosystem: **gas production** (CH_4 , O_2), **specific pigmentation** (fluorescence), **specific red-ox** or **thermal** activity non chemically explainable, presence of **specific macromolecules** linked to replication or recognition properties, amplification of molecular biomarkers (structural genes, etc) by PCR (*Polymerase Chain Reaction*) or by *in vitro* culture.

To summarize:

- **Metabolic activity** : assimilation, and/or release of metabolites
- **Replication**
- **Molecular signatures** : biomacromolecules
- **Homochirality**
- **Rapid evolution of characteristics** (morphology, chemical composition, etc)

Signatures of extinct Life

Structural biosignatures

Direct : Morphology (individual level), biofilms (colonies)

Indirect : biocorrosion of biomineratisation structures (specific biotransformations, not reached by purely chemical processes)

Chemical biosignatures

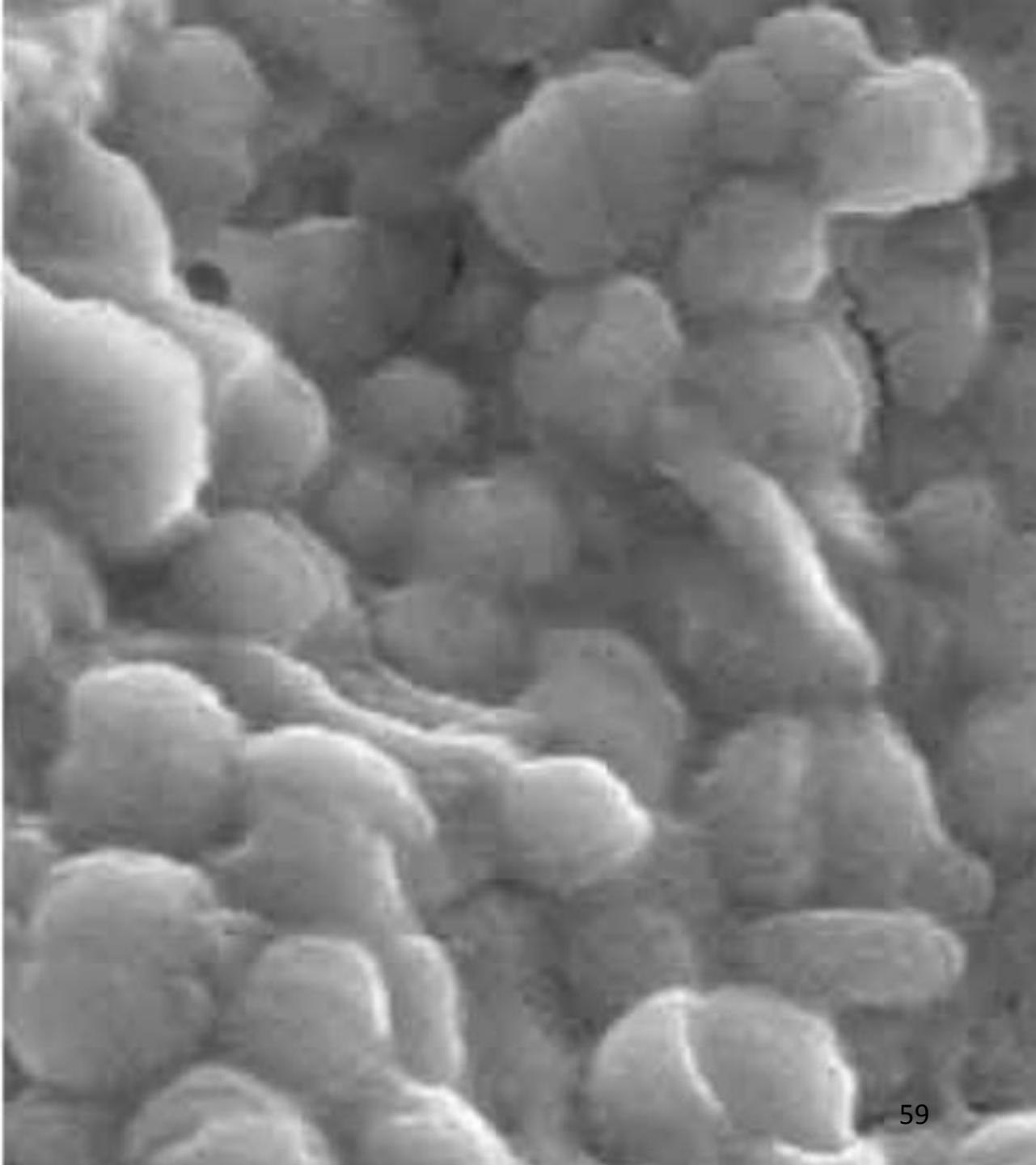
Organic : degradation of biogenic organic matter during fossilisation processes: lipidic biomarkers produced by the thermal and chemical degradation of cellular membranes constituents

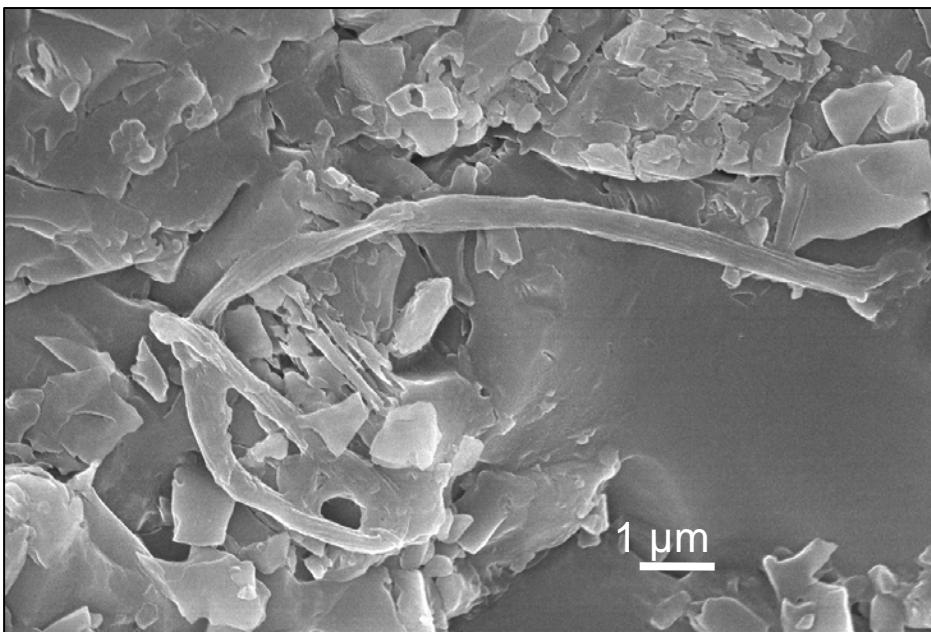
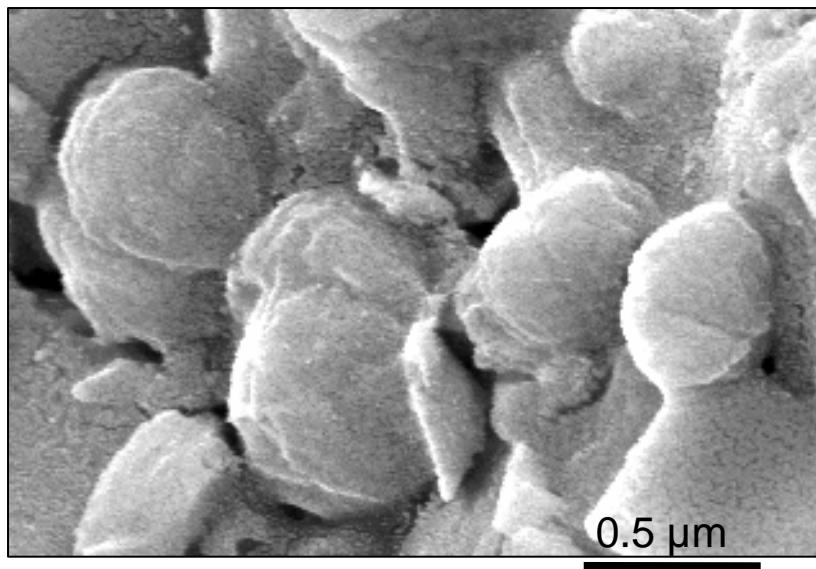
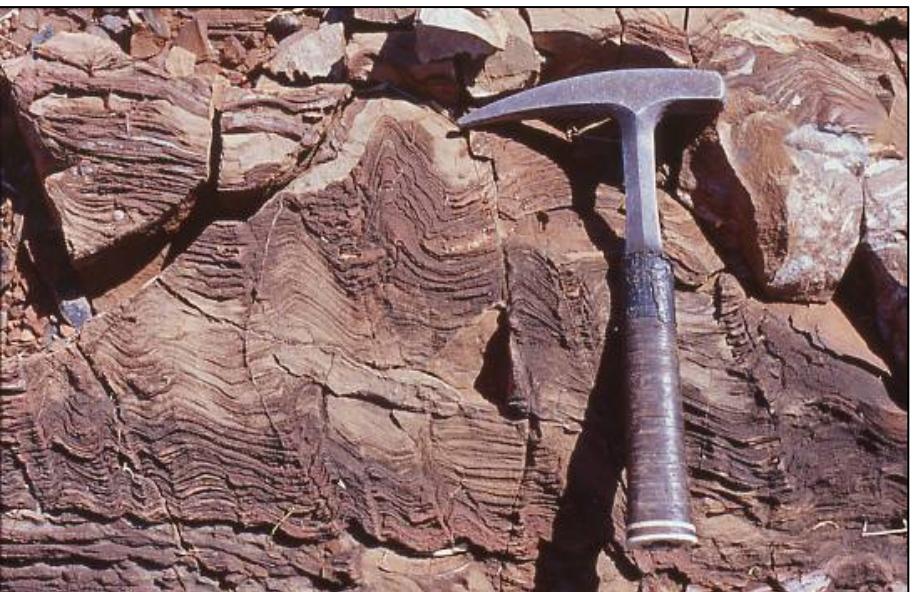
Mineral (inorganic) : Red-Ox biological processes can produce secondary minerals with specific crystallochemical properties (symmetry, stoichiometry, etc): biochemical cycle of iron: blue green iron FeII-FeIII (green rust), bio-magnetite, etc..

Isotopic : enrichment in light isotopes ^{12}C , ^{14}N , ^{32}S

Chiral : important enantiomeric excess (amino acids, etc)

**About 3.5 Ga old
fossil bacteria
from South Africa**



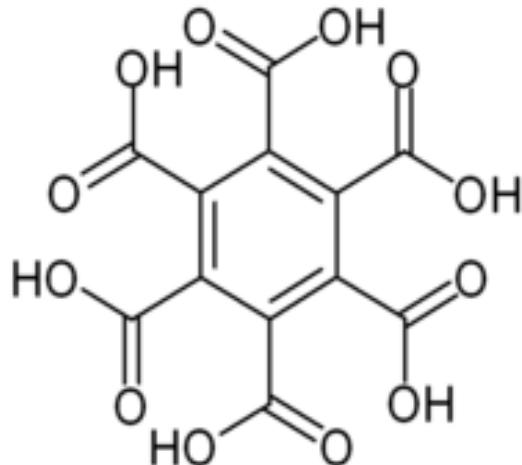


Westall, 2003; Westall et al., 2006

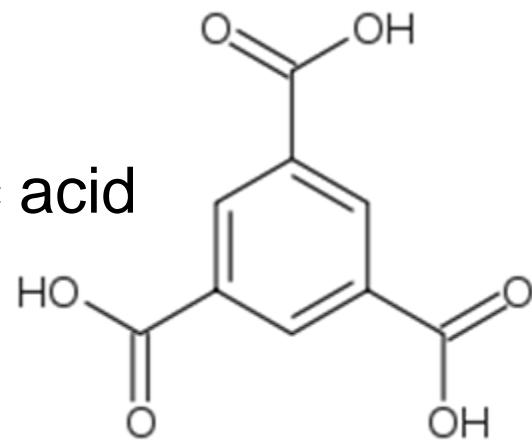
ORGANICS ON MARS ? : é What To Search For ?

- low MW cpds, including C₁-C₄ hydrocarbons, their oxidative products : alcohols, carbonyl compounds, carboxylic acids and peroxy-acids
- cpds of higher thermal stability, e.i. benzoic acid and its derivatives
- higher MW cpds of biological or prebiotic interest : amino-acids, and heterocyclic bases (mainly purine bases, such as adenine)
- macromolecular cpds : peptides, oligopeptides or oligopeptide-like compounds, kerogen or kerogen-like compounds
- chirality : search for enantiomeric excess in the low MW organics, search for tacticity in the macromolecular organics
- detailed isotopic analysis of biogenic elements, specially C, O, N & S
- detailed analysis of the oxidants in the sample : quantitative analysis of H₂O₂, other peroxides, superoxides, other oxidants
- correlation between :
 - * organic and inorganic inventories in the sample
 - * chemical composition and morphology
 - * concentration of the organics and depth
 - * organics and oxidants concentrations

Methane CH₄



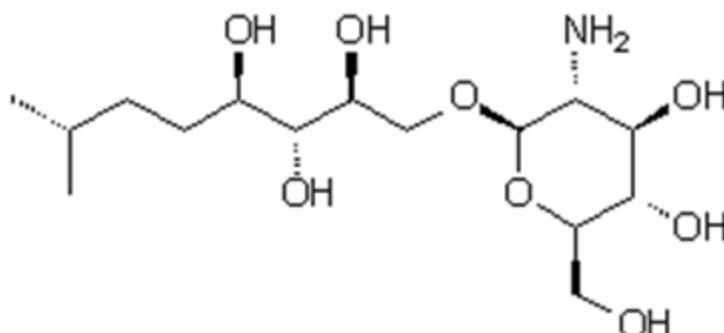
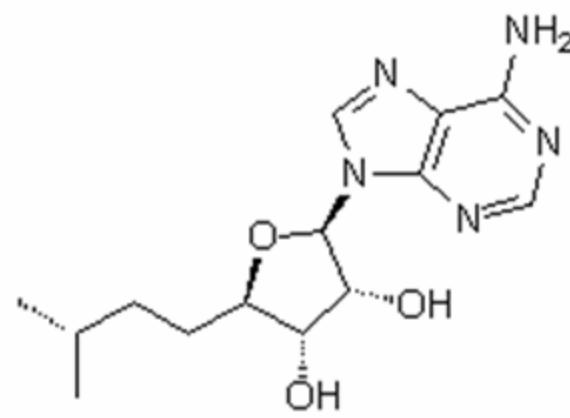
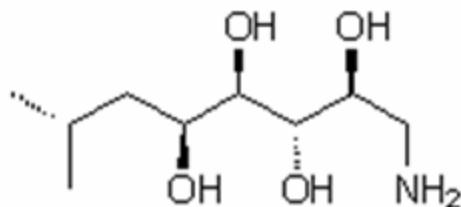
Ethane C₂H₆



Trimesic acid

Mellitic acid

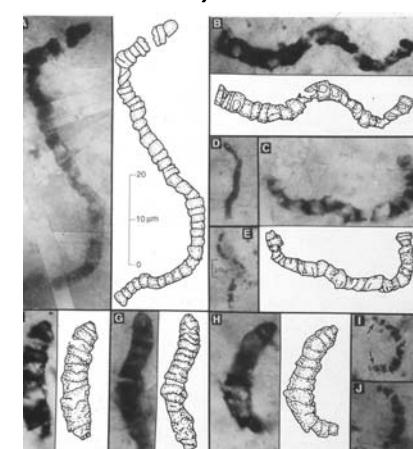
Hopanes



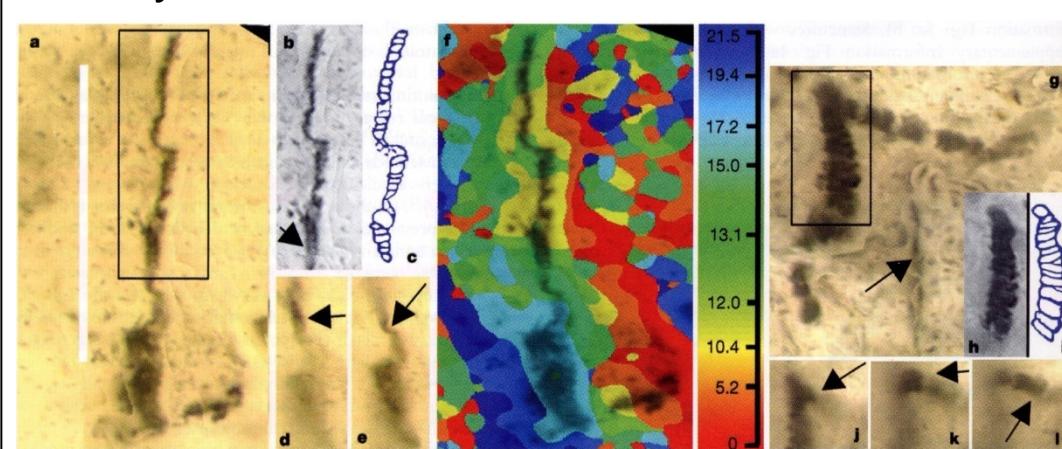
partial structures
of some
complex hopanoids

But there are potential problems:

e.g. Schopf/Brasier controversies on the biogenicity of carbonaceous structures from the 3.465 Gy old Apex Chert (Warrawoona Formation, Western Australia) considered for years as the Earth's oldest fossils



Schopf (1993)



Brasier et al. (2002)

Structures

Fossil cyanobacteria

Hydrothermal artefact

Kerogen

Biogenic

Fischer Topsch artefact

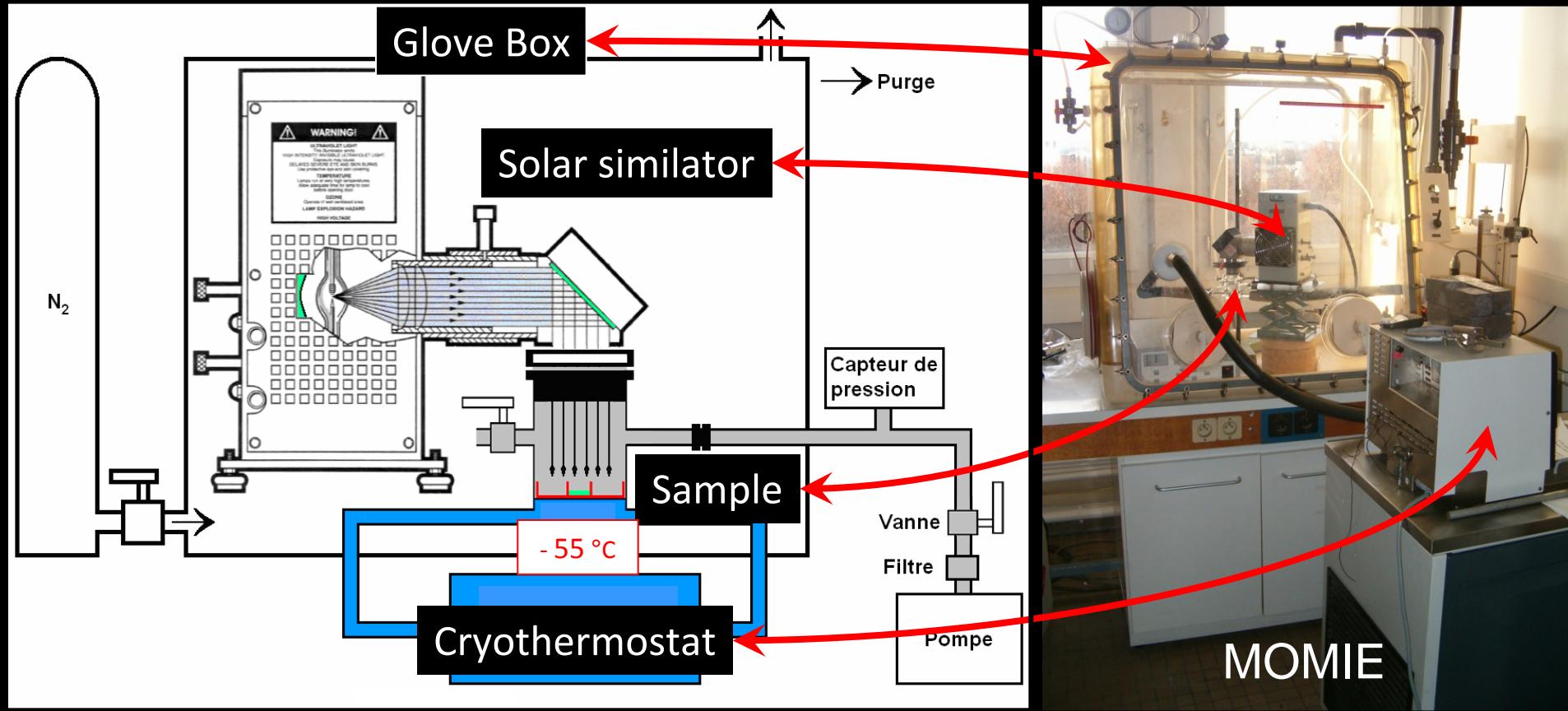
$\delta^{13}\text{C}$

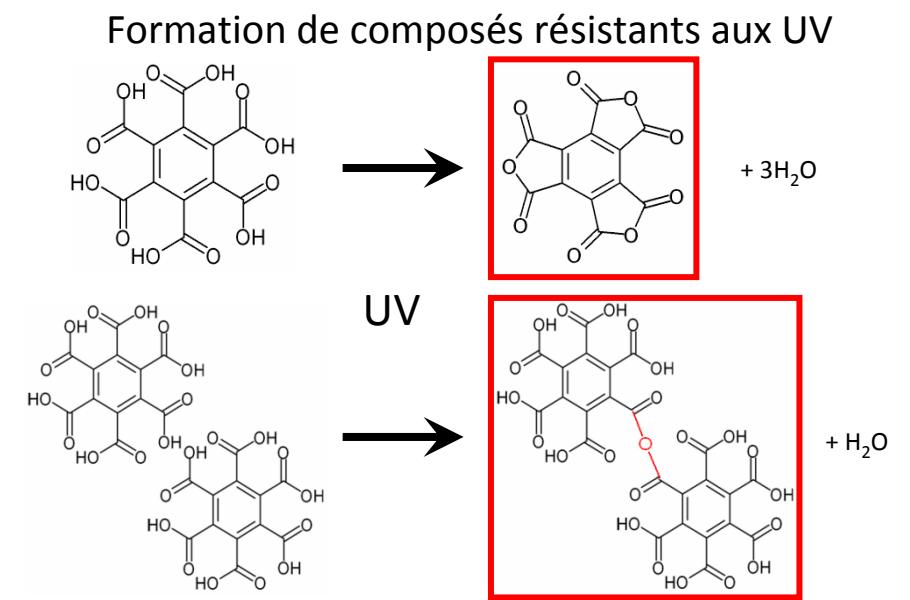
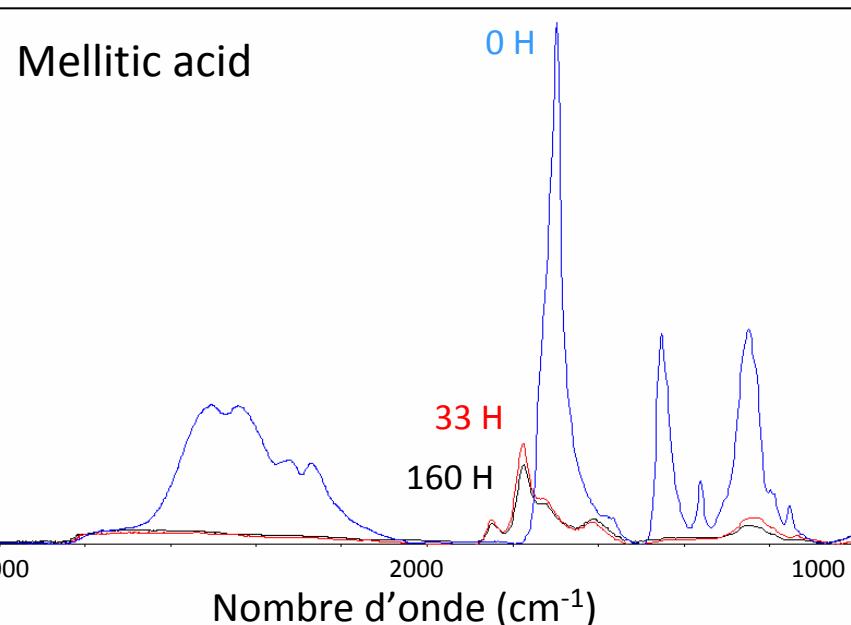
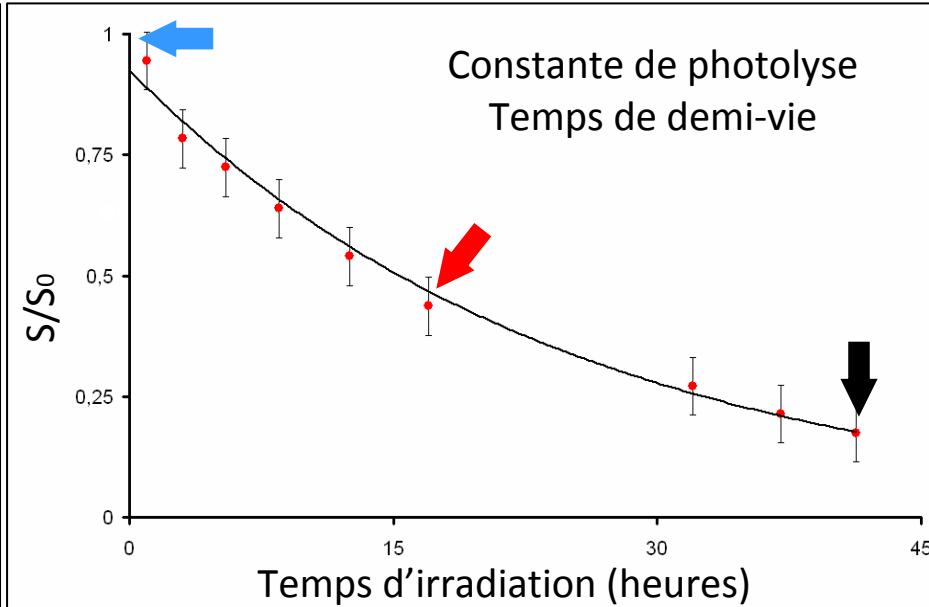
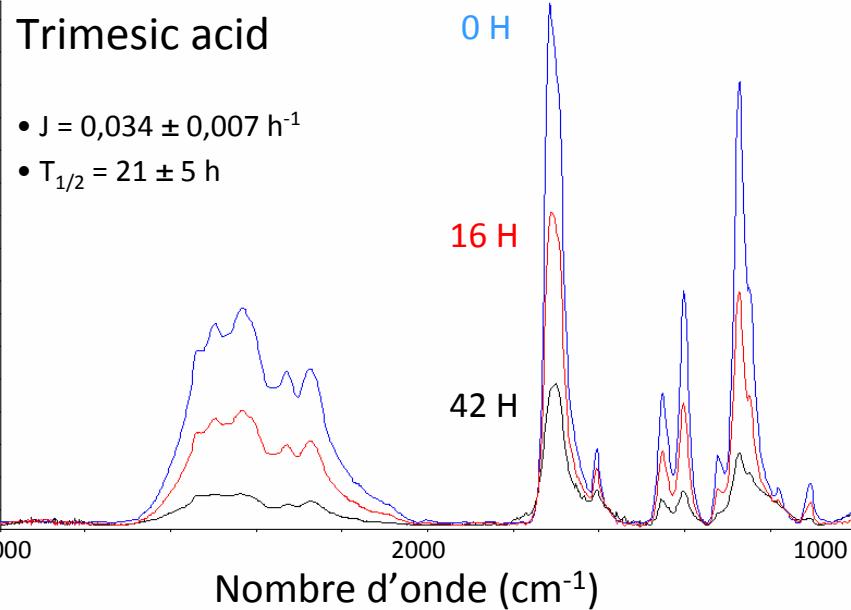
-14 to -42‰
biogenic

-16 to -26‰
Fischer Topsch
(N. Grassineau (co-author) – biogenic)

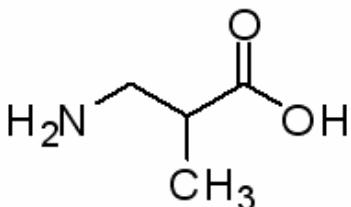
MOMIE : Martian Organic Molecules Irradiation and Evolution

- Inventory of the organics which may be present on Mars
- Study of their evolution under UV irradiation (solar simulator)
- Study of their evolution in the presence of oxidant (H_2O_2)





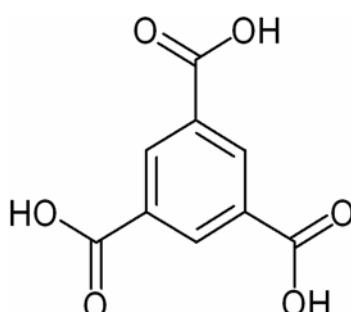
AIB



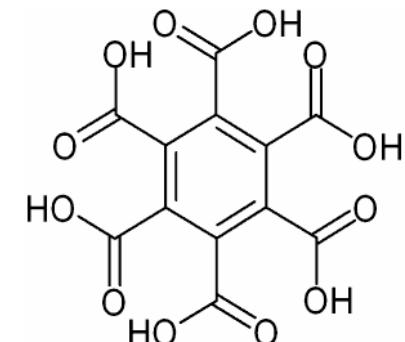
Phtalic Acid



Trimesic Acid



Mellitic Acid

**Molecule****J(s-1)****Rel uncert.****Half Life at 1 AU (d)****Half Life at Mars (d)**

AIB*	6,6E-07	26%	12	35
phtalic acid	7,5E-07	24%	11	31
trimesic acid	1,9E-06	21%	4	12
mellitic acid	4,5E-06	23%	2	5
AIB + MSA**	1,0E-06	44%	8	22
phtalic acid + MSA	1,2E-06	12%	7	20
trimesic acid + MSA	No Data		No Data	No Data
mellitic acid + MSA	No Data		No Data	No Data

* AIB = α -aminoisobutyric acid

** MSA = Martian Soil Analog (JSC Mars 1 - Allen et al., 1998)

No protection effect due to the presence of martian soil analogue
J increases !

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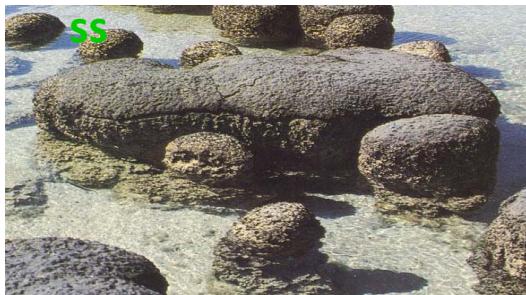
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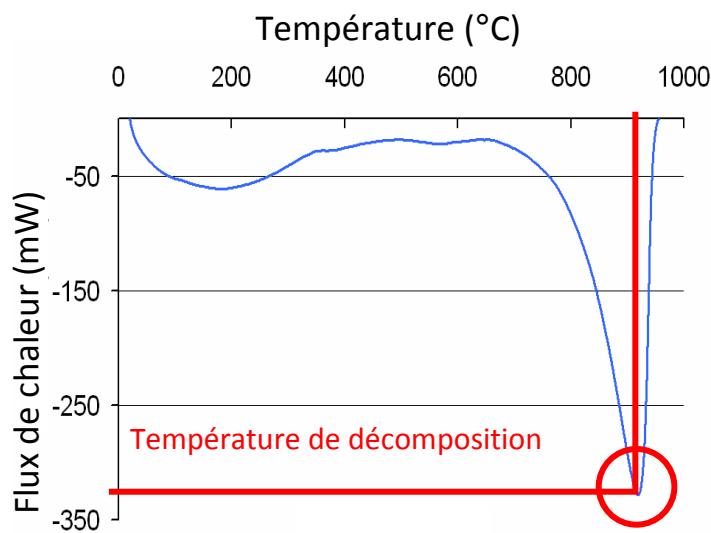
Characterisation of specific thermal degradation of biominerals

Biocarbonate

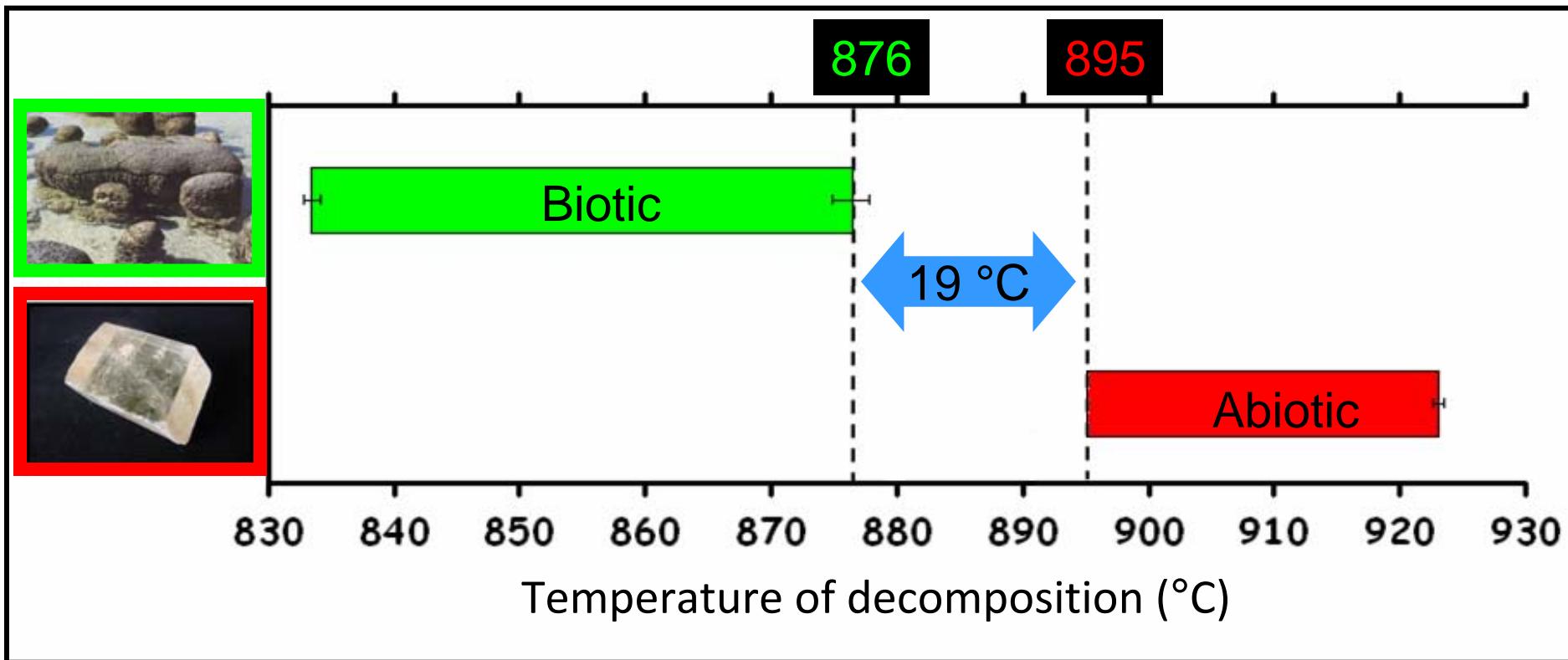


DTA-TG
Differential thermal analysis -
thermogravimetry

Abiotic Carbonates



From 70 studied samples: clear separation between biotic and abiotic origin of carbonates



SEARCH FOR ORGANICS

in situ

- GC-MS coupled to Pyrolysis + chemical derivatization with multi GC columns including chiral separation (expected sensitivity : ppb)
- MS coupled to Laser Ablation-Inductive Coupled Plasma-(LA-ICP-MS) for determination of organic and inorganic phases
- Capillary electrophoresis, HPLC and/or supercritical chromatography for direct analysis of high MW organics and/or fluid extraction

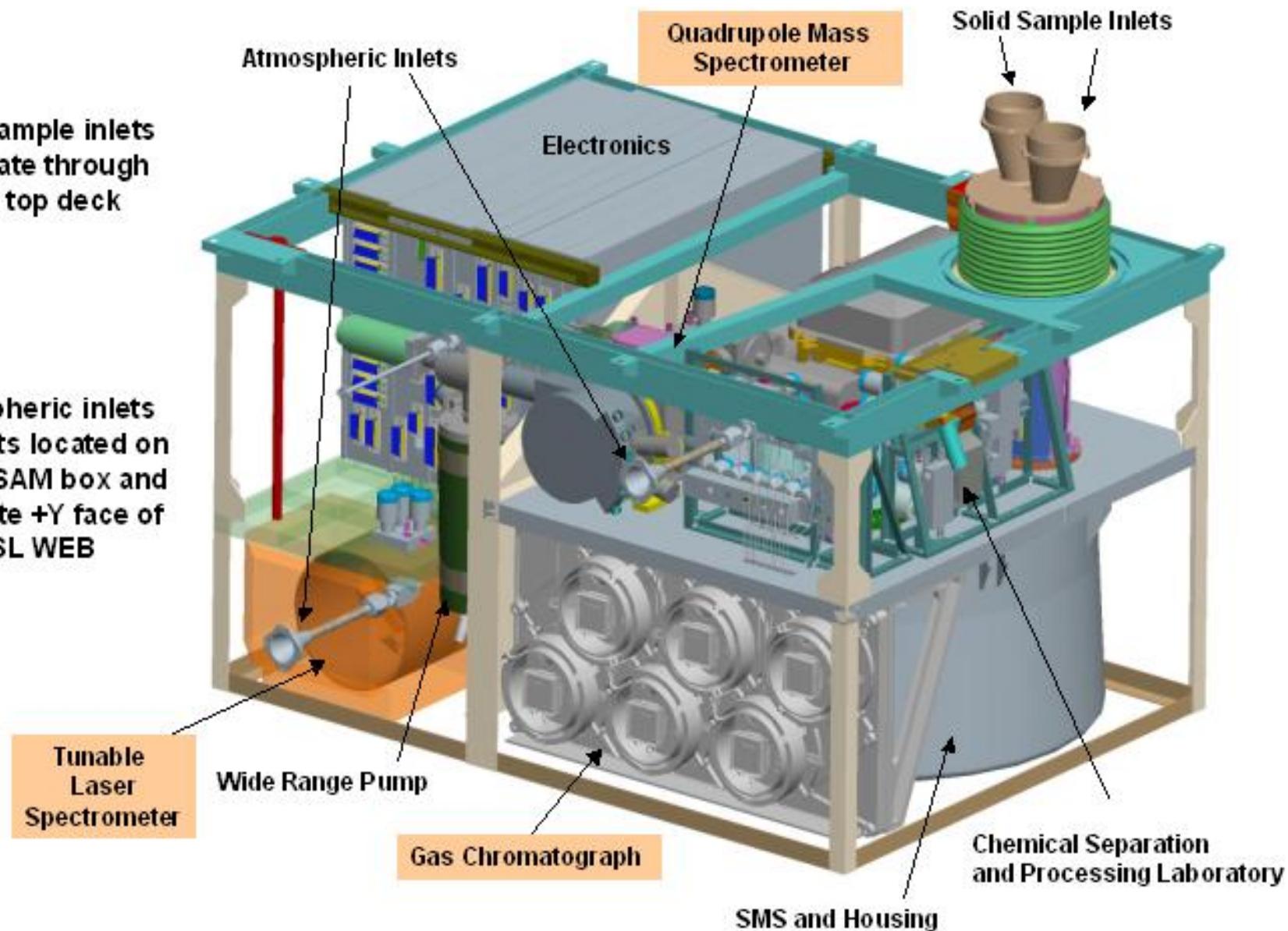
Returned samples

- Same techniques + a variety of analytical techniques available or under development several laboratories :
- High resol. MS
- Capillary electrophoresis / Laser induced fluorescence (CE-LIF)
- Enzyme Linked Immuno Sorbent Assays (ELISA)

THE SAM EXPERIMENT OF THE MSL'11 MISSION

Solid sample inlets
penetrate through
MSL top deck

Atmospheric inlets
and vents located on
side of SAM box and
penetrate +Y face of
MSL WEB

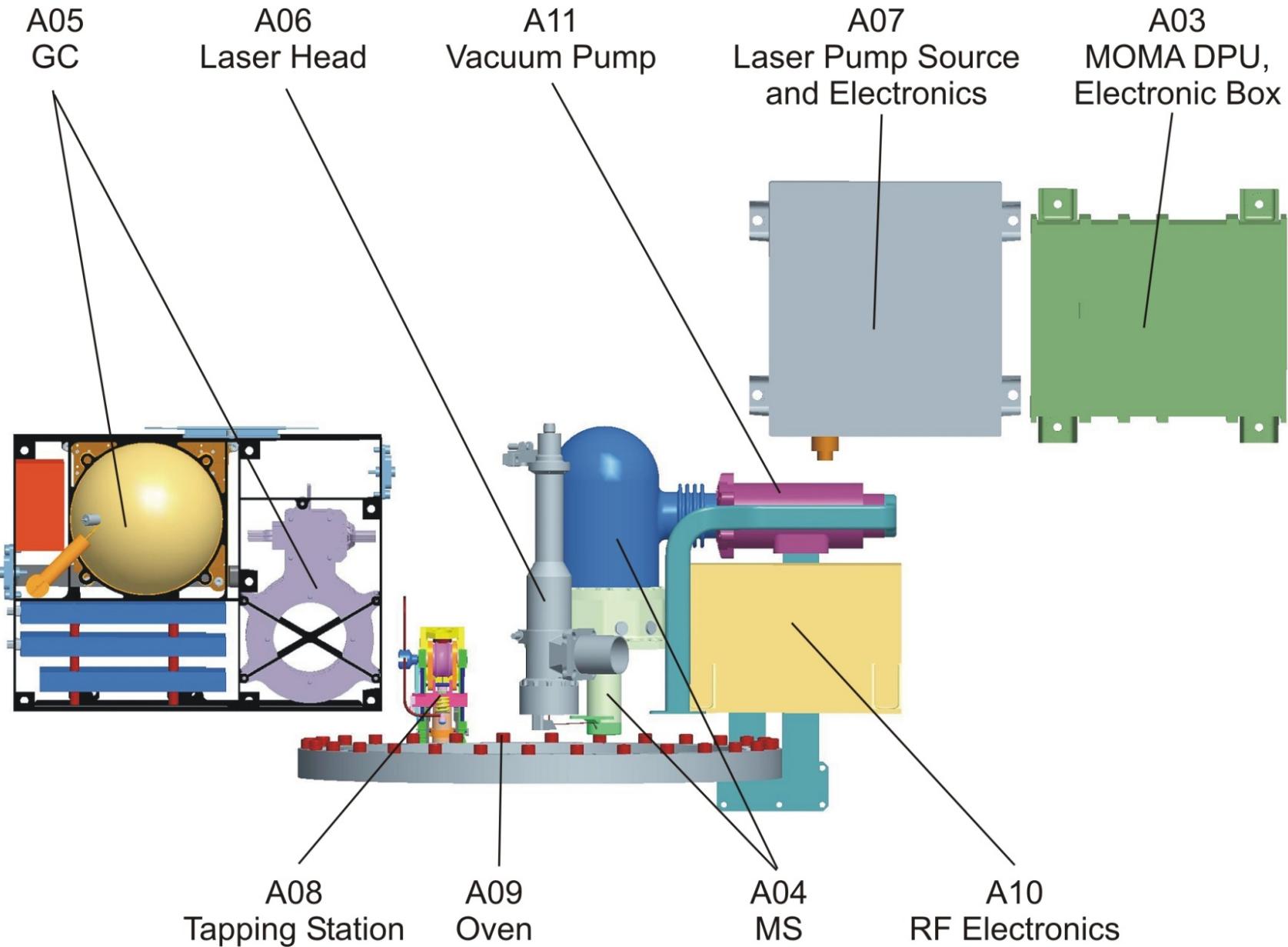


- **Optical Colour Microscope (low & high resolution)**
 - Detection of microorganisms, fossil structures & mineralogical studies.
 - Resolution: 0.1 mm down to 1 mm.
- **Combined Laser Plasma and Raman Spectrometers**
 - Provide complementary information, useful for the identification of organics and of the environment where the sample is obtained.
 - Raman spectrometer => non-polar ($-\text{C}-\text{C}-$ and $-\text{C}=\text{C}-$) molecular bonds.
 - LPS characterises the atomic composition of the sample.
- **Life Marker Chip**
 - New technology instrument based on antibodies and organic molecules attached to well-known locations on a chip matrix.
 - A solution with Mars soil and a chromophore substance is washed over the chip.
 - The chip is illuminated, and chip spots fluoresce where a match exists.

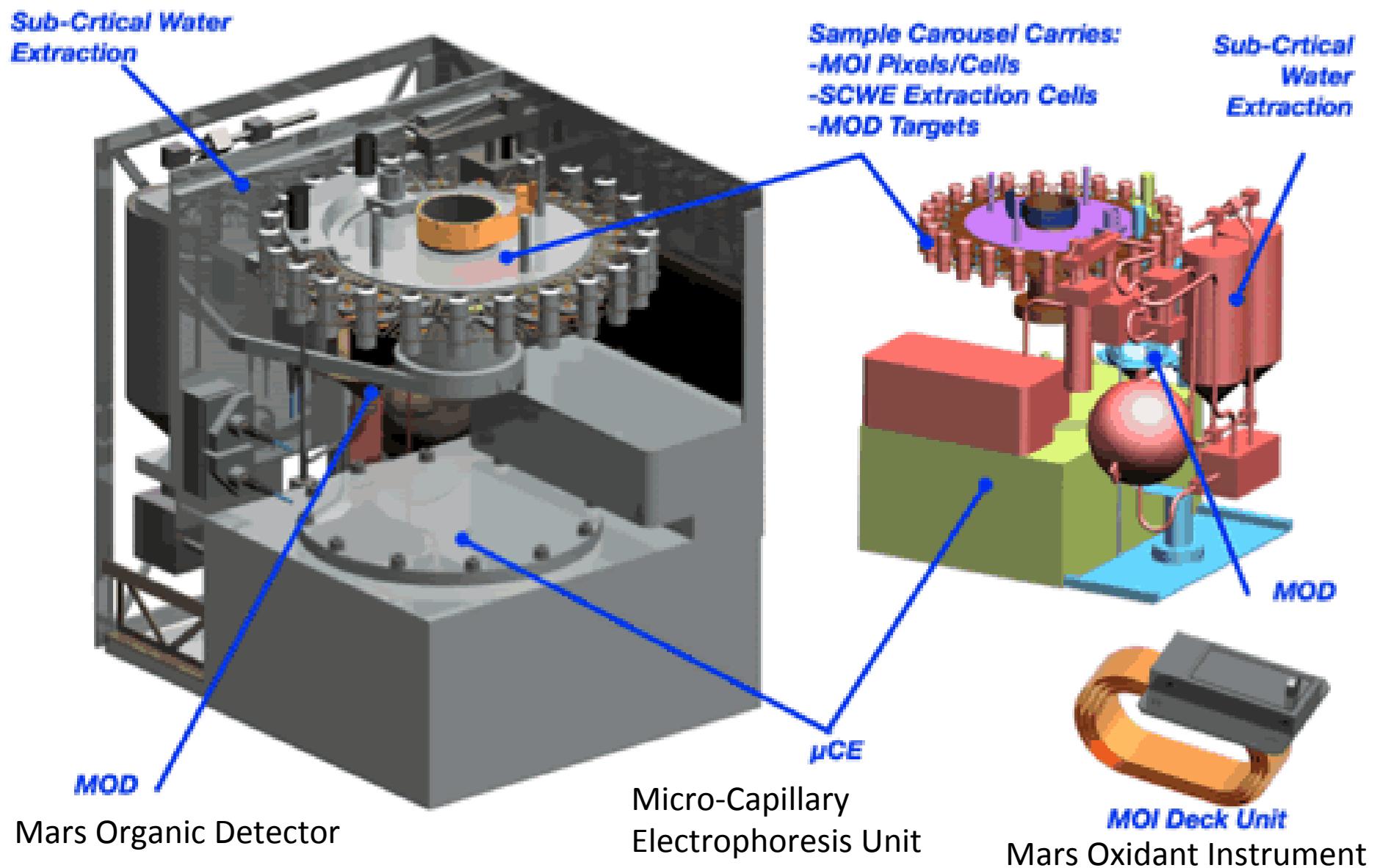
- **Oxi/Pyr-GCMS**

- Oxidant detection
- Gas Chromatography
- Mass Spectroscopy
- Chirality Measurements
- For determining the isotopic, elemental, organic and inorganic molecular compositions, and chirality.

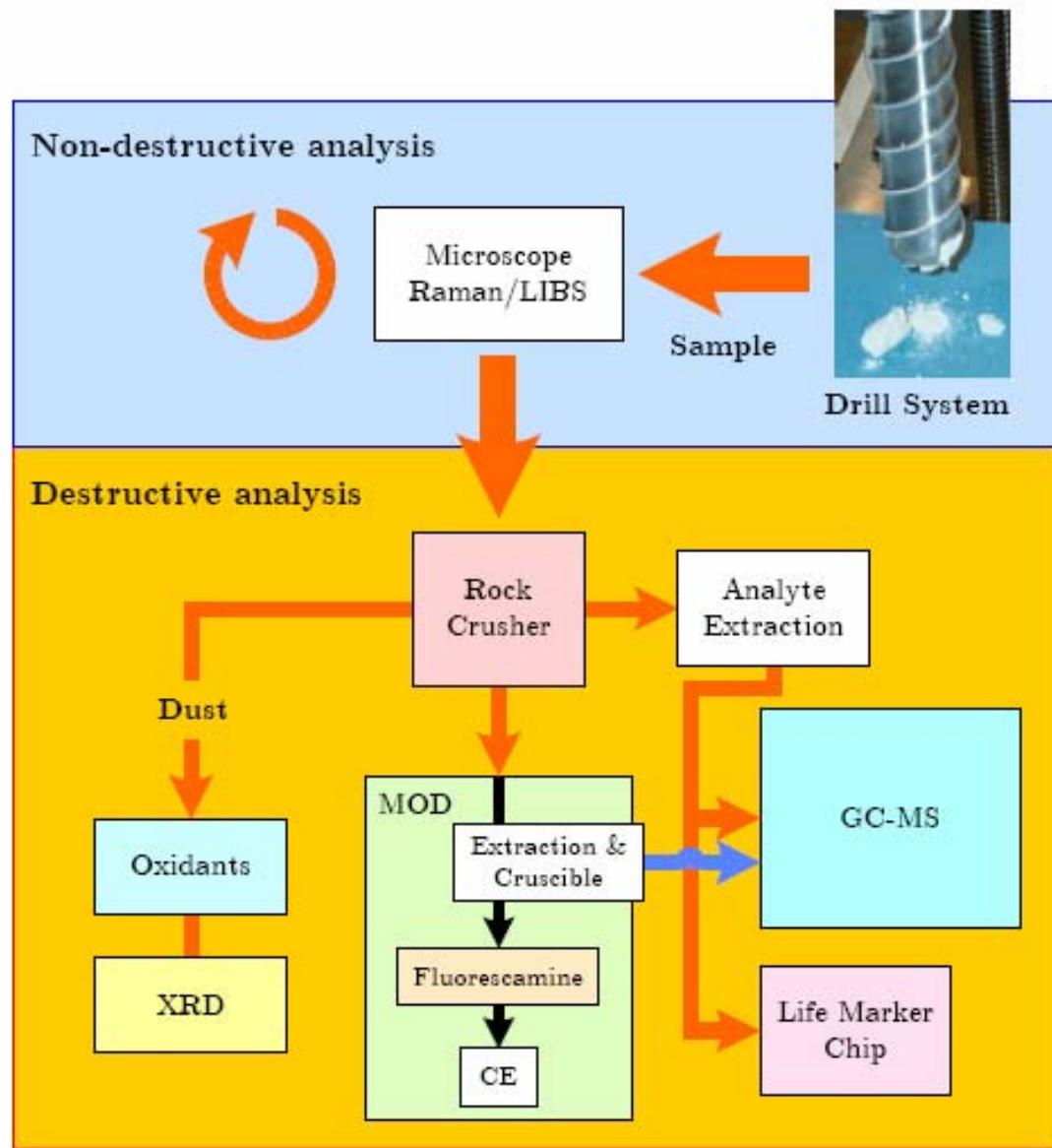
MOMA – Mars Organic Matter Analyzer



UREY Experiment



PASTEUR & EXOMARS



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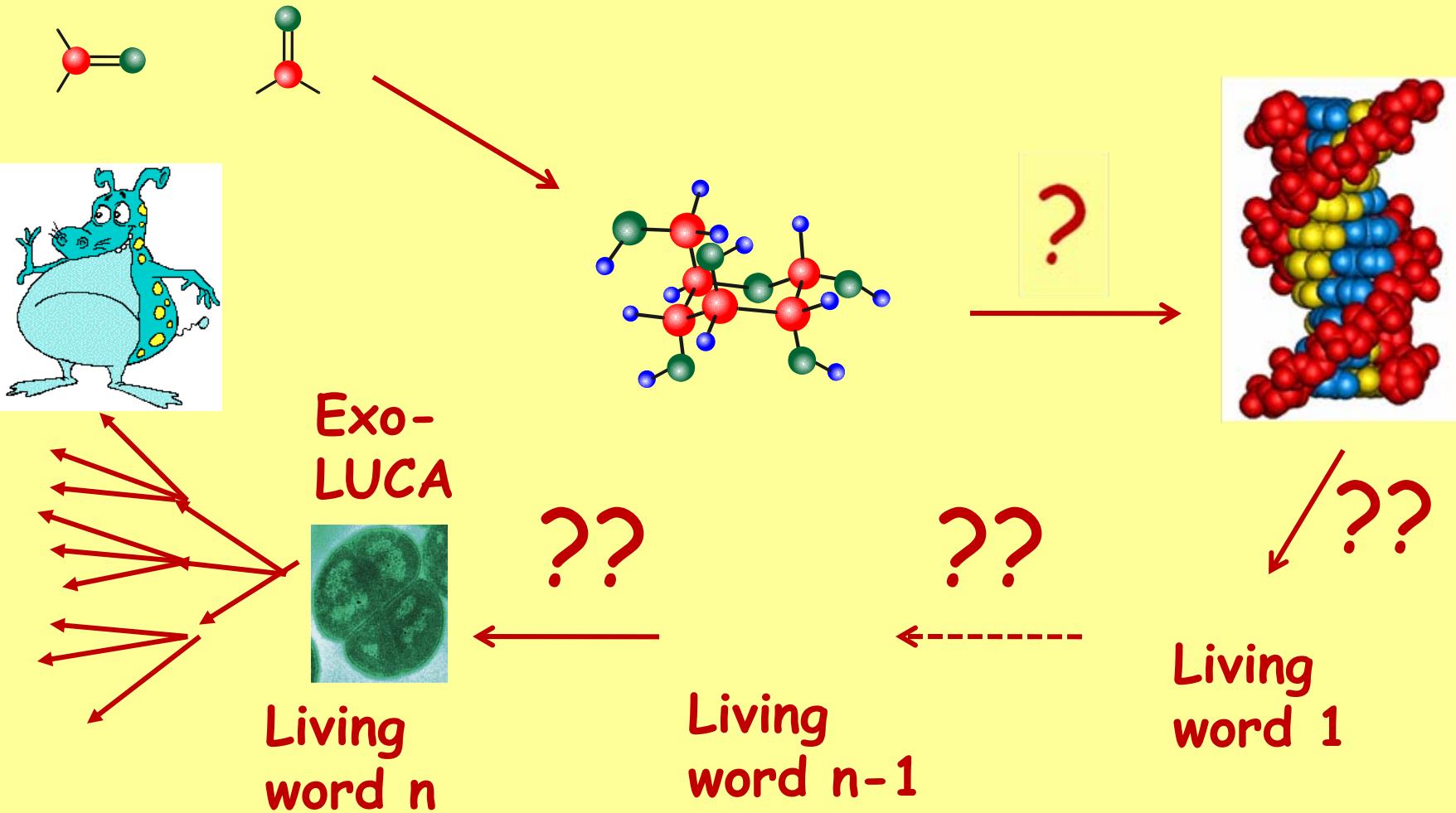
How to search for?

The PP aspects and future prospects

COSPAR recommendation on Planetary Protection

Category	1	2	3	4	5
Prevention of		Forward	contamination		Back
Biological interest	No	Significant	Significant	Significant	
Probability of contamination	Any	Remote	Significant	Significant	Unknown
Type of mission	Any	Any	Orbiter / Fly-by	Lander	Earth Return
	Mercury Venus Moon Sun Asteroids (except C)	Jupiter Saturn Uranus Neptune Pluto Comets C-asteroids	Mars Europa	Mars Europa	Earth-Moon System
Range of requirements					↗

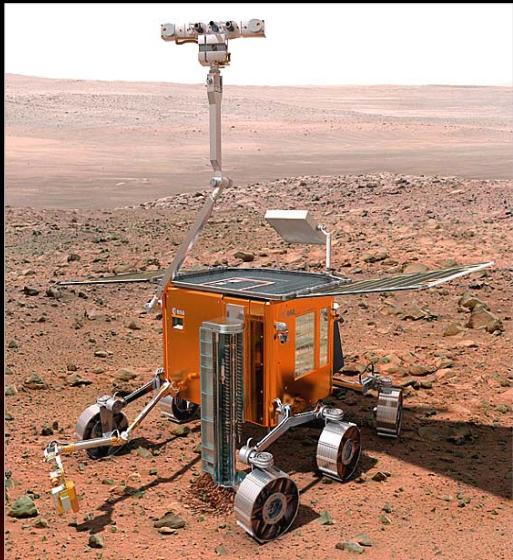
Carbonaceous matter + liquid water + Energy



Exobiology and Mars

With my exobiological thanks for your attention

Mars Robotic Exploration Programme



→ ExoMars 2016

MREP



→ 2018

→ 2020

→ ...

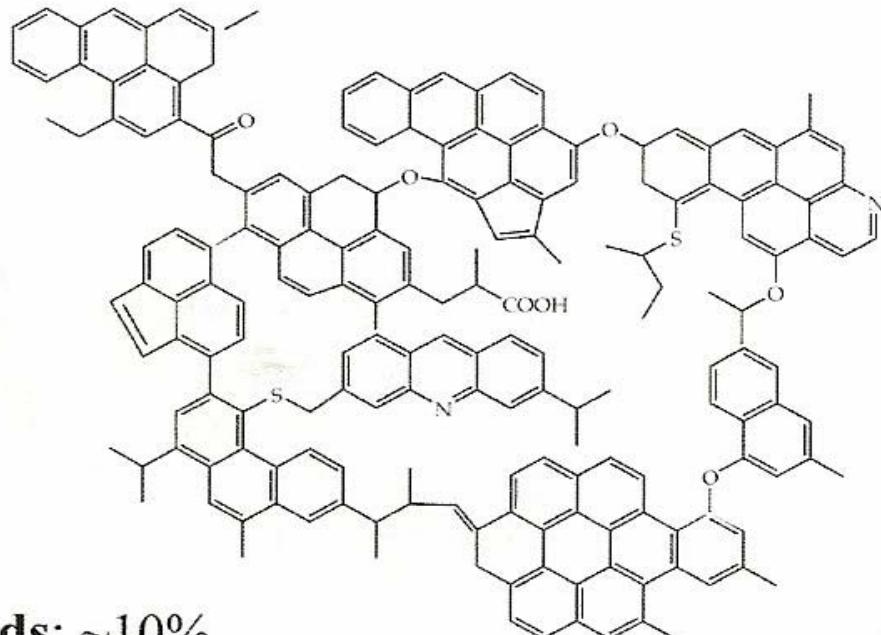
→ Mars Sample Return



The insoluble organic matter

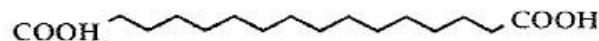
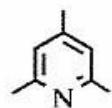
Elemental composition: $C_{100}H_{71}N_3O_{12}S_2$

Macromolecular material: ~80%



Structurally differentiated: ~10%
e.g., nano globules and tubes

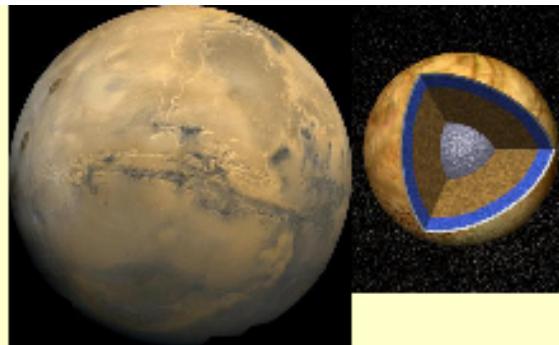
Hydrothermally freeable compounds: ~10%
e.g. C₃-C₁₇ dicarboxylic acids and methylated pyridines



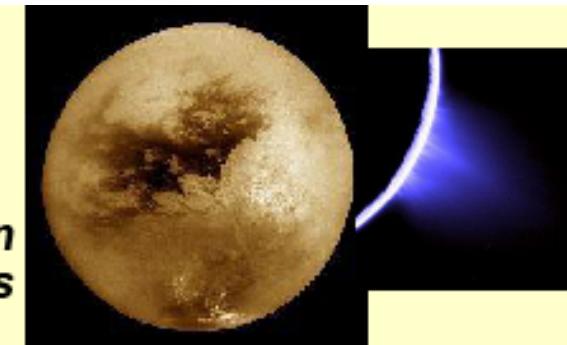
Exotic carbon from interstellar grains: ppm
e.g., diamond, graphite, and fullerenes; SiC; Si₃N₄

From Pizzarello, in *Prebiotic Evolution and Astrobiology*, Wong & Lazcano Eds, Landes Biosciences, pp. 46 (2009)

Interstellar Molecules



Mars
Europa



Titan
Enceladus

Comets



SOURCES:
Comets, dust
meteorites



Meteorites



bombardment

-4,55 Ga

Isua

-3,8 Ga

Primitive Earth

CONDITIONS:
Chemical,
Environmental

RESISTANCE
to extreme conditions
T, P, pH, radiations...
Oceans, antarctic,
space



Exoplanets
 O_2-O_3 signal

Toward homochirality

Organics
Liquid H₂O
D/H

Auto-replication
Mutation
Pre-RNA world

RNA
World

Primitive
Cell
DNA world
LUCA



stromatolites

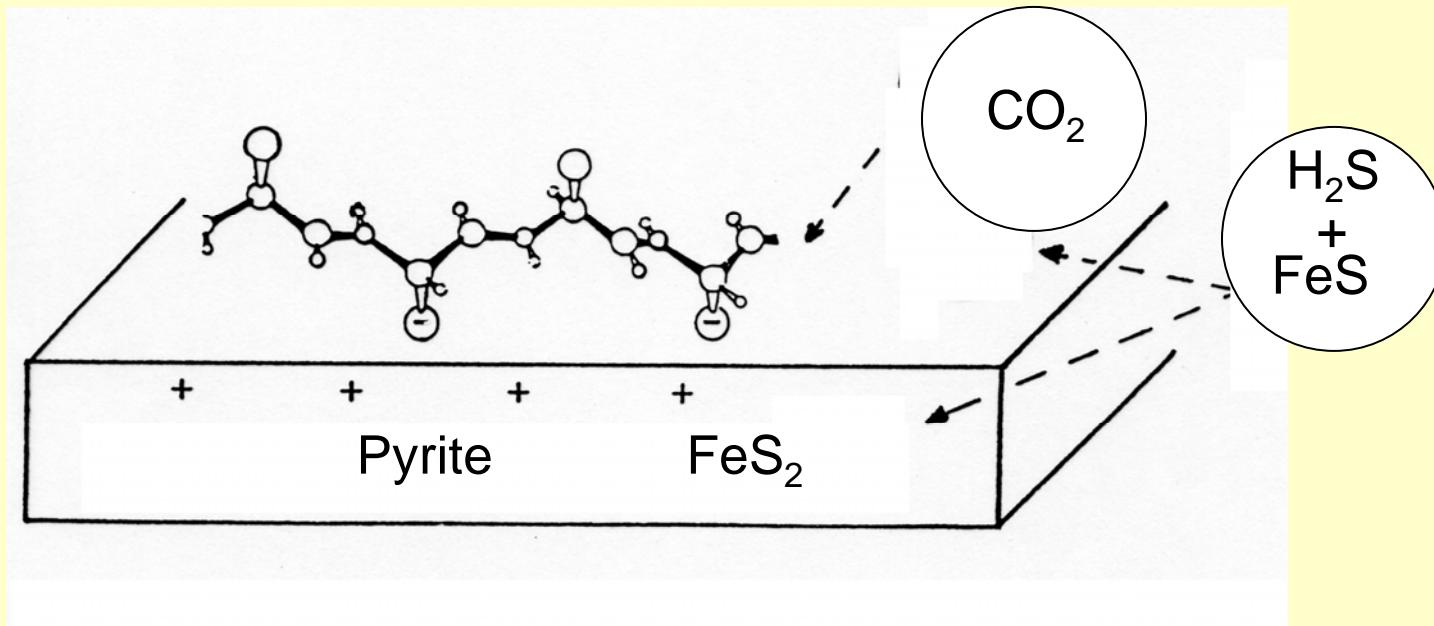
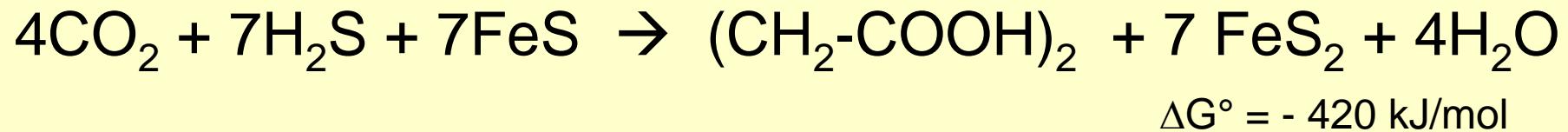
-3,5 Ga



An Iron-Sulfur world?

Mineral surface based reaction system

Chemoautotrophic mechanism « pyrite-pull reaction »



Carbonaceous matter + liquid water + Energy

