The emergence of life on Earth: recent advances, old problems

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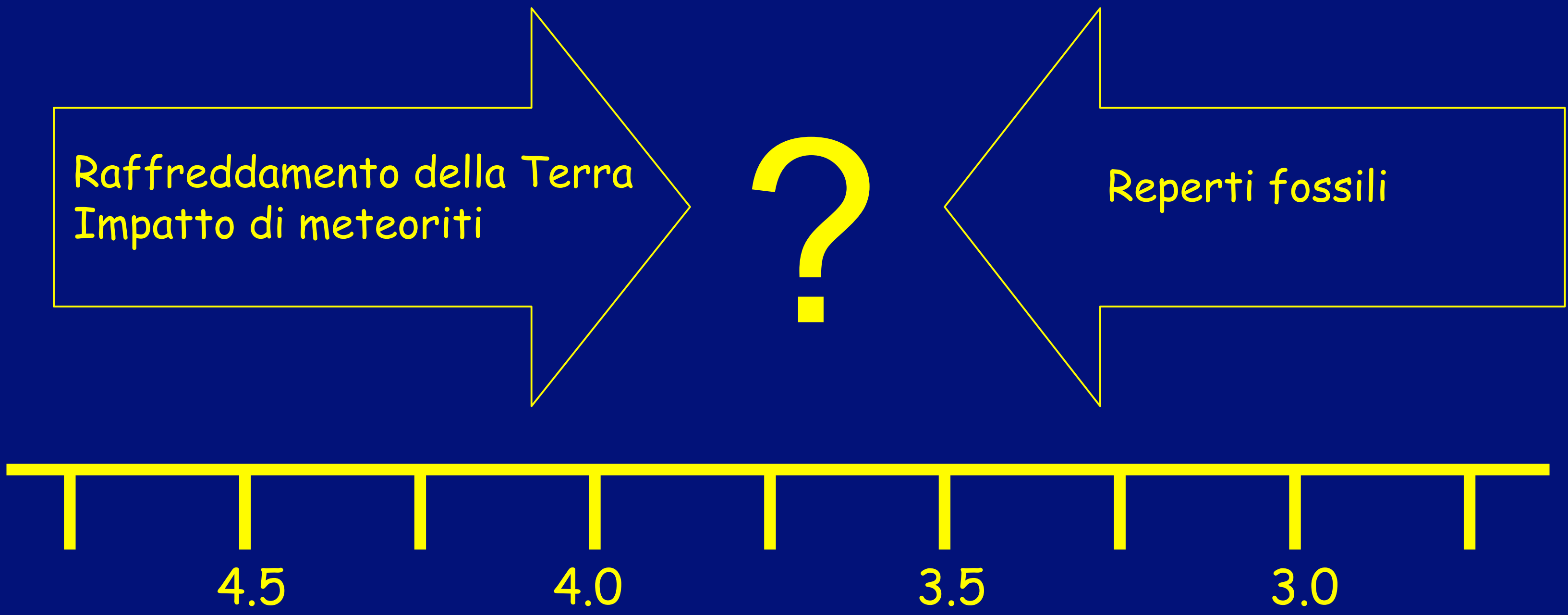
Bologna 2007

La scala temporale dell'origine della vita sulla terra



Età della Terra (miliardi di anni fa)

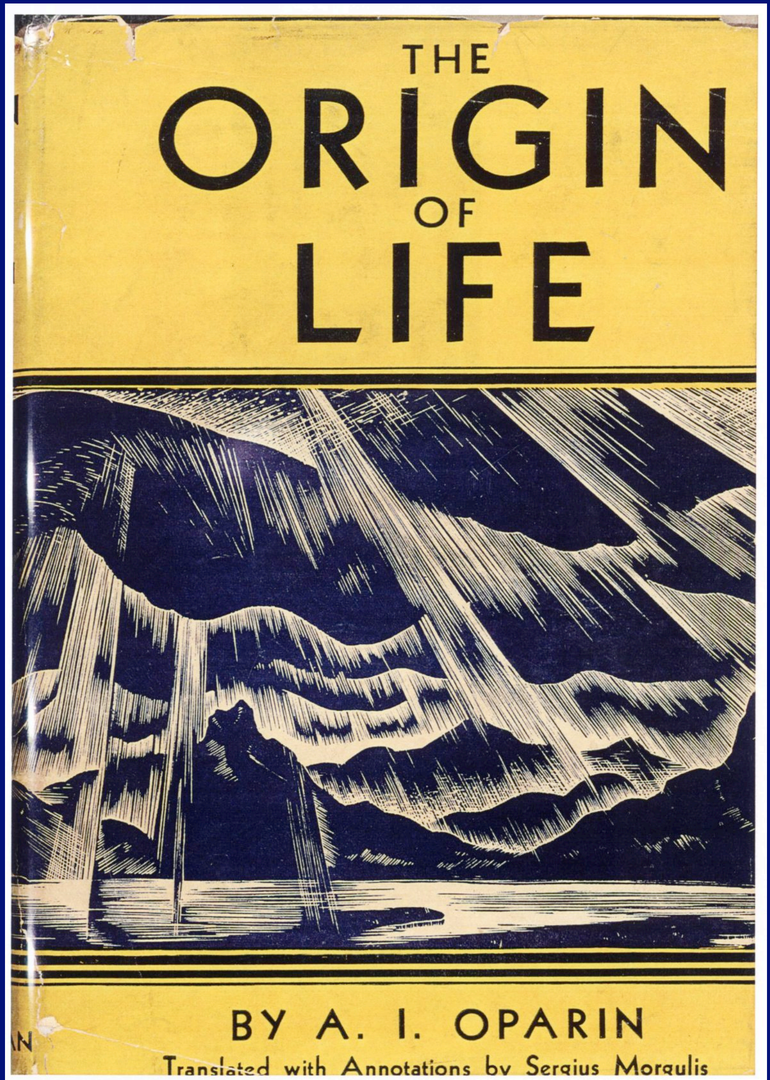
The origin of life was

a) autotrophic — capable of synthesizing its own components from CO_2

b) heterotrophic — formed from a primitive soup

c) extraterrestrial — came from outer space (panspermia)

Un'origine eterotrofa della vita?



atmosfera riducente

↓

sintesi di composti organici

↓

zuppa primordiale

↓

eterotrofi primordiale

Some interstellar molecules

H_2, OH, SiS, HCl, NaCl, KCl, CH, CH^+, CN, CO, CS, C_2

H_2O, H_2S, N_2H^+, SO_2, HCO^+, HCN, C_2H, C_3, C_2O, COS

NH_3, H_2CO, HNCO, H_2CS, C_2H_2

SiH_4, HC_3N, H_2CN, CH_4, C_5, $H_2C{=}C{=}O$, HCOOH, HNCO

CH_3OH, CH_3CCN, $HCONH_2$

CH_3COH, CH_3C_2H, CH_3NH_2, H_2CCHCN, HC_5N

$HCOOCH_3$, CH_3CH_2, $(CH_3)\ _2O$, HCN_7N

HC_9N, $HC_{11}N$

Laepis ex caelis: il meteorite di Murchison, antico di 4.6 miliardi di anni

Australia, 28 settembre, 1969

Composti presenti nel meteorite di Murchison

Idrocarburi aromatici
Idrocarburi alifatici
Acidi solfonici
Acidi fosfonici

Acidi monocarbossilici (C_1-C_8)
Acidi dicarbossilici (C_2-C_5)
Amine (C_1-C_4)

Piridine
Chinoline
Polipirroli

Alcoli (C_1-C_4)
Aldeidi (C_2-C_4)
Polioli (C_2-C_4)

Chetoni (C_3-C_5)
Idrossiacidi (C_2-C_9)
Aminoacidi

Urea
Purine
Pirimidine

L' atmosfera prebiotica di Urey

$C + 2H_2 \rightarrow CH_4$

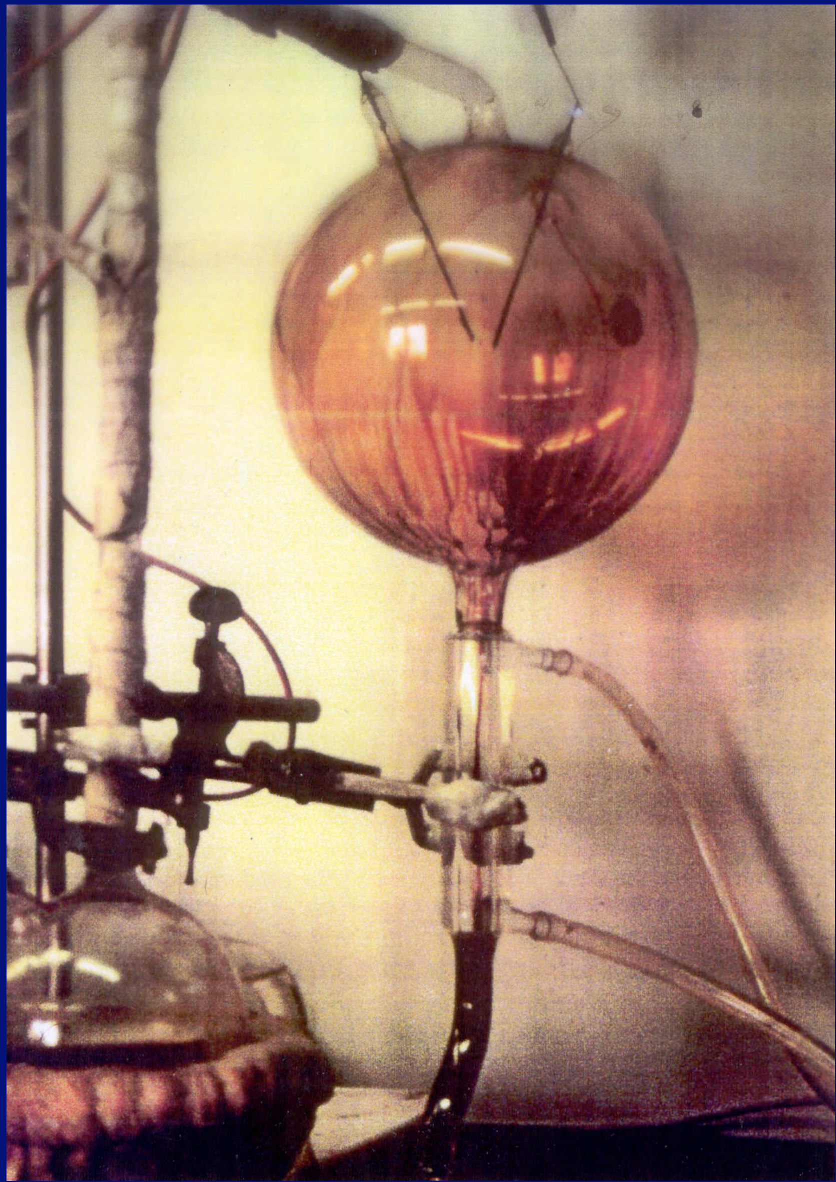
$N_2 + 3H_2 \rightarrow NH_3$

$O_2 + 2H_2 \rightarrow H_2O$

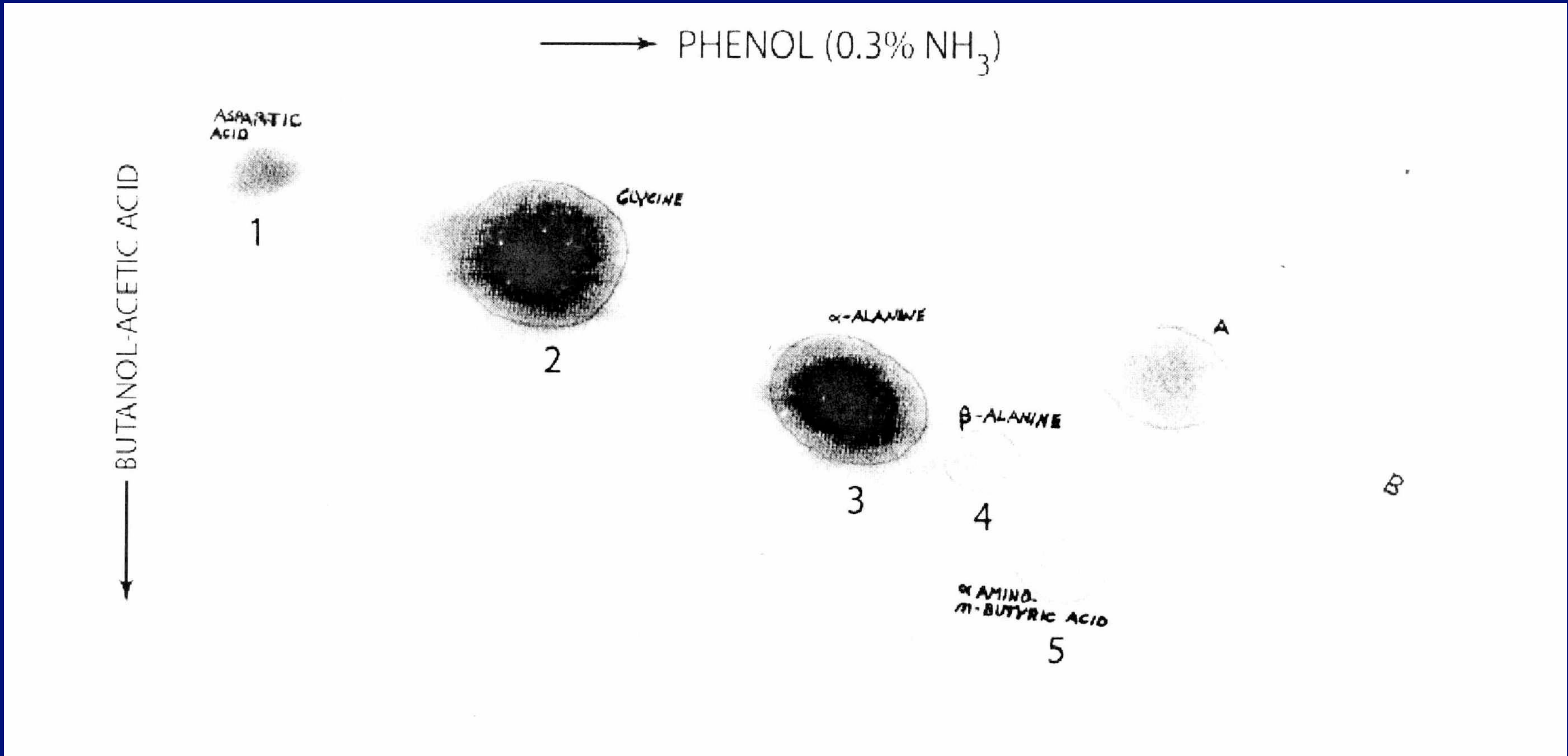
$S + H_2 \rightarrow H_2S$

$CO_2 + 6H_2 \rightarrow CH_4 + 2H_2O$

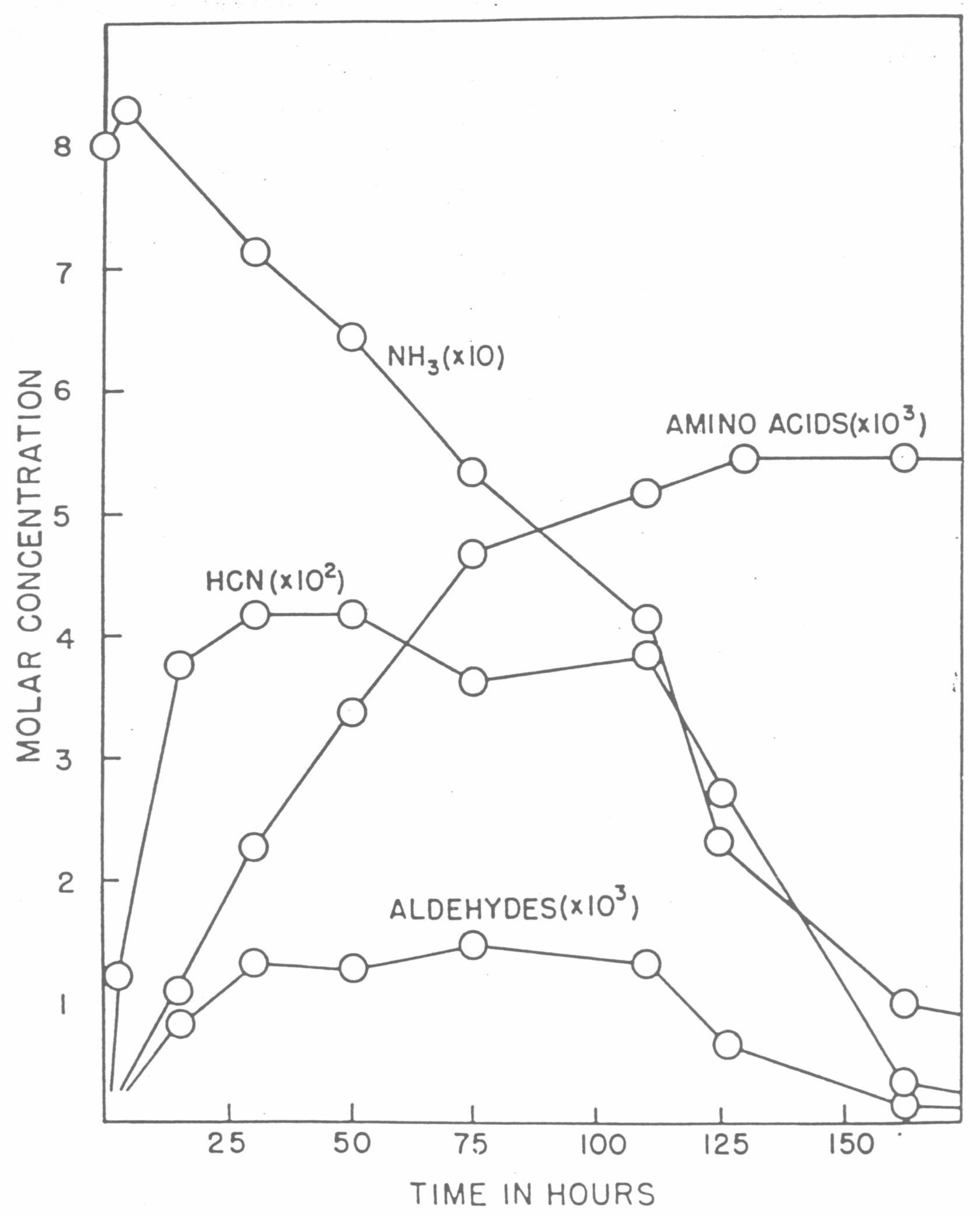
L'esperimento di Miller nel 1953



Sintesi prebiotiche di aminoacidi



Miller, 1953



NH3(x10)
AMINO ACIDS(x10^3)
HCN(x10^2)
ALDEHYDES(x10^3)
MOLAR CONCENTRATION
TIME IN HOURS
1
2
3
4
5
6
7
8
25
50
75
100
125
150

$$RCHO + NH_3 + HCN \underset{}{\overset{K}{\rightleftharpoons}} RCH(NH_2)CN + H_2O$$

$$RCH(NH_2)CN + 2H_2O \xrightarrow{k} RCH(NH_2)COOH + NH_3$$

$$RCHO + HCN \overset{H}{\rightleftharpoons} RCH(OH)CN$$

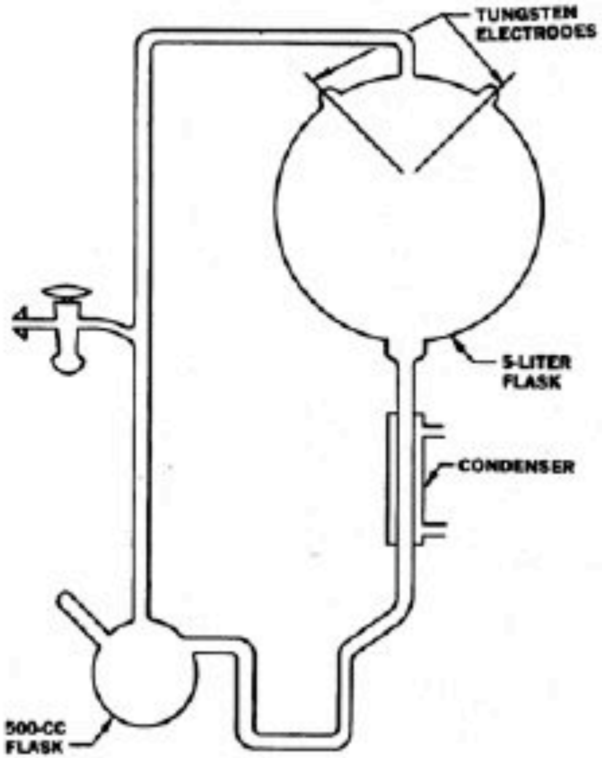
$$RCH(OH)CN + 2H_2O \xrightarrow{h} RCH(OH)COOH + NH_3$$

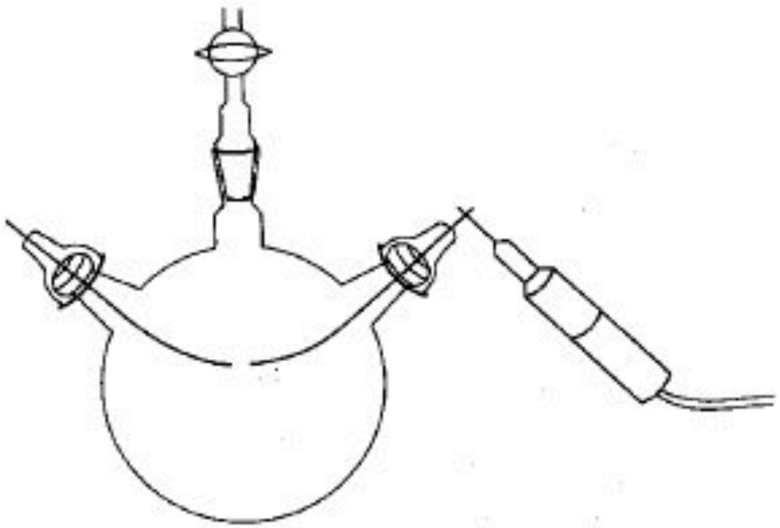
Types of planetary atmospheres

Reducing: CH_4, NH_3, N_2, H_2O, H_2
CO_2, N_2, H_2O, H_2
CO_2, H_2, H_2O

Neutral: CO_2, N_2, H_2O

Oxidizing: CO_2, N_2, H_2O, O_2

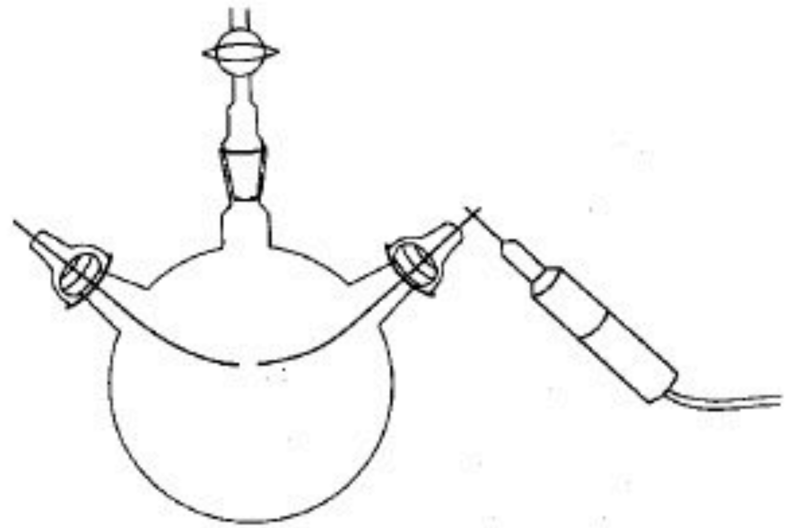

TUNGSTEN ELECTRODES
5-LITER FLASK
CONDENSER
500-CC FLASK



Prebiotic organic synthesis in neutral planetary atmospheres

Experimental conditions:

100 mL water
100 mm CO_2/100 mm N_2
48 hrs, 23 °C



Products:

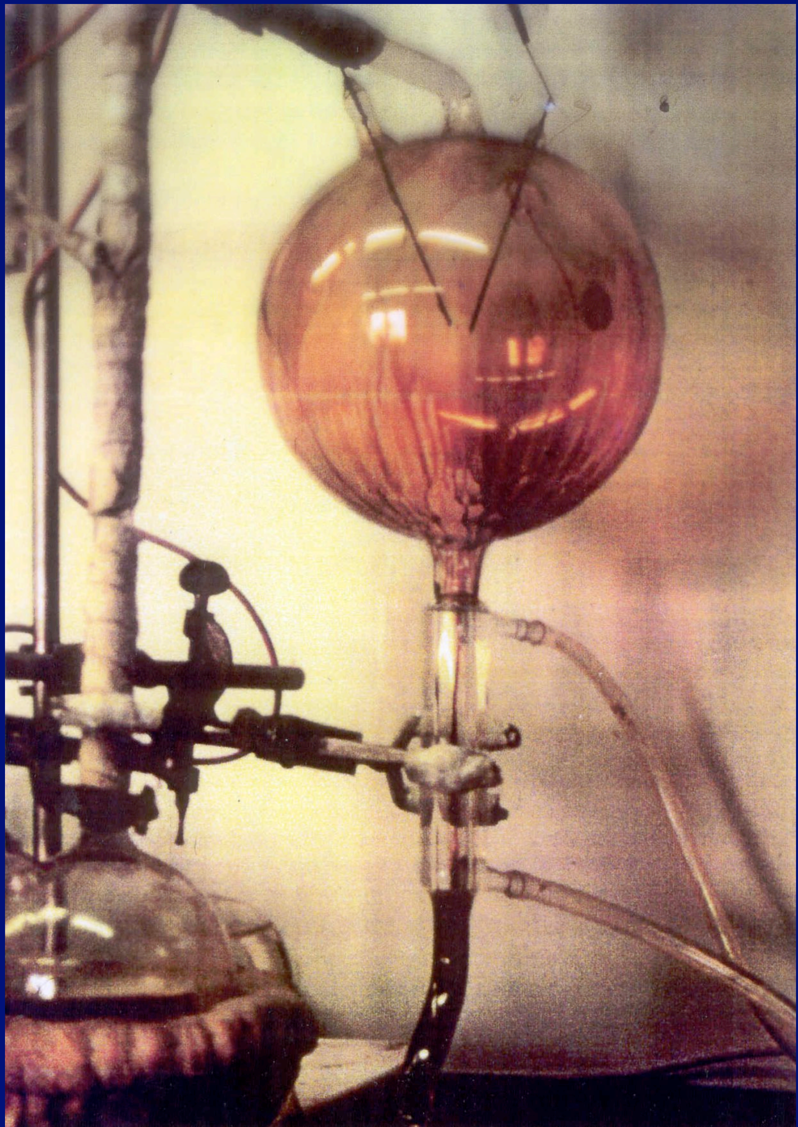
HCN, NH_3, $HCHO$, CH_3CHO,
$HOCCHO$, $HOCCO_2H$

plus HNO_2, HNO_3

and, of course, negligible yields of amino acids (approx. 10^{-2}%)

Bada, G. L., Chalmers, J., Cleaves, H. J., Lazcano, A. & Miller, S. L., in prep.

Prebiotic synthesis under reducing and neutral conditions



CH_4, NH_3, H_2 & H_2O
(Miller, 1953)

CO_2, N_2 & H_2O
(Bada, Chalmers, Cleaves, Lazcano & Miller, 2006)

Prebiotic organic synthesis in neutral planetary atmospheres

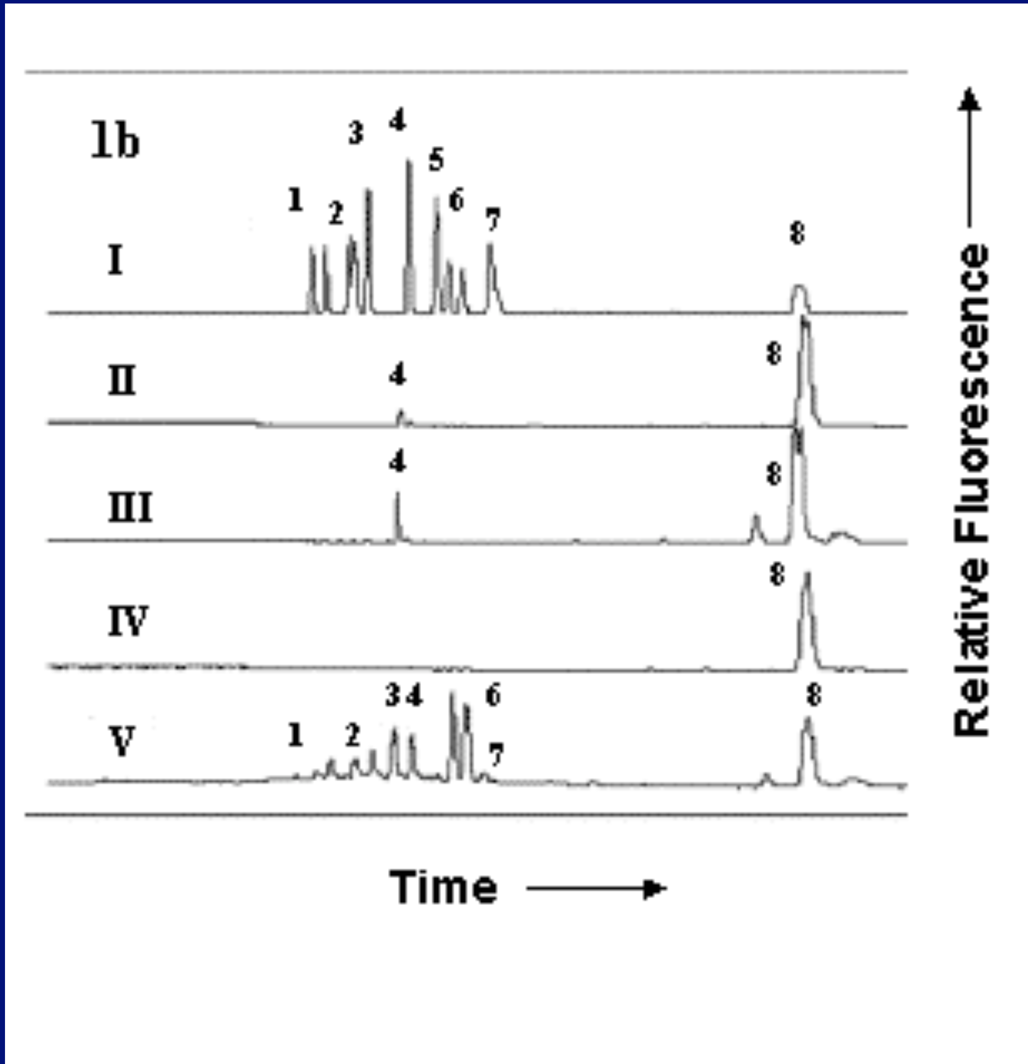
I. amino acid standard

II. CO_2/N_2 not sparked

III. $CO_2/N_2 + CaCO_3$, sparked, hydrolyzed with no ascorbate

IV. CO_2/N_2 sparked, hydrolyzed with no ascorbate

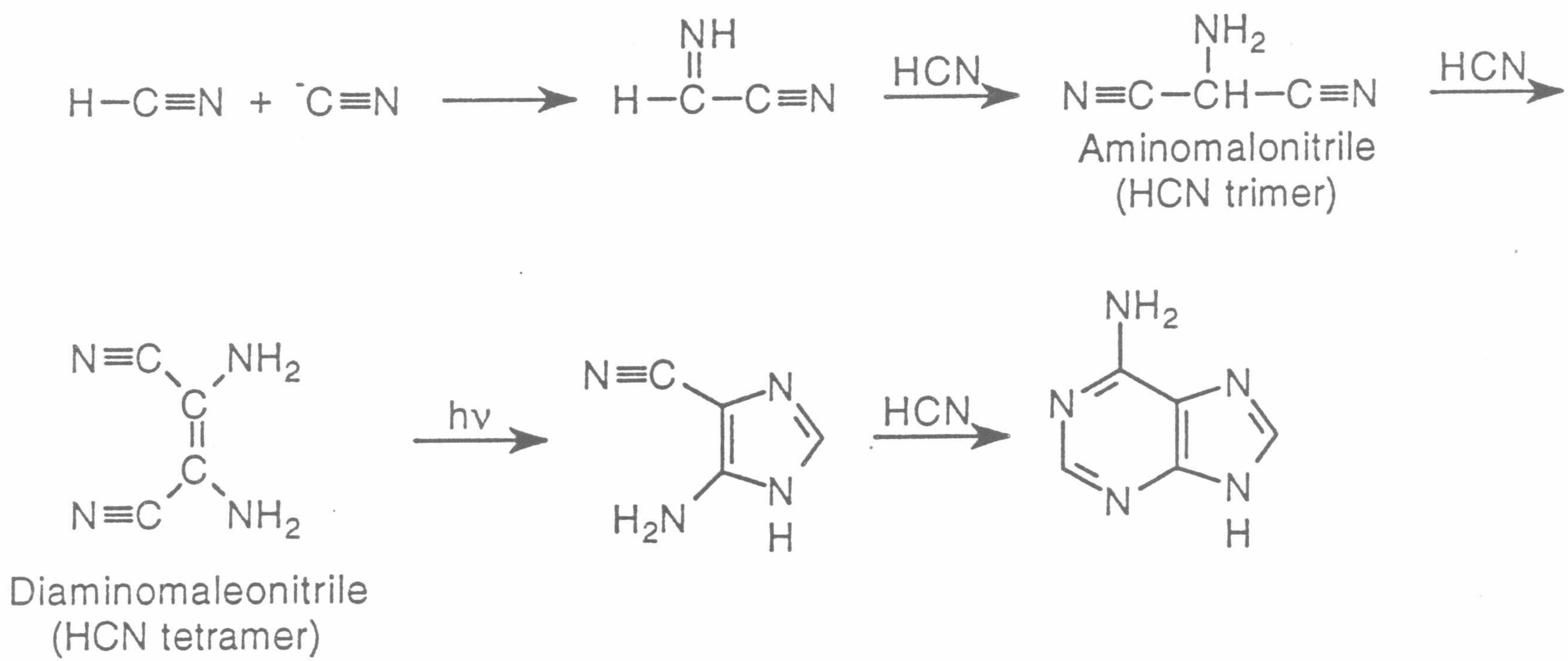
V. $CO_2/N_2 + CaCO_3$, sparked, hydrolyzed, ascorbate



(1) DL aspartic acid; (2) DL glutamic acid; (3) DL serine; (4) glycine; (5) β-alanine; (6) DL alanine; (7) α-amino isobutyric acid; (8) DL norleucine (internal standard)

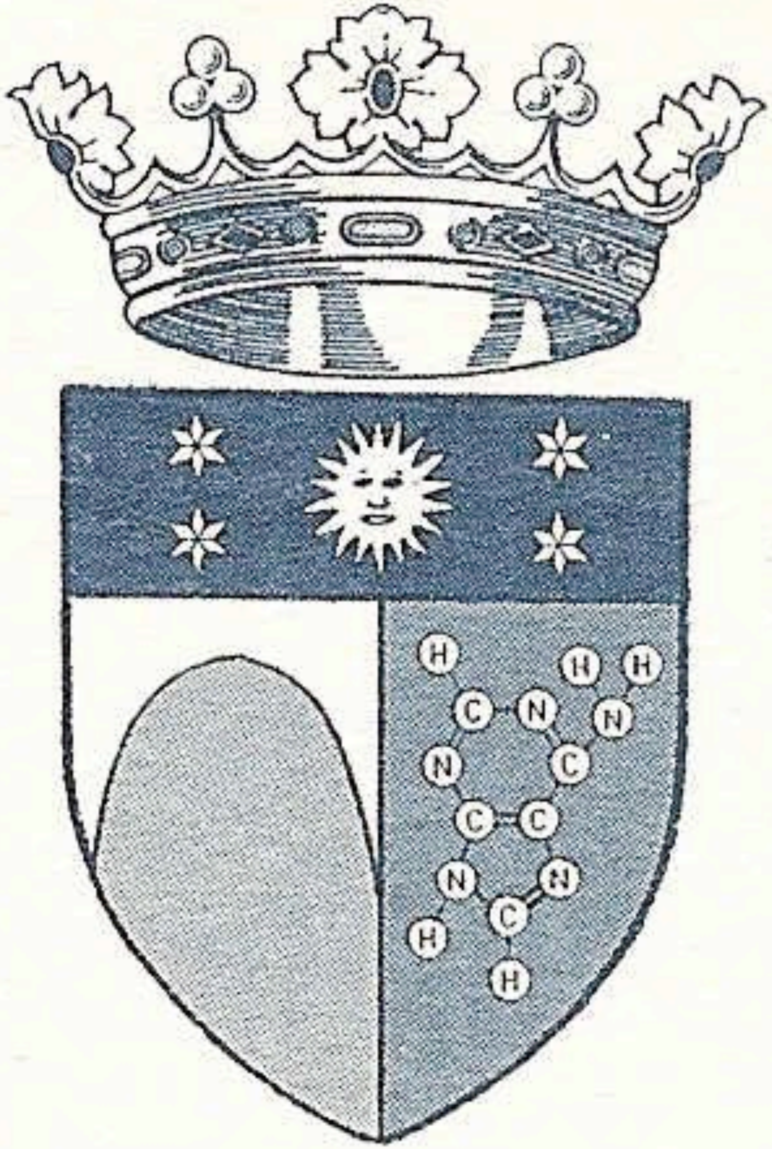
5 HCN → adenina

Joan Oro

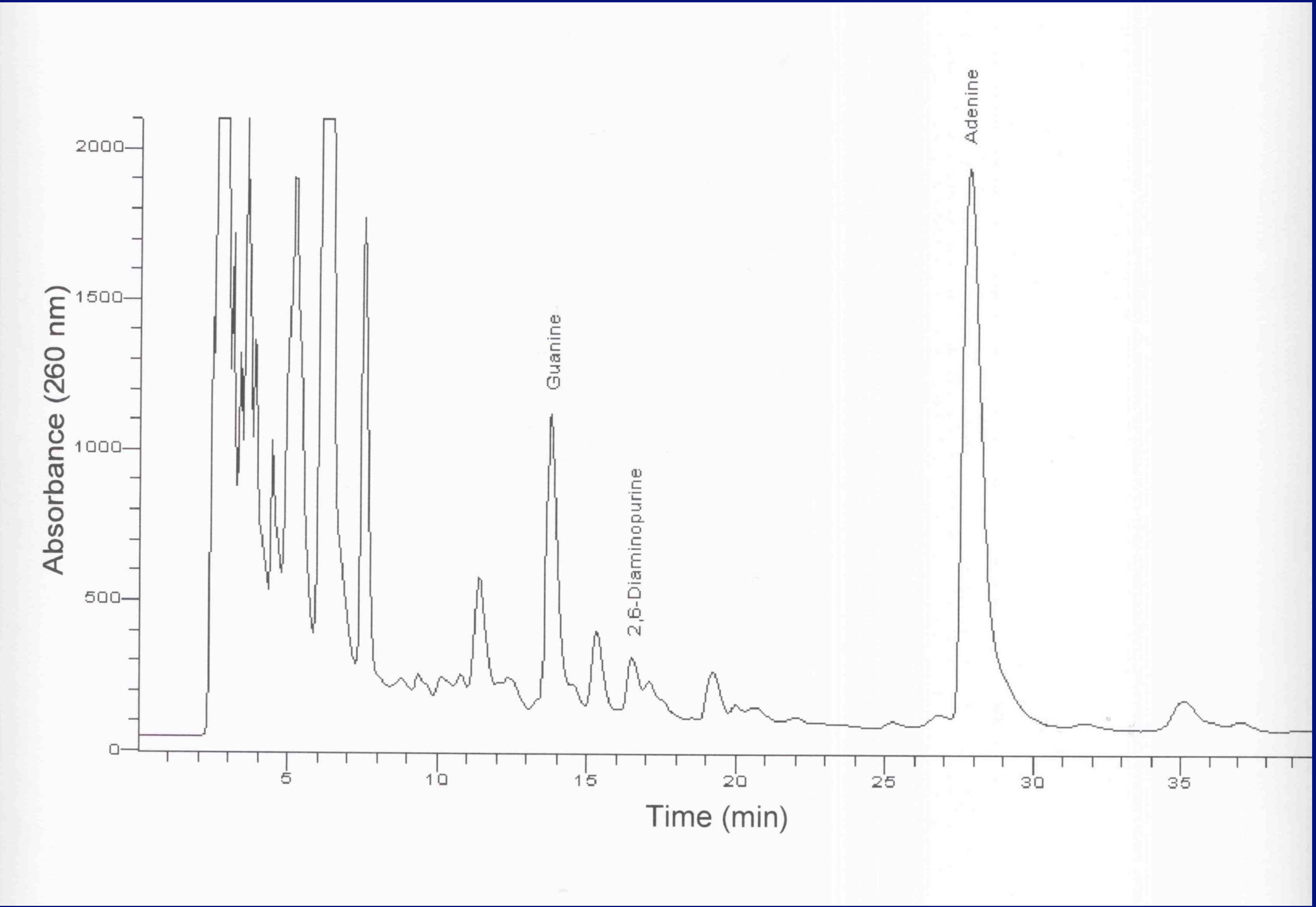

H−C≡N + ⁻C≡N
NH
H−C−C≡N
HCN
NH2
N≡C−CH−C≡N
Aminomalonitrile
(HCN trimer)
HCN
N≡C NH2
C
C
N≡C NH2
Diaminomaleonitrile
(HCN tetramer)
hν
N≡C
N
N
H2N
H
HCN
NH2
N
N
N
N
H

5 HCN ⟶ adenina

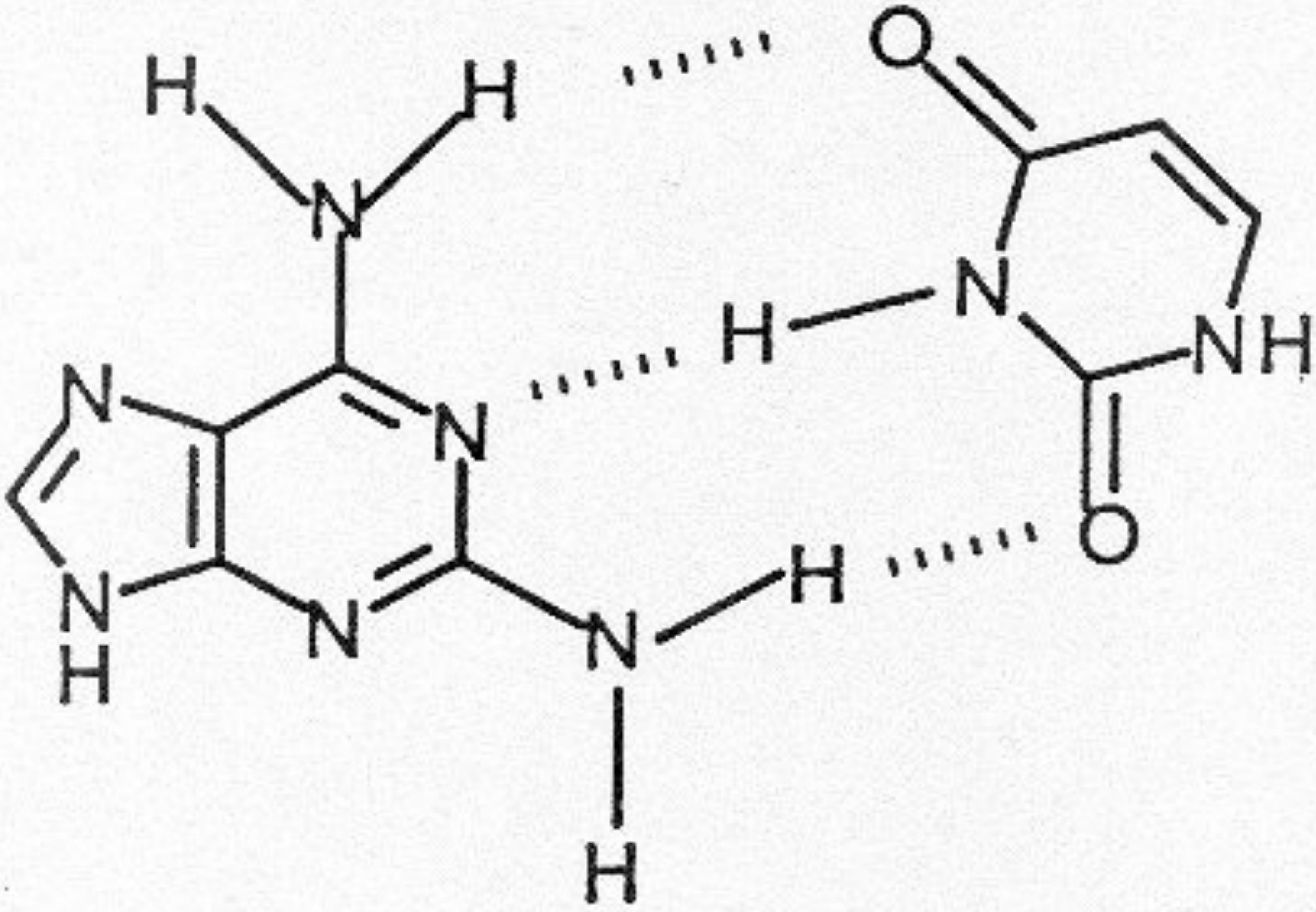
Joan d' Oro


H
H H
C N N
N C
C C
N N
H C
H

Chromatogram of NH_4CN polymerization at 80 °C



Borquez, Cleaves, Lazcano & Miller (2004) *Origins Life Evol. Biosph.* **35**: 537



H
H
N
O
N
H
N
NH
N
H
N
O
H
N
H
N
H

Sintesi prebiotiche che funzionano

1. **Aminoacidi dalla sintesi di Strecker**
2. **Purine dalla polimerizzazione di HCN**
3. **Pirimidine da cianoacetilene & urea**
4. **Zuccheri dalla polimerizzazione di HCHO**

Abiotic synthesis under hydrothermal vent conditions

$$2CH_3\text{-}SH + CO \xrightarrow{NiS/FeS} CH_3CO(SCH_3) + H_2S$$

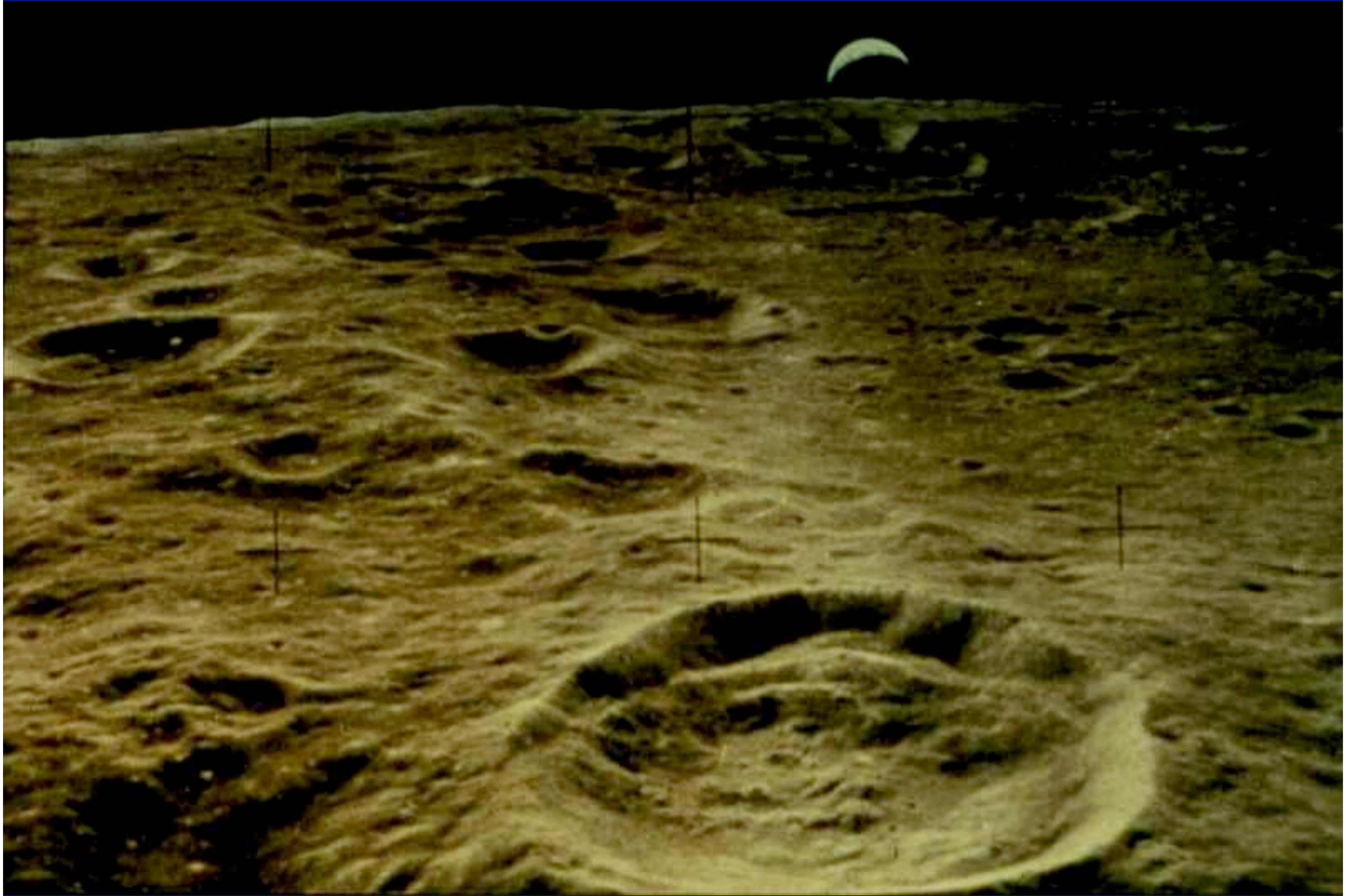
$$CH_3\text{-}SH + CO + H_2O \xrightarrow{NiS/FeS} CH_3\text{-}COOH + H_2S$$

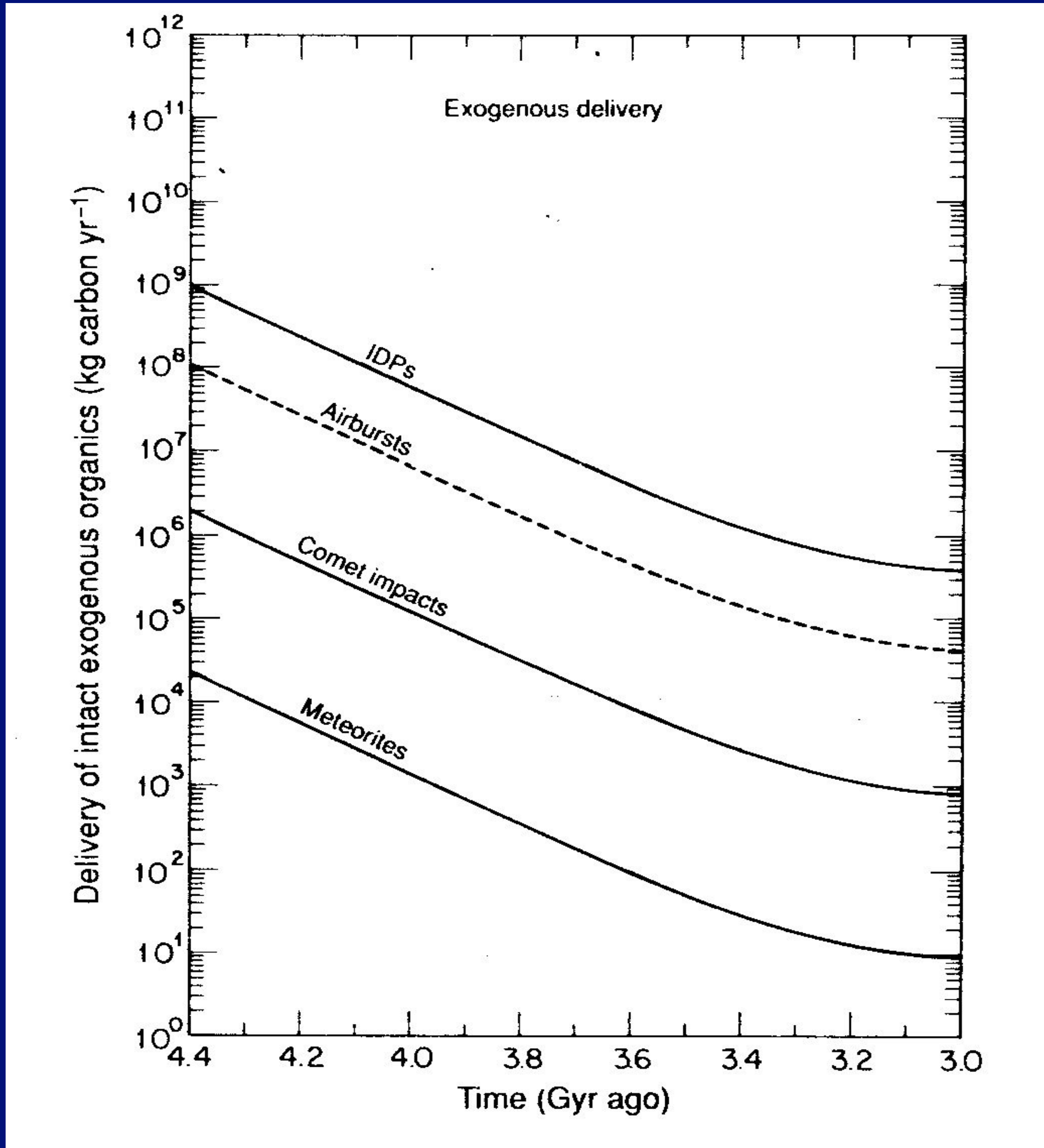
$$\text{amino acids} + CO \xrightarrow{NiS/FeS} \text{dipeptides}$$

An extraterrestrial origin of organic compounds?

The Murchison meteorite

Meteor Crater, Arizona



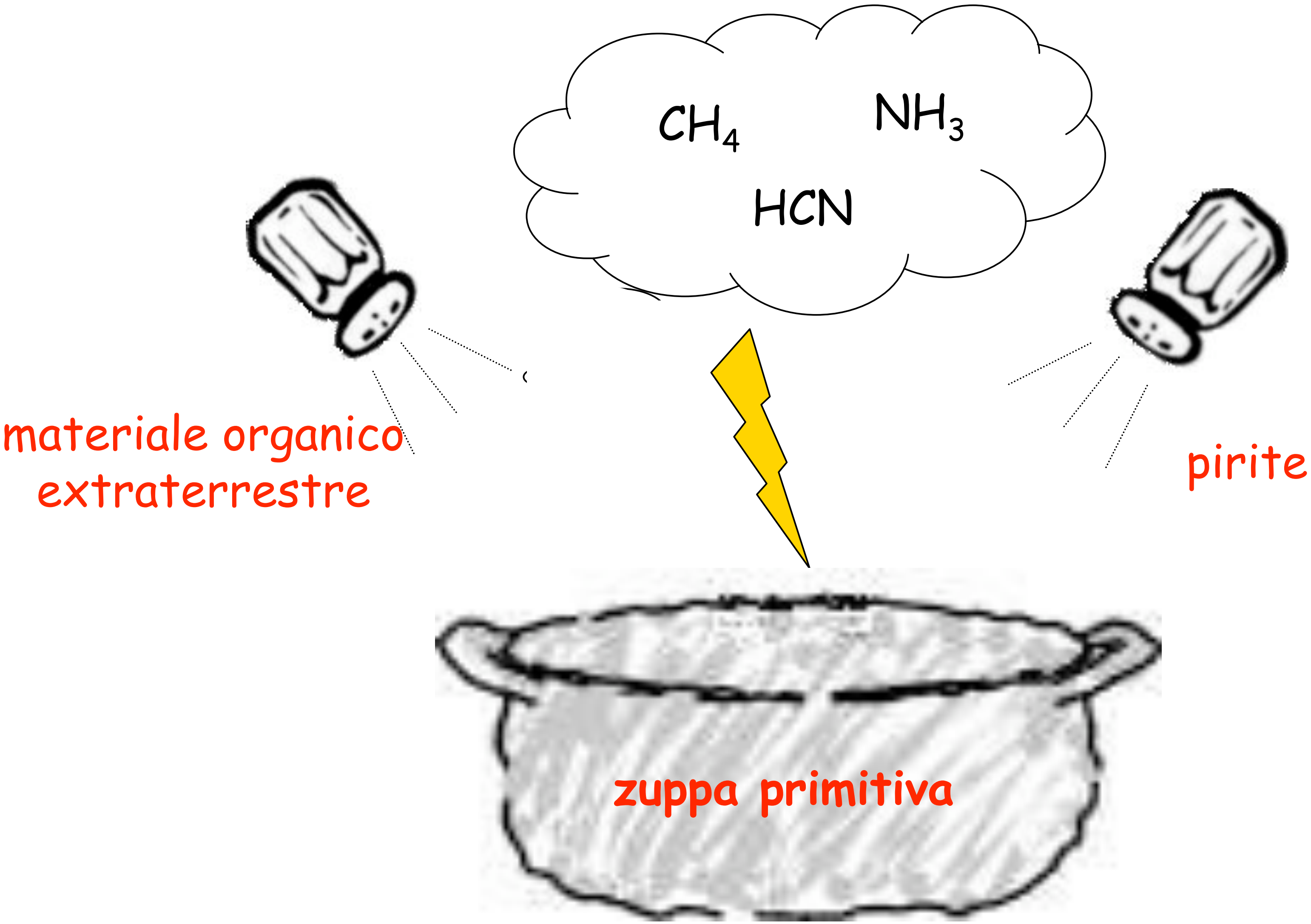


Chyba & Sagan (1992)

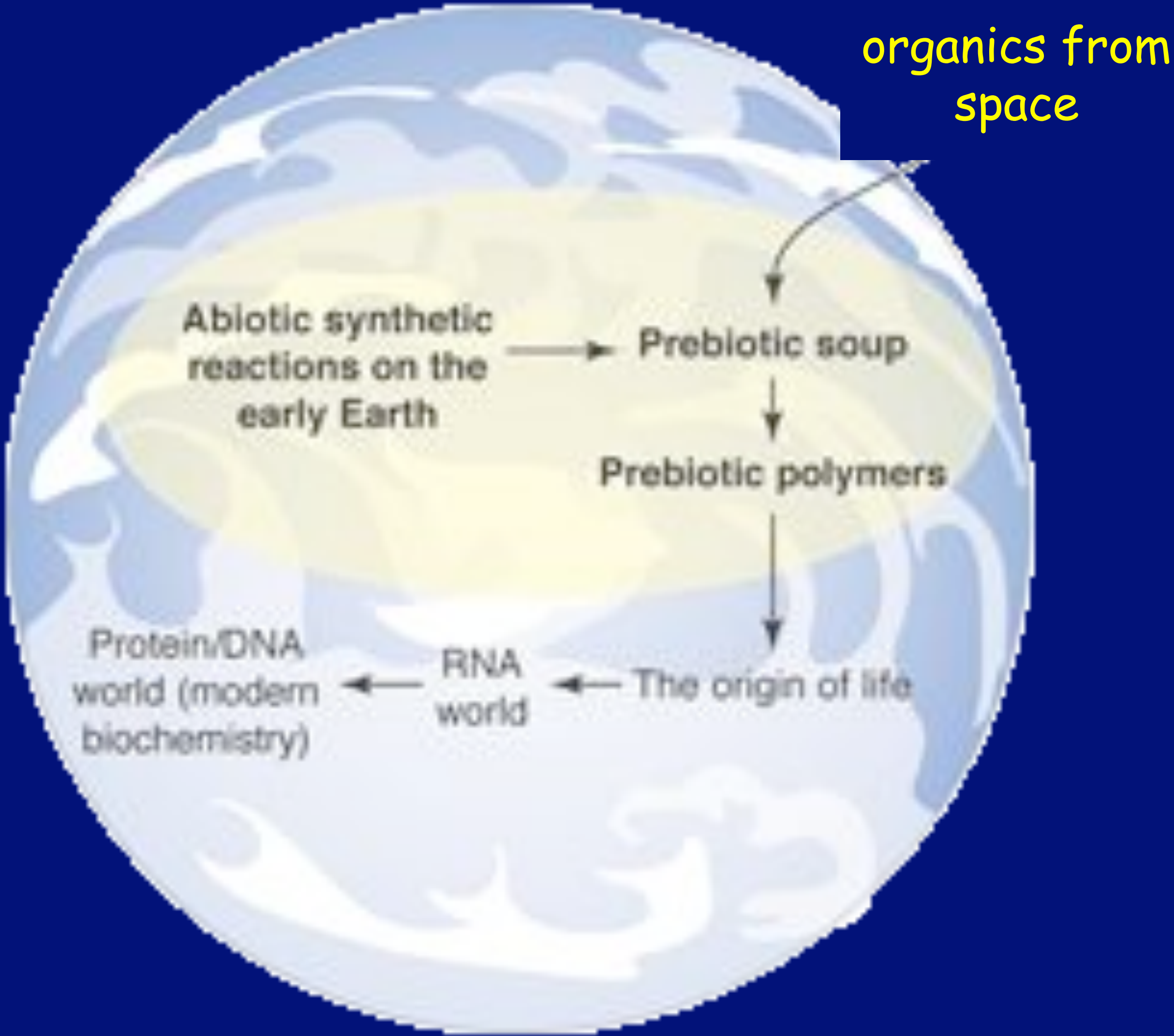
Prebiotic sources of organic compounds

1) anoxic interfase ocean/atmosphere
2) input in meteorites
3) high-temperature vent chemistry

Troppi cuochi hanno rovinato la zuppa?



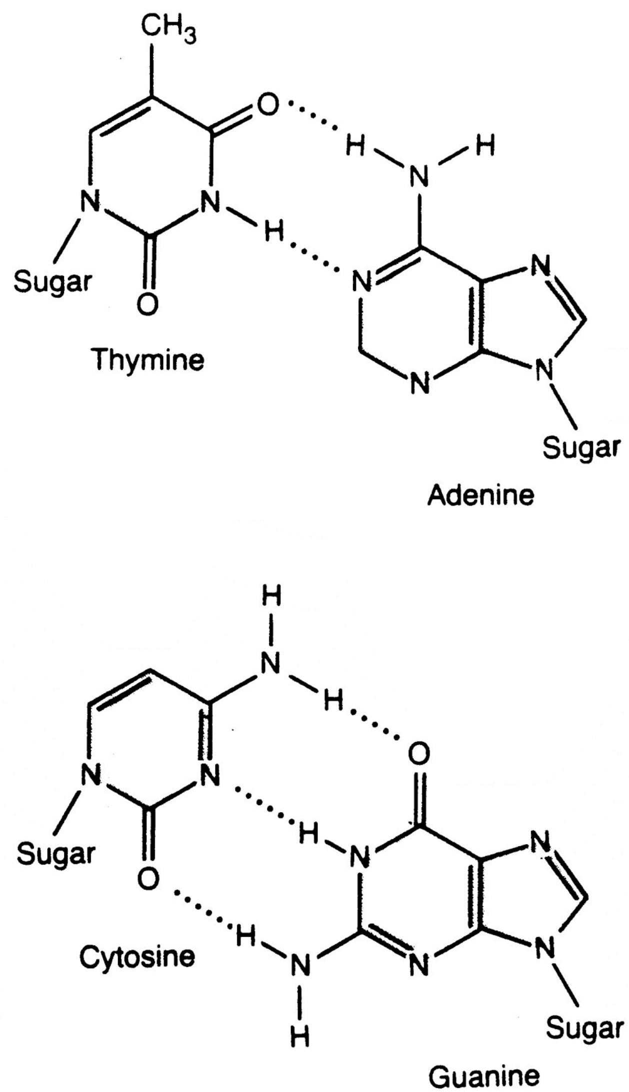
CH_4
NH_3
HCN
materiale organico extraterrestre
pirite
zuppa primitiva

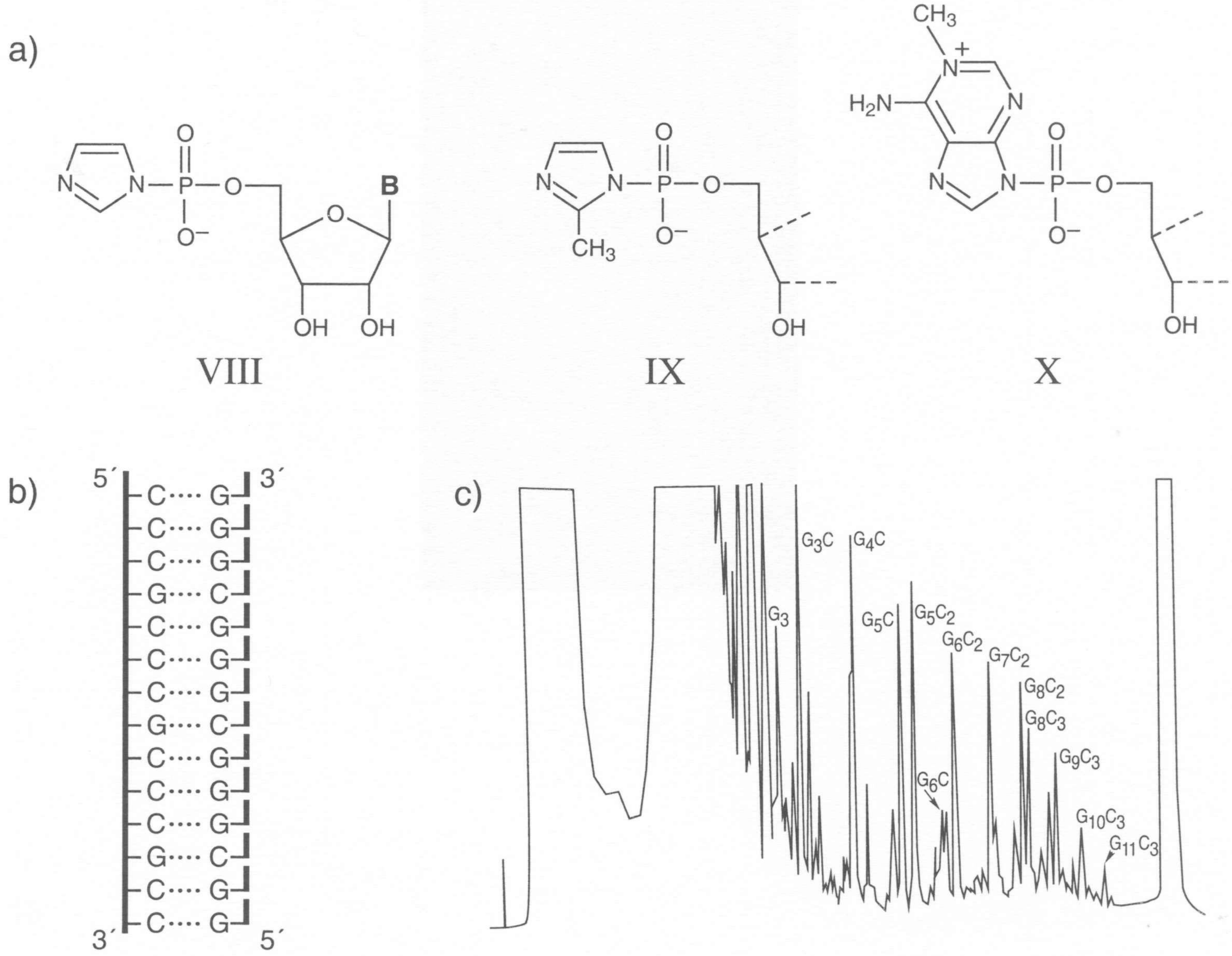


Bada & Lazcano (2002) *Science* **296**: 1982


*U
*A
*A
*A
*U
A
U
U
*U
A
*U
*A
montmorillonite
Ferris 2002

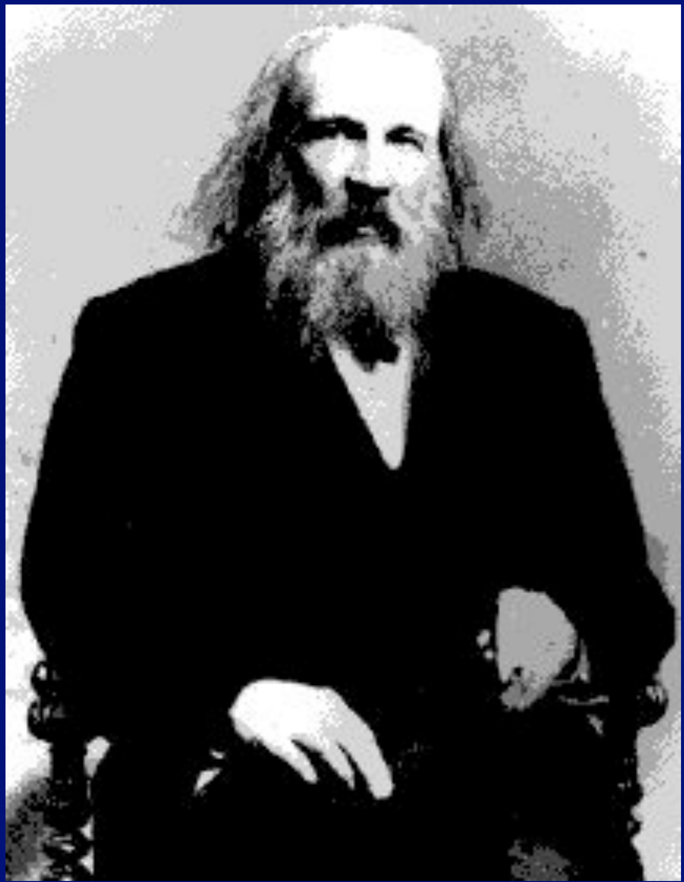
L'appaiamento delle basi é "gratis"




a)
CH_3
N
H_2N
O
P
O
O^-
B
OH
VIII
IX
X
b)
5´
3´
C···· G
G···· C
c)
G_3C
G_4C
G_3
G_5C
G_5C_2
G_6C_2
G_7C_2
G_8C_2
G_8C_3
G_9C_3
G_6C
$G_{10}C_3$
$G_{11}C_3$

Orgel, 2004

Mendeleyev e l'origine abiotica dell'olio

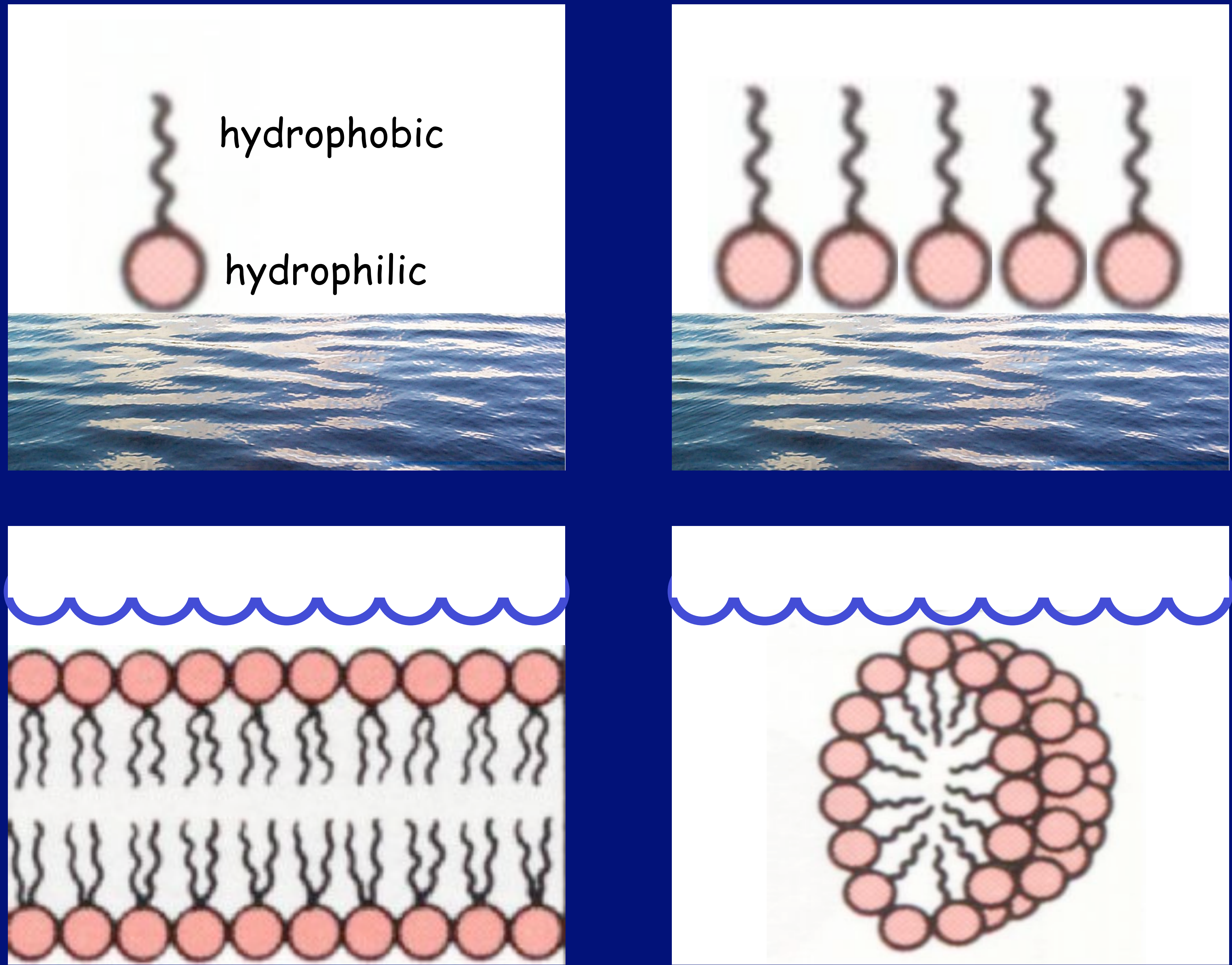


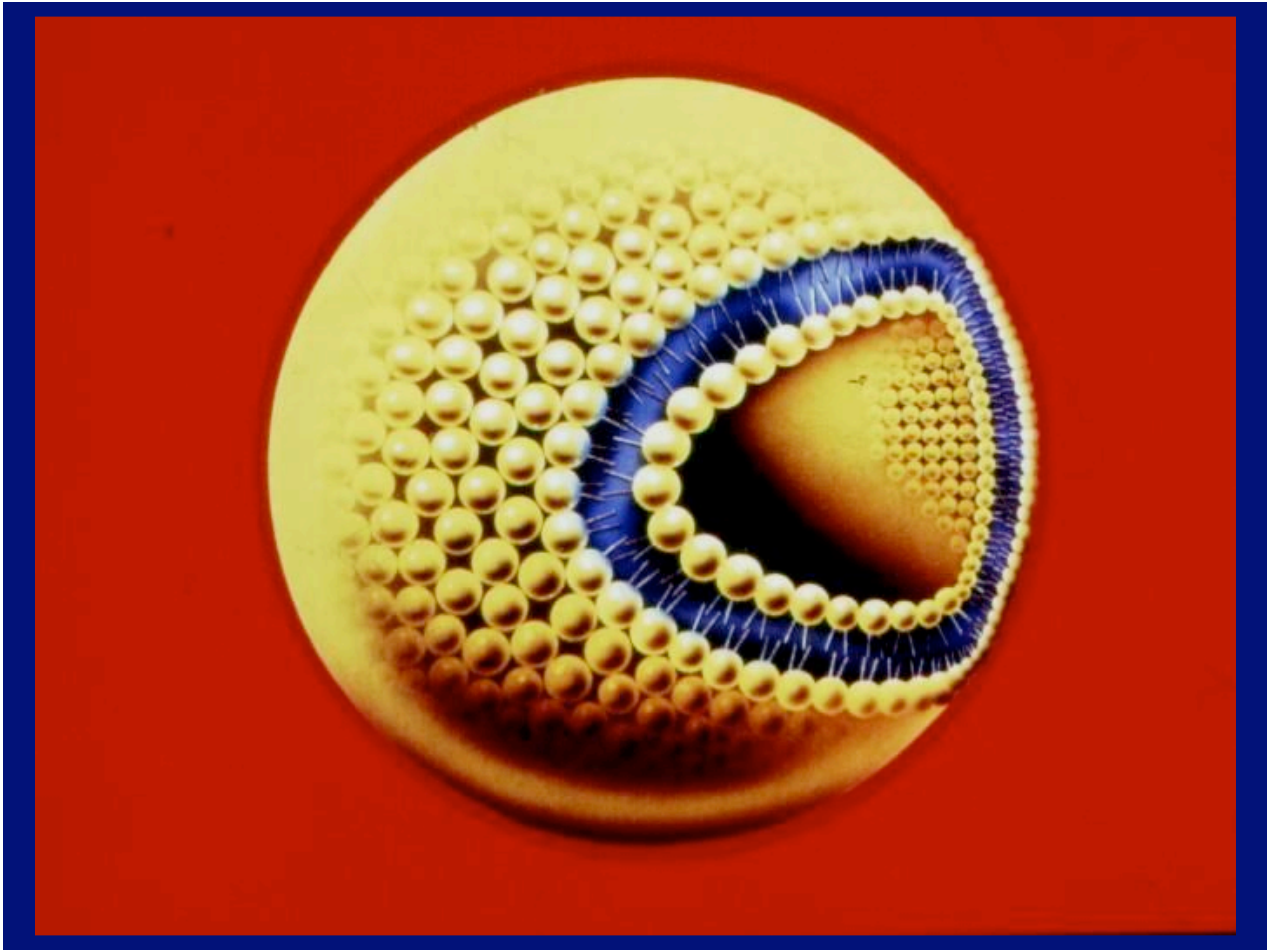
$Fe_3C + H_2O \longrightarrow$ idrocarburi

Dagli idrocarburi ai composti anfifilici

1) $Fe_3C + H_2O \longrightarrow$ alcani + alcheni

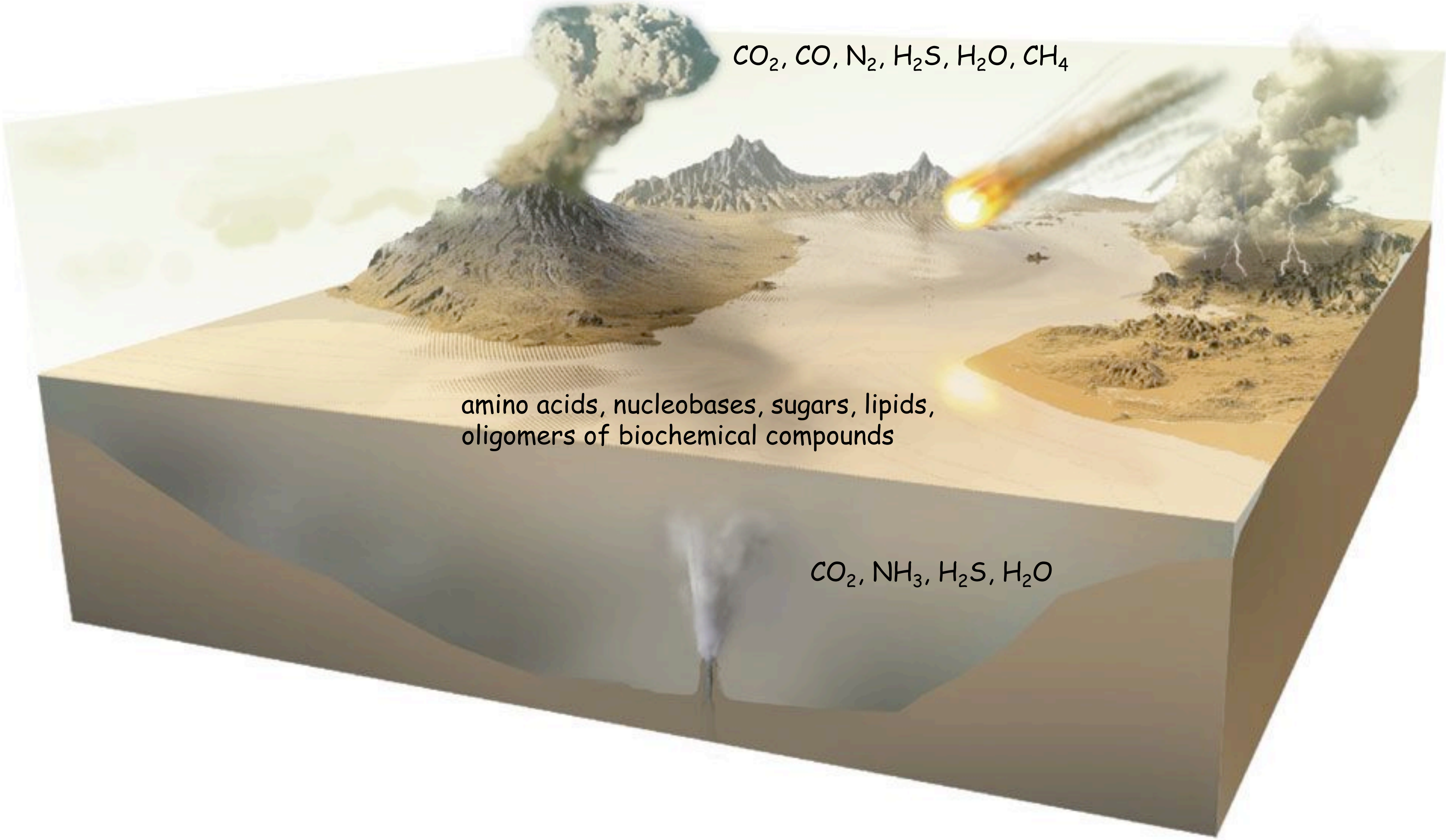
2) alcheni $\xrightarrow{\text{condizioni acide}}$ alcoli


hydrophobic
hydrophilic



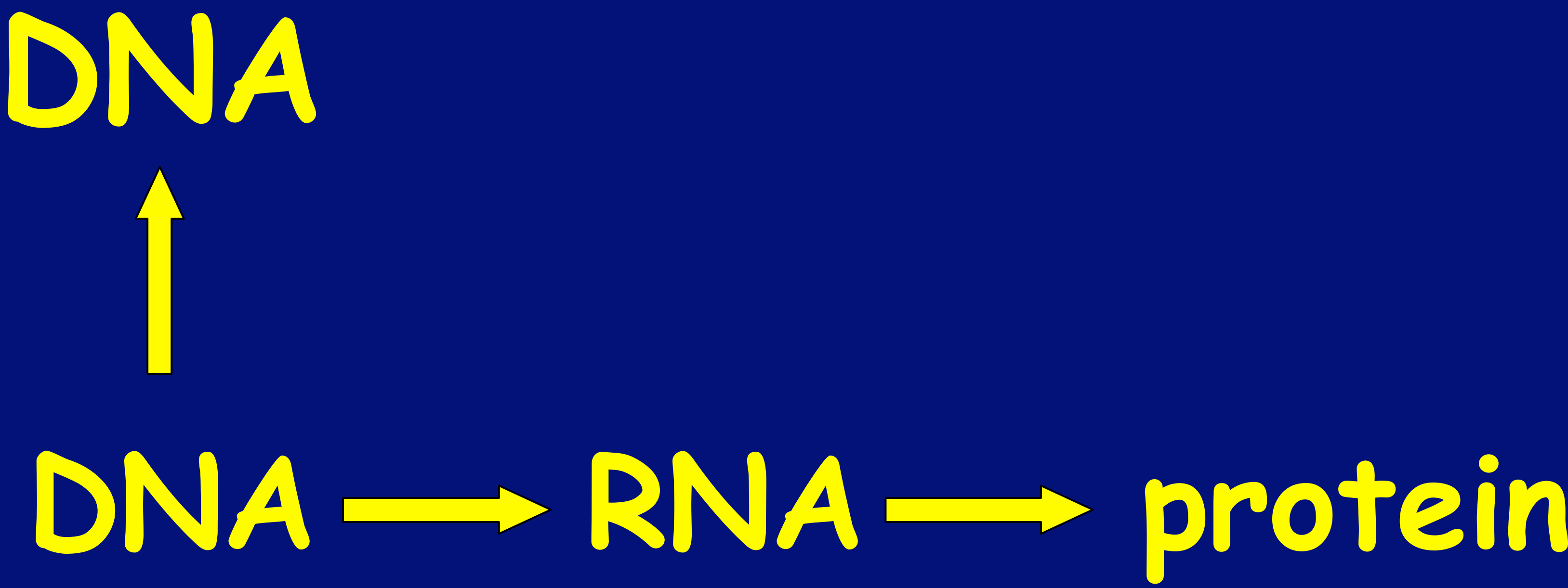
I dati suggeriscono che prima dell'origine della vita già esistevano:

- molti agenti catalitici diversi
- polimeri con sequenze di nucleobasi
- composti capaci di formare membrane



Lazcano, *Natural History* (Feb/2006)


Campbell's
CONDENSADA
SE CONVIERTE EN EL DOBLE
SOPA
Primitiva


DNA
DNA
RNA
protein

The RNA world hypothesis

replicative RNA

catalytic RNA

plus many other things: amino acids, lipids, sugars, clays, metallic cations, etc!

RNA World

↑

?

catalytic & replicative RNAs

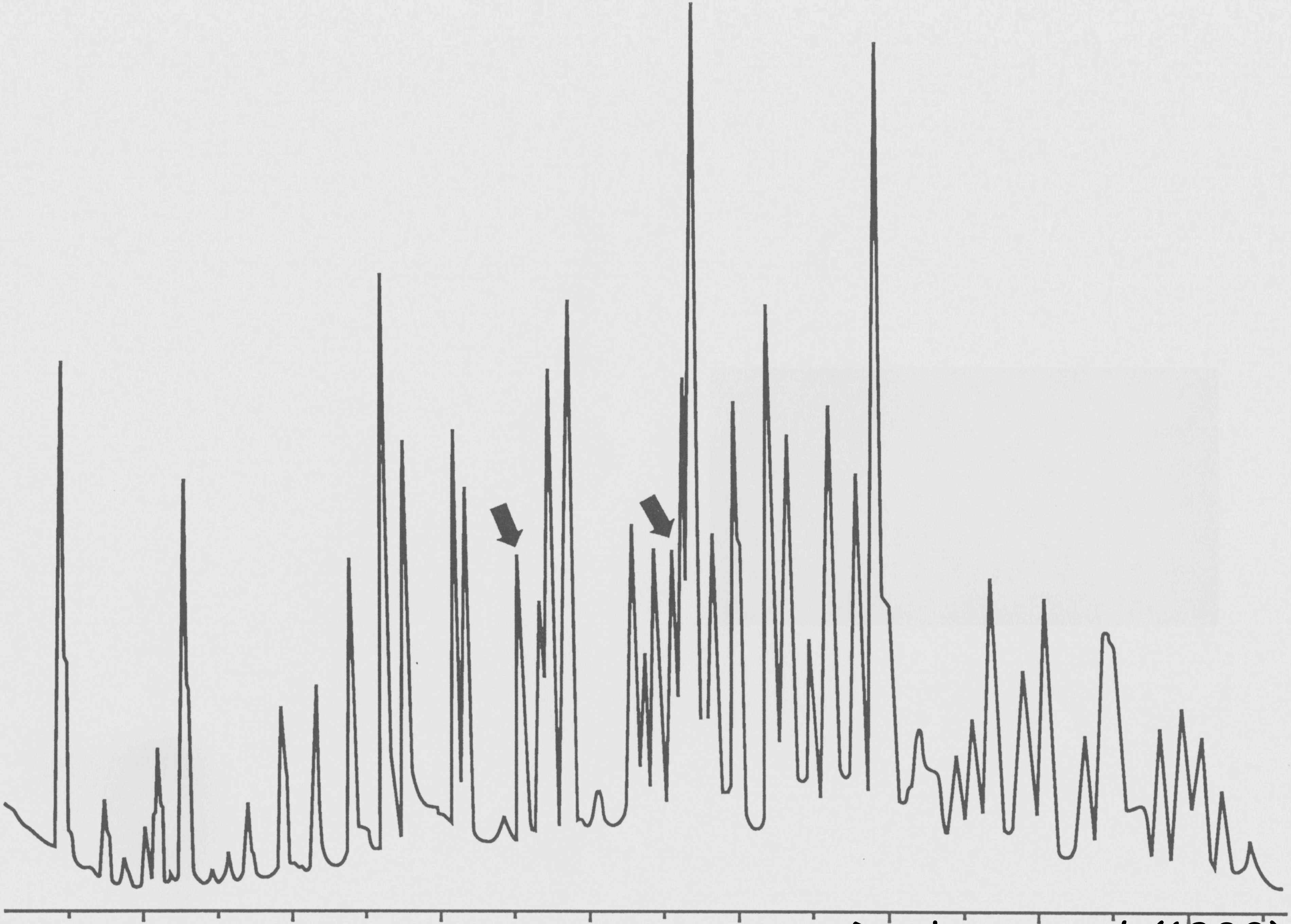
↑

?

prebiotic soup

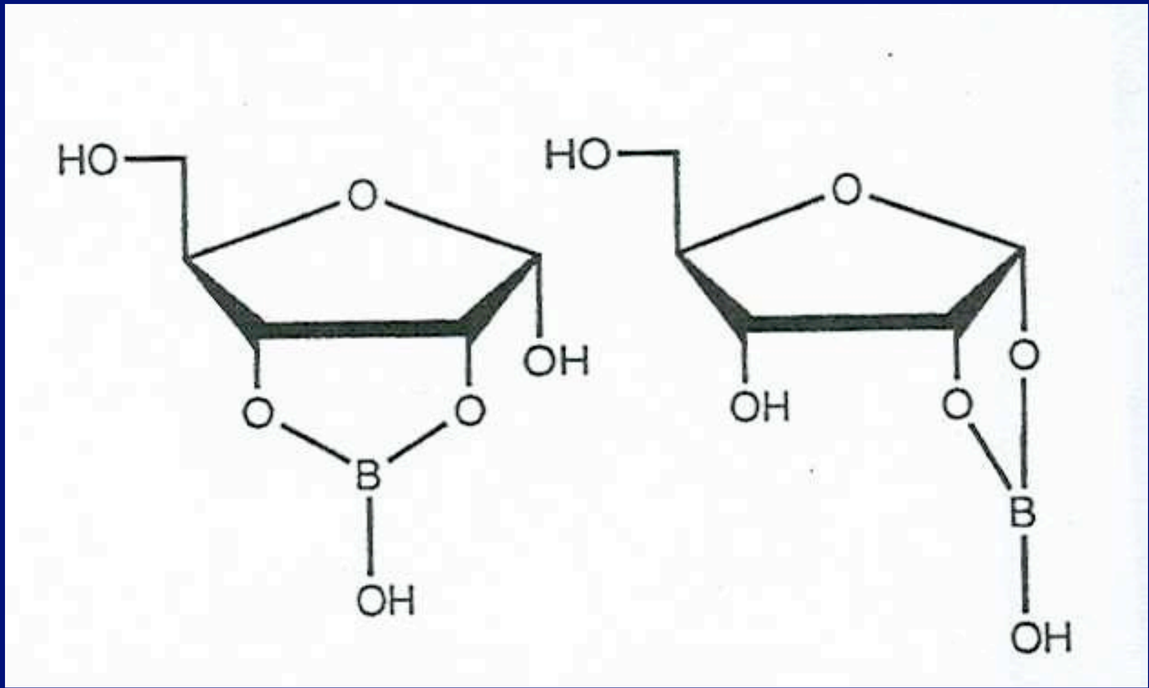
Butlerov´s formose reaction

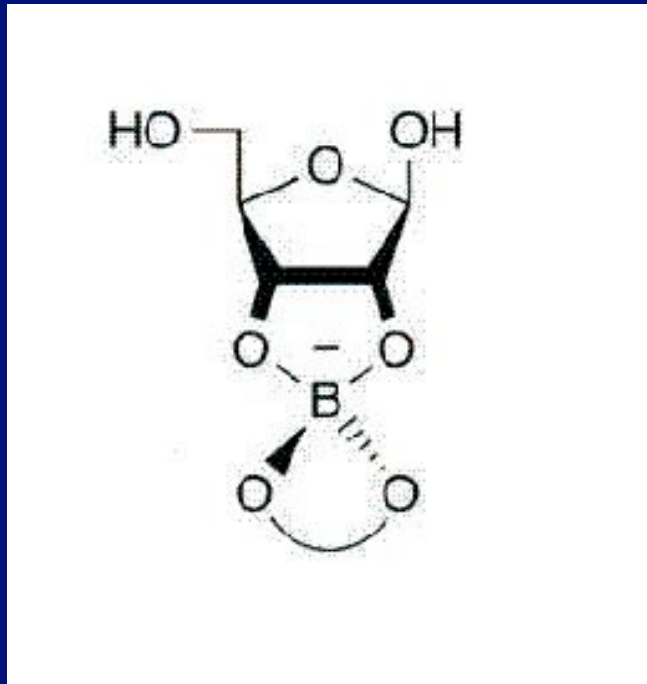
$$H_2CO \xrightarrow{OH^-} \text{sugars}$$



Decker *et al* (1982)

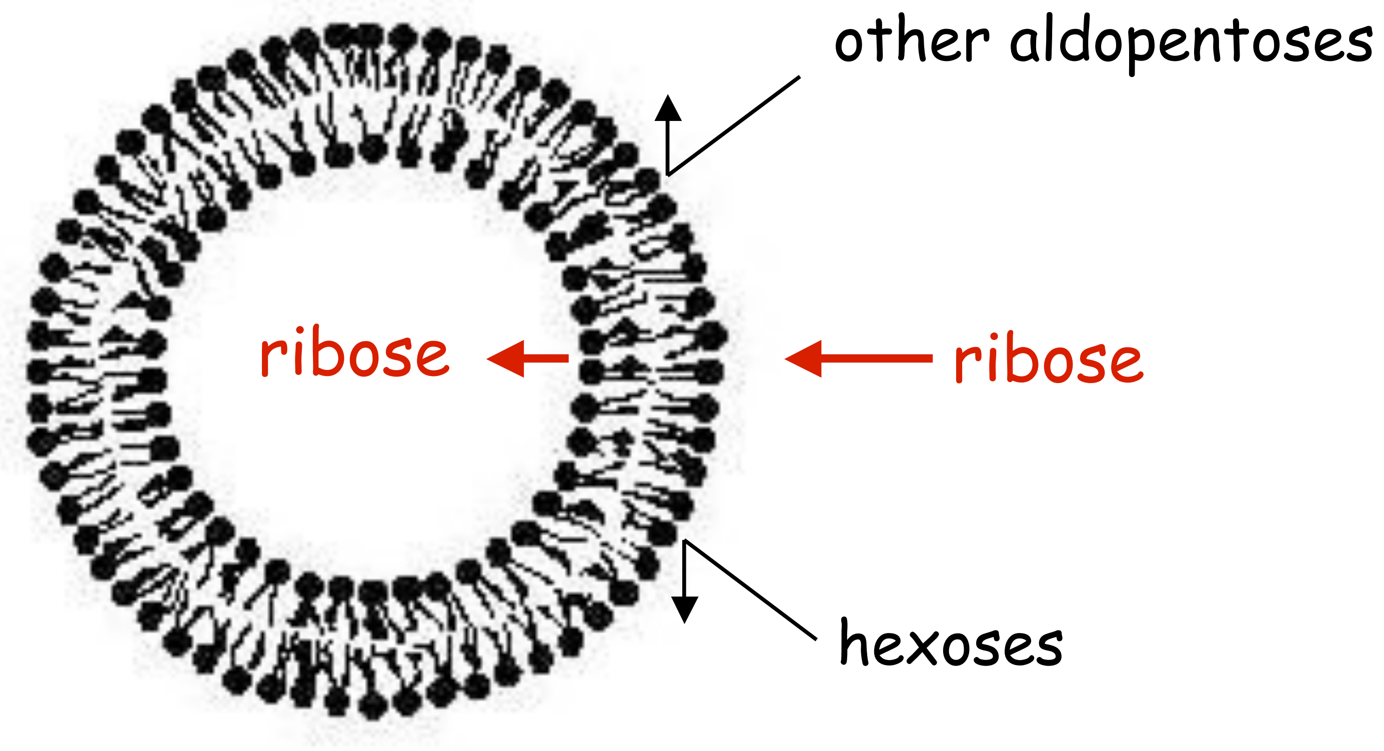
Preferential sequestration of ribose by boron: the key to a prebiotic origin of the RNA world?





Prieur (2001) *C.R.Acad. Sci. Chimie* **4**: 667

Ricardo *et al.* (2004) *Science* **303**: 194

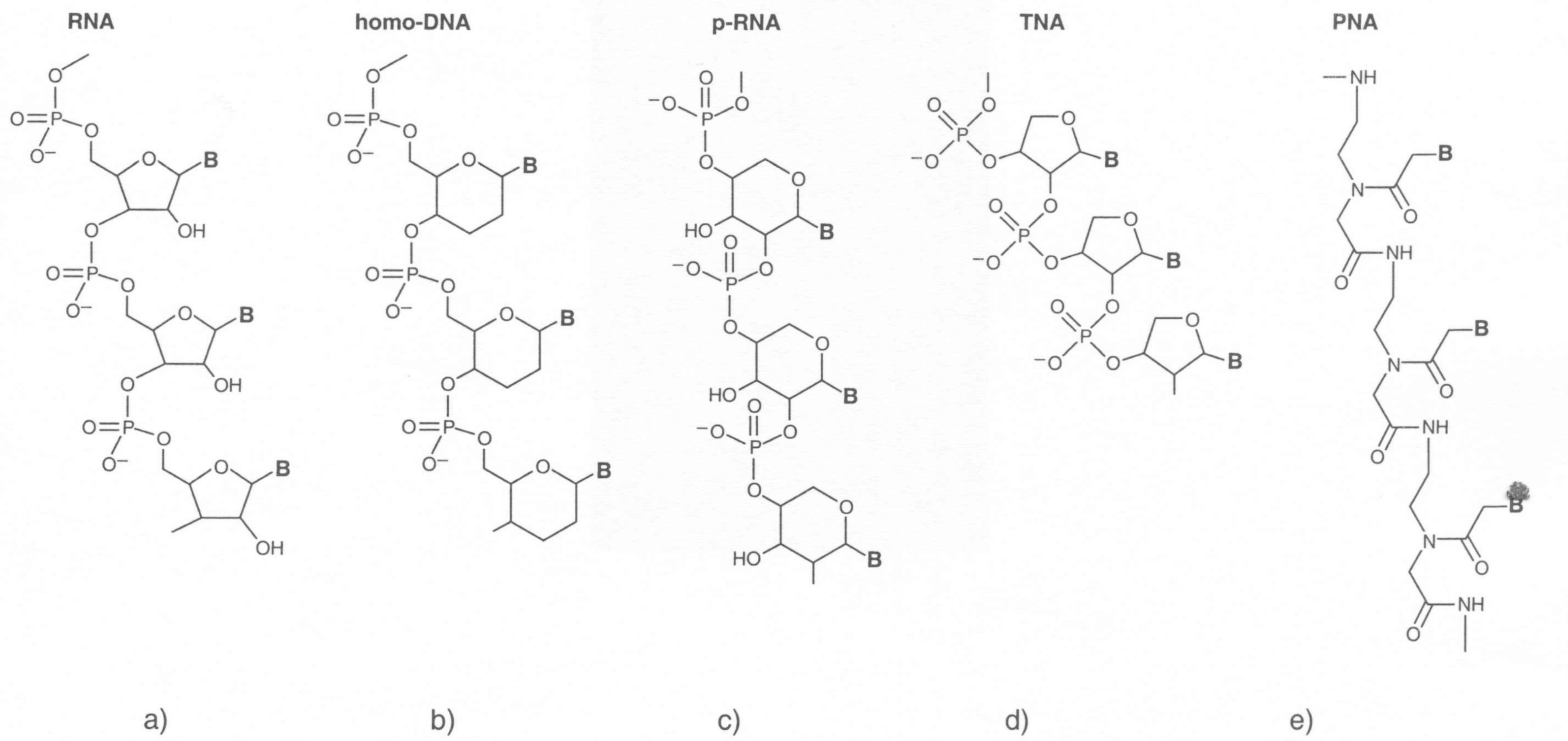


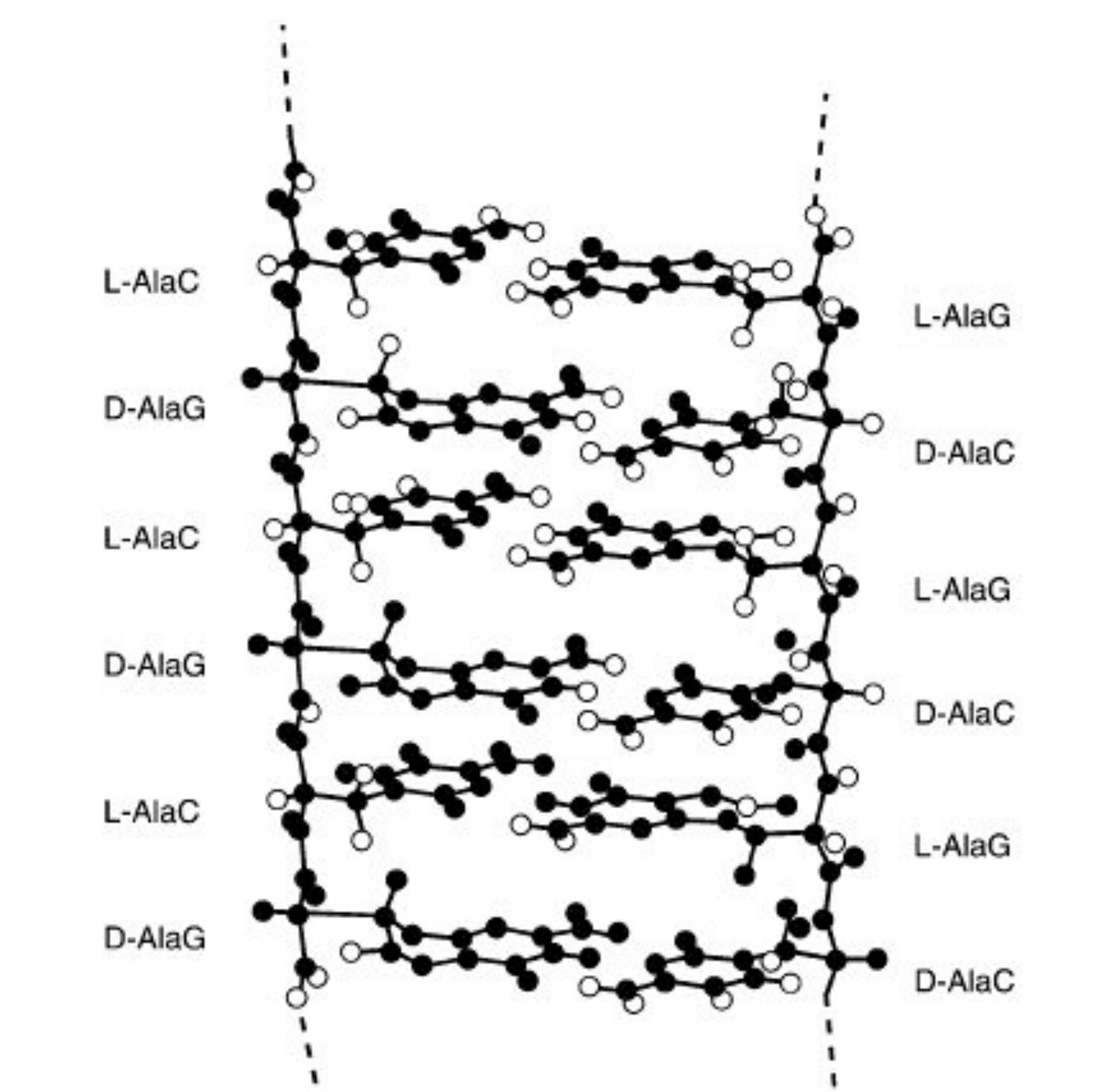
Sacerdote & Szostak, 2005

RNA world

Unknown prebiotic chemical processes?

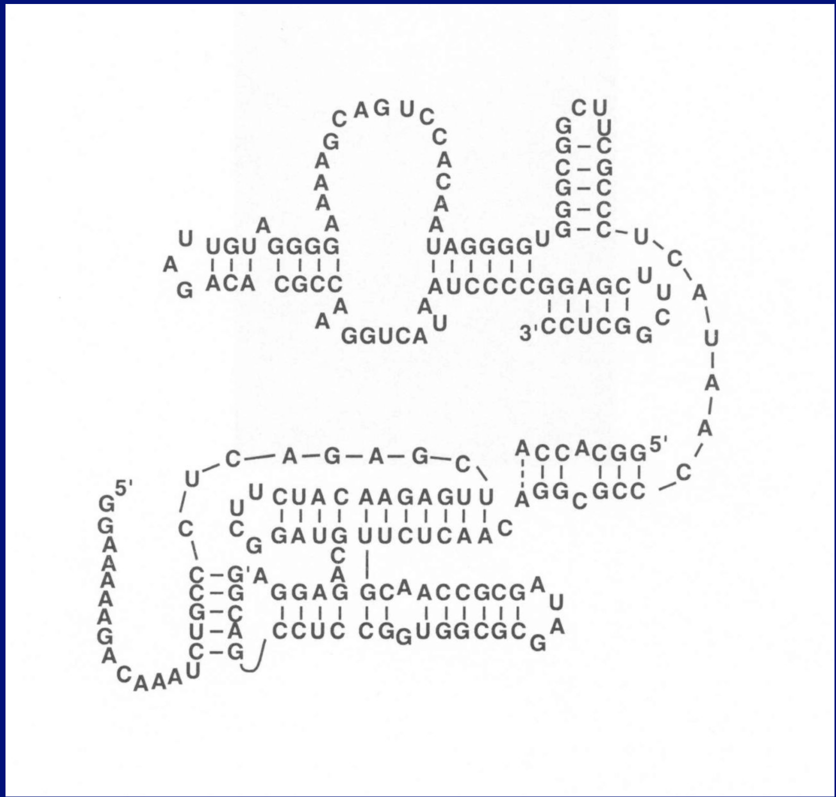
Evolutionary outcome of pre-RNA worlds?


RNA
homo-DNA
p-RNA
TNA
PNA
a)
b)
c)
d)
e)

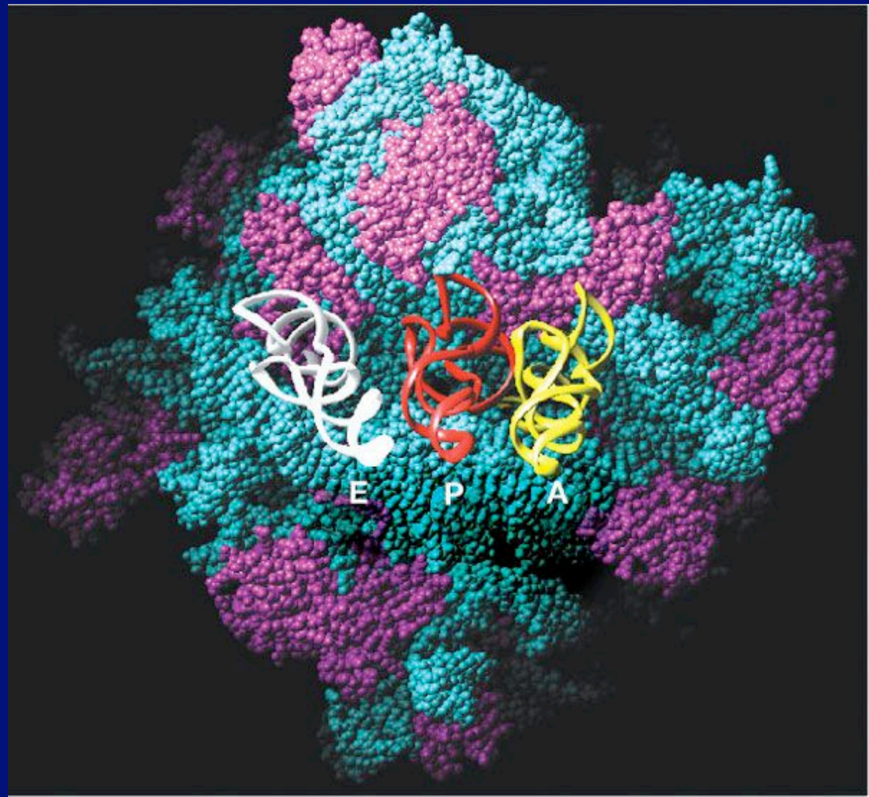


L-AlaC
L-AlaG
D-AlaG
D-AlaC
L-AlaC
L-AlaG
D-AlaG
D-AlaC
L-AlaC
L-AlaG
D-AlaG
D-AlaC

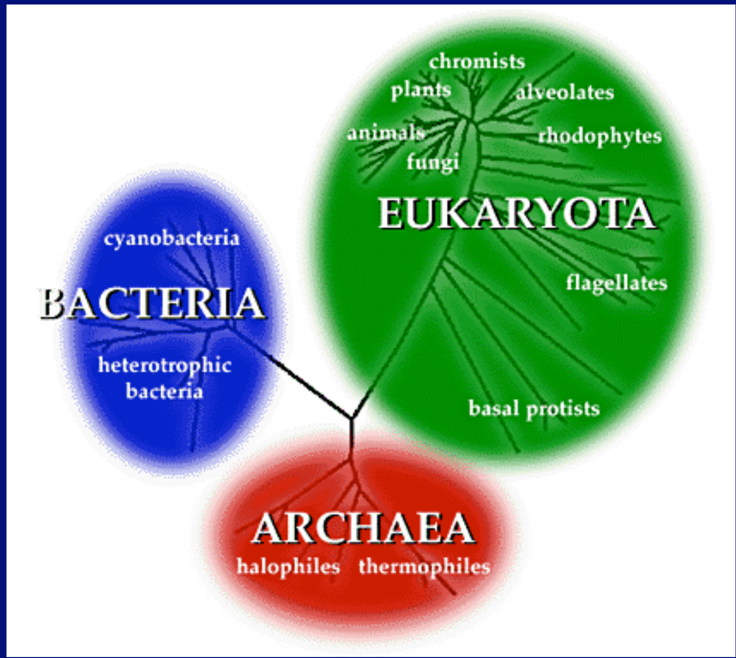
Alcune capacità catalitiche dell' RNA



Piccoli ribozimi possono esibire capacità replicative (Strobel, 2001)



L'Rna ribosomale catalizza la formazione del legame peptidico (Moore & Steitz, 2002)

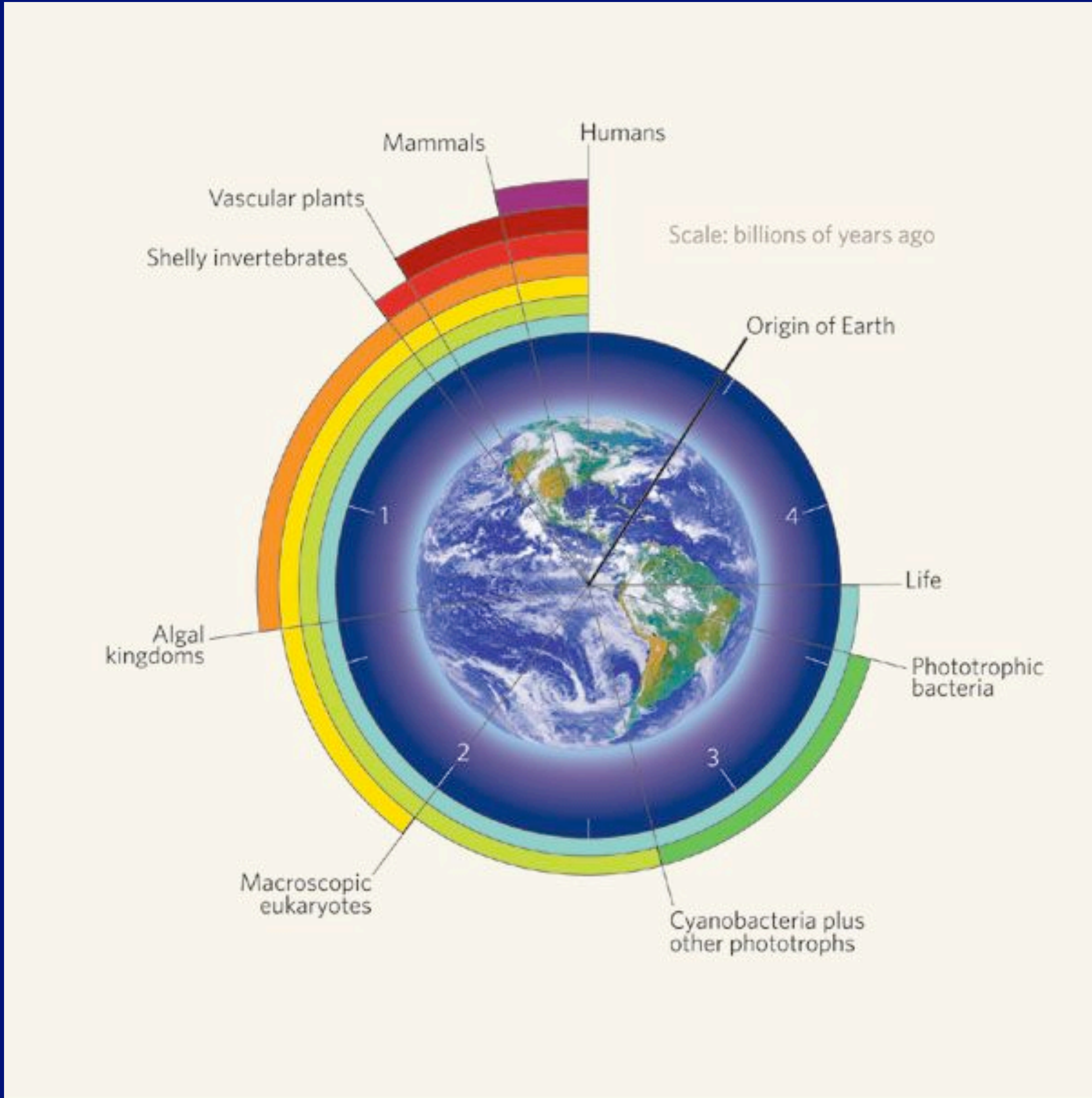


DNA, RNA & proteins

RNA + proteins

RNA world

?



DesMarais (2005) *Nature* 437: 827