Astrobiology
Lecture 5

Life in a cosmic context

University of Trieste, 2023
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Diversity and unity of terrestrial life

Terrestrial life shows a great diversity of species

Species: organisms that have a genetic pool sufficiently similar to be able to breed among themselves

The number of species currently living on Earth is in the order of 10^7 (of which $\sim 10^6$ are documented)

The total number of extinct species in the course of the evolution is estimated to be in the order of a few 10^9

The largest diversity is found in the unicellular world

Unity of terrestrial biomolecules

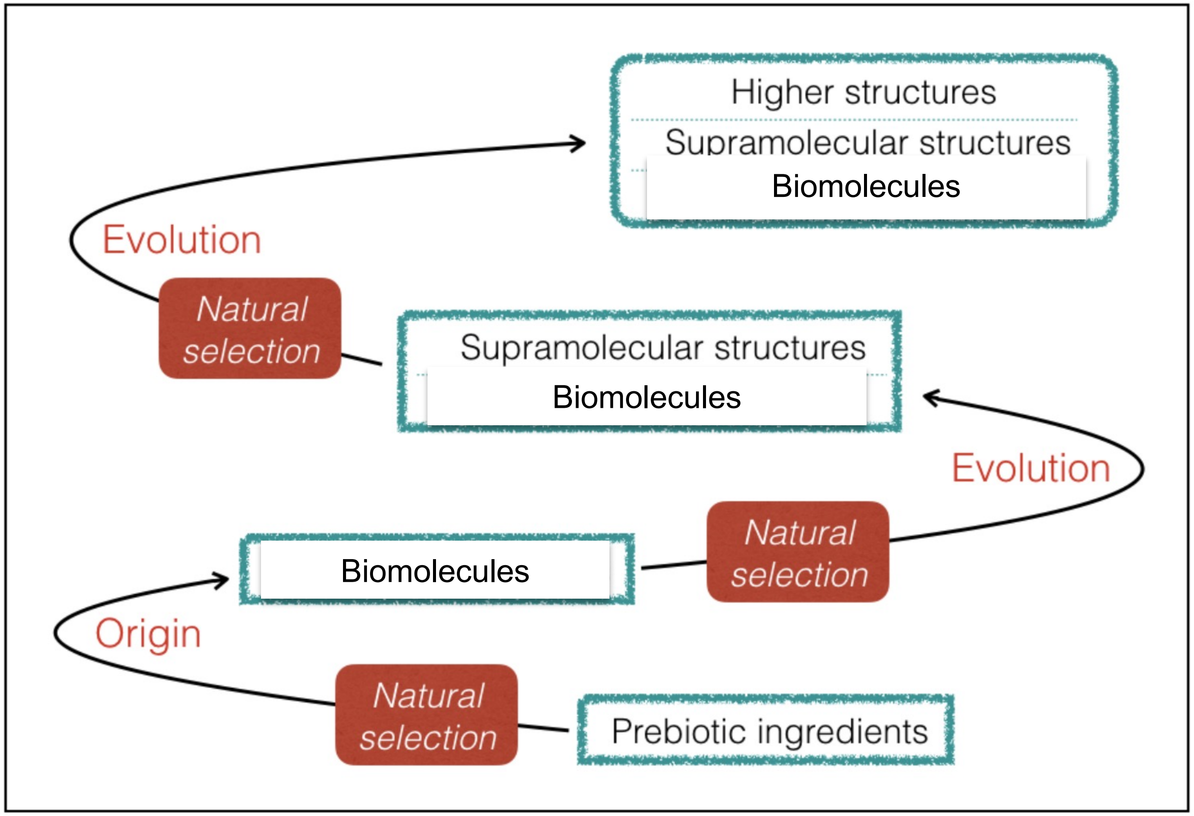
Despite the extremely large diversity of species,
all terrestial organisms show a remarkable unity at the molecular level

The genetic code is shared by all organisms,
from bacteria to men (with rare cases of minor variations)

All terrestrial life uses a well-defined set of biomolecules
selected among countless possibilities provided by organic chemistry
ATP, RNA, DNA, 20 L-aminoacids …

The species, although differentiated via Darwinian evolution, have preserved the same pool of biomolecules

The evolutionary diversity between different species arises at the supramolecular and higher levels

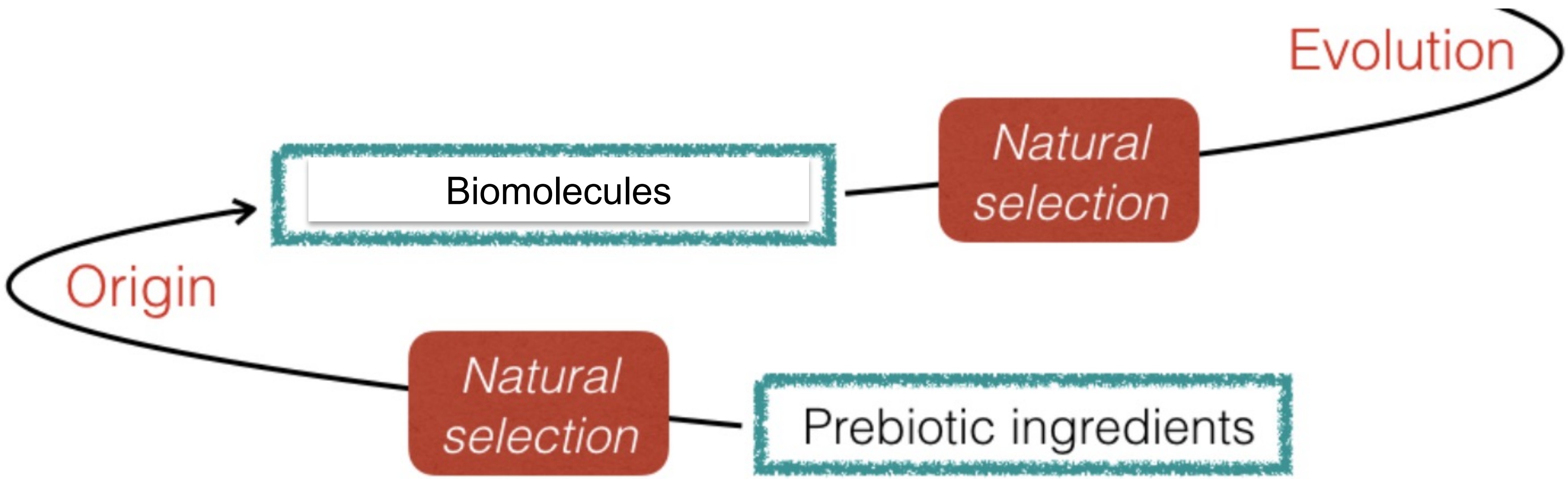


The unity of terrestrial biomolecules may indicate that:

all terrestrial organisms share a common origin

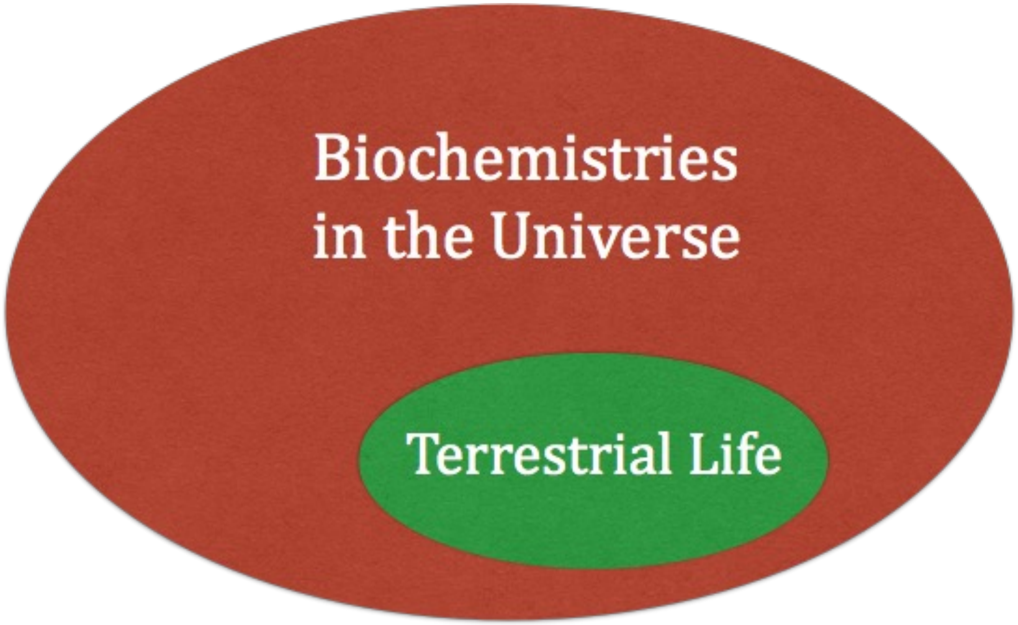
and/or that

terrestrial biomolecules are the best fit molecular constituents
with metabolic and genetic capabilities
that may emerge from spontaneous prebiotic pathways



Possible types of chemical life in the Universe

In order to set the life that we know in a cosmic context
we may consider terrestrial life as a special case
of a more universal chemical phenomenon



Constraints on possible types of biochemistry

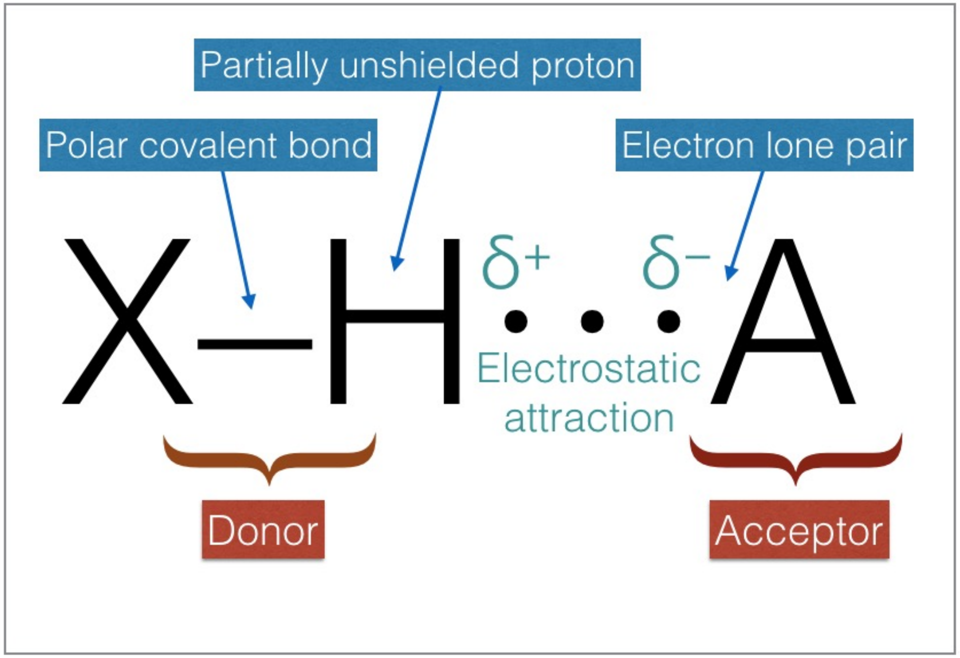
Metabolic and genetic molecules require different types of chemical bonds:

1: Covalent bonds holding the atomic chains of biomolecules

2: Weak, directional chemical bonds for intermolecular or intramolecular interactions

Hydrogen bonds are the only type of chemical bonds that can provide weak, directional interactions required for metabolic and genetic molecular processes

(see Vladilo & Hassanali, *Life*, 2018, 8, 1)



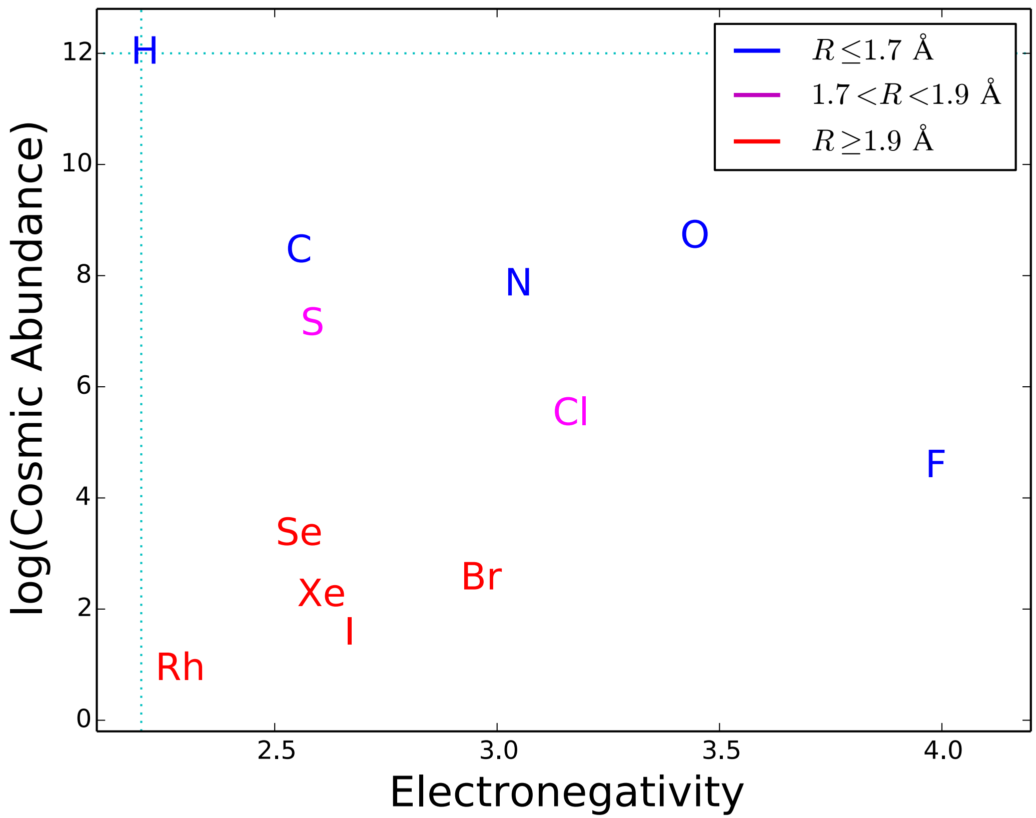
Hydrogen bonds and life in the universe:

Constraints on possible types of biochemistry

Based on the electronegativity (the tendency to attract electrons), only a few elements are suitable for hydrogen bonding

Among cosmically abundant elements, mostly N, O and C

Viable biochemistries are constrained by the necessity of hydrogen bonding



Hypothetical, non-terrestrial biochemistries

Is it possible to replace carbon ?

Silicon has been considered as a potential alternative

Silicon versus carbon

Silicon and carbon lie in the same column of the Periodic Table

Silicon based chemistry, however, is by far less flexible than carbon chemistry

- −Si is not able to form double covalent bonds with the same easiness as C
- −The larger volume occupied by the external electronic orbitals of silicon tend to reduce the superposition of *p* orbitals

The properties of silicon and carbon are quite different in many respects

- −For instance, the electronegativities are different
- −According to the Pauling's scale of electronegativity:

$$\chi(H)=2.2 \qquad \chi(C)=2.55 \qquad \chi(Si)=1.90$$

- −As a result, the polarities of C–H bond are inverted compared to the polarities of Si–H bonds

$$\delta^- \text{ C–H } \delta^+ \qquad\qquad \delta^+ \text{ Si–H } \delta^-$$

Prevents formation of hydrogen bonds

Role of silicon in biochemistry

Due to its electronegativity, lower than that of hydrogen, Si is not able to participate in hydrogen bonding

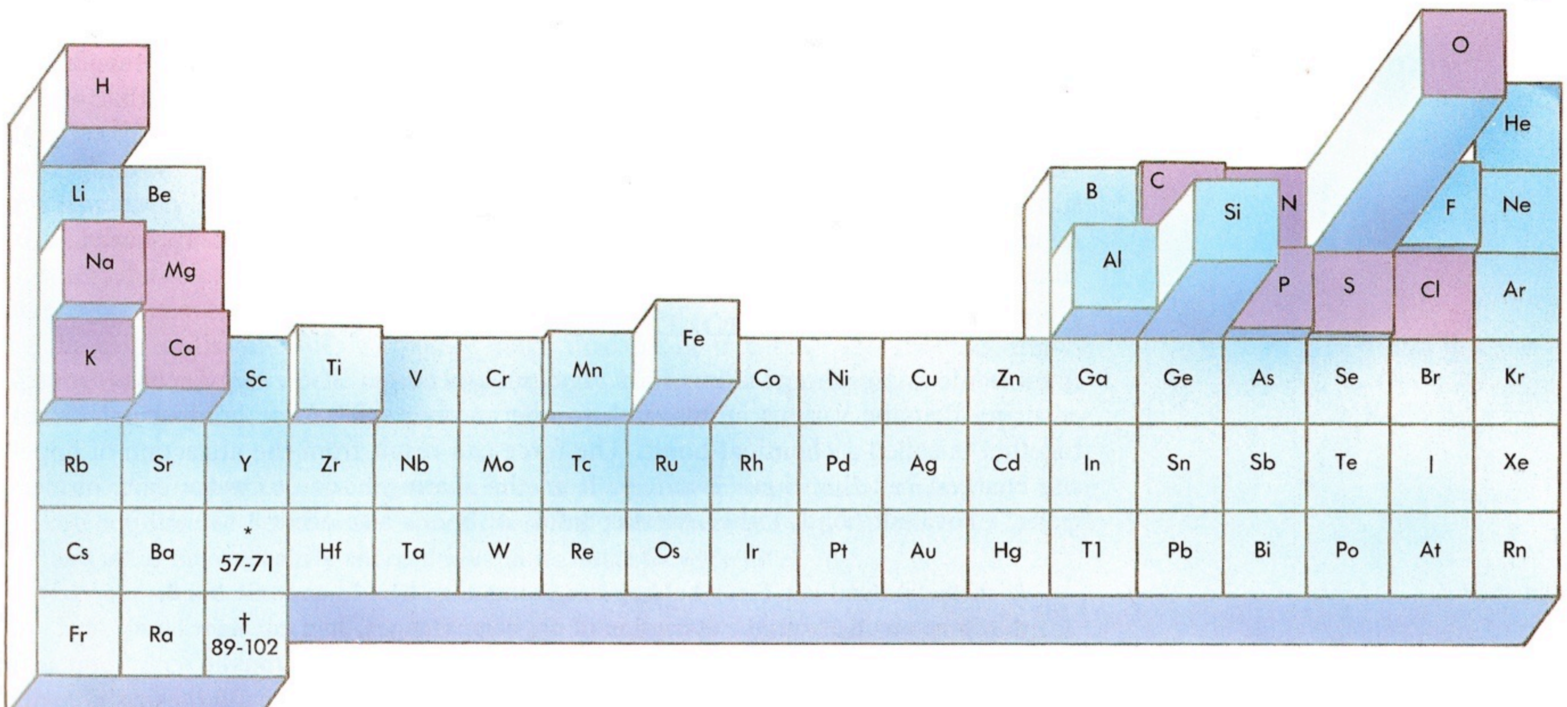
Based on the hydrogen bond requirements, Si can hardly play a role in the chemical groups of genetic and metabolic molecules

The example of terrestrial life shows that Si can play other roles in living organisms, typically related to structural support

- One of the best examples is the presence of silicates in the shells of diatoms (unicellular algae)
- Silicon, in different forms, is employed also by plants (e.g., to form rigid protrusions) and animals (e.g., in hair, nails, and bones)

The chemical abundances of elements in the Earth crust
provide hints on the relative importance of silicon and carbon in biochemistry

Legenda: the biological elements are shown in pink color
Abundances in the earth crust are indicated by the height of boxes



Life prefers carbon-based biochemistry, rather than silicon-based biochemistry, despite the high value of the Si/C abundance ratio at the surface of the Earth

Hypothetical, non-terrestrial biochemistries

Is it possible to replace water ?

Cosmically abundant molecules have been considered as potential alternatives to water

Comparison of water with other molecules

Main properties of water and of some polar or non-polar molecules

Proprietà	Note	H_2O	NH_3	HCN	HF	H_2S	CH_3OH	N_2H_4	CH_4	C_2H_6
μ	(a)	18.0	17.0	27.0	20.0	34.1	32.0	32.1	16.0	30.1
ρ	(b)	0.997	0.696	0.684	0.818	1.393	0.793	1.00	0.426	0.572
p	(c)	1.85	1.46	2.99	1.83	0.98	1.6	1.9	0.00	0.00
T_{fus}	(d)	0	−78	−13	−83	−86	−94	2	−182	−172
T_{boil}	(d)	100	−33	26	20	−60	65	114	−162	−89
ΔT_{liq}	(e)	100	44	39	103	26	159	111	20	83
ΔH_{vap}	(f)	40.7	23.3	25.2	30.3	18.7	40.5	40.9	8.2	14.7
$\Pi_i\, a_i$	(g)	-3.4	-4.3	-7.9	-7.6	-4.9	-7.1	-8.5	-3.8	-7.5

(a) Peso molecolare in unità di masse atomiche. (b) Densità in g/ml. (c) Momento di dipolo in debye (1 D $= 10^{-10}$ esu · Å). (d) Punti di fusione e di ebollizione in °C alla pressione di 1 bar. (e) Intervallo di temperature in cui il composto è in fase liquida alla pressione di 1 bar. (f) Entalpia di vaporizzazione in kJ/mol. (g) Disponibilità cosmica.

Critical factors:

polarity, liquid phase interval, specific heat, cosmic abundance

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The comparison with other molecules generally favours water as an optimal medium for life

Other polar solvents, such as HF, have some interesting properties, but are by far less abundant than water in the cosmos.

Here the index in the row (g) represents the product of the cosmic abundances of the elements that compose the molecule

Water also has a relatively high specific heat, which is useful to stabilize the temperature of living systems

Hydrazine

- N_2H_4 is liquid in a broad range of temperatures and is an excellent polar solvent, with polar strength similar to that of H_2O
- Also its dielectric constant and viscosity are very similar to water

- Hydrazine is a very reactive molecule and decomposes extremely fast in the presence of oxygen, therefore it not a good solvent for life if oxygen is present
  - Low temperatures in an anoxic environment perhaps would be conducive to controlled biochemical reactions at a reasonable speed
  - Hydrazine is not an abundant molecule

- In summary, hydrazine does not appear to be a promising solvent candidate despite having some favourable properties

Ammonia

- NH_3 is polar, with polar strength similar to that of H_2O
  - The weaker capability of hydrogen bonding (compared to water) makes ammonia less ideal to form of a molecular network able to support interactions between biomolecules

- NH_3 is liquid at lower temperatures than water
  - An hypothetical life with liquid ammonia as a medium would operate at low temperatures, meaning <u>slow chemical reactions and low thermal energy</u>

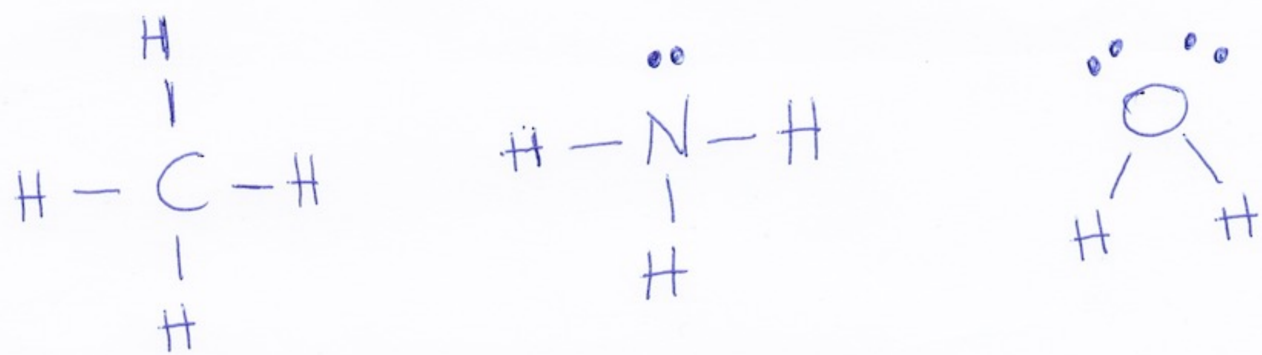
- Like water, ammonia undergoes molecular autoionisation to form its acid and base conjugates:
  - $2\ NH_3\ (aq) \leftarrow\rightarrow NH_4^+\ (aq) + NH_2^-\ (aq)$
- These ions are less suitable than H^+ and OH^- for charge transportation and for taking part in metabolic pathways

Non-polar hydrocarbons

- CH_4 and C_2H_6 are non polar
  - They are not able to form a network of hydrogen bonds able to support the interactions between genetic and catalytic molecules
- They are liquid at very low temperatures
  - An hypothetical life based on liquid CH_4 and C_2H_6 would be characterized by very slow chemical reactions and very low thermal energy
- In principle, bilayers could still be formed in liquid hydrocarbons
  - with reversed shape

The medium of life in exobiology: water versus other solvents

Among cosmically abundant molecules,
water has the highest capability of hydrogen bonding



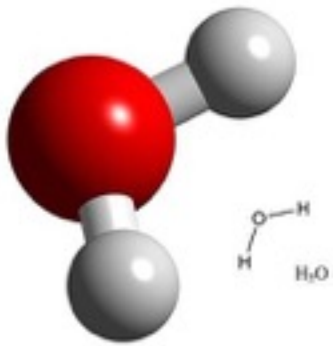
4 donors no acceptors	3 donors 1 acceptor	2 donors 2 acceptors

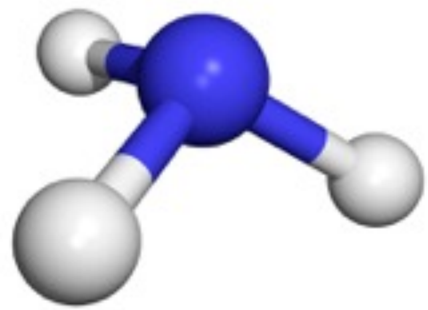
As a result, water has the capability of forming
a molecular network that supports and actively interacts
with the molecules specialized in genetic and catalytic properties

Hydrogen bonds and the molecular medium of life processes

Among cosmically abundant molecules,

water has the best capability to form a 3D network of hydrogen bonds





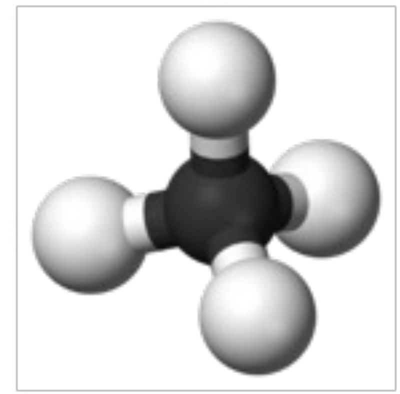


Table 4. Hydrogen bond (HB) properties of cosmically abundant, small molecules.

	HB strength and directionality	Number[a] of HB donors	Number[b] of HB acceptors	Potential HB partners	Capability of HB network formation	Multiplicity of H bonding in the HB network
CH_4	Weak	4	0	Only acceptors	Absent	—
NH_3	Strong	3	1	Acceptors & donors	Present (1D)	Absent
H_2O	Strong	2	2	Acceptors & donors	Present (3D)	Present

[a] The number of hydrogen bond donors equals the number of hydrogen atoms in each molecule.

[b] The number of hydrogen bond acceptors is the number of lone pairs of electrons in the outer shells of C, N or O.

Types of chemical life in the universe

- The special properties of water and carbon
- The hydrogen bond requirements
- The high cosmic abundances of H, O, N and C

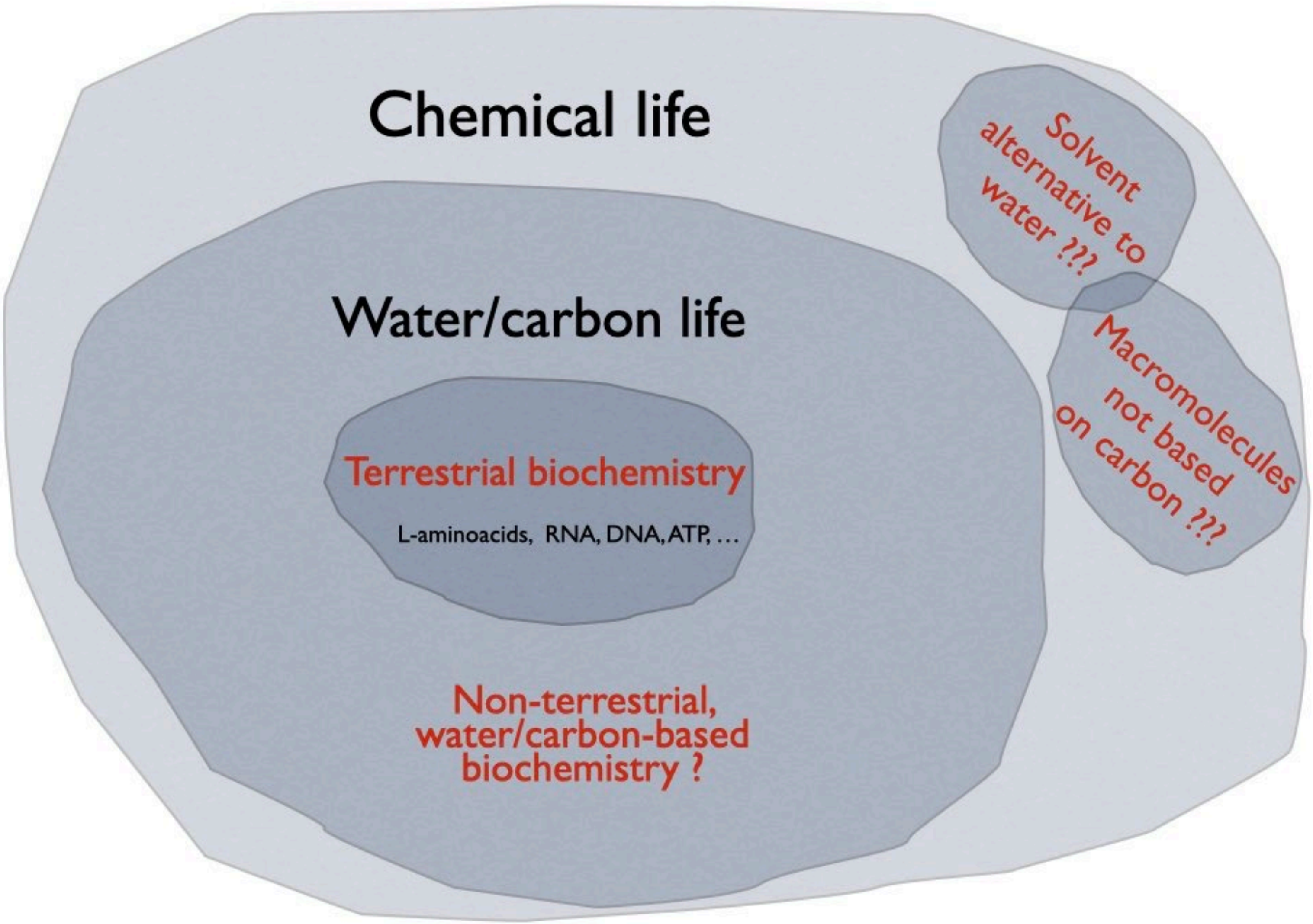
suggest that water and carbon-based biochemistry is the most likely type of biochemistry that may exist in the universe

We cannot exclude that alternative biochemistries may exist, but their viability needs to be investigated

Life based on carbon and water does not need to be "terrestrial":

We may expect significant differences at the level of molecular constituents with respect to terrestrial biomolecules

Possible types of chemical life in the Universe



Life based on carbon and water may show significant differences with respect to the terrestrial one

Genetic information

In non-terrestrial organisms, the genetic information might be coded using molecules other than the RNA and DNA

Also the genetic code might be different

Chirality

In non-terrestrial organisms, biological macromolecules might have a type of chirality different from that of terrestrial life (as an example the amino acids, if present, might have D, rather than L, chirality)

Unless there are some specific processes that bias the molecular chirality (e.g. parity violation in beta decays)

Testing alternative biochemistries starting from manipulations of terrestrial life

The viability of alternative forms of chemical life can be tested
in the framework of biotechnology studies

Synthetic biology

Emerging scientific field at the cross road between
biotechnology and nanotechnology

Artificial design and engineering of biological systems and living organisms for purposes of improving applications for industry or biological research

Xenobiology

Novel biological systems and biochemistries
that differ from the canonical DNA-RNA-20 amino acid system

Expanding the genetic alphabet

Some experiments target the replacement or enlargement of the genetic alphabet of DNA with unnatural base pairs

The viability of candidate bases for possible incorporation in the DNA is being tested

For example, DNA has been designed that has - instead of the four standard bases A,T,G, and C - six bases A, T, G, C, and the two new ones P and Z

New candidate bases may potentially yield a large number of base pairs

Genetic code engineering

One of the goals of xenobiology is to rewrite the genetic code.

The repertoire of 20 canonical amino acids can in principle be expanded.

Existing codons can in principle be reprogrammed

An even more radical approach is the change of a triplet codon to a quadruplet and even pentaplet codon

New types of enzymes can in principle be synthesized

Experiments of this type are under way and have already shown the feasibility of changes of this type in a limited number of cases