#### Astrobiology Life in a cosmic context

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# The diversity of terrestrial life

Terrestrial life shows a great diversity, with a large number of species

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

The total number of extinct species in the course of the evolution of terrestrial life is estimated to be in the order of a few 10<sup>9</sup>

The largest diversity is found in the unicellular world, rather than among multicellular organisms

# The unity of terrestrial life

Despite their extremely large diversity, all terrestial organisms show a remarkable unity <u>at the molecular level</u>

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

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

# The unity of terrestrial life

The unity of terrestrial life suggests a <u>common origin</u> of all terrestrial organisms

The unity of terrestrial life may also suggest that the biomolecules that we know:

are the result of the <u>most probable chemical pathways</u>
are <u>best fit for their specific functions</u>

# Possible types of chemical life in the Universe

Terrestrial life as a special case of a more universal chemical phenomenon

Biochemistries in the Universe

**Terrestrial Life** 

Hypothetical, non-terrestrial biochemistries

Is it possible to replace carbon?

Silicon has been considered as a potential alternative to carbon

#### Silicon versus carbon

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

-Silicon has been proposed as a possible alternative for biological molecules

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 (i.e. the tendency to attract electrons) are different

-According to the Pauling's scale of electronegativity:

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

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

 $\delta^-$  C-H  $\delta^+$   $\delta^+$  Si-H  $\delta^-$ 

#### Role of silicon in biochemistry

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

Therefore, silicon cannot play a role in the chemical groups involved in intermolecular, hydrogen-bond interactions essential for life molecular processes, such as intermolecular recognition, molecular replication, or molecular folding

The example of terrestrial life shows that silicon 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 larger flexibility of carbon, compared to silicon, is supported by astronomical observations of interstellar molecules

Complex gas-phase molecules based on Si have not been found Si tends to be incorporated in the form of silicates in the refractory component of dust grains

Table 5.4 Some complex carbon compounds detected in the interstellar medium and meteorites.

Number of Atoms								
6	7	8	9	> 9				
$C_5H$ , $HCH_2OH$	$\mathrm{CH}_3\mathrm{C}_2\mathrm{H}$	$CH_3OCHO$	$(CH_3)_2O$	$(CH_3)_2CO$				
$\rm NH_2CHO$ ,	$\rm CH_3 CHO$	$\mathrm{CH}_3\mathrm{C}_3\mathrm{N}$	$\rm CH_3 CH_2 OH$	$\mathrm{HC}_{9}\mathrm{N}$				
$\rm CH_3CN$	$HC_5N, C_6H$	$C_7H, H_2C_6$	$\mathrm{CH}_3\mathrm{CH}_2\mathrm{CN}$	$HC_{11}N$				
$CH_3NC$ ,	$\mathrm{CH}_3\mathrm{NH}_2$		$HC_7N$	$C_6H_6, C_{60}^+$				
$\rm CH_3SH$	$\rm CH_2 CHCN$		$CH_3C_4H, C_8H$	PAHs,				
$H_2C_4,$	$C_2H_4O$		$\mathrm{CH}_3\mathrm{C}_4\mathrm{N}$	glycine?				
$\mathrm{HCC}_{2}\mathrm{HO},$								
$C_5H, C_5N,$								
$C_5O$								

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

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



Despite the highest abundance of silicon, terrestrial life has "chosen" carbon

This provides further evidence that carbon-based biochemistry is more flexible than silicon-based biochemistry

#### Molecular processes and chemical interactions of life

Molecular interactions of life require different types of chemical bonds

- 1: Structural bonds holding the atomic chains of biomolecules
- 2: Non-invasive interactions between atomic chains and molecules
- 3: Weak, directional interactions for intermolecular recognition

Hydrogen bonds are the only type of chemical bonds that can effectively carry out type-2 and type-3 interactions



### Hydrogen bonds and life in the universe: Constraints on possible types of biochemistry



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										
ſ	Proprietà	Note	$H_2O$	NH <sub>3</sub>	HCN	HF	$H_2S$	CH <sub>3</sub> OH	$N_2H_4$	$CH_4$	$C_2H_6$
Ì	$\mu$	(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
	$T_{ m fus}$	(d)	0	-78	-13	-83	-86	-94	2	-182	-172
	$T_{ m boil}$	(d)	100	-33	26	20	-60	65	114	-162	-89
	$\Delta T_{ m lig}$	(e)	100	44	39	103	26	159	111	20	83
	$\Delta H_{\mathrm{vap}}$	(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

#### Comparison of water with other molecules

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Proprietà	Note	H <sub>2</sub> O	NH <sub>3</sub>	HCN	HF	$H_2S$	CH <sub>3</sub> OH	$N_2H_4$	CH <sub>4</sub>	$C_2H_6$
$\mu$	<i>(a)</i>	18.0	17.0	27.0	20.0	34.1	32.0	32.1	16.0	30.1
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The comparison with other molecules generally favours water as an optimal medium for life

For instance other polar solvents, such as HF, are interesting in principle, 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 atoms that compose the molecule.

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

#### 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<sub>3</sub> 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</u> <u>low thermal energy</u>
- Like water, ammonia undergoes molecular autoionisation to form its acid and base conjugates:

 $-2 \operatorname{NH}_{3}(\operatorname{aq}) \leftrightarrow \operatorname{NH}_{4^{+}}(\operatorname{aq}) + \operatorname{NH}_{2^{-}}(\operatorname{aq})$ 

• These ions are larger than H<sup>+</sup> and OH<sup>-</sup> ions and are less suitable for charge transportation and for taking part in metabolic pathways

### 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, making it an ideal rocket fuel, but not a good solvent for life in the presence of oxygen
  - 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

#### 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 <u>slow chemical reactions</u> and very <u>low</u> <u>thermal energy</u>
- In principle, micelles and bilayers could still be formed in liquid hydrocarbons
  - with reversed shape, if we use amphiphilic molecules with polar heads
  - with "typical" shape, if we use amphiphilic molecules with nonpolar heads

### The medium of life in exobiology: water versus other solvents

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



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 <sup>a</sup> of HB donors	Number <sup>b</sup> 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

<sup>*a*</sup> The number of hydrogen bond donors equals the number of hydrogen atoms in each molecule. <sup>*b*</sup> 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
- all suggest that water and carbon-based biochemistry is the most likely type of biochemistry existing 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

# 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)

# 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

# Testing alternative biochemistries starting from manipulations of terrestrial life

The current advancements in biotechnology provide the possibility to test the viability of alternative forms of chemical life

#### 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

Xenobiology (XB) is a subfield of synthetic biology that describes a form of biology that is not found in nature

In practice it describes novel biological systems and biochemistries that differ from the canonical DNA-RNA-20 amino acid system (i.e., the classical central dogma in molecular biology)

Originally a research on alternative forms of DNA was driven by the question of how life evolved on earth and why RNA and DNA were selected by (chemical) evolution over other possible nucleic acid structures

# Expanding the genetic alphabet

Instead of modifying the backbones, other experiments target the replacement or enlargement of the genetic alphabet of DNA with <u>unnatural base pairs</u>

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

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

# Alternative biomolecules for metabolism

New types of enzymes can in principle be synthesized

This possibility can be expanded by changing the repertoire of 20 canonical amino acids

The experiments of xenobiology may eventually demonstrate that life based on carbon and water can potentially use a broad spectrum of biomolecules

An interesting question related to alternative forms of carbon-water life is whether such forms can interact with life-as-we-know-it