# Exobiology 1

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Origin of life

*The fundamental question*

Formation of Earth 4.6Ga

Evidence of life on Earth 3.5Ga on ancient rocks \(\Rightarrow\) **life developed rapidly**

**Spontaneous generation hypothesis**: based on observation of spontaneous apparition of flies and maggots on rotting meat, lice from sweats, eels and fish from sea mud, frogs and mice from moist soil

1668 **Francesco Redi**: demonstrates that maggots are larvae of flies \(\Rightarrow\) if meat kept in sealed container no maggots appear

1676 **Anthony van Leeuwenhoek**: discover micro-organism \(\Rightarrow\) consistent with spontaneous generation?

1862 **Louis Pasteur**: if a solution is properly sterilized and excluded from contact with micro-organisms it remains sterile indefinitely

**All life comes from life \(\Rightarrow\) poses the problem of origin of life itself**

*Inescapable logical conclusion: life arises from non-living materials present in the Universe*
Definitions of life

More than one definition

NASA definition (Gerald Joyce): life is a self sustaining chemical system capable of undergoing Darwinian evolution

Basic characteristics:

1. Capacity of self-sustention + self-replication
2. Capacity of evolution (Darwin)?

Reproduction ⇒ Evolution

- During self-replication, a system produce copies of himself
- Imperfection of copying process or mutation during the process produces different characteristics
- Natural selection favors particular characteristics
- Increases chance of survival and self-replication

Charles Darwin (1809-1882): Descent with modifications
- Any population consists of individuals that are slightly different from one another
- A different characteristics that gives an advantage to stay alive increases also the chance of the individual to reproduce
- Evolution of trait of individual

Ex. Galapagos finches: in arid environment birds with beaks better suited for eating cactus ⇒ they get more food ⇒ gain better condition to mate ⇒ survival of fittest

Natural selection: variations already exist in population, nature only select the best adapted varieties

NASA definition of life = can only be applied to population ⇒ exclude single specimen, artifacts, chemical and artificial life forms (Pier Luigi Luisi 2006)
Complementary (more basic) = energy + material must be extracted from surrounding ⇒ some sort of apparatus (metabolism) must be present to govern + facilitate chemistry of life

Metabolism (Merriam-Webster definition):
1a: the sum of the processes in the buildup and destruction of protoplasm; specifically: the chemical changes in living cells by which energy is provided for vital processes and activities and new material is assimilated b: the sum of the processes by which a particular substance is handled in the living body c: the sum of the metabolic activities taking place in a particular environment <the metabolism of a lake>
2: metamorphosis 2 —usually used in combination <holometabolism>

Alexander Oparin (1961): 6 properties
1. Capability of exchange of material with surrounding medium
2. Capability of growth
3. Capability of population growth
4. Capability of self reproduction
5. Capability of movement
6. Capability of being excited

Definition of life is not easy because leaving systems are complex structures ⇒ must have started as simple bodies which transformed gradually over extended period of time (~4 Ga) into more and more complex and individualized entities – this complexification history must be included in definition of leaving things

The myth of life – often the definition of life includes concepts which are not clear – like, for example the entropy - life is conceived as violating thermodynamic entropy (e.g. Erwin Schrödinger 1944 book: What is Life?)

This is probably not correct, because it considers leaving systems as closed ones, while they are really connected with their environment – as a result of metabolisms, internal entropy may decrease, but this is temporarily (all leaving systems degrades over time) and most probably this happens at the expense of an increase of entropy in its environment
**Working definition** – *individualized – chemical system* - capable of **metabolic processes**

A. Self maintenance of structures
   a. **Isolation** = protection from environment ↔ **membranes**
   b. Growth = accumulation of specific substances
      i. Reproduction - **Mitosis**
         a. Mutations (random)
         b. Sexual exchanges (specific)
            i. evolution

B. Exchange of information + material with surrounding
   a) Sensing of environment - photosensitivity + gravitosensitivity
      i. Senses
         I. Intelligence and Consciousness – (assimilation + integration + synthesis)
   b) Mobility ⇒ random ⇒ specific
   c) Chemical compatibility
      i. nutrition

C. Transformation of matter into energy (physical + chemical energy) and specific products or byproducts
Basic constituents

All currently known life forms utilize carbon-based organic compounds

Carbon

- Chemical versatility: can form chemical bonds with many different atoms
- Can form organic compounds that easily dissolve in water
- Only element that can form molecules of sufficient sizes to perform functions necessary for life

Organic compounds also contain: H, O, N, S, P + Fe, Mg, Zn

Most abundant elements (atoms/100000 total atoms)

<table>
<thead>
<tr>
<th>Order</th>
<th>Universe</th>
<th>Humans</th>
<th>Ocean</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>92714</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>7185</td>
<td>O</td>
</tr>
<tr>
<td>3</td>
<td>O</td>
<td>50</td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td>Ne</td>
<td>20</td>
<td>N</td>
</tr>
<tr>
<td>5</td>
<td>N</td>
<td>15</td>
<td>Ca</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>8</td>
<td>P</td>
</tr>
<tr>
<td>7</td>
<td>Si</td>
<td>2.3</td>
<td>S-S</td>
</tr>
<tr>
<td>8</td>
<td>Mg</td>
<td>2.1</td>
<td>Na</td>
</tr>
<tr>
<td>9</td>
<td>Fe</td>
<td>1.4</td>
<td>K</td>
</tr>
<tr>
<td>10</td>
<td>S</td>
<td>0.9</td>
<td>Cl</td>
</tr>
</tbody>
</table>

He and Ne chemically non active – do not bind with other atoms

- First 4 elements of life among most common in Universe – as expected
- First 2 elements of life + traces of minerals (Ca, Na, K and Cl) most common in Ocean ⇒ strong relation between water and life
- What is the origin of P?
Living tissues formed by 70% in mass of water

Water

- Fundamental for development of living organisms ⇒ facilitate interactions of organisms with each others
- The natural solvent ⇒ molecules can dissolve easily facilitating reactions
- Exist as liquid in temperature range not too cold to sustain biochemical reactions and not too hot to stop many organic bonds to form
  - Alternative = Ammonia – liquid at lower temperatures ⇒ too cold for chemical reactions

Water is a Polar solvent

- Each side carries a different electrical charge
- Two molecules interact to form a H bonds (a)
- Polar organic molecules readily dissolve (b) in water
  - Polar = hydrophilic molecule (water lovers)
- Apolar = hydrophobic molecule (water haters) – not dissolved by water (c)
**Organic molecules**

Except for water most molecules in living systems are large organic molecules.

### Table 1.2 Types and abundances of the molecules that make up a bacterium.

<table>
<thead>
<tr>
<th></th>
<th>Percent of total weight</th>
<th>Number of types of molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>inorganic ions, e.g. Na(^+), K(^+) and Ca(^{2+})</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>small organic molecules ((&lt;1000) atomic units), e.g. fatty acids, sugars, amino acids, nucleotides</td>
<td>7</td>
<td>750</td>
</tr>
<tr>
<td>large organic molecules ((&gt;100000) atomic units), e.g. collections of lipids, carbohydrates, proteins, nucleic acids</td>
<td>22</td>
<td>5000</td>
</tr>
</tbody>
</table>

4 types with different functions:

1. Lipids
2. Carbohydrates
3. Proteins
4. Nucleic acids

Individual organic molecules = **monomers** combine to form complex molecules = **polymers**
Lipids - fats and oils

- Different groups – 1 hydrophobic + 1 hydrophilic end
- Poorly soluble in water ⇒ rarely found as individual molecules
- Arrange themselves into weakly bonded aggregates = macromolecules
- Convenient and compact way to store energy
- Weak bonding ⇒ high degree of flexibility ⇒ useful for membranes

<table>
<thead>
<tr>
<th>hydrophilic end</th>
<th>COOH</th>
<th>COOH</th>
<th>-O=C=O</th>
<th>-O=C=O</th>
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<tr>
<td>CH₂</td>
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</tbody>
</table>

octadecanoic acid (stearic acid) octadecenoic acid (oleic acid)
Carbohydrates

- Molecules with many hydroxyl (–OH) groups
- Hydroxyls are polar ⇒ soluble in water
- Sugars = common carbohydrates
  - Form rings like structures when dissolved in water
  - Pentose ⇒ 5 atoms; hexose ⇒ 6 atoms
- Polysaccharides = large carbohydrates structures = sugar monomers connected together
  - Polymerization: occurs by reactions that involve the loss of water
  - Useful energy stores + structure support of organisms
Proteins

- Most complex macromolecules in living systems
- Long trains of amino acids (a) linked together by polymerization (b)

![Amino acid structure](image)

- 20 different amino acids
- Most important of life chemicals + various numbers of roles
  - Structures (fingernails, hair, etc.)
  - Catalyst - ex. Digestion ⇒ enzymes

Nucleic acids

- Largest macromolecules in living systems
- Exist as collection of nucleotides (a) linked together in long linear polymers (b)
- Formation process involves loss of water = polymerization
- Structure of nucleotide - contains:
  - Five carbon sugar molecules
  - One or more phosphate groups
  - Nitrogen compound (nitrogenous base)
DNA: deoxyribonucleic acids

- Contains four different nucleotides each possessing identical sugar and phosphate groups but different bases
  - Adenine – A
  - Guanine – G
  - Cytosine – C
  - Thymine – T

- Form two long molecules strands that coil about each other like an helix
- Bonds = 2 nucleotides each contributing ½
- Bases always match: A-T and G-C
- Bases attached to helical strands by sugar groups connected together by phosphate groups

*DNA is a structure that enables a biological molecule to replicate itself*
Replication process of DNA

- Special protein (enzyme) separate the strands
- The single strands hook up with spare nucleotides present in liquid surrounding molecules
- Each base latches on to complementary bases
- Sugar + phosphate groups join to form an helix $\Rightarrow$ 2 new DNA formed

![Diagram of DNA replication process](image)

**DNA also account for variations between individuals of same species and for differences between species**

**DNA hybridization** – a technique to determine the level of similarity of species

- Closely related species have similar nucleotides sequences and splice relatively well
- DNA unzipped by heating and combined with other DNA species
- Mixture cooled to allow different strands to splice together
- The strength of bonding is proportional to species relationship
- When heated again the less related species unzip at lower temperature
Other functions of DNA

- Keeping and passing information
  - Genetic code = sequences of bases in the molecules
- Govern protein synthesis
  - Direct production of 1000s of proteins needed for structures + functions of living systems

RNA: Ribonucleic acids

- Different from DNA
  - Sugar components = ribose
  - Thymine replaced by Uracil, which pairs with Adenine – A-U

The transcription of DNA passes by messenger RNA (mRNA)

Protein production

- DNA unzip
- Form mRNA which is released in the system
- DNA reform
- Released mRNA carries its own version of DNA into a region containing free amino acids
- Molecules factories (ribosomes) use the mRNA to combine the amino acids into long protein chains
The Cell

Cell = basic structure unit of all present-day organisms – if you can explain the origin of cells then you can explain the origin of life

- Facilitate biochemical reactions and store genetic information
- Vary in number, shape and functions
- Bacteria = single cell organism – possibly “first” form (or model of first form) of life
- Humans $10^{12}$ cells

Cell structure
- A small bag of molecules separated from the outside world by a membrane
- At the center reside strands of DNA surrounded by cytosol (salt water solution) + enzymes (proteins) + ribosomes
- Soft membranes formed by lipids and proteins protect the content of the cell
- The cell rigidity come from a wall made of carbohydrates molecules + short chains of amino acids
- Separate during DNA replication
Two forms of cells – without a nucleus = **prokaryotes** (Old Greek pro- before + karyon nut or kernel) and with a nucleus = **eukaryotes**

- Eukaryotes do have "true" nuclei containing their DNA, whereas the genetic material in prokaryotes is not membrane-bound
- Most prokaryotes are unicellular, while most eukaryotes are multicellular
- Most prokaryotes are **bacteria**, and the two terms are often treated as synonyms
- Prokaryotes are smaller than eukaryotes

While prokaryotes are nearly always unicellular, some are capable of forming groups of cells called colonies. Individuals that make up such bacterial colonies most often still act independent of one another. Colonies are formed by organisms that remain attached following cell division, sometimes through the help of a secreted slimy layer.

Prokaryotes are separated in two domains: **bacteria** and **Archaea** (Carl Woese 1977)
Prokaryotes are found in nearly all environments on earth

Archaea seem to thrive in harsh conditions, such as high temperatures, thermophiles, or salinity, halophiles = extremophiles

Many prokaryotes live in or on the bodies of other organisms, including humans.

First living cells = some form of prokaryote - may have developed out of protobionts

- Fossilized prokaryotes ~ 3.5 Ma old have been discovered
- Most successful and abundant organism even today

Eukaryotes only formed later, from symbiosis of multiple prokaryote ancestors

- First evidence in the fossil record appears ~ 1.7 Ga years ago, although genetic evidence suggests they could have formed as early as 3 Ga years ago

Prokaryotes diversified greatly throughout their long existence

- The metabolism of prokaryotes is far more varied than that of eukaryotes, leading to many highly distinct types of prokaryotes
  - For example, in addition to using photosynthesis or organic compounds for energy like eukaryotes do, prokaryotes may obtain energy from inorganic chemicals such as hydrogen sulfide

Protobionts are organisms that are controversially considered to have possibly been the precursors to prokaryotic cells

- Aggregate of abiotically produced organic molecules surrounded by a membrane or a membrane-like structure

- Have spontaneously formed early in the earth's development, according to the laws of physics and chemistry.

- Exhibit some of the properties associated with life, including simple reproduction and metabolism, as well as the maintenance of an internal chemical environment different from that of their surroundings.

- Key step in the origin of life on earth - Sidney W. Fox and Aleksandr Oparin – experiments in conditions much like what the early Earth is thought to have been like - liposomes and microspheres, which have membrane structure similar to the phospholipid bilayer found in cells form naturally
Identification of past and present life

Biological markers (or biomarkers)

- First used for petroleum exploration
- Used to determine when and where the correct environments existed in the geological past to produce and accumulate fossil fuels
- Most useful tool – biomarkers are specific to particular organisms in organic rich rocks
- Diagnostic value of the biomarker increases when the organisms are restricted to a certain environments

In astrobiology biomarker = any evidence that indicates present or past life detected in situ or remotely

1999 Des Marais & Walter - principal biomarkers

- Cellular remains
- Textural structures in sediments that record structures and/or functions of biological communities
- Biologically produced (biogenic) organic matter
- Minerals whose deposition was affected by biological processes
- Stable isotopic patterns that reflect biological activity
- Atmospheric constituents whose relative concentrations require a biological source

Problems: definition of biomarker is subjective - Ex. Aromatic Hydrocarbons

- Class of organic molecules that can be generated by heat + pressure on biological remains of living organism
- Major component of coal = fossil remains of land plants
- However, can also be produced by non living things like combustion engines or giant stars

Approaches to study the origin of life

1. **Bottom-up** – focuses on collection of inanimate elements, molecules and minerals with known properties and attempt to figure out how they combine to form living organisms
2. **Top-down** – looks at present biology and uses this information to extrapolate back towards simplest living entities

The two methods should converge, although how is not obvious
**Origin of Organic matter in the Universe**

A **chemical compound** is a substance consisting of two or more elements chemically bonded.

An **organic compound** is any member of a large class of chemical compounds whose molecules contain carbon.

Carbon-rich red giant stars produce large amounts of Organic Molecules

- Chemical reactions similar to those in candle flame \(\Rightarrow\) ex. aromatic hydrocarbons
- Stellar winds expel the molecules into space
- Could be caught-up in environments - **molecular clouds** - where organic matter may be created

**Molecular clouds**

- Coldest (10-20K) and densest parts of ISM
- Key role in evolution of galaxies \(\Rightarrow\) stars + planets form in these systems
  - Deeply embedded clumps of IS gas + dust collapse under their own gravitational attraction
- Numerous different organic molecules identified in IS clouds and **circumstellar envelopes**
- The largest quantity of organic molecules in our Galaxy found in Molecular clouds
  - Form through complicated networks of chemical reactions
  - Any gas hitting dust grain freeze out on it forming icy mantle
  - Once organic compounds attached to grain chemical reactions catalyzed by grain surface and reaction products are processed further by UV and CRs
Molecules detected in ISM + circumstellar envelopes

<table>
<thead>
<tr>
<th>hydrogen species</th>
<th>HD</th>
<th>H$_3^+$</th>
<th>H$_2$D$^+$</th>
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<tr>
<td>CH</td>
<td>CH$^+$</td>
<td>C$_2$</td>
<td>C$_2$H</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>C$_2$H$_2$</td>
<td>C$_3$H (lin)</td>
<td>C$_3$H (circ)</td>
</tr>
<tr>
<td>H$_2$CCC (lin)</td>
<td>C$_4$H</td>
<td>C$_5$</td>
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<td>C$_6$</td>
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<table>
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<tr>
<td>C$_5$O</td>
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<td>CH$_3$OCH$_3$</td>
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<td>CH$_3$C$_2$N</td>
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<table>
<thead>
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<tbody>
<tr>
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<table>
<thead>
<tr>
<th>other species</th>
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<tr>
<td>SH</td>
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<tr>
<td>SIC</td>
</tr>
<tr>
<td>AlCl</td>
</tr>
<tr>
<td>H$_2$S</td>
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<tr>
<td>NaCN</td>
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<tr>
<td>HSiC$_2$</td>
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</tbody>
</table>

Note: (circ) denotes circular molecules and (lin) denotes linear molecules.

- Further chemistry in warm (200-400K) and dense (100 H$_2$ mol/cm$^3$) areas of gas around recently formed stars
  - **Hot cores** most chemically diverse regions of ISM
  - When star form, radiation evaporates ice and molecules return to gas phase
  - **Solar nebula** = spinning disk of dust + gas
  - Inherit variety of organic molecules from its molecular cloud
  - Some organic matter synthesized anew?
  - Transform into solar system (how?)
Synthesis of organic molecules on early Earth

Much of chemistry of Universe is organic chemistry

- Organic compounds relatively simple molecules compared to organic molecules in living organisms

Surfaces of planets + atmosphere = next opportunity for generation of complex organic molecules

Energy sources

Energy is required to sustain and maintain order

- Two roles of energy for origin of life:
  1. Fuel reactions to synthesize organic matter
  2. Sustain primitive life

<table>
<thead>
<tr>
<th>Sources of energy</th>
<th>J m(^2) yr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun</td>
<td>1.09 \times 10^6</td>
</tr>
<tr>
<td>UV light</td>
<td>1.68 \times 10^3</td>
</tr>
<tr>
<td>Electric discharges (lightning)</td>
<td>1.68</td>
</tr>
<tr>
<td>Cosmic rays</td>
<td>6.0 \times 10^{-4}</td>
</tr>
<tr>
<td>Radioactivity</td>
<td>0.33</td>
</tr>
<tr>
<td>Volcanoes</td>
<td>0.05</td>
</tr>
<tr>
<td>Shock waves (atmospheric entry)</td>
<td>0.46</td>
</tr>
</tbody>
</table>

- Early Sun was 20-30% weaker than today
- Electric discharges – to weak to have played important role
Miller-Urey experiment

Early 1950’s

- Flask of water = primordial ocean
- Heated flask = primitive hydrosphere
- Other flask = primitive atmosphere
  - CH₄ (methane) + NH₃ (ammonia) + H₂ + water vapor
- Continuous electric discharges = lightning
- Interaction of gas + accumulation of products = formation of amino acids

**Ease of production ⇒ phenomenon very common in Universe**

- Miller-Urey experiment has been reproduced many times using different energy sources and slightly different mixtures of gas ⇒ each time biological useful molecules were produced
- However, recent models have shown that early Earth atmosphere was not rich in methane or ammonia because these are easily destroyed by sunlight
  - More stable CO₂ + N + H₂O dominate

⇒ *In situ* production of life organic molecules more difficult than previously thought
Murchison meteorite

Discovered at Murchison, near Melbourne Victoria in Australia (1969)

Carbonaceous chondrite ⇒ origin somewhere between Mars and Jupiter

Unaltered since birth of solar system?

Solvent smells coming from the stone ⇒ evidence for organic molecules

Analysis in Apollo mission laboratory ⇒ several classes of organic compounds found, similar than in Miller-Urey experiment

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Abundance in the Miller–Urey experiment</th>
<th>Abundance in the Murchison meteorite</th>
<th>Found in proteins on Earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>glycine</td>
<td>●●●●</td>
<td>●●●●</td>
<td>yes</td>
</tr>
<tr>
<td>alanine</td>
<td>●●●●</td>
<td>●●●●</td>
<td>yes</td>
</tr>
<tr>
<td>ω-amino-N-butyric acid</td>
<td>●●●</td>
<td>●●●●</td>
<td>no</td>
</tr>
<tr>
<td>α-aminoisobutyric acid</td>
<td>●●●●</td>
<td>●●●</td>
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<tr>
<td>valine</td>
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<td>●●●</td>
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<tr>
<td>norvaline</td>
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<tr>
<td>isovaline</td>
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</tr>
<tr>
<td>proline</td>
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<tr>
<td>pipelic acid</td>
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<tr>
<td>aspartic acid</td>
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<tr>
<td>glutamic acid</td>
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<tr>
<td>β-alanine</td>
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<td>●●●●</td>
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<tr>
<td>β-amino-N-butyric acid</td>
<td>●●</td>
<td>●●●●</td>
<td>no</td>
</tr>
<tr>
<td>β-aminoisobutyric acid</td>
<td>●●</td>
<td>●●●●</td>
<td>no</td>
</tr>
<tr>
<td>γ-aminoobutyric acid</td>
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</tr>
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<td>sarcosine</td>
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<td>N-ethylglycine</td>
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</tr>
<tr>
<td>N-methylisocitrine</td>
<td>●●</td>
<td>●●●●</td>
<td>no</td>
</tr>
</tbody>
</table>

- Early Solar system ⇒ organic chemistry must have taken place
  - Simple organic molecules available in reasonable amount in early solar system
- Polymerization on Earth ⇒ produced life?
Problem

- Abundance of C = indicator of amount of **abiotic organic matter**
- Inwards of asteroids belt organic matter declines abruptly
- Although liquid water present early on Earth, maybe also on Mars, but not outwards ⇒ zone where liquid water exist not more extended than 1.7 A.U.
- Paradoxal situation = organic molecules abundant where there is no liquid water
Origin from space

1961, Juan Oró - abundance of elements composing life more similar to abundance of elements in Universe than on Earth ⇒ organic matter was delivered by meteorites + comets that formed in regions rich in organic molecules

Table 1.6 The biological role and types of organic molecules (both monomers and polymers) found in life and in meteorites.

<table>
<thead>
<tr>
<th>Role</th>
<th>Life</th>
<th>Murchison meteorite</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>lipids (hydrocarbons and acids)</td>
<td>membranes, energy storage</td>
<td>yes</td>
</tr>
<tr>
<td>sugars (monosaccharides)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>polysaccharides (polymerized sugars)</td>
<td>support, energy storage</td>
<td>yes</td>
</tr>
<tr>
<td>amino acids</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>proteins (polymerized amino acids)</td>
<td>many (support, enzymes, etc.)</td>
<td>yes</td>
</tr>
<tr>
<td>phosphate</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>nitrogenous bases</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>nucleic acids (polymerized sugars, phosphates and nitrogenous bases)</td>
<td>genetic information</td>
<td>yes</td>
</tr>
</tbody>
</table>

Largest contribution = meteors

- Rate of meteor showers was higher 4 to 3.8 Ga in the past = last heavy bombardment

- Evidence on Moon clearer than for Earth because of absence of weathering

- Problem: no organic molecules on the Moon?

Cyril Ponnampenura (Laboratory of Chemical Evolution, Dept. of Chemistry, University of Maryland, 20742 College Park, Md., USA) “The analysis, so far, has not revealed with certainty a single organic compound of biological significance. However, the finding of methane, carbon monoxide, carbides, etc. could be considered in the context of cosmic evolution.”
Other evidence of space origin = origin of chirality

- Definition of chirality: any object whose mirror image is non-superimposed (chiral Greek word for hand-like)

  Right-hand = D (destro)  \hspace{1cm} \text{Left-hand} = \text{L (levo)}

- Due to Carbon, organic molecules are chiral

When all the carbon atoms in molecules have less than 4 different structures bond to it ⇒ \text{achiral}

When all the carbon atoms in molecules have 4 different structures bond to it ⇒ \text{chiral}
• Glycine is achiral while Alanine is chiral

![Chemical structures of Glycine and Alanine](image)

• In the absence of life, chemical reactions that make amino acids create an equal amount of D and L \( \Rightarrow \) racemic mixture

![Diagram of chiral amino acid alanine](image)

**Figure 1.25** The chiral amino acid alanine can be present as left- and right-handed forms.

• Life on Earth uses only L amino acids to produce proteins \( \Rightarrow \) out of 20 amino acids, 19 are chiral except Glycine

• Mixing D and L amino acids in proteins \( \Rightarrow \) hindered proteins to do their biological functions

• Early in the history of life, L organic compound were favored in some way?
Breakthrough comes from space

- Evidence of excess of L organic matter found in meteorites
- Evidence for Ultraviolet Circularly Polarized light (UVCPL) phenomenon discovered
  - Electric field direction rotates along the beam
  - Rotation = chiral phenomenon $\Rightarrow$ L or D
  - Chiral substances have different absorption intensities for L or D
  - Photolysis (destruction of molecules by light) occurs when photons are absorbed
  - UVCPL destruct one form more readily than other
  - Orion region produce large amount of UVCPL $\Rightarrow$ chiral amino acids in excess of L or D? (see Baley J. et. al. 1998, Science, 281, 672)

*Fig. 1. Circular polarization image of the OMC-1 star-formation region in Orion at 2.2 $\mu$m (K, band). (Right) Percentage circular polarization ranging from $-5\%$ (black) to $+17\%$ (white). Polarization accuracy ranges from about 0.1% in the brighter regions to 1% in the fainter regions. By convention, positive polarization means that the electric vector is seen to rotate counterclockwise in a fixed plane by an observer looking at the source. (Left) The total IR intensity. The bright source at coordinates (0,0) is the Becklin-Neugebauer object. The size of a typical protostellar disk (~100 astronomical units) is less than 1 arc sec at the 450 pc distance of OMC-1 and therefore much smaller than the observed polarization structure.*

*If similar phenomenon happened during formation of the Sun $\Rightarrow$ bombardment of early solar system by UVCPL could have increased the number of chiral L molecules in meteorites that would have seeded the young Earth*
Panspermia

- Theory that suggested that Earth was bombarded by viable micro-organisms
- Developed by Fred Hoyle and Chandra Wickramasinghe
- Amount of organic material fallen per $10^6$ yrs around time of origin of life: $10^{16} - 10^{18}$ kg → 1.6cm to 1.6m spreaded over surface of Earth
- Most fell in the Ocean → buried in sediments
- Problems: mechanism to form in space (comets)?
  - Deep Impact’s probe collided with Tempel-1 on 4 July, 2005
  - [http://www.nasa.gov/mission_pages/deepimpact/media/deepimpact_water_ice.html](http://www.nasa.gov/mission_pages/deepimpact/media/deepimpact_water_ice.html) - Deep Impact Team Reports First Evidence of Cometary Ice on comet Tempel 1 (NASA 02.03.06)

The comet’s surface features three pockets of thin ice. The area the ice covers is small. The surface area of Tempel 1 is roughly 45 square miles or 1.2 billion square feet. The ice, however, covers roughly 300,000 square feet. And only 6 percent of that area consists of pure water ice. The rest is dust.

Other key findings include an abundance of organic matter (hydrocarbons) mixed with carbonates and clays (clays and carbonates need liquid water to form) as well as its likely origins – the region of the solar system now occupied by Uranus and Neptune.

- ALH 84001 – meteorites from Mars – in 1996, NASA suggest fossil evidence of microorganisms are found on the rock – but very controversial
  - Problems: even more difficult to explain formation of life on Mars than on Earth…so what is the point?
  - In fact would be evidence that life can travel on Meteorite – but not really the case either
**Complexification**

Some form of concentration mechanisms necessary for organic matter to take part in chemical reactions to produce more complex molecules

Possibilities:

1. Marginal environment
   - Lagoons + tidal pools: evaporation causes residual liquid to contain higher proportion of organic molecules
2. Freezing aqueous solution
   - Increases concentration of dissolved organic compounds because water freeze faster
3. Surfaces clays + other minerals
   - Traps for organic molecules – clay can accommodate organic molecules on and within their structures

**Polymerization**

*Complexification mechanism very poorly understood*

**Polymers are produced by a reaction involving the loss of water molecules**

- OH groups of sugar monomers can combine to form a bond following the release of water molecules
- $-\text{NH}_2 + -\text{COOH}$ form bonds following release of water
- Ends of larger molecules still contain reactive OH groups $\Rightarrow$ polymerization can continue

$\Rightarrow$ **Polymerization** can generate large molecules

Problems:

- Water is a destructive compound, that will break down polymers not build them
- Higher level of complexity of some macromolecules need more sophisticated methods $\Rightarrow$ **Catalytic properties of proteins enzymes**
Origin of cells

A self assembly process:

- Certain kinds of organic compounds have both hydrophobic + hydrophilic properties = amphiphiles (love both)
- Polar heads with small electrical charges ⇒ soluble in polar solvents like water
- Uncharged tails less soluble
- Amphiphiles molecules added to water sit at surface with hydrophilic heads in the water and hydrophobic tails in the air ⇒ formation is spontaneous
- Single layer of molecules = monomer = 2D surface
- Shaking mixture ⇒ spherical structures call micells

- Larger collections amphiphiles molecules form double layer structures = bilayer
- 3D structures = bilayer vesicles

- Can be used by organisms to preserve integrity of their cells
- Original membrane bound environment for cellular life?
In 1924, Alexander Oparin added proteins to water ⇒ grouped together form droplets = coacervates (Latin word for clustered or heaped)

• Many different polymers form coacervates: nucleic acids + polysaccharides
• Coacervates ⇒ property of physical chemistry related to polarity of molecules and ability to form hydrogen bonds in water
• Many substances when added to coacervates preparation can become preferentially incorporated into the droplets ⇒ prebiotic chemical factories?

In 1958, Sidney Fox heated mixtures of amino acids causing polymerization by reactions involving loss of water

• Amino acids polymers = proteinoids
• When dissolved in hot water and cooled ⇒ small spheres 2μm = microspheres
• Double wall resembling a membrane could shrink or swell depending on salt concentration
• If left for several weeks absorption of proteinoid produce buds
• Occasionally separate to form second generation of microspheres

In 1985, David Deamer extracted organic molecules from Murchison meteorite and added it to water ⇒ form membranes bounded bubbles

![Figure 1.30](image1) (a) Coacervates and (b) proteinoid microspheres. (a) sourced from www.angelfire.com; (b) sourced from University of Hamburg website)

![Figure 1.31](image2) Bilayers generated from the Murchison meteorite organic matter. (Dr. David Deamer)

Mixed with a collection of molecules and then dehydrated on the early earth. When hydrated again, small chemical factories may have developed into primitive cells.
Role of minerals

Development of first living cell involves a sequence of chemical transformations to achieve a greater level of structures and complexity than available in starting materials.

Minerals critical function in this process – 4 key roles

1. **Hosts for assembling chemical systems protecting them for dispersal and destruction**
   - Ex. Volcanic rocks have small pockets of air created by gas expansion when rocks was molten
   - Other minerals develop microscopic pits following weathering
   - These compartments could have housed a small chemical mixtures

2. **Support structures for molecules to accumulate and interact**
   - Effective way to assemble molecules from dilute solution is to concentrate them on a flat surface
   - Experiment:
     - Solution containing amino acids are evaporated in a vessel containing clays
     - Amino acids concentrate on the clay surface
     - Polymerize into short protein-like chains

3. **Aided the selectivity of certain biologically useful molecules**
   - Many have crystal faces that are mirror images of each other
   - Ex. Calcite bond strongly to amino acids
   - When submerged in racemic solutions of amino acids L and D forms of amino acids bond to different crystal faces
   - Under right conditions (?) excess of L molecules?
   - Alternative = natural selection then choose L?
4. **Catalysts**

- One element to produce biologically useful material = Nitrogen present as unreactive gas
- Primitive organisms must have found a way of converting N gas to a form assimilable by life
- Industrial process: N + H passed over metallic surface to generate ammonia
- Similar reaction on early earth $\Rightarrow$ ammonia = valuable source of N for biological reactions
- **Hydrothermal vents** = process where N + H passed over Fe oxide surface

1988, **Gunter Wächtershäuser** – Iron + Nickel sulfides could have served as a template, catalyst and energy source for production of biological molecules

- First living things = coating stuck to the surfaces of crystals
- If the mineral acted as a catalyst then primitive life metabolism proceeded in the absence of enzymes
From chemical to biological system

RNA world

Dilemma:
- Nucleic acids have the genetic information to reproduce themselves, but they need proteins to catalyze the reactions
- Proteins catalyze reactions, but cannot reproduce without the information supplied by the nucleic acids
- Which molecules could have existed without the other: DNA, RNA or proteins enzymes?

Mid 1980 – RNA was found to be able to perform some of the enzymatic functions needed for replication (Sidney Altman & Thomas Cech, Nobel prize for chemistry 1989)

RNA with catalytic properties = ribozymes

Because RNA molecules can store genetic information and act as catalysts
- Protein unnecessary for simple life functions?
- RNA might have been able to replicate and evolve without specialized proteins?

RNA world may have preceded the DNA+RNA+PROTEIN world

Evidences in favor of RNA world hypothesis
1. Nucleotides in RNA are more readily synthesized than nucleotides in DNA
2. DNA may have evolved from RNA, because of higher stability ⇒ DNA replaced RNA
3. RNA evolved before protein, because no plausible scenario of replication of proteins exist without RNA
Ex. Retrovirus

Diagram of a Retrovirus

- Virus = infectious parasite without cellular home
  - Without host, virus does not carry functions of living cell (respiration, growth, etc.)
  - Within host cell, steal cell energy and highjack ability to synthesize proteins and nucleic acids to replicate themselves
- Fragment of RNA nucleic acids within protein coat (capsid) and surrounded by a lipid envelop
- Envelope contains polypeptide chains including receptor binding proteins which link to the membrane receptors of the host cell, initiating the process of infection
- Small in size 10-200nm
- Some virus do not kill the host but persist within them in one form or another
- Cancer-virus = HIV (human immunodeficiency virus - the virus that causes AIDS = acquired immune deficiency syndrome) evolve at $10^6$ times the rate of nuclear DNA
- Retrovirus replication $\Rightarrow$ reverse of normal cellular process using enzyme reverse transcriptase (RTase)
  - When a retrovirus infects a cell, it injects its RNA into the cytoplasm of that cell along with the reverse transcriptase enzyme which causes synthesis of a complementary DNA molecule (cDNA) using virus RNA as a template
- Retrovirus = legacy of darkest ancestors?
**Primitive biochemistries**

*Energy sources are captured by life and utilized via metabolic processes*

Most important source of energy = sunlight ⇒ *photosynthesis*
- Production of carbohydrates from water and carbon dioxide
- Using S: \( n\text{CO}_2 + n\text{H}_2\text{S} \rightarrow (\text{CH}_2\text{O})_n + n\text{H}_2\text{O} + n\text{S} \)
- Used by plants today: \( n\text{CO}_2 + n\text{H}_2\text{O} + \text{energy} \rightarrow (\text{CH}_2\text{O})_n + n\text{O}_2 \)

**Alternative energies**

1. **Chemosynthesis**: deep sea hydrothermal vents populated with a range of organisms
   - Sea water circulating through new, hot ocean crust at mid ocean ridges is heated
   - Hot sea water dissolves and exchanges chemicals with the rocks
   - Mineral rich hot water vent back into the sea at temperature \( \sim 400^\circ\text{C} \)
   - Only great pressure stop water from boiling
   - Hydrothermal systems occur deep in earth crust where water and heat are present
   - Chemosynthetic life forms produced ⇒ *deep hot biosphere*, where amount of organic matter rival that on surface

**Autotrophs**: Organisms that utilize photosynthesis and chemosynthesis to generate organic compounds from energy and simple inorganic substances – carbohydrates are used to generate energy-rich bonds that can be used by metabolisms

2. **Fermentation + respiration – two most common metabolisms**
   - **Fermentation**: glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{CO}_2 + \text{ethanol CH}_3\text{CH}_2\text{OH} \) or lactic acid \( \text{C}_3\text{H}_6\text{O}_3 \) for a net gain of 2 energetic-rich phosphate bonds
   - **Respiration**: glucose transformed into dioxide of carbon and water for a net gain of 36 energetic-rich phosphate bonds \( (\text{CH}_2\text{O})_n + n\text{O}_2 \rightarrow n\text{CO}_2 + n\text{H}_2\text{O} + \text{energy} \)

**Heterotrophs**: consume Autotrophs
Molecular Phylogeny

Life
- History extends over 4 GA
- Started with single and simple common ancestor
- All life on earth are related

Genetically based phylogenetic tree
- Life builds from what came before
- Recorded in present genetic material
- Sequence of nucleotides in RNA and DNA
- **Phylogenetic tree:** examine similar molecules in different creatures
  - If parts are alike ⇒ must been inherited by organisms from common ancestor

- More modern tree (Carl Woese 1970’s): build from genetic information obtained from sub units of ribosomal RNA compared between different organisms
  - Hierarchy of evolutionary innovations
  - The longer a branch the greater the difference in ribosomal RNA
  - 3 domains: **Bacteria + Archaea + Eukarya**
  - Branches ⇒ more closely related species
  - Ancestral groups (roots) ⇒ deepest and shortest branches = **thermophiles + hyperthermophiles**
  - Source of evolution moved from high to low temperature?
  - Majority of deepest branching organisms do not use light ⇒ photosynthesis later development?
  - Last common ancestor similar to heat loving chemosynthetic organisms that populated hydrothermal vents today?
Carl Woese’s tree of life, comparing among many different organisms the sequence of a gene that encodes a ribosomal RNA (rRNA). The tree, and supporting research from other fields, led to the speculation that life originated in very hot environments, perhaps in the hydrothermal vent systems found deep underwater around the globe. Woese’s original tree, and the resulting speculation that life arose in a hot environment have become widely accepted among researchers (since 1996), and have taken on the status of textbook explanations of the origin of life.
Recent controversy = more likely that life originated at low temperatures

Phylogenetic tree (Stetter 1996) modified from Woese et al. (1990), demonstrating the thermophilic root of the last universal common ancestor (in red) but also the putative mesophilic progenote (Forterre and Philippe 1999). The "primitive" nature of Fe III reducers (green) are also evident (Liu et al. 1997; Vargas et al. 1998) - Credit: gla.ac.uk

The tree differs in some striking ways from the one that has become standard. First, the hyperthermophilic bacteria do not appear near the trunk of the tree. Instead the reanalysis shows them up among the leaves, part of a large, bushy crown group that includes most of the bacteria.

Philippe: "One could have guessed from the discovery of hyperthermophilic organisms that they are specialized, and thus very evolved."