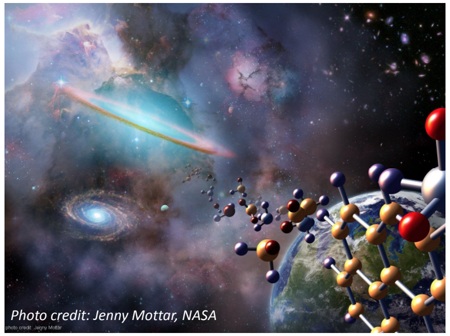
The molecular origins of life



SoSe 2017 HD

Zbigniew Pianowski

7 lectures (90 min. each) in English
Mondays 16:00-17:30, INF 272, kHS

1st lecture: 8th May. 2017

Following lecture terms:
15th, 22th May
then 12th, 19th June, and
3rd, 10th July

NO LECTURE ON: 29th May., 5th June, 26th June

The most actual dates, handouts – on the website:
http://www.ioc.kit.edu/pianowski/ and by Moodle

Mailing list for changes and supplementary information

General references

K. W. Plaxco, M. Gross *Astrobiology. A brief introduction.* 2nd Ed.
(EN, The Jonh Hopkins Univ. Press)
Astrobiologie für Einsteiger (DE, Wiley-VCH)

K. Ruiz-Mirazo, C. Briones, A. Escosura *Prebiotic Systems Chemistry: New Perspectives for the Origins of Life.*
Chemical Reviews, 2014, 114, pp. 285-366

A. Pross *What is Life? How Chemistry Becomes Biology.*
(Oxford Univ. Press)

Overview of the course

Lecture 1	***Introduction to life***
Lecture 2	*The primordial soup – Aminoacids*
Lecture 3	*The primordial soup – Lipids, Sugars*
Lecture 4	*The primordial soup – Nucleobases, cyanosulfidic chemistry*
Lecture 5	*Oligomerization, Systems Chemistry*
Lecture 6	*Self-assembly, metabolism, RNA world*
Lecture 7	*Protocells, LUCA, extremophilic organisms*

Continuation – The molecular origins of life II: Synthetic life

Artificial genetic polymers – oligonucleotide analogues: structures, applications, hypothetical roles in biogenesis;

unnatural base pairing – expansion of the genetic alphabet;

The re-born RNA world – artificial ribozymes for efficient catalysis and recognition; SELEX, DNAzymes, foldamers;

Unnatural aminoacids (UAAs) for protein modifications – covalent modifications of proteins, biosynthetic incorporation of UAAs

Designed enzymes – production of enzymes with unknown or unnatural properties, protein engineering, *ab initio* protein design, directed evolution, theozymes;

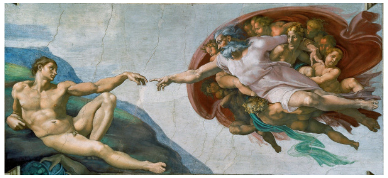
Artificial lipid vescicles – dividing compartments as models for protocell multiplication;

Synthetic biological circuits – riboswitches, time-delay circuits, oscilators, optogenetics;

Design of artificial organisms – minimal genome project, Synthia – fully artificial genome resulting in living bacterial species

People always liked to know...

Where do we come from?



Michelangelo, the Sistine Chapel

Are we alone in the Universe?

Alien, by Ridley Scott

Can we create life?

Young Frankenstein, by Mel Brooks

Nowadays, molecular sciences and particularly chemistry seem to be in the position to adress these questions

How science can adress these questions

What science can't do:

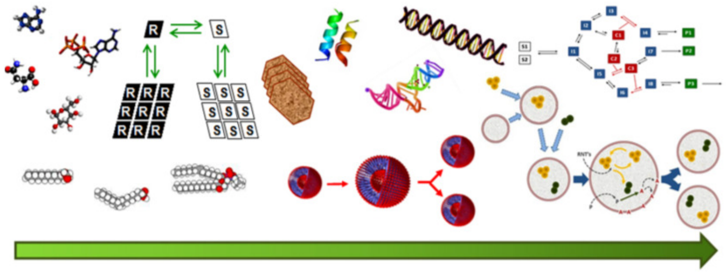
Exactelly repeat the process of life creation from elements and simple low MW molecules
Not enough resources (time, money) to perform the experiment

Science can demonstrate:

- The origin and abundance of elements and small molecules in the Universe
- How the small molecules self-assemble into biopolymers and complex systems
- How to dissect the origin of life into subsequent and overlaping stages
- How the particular stages can be achieved in the lab under abiotic conditions

Important stages of the origin of life

biomolecules – biopolymers – self-replication – metabolism - compartmentalization



Increasing complexity from molecules to systems

Aspects of chemistry involved:

- Supramolecular chemistry
- Self-assembly
- Autocatalysis
- Organic chemistry
- Biochemistry
- Templated reactions
- Systems chemistry
- Geochemistry
- Astrochemistry

Feedback from:

- Biology
- Physics
- Mathematics and modelling
- Astronomy
- Geology

Definitions of life

Erwin Schrödinger (1943):
Life: heredity and thermodynamics

Order from order
genetics

The Nobel Foundation

Order from disorder
ordered arrangements of molecules (cells, tissues) within themselves on the expense of increasing disorder of the environment

Definitions of life

Life is a self-replicating chemical system capable of evolution (NASA, 2009)

Self-replicating: copies itself
Chemical system: based on assembly of molecules
Evolvable: adapt to the surroundings

The definition not exhaustive
Mules (donkey/horse)
Infertile or old organisms
Viruses

The definition covers all species, not necessary individuals

Definitions of life

Life is a self-sustaining kinetically stable dynamic reaction network derived from the replication reaction
(A. Pross, 2012)

Non-living systems → thermodynamic stability
Living systems →dynamic kinetic stability (DKS)
Better at making more of itself (replicating) → more stable in the DKS sense

„self-sustaining" - orders itself on the expense of the external world (2nd LT)

Death is reversion of a system from the kinetic, replicative world back to the thermodynamic world

Constrains for the origin of life

Elements – Solvents – Energy – Other limitations

Elements of life

Carbon-based life well-justified:

- self-replicating chemical systems need sufficient complexity
- Carbon is tetravalent and can form complex structures (unlike H, He, Li, O, or F)
- Fourth most common element in the Solar system
- Energy of C-C bond comparable to C-O, C-N and C-H – easy exchange between elements

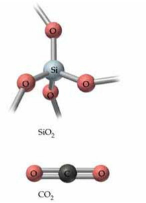
Alternatives: silicon-based life...

- Also can form complex structures, multivalent
- Second most abundant element on Earth's surface (far beyond C)
- Si-O bond far more stable than Si-Si, Si-H or Si-N → oxidation almost irreversible

Elements of life

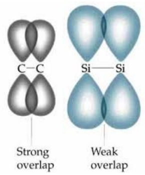
Carbon-based life:

- Two carbon atoms form double and triple bonds with increasing stability
- Same is true for binding oxygen and nitrogen to carbon
- Methane CH_4 – kinetically stable on air
- Substitution on carbon with high activation bareer CH_3X → CH_3^+ → CH_3Y



Silicon-based life:

- Multiple Si-Si bonds unstable (3s and 3p orbitals do not hybridize efficiently)
- Silane SiH_4 – pyrophoric on air, low E_{akt}
- Substitution on silicone by low-energy pentavalent intermediate (3d orbital binding)



Solvents of life

Life requires a solvent to move molecules around

Terrestrial organisms based on water

Advantages of water:

- ice floats → nutrient transport, temperature modulation
- High heat capacity 4.2 J/g*^{0}C (3x of rocks or metals), heat of vaporization 41 J/g
  → both help to moderate Earth's climate
- Liquidity range – 100^{0}C
- High dielectric constant – water is a very good solvent
- High molecular density 55.5 mol/L – „hydrophobic effect":
  H_2O forces dissolved molecules to organize to minimize the enthropic cost
- H, O – very abundant in the Universe (1st, 3rd)
  H_2O – 2nd most abundant after H_2

Solvents of life

Alternative solvents

HF, NH_3, CH_4, H_2

TABLE 1.3
Physical properties of potential biological solvents

Solvent	Formula	Liquid range (°C, at atmospheric pressure)	Molar density (mol/L)	Heat capacity (J/g K)	Heat of vaporization (J/g)	Dielectric constant	Density ratio: solid to liquid
Water	H_2O	0 to +100	55.5	4.2	41	80	0.9
Hydrogen fluoride	HF	−83 to +20	48.0	3.3	0.4	84	1.8
Ammonia	NH_3	−78 to −34	40.0	4.6	23	25	1.2
Methane	CH_4	−182 to −161	26.4	2.9	8	2	1.1
Hydrogen	H_2	−259 to −253	35.0	0.008	0.5	1	1.3

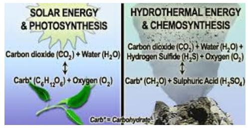
HF – similar physical properties to water,
but fluorine cosmologically rare (100,000 x less than oxygen)

Energy for life

Life creates order from disorder → need for energy

High energy photons absorbed by plants
→ nutrients absorbed by animals;
both patterns used to run metabolic processes

However, not the only available source of energy
Geothermal, chemical energy
→ Further lecture on extremophiles



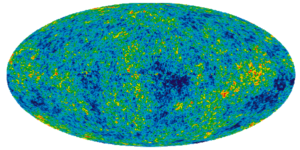
Energy-producing oxidation reaction	Type of bacteria
$2H_2 + O_2 \rightarrow 2H_2O$	Hydrogen bacteria
$2H_2S \rightarrow S \rightarrow S_2O_3^{2-} \rightarrow SO_4^{2-}$	Colorless sulfur bacteria
$Fe^{2+} \rightarrow Fe^{3+}$	Iron bacteria
$NH_3 \rightarrow NO_2^- \rightarrow NO_3^-$	Nitrate, nitrite bacteria

Life requires a condensed medium → rocky solid planets with available solvent
Life requires time to be formed → unstable environment (overheating, asteroids, supernovae) is detrimental

Origins of a habitable Universe

Echoes of the earliest Universe

Cosmic microwave background
(Penzias, Wilson, 1965 Bell ATnT)



Red shift of spectral lines in far galaxies – Doppler shift (Hubble, 1929)

Theory of the Big Bang – Gamow (1948):

Heat of the Big Bang dissipated in the Universe as the 4K residual radiation
Expansion would cause red shift of the spectral lines in distant objects that shift away

Origin of the Universe

10^{13} K: equilibrium: 2 photons=nucleon+antinucleon

Mutual anihilation of nucleons/antinucleons was not symmetric.
The sight excess (>1 ppb) of the matter vs. antimatter remained and forms the currently known „visible" part of the Universe

$3x10^9$ K: electron/positron equilibrium settled (again c.a. 1 ppb e^- excess);
Universe – dense see of unbound nucleons above $1x10^9$ K (100 s old)

3.5-5 min old – 20% of the ^1H converted into ^4He

Further nuclei DID NOT form during the Big Bang – unstable until ^{12}C (which requires unlikely collision of *three* ^4He to be formed)

Origin of the Universe, Galaxies and Stars

5 min old: rapid expansion of the Universe – dilution of ^4He (rate of ^4He*3 collision negligible)

3000 K – (377.000 years old U) recombination of plasma (e^- + nuclei) into atoms –
Plasma scatters light – only after the recombination Universe became transparent

Before recombination, disturbances in matter density were reflected by disturbances in photon density → microwave background is a „fossil" of the early Universe's density,
Its fluctuations reflect fluctuations of matter's density
These fluctuations detected by COBE (1990s, 2006 Nobel Prize)

100.000.000 years – protogalaxies formed (10^9 Sun masses) and continuously merge into galaxies until now

700.000.000 years - formation of first stars → self-attracting matter squeezed itself until synthesis of heavier nuclei by nuclear fusion begun

First Galaxies and Stars

150 Mio. K – Star that burned all its ^{1}H (red giants), beginns to synthesize ^{12}C and ^{16}O from ^{4}He,

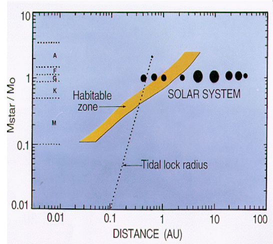
If it is big enough (>8 Sun masses), it can ignite ^{12}C and ^{16}O to form ^{24}Mg, ^{23}Mg ($-^{0}n$),
^{23}Na ($-^{1}H^{+}$), and ^{28}Si
Last step: $2x^{28}Si$ → ^{56}Fe
The iron core self-collapses into neutron star (fusion of e^{-} and H^{+}) 10 km-wide
→ a shockwave of free neutrons that freely recombine with surrounding nuclei,
excess of neutrons converts to protons (and e^{-}) yielding atoms heavier than ^{56}Fe,
the released energy boosts outer layers of the star into space with a few % light speed
→ Supernova

The heavy „metals” are then spread around Universe and can „dope” lighter star systems

Stellar requirements for evolution of life

- The sun is solitary, 85% stars are multiple
- The sun is relatively massive (within top 10%)
- Small stars have very small „habitable zones”, very close to itself → difficult to harbor a planet
- „Tidal lock” – tidal energy converts planet rotation into heat and „locks” its position so that it faces the star with one side only (high constant gradients of heat distribution)

Habitable zone – the region where liquid water can form
„tidal lock” – detrimental below 40% of the Sun mass
Too large star – fast burnout and explosion before life develops
(Sun =11 Bio. Years lifetime, 2 Sun masses = only 1 Bio. Ys. life)



Only 5% of all known stars are large enough to avoid tidal lock and small enough to be stable

Galactic requirements for evolution of life

Distance from the galaxy center matters!
Sun orbit – 26000 Light years from the center (225 Mio yrs. to make the full circle)

Closer to the center – density of stars increases → probability of supernova explosions increases highly → any planet nearby would be sterilized on much shorter timescales than needed for evolution of life
Even closer → X-rays from black hole(s) in the center would fry any biomolecule rapidly

Far beyond the Sun's orbit – mostly type II metal-poor stars → no heavier elements than carbon and oxygen → planet formation inhibited

GHZ – Galactic Habitable Zone – weekly populated (c.a. 10% stars from the Milky Way)

Moreover, a star must REMAIN in the GHZ all the time to host life development
Less than 5% of all stars do

Origins of a habitable universe - Summary

$P_{habitable} = P_{solitary} * P_{size} * P_{GHZ} = 0.00075$

1 star in 1300 seems to be habitable
Still 100.000.000.000 stars in our Galaxy
And 100.000.000.000 galaxies in the Universe

Good understanding of the origins of the Universe
– the Big Bang model highly quantitative and confirmed

Too dense universe → wouldn't survive long enough to host life
Too sparse universe → Galaxies, stars and heavy elements would not have formed

The size of the Sun, its location in our galaxy, and its regular orbit (low eccentricity) optimal to support life development.

We have defined size range and optimal location (HZ, GHZ) for other life-friendly worlds.

Origins of a habitable planet

Evolution of the solar system

Condensation of the pre-solar nebula: most matter into the proto-sun, but c.a. 0.1%-2% remained in the acretion disc

The central nebula collapses under its own gravity, warms up (potential energy of gravity → kinetic energy of particles) and ignites as a star when reaches 10 Mio. K (H→ He)

This young star was hotter than the current Sun, rotated faster, and expels a strong stream of charged particles (the stellar wind)

Rest of the matter in the nebula accumulates in the equatorial plane of the star due to non-gravitational forces

Evolution of the solar system

The disc of matter is heated from the star and by friction movements of the matter inside

The inner portions of the disc →1000 K, strong temperature and pressure gradient outwards

Liquids not stable at low pressures in the solar nebula → only sublimation relevant

Close to the inner edge (warm) – only metals and most „refractory" oxides (alumina) condensed
Mid-distance – other, less refractory silicates also condensed
Large distance – water, ammonia, methane also form ices and thus condense

Conglomerations of particles continue to condense and form km-sized planetesimals, frequent collisions led to accretion – the km-sized bodies become gravitationally attractive for gases available around – growth of proto-planets

Evolution of the solar system

Composition of planetesimals depends on their distance from the star:
Metal-rich – center
Silicate-rich – middle
Volatile-rich – outer part

The equilibrium condensation model
temperature determines equilibrium chemistry which defines the composition
The prediction is rough because some particles are scattered away from their origin

Exceptions: volatiles on Earth and Venus, composition of the Moon

Composition of the planets

Mercury: dense, highly refractory metals (8 g/cm^3), tiny outer silicate (3 g/cm^3) shell – 5.4 g/cm^3 avg. density (50/50), has magnetic field (conducting metallic core)
Venus: 5.3 g/cm^3; but 14x more massive than Mercury – corrected with mass compression rock-to-metal ratio 3:1 (uncompressed 4.2 g/cm^3)
Earth: 5.5 g/cm^3; 17x Mercury mass, rock-to-metal ratio 3:1 (uncompr. 4.2 g/cm^3)
Mars: 4.0 g/cm^3; rock-to-metal ratio >5:1 (uncompr. 3.3 g/cm^3)

Venus, Earth and Mars far enough from Sun to have significant silicate condensation, thick rocky mantle surrounding small metallic core
Asteroid belt – separates terrestrial planets from the outer Solar System

Jupiter: 1.3 g/cm^3 > 300 masses of Earth; Saturn: 0.7 g/cm^3; > 90 masses of Earth
Uranus: 1.3 g/cm^3 > 15 masses of Earth; Neptune: 1.6 g/cm^3; > 17 masses of Earth
Pluto: 2.0 g/cm^3; 0.003 masses of Earth

the outer Solar System dominated by Jupiter

Composition of the planets - Jupiter

Water – a major component of the solar nebula, but under the very low pressure does not condense above 150 K („snow line” in the nebula).

Asteroids that form above 2.7 AU contain significant amount of water

Jupiter – 5.21 AU – first planet beyond the snow line – silicates and water condensed in largest amounts of the whole Solar System around a small metal core, and formed a proto-Jupiter (10-15 Earth masses, fast), then gravity strong enough to pull in all available gases from around, until it mainly consisted of H_2 and He (strongly pressurized)

Composition of the planets – Saturn and beyond

Saturn – 9.58 AU – similar to Jupiter, but less gases available because the nebula less dense

Uranus, Neptune – even less dense nebula region, but so cold that ammonia and methane can condense → rock-and-ice cores of several Earth masses, but not massive enough to efficiently attract H_2 and He

Pluto, Eris – small icy bodies, density c.a. 2 g/cm^3 – equal parts rocks and ice

Timeframe – chondritic meteorites, contain the oldest matter in the Solar System
Dated for 4.559 Bio. Years old (+/- 20 Mio. Yrs.)
Accrecion of planetesimals into planets took 10-100 Mio. Yrs. (short!), then any remaining dust and gases blown away by the solar wind

Origin of the Moon

Origin hypotheses:
Wife – coming from elsewhere
Sister – formed in the neighbourhood and failed to accrete
Daughter – originated from Earth

Apollo mission brought lunar rock samples:
Isotopic distribution like on Earth – contradictory to the „wife” hypothesis

Surface of the Moon is different from the Earth surface – lack of „volatile” metals like sodium, the Moon's density only 3.4 g/cm^3→ contains almost entirely silicates- contradictory to the „sister” hypothesis

Currenly „Daughter-like” Moon's origin – impact of a Mars-size object into Earth splashed a big chunk of liquid rock from its mantle (mostly silicates) into space
Isotope dating (^{182}Hf/^{182}W): Moon formed 30 Mio. Yrs after accretion

Origin of volatiles on terrestrial planets

Proto-Earth was too hot to condense water (but 0.035% Earth mass is water!!)

Water came from beyond the snow line:
Big outer planets (especially Jupiter) ejected the remaining planetasimales from their neighbourhood into outer space (Kuiper Belt) or inwards the Solar system.
The latter ones delivered volatiles to Earth and other terrestrial planets by crushing on them.
(carbonaceous chondrites contain 5-20% water, 5% total carbon and 3% organic materials – mainly polyaromatic hydrocarbons)
The big planets also „cleaned up” – late heavy bombardment 3.8 Bio. Yrs. ago was the last intensive impact period. Then no more planetasimales present.
An impact of a 100-km-wide object can sterilize the surface of the whole planet, but nothing like that happened since.

Fate of volatiles on terrestrial planets

Mercury – most of the volatiles delivered by planetosimales bombardment escaped into space. Exeptions: craters at the poles
No seasons at Mercury (rotation axis does not move), so bottoms of these craters always in shade (chilled to few Kelvins) → cold traps, filled with ice
Same situation on the Moon, but gravity much weaker, so smaller amounts of water ice left

Mars – weak atmosphere, significant amount of water ice detected in polar caps (mix of water ice and frozen CO_2), and underground in the polar regions, but in the past most likely to have much of surface water (geological structures – canyons – and sedimentary rocks characteristic for running water)
Liquid water still possible around warm volcanoes under the crust

Fate of volatiles on terrestrial planets

Venus – the closest Earth's sibling
Still, drastically different for water abundance – dry as a bone
Atmosphere: 30 ppm water vapor (Earth: 1.000-40.000 ppm + 120.000 more in oceans)
Atmospheric pressure on Venus' surface: 90 atm (96.5% CO_2, 3.5% N_2)
Strong greenhouse effect: 460^{0}C on the surface.

Why?

On Earth, the same load of CO_2 bound in limestone because liquid water still present: CO_2 dissolves in water, when it warms, together with Ca and Mg ions. These precipitate as $CaCO_3$ and $MgCO_3$ and sequester CO_2 until volcanic activity liberates it again.
When Earth gets too cold, water freezes („snowball Earth"), so no contact with CO_2 anymore.
Then due to plate tectonics the limestone is transported inside and decomposed due to heating (volcanic activity), CO_2 is liberated again to the atmosphere → warming up

Liquid water + plate tectonics (water-dependent?) → temperature stabilization

Fate of volatiles on terrestrial planets

Venus had a lot of water, but lost it.

D_2O evaporates slower than H_2O.
Jupiter due to strong gravity did not lose any of its primordial hydrogen
Jupiter's H:D ratio is 44.000:1 (the primordial ratio of the solar system)
Venus: 60:1 (700x less!) → it supposed to have lost several OCEANS of water
Earth: 6000:1 (7x less) → it also lost some water, but proportionally much less

Blackbody temperature on the Earth's orbit is 255 K (-18^{0}C) → outer shell of Earth's atmosphere is well below freezing of water → any water vapor condenses and falls back as rain or snow
Venus' atmosphere is warmer than 0^{0}C → water difuses to its top
UV light from Sun → water photolysis to H_2 and O_2, part of the H_2 irreversibly escapes with the solar wind.
Over last 4 Bio. Yrs. almost all water lost that way.

Origins of a habitable planet - conclusions

Earth formed in the inner region of the solar nebula
Predominantly composed of refractory metals and silicates – non-biogenic materials
Jupiter provided proto-Earth with icy, volatile-rich material, and allowed cleanup of the Solar System from planetasimales, so no more big, planet-sterilizing impact possible anymore.
Earth is optimally positioned (0.95-1.15 AU) to maintain the acquired water as liquid, and stable surface temperature over billions years.