# The origin of life

### **Curators: Thomas Henning**

Max Planck Institute for Astronomy Andrei Lupas Max Planck Institute for Developmental Biology

# The origin of life at a glance

The study of the fundamental pathways from non-living matter to life, starting with the build-up of simple organic molecules, over the synthesis of nucleotides and finally to the formation of RNA and DNA - the messenger material for all present life on Earth - is entering a phase where major progress can be expected. In parallel, the discovery of planets outside of the Solar System and the detection of Earth-like planets in regions around other stars where liquid water can exist has opened up a new line of research with the goal to find life elsewhere by tracing biological activity on other planets through the spectroscopy of their atmospheres.

## The research topic

The origin of life has preoccupied humans since the dawn of civilization and has led to a wide range of creation myths involving superhuman agents. The ancient Greek were the first to seek a scientific explanation and proposed spontaneous generation as a path for the emergence of complex organic forms from simpler inorganic matter. With the rise of European science after the Middle Ages, biologists gradually refuted this hypothesis, showing instead a seemingly unbridgeable gulf between life and inanimate matter ("omne vivum ex vivo"). At the same time, however, chemists gradually proved the validity of chemical principles across all matter, living and dead, leading them from the synthesis of an organic substance from inorganic precursors (urea) to the establishment of organic chemistry and biochemistry as scientific disciplines.

From the late 1800s onwards, these twin developments triggered a flourishing of thought on the chemical origins of life on a pre-biotic Earth, from Charles Darwin's sketchy "warm little pond" speculation (1871) to the elaborate chemical hypotheses of Alexander Oparin (1924). With the exploration of these hypotheses starting in 1953, Stanley Miller brought these thoughts into the realm of experimental science and founded the new field of origin-of-life studies. These studies were notably broadened and strengthened by theoretical approaches, ranging from philosophical speculations - with Fermi's paradox as a good example (Jones et al. 1985) - to physical argumentation (Schrödinger 1951) and non-linear thermodynamics (Nicolis & Prigogine 1977). A large boost for these efforts was provided by advances in

astronomy and space exploration (the "space age"), which placed the possibility of life outside Earth into the centre of public attention. All these developments led to more specific formulations of the origin-of-life question, which we would summarize as follows:

Under which conditions can molecules form living cells? Is the transition from complex molecules to biological systems inevitable under the right conditions? How diverse can life be in its simplest forms? Does life on other planets exist? Can we find evidence for life through remote spectroscopy of planetary atmospheres (Fig. 1)?



**Fig. 1:** Apart from Mercury the other three of the four terrestrial planets in our Solar System -Venus, Earth, and Mars - contain an atmosphere. Their composition and spectral signatures are very different. Ozone together with water in combination with other molecular tracers may indicate the presence of life as seen in the spectrum of Earth. Source: ESA 2001.

Despite early successes and temporary revivals, e.g., with the studies on the selforganisation of pre-biotic systems by Eigen & Schuster (1979), the iron-sulfur chemistry of Wächtershäuser (1990), or repeated - though unfortunately erroneous - reports of microfossils in meteorites, origin-of-life studies gradually ran out of steam from the mid 1980s on, due to their inability to provide conclusive breakthroughs on any of the questions above.

With the seminal discovery of the first extra-solar planet around another Solar-type star by Mayor & Queloz (1995), the finding that low-mass planets are abundant (Fressin et al. 2013, Bonfils et al. 2013), the possibility to synthesise activated pyrimidine ribonucleotides under early Earth conditions (Powner et al. 2009), and the possibility to build a minimal cell under a variety of chemical conditions (Szostak et al. 2001, Forster & Church 2006), the situation has changed decisively. However, further breakthroughs in this area will likely require challenging, sustained, and coherent research programs, offering large payoffs in return.

# Status of the field

The study of the origin of life on Earth and even more so that of life on other planets is currently an amorphous research topic, with uncertainties that place some aspects closer to science fiction than to science. We may well, for example, never be able to determine the exact conditions on Earth four billion years ago when a complex mixture of molecules - the "Ursuppe" - finally made the transition from non-life to life (Fig. 2). The original Miller-Urey experiment was performed at a time when the atmosphere on Earth was thought to be composed primarily of NH<sub>3</sub> and CH<sub>4</sub>. Today, we assume that the early Earth atmosphere was dominated by CO<sub>2</sub> and N<sub>2</sub>, with the fraction of out-gassed atomic hydrogen under heavy debate. This already demonstrates the uncertainties in our knowledge of the early Earth.



**Fig. 2**: Life on Earth evolved around 3.5 billion years ago. Evidence comes from ancient microfossiles and old rock structures in South Africa and Australia, called stromatolites. These structures are built by thin films from microbes which capture mud and finally form layered rock structures. Stromatolites in the 3.4 billion year old Strelley Pool Chert Formation (Trendall, Western Australia). Source: Dr. Christian Hallmann (MPI for Biogeochemistry, Jena).

Furthermore, so far, we do not have any example of life outside Earth. Life, as we know it, is a cell-based system with a DNA-based genome that is translated to a rather complex protein world. It is characterized by self-reproduction, the transmission of information, Darwinian evolution, and the conversion of material from higher to lower energy states through metabolic processes. The extent to which these properties are required for the formation of life, as opposed to just one possible solution, are at this point unknown and a matter of pure speculation.

The situation is reminiscent of the research field of planet formation until 1995 when the first extra-solar planet was discovered. All planet formation theories were calibrated on the

Solar System as the *only* example for a planetary system we were able to study. Meanwhile, more than 1000 extra-solar planets have been discovered, from Hot Jupiters to Super-Earths, from planets on highly eccentric orbits to those in resonances, revealing an amazing diversity of "other" worlds. Despite this observed extreme diversity of planetary systems, the "historical" Kant-Laplace hypothesis, which postulated the joint formation of planetary systems and their central stars from dusty gas disks, still provides an extremely successful framework for our understanding of planet formation. Of course, new elements had to be added to models of planet formation such as planet-planet interactions and planet migration as well as the chemical and physical structure of protoplanetary disks which we now know through a wealth of multi-wavelength observations. However, the basic physical framework has remained the same.

As we started with the Solar System as the only example to develop planet formation models, we better start from living systems close to what we know if we want to investigate the origin of life, but be open to the investigation of other life forms (Joyce et al. 2012).

A comprehensive study of the origins of life certainly needs a combination of various research fields, ranging from organic and macromolecular chemistry, over biology and biochemistry, biogeochemistry, climate research to astrophysics.

#### **International activities**

The field is still emerging, certainly in the aspects that link astrophysics to biochemistry, but it is rapidly developing at a number of research institutions. Harvard University has started the "Pathways to Origins of Life" initiative and is closely collaborating with the MIT geobiology laboratories and its exoplanet atmosphere group. The University College London has initiated an "Origins of Life" program as well as the University of Cambridge in the UK. At Tokyo Tech in Japan the new Earth-Life Science Institute has just been launched as a major initiative in the origins of life research field.

The Max Planck Society could realistically offer a structure and perspective that is unique in its temporal horizon and scope through its various institutes in (geo)-chemistry, biology, biochemistry and astronomy.

#### **Research opportunities and benefits**

Particularly interesting research opportunities exist in organic macromolecular chemistry, exoplanet atmosphere research, and isotopic geochemistry. Other important research directions for an "Origins of Life" initiative such as the build-up of synthetic minimal cells, the study of protein evolution, and the investigation of error propagation in biological

systems will be pursued in existing Max Planck Institutes. In the following, three research opportunities are described in more detail as examples for existing research opportunities.

#### **Topic 1: The origin of RNA**

A fundamental question in the origins of life is how biological macromolecules were first produced on early Earth from precursor material. Given its ability to both encode information and catalyze reactions, RNA has been proposed to have represented the original "molecule of life" (the "RNA world"), before the transition to DNA- and protein-based life occurred (Fig. 3). This hypothesis gained considerable support when it became clear that the core particle mediating protein synthesis, the ribosome, is a ribozyme. The essential reaction of this hypothesis (Joyce & Orgel 1999), a ribozyme-catalyzed, template-driven polymerization of RNA, which is not observed in nature today, has also been achieved (Johnston et al. 2001, Wochner et al. 2011), albeit by molecules of considerable molecular complexity.



**Fig. 3:** Before the modern chemistry of life, which uses DNA as the repository of information and proteins as catalysts, became established, both activities may have been provided by RNA molecules (the "RNA world"), such as the hammerhead ribozyme, which can catalyze the reversible cleavage and joining of other RNA molecules. Source: A. Lupas (MPI for Developmental Biology, Tübingen).

Given the complexity of the simplest ribozymes mediating transcription and translation and the ongoing failure to obtain activated ribonculeotides from ribose and nucleobases, the RNA-world hypothesis faces substantial challenges, although these may gradually be overcome (Fig. 4; Ricardo & Benner 2007, Mast et al. 2013). In order to sidestep these issues, pre-RNA world hypotheses have also been proposed, where other, simpler replicators

preceded RNA as the genetic material (e.g. Shapiro 2007). For example, cyclic nucleotides can polymerize in water and form chains of over 100 nucleotides, due to their higher reactivity (Constanzo et al., 2009).



**Fig. 4:** Although the formose reaction, by which formaldehyde (CH2O) forms complex mixtures of carbohydrates through self-condensation, has been known since 1861, its ability to generate building blocks for biological macromolecules has been questioned in light of the rapid further reaction of the carbohydrates to tar. The discovery that its products, particularly ribose, could be stabilized by borate has resolved an essential obstacle to scenarios for the abiotic emergence of RNA. Source: Ricardo et al., Science (2004) 303:196.

The abiotic synthesis of activated building blocks (both of ribonucleotides and more reactive analogs), their assembly into information-containing polymers, and the origins of homochirality form the core of the research program on the chemical origin of life proposed for the center (for a discussion of these questions, see also the special issue of Nature Chemistry 5, 5, 2013). Several important advances have been made in recent years, suggesting a substantial gain of momentum in this field. Thus, the Sutherland group obtained activated pyrimidine ribonucleotides under prebiotically plausible conditions (Powner et al., 2009), and did so in a short sequence of reactions that bypass free ribose and the nucleobases, instead proceeding through arabinose amino-oxazoline and anhydronucleoside intermediates. Building on this breakthrough, both the Sutherland and Powner laboratories recently provided important further advances, notably a common photoredox reaction scheme for the synthesis of both ribonucleotides and proteinogenic amino-acids, and an acetylation scheme facilitating oligoribonucleotide ligation.

Particularly interesting are approaches employing geochemical or geothermal gradients - as expected on early Earth - for the synthesis of components for life (Fig. 5). Recent experiments demonstrated the escalated polymerization of nucleotides by a spatially confined thermal gradient - a situation which certainly is a viable scenario on early Earth (e.g. Mast et al. 2013). The thermal gradient led to an accumulation of monomers by thermophoresis and convection, while retaining larger polymers exponentially better. One

could imagine other scenarios where photophoresis could have served as a trap and where one could investigate the relative efficiency of the various traps. Such approaches would provide an attractive interface to the geochemical research proposed as Topic 3 and to astrophysics where other planetary "landscapes" will be characterized.



**Fig. 5:** The emergence of the building blocks of biological polymers and their assembly into macromolecules are thought to have occurred in environments with strong chemical and thermal gradients, such as would have been provided by this black smoker at a mid-ocean ridge hydrothermal vent in the Atlantic ocean. Source: OAR/National Undersea Research Program (NURP), National Oceanic & Atmospheric Adminstration (NOAA).

Once nucleic acid polymers had emerged, they would not only have encoded information and catalyzed reactions, resulting in rounds of accumulation, replication and polymerization that autocatalytically increased the molecular complexity of the system, but would also have provided structural templates for the accretion and elongation of other nascent biopolymers, such as saccharides, lipids, and particularly peptides. Peptides of increasing length and complexity, initially generated abiotically, but soon ligated by primordial versions of the ribosome, would have offered a range of attractive benefits to the emerging RNA world, such as folding efficiency, thermostability and improved catalysis. These peptides would have provided the building blocks for the proteins that underpin all functions of life today (Fig 6).



**Fig. 6:** Life today is built on the catalytic activity of proteins, but the elaborately folded structures they require for catalysis are too complex to have arisen by random concatenation of amino acids. A likely path to their emergence is the repetition, recombination and elaboration of shorter peptides that evolved in the context of RNA catalysis and replication. Source: A. Lupas (MPI for Developmental Biology, Tübingen).

# Topic 2: Characterization of exoplanet atmospheres - search for biological activity

Since the discovery of extra-solar planets around Sun-like stars only 19 years ago, the hunt for and study of these amazing objects has seen an enormous growth and is developing into a major branch of astronomy. We presently know close to 1000 extra-solar planets, including multi-planetary systems, hot and very hot Jupiters and Neptunes, planets in resonances and on eccentric orbits, and at large distances from their central stars (Seager 2010, Perryman 2011). The most surprising result of these early studies is the huge diversity in planetary system architectures, far beyond our theoretical imagination that had been mostly shaped by our knowledge from the solar system. The explanation how we can understand this huge diversity of planetary systems is presently one of the greatest challenges of modern astrophysics.

Giant extra-solar planets are easier to find. Five years ago we were still speculating how frequent Earth-type planets and Super-Earths (massive terrestrial planets) would be. From knowing only three examples in the Solar System, Earth, Mars, and Venus, we now have discovered that these low-mass planets are very frequent thanks to the amazing success of the US-led Kepler exo-planet transit mission (Lissauer et al. 2011, Howard et al. 2012, Borucki et al. 2011, 2013; Fressin et al. 2013). In addition, radial velocity studies of low-mass M stars have demonstrated that Super-Earths are likely very abundant (Bonfils et al. 2013). Based on results of the Kepler mission, Petigura et al. (2013) estimated that about 6%

of Sun-like stars harbour an Earth-size planet with orbital periods between 200 and 400 days.

But not only that, we could also determine very precisely the mass and radius of some of these planets and could thereby constrain their mean density, an important parameter for constraining their internal structure (Valencia et al. 2007). First results indicate that super-Earths are geologically more active, with more vigorous plate tectonics. These studies begin to reveal the second level of diversity, in the interior structure of planets themselves (Sasselov et al. 2008).

Recently, the *Kepler* mission returned a number of Super-Earths in the habitable zone - defined as the region around the central stars where liquid water can exist. The planet Kepler-22b is such a 2.4 Earth radius planet in the habitable zone around a Sun-like star (Borucki et al. 2012). The Kepler-62 system (Fig. 7) contains at least 5 planets with even 2 planets of 1.4 and 1.6 Earth radii in the habitable zone (Borucki et al. 2013). Based on advanced models both planets could be solid, either with a rocky composition or composed of mostly solid water.



**Fig. 7:** The Kepler-62 planetary system as discovered by NASA's Kepler mission compared to the Solar System. The central star of the Kepler-62 system has a spectral type of K2V and is smaller and cooler than the Sun. The two planets Kepler-62e and 62f are the smallest exoplanets yet found in a habitable zone. Source: NASA.

The next step in the characterization of exoplanets has already started: The characterization of the thermal and chemical structure of exoplanetary atmospheres, leading to the discovery of water, methane, ammonia and other species in the atmospheres of giant planets. The first transmission spectra of the Super-Earth GJ 1214b have been obtained recently (Desert et al. 2011, Bean et al. 2011, Fraine et al. 2013). The investigation of this object led to the conclusion that the planet's atmosphere must be dominated by water in mass or contains optically thick high-altitudes clouds or haze with the latter being more probable based on a detailed analysis of the data.

The observational characterization of the atmospheres of Super-Earths and Earth-like planets remains a technological challenge. High-contrast adaptive optics-assisted imaging at the next generation of 30-40m class telescopes (e.g. Crossfield et al. 2013), radial-velocity correlated high-resolution spectroscopy at these telescopes (e.g. Snellen et al. 2013) and transit spectroscopy with instruments on the *James Webb Space Telescope* (e.g. Fortney et al. 2013) together with dedicated space missions and ground-based instruments will all play their role in the race to characterize these atmospheres.

With our knowledge of the interior and surface conditions of super-Earths and Earth-like planets, including the Solar system planets Earth and Mars, we are able to calculate planetary spectra. Dedicated modelling efforts to understand the structure of these atmospheres, from giant to terrestrial planets, have started in a number of groups (e.g. Burrows et al. 2011, Fortney et al. 2011, Kaltenegger & Sasselov 2011, Kaltenegger et al. 2011, Howe & Burrows 2013). These studies will help to define the habitability and the best biomarkers for the variety of planetary atmospheres and environmental conditions (Kaltenegger et al. 2010, Rauer et al. 2011, Hedge & Kaltenegger 2013, Greenfell et al. 2013).

This research can be directly connected to the question if we can better characterize the early carbon and nitrogen cycle on Earth, using isotopic techniques to determine the nitrogen and carbon isotopic compositions of pre-Cambrian sedimentary organic matter and individual organic compounds as performed in the research group of C. Hallmann (MPI for Biogeochemistry). The evolution of the geochemical cycles of essential elements (e.g. C, O, P, N, S), climatic changes, and modification of the Earth's litosphere require a comprehensive understanding of the interaction between the geo-sphere and life on Earth.

Planets are driven to a set of global geochemical quasi-equilibria by global geo-cycles over geological timescales. On Earth this is the well-characterized carbon-silicate cycle, leading to a long-term stabilization of the Earth's surface temperature (Walker et al. 1981). Alternative cycles such as a sulfur cycle (Halevy et al. 2010, Kaltenegger & Sasselov 2010) certainly exist and will lead to a different chemical and thermal "landscape" on other Earth-type planets. Tectonics and plate tectonics will be major players in defining the operation of these cycles. Much can be learned from Earth, but needs to be extended to other planetary conditions; this is the first step into comparative "geo"chemistry and planetology.

# **Topic 3: Chemical inventory of Earth and dating of important events**

Astronomers have not only observed other planets, but made major progress in the characterization of proto-planetary disks around young stars, the cradles of new solar systems (Henning & Meeus 2011). Apart from constraining their physical parameters and lifetimes, we are starting to provide an inventory of molecules in these disks, from water to more complex organic molecules such as polycyclic aromatic hydrocarbons (e.g. Pascucci et al. 2009, Pontoppidan et al. 2010, Hogerheijde et al. 2011; see Henning & Semenov 2013 for a review). We can now ask the question how was water formed in these disks and delivered to early Earth? Are we seeing evidence for early delivery by hydrous silicate particles or late delivery by wet solar system bodies? What is the pathway to more complex molecules, including simple amino acids?

These complex organic molecules from our own early Solar System are preserved in primitive meteorites and comets. They can be studied in the laboratory with modern analytic techniques such as laser-assisted mass spectroscopy or nano-SIMS isotopic analysis. More than 100 different amino acids have been found in the so-called chondritic meteorites with Murchison, Allende, and Orgueil being prominent examples. The origin of these amino acids is widely debated, ranging from their chemical formation in the Solar System to delivery from the parent molecular cloud (Throop 2011). A promising approach to understand the origin of water and amino-acids would be a dedicated study of their D/H ratios and a comparison with solar-system bodies and material in proto-planetary disks.

An interesting aspect of these studies is the chirality problem (see Meierhenrich 2008): all amino acids in proteins are "left-handed". Most of the chiral amino acids in meteorites form a racemic mixture. However, non-racemic isovaline was observed in the aqueously altered carbonaceous chondrites Muchison, Orgueil, SCO 06043, and GRO 95577 with L-isovaline excess, ranging from 11 to 19% (Glavin et al. 2010). These authors concluded that aqueous alteration may have played an important role in the amplification of small initial L--handed isovaline excesses on the parent bodies. An interesting related - although debatable - hypothesis is the exogeneous delivery of biological important molecules to early Earth. Dipeptides have been found in the Murchison meteorite, but their production pathway in space was not known. Recently, Kaiser et al. (2013) demonstrated that dipeptides can be formed in molecular ice analogue materials by irradiation and annealing.

The results from the STARDUST mission, returning primitive material from comet 81P/Wild2 has recently added an enormous amount of information on cosmochemical events in the early Solar nebula and the analysis of the returned material will continue in the coming years (e.g., Brownlee et al. 2006, Zolensky et al. 2008, Matrajt et al. 2013).

This research into primitive organic molecules on early Earth can be connected to the search of early hydrocarbon biomarkers in the most ancient sediments on Earth. Here dedicated techniques have to be developed, and the molecular classes of PAHs and diamondoids may turn out to be interesting tracers of early biological activity (e.g. Grice et al. 2009). PAHs and

the cage-like saturated hydrocarbons are a very interesting class of molecules and have also attracted the attention of the laboratory astrophysics group at MPIA (e.g. Henning & Salama 1998, Jäger et al. 2011, Steglich et al. 2011).

Dedicated chemical and isotopic analysis of primitive material from the Solar System does not only allow to trace the earliest evidence for life on Earth, but also allows to reconstruct the decisive steps which led to the formation of Earth. Long-lived isotopic chronometers (e.g. <sup>238, 235</sup>U, <sup>206,207</sup>Pb, <sup>147</sup>Sm, <sup>143</sup>Nd, <sup>187</sup>Re, <sup>187</sup>Os) provide strong constraints on the chronology and differentiation processes during the early Solar System evolution (e.g. Begemann et al. 2001, Dickin 2005). The isotopic record of extinct radionuclides (e.g. <sup>26</sup>Al and <sup>182</sup> Hf) has the potential to provide reliable constraints on the planetesimal and planet core formation, and the evolution of the mantle and crust in planets (e.g. Podosek & Cassen 1994, Petaev & Wood 1998, Kleine et al. 2002). The various research results on ordinary and carbonaceous chondrites (stony meteorites) indicate that the timescale between the formation of the oldest material in the Solar system- the Calcium-Aluminium-rich inclusions (CAI) - and the chondrules is only 1-2 Myr (Amelin et al. 2002) and that achondritic parent bodies may have formed and differentiated within 2-4 Myr after the formation of the Solar System (Fig. 8). Jupiter probably reached its current mass 3-5 Myr after CAI formation (Scott 2006). This places the lifetime of the Solar nebula well within the lifetimes of protoplanetary disks constrained by astronomical observations.



**Fig. 8**: Carbonaceous chondrites - a certain class of primitive meteorites contain small white patches of refractory minerals. These calcium-aluminium-rich inclusions (CAIs) are the first condensates in the Solar System with an age of 4.567 billion years. The picture shows a piece of the Allende meteorite with the CAIs. Source: NASA

The various steps in the evolution of planet Earth are related to various fractionation steps: volatile/refractory fractionation during planetesimal formation, litophile/siderophile fractionation during core formation, and compatible/incompatible litophile fractionation during silicate differentiation. This has to be taken into account in analysing isotopic records.

For understanding and diagnosing life on planets, the structure and composition of the early Earth atmosphere and its interaction with the planetary core/crust system are crucial. The accretion of a massive gas atmosphere with Solar composition is a direct result of accretion of planetary matter from a gas-rich proto-planetary disk if the planet attains a mass of roughly 10% of today's Earth mass (Hayashi et al. 1979, Rafikov 2006). The accretion process of this atmosphere seems to be relatively rapid (Wetherill & Stewart 1993), although many of the important processes are not well understood. They include the infall rate of various components (dust, water, organics), the rise of oxygen, and the atmosphere circulation (Kasting 1993, Grenfell et al. 2010). The logical next step is to explore the evolution of the Earth atmosphere over time, from the period of planet formation to the emergence of complex life on Earth. An amazing observation is the fact that the period of Late Heavy Bombardment 3.8 Gyrs ago seems to coincide with the earliest track records of life on Earth. With the flood of atmosphere spectra of exo-planets to be expected over the coming years, we can place this research topic in a wider context of astrophysical research on planets similar and substantially different than Earth, e.g. super-Earths and ocean planets. Here the boundary conditions of the interiors and surfaces of such planets as well as the external conditions such as UV irradiation have to be taken into account.

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