

SESSION 1: THE ORIGINS OF LIFE

Origins of life systems chemistry

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By reconciling previously conflicting views about the origin of life – in which one or other cellular subsystem precedes, and then ‘invents’ the others – a new *modus operandi* for its study is suggested. Guided by this, a cyanosulfidic protometabolism is uncovered which uses UV light and the stoichiometric reducing power of hydrogen sulfide to convert hydrogen cyanide, and a couple of other prebiotic feedstock molecules which can be derived therefrom, into nucleic acid, peptide and lipid building blocks. Copper plays several key roles in this chemistry, thus, for example, copper(I)-copper(II) photoredox chemistry generates hydrated electrons, and copper(I) catalysed cross coupling and copper(II) driven oxidative cross-coupling reactions generate key feedstock molecules. Geochemical scenarios consistent with this protometabolism are outlined. Finally, the transition of a system from the inanimate to the animate state is considered in the context of there being intermediate stages of partial ‘aliveness’.

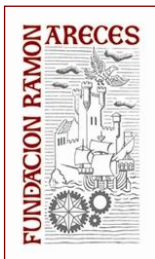
Reference: B.H. Patel, C. Percivalle, D.J. Ritson, C.D. Duffy and J.D. Sutherland (2015). 'Common origins of RNA, protein and lipid precursors in a cyanosulfidic protometabolism'. *Nature Chemistry* 7: 301-307.

Competition and cooperation of simple replicons

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In chemistry and biology three different kinds of chemical reaction networks are properly distinguished: (i) ordinary chemical reaction networks as they are discussed, for example, in prebiotic chemistry or in chemical technology, (ii) biochemical reaction networks where almost all reaction steps are catalyzed by protein enzymes as found in cellular metabolism, and (iii) autocatalytic reaction networks that contain one or more reaction steps, which follow an overall process of the general type $A + n X \rightarrow (n+1) X$ where A is the material to be consumed by the reaction and X is either a template and/or a catalyst. For $n = 1$ the process is simple autocatalysis or conventional template induced reproduction. The case $n = 2$ deals with catalyzed reproduction as found, for example, in



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symbiosis. Reaction networks of class (i) and (ii) differ essentially in two aspects from autocatalytic networks: template action and cooperative network dynamics. Template action gives rise to genetics and reaction dynamics leads to selection, quasispecies formation and Darwinian evolution for $n = 1$ or the formation of dynamically coupled and replicating symbiotic units for $n = 2$. A model is presented that combines the features of autocatalytic networks with $n = 1$ and $n = 2$ (Phil.Trans.R.Soc.B 371:20150439, 2016). Such a system shows selection at scarcity of resources being tantamount to low concentration of A, and cooperative dynamics at high concentrations. RNA molecules with suitable properties provide all prerequisites for template action and catalysis and the relation of the model with network formation among cooperative RNA replicators is discussed (Science 323:1229-1232, 2009; Nature 491:72-77, 2012).

The origins and early evolution of metabolic pathways

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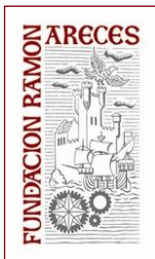
Current research on the origins of life follows the Darwinian principle of material causes operating in an evolutionary context, as advocated by A. I. Oparin and J. B. S. Haldane in the 1920s. The simplest living entity relies on the cooperation of metabolic networks and replicative genomes inside a lipid boundary. How did these functionally integrated complex systems arise in the early Earth? Diverse research projects in systems chemistry have explored the prebiotic plausibility of each of the autocatalytic subsystems and combinations thereof: self-maintained networks of small molecules, self-replicative polymers, and self-reproductive vesicles. The metabolism of the Last Common Ancestor could be reconstructed by comparative biochemistry, albeit apparently easy questions, such as the existence of an ancient autotrophic metabolism at the roots of the tree of life, are very hard to answer. Even harder is to establish the connection of the early metabolic pathways with the abiotic cosmo/geo-chemical environments. Behind the present fuzzy panorama, a common theme emerges: the role played by the substrate ambiguity and multifunctionality of the catalysers in the origin and evolution of metabolism.

The origins of cellular life on Earth

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The earliest living cells must have had very simple structures in order to emerge spontaneously from the chemistry of the early earth. We are attempting to synthesize such simple artificial cells in order to discover plausible pathways for the transition from chemistry to biology. Very primitive cells may have consisted of a self-replicating nucleic acid genome, encapsulated by a self-replicating cell membrane. We have recently described robust pathways for the coupled growth and division of primitive cell membranes



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composed of fatty acids, which were likely to have been available prebiotically. However, no process for the replication of a nucleic acid genome, independent of evolved enzymatic machinery, has yet been described. I will discuss our recent progress towards the realization of an efficient and accurate system for the chemical replication of RNA.

SESSION 2: DIVERSIFICATION OF LIFE AND EXTREMOPHILES

Microorganisms in hot springs from Costa Rica to Antarctica

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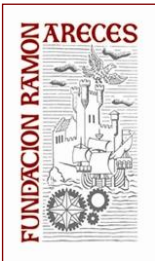
Extreme environments impose severe demands on the metabolism and molecular buildup of living beings. The necessary adaptations have been acquired in evolution by a limited number of species. As a result, extreme environments are usually less diverse and ecological relationships are simplified with respect to environments with milder conditions. We took advantage of this reduced diversity to analyze the community metabolism in hot spring microbial mats in Chilean Patagonia, by metagenomics and metatranscriptomics at different temperatures. We were able to reconstruct several genomes from these sequences and assign roles in the carbon and nitrogen cycles to specific microorganisms. In addition, hot springs are hot 'islands' in a temperate 'ocean'. Thus, we analyzed the community composition in hot spring microbial mats in Costa Rica, northern and southern Chile and the Antarctic Peninsula to determine whether thermophilic microorganisms are cosmopolitan or whether there are barriers to their dispersal.

Some like it salty: life in hypersaline environments

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Hypersaline environment have salt concentrations well above salt water and constitute extreme systems that are widely distributed in the planet. Indeed, hypersaline water masses are comparable in volume to freshwater in lakes and rivers. In spite of the extreme conditions imposed by high salt and low water activity, hypersaline systems are inhabited by a group of very specialized extremophilic microbiota. Archaea belonging the the Euryarchaea and to the Nanonaloarchaea (belonging to the so-called 'microbial dark matter') normally dominate these systems, although eukaryotes and Bacteria may also play relevant roles. These organisms have developed mechanisms that allow them no only to survive but to thrive in the harsh conditions imposed by high salt and low water activity. For instance, very frequently extremely halophilic microbes use a salt-in strategy in which



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the high external osmotic pressure is compensated by accumulating inorganic salts in the cytoplasm, which imposes constraints to intracellular proteins. Finally, hypersaline brines harbor the highest concentration of virus-like particles reported so far for aquatic environments and thus are excellent scenarios for studying virus-hosts interactions. In addition to their ecological and evolutionary interest, extremely halophilic microbes can be considered as models for the study of life in extraterrestrial systems such as the Jupiter's moon Europa or Mars, where salt deposits have been found. Thus, the study of extreme halophiles could shed light on the putative mechanisms of evolution and adaptation of life in other planets.

Getting under Atacama's rocky skin: life's last refuge

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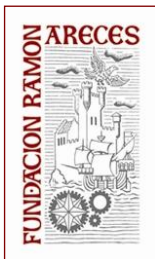
The last few decades have shown a surge of interest in the world of microorganisms that live in extreme environments. It can be argued that the combination of extreme conditions existing on the deserts present one of the most extreme environmental settings faced by microbial life. Microbial cells in extremely arid deserts need to withstand the severe biochemical stresses created by the lack of water, exposure to high levels of UV and photosynthetic active radiation, along with temperature fluctuations and/or high salinity. In this inhospitable environment, microbial life has found the refuge in very specific microhabitats - inside the rocks - within so called endolithic habitat. Endolithic colonization can be viewed as a stress avoidance strategy, where the architecture of habitable rocks provides efficient protection from incident lethal UV radiation, thermal buffering, and physical stability and first of all enhanced moisture availability. The study of the Atacama's extremophilic and extremotolerant microorganisms has therefore important implications for the understanding of the limits of life on Earth, as well as may provide us with clues on the possibility of the existence of similar life elsewhere in the Universe.

Life in extremely acidic environments: Rio Tinto as a Mars terrestrial analog

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The NASA Astrobiology roadmap underlines the importance of extreme environments and the microorganisms that live on them to evaluate the possible existence of life outside planet Earth. Between the extremophiles acidophiles are of special interest because the extreme environmental conditions in which they thrive are the metabolic product of chemolithotrophic microorganisms that obtain their energy from inorganic mineral substrates, like pyrite, a property that places them among the best candidates for a successful primitive energy conservation system. A thorough geomicrobiological



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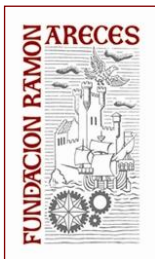
characterization of an extreme acidic environment, Río Tinto, has revealed the importance of the iron cycle in the water column of the river and detected a high level of metabolic diversity on the sediments and subsurface of the Iberian Pyrite Belt due to the presence of micro-niches with environmental conditions quite different from the bulky acidic conditions and high redox potentials existing in the river. The identification of iron oxides and iron sulfates on the surface of Mars, similar to those produced in the Tinto basin by the metabolic activity of chemolithotrophic microorganisms, has given Río Tinto the status of a geochemical and mineralogical terrestrial analog of Mars. The argument that Mars' environmental conditions are not suitable for biological methane productions could be easily challenged by the methane production observed in the sediments of Río Tinto and the subsurface of the Iberian Pyrite Belt.

SESSION 3: THE SEARCH OF LIFE BEYOND EARTH

Characterization and synthesis of organic matter in comets and meteorites
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Comets are relics of the formation of our solar system that contain a fraction of organic matter rich in oxygen and nitrogen. These molecules were probably formed in pre-cometary dust particles exposed to radiation. Some meteorites of asteroidal origin, in particular carbonaceous chondrites like Murchison, host a suite of amino acids, sugar-related molecules, and other species of prebiotic interest. The delivery of exogenous matter via comets, meteorites and interplanetary dust could have played a role in the appearance of life on Earth. The formation of relatively complex molecules in pre-cometary dust grains covered by ice mantles has been simulated experimentally under vacuum. Photon (UV and X-rays) and cosmic-ray (protons, electrons, heavier nuclei) irradiation of ice mixtures containing H₂O, CO, CO₂, CH₃OH, and NH₃, forms radicals that react with other radicals or with molecules in the ice. Among other organic species of prebiotic interest, amino acids and sugars were produced in these experiments. There is, however, a large gap between the laboratory results and the reduced set of organic molecules inferred from observations of the interstellar medium and cometary missions. The ESA-Rosetta mission has contributed to fill this gap with the detection of desorbing molecules from the comet nucleus using the ROSINA mass spectrometer, and the chemical analysis



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of the dust during landing on the nucleus by the Ptolemy and COSAC instruments. These findings will be interpreted after comparison to the available laboratory data on ice irradiation and warm-up. The possible formation routes of some organic species in ice mixtures will be discussed.

The detection and characterization of Earth-like extrasolar planets

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Planets appear to be ubiquitous in the Galaxy. Their properties and the architecture of planetary systems are much richer and more varied than previously anticipated. The last two decades have witnessed a tremendous advance in our knowledge of planetary-mass worlds: they exist not only around stars but also reveal themselves as companions to brown dwarfs and free floating in the Milky Way, thus challenging all current theories for the formation of stars, planets and planetary systems. The first discoveries of planets orbiting stars others than the Sun were announced in the 1990s, and young giant planets in isolation were found a few years later. Today, over 3,000 planets are known, a similar number of candidates is still awaiting confirmation, and only a few have well characterized atmospheres, including super-Earths (i.e., planets slightly more massive and bigger than our own world). Observations of planets, particularly Earth-like planets, demand the most sophisticated space- and ground-based telescopes; the extrasolar planetary research has become one major science driver for future instrumental development. In this presentation, we shall review the most impacting discoveries and our current understanding of the properties of extrasolar planets. Special attention will be given to the search for rocky planets in the habitable zones of their parent stars.

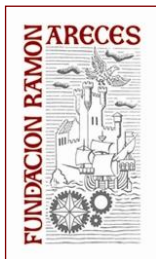
The search for life in ocean worlds of the outer Solar System

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At least five moons in the outer Solar System may harbor liquid water oceans: Europa, Ganymede, Callisto, Enceladus and Titan. These oceans have likely persisted for much of the history of the Solar System and, as a result, they are highly compelling targets in our search for life beyond Earth. In this talk I will explain the science behind why we think we know these oceans exist and what we know about the physical and chemical conditions that likely persist on these worlds. I will focus on the surface chemistry of Jupiter's moon Europa and connect laboratory spectroscopic measurements to ground and space-based observations of Europa's surface.

References: F. Raulin, K.P. Hand, C.P. McKay and M. Viso (2010). 'Exobiology and Planetary Protection of icy moons'. *Space Science Reviews* 153: 511-535. K.P. Hand and R.W. Carlson (2015). 'Sea Salt on Europa'. *Natural History* 123: 34-37.



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