Program

LUNAR AND PLANETARY INSTITUTE

USRA

XVIIIth International Conference on the Origin of Life

July 16–21, 2017 • San Diego, California

Institutional Support
International Society for the Study of the Origin of Life
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University of California, San Diego

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Abstracts for this conference are available via the conference website at

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Guide to Sessions

Sunday, July 16, 2017

4:00 p.m.	Price Center Ballroom West	Plenary Opening Lecture

Monday, July 17, 2017

8:30 a.m.	Price Center Theatre	Exoplanets from an Origin of Life Perspective and the Search for Life and Its Precursors in the Solar System
2:00 p.m.	Price Center Theatre	Meteorites, Comets and the Fate of Their Organic Matter I
4:10 p.m.	Price Center Theatre	Meteorites, Comets and the Fate of Their Organic Matter II
7:00 p.m.	Price Center Theatre	Panel: How can Exoplanet Research take Advantage of the Cooperation with Origin of Life Studies?

Tuesday, July 18, 2017

8:30 a.m.	Price Center Theatre	The Environmental Conditions for the Origin of Life on the Early Earth
11:00 a.m.	Price Center Theatre	The Environmental Context and Early Life on Earth
2:00 p.m.	Price Center Theatre	The Formation and Evolution of Organics on the Early Earth
4:10 p.m.	Price Center Theatre	The Role of Minerals in the Fate of Organic Matter and Chemical Evolution
7:00 p.m.	Price Center Theatre	Panel: The Role of Minerals in the Fate of Organic Matter and Chemical Evolution

Wednesday, July 19, 2017

8:30 a.m.	Price Center Theatre	Chemical Evolution Towards the Transition of Life
1:00–5:00 p.m.		Excursion to the Birch Aquarium (purchase required)
1:30–4:00 p.m.		Closed ISSOL Business Meeting
4:30–5:30 p.m.		Open ISSOL Business Meeting
7:00 p.m.	Price Center Theatre	Panel: 64 Years After Miller Experiment, Can the Formation of Building Blocks of Life be Considered as Solved?

Thursday, July 20, 2017

8:30 a.m.	Price Center Theatre	Self-Organization and Prebiotic Molecular Systems
11:00 a.m.	Price Center Theatre	The Interplay of the Different Subsystems for the Origin of Life: Fatty Acids or Other Compartment–Forming Systems/Amino Acids/Nucleotides
2:00 p.m.	Price Center Theatre	Early Metabolisms and Development of Compartmentation
2:40 p.m.	Price Center Theatre	Panel: The Role of Compartments
4:10 p.m.	Price Center Theatre	Genetic Information and Function in the Early Stages of Life
7:00 p.m.	Price Center Theatre	Special Session in Honor of Jim Ferris: From the Prebiotic Synthesis of Bases and Polymerization to RNA World Research/Concepts

Friday, July 21, 2017

8:30 a.m.	Price Center Theatre	Evolution: The Driving Force for Evolution at the Chemical and Biological Stages
9:30 a.m.	Price Center Theatre	Panel: Evolution: The Driving Force for Evolution at the Chemical and Biological Stages
11:00 a.m.	Price Center Theatre	Evolution: Before and After LUCA/Evolution of Metabolism
2:00 p.m.	Price Center Theatre	Evolution: Competition, Cooperativity, Complexity and Ecology

Posters

Price Center Ballroom East and Forum Posters will be on Display for the Entire Week.

Presenters are Requested to be Present at Their Poster During the Last Half-Hour Break of the Evening

Exoplanets from an Origin of Life Perspective and the Search for Life and It's Precursors in the Solar System

Meteorites, Comets and the Fate of Their Organic Matter

Environmental Conditions for the Origin of Life on the Early Earth

The Formation and Evolution of Organics on the Early Earth

The Role of Minerals in the Fate of Organic Matter and Chemical Evolution

Chemical Evolution Towards the Transition of Life

Self-Organization and Prebiotic Molecular Systems

Interplay of the Different Subsystems for the Origin of Life: Fatty Acids or Other Compartment-Forming Systems/Amino Acids/Nucleotides

Early Metabolisms and Development of Compartmentation

Genetic Information and Function in the Early Stages of Life

Special Session in Honor of Jim Ferris: From the Prebiotic Synthesis of Bases and Polymerization to RNA World Research/Concepts

Evolution: The Driving Force for Evolution at the Chemical and Biological Stages

Evolution: Before and After LUCA/Evolution of Metabolism

Evolution: Competition, Cooperativity, Complexity and Ecology

Sunday, July 16, 2017
PLENARY OPENING LECTURE
4:00 p.m. Price Center Ballroom West

Chair: Ulrich Muller

4:00 p.m. Muller U. F. *
Welcome Lecture

4:15 p.m. Szostak J. W. *
The Nonenzymatic Copying of RNA Templates **[#4109]**
I will discuss recent progress in the chemical replication of short RNA templates.

Monday, July 17, 2017
EXOPLANETS FROM AN ORIGIN OF LIFE PERSPECTIVE AND
THE SEARCH FOR LIFE AND ITS PRECURSORS IN THE SOLAR SYSTEM
8:30 a.m. Price Center Theatre

Chair: Dimitar Sasselov

8:30 a.m. Seager S. *
Searching for Signs of Life on Exoplanets **[#4227]**
The search for life in other planetary systems is a relatively new but exciting endeavor. The ambitious goal of identifying a habitable or inhabited exoplanet is within reach.

9:25 a.m. Tian F. *
Exoplanet Habitability and Biosignature Detection **[#4076]**
In this talk the most recent developments on planetary habitability and biosignature detections will be discussed.

9:50 a.m. Lineweaver C. H. * Chopra A.
The Case for a Gaian Bottleneck: The Biology of Habitability (i.e. The Potential Non-Dominance of Abiotic Factors in Creating Circumstellar Habitable Zones) **[#4148]**
We present the Gaian Bottleneck Hypothesis: If life emerges on a planet, it only rarely evolves quickly enough to regulate greenhouse gases and albedo, thereby maintaining surface temperatures compatible with liquid water and habitability.

10:15 a.m. *Coffee Break*

10:45 a.m. Des Marais D. J. *
Exploring Mars for Evidence of Habitable Environments and Life **[#4214]**
The climate of Mars has been more similar to Earth's climate than to that of any other planet in our solar system. Still, Mars represents a different example of how planetary environments and processes might affect the presence of life.

11:40 a.m. Hand K. P. *
The Search for Signs of a Second Origin of Life in Ocean Worlds of the Outer Solar System **[#4205]**
The best places to test the 'biology hypothesis' are ocean worlds of our outer solar system (e.g. Europa and Enceladus). Experiments to characterize organics on ocean worlds, pathways for origins, and future in situ missions will be described.

12:05 p.m. Le Sergeant d Hendecourt L. *
From Astrochemistry to Astrobiology: The Importance of Cosmic Ices for the Exogeneous Delivery of Organic Matter onto Telluric Planets Toward the Onset of Prebiotic Chemistry **[#4101]**
Cosmic ices are observed in molecular clouds out of which stars, planets and debris form. Ices, submitted to energetic and thermal processes in the laboratory form a rich organic chemistry in which bricks of biological importance are detected.

12:30 p.m. *Lunch*

Monday, July 17, 2017
METEORITES, COMETS AND THE FATE OF THEIR ORGANIC MATTER I
2:00 p.m. Price Center Theatre

Chair: Hiroshi Naraoka

2:00p.m. Bredehöft J. H. * Schmidt F. Goesmann F.
The Organics on the Nucleus of 67P/C-G and How They Might have Gotten There **[#4091]**
The COSAC instrument aboard Rosetta mission lander Philae identified a suite of 16 small organic molecules on the nuclues of comet 67P/Churyumov-Greasimenko. Laboratory studies show a complex inter-relation between these and possibly other compounds.

2:20 p.m. Cottin H. * Altwegg K. Baklouti D. Bardyn A. Briois C. Engrand C. Fray N. Le Roy L. Modica P. Raulin F. Schulz R. Siljestrom S. Thirkell L. Isnard R.
Comets and Astrobiology, (Re)Assessment for Comet 67P After Rosetta **[#4082]**
The form in which carbon has been delivered to the early Earth by comets, and implications for the origin of life, will be discussed with regard to the new inventory of organic matter detected by Rosetta instruments in comet 67P.

2:40 p.m. Yabuta H. * Noguchi T. Itoh S. Nakamura T. Okazaki R. Tachibana S. Terada K. Ebihara M. Nagahara H.
Coevolution of Organic and Inorganic Compounds in the Early Solar System Revealed from Antarctic Micrometeorites **[#4216]**
We investigated Antarctic micrometeorites and revealed that the precursor compositions of meteoritic organics prior to parent body aqueous alteration were enriched in carboxyls, aliphatic carbon, and nitriles or pyrimidines.

3:00 p.m. Martins Z. * Modica P. Zanda B. d'Hendecourt L.
The Degree of Aqueous Alteration of Carbonaceous Chondrites and its Influence on the Soluble Organic Content **[#4114]**
The degree of aqueous alteration on the parent body of CM chondrites appears to have influenced the distribution and relative abundance of their soluble organic compounds.

3:20 p.m. Kebukawa Y. * Chan Q. H. S. Misawa S. Matsukuma J. Tachibana S. Kobayashi K. Zolensky M. E.
Synthesis of Amino Acid Precursors with Organic Solids in Planetesimals with Liquid Water **[#4062]**
We demonstrated synthesis of a complex suite of amino acids simultaneously with IOM via hydrothermal experiments starting from formaldehyde, glycolaldehyde and ammonia, simulating the aqueous processing in the planetesimals.

3:40 p.m. *Coffee Break*

Monday, July 17, 2017
METEORITES, COMETS AND THE FATE OF THEIR ORGANIC MATTER II
4:10 p.m. Price Center Theatre

Chair: George Cooper

4:10 p.m. Rios A. C. * Cooper G.
A Prebiotic Pyruvate Reaction Network that Leads to a Continuous Production of Metabolic Compounds: Evidence from Carbonaceous Chondrites? **[#4171]**
We attempt to show that the chemistry of pyruvate leads to the sustained production of labile compounds found in carbonaceous chondrites and its implications for a proto-metabolism.

4:30 p.m. Meinert C. * Jones N. C. Hoffmann S. V. Nahon L. d'Hendecourt L. Meierhenrich U. J.
Chiral Sugar and Amino Acid Formation in Simulated Cometary Matter Inches Closer to Explaining the Emergence of Homochiral Life **[#4029]**
Simulated cometary ice experiments have indicated that circularly polarised light could be the initial source of life's handedness. We detected chiral sugars, amino acids and their molecular precursors within these interstellar achiral ice analogues.

4:50 p.m. Pizzarello S. * Yarnes C. T.
Chiral Molecules in Space and Their Likely Passage to Planetary Bodies as Recorded by Meteorites **[#4110]**
We searched Murchison meteorite extracts for propylene oxide (PO), the only chiral molecule discovered so far outside solar environments[3], and detected its possible derivative.

5:10 p.m. Chan Q. H. S. * Zolensky M. E. Kebukawa Y. Fries M. Ito M. Steele A.
Organic Matter in Extraterrestrial Water-Bearing Salt Crystals **[#4069]**
Abundant, primitive, and highly-diverse ^{15}N-rich organic compounds were detected in brine-water bearing halite crystals that were synthesized on a cryovolcanically-active asteroid.

5:25 p.m. Glavin D. P. * Aponte J. C. Blackmond D. G. Burton A. S. Dworkin J. P. Elsila J. E.
L-Amino Acid Enantiomeric Excesses in Meteorites: Formation Mechanisms and Implications for the Origin of Homochirality **[#4059]**
Large L-amino acid excesses have been discovered in carbonaceous meteorites that have experienced aqueous alteration on their parent bodies. Plausible amplification mechanisms and the implications for the origin of homochirality will be discussed.

5:40 p.m. *Session Adjourns*

Monday, July 17, 2017
HOW CAN EXOPLANET RESEARCH TAKE ADVANTAGE OF THE COOPERATION WITH ORIGIN OF LIFE STUDIES?
7:00 p.m. Price Center Theatre

Moderator: **Dimitar Sasselov**

Panel Members: **Sara Seager**
Charles Lineweaver
Feng Tian

This session explores how the relatively new field of exoplanet research can potentially utilize knowledge gained from origin of life studies.

Tuesday, July 18, 2017
THE ENVIRONMENTAL CONDITIONS FOR THE ORIGIN OF LIFE ON THE EARLY EARTH
8:30 a.m. Price Center Theatre

Chair: Francis Westall

8:30 a.m. Ueno Y. * Endo Y. Zang X. Kawade W.
Revisiting Redox State of the Early Earth's Atmosphere and Prebiotic Synthesis **[#4129]**
Our recent experiment showed that Archean atmosphere would have been reducing, possibly including and levels of CO or CH_4 to explain S-MIF record. In such a CO-bearing atmosphere, UV induced photochemistry can create various building blocks of life.

9:10 a.m. Damer B. F. * Djokic T. Van Kranendonk M. J. Deamer D. W.
Oldest Convincing Evidence for Life on Earth Discovered in Archaean Subaerial Hot Springs: Implications for an Origin of Life on Land **[#4162]**
New discoveries of well-preserved stromatolites in a 3.48 Ga Archean hot spring in Western Australia depict a vibrant microbial community thriving in fresh water on land, suggesting this as a locality for the origin and early evolution of life.

9:30 a.m. Kakegawa T. *
High Abundance of Borate in Hadean Proto-Arc Environments to Form Prebiotic Ribose and Nucleotide?: Geological Constraints from Isua Supracrustal Belt **[#4074]**
New geological information from Isua Supracrustal Belt gives a model to illustrate where and how prebiotic ribose and nucleotide formed. This geological model is consisting with current prebiotic experimental results.

9:50 a.m. Pasek M. A. * Herschy B.
Solubilization and Activation of Phosphorus on the Early Earth **[#4117]**
We present here a new route to the formation of reactive phosphorus compounds. This route couples redox chemistry of phosphorus (reduction by iron, oxidation by simple oxidants) to the production of polyphosphates.

10:10 a.m. Morasch M. * Liu J. Braun D.
Thermally Driven Accumulation and Dry-Wet Cycles of Nucleotides **[#4153]**
We show how a nonequilibrium system in form of a temperature gradient across porous rock creates high local concentrations and dry-wet cycles of nucleotides and other molecules.

10:30 a.m. *Coffee Break*

Tuesday, July 18, 2017
THE ENVIRONMENTAL CONTEXT AND EARLY LIFE ON EARTH
11:00 a.m. Price Center Theatre

Chair: **David DesMarais**

11:00 a.m. Westall F. * Hickman-Lewis K. Cavalazzi B. Gautret P. Campbell K. A. Breheret J. Foucher F. Hinman N. Sorieul S.
A Hydrothermal Setting for Early Life **[#4125]**
Ubiquitous contemporaneous hydrothermal activity and input from the macroscopic to elemental scale into the early Earth environment suggests that its microbial inhabitants must have been at least mesophilic, if not thermophilic.

11:30 p.m. Arrhenius G. * Pérez-Montaño S. H. van Zuilen M. A. Misra A. Lepland A. Daraio C.
Earliest Life on Earth **[#4217]**
The carbon from decaying organic matter forms as the rhombohedral type of graphite .This form also occurs in the 3.8 Gyr old Isua rock and may be taken as evidence of life or conversion of hexagonal graphite under tectonic stress.

12:00p.m. Bassez M. P.
Geobiotropy: The Evolution of Rocks in Symbiosis with Prebiotic Chemistry **[#4045]**
In their interaction with water, minerals inside rocks transform with production of elements and small molecules which intervene in prebiotic syntheses. This chemical evolution between the world of rocks and the world of life is called geobiotropy.

12:30 p.m. *Lunch*

Tuesday, July 18, 2017
THE FORMATION AND EVOLUTION OF ORGANICS ON THE EARLY EARTH
2:00 p.m. Price Center Theatre

Chair: Kensei Kobayashi

2:00 p.m. Vaida V. * Rapf R. J. Perkins R. J.
Harnessing Energy from Stellar Radiation to Build Chemical Complexity for Life **[#4116]**
This presentation discusses results of our laboratory experiments modeling the use of sunlight to generate abiotically the chemical complexity needed for the synthesis of biopolymers necessary for life, using the chemistry of pyruvic acid.

2:20 p.m. Burton A. S. * Berger E. L.
Chiral Selectivity as a Bridge to Homochirality **[#4119]**
We investigate the transition from racemic, abiotic chemistry to homochiral polymers used in proteins; exploring the polymerization behavior of chiral amino acids to determine if they show a preference for homochiral or heterochiral polymerization.

2:40 p.m. Saitta A. M. * Pietrucci F.
From Quantum Computational Physics to the Origins of Life **[#4046]**
Quantum atomistic computational methods have yet to make a breakthrough in prebiotic chemistry. Here I present, via our new topological approach to chemical networks, ab initio studies from Miller experiment to RNA nucleotide synthesis in solution.

3:00 p.m. Forsythe J. G. Weber A. L. *
Prebiotic Peptide (Amide) Bond Synthesis Accelerated by Glycerol and Bicarbonate Under Neutral to Alkaline Dry-Down Conditions **[#4064]**
We report a new process for robust peptide bond synthesis in the pH 6–10 range that involves dry-down heating of amino acids in the presence of glycerol and bicarbonate (substrates: L-alanine, L-2-aminobutyric acid, β-alanine, isoserine).

FLASH TALKS HIGHLIGHTING POSTERS

3:20 p.m. Bada J. L. * Chalmers J. Burton A. Scheu B. Cimarelli C. Dinwell D. B.
Laboratory Simulated Volcanic Lightning and Prebiotic Synthesis **[#4102]**

3:25 p.m. Schreiber U. * Mayer C. Bronja A. Schmitz O. J.
Archean Fluid Inclusion of Hydrothermal Quartz Minerals — Archives of Prebiotic Chemistry on Early Earth? **[#4018]**

3:30 p.m. Kolb V. M. *
Prebiotic Organic Reactions in Water **[#4025]**

3:32 p.m. Gavette J. V. * Krishnamurthy R. Springsteen G.
Exploring the Role and Reaction Constraints of Malonate Within the Context of the "Glyoxylate Scenario" **[#4167]**

3:34 p.m. Jaipaul R. Tewari B. B. *
Interaction of Alanine and Aspartic Acid with Aluminum, Iron and Zinc Oxides and its Relevance in Chemical Evolution **[#4033]**

3:36 p.m. Kim H. J. *
Stereoselective Prebiotic Nucleotide Synthesis for Threose Nucleic Acid **[#4184]**

3:38 p.m. Takahashi J.
Biological Homochirality and Symmertry Breaking of the Universe **[#4156]**

3:40 p.m. *Coffee Break*

Tuesday, July 18, 2017
THE ROLE OF MINERALS IN THE FATE OF ORGANIC MATTER AND CHEMICAL EVOLUTION
4:10 p.m. Price Center Theatre

Chair: Matthew Pasek

4:10 p.m. Cooper G. J. T. * Surman A. J. Cronin L.
Steering Complex Reaction Networks with Minerals **[#4056]**
Uncontrolled condensation reactions are expected to produce a combinatorial explosion. However, this can be tamed; Environmental changes (i.e. minerals) can programme the condensation amino acids into consistently different products/structures.

4:50 p.m. Akouche M. Jaber M. Maurel M.-C. Lambert J.-F. Georgelin T. *
A Molecular Vestige of the Origin of Life on Minerals: Phosphorybosyl-Disphosphate **[#4085]**
Nucleotides were synthesized from Ribose, Adenine, and phosphates on silica surfaces in one pot process. A important molecular intermediate was enlightened, the phosphoribosyl pyrophosphate. This molecule is a molecular relic of early earth.

5:10 p.m. Piedrafita G. * Castro C. Messner C. Griffin J. L. Ralser M.
High-Throughput Kinetic Screening of Non-Enzymatic Metabolic Conversions Driven by Single Amino Acids **[#4213]**
A screening for catalytic effects of single amino acids on central metabolism is done by high-throughput LC/MS experiments, finding several non-enzymatic reactions driven by cysteine/iron(II), with implications on evolution of first biocatalysts.

5:30 p.m. *Session Adjourns*

Tuesday, July 18, 2017
THE ROLE OF MINERALS IN THE FATE OF ORGANIC MATTER AND CHEMICAL EVOLUTION
7:00 p.m. Price Center Theatre

Moderator: **Jean-Francois Lambert**

Panel Members: **Robert Hazen**
Matthew Pasek

This session discusses issues comprising prebiotic minerals in the origin and/or evolution of early organic matter.

Wednesday, July 19, 2017
CHEMICAL EVOLUTION TOWARDS THE TRANSITION OF LIFE
8:30 a.m. Price Center Theatre

Chairs: **Ramanarayanan Krishnamurthy**
Yitzhak Tor

8:30 a.m. Deamer D. W. * Damer B. F. Van Kranendonk M. J. Djokic T.
An Origin of Life in Cycling Hot Spring Pools: Emerging Evidence from Chemistry, Geology and Computational Studies **[#4130]**
New evidence for an origin of life in a hot spring setting on land is supported by three studies: chemical (polymerization in wet-dry cycles), geological (stromatolites in a 3.48 Ga geothermal field) and computational (verifying the kinetic trap).

8:50 a.m. Parker E. T. * Forsythe J. G. Fernandez F. M.
An Evaluation of the Prebiotic Plausibility of Depsipeptide Synthesis Under Possible Primitive Conditions **[#4163]**
This research evaluates the primordial plausibility of generating depsipeptides (containing mixed amide/ester linkages) from prebiotic simulation experiments, as literature reports surmise depsipeptides may enable primitive polypeptide synthesis.

9:10 a.m. Camprubi E. * Lane N.
Alkaline Hydrothermal Vents as Electrochemical Reactors Driving an Auto-Trophic Origin of Life **[#4168]**
We report the reduction of CO_2 to formaldehyde under simulated alkaline hydrothermal conditions. Formaldehyde is transformed into relevant sugars via the formose reaction. Acetyl phosphate can also be synthesised and phosphorylates organic molecules.

9:30 a.m. Furukawa Y. * Takeuchi Y. Kobayashi T. Sekine T. Kakegawa T.
Amino Acid Formation by Asteroid Impacts on Ammonia-Free Oceans **[#4075]**
Impacts of asteroids have potential to have provided inorganic reductants to the prebiotic Earth. This study shows the results of experiments simulating post-impact reactions and shows the formation of amino acids with N_2 as the nitrogen source.

9:50 a.m. Becker S. * Carell T.
Parallel Prebiotic Origin of Canonical and Non-Canonical Purine Nucleosides **[#4118]**
RNA of all living organisms is highly modified. It is unclear if these non-canonical bases are ancestors of an early Earth or biological inventions. We investigated a prebiotic pathway that leads to canonical and non-canonical purine nucleosides.

10:10 a.m. Ashkenasy G. * Chotera A.
Chemical Evolution Routes to Functional Peptide-Nucleic Acid Chimeras **[#4120]**
We discuss a prebiotic system relevant for the pre-LUCA transition from RNA or peptides alone into today's DNA-RNA-proteins triad, highlighting structure and function synergies along a putative trajectory producing DNA-peptide conjugate assemblies.

10:30 a.m. *Coffee Break*

11:00 a.m. Petrov A. S. * Gavette J. V. Krishnamurthy R. Hud N. V.
Exploring the Stability of DNA/RNA Chimeras by MD simulations: Could Early Life have Utilized Mixed DNA/RNA Duplexes? **[#4198]**
We report an MD study of a DNA to RNA transition by two pathways that are different by the order of purine and pyrimidine mutations. The results reveal substantial differences in the structure and energetics of these transitions.

11:20 a.m. Bhowmik S. * Stoop M. Krishnamurthy R.
Heterogeneity to Homogeneity: Synthesis, Base Pairing, and Ligation Studies of 4',3'-XyluloNA/RNA and TNA/RNA Chimeric Sequences **[#4219]**
Based on the reality of "prebiotic clutter," we herein present an alternate model for pre-RNA to RNA transition, which starts, not with homogeneous-backbone system, but rather with mixtures of heterogeneous-backbone of chimeric "pre-RNA/RNA."

11:40 a.m. Liu Y. * Shu W. Y. Yu Y. F. Ji Z. L. Zhao Y. F.
Ser-His Dipeptide : A Potential Candidate of the Prototype for Serine Protease **[#4026]**
Ser-His is a magical dipeptide with protease activity. It is obtained easily in prebiotic conditions, could hydrolyze all 20 amino acids with different efficiencies and substrate proteins broad spectrum. It maybe a potential candidate of the serine protease prototype.

12:00 p.m. Mariani A. * Sutherland J. D.
Non-Enzymatic RNA Backbone Proofreading by Energy-Dissipative Recycling **[#4054]**
Degradation and repair of non-natural backbone linkages as a plausible scenario for the prebiotic evolution of RNA on the early Earth.

12:20 p.m. Pressman A. D. * Moretti J. E. Campbell G. W. Muller U. F. Chen I. A.
Estimating Ribozyme Kinetics from Analysis of In Vitro Selection **[#4147]**
Accurately mapping the pathways of potential evolution in an RNA world would require better methods for approximating ribozyme activity. We demonstrate a mathematical process for high-throughput estimation of activity across a ribozyme landscape.

12:40 p.m. *Session Adjourns*

Wednesday, July 19, 2017
64 YEARS AFTER MILLER EXPERIMENT,
CAN THE FORMATION OF BUILDING BLOCKS OF LIFE BE CONSIDERED AS SOLVED?
7:00 p.m. Price Center Theatre

Moderator: **Antonio Lazcano**

Panel Members: **Jack Szostak**
Steven Benner
Nicholas Hud
Donna Blackmond

Thursday, July 20, 2017
SELF-ORGANIZATION AND PREBIOTIC MOLECULAR SYSTEMS
8:30 a.m. Price Center Theatre

Chair: Matthew Powner

8:30 a.m. Otto S. *
Can We Make Life in the Lab? Emergence and Evolution of Self-Replicating Molecules from Dynamic Molecular Networks **[#4089]**
Self-replicating molecules can emerge spontaneously from mixtures of interconverting molecules. Self-assembly of molecules drives their replication. In a replication-destruction regime Darwinian evolution of such systems is feasible.

9:10 a.m. Devaraj N. K. *
In Situ Synthesis of Lipid Membranes **[#4030]**
We have a strong interest in applying covalent coupling reactions to the formation and modification of lipid membranes. We have utilized chemoselective reactions, such as copper-catalyzed triazole formation or the native chemical ligation.

9:30 a.m. Lozoya Colinas A. * He C. Gállego I. Grover M. A. Hud N. V.
Viscosity-Mediated Replication of an RNA Duplex Containing a Ribozyme Motif **[#4180]**
An important goal in the origins of life field is the demonstration of an RNA system that can undergo sustained cycles of replication. Here we propose a replication system enabled by a viscous solvent of a gene-length RNA duplex containing a ribozyme sequence.

9:50 a.m. Ross D. S. *
The Questionable Prospect of Deep Sea Alkaline Vents as Origin Sites **[#4032]**
It is argued that the faulty application of both kinetic and thermodynamic factors employed in its support invalidates the notion that deep sea alkaline vents were the sites of the life's origins.

10:10 a.m. Mayer C. * Schreiber U. Dávila M. J. Bronja A. Schmitz O. J.
Evolution of Prebiotic Peptides in Amphiphilic Environments **[#4017]**
We present experimental evidence that vesicles, spontaneously forming in tectonic fault zones in the Earth's crust, are capable of selecting and accumulating hydrothermally generated peptide molecules which integrate into the vesicle membrane.

10:30 a.m. *Coffee Break*

Thursday, July 20, 2017
THE INTERPLAY OF THE DIFFERENT SUBSYSTEMS FOR THE ORIGIN OF LIFE: FATTY ACIDS OR OTHER COMPARTMENT–FORMING SYSTEMS/AMINO ACIDS/NUCLEOTIDES
11:00 a.m. Price Center Theatre

Chair: Greg Springsteen

11:00 a.m. Joshi M. P. Rajamani S. *
Stability of Amphiphilic Systems in Terrestrial Hydrothermal Fields and its Implications for the Origin of Cellular Life **[#4149]**
Characterization of the stability of prebiotically relevant amphiphiles in hot spring samples collected from high altitude locations of Ladakh region in India; an Astrobiologically relevant site for studying life under extreme conditions.

11:20 a.m. Black R. A. * Gordon M. T. Cornell C. Ramsay A. Keller S. L.
Polymer Building Blocks and Dipeptides Stabilize Fatty Acid Vesicles **[#4128]**
How did the biological polymers, RNA and protein, became associated with a membrane? We present evidence that the building blocks of the polymers bind to fatty acid bilayers, and that this binding increases the formation and stability of membranes.

11:40 a.m. Tsuji G. Fujii S. Sunami T. Yomo T. *
Sustainable Proliferation of Liposomes Compatible with Inner RNA Replication **[#4040]**
We demonstrate the concurrent incorporation of nutrients and membranes into RNA-containing liposomes. The proliferation of liposomes, RNA replication, and distribution of the replicated RNA to daughter liposomes were observed compatibly by 10 cycles.

12:00 p.m. Fraccia T. P. Smith G. P. Todisco M. Zanchetta G. Clark N. A. Bellini T.
Liquid Crystal Self-Assembly of Short RNA/DNA Oligomers as Autocatalytic Pathway for Ribozymes Formation **[#4065]**
The collective behavior of short DNA/RNA oligomers and mononucleotides suggests a pathway by which linear self-assembly and spontaneous liquid crystal ordering might have enhanced the prebiotic formation of long and potentially active RNA polymers.

12:20 p.m. *Lunch*

Thursday, July 20, 2017
EARLY METABOLISMS AND DEVELOPMENT OF COMPARTMENTATION
2:00 p.m. Price Center Theatre

Chair: Sheref Mansy

2:00 p.m. Mast C. B. Möller F. Lanzmich S. Keil L. Braun D. *
Hosting Early Evolution in Heated Pores of Rock **[#4037]**
Recent experiments with non-equilibrium micro-systems suggest that porous rock conditions drive early molecular evolution in many ways, including accumulation, polymerization, replication, length selection and gelation.

2:20 p.m. Moran J. *
Can Autotrophic Carbon-Fixing Pathways be Catalyzed Without Enzymes? **[#4055]**
This talk summarizes our efforts to identify non-enzymatic catalysts for the reductive Krebs cycle and the AcCoA pathway in order to understand primordial metabolism. Productive and parasitic reactions are also discussed.

Thursday, July 20, 2017
THE ROLE OF COMPARTMENTS
2:40 p.m. Price Center Theatre

Moderator: **Sijbren Otto**

Panel Members: **Roy Black**
David Deamer
Andrew Pohorille

3:40 p.m. *Coffee Break*

Thursday, July 20, 2017
GENETIC INFORMATION AND FUNCTION IN THE EARLY STAGES OF LIFE
4:10 p.m. Price Center Theatre

Chair: Luke Leman

4:10 p.m. Akoopie A. * Müller U. F.
Identification of the NTP Binding Site in the Polymerase Ribozyme **[#4079]**
To test how an RNA world organism could have functioned, an RNA polymerase ribozyme was previously developed. Using *in vitro* evolution we confirm that the NTP binding site of this ribozyme is within the purine-rich loop of its accessory domain.

4:30 p.m. Tagami S. * Attwater J. Holliger P.
Simple Non-Coded Peptides Enhance RNA Polymerase Ribozyme Function **[#4136]**
Simple positively charged peptides could stimulate activity and evolution of an RNA polymerase ribozyme. This work shows how simple peptides could have supported ribozymes in the RNA world even before the emergence of the genetic code.

4:50 p.m. Horning D. P. Samantha B. Tjhung K. F. Joyce G. F. *
RNA-Catalyzed Polymerization and Replication of RNA **[#4067]**
In an effort to reconstruct RNA-based life, in vitro evolution was used to obtain an RNA polymerase ribozyme that can synthesize a variety of complex functional RNAs and can catalyze the exponential amplification of short RNAs.

5:10 p.m. Meringer M. Butch C. Burger P. Goodwin J. Cleaves H. J. II *
Computational Exploration of the Chemical Space of Nucleic Acid-Like Compounds **[#4078]**
Using graph theory-based structure generation, we have exhaustively computed the chemical isomer space of the natural ribosides (compounds of formula $C_5H_9O_4B$, where B is a nucleobase) as well as a much wider range of formulas from C3 to C8.

5:30 p.m. *Session Adjourns*

Thursday, July 20, 2017
SPECIAL SESSION IN HONOR OF JIM FERRIS:
FROM THE PREBIOTIC SYNTHESIS OF BASES AND
POLYMERIZATION TO RNA WORLD RESEARCH/CONCEPTS
7:00 p.m. Price Center Theatre

Chair: Alan Schwartz

7:00 p.m. Schwartz A. *
Chairman of the Special Session

7:15 p.m. Powner M. W. *
Prebiotic Synthesis: Selection Overcoming Clutter **[#4072]**
A mechanism to efficiently and selectively direct multistep prebiotic synthesis of nucleotides and amino acids from complex mixtures, a divergent synthesis of pyrimidine and purine nucleotides, and prebiotic triose glycolysis will be presented.

7:40 p.m. Pressman A. Saha R. Müller U. Chen I. *
Fitness in the RNA World **[#4223]**
Life probably progressed through a primitive form based on RNA, in which RNA acted as both a genetic material and a catalyst for biochemistry. Understanding the evolution of RNA is therefore central to understanding the origin of life.

7:55 p.m. Williams L. D. * Kovacs N. Petrov A. Lanier K.
Frozen in Time: The History of the Ribosome **[#4222]**
Translation provides a window into the essential nature of biology.

Friday, July 21, 2017
EVOLUTION: THE DRIVING FORCE FOR EVOLUTION
AT THE CHEMICAL AND BIOLOGICAL STAGES
8:30 a.m. Price Center Theatre

Chair: Irene Chen

8:30 a.m. Pascal R. Pross A. *
A Roadmap Toward Synthetic Protolife **[#4151]**
In this lecture it will be argued that a strategy for the synthesis of protolife requires the characterization of the physicochemical state of life's primordial beginnings, not just its material composition.

8:50 a.m. Petrie K. L. * Meyer J. R.
Bypassing Evolutionary Roadblocks: Phenotypic Diversity in Isogenic Population Bridges Tradeoff in Evolution of a New Function **[#4080]**
A novel mechanism of innovation bridges fitness valleys by violating the one gene-one phenotype dogma. Protein products of a single gene partition into populations, some of which carry out a new function and some the old, avoiding tradeoffs.

9:10 a.m. Fujishima K. * Greenberg D. Kobayashi A. Kuruma Y. Mizuuchi R. Rothchild L. J. Ditzler M. A.
In Vitro RNA-Peptide Co-Evolution System for Screening ATP-Binding RNP **[#4218]**
Understanding the historical trajectories of the co-evolution of RNA and proteins to RNA-protein complexes (RNPs) using ATP-binding function as a selective pressure.

Friday, July 21, 2017
EVOLUTION: THE DRIVING FORCE FOR EVOLUTION
AT THE CHEMICAL AND BIOLOGICAL STAGES
9:30 a.m. Price Center Theatre

Moderator: **David Deamer**

Panel Members: **Gerald Joyce**
Addy Pross

10:30 p.m. *Coffee Break*

Friday, July 21, 2017
EVOLUTION: BEFORE AND AFTER LUCA/EVOLUTION OF METABOLISM
11:00 a.m. Price Center Theatre

Chair: Niles Lehman

11:00 a.m. Lancet D. * Zidovetzki R. Shenhav B. Markovitch O.
Metabolic GARD: Replicating Catalytic Network of Lipid-Anchored Metabolites **[#4061]**
We propose a computer-simulated M-GARD model, with mutually catalytic metabolic network of amphiphiles. It can show compositional reproduction of both bilayer and lumen content of lipid vesicles, thus joining metabolism, compartment and replication.

11:20 a.m. Gaut N. Heili J. Gomez-Garcia J. Engelhart A. Adamala K. *
Pre-LUCA Cells: Life but Not Alive **[#4200]**
We study late, immediately pre-LUCA stages of prebiotic evolution using synthetic minimal cell bioreactors.

11:40 a.m. Bonfio C. Scintilla S. Shah S. Evans D. J. Jin L. Szostak J. W. Sasselov D. D. Sutherland J. D. Mansy S. S. *
Model Prebiotic Iron-Sulfur Peptides **[#4090]**
Iron-sulfur clusters form easily in aqueous solution in the presence of thiolates and iron ions. Polymerization of short, iron-sulfur binding tripeptide sequences leads to ferredoxin-like ligand spacing and activity.

12:00 p.m. Czárán T. Könnyü B. * Szathmáry E.
Metabolically Coupled Replicator Systems: Overview of an RNA-World Model Concept of Prebiotic Evolution on Mineral Surfaces **[#4034]**
Metabolically Coupled Replicator Systems: Overview of an RNA-world model concept of prebiotic evolution on mineral surfaces.

12:20 p.m. *Lunch*

Friday, July 21, 2017
EVOLUTION: COMPETITION, COOPERATIVITY, COMPLEXITY AND ECOLOGY
2:00 p.m. Price Center Theatre

Chair: Nick Hud

2:00 p.m. Lehman N. *
Molecular Cooperation: A Self-Less Origin of Life **[#4122]**
The role of molecular cooperation in the origins of life will be discussed. The distinction between reproduction and replication will be made, with a conclusion that the former preceded the latter, by recombination. The origins of life was self-less.

2:40 p.m. Furubayashi T. * Bansho Y. Motooka D. Nakamura S. Ichihashi N.
In Vitro "Evolutionary Arms-Races" Between Hosts and Parasites in an Artificial RNA Replication System **[#4081]**
We performed coevolution of artificial RNA self-replicators and parasitic replicators in microdroplets. We observed evolutionary arms-races with oscillating population dynamics and faster evolution of self-replicators caused by parasitic replicators.

3:00 p.m. Bansho Y. Furubayashi T. Ichihashi N. *
Host-Parasite Oscillation Dynamics and Evolution in a Compartmentalized RNA Replication System **[#4001]**
We have constructed an evolvable RNA-protein replication system. Here, we report that a parasitic RNA spontaneously appears in this system and shows oscillating population dynamics only when the system is compartmentalized.

3:20 p.m. Mizuuchi R. * Ichihashi N.
Darwinian Evolution of Mutualistic RNA Replicators with Different Genes **[#4077]**
We report a sustainable long-term replication and evolution of two distinct cooperative RNA replicators encoding different genes. One of the RNAs evolved to maintain or increase the cooperativity, despite selective advantage of selfish mutations.

3:40 p.m. *Coffee Break*

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening Break.

POSTER SESSION: EXOPLANETS FROM AN ORIGIN OF LIFE PERSPECTIVE AND THE SEARCH FOR LIFE AND ITS PRECURSORS IN THE SOLAR SYSTEM
Price Center Ballroom East

Gros C.
Restarting Over: Alternative Evolutionary Pathways for Terrestrial Life on Oxygen Planets **[#4043]**
Up to 30 billion planets with massive abiotic oxygen partial pressures have be estimated to exist in our galaxy. It is hence an important question, whether primordial oxygen would preempt abiogenesis together.

Vladilo G. Silva L. Murante G. Provenzale A.
Constraining the Epoch of the Potential Emergence of Life in Exoplanets **[#4220]**
We use a specially designed climate model to track the onset of conditions suitable for the emergence of life in Earth-like exoplanets. We apply this methodology to the best example of habitable Earth-size exoplanet orbiting a sun-like star.

Westall F. Zipfel J. Foucher F. Smith C. Russell S. Hickman-Lewis K. Viso M.
Life on Mars: Returned Samples and Their Storage, the EURO-CARES Project **[#4096]**
Definitive detection of life on Mars will likely require study of samples returned to Earth. The EURO-CARES project looks at curation and storage of such samples. We discuss the importance and use of different kinds of analogue materials in such a facility.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: METEORITES, COMETS AND THE FATE OF THEIR ORGANIC MATTER
Price Center Ballroom East

Schulz R. Kissel J. Silen J.
The Composition of Comets – Overview of 30 Years of Investigations **[#4050]**
In the 30 years of comet composition investigations important progress was made in identifying the composition and chemistry of comets. An overview will be given of the most important milestones with special emphasis to organic material.

Zellner N. E. B. McCaffrey V. P. Butler J. Crake C. L.
Assessing the Abundances of Sugar Molecules on Comet Nuclei **[#4182]**
Simple sugars have been detected on comets and have been shown to survive and become more complex under impact conditions. We present estimates of the amounts that may have been delivered by comets and thus available for life as we know it.

Kobayashi K. Mita H. Kebukawa Y. Nakagawa K. Ishiyama K. Aoki R. Harada T. Misawa S. Uchimura E. Sato T. Naito K. Minematsu S. Imai E. Yano H. Hashimoto H. Yokobori S. Yamagishi A.
Stability of Amino Acid-Related Compounds in Space — Preliminary Results of the Tanpopo Organic Exposure Experiment **[#4131]**
The Tanpopo Mission is the space mission utilizing ISS, including collection of cosmic dusts and space exposure of amino acid-related compounds. Here we report the first analytical results of the organic exposure experiment in the Tanpopo mission.

Dworkin J. P. OSIRIS-REx Team
Status of the OSIRIS-REx Sample Return Mission **[#4095]**
Latest status and plans of NASA's OSIRIS-REx mission, which launched in 2016 and will return pristine regolith from near-Earth asteroid Bennu for organic and mineral analyses.

Lyons J. R. Gharib-Nezhad E. Ayres T. R.
The Initial C Isotope Ratio for the Solar System **[#4186]**
Using spectroscopic observations of CO in the solar photosphere, we have determined the $^{13}C/^{12}C$ ratio for the Sun, and therefore for the bulk initial solar system. The Sun is light in ^{13}C by 50 ‰ compared to bulk Earth and marine carbonates.

Heckman T. Pravdo S.
Fuller Clarke Sphere **[#4154]**
A Geodesic Sphere constructed around the planet for defense, scientific study, urban, commercial and industrial use analogous to a Dyson Sphere. Clarke Space Elevators are also implemented in the design located at the icosahedral vertex points.

Berger E. L. Burton A. S. Locke D.
Amino Acid Contents of Meteorite Mineral Separates **[#4094]**
We investigate the relationship between parent body conditions, mineralogy, and amino acid composition, by analyzing meteoric mineral separates using liquid chromatography-mass spectrometry, scanning electron microscopy, and x-ray diffraction.

Koga T. Naraoka H.
The Discovery of New Meteoritic Amino Acids in the Murchison Meteorite: Implication for New Formation Mechanisms of Meteoritic Amino Acids **[#4003]**
The ten new amino acids have been newly identified from the Murchison extract. The formose reaction with ammonia in the presence of minerals is an important formation pathway to produce meteoritic amino acids on the meteorite parent body.

Aponte J. C. Dworkin J. P. Elsila J. E.
Amines in Carbonaceous Meteorites **[#4057]**
Aliphatic amines in aqueous altered, thermally metamorphosed, and non-altered carbonaceous chondrites.

Naraoka H. Yamashita Y. Koga T.
Formose Reactions with Ammonia Prevailing for the Synthesis of Meteoritic Soluble Organic Matter **[#4083]**
Formose reactions with ammonia in the presence of minerals are an important process to produce meteoritic soluble organic matters through aqueous alteration on the meteorite parent body.

Cooper G.
Enantiomer Excesses in Carbonaceous Meteorites **[#4210]**
Enantiomer excesses in meteorites and laboratory attempts at duplication will be discussed.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: ENVIRONMENTAL CONDITIONS FOR THE ORIGIN OF LIFE ON THE EARLY EARTH
Price Center Ballroom East

Laneuville M. Kameya M. Cleaves H. J. II
Earth Without Life: A Systems Model of a Global Abiotic Nitrogen Cycle **[#4155]**
N is the major component of the atmosphere and plays important roles in biochemistry. Presently, the surface N-cycle is dominated by biology. However, before the origin of life, abiotic N-cycling would have set the stage for the origin of life.

Westall F. Hickman-Lewis K. Hinman N. Gautret P. Campbell K. A. Breheret J. Foucher F. Hubert A. Sorieul S. Dass A. V. Kee T. Georgelin T. Brack A.
A Hydrothermal-Sedimentary Origin of Life Scenario **[#4098]**
The Hadean, carbon-containing volcanic sediments represented a global reservoir of mini reactors characterised by porosity, reactive mineral surfaces, physical and chemical disequilibria, and flushed by hydrothermal fluids.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: THE FORMATION AND EVOLUTION OF ORGANICS ON THE EARLY EARTH
Price Center Ballroom East

Kobayashi K. Aoki R. Kebukawa Y. Shibata H. Fukuda H. Oguri Y. Airapetian V. S.
Roles of Solar Energetic Particles in Production of Bioorganic Compounds in Primitive Earth Atmosphere **[#4133]**
We examined the formation of amino acids from slightly reducing gas mixtures by proton irradiation to simulate the action of solar energetic particles (SEPs), and found that SEPs were promising energies for prebiotic synthesis of N-bearing organics.

Schreiber U. Mayer C. Bronja A. Schmitz O. J.
Archean Fluid Inclusion of Hydrothermal Quartz Minerals — Archives of Prebiotic Chemistry on Early Earth? **[#4018]**
Fluid inclusions in quartz crystals grown in the hydro-thermal environment of the continental crust during the Archean period contain a rich collection of organic compounds which are highly relevant for molecular evolution.

Kolb V. M.
Prebiotic Organic Reactions in Water **[#4025]**
Reactions of organic compounds which are not soluble in water may still occur in water, by the “on-water” mechanism or in supercritical water, which behaves as acetone and has acid/base catalytic properties.

Gavette J. V. Krishnamurthy R. Springsteen G.
Exploring the Role and Reaction Constraints of Malonate Within the Context of the “Glyoxylate Scenario” **[#4167]**
Exploration of the reaction conditions that influence the aldol addition of malonate and glyoxylate to understand their prebiotic importance.

Jaipaul R. Tewari B. B.
Interaction of Alanine and Aspartic Acid with Aluminum, Iron and Zinc Oxides and its Relevance in Chemical Evolution **[#4033]**
Studies on adsorptive interaction of alanine and aspartic acid with aluminum, iron and zinc oxides and its relevance to chemical evolution and origins of life.

Kim H. J.
Stereoselective Prebiotic Nucleotide Synthesis for Threose Nucleic Acid **[#4184]**
The reaction of threose-1,2-cyclic phosphate and adenine provided threose-adenine nucleoside 2’-phosphate under prebiotic plausible condition. This will be the first example of prebiotic synthesis of nucleotide from sugar and nucleic base.

Takahashi J.
Biological Homochirality and Symmertry Breaking of the Universe **[#4156]**
Scenarios for the origin of terrestrial bioorganic homochirality (enantiomeric domination of L-form amino acids in proteins and D-form sugars in DNA/RNA), Cosmic Scenario and Intrinsic Scenario, will be discussed.

Alvarez-Carreño C. Becerra A. Lazcano A.
Norvaline and Norleucine may have been more Abundant Protein Components During Early Stages of Cell Evolution **[#4103]**
Major prebiotic products are absent from the inventory of protein amino acids. We discuss the case of two hydrophobic amino acids: norvaline and norleucine.

Sorden S. Cooper G.
Increasing the Relative Production of Ribose Under Mild Prebiotic Conditions **[#4127]**
In the classic formose reaction, ribose is produced in low abundance relative to other sugars. We manipulated various parameters in formose-type reactions and found that the relative abundance of ribose can be significantly increased.

Adam Z. R. Fahrenbach A. C. Hongo Y. Cleaves H. J. II Ruiqin Y. Yoda I. Aono M.
Production and Concentration of Water-Alternative Solvents on the Prebiotic Earth **[#4204]**
Water creates special problems for prebiotic chemistry, notably that biopolymers are corroded by water. We report the conversion of aqueous acetonitrile and hydrogen cyanide into formamide under conditions mimicking exposure to radioactive minerals.

Lago J. L. Pasek M. A.
The Robustness of the Urea-Ammonium Formate-Water Mixture as a Prebiotic Solvent **[#4027]**
We propose a semi-aqueous solvent consisting of urea, ammonium formate, and water as a prebiotic solvent in which phosphorylation of nucleosides can occur spontaneously in appreciable quantities under mild conditions.

Burcar B. T. Pasek M. Gull M. Cafferty B. J. Velasco F. Menor-Salvan C. Hud N. V.
Phosphorylation in Urea-Rich Eutectic Solvents **[#4195]**
Phosphorylation reactions have been viewed as problematic due to phosphate sequestration in minerals and thermodynamically unfavorable reactions. Phosphorylation in urea-rich eutectics successfully phosphorylate, addressing these major issues.

Surman A. J. Rodriguez-Garcia M. Abul-Haija Y. Cooper G. J. T. Donkers K. Planchat i Barbarà J. M. Kube J. Mullin M. Hezwani M. Cronin L.
Can a Reaction's Environment Program its Outcome, and Does it Matter? **[#4006]**
Where most eschew reactions producing complex mixtures ('tar') and prefer to plan 'clean' syntheses, we embrace complexity. We show that environments can steer 'messy' reactions, and ask if this can yield significant difference in structure and function.

Aguilar-Ovando E. Buhse T. Negrón-Mendoza A.
Evaluation of Glyceraldehyde Under Simulated Prebiotic Conditions **[#4009]**
The aim of this work is to compare the behavior under irradiation of solid and aqueous DL-glyceraldehyde simulating prebiotic conditions. The results show the formation of sugar-like products of prebiotic significance as function of irradiation dose.

Febrian R. Roddy J. P. Devall C. T. Bracher P. J.
The Effects of Metal Ions on Reactions of Thioesters in Simulated Prebiotic Environments **[#4172]**
Our project explores the effects of various metals which are conjectured to have been present in the ancient ocean on the hydrolysis, aminolysis, and thiol–exchange reactions of thioesters in complex aqueous solutions.

Bracher P. J. Campbell T. D. Cheneler M. L. Devall C. T. Febrian R. Hart C. A. Roddy J. P.
Using Reaction Kinetics to Assess Chemistry of Prospective Importance to the Origin of Life **[#4173]**
This presentation concerns the use of physical-organic chemistry and the measurement of kinetics to assess proposed models for peptide coupling and reactions of thioesters with respect to the origin of life.

Frenkel-Pinter M. Yu S-S. Solano M. D. Forsythe J. G. Fernandez F. M. Grover M. A. Hud N. V.
Self-Assembly of Plausible Proto-Peptides **[#4150]**
Applying dry-hot conditions drives oligomerization of short, chemically synthesized depsipeptides (i.e. peptides that are composed of hydroxy and amino acids) into long oligomers, and a structural shift coincides with polymer growth.

Yi R. Q. Aono M. S. Cleaves H. J. Hara M. H.
The Formation of Oligopeptides in Good Yield Under Geyser System Model **[#4159]**
A one-pot wet-dry geyser reactor system was developed to explain how unactivated amino acids were condensed to oligopeptides.

Bahn P. R. Pravdo S. H.
Quad Amino Acids **[#4022]**
Amino acids are usually thought of as trifunctional chemicals having the amino group, the carboxyl group and the side chain. We propose synthesizing quadfunctional amino acids by replacing the hydrogen on the alpha carbon with a second side chain.

Vázquez-Salazar A. Tan G. Stockton A. Fani R. Becerra A. Lazcano A.
Can an Imidazole be Formed from an Alanyl-Seryl-Glycine Tripeptide Under Possible Prebiotic Conditions? **[#4013]**
We discuss the special role that the imidazole group and its derivatives play in extant biology. We also propose a possible prebiotic synthesis of an imidazolide, based on the biosynthesis of 4-methylidene-imidazole-one (MIO).

Bada J. L. Chalmers J. Burton A. Scheu B. Cimarelli C. Dinwell D. B.
Laboratory Simulated Volcanic Lightning and Prebiotic Synthesis **[#4102]**
We report here results from experiments using the laboratory-based generation of volcanic lightning in the presence volcanic ash and various gas mixtures. Glycine and well as other possible amino acids are readily synthesized in these simulations.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: THE ROLE OF MINERALS IN THE FATE OF ORGANIC MATTER AND CHEMICAL EVOLUTION
Price Center Ballroom East

Lambert J. F. Sakhno Y. Battistella A. Ribetto B. Mezzetti A. Georgelin T. Jaber M. Michot L.
Could Mineral Surfaces have Oriented Amino Acid Polymerization Towards Useful Products? **[#4152]**
We investigated selective amino acid polymerization on the surface of silicic minerals. Specific amino acid couples were deposited on silica or clays, thermally activated, and the oligomers formed were analyzed. Very different behaviors were observed.

Cameron R. D. Hermis N. Chin K. LeBlanc G. Barge L. M.
Electrochemistry of Early Earth Hydrothermal Chimneys and Simulations of Possible Prebiotic Metabolic Pathways **[#4176]**
We present the results of artificial seafloor hydrothermal chimney experiments, using using electrodes placed across the chimney wall to analyze the surface charge potential at the interface of the chimney/ocean/hydrothermal fluid.

Flores E. VanderVelde D. Russell M. J. Baum M. M. Barge L. M.
Redox and pH Gradients Drive Amino Acid Synthesis at Hydrothermal Vents **[#4178]**
We conducted experiments to test if amino acids could be synthesized in the presence of the redox-sensitive iron oxyhydroxides in simulated hydrothermal vent gradient conditions.

Barge L. M. Flores E. Abedian Y. Maltais T. Cameron R. Hermis N. Chin K.
Russell M. J. Baum M. M.
Effects of pH and Redox Gradients on Prebiotic Organic Synthesis and the Generation of Free Energy in Simulated Hydrothermal Systems **[#4179]**
Hydrothermal minerals in alkaline vents can promote phosphorus and organic concentration, redox reactions driven by catalytic metal sulfides, and the ambient pH and redox gradients can affect the synthesis of organics.

Abedian Y. Maltais T. VanderVelde D. Flores E. Barge L. M.
Phosphorous and Amino Acid Adsorption in Early Earth Seafloor Minerals **[#4177]**
In this work, we simulated early Earth iron hydroxide seafloor precipitates and measured their ability to absorb phosphate and phosphite; we also tested how P adsorption was affected by the presence of amino acids (alanine or aspartate).

Villafañe S. Baú J. Zaia D. Colín M. Negrón A. Heredia A.
Salinity Effect on Adsorption of Nucleic Acids Compounds onto Montmorillonite: A Prebiotic Chemistry Experiment **[#4039]**
Absorption of nucleic acids compounds in clay was studied using a primitive ocean analog. Results showed that the absorption process could be affected by high concentration of salts that are involved in the competition for available sites of mineral.

Afrin R. Ganbaatar N. Aono M. Yano T. Hara M.
Amino Acids Adsorption to Mineral Surfaces: Basis for Prebiotic Molecule Accumulation Studied at Nanoscale **[#4070]**
The single molecule force spectroscopy technique based on AFM was used to verify the binding interaction of several amino acids to pyrite surface. Results indicated the ionic nature of adsorption/desorption reaction on the pyrite substrate.

Hammer A. C. Corbit B. C. Doloboff I. J. Barge L. M.
Structural and Compositional Diversity in Iron-Based Hydrothermal Chimney Simulants Grown with Functionalized Organics **[#4208]**
Alkaline hydrothermal chimneys are a potential environment for origin of life. We show that iron-based chimney simulants show structural and compositional gradients indicative of their growth environments and that they are altered by organic dopants.

Cruz-Castañeda J. Negrón-Mendoza A. Ramos-Bernal S. Colín-García M.
Heredia A. Fuentes-Carreón C.
Stability of the D-Ribose-Na+Montmorillonite and DL-Glyceraldehyde-Na+Montmorillonite Systems in Aqueous Suspension Under Gamma Radiation Fields at pH 7 and 92°C: Implications in Chemical Evolution **[#4007]**
The objective of this project is focused on studying the stability of aldoses-clay suspensions, under gamma irradiation. To this end, we study the radiolysis of these systems by varying the irradiation dose and the ratio aldose-clay at pH 7 and 92°C.

Meléndez-López A. L. Negrón-Mendoza A. Ramos-Bernal S. Colín-García M. Heredia A.
Effects of Gamma Irradiation in Nucleic Acids Bases Co-Adsorbed in a Na-Montmorillonite and Fe-Montmorillonite: Relevance in Chemical Evolution **[#4008]**
Our aim is to study the role of clays in chemical evolution as protector agent under ? radiation. We study the co-adsorption of adenine and thymine-clay systems at different irradiation doses, pH to evaluate the adsorption and degree of decomposition.

Biondi E. Furukawa Y. Howell L. Benner S. A.
Adsorption of RNA on Mineral Surfaces and Mineral Precipitates **[#4188]**
We show trends in the interaction of RNA with natural minerals, synthetic mineral specimens, and co-precipitated pairs of synthetic minerals, overcoming the issues related to the study of the interactions between RNA and different mineral sources.

Posters will be on Display for the Entire Week.
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POSTER SESSION: CHEMICAL EVOLUTION TOWARDS THE TRANSITION OF LIFE
Price Center Ballroom East

Gupta V. K.
Photochemical Synthesis of Bioinspired inorganic-Organic Hybrid Protocell-Like Self-Sustaining Supramolecular Assemblies, "Jeewanu" in a Laboratory sSimulated Possible Prebiotic Atmosphere **[#4012]**
Photosynergistic collaboration of non-linear coherent processes at mesoscopic level led to emergence of biomimetic hybrid supramolecular assemblies similar to Jeewanu capable of showing various functional properties viz. self-organisation and self-sustenance.

Wang W. Q. Gong G. Y. Shen X. C. Qiao B. H. Li J. J.
Magnetic Field Dependence of Heat Capacity Study on the (e-p) Bose-Einstein Condensation Through the Hydrogen onto D, L-Valine Optical Lattice **[#4031]**
For the aim to investigate the role of chirality and helicity between D- and L-valine crystal lattices under Debye temperature 2 K to 20 K, the magnetic field dependence of zero-field and 1, 3 and 5 Tesla on the heat capacity were measured.

Konstantinov K. K. Konstantinova A. F.
Importance of Sedimentation for Chiral Symmetry Breaking in Far from Equilibrium Peptide Systems **[#4134]**
Considered chiral symmetry breaking in complex far from equilibrium chemical systems. Shown that effective averaging of chemical reactions does not allow chiral symmetry breaking but it does not apply to phase transition during sedimentation process.

Zhao Y. F. Liu Y. Xu P. X. Han D. X.
The Model for Genetic Code Origin Study Based on the Dipeptide Yields Variation with the Nucleosides **[#4028]**
A simplified and effective chemical model containing phosphorous compounds, amino acids and nucleosides, was built up for the study the translation mechanism of genetic code origin.

Matsubara Y. J. Kaneko K.
Optimal Size for Emergence of Self-Replicating Polymer System **[#4141]**
For the origins of life, emergence of an active state with catalytic polymers synthesized by their own is necessary. We present a universal formula for the optimal system-size that minimizes the transition time for such state.

Myrgorodska I. Fletcher S. P.
Induction of Asymmetry in Formose Reaction **[#4087]**
In the present work we investigated influence of different chiral species, including amino acids and sugar derivatives, on the enantioseleve outcome of the fomose reaction.

Blokhuis A. W. P. Lacoste D. Nghe P.
Thermodynamics of Sequence and Exploration in Prebiotic Scenarios **[#4004]**
We study the thermodynamics of polymers with sequence, for exchange and ligation reactions. We show novel ways of obtaining long polymers and derive thermodynamic costs for exploration and maintenance. These costs strongly impact prebiotic scenarios.

Ikehara K.
Necessities for the First Life to Emerge **[#4051]**
For the first life to emerge, the first protein must be produced by random joining of amino acids in protein 0th-order structure. In addition, the first genetic code and the first double-stranded gene must encode the protein 0th-order structure.

Wong S. B. Gately M. Young E. Krishnamurthy R. Weber A. L. Campbell T.
Pyrazine Nucleic Acids: From Small Molecules to Proto-Informational Polymers **[#4183]**
Pyrazine nucleosides are derivable from amino acid amides and pentoses under plausibly prebiotic conditions. Pyrazines share features similar to adenine or thymine, and may behave as an informational polymer when polymerized as pyrazine nucleic acid.

Panchal Z. Oye M. Deamer D. Vercoutere W.
Non-Enzymatic Synthesis of Duplex Nucleic Acid **[#4209]**
The earliest forms of life would likely have a protocellular form, with a membrane encapsulating some form of linear charged polymer that would have genetic properties; we simulate the plausible prebiotic conditions and use a nanopore for analysis.

Norkus R. Damer B. F. Deamer D. W.
A Hot Spring Origin of Life and Early Adaptive Pathway from Woese Progenotes to Marine Stromatolites **[#4132]**
An origin of life on land is visualized as: organic compounds accumulating in hydrothermal pools, wet-dry cycling of protocells encapsulating synthesized polymers, arising of a Woese progenote and its evolution into living microbial communities.

Kawamura K.
Two Gene Hypothesis for the Initiation of Life-Like Systems Towards the RNA World **[#4049]**
The minimum number of genes for initiation of life-like systems was deduced from the characteristics of RNA molecules and of life-like systems, and I propose what functions with RNA molecules were essential for emergence of life.

Mungi C. V. Singh S. Chugh J. Rajamani S.
Synthesis and Characterization of Informational Molecules Formed Under Prebiotic Conditions **[#4068]**
Effects of simple prebiotic conditions such as low pH, high temperature and dry heating on synthesis of RNA-like molecules is studied and chemical alternatives to modern RNA which may be stable under harsh conditions are suggested.

Kobayashi A. Fujishima K.
Improving mRNA-Display for In Vitro RNA-Protein Co-Evolution **[#4084]**
Optimization of mRNA-display using in vitro translation to achieve stable and efficient screening of the acquisition of primitive functional RNA-peptide complex through iterative optimization of the accompanying puromycin chemistry conditions.

Scanes R. J. H. Fletcher S. P.
Design of Novel Asymmetric Autocatalytic Systems **[#4107]**
Investigation into novel autocatalytic systems using organocatalysis.

Suárez-Marina I. Rodriguez-Garcia M. Surman A. J. Cooper G. J. T. Cronin L.
Automated Oligopeptide Formation Under Simple Programmable Conditions **[#4042]**
Traditionally, prebiotic chemistry has investigated the formation of life's precursors under very specific conditions thought to be "plausible". Herein, we explore peptide formation studying several parameters at once by using an automated platform.

Conwell C. C. Parsons C. J. Grover M. A.
Educating About Origins of Life Research: The Power of Collaboration **[#4170]**
The Center for Chemical Evolution has a unique opportunity to pursue outreach and education related to origins of life research. Through a partnership, we have created four videos that have educated over 1 million viewers about scientific concepts.

Guillemin J. C. Trolez Y.
Synthesis of Cyanopolyynes for Photochemical and Spectroscopic Studies **[#4175]**
Synthesis of cyanoacetylene derivatives, spectroscopic and photochemical studies.

Hawker J. Christensen E.
Introduction to Astrobiology: A Model for Integrating Research into an Undergraduate Class **[#4187]**
We describe a research based learning college course, co-taught by two instructors, that introduces undergraduate students, including non-science majors, to the field of Astrobiology.

Bonfio C. Valer L. Scintilla S. Shah S. Evans D. J. Jin L. Szostak J. W. Sasselov D. D. Sutherland J. D. Mansy S. S.
UV-Light Driven Prebiotic Synthesis of Iron-Sulfur Clusters **[#4016]**
Photolysis and photooxidation drive the prebiotic synthesis of iron-sulfur peptides under model early Earth conditions.

Tirumalai M. R. Paci M. Tran Q. Marathe A. Chavan D. Dusi V. Fox G. E.
Understanding Increase in Complexity in the RNA World Using a Two Enzyme System **[#4224]**
The dynamics of the emergence of complexity in an RNA World is an important problem in the quest towards understanding the origins of life.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: SELF-ORGANIZATION AND PREBIOTIC MOLECULAR SYSTEMS
Price Center Ballroom East

Jayathilaka T. S. Lehman N.
Self-Assembly of Multiple Small RNA Fragments into an Autocatalytic Prebiotic System **[#4011]**
This study describes a system that models prebiotic self-assembly of the catalytically active Azoarcus group I intron through the recombination of five shorter inactive RNA oligonucleotides.

Kua J.
Constructing Free Energy Maps of Oligomerization Reactions in Solution **[#4038]**
Using first principles computational chemistry, we have constructed free energy maps detailing the thermodynamics and kinetics in systems of molecules with their corresponding oligomers in aqueous solution relevant to prebiotic chemistry.

Todisco M. Fraccia T. P. Smith G. P. Zanchetta G. Clark N. A. Bellini T.
Non-Enzymatic Ligation of Short RNA Oligomers Enhanced by Supramolecular Self-Assembly and Liquid Crystal Ordering **[#4066]**
Short RNA molecules self-assembled into liquid crystals show an enhanced non-enzymatic ligation efficiency between their terminals, producing longer polymers (~6n) than the ones produced under the same conditions in a disordered solution (~2n).

Famiano M. A. Boyd R. N. Kajino T. Onaka T.
Selection of Amino Acid Chirality via Weak Interactions in External Fields **[#4073]**
A model has been developed in which the selective destruction of chiral states in high magnetic fields can create enantiomeric excesses of about one part in one million. This selection is implemented through weak interactions on nuclei in amino acids.

Arsene S. Ameta S. Nghe P. Lehman N. Griffiths A. D.
Networks of RNA Replicators in Origin of Life **[#4088]**
A diverse library of networks of RNA replicators based on Azoarcus group I intron can be analyzed using a high-throughput experimental set-up in order to study network topologies, node-fitness and robustness in the context of origin of life.

Morrow S. M. Bissette A. J. Kukura P. Fletcher S. P.
Chirality and Physical Autocatalysis **[#4092]**
In this work we aim to establish asymmetric variants of physical autocatalytic reactions for the amplification of chirality.

Post E. A. J. Bissette A. J. Fletcher S. P.
Probing the Mechanism of Self-Reproducing Micelles **[#4093]**
The work presented here describes a novel physical autocatalytic reaction where new bonds are formed via a copper-catalysed azide-alkyne cycloaddition.

Berg M.F. B. Krismer M. K. Christensen M. C. Hermsen M. H. Vetsigian K. V. Baum D. B.
Selection for the Spontaneous Appearance of Lifelike Chemistry In Vitro **[#4097]**
We are using a novel class of experiments, modeled after microbial artificial ecosystem selection experiments to evaluate whether evolvable autocatalytic systems can emerge spontaneously in the laboratory.

Dalai P. Ustriyana P. Sahai N.
Magnesium Tolerance and Preferential Selectivity of a Lipid in Binary Lipid Systems: An Evolutionary Approach to Modern Membranes **[#4104]**
We investigated the mechanisms for increased ion tolerance and preferential selectivity of a lipid in a mixed lipid system in the presence of Mg2+ as an environmental selection pressure for membrane evolution from fatty acids to phospholipids.

Sahai N. Dalai P. Kaddour H.
Protocell Self Assembly as Predicted by Mineral Surface Chemistry **[#4105]**
A structure-activity correlation between mineral surface properties and the enhancement of model protocell formation rates was identified for the first time. Modified DLVO theory for mineral-lipid interactions provides the mechanism.

Hansma H. G.
Between Mica Sheets: Better than Membranes at the Origin of Life? **[#4113]**
Organelles without membranes are found in all types of cells. They typically contain RNA and protein and may have preceded membrane-bound structures at the origins of life, where they would have been well sheltered in the spaces between mica sheets.

Bhattacharya A. Devaraj N. K.
Spontaneous Phospholipid Membrane Formation by Chemoselective Ligation Reactions **[#4115]**
We describe a simple chemoselective reaction between histidine-functionalized lysolipid and a fatty acyl thioester to generate phospholipid membranes de novo. Such strategies can provide insight into the origin and early evolution of membranes.

Jin L. Szostak J.
Fe_2+ in Prebiotic Non-Enzymatic RNA Chemistry and Early Compartmentation **[#4165]**
We studied Fe(II) catalytic effect on non-enzymatic RNA replication, ligation and hydrolysis along with the effect of pH and cation concentration. Also, these reactions were compatible inside fatty acid protocells with the help of small chelators.

Kühnlein A. Mast C. B. Benk A. Spatz J. P. Braun D.
Driving Early Biochemical Reactions by the Thermal Accumulation of ATP over ADP/AMP? **[#4142]**
We propose a system which uses the prebiotically realistic thermal trap to locally shift the equilibrium of ADP and ATP towards an ATP bias and thereby allows biochemical reactions to take off.

Evans A. C. Kading J.
Continuous Processing Approaches for Prebiotic Syntheses of 2-Amino-Oxazole and Subsequent Ribo/Arabino Furanosyl Amino-Oxazolines **[#4124]**
Under mild continuous processing prebiotic conditions, the precursors to nucleic acids can be formed. Glycolaldehyde and cyanamide efficiently form 2-amino-oxazole, which can then be reacted in flow series to form furanosyl amino-oxazolines.

Ito S. Haruna T. Sakurazawa S.
Formation of Outer Shells from Proteinoid Microspheres **[#4174]**
Proteinoid microspheres form outer shells with thermal gradient. We conducted experiments to verify this mechanism. We found that formation of outer shells was caused by dissolution of microspheres and the flow promotes the formation of outer shells.

Fialho D. M. Cafferty B. J. Clarke K. C. Khanam J. Moore M. K. Watkins K. A. Schuster G. B. Krishnamurthy R. Hud N. V.
Glycosylation of Noncanonical Nucleobases in Water: Implications for the Evolution of Early Genetic Polymers **[#4193]**
Unlike the canonical nucleobases, 2,4,6-triaminopyrimidine can react with sugars (including ribose) in water to form glycosides. These monomeric glycosides have the propensity to self-assemble in water.

Leman L. J. Masaki Y. Ura Y. Beierle J. M. Ghadiri M. R.
Dynamic Chemical Assembly of Peptide Nucleic Acids **[#4111]**
We report on the development of dynamic, sequence-adaptive peptide nucleic acids that efficiently assemble in aqueous solution via reversible covalent reactions from simple peptides and nucleobase units.

Guillemin J. C. Tarasevych A. V. Vives T. Snytnikov V. N.
A Path to Homochirality on the Primitive Earth: High Temperature Sublimation of Enantioenriched α-Alkylated-α-Amino Acids **[#4138]**
The high temperature sublimation of alpha-alkylated-alpha-amino acids containing one enantioenriched derivative leads to enantioenrichments of all components with the same handedness.

Bartlett S. J. Witkowski O. Giovannelli D.
Cognition and Learning: A Primary Determinant and Seed of Life **[#4140]**
We propose a new line of inquiry for origin of life research: the emergence of learning in prebiotically relevant systems. Understanding the origin of learning would provide key insights in the search for the origin of life on Earth and elsewhere.

Karunakaran S. C. Cafferty B. J. Hud N. V. Schuster G. B.
Influence of Nucleic Acid Intercalators on Model Proto-Nucleotide Supramolecular Assemblies **[#4160]**
We are investigating the potential for known nucleic acids intercalators, as model midwife molecules, to alter the supramolecular structures formed by self-assembling model proto-nucleobases.

Yu S. S. Solano M. D. Blanchard M. K. Soper-Hopper M. T. Krishnamurty R. Fernandez F. M. Hud N. V. Schork F. J. Grover M. A.
Growth of Proto-Peptides by Continuous Feeding of Monomers **[#4161]**
The formation of peptides on the early Earth is a long-standing problem in prebiotic chemistry. An environmental cycle is presented to elongate peptides produced via the ester-amide exchange reaction, by periodically feeding with monomers.

Glass K. Oye M. Deamer D. Vercoutere W.
Assessment of Secondary Structure in Nucleic Acid Produced in Simulated Prebiotic Conditions **[#4211]**
The earliest forms of life would likely have a protocellular form, with a membrane encapsulating some form of linear charged polymer that would have enzymatic as well as genetic properties. Our experiments mimic these conditions.

Colomer I. Fletcher S. P.
Physical Autocatalysis Triggered by a Transition Metal-Catalyzed Reaction **[#4145]**
We highlight here the importance of merging transition metal-catalyzed reactions and new modes of autoinduction or physical autocatalysis, using simple non-activated molecules, such as alkenes.

Ameta S. Arsene S. Nghe P. Lehman N. Griffiths A. D.
Autocatalytic sets of RNA Replicators in Origin of Life **[#4143]**
Autocatalytic sets based on Azoarcus' group I intron ribozyme can form networks of replicators. Using a high-throughput experimental set-up, we have analyzed a diverse library of RNA networks to study network topologies, node-fitness and robustness.

Posters will be on Display for the Entire Week.
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POSTER SESSION: INTERPLAY OF THE DIFFERENT SUBSYSTEMS FOR THE ORIGIN OF LIFE: FATTY ACIDS OR OTHER COMPARTMENT-FORMING SYSTEMS/AMINO ACIDS/NUCLEOTIDES
Price Center Ballroom East

Bapat N. V. Rajamani S.
Effect of Co-Solutes on Template-Directed Nonenzymatic Copying of RNA **[#4005]**
Given the heterogeneous nature of the prebiotic milieu, we report here, the effect of presence of lipid vesicles and Polyethylene Glycol (PEG) as co-solutes on the rate and accuracy of enzyme-free template-directed RNA primer extension reactions.

Yu Y. F. Shu W. Y. Liu Y. Zhao Y. F.
Co-Origin of Oligopeptide/Oligonucleotide/Membrane with an N-Phosphoryl Amino Acid Model in Origin of Life **[#4044]**
Co-origin theory receives much concern in recent years. We bring in an N-phosphoryl amino acid model to demonstrate the reasonability of this theory. Herein, we expect an oral presentation to elucidate the importance of phosphorus in origin of life.

Sproul G. D.
Protolife Membrane Composition **[#4108]**
A simpler membrane than with phospholipids was likely found among protocells. Using synthetic conditions that have been shown to produce peptides, fatty acids react with amino acids or peptides to form amphiphilic lipoamino acids and lipopeptides.

Dass A. V. Georgelin T. Kee T. P. Brack A. Westall F.
Hydrogels: Lets Thicken the Prebiotic Soup **[#4146]**
We introduce a new class of material that could be interesting in prebiotic chemistry: The silica hydrogel. Inorganic cells could have provided an alternative mode of compatmentalisation on early earth.

Campbell T. D. Febrian R. Bracher P. J.
Mixtures of Hygroscopic Salts and Urea as Prebiotic Media for the Condensation of Amino Acids **[#4192]**
Here, we describe a model in which mixtures of simple salts and urea are able to absorb limited amounts water from the atmosphere and serve as media to host reactions of prospective importance to the origin of life on Earth.

Sweeney K. J. Müller U. F.
Lanthanide Cofactors for Triphosphorylation Ribozymes **[#4112]**
RNA world organisms could have used trimetaphosphate as energy source for thermodynamically unfavorable RNA polymerization. Using in vitro selection we show here that Lanthanides can serve as cofactors for ribozyme-catalyzed RNA triphosphorylation.

Misuraca L. Natali F. da Silva L. Peters J. Zaccai G. Deamer D. Maurell M. C.
Dynamics of Adenosine Monophosphate in Lipid and Salty Environment **[#4228]**
One of the fundamental questions, which concern the Origin of Life studies, is how the first nucleic acids were synthesized starting from the monomeric constituents, in a probiotic environment.

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POSTER SESSION: EARLY METABOLISMS AND DEVELOPMENT OF COMPARTMENTATION
Price Center Ballroom East

Wei C. Pohorille A.
Coupling Between Metabolism and Compartmentalization: Vesicle Growth in the Presence of Dipeptides **[#4135]**
Extensive molecular dynamics simulations demonstrate low energy pathway for fast fusion of vesicle mediated by membrane-bound hydrophobic dipeptides and facilitated flip-flop transport of fatty acid molecule for transmembrane proton transfer.

Maltais T. R. VanderVelde D. LaRowe D. Goldman A. D. Barge L. M.
Which Came First, Proteins or Cofactors? Recreating Metabolic Reactions of the Early Earth **[#4158]**
We test whether cofactors can promote parts of core metabolic pathways by examining Coenzyeme A (CoA), the cofactor central to citrate synthesis in the citric acid cycle, as a target for examining cofactor activity without its protein enzyme.

Piedrafita G. Monnard P.-A. Mavelli F. Ruiz-Mirazo K.
Permeability-Driven Selection in a Semi-Empirical Protocell Model: The Roots of Prebiotic 'Systems' Evolution **[#4212]**
A semi-empirical model of self-reproducing protocells is built. Based on in vitro permeability assays we show how differential permeability linked to changes in membrane composition could have enabled a mechanism of selection between protocells.

Heili J. Gaut N. Han Q. Gomez-Garcia J. Szostak J. W. Adamala K. P. Engelhart A. E.
Functional Interactions Between Early Biopolymers and Primitive Cells **[#4207]**
Recently, we have demonstrated that compartmentalized biomolecules exhibit functional behaviors not observed in bulk solution. We suggest that numerous synthetic and regulatory processes might have been enabled by membrane-biomolecule interactions.

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POSTER SESSION: GENETIC INFORMATION AND FUNCTION IN THE EARLY STAGES OF LIFE
Price Center Ballroom East

Zamudio G. S. José M. V.
Information Analysis is Used to Determine the Identity Elements of the Operational tRNA Code **[#4015]**
We obtained the identity elements (IE) of the 20 tRNAS of the 20 canonical amino acids from about 53,000 sequences. We use the variation of information along the 76 nucleotides of each tRNA molecule. We expand the current catalogue of IE.

Edeleva E. V. Schwintek P. J. Braun D.
Elucidating Signatures of the Genetic Code with Binding Assays **[#4036]**
What defined specific assignment of amino acids to their cognate codons during the emergence of the genetic code? In this project, we develop experimental strategies to test the stereochemical theory of the genetic code origin.

Ying J. X. Liu Y. Xu P. X. Zhao Y. F.
Synergistic Effects of Nucleosides on Amino Acid Dipeptide Yields in Aqueous Conditions **[#4041]**
Our concern is the synergistic effect of codon and anti-codon (A/U, C/G) on the forming peptide of amino acid. Experimental results reveal that the yield of dipeptide formation (Phe-Phe) is indeed affected by the double nucleoside synergistic effect.

Maurel M.-C.
From Viroids and Ribozymes RNA Back and Forth **[#4063]**
We recently demonstrated that viroids replicate in non-specific hosts, emphasizing their adaptability to different environments. These results exemplify the plasticity and efficiency of small RNAs, viroïds and ribozymes.

Tjhung K. F. Joyce G. F.
Advancing Polymerase Ribozymes Towards Self-Replication **[#4126]**
Autocatalytic replication and evolution in vitro by (i) a cross-chiral RNA polymerase catalyzing polymerization of mononucleotides of the opposite handedness; (ii) non-covalent assembly of component fragments of an existing RNA polymerase ribozyme.

Wei C. Pohorille A. Popovic M. Ditzler M.
Exploring Connectivity in Sequence Space of Functional RNA **[#4137]**
Connectivity between clusters on the sequence space of RNA ligase ribozymes selected through in vitro evolution is investigated to shred light on evolution paths. Common motifs for activity are shown with increased complexity for longer molecules.

Takeuchi N. Hogeweg P. Kaneko K.
The Origin of a Genome Through Spontaneous Symmetry Breaking: A Computational Modeling Study **[#4139]**
Differentiation between templates and catalysts is a fundamental property of life. We use individual-based modeling to show that such differentiation could first emerge in primitive cells owing to an evolutionary conflict between molecules and cells.

Popovi? M. Wei C. Pohorille A. Ditzler M. A.
Modular Growth and Structural Remodeling in Early RNA Evolution **[#4164]**
By combining exhaustive mapping of fitness landscapes for short RNAs with structure guided mapping for long RNAs, we investigated RNA fitness landscapes as a function of polymer length.

Plebanek A. J. Ditzler M. A.
Sequence Duplication as an Evolutionary Mechanism in Functional RNAs **[#4190]**
Understanding the adaptive mechanisms available to RNA is useful when reconstructing the early evolutionary history of life, especially in an "RNA World" context. This study explores how a duplication event can enable new functions to evolve in RNA.

Biondi E. Yang Z. Zhang L. Dasgupta S. Piccirilli J. A. Leal N. A. Benner S. A.
Developing a Molecular Biology for Alternative Biopolymers in Early Evolution **[#4191]**
We report the further development and applications of a molecular biology for an artificial genetic system composed of nucleic acid-like biopolymers made from six different building blocks (Artificially Expanded Genetic Alphabet, or AEGIS).

Neme R. Landweber L. F.
Molecular Innovation in Ciliates with Complex Genome Rearrangements **[#4194]**
We study molecular innovation in several ciliate species with unique massive genome rearrangements to understand how a radically distinct genome architecture can shape the process of acquiring new functions, genes and structures.

José M. V. Morgado E. R.
The Total Number of Possible Genetic Codes with 64 Triplets, 20 Amino Acids, and One Stop Signal **[#4121]**
Given the recent discovery of several exo-planets which may show conditions for the existence of life, we count all the possible genetic codes with some property in common with our current genetic code.

Horning D. P. Joyce G. F.
Amplification of RNA by an RNA Polymerase Ribozyme **[#4024]**
An RNA polymerase ribozyme can synthesize structured, functional RNAs, transcribe RNA into nucleic acid analogs, and amplify RNA via a protein-free form of the polymerase chain reaction. Directed evolution towards a general RNA replicase is underway.

Cai H. H. Lin R. C. Xu P. X. Liu Y. Zhao Y. F.
A New Method to Verify of the Triplet Code **[#4058]**
This protocol chose the DNA chain and dipeptide to prove the genetic code reflected by the synergistic effect between the oligonucleotide and dipeptide under the UV radiation. The proposed method showed a new insight to research the genetic code.

Rothschild-Mancinelli B. Horfall L.
Elucidating the Evolution of Metallo-ß-Lactamases Through Ancestral Gen Reconstruction **[#4226]**
Proteins are the core of an organism's survival and adaptation, therefore under-standing their evolutionary history is critical to knowing their ability to survive.

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Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: SPECIAL SESSION IN HONOR OF JIM FERRIS:
FROM THE PREBIOTIC SYNTHESIS OF BASES AND POLYMERIZATION
TO RNA WORLD RESEARCH/CONCEPTS
Price Center Ballroom East

Sawant A. A. Rajamani S.
Synthesis and Characterization of a Putative Pre-RNA World Ribonucleoside Precursor **[#4221]**
We describe chemical synthesis and characterization of a putative pre-RNA world ribonucleoside precursor and Oligomers of these ribonucleoside precursor are expected to preserve information transfer capability of RNA.

Bahn P. R.
Tetrahedral Chart of the 4 Commonly Occurring RNA Bases **[#4019]**
A useful heuristic device for learning the names, chemical structures, and 1-letter symbols of the four commonly occurring RNA bases was made by putting such information on the four faces of a tetrahedron, which can be used generate random RNA sequences.

Rodriguez L. E. House C. H. Callahan M. P.
Nitrogen Heterocycles in Miller-Urey Spark-Discharge Mixtures: Using Chemical Trends to Elucidate Plausible Pre-RNAs on the Early Earth **[#4144]**
We incubated 53 nitrogen heterocycles with spark-discharge mixtures and found that they react with only a handful of nitriles to yield adducts that may polymerize. Whether these adducts can form a monomer of Peptide Nucleic Acid was investigated.

Pérez-Villa A. Georgelin T. Lambert J-F. Guyot F. Maurel M.-C. Saitta A. M. Pietrucci F.
Molecular Modeling of RNA Nucleotides Under Hydrothermal Prebiotic Conditions **[#4157]**
We study ribonucleotides synthesis by ab initio molecular dynamics in combination with free-energy methods under hydrothermal prebiotic conditions. In addition, we performed NMR and MS experiments to complement the results from the in silico modeling.

Wang H. Y. Han D. X. Zhao Y. F.
Based on the Hydrothermal Sediment Samples in the Extreme Environment to Study the Origin of Life **[#4010]**
We demonstrate that amino-acid homochirality, as a unique feature of life, might have originated synchronously with the Genetic Code.

Kawamura K. Konagaya N. Maruoka Y.
Mineral-Mediated Chemical Evolution of RNA and Related Molecules Compatible with the Hadean Environments **[#4048]**
We show a possible RNA world senario compatible with the Hadean environments on the basis of hydrothermal micro-flow reactor experiments associated with catalytic roles of minerals for the formation of RNA even under hydrothermal conditions.

Ertem G.
Role of Minerals in the Formation and Preservation of RNA Oligomers in the Events Leading to the Origin of Life **[#4100]**
Montmorillonite catalyses formation of RNA oligomers which serve as template for formation of complementary RNA oligomers. Minerals protect RNA and protein monomers from UV and gamma radiation demonstrating minerals' role in events leading to origin of life.

Rogers K. L. Burcar B. Ackerson M. Riggi V. Watson E. B. McGown L. B.
Early Earth Environments for an Emerging RNA World — More Widespread than Previously Thought? **[#4206]**
Expanding the potential for an RNA World, we show that several mineral catalysts, beyond montmorillonite, can catalyze the polymerization of activated 5'-adenosine monophosphate under high pressure conditions.

Tupper A. S. Shi K. Higgs P. G.
The Role of Templating in the Emergence of RNA from the Prebiotic Chemical Mixture **[#4166]**
If template-directed sysnthesis operates in the prebiotic mixture, strands with uniform chirality, monomer alphabet, and bond type will emerge. This leads to selection of uniform RNA at the level of oligomers before the origin of ribozymes.

Smith G. P. Fraccia T. P. Todisco M. Zanchetta G. Zhu C. Bellini T. Clark N. A.
Liquid Crystal Formation by Base-Pairing and Duplex Stacking of Mononucleoside Triphosphates in Aqueous Solution **[#4185]**
We observe for the first time duplex columnar liquid crystal order in aqueous solution of dATP/dTTP and dGTP/dCTP at high concentrations (~700 mg/mL) and low temperature (5°C). This sets up experimentation on natural self-ligating liquid crystals.

Smith G. P. Fraccia T. P. Todisco M. Zhu C. Bellini T. Walba D. M. Clark N. A.
Intricate Behavior of 4-Base NanoDNA Sequences: An Intersection Between Condensed Matter and RNA World **[#4197]**
As a bridge between ligation mediated by intermediate length nanoDNA oligomers and liquid crystals formed from single-base monomers, we pursue a general characterization of the self-assembly and phase behavior of particularly short 4-base DNA.

Hayden E. E. Smith G. P. Fraccia T. P. Todisco M. Bellini T. Clark N. A.
Liquid Crystal Phases of RNA Mononucleoside Triphosphates in Aqueous Solution **[#4199]**
Recently it has been shown that Deoxynucleoside Triphosphates (dNTPs) in aqueous solution form duplex base pair stacks that form columnar liquid crystal phases; here we investigate the self-assembly behavior of Ribonucleosidal Triphosphates (rNTPs).

Theis J. G. Smith G. P. Yi Y. Clark N. A.
Liquid Crystal Phase Behavior of Aqueous Mixtures of Sunset Yellow and a DNA Dodecamer **[#4202]**
We explore the molecular separation and partitioning of Sunset Yellow dye and self-complementary Dodecamer DNA molecules in stacked aggregates to exemplify a condensed matter route to chemical selection.

Lanier K. A. Kovacs N. A. Petrov A. S. Williams L. D.
The Ribosome: A Window in Time **[#4189]**
Our results support a model in which protein folding was an emergent phenomenon of interactions with RNA, and that the evolution of the ribosome was the maturation of the symbiotic relationship between RNA and protein.

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POSTER SESSION: EVOLUTION: THE DRIVING FORCE FOR EVOLUTION AT THE CHEMICAL AND BIOLOGICAL STAGES
Price Center Ballroom East

Kompanichenko V. N.
Formation of Initial Cellular Structures Through Thermodynamic Inversion **[#4021]**
The moment of a living unit arising consists in thermodynamic inversion, when the appeared 'over-entropy' free energy transforms the network of reactions in a prebiotic microsystem into functional way.

Ikehara K. Oi R.
Protein 0th-Order Structure is Encoded onto GC-NSF(a) Base Sequence **[#4052]**
Entirely new gene/protein is easily produced, because protein 0th-order structure is written onto antisense sequence of GC-rich gene or GC-NSF(a), so that a catalytic activity necessary to adapt for a new environment can be obtained.

Oi R. Ikehara K.
Direct Evidence for GC-NSF(a) Hypothesis on Creation of Entirely New Gene/Protein **[#4053]**
Every amino acid sequence (AAS) encoded by antisense sequence of GC-rich gene (GC-NSF(a)) of a genome was homology-searched against all proteins encoded by the same genome. It was found that entirely new gene has been generated from GC-NSF(a).

Brown G. D.
The Diel Theory of Evolution: Shedding Light/Dark on Abiogenesis **[#4196]**
The importance of photochemistry for abiogenesis has been appreciated since Oparin, but the day/night cycle has, surprisingly, been almost entirely ignored. The diel theory of evolution raises the rotating Earth to the status of prebiotic tinkerer.

Popović M. Ditzler M. A.
Impact of Molecular Crowding on in vitro Ribozyme Evolution **[#4201]**
We investigated the impact of molecular crowding on the evolution of ligase ribozymes. We evolved populations of ligase ribozymes in dilute and crowded buffered solutions.

Petrov A. S. Gulen B. Williams L. D.
The LSU is from Mars, the SSU is from Venus **[#4203]**
We discuss the evolution of the Ribosome within the framework of the accretion model and focus on difference and similarities between the large and small subunits in terms of their function, shape, morphology and rigidity.

Tirumalai M. R. Kaelber J. T. Park D. Chiu W. Fox G. E.
Complexity in Ribosomal Evolution — A Case Study of an Evolutionarily Divergent Recent Insertion in the 5S RNA **[#4225]**
Understanding ribosomal evolution is central to understanding origins of translation dating back to the RNA world and therefore could help understand better, the 'origins of life' as we know it.

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: EVOLUTION:
BEFORE AND AFTER LUCA/EVOLUTION OF METABOLISM
Price Center Ballroom East

Reyes-Prieto F. Hernández-Morales R. Jácome R. Becerra A. Lazcano A.
Coenzymes, Viruses and the RNA World **[#4023]**
Bioinformatic search for homologous sequences involved in ribonucleotidyl-coenzyme biosynthesis has shown that they are absent in RNA viral genomes, indicating that RNA viruses may not be direct holdovers from an ancient RNA/protein world.

Broddrick J. T. Yurkovich J. T. Palsson B. O.
Metabolic Modeling of the Last Universal Common Ancestor **[#4215]**
The origin and diversity of life on earth are intimately linked to metabolic processes. Using recent assessments of early metabolic capabilities, we construct a metabolic model of a primordial organism that could be representative of the LUCA.

Palacios-Pérez M. Andrade-Díaz F. José M. V.
A Proposal of the Ur-Proteome **[#4014]**
We uncover the plausible Ur-proteome encoded in RNY chains. The Ur-proteome obtained worked as Cofactor Stabilising Binding Sites (CSBS), i.e. the primitive bindome. CSBSs were the first proteins modules in progenotes.

Guimaraes R. C.
The Logic that Emerges from the Self-Referential Genetic Code **[#4060]**
The Self-Referential Model for the structure & formation of the genetic code is based on (proto)tRNA Dimer-Directed Protein Synthesis. Peptides that are stable and binders of the (proto)tRNAs evolve into the aminoacyl-tRNA synthetases.

Shannon G. Wei C. Pohorille A.
Exploring the Evolutionary Accident Hypothesis: Are Extant Protein Folds the Fittest or the Luckiest? **[#4181]**
Here we aim to test the "Evolutionary Accident Hypothesis" by attempting to prove the evolvability of a synthetic ATP-binding protein with a fold that is not observed in nature.

Campillo-Balderas J. A. Cruz-González-Luna C. Muñoz-Velasco I. Lazcano A. Becerra A.
Host Phylogeny and Viral Genome Size Suggest that Viruses may be Antique, but not Primitive **[#4047]**
Viruses are not relicts from an ancient RNA/protein World and their origin is related to the phylogeny of their hosts. They may be antique, but not primitive.

Jácome R. Becerra A. Ponce de León S. Lazcano A.
Structural Analysis of Monomeric RNA-Dependent Polymerases **[#4099]**
RNA-dependent polymerases are key enzymes in the viral cycle. They all share a right-hand form with three functional subdomains: palm, fingers and thumb. The palm subdomain might be one of the oldest structural domains in extant cells and viruses.

Jheeta S.
Hypothesis: ncRNA — Cellular Activity Controller? **[#4169]**
This is a hypothesis abstract: ncRNA — cellular activity controller?

Posters will be on Display for the Entire Week.
Presenters are Requested to be Present at Their Poster the Last Half-Hour Break of the Evening.

POSTER SESSION: EVOLUTION:
COMPETITION, COOPERATIVITY, COMPLEXITY AND ECOLOGY
Price Center Ballroom East

Motamedi Sh. Brazelton W. J.
Exploration of Novel Subsurface Microbial Communities Within Seafloor Mantle Rocks **[#4106]**
Extraction of DNA from serpentine rock samples that were collected during IODP Expedition 357 to the Atlantis Massif. These samples will be used for environmental 16S rRNA gene sequencing and microbial community composition analyses.

Kamimura A. Kaneko K.
Transition to Diversification by Limitation and Competition for Multiple Resources in Catalytic Reaction Networks **[#4123]**
A general mechanism of diversification is studied by resource competitions both at molecule and cell levels, and quantitative relationships are predicted between molecule diversity and resource abundances to achieve maximum growth speed.

Könny? B. Szilágyi A. Czárán T.
In Silico Ribozyme Evolution in a Metabolically Coupled RNA Population **[#4035]**
In silico ribozyme evolution in a metabolically coupled RNA population.

PRINT ONLY

Agmon E. * Stockwell B. R.

Computational Models of Heterogeneous Lipid Assemblies **[#4002]**

This work uses coarse-grained molecular dynamics to model heterogeneous lipid assemblies. Different assemblies have different properties, such as fluidity, permeability, and rigidity.

WITHDRAWN

Clarke P. A. * Steer A. M. Burroughs L. Bia N. Smith D. K.
Potentially Prebiotic Asymmetric Synthesis of Carbohydrates **[#4086]**
This lecture will present our results on the amino ester and amino nitrile promoted formation of D-carbohydrates, including 2-deoxy-D-ribose, under potentially prebiotic conditions.

Jia T. Z. Pappas C. G. Ulijn R. V. Szostak J. W.
Self-Assembled Cationic Tripeptide Nanostructures as Prebiotic RNA Binders **[#4020]**
Sustained RNA replication on the early earth was a crucial process necessary for the rapid proliferation of early life. Here, we probe the ability of small, self-assembled tripeptide nanostructures to scaffold RNA and promote RNA replication.

Knoll A. H. *
The Proterozoic Eon: Life and Environments in Earth's Middle Age **[#4071]**
Sedimentary rocks of the Proterozoic Eon preserve an increasingly well resolved record of life and environments that informs our understanding of both the earlier Archean Eon and the familiar world of the Phanerozoic.

Phosphorous and Amino Acid Adsorption in Early Earth Seafloor Minerals

Y. Abedian[1,2,4], T. Maltais[1], D. VanderVelde[3], E. Flores[1,2], L. M. Barge[1,2]

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Phosphorous (P) has always played a crucial role in living organisms and nature: it can be observed in the structure of DNA and RNA, exists in ATP which has an essential role in energy storage, and is present in many metabolic intermediates [1]. The precise role, form, and geological source of P in origin of life reactions is heavily debated. One issue is the very dilute concentration of phosphate that would have been present in the early Earth's oceans [2]; the reduced form, phosphite, has also been proposed as a likely prebiotic source [3]. A possible mechanism for concentrating P species for prebiotic chemistry is adsorption in minerals. In particular, iron oxyhydroxides including green rust are good phosphate adsorbers [4], are formed in natural environments, and would have been a common component in hydrothermal chimneys and sediments forming in the early iron-rich oceans [5]. The presence of amino acids with P species in the mineral precipitates is also significant as this system may have eventually led to peptide-phosphorus feedbacks and nests [6]. In this work, we simulated early Earth iron hydroxide seafloor precipitates and measured their ability to absorb phosphate and phosphite; we also tested how P adsorption was affected by the presence of amino acids (alanine or aspartate). By monitoring reactions with ^{31}P and ^{1}H NMR spectroscopy, both phosphate and phosphite were clearly adsorbed and concentrated into the iron hydroxides after 24 hours (phosphate more strongly than phosphite). The amount of P adsorbed in the iron hydroxides was also affected by the simultaneous presence of amino acids, with alanine presence demonstrating greater phosphate absorption than when aspartic acid was present. However, it appears that after several days to one week the additional adsorbed phosphate was released back into solution, and the P content of the solid phases began to equilibrate. These preliminary results suggest that iron hydroxides in early Earth hydrothermal/seafloor systems could have concentrated P species present in dilute concentration in the ocean and retained them in the mineral reaction system for prebiotic chemistry, but the degree to which phosphate or phosphite is adsorbed into minerals would also depend strongly on the amino acids (and presumably other organic species) that are present. More work is needed to determine which mineral / ocean / hydrothermal chemistries are most likely to support the emergence of organic-mineral-phosphorus feedbacks.

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July 16-21, 2017 at UC San Diego, CA, USA

PRODUCTION AND CONCENTRATION OF WATER-ALTERNATIVE SOLVENTS ON THE PREBIOTIC EARTH

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Introduction: Water creates special problems for prebiotic chemistry, notably that biopolymers are corroded by water[1]. The synthesis and concentration of water-alternative solvents with favorable properties for the formation of a variety of prebiotic polymers on the early Earth may have been one means of minimizing water's detrimental effects on these molecules. Formamide ($HCONH_2$), which is a liquid under normal terrestrial surface temperature and pressure conditions, has been advanced as an alternative to water that could enable chemical complexification[2]. It has the advantageous properties of promoting dehydration condensation reactions and solubilizing phosphate minerals. It has also been shown to serve as a feedstock for several biologically relevant compounds including nucleobases, amino acids and carboxylic acids when placed in contact with a variety of mineral catalysts at elevated temperatures[3]. However, it is unclear whether formamide (or other high boiling temperature amides or nitriles) may be produced in sufficient quantities, or in environments that can reach sufficiently high tempeartures, to carry out reactions of prebiotic significance. We report here the conversion of aqueous acetonitrile and hydrogen cyanide into formamide, acetamide, succinonitrile and a host of other compounds by γ-irradiation under conditions mimicking exposure to radioactive minerals. The formamide may be concentrated upon evaporation of water in near-surface geochemical settings. The maximum observed yield of formamide from 100 mM aqueous acetonitrile was ~0.55%. We estimate that starting with production of acetonitrile from irradiation of atmospheric N_2 and CH_4 or radiolysis of ambient hydrogen cyanide, a radioactive placer deposit[4] can produce about 0.3-4.5 moles of formamide km^{-2} $year^{-1}$. A natural uranium fission zone 10 m in diameter with 10kW total power output, comparable to the Oklo reactors in Gabon[5], can produce up to 0.1-1.7 moles of formamide m^{-2} $year^{-1}$ from initial acetonitrile and hydrogen cyanide, which is 2-6 orders of magnitude greater than other proposed scenarios of formamide production for which reaching neat concentrations of formamide are problematic. Radioactive mineral deposits capable of producing and trapping formamide would also place the solvent in contact with a variety of placer mineral types relevant to prebiotic chemistry, including monazite ((Sm, Gd, Ce, Th)PO_4), rutile (TiO_2), pyrite (FeS_2) and apatite ($Ca_{10}(PO_4)_6(OH)_2$)[6]. Radioactive mineral deposits may thus be favorable settings for prebiotic polymer formation through a combination of emergent geologic processes and formamide-mediated organic chemistry.

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Amino Acids Adsorption to Mineral Surfaces: Basis for Prebiotic Molecule Accumulation Studied at Nanoscale

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Introduction: In the study of origin of life, selective accumulation of abiotically synthesized amino acids to a high enough concentration for the subsequent creation of functional peptides and proteins has been regarded as a very important but least understood step. It is often discussed that certain mineral surfaces played a role in adsorbing amino acids selectively for further polymerization reactions [1]. Adsorption of amino acids to various mineral surfaces or to lipid vesicles has been proposed and studied both experimentally and theoretically but more solid knowledge about this process is expected to be established [2,3].

Experiment: In the present study, the single molecule force spectroscopy technique based on atomic force microscopy (AFM) was used to verify the binding-interaction of several amino acids to pyrite and other mineral surfaces. Amino acid molecules were covalently crosslinked to an AFM probe and their unbinding event from the mineral surface was investigated.

Resutlts and Discussion: Our results clearly indicated the ionic nature of the single molecular adsorption/desorption reaction on the pyrite substrate. Changes in the local reaction environment may have influenced the binding reaction in addition to surface properties of pyrite as investigated by Raman spectroscopy and other surface science related techniques [4].

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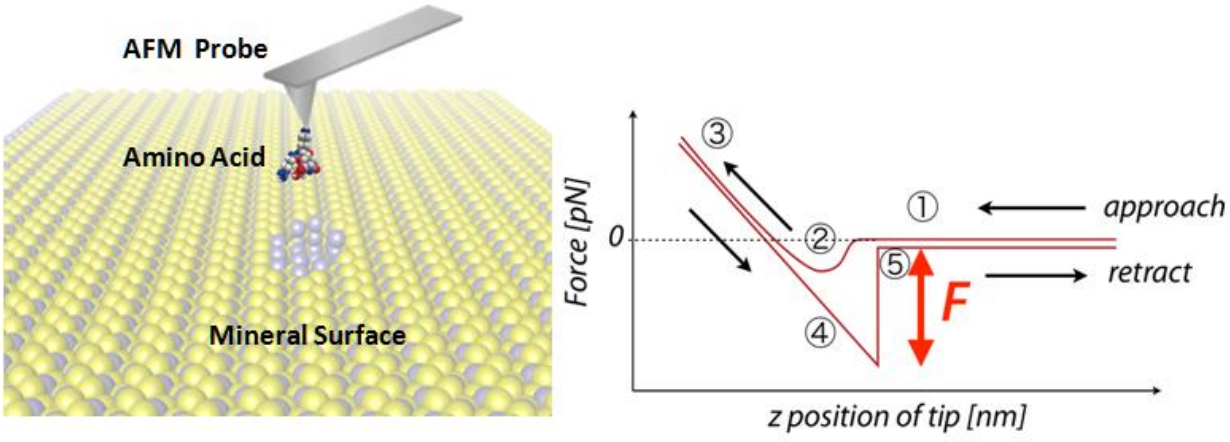

Figure 1. Schematic presentation of general principle of this work based on single molecule force measurements of AFM .

Computational Models of Heterogeneous Lipid Assemblies

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Introduction: Computational models of lipid assemblies provide flexible tools for investigating the principles and processes that lead to early membrane formation, the stabilization of protocells, growth, division, and selection. Several ventures have aimed to establish a modeling framework for protocells [1,2,3]; these simplify the chemistry of the real world while preserving key functional properties, allowing us to observe how protocells might emerge. Thousands of experiments can run systematically in-silico, and provide access to information on every component of the system. This enables us to explore a vast landscape of initial conditions and behaviors, posing predictions that directly complement in-vitro experimentation.

Model: The work presented uses coarse-grained molecular dynamics [4] to model heterogeneous lipid assemblies. At present, the model consists of about 100 different lipids, including simple fatty acids that can be saturated or unsaturated, and more complex lipids such as phospholipids, cardiolipins, sterols. These are combined in different compositions, and then simulations reveal how these compositions self-assemble into bilayer structures, vesicles, micelle, and more potentially more complex structures such as multilamellar and multivesicular vesicles. They can be brought in contact with different environments, which consist of varying temperatures, pHs, obstacles, and different molecules.

Results: Each resulting lipid assembly and environment pairing is then analyzed according to functional properties such as permeation of neutral molecules and ions, robustness to fluctuations, fluidity, and order. Membranes can demonstrate the formation of microdomains with different functional properties. The model is currently applied to study the effects of regulated cell death, in which lipid oxidation increases following the inhibition of a lipid repair enzyme. Future work will look at interactions of different lipid assemblies with simple polypeptides to determine whether they can assist with folding.

Goals: The long-term goal of this project is to observe a minimal form of Darwinian selection, in which protocells change and adapt over a few generation of growth and division. The work has begun with simple bilayers and vesicles, but will extend to vesicles with internal metabolisms, and ultimately vesicles with metabolisms that synthesize lipids. Developing and analyzing models will force us to confront many theoretical challenges related to the transition to Darwinian selection, and will deepen our understanding of this fundamental step in life's origins. In tackling these challenges, we can develop novel concepts and techniques that can directly complement and inform in-vitro work that aims to synthesize protocells in a lab setting.

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Evaluation of Glyceraldehyde Under Simulated Prebiotic Conditions

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Introduction: Prebiotic origin of sugars, like ribose (a central subunit of RNA) remains unknown [1]. So, a probable mechanism that leads to their synthesis from simpler molecules in space or primitive Earth like conditions still requires to be elucidated. The study of possible precursors, like glyceraldehyde (the simplest triosa), subjected to different sets of simulated prebiotic conditions is then useful to try to understand the pathways that might had originated this kind of building blocks of life. Considering that information about the radiation chemistry of ketones and aldehydes, whether in aqueous solution or in solid state, is scarce, the aim of the present work was to observe the behavior of DL-glyceraldehyde in solid state when irradiated with ionizing radiation (from a gamma ray source) at different doses and temperatures, and in absence of oxygen, compared to what was previously observed in aqueous solutions. By using Electronic Paramagnetic Resonance (EPR), polarography, and High Performance Liquid Chromatography (HPLC) coupled to Mas Spectroscopy (MS), it was determined that solid DL-glyceraldehyde produces stable free-radical species even at low doses. Low and room temperature showed the same spectral composite EPR patterns, with different concentration of species due to the stability of polyalcohols' primary radicals, that are usually very unstable and are observed in higher concentration at low temperatures. As observed in aqueous solutions, the decomposition of glyceraldehyde is a function of irradiation dose. As in aqueous solution, malonaldehyde was detected in small amounts by HPLC-MS. In aqueous solution were identified products of radiolysis like ethylene glycol and glycolaldehyde, which are considered intermediates for sugars and sugar like molecules [1], and have been identified in comets and solar-type protostars [2].

Aknowledgement: project CONACYT-ANR 188689.

References:

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Identification of the NTP binding site in the polymerase ribozyme

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The RNA world hypothesis describes an early stage in the evolution of life in which RNA would have served as genome and the only genome-encoded catalyst. RNA world organisms would have required catalysts for the template-dependent polymerization of RNA polymer for the replication of RNA polymers. A ribozyme (catalytic RNA) for the template-dependent polymerization of RNA was developed by the Bartel lab [1].

The structure of this polymerase ribozyme has been partially elucidated. Crystal structures of the catalytic core show the positions of critical residues and functional groups contributing to catalysis [2]. The structure of the ribozyme's accessory domain, which is important for binding of nucleoside triphosphates (NTPs), has not been determined. Results from the Unrau lab suggest that NTPs are bound by a purine-rich loop in the accessory domain [3].

To test the location of NTP binding we performed an in vitro evolution experiment of the polymerase ribozyme in the presence of a modified NTP, 6-thio GTP (6sGTP). After ten rounds of evolution, 27 clones were analyzed for their sequence, and their ability to utilize 6sGTP. All clones showed a specific mutation in the purine-rich loop. The most efficient clone was ~200-fold more efficient in utilizing 6sGTP, and contained six mutations. Reverting the mutation in the purine-rich loop reduced activity to within ~2-fold of the starting construct, and introducing this mutation alone into the starting construct raised activity to ~3-fold within the activity of the most active clone. SHAPE analysis suggested a change in flexibility of the purine-rich loop by the mutation. Together, these results confirm that the purine-rich loop of the polymerase ribozyme is the central part of the accessory domain responsible for binding NTPs.

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A molecular vestige of the origin of life on minerals : phosphorybosyl-diphosphate

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In the "RNA world" prebiotic scenario, ribonucleotide polymers are considered as the first biochemical species to have emerged. These play a fundamental role in metabolism but their formation involves a particular problem since their synthesis is thermodynamically unfavorable.This is a significant question in the frame of the "RNA world", which explains later stages of evolution, but requires the previous existence of nucleosides and nucleotides. In solution, synthesis routes of nucleotides have been described [1] that involve unstable chemical intermediates or noncanonical nucleobases. Another possible pathway to nucleotides involves mineral surfaces, which have been considered in prebiotic processes at least since the work of Bernal in 1951 [2]. Mineral surface scenarii have been tested for several prebiotic reactions[3], such as phosphorylations, phosphate polymerization or nucleotide oligomerization[4]. No matter how interesting these studies may be, they do not solve the thermodynamical problem because they do not start from "naked" monomers, but from activated nucleotides whose polymerisation is already thermodynamically favored. Thus, the assembly of the individual elements of the nucleotide, as well as its later polymerization to RNA on a mineral surface are a great prebiotic challenge. Our current research focuses on the synthesis of nucleotides and oligonucleotides from their elementary components : α-D-ribofuranose, canonical nucleobases (adenine) and the inorganic monophosphate on amorphous silica surface. In our experiments, reaction products were analyzed by in situ infrared spectroscopy, solid state NMR spectroscopy and mass spectrometry. When adenine, ribose and phosphate were adsorbed on minerals, the one pot formation of adenosine monophosphates was observed after activation at moderate temperatures (70 °C). A key intermediate was observed : phosphoribosylpyrophosphate (PRPP). In our proposition, the main reaction (the endergonic step)[5] in the nucleotides formation mechanism is the PRPP synthesis. Minerals act as metabolic support for the formation of PRPP and then the formation of nucleotides can occur. For the first time, a metabolic intermediate was analyzed in prebiotic way. The PRPP is probably a molecular relic of the origin of life. Our results have also shown, in a second pot reaction, the formation of dimer of nucleotide on mineral surfaces.

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Norvaline and norleucine may have been more abundant protein components during early stages of cell evolution

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Introduction: The nature of the evolutionary process that led to the selection of the L α-amino acids found in proteins is an unsolved issue in the study of the origin of life. Major prebiotic products are absent from the inventory of protein amino acids. We discuss the case of two hydrophobic amino acids: norvaline and norleucine.

L-Norvaline and L-Norleucine are incorporated into proteins: The intracellular accumulation of norleucine and norvaline results from the low-substrate specificity of the branched-chain amino acid pathway enzymes [4, 5]. Under anaerobic conditions, such as those that likely existed in the primitive environment prior to the development of an oxidizing atmosphere, high glucose concentrations lead to a rapid accumulation of pyruvate, which is immediately used as an alternative substrate for direct keto chain elongation to α-ketobutyrate first, and then to α-ketovalerate which undergoes transamination and forms L-norvaline [6]. Norleucine is also a by-product of the leucine biosynthetic pathway enzymes starting from pyruvate or α-ketoisovalerate, and can be misincorporated in place of methionine in recombinant proteins [5].

Conclusions: The exhaustion of the prebiotic budget of norvaline, norleucine and other non-proteinic amino acids did not stop their misincorporation into proteins. The mechanisms described here may have operated during the early stages of biochemical evolution, but continued afterwards when the development of the biosynthesis of branches-chain amino acids led to norvaline and norleucine as by-products [7].

The incorporation in proteins of norvaline in place of leucine is an outcome of the combination of the substrate ambiguity and multifunctionality of both leucyl-tRNA synthase and the branched-chain amino acid biosynthetic enzymes. Such functional flexibilities may confer evolutionary advantages, especially under anaerobic conditions that favor the accumulation of pyruvate.

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Autocatalytic sets of RNA replicators in origin of life

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Introduction: Autocatalytic sets must have been an intriguing feature of prebiotic molecules to generate first life-like scenarios on Earth [1-3]. Such autocatalytic sets brings a network-based perspective in origin-of-life where ideas of cooperativity between earlier molecules [1], collective fitness [2,4] and storing information in group of molecules [5] can be applied. Though there is considerable theoretical work promoting the network-based approach in origin-of-life [2,3,6], empirical studies targeting different properties of network in context of origin-of-life are still scarce. Recently, small RNA fragments of *Azoarcus* group I intron have been shown to spontaneously recombine to generate fully-functional ribozymes by forming cooperative and autocatalytic networks [7,8]. Such RNA recombination system have potential of overcoming the hurdle of error-catastrophe in a pure replication-based origin-of-life system [9]. However, here individual networks in isolation were not studied. In the current work, we are exploiting RNA networks formed by *Azoarcus* group I intron ribozyme to assess different network-level parameters [4,6] with an ultimate goal of demonstrating Darwinian-like evolution with such rudimentary RNA system. In order to explore the total network space, we have developed a high-throughput experimental set-up by combining droplet-microfluidics[10] with next-generation sequencing by which RNA networks can be sequenced in each droplet at an unprecedented resolution (Figure1).

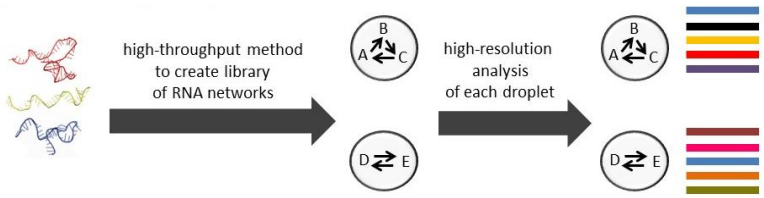

Figure 1 – Schematic representation of a high-throughput method to create a diverse library of RNA networks from the fragments of *Azoarcus* group I intron ribozyme. Using droplet-based microfluidics each of the network from the library can be analyzed at high-resuloution.

Using this set-up, we have analyzed a diverse RNA network library containing between 2-12 membered networks. Initial analysis revealed that network topology could be a strong determinant for growth of a network. More efforts are now focused on evaluating the relation between network topology and 'fitness' and future experiment will also address robustness and evolvability of such networks.

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Amines in Carbonaceous Meteorites

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Carbonaceous chondrites are primitive stony meteorites that are subdivided into eight groups, according their mineralogical composition and oxygen isotope ratios [1]. Carbonaceous chondrites contain a diverse variety of solvent-soluble organic compounds which include aliphatic monoamines (hereafter called "amines"). We have investigated the molecular abundance and distributions of amines in the CI, CM, CR, CO, CV, and CK chondrites finding that the concentration of meteoritic amines mostly correlates with the levels of aquesous and thermal processing occurred inside asteroid parent body (Figure 1). The abundance of amines decreases with increasing aqueous alteration; for example, amines are between one and two orders of magnitude less abundant in CI1 and CM1/2 compared to less aqueously altered CR2 chondrites [2,3]. A similar detrimental effect on the abundance of amines may be exerted by extensive thermal metamorphism such that occurred in CV3, CK4 and CK5 chondrites. The relationship observed between parent body processes and amine concentration, however, does not apply to the CO3 chondrites we have studied (DOM 08006 and MIL 05013), as these chondrites represent some of the least aquesously and thermally altered carbonaceous chondrites available in the Antartic meteorite catalog, yet they exhibit low amine contents. We will discuss these results, along with the isotopic and enantiomeric data collected, and the potential parent-daughter relationships that may exist between meteoritic amines and amino acids. Our collective data is critical for understanding the chemical inventory of the early Solar System, the primordial synthesis of organic matter, and how life could have appeared on Earth.

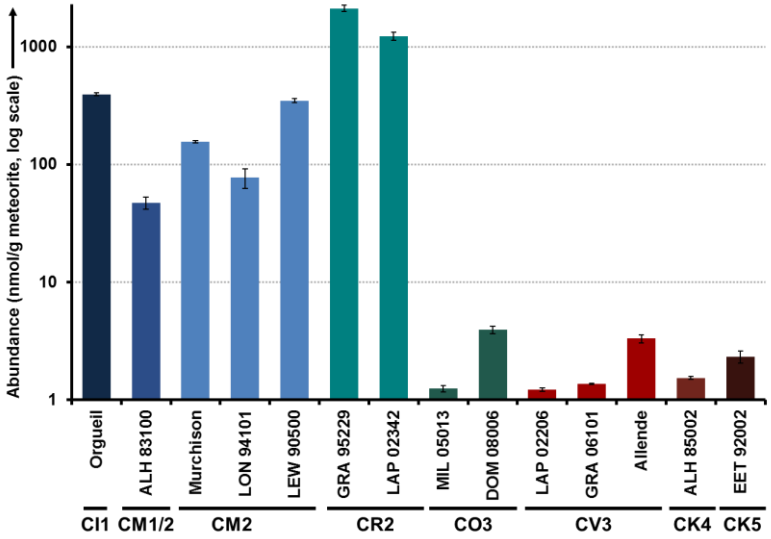

Figure 1 – Total abundance of amines in acid-hydrolyzed hot water extracts of the carbonaceous chondrites studied.

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Earliest life on Earth

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The banded iron formation at Isua in southern West Greenland with an age of 3.8 billion years is one of the oldest known sedimentary rocks and contains potential information about the earliest life on Earth. In these rocks time, temperature and pressure have led to the complete obliteration of any microfossil shapes by destruction or recrystallization of the biomaterials, including carbon to graphite [1]. On the basis of carbon isotope fractionation and structural studies it has been suggested that this graphite is of biogenic origin [2,3]. Graphite also occurs abundantly in nature in forms of inorganic origin from crustal fluids [4] and also from disproportionation of divalent transition metal-, mainly iron carbonates. Such deposits may be confused with the graphite produced by decomposition of organic matter unless physical criteria can be found that distinguish between these genetically different types. Graphite crystallizes in two modifications one metastable with rhombohedral layer stacking the other being the stable hexagonal end member. We found that the graphite in these oldest rocks, have a high proportion of rhombohedral graphite [5]. A caveat for a generalized interpretation of rhombohedral graphite as an indicator of origin from organic matter and therefore of life comes from the observation that hexagonal graphite may convert to the rhombohedral form when exposed to extreme pressure and stress [6,7,8]. The seemingly undistorted microlamination [2] in the Isua carbonaceous shale does not give any clear indication of such deformation but independent signs of subtle metamorphic effects must be sought before final conclusions can be drawn about the evidence from carbon crystal structure alone. We have recently found that the disordered graphite nanocrystals from an early stage of graphitization of clearly biogenic deposits consistently have assumed the rhombohedral structure. This may suggest but does not prove that the rhombohedral carbon in the oldest rocks is biogenic - further evidence is needed to distinguish between rhombohedral graphite formed by decay of organic matter and the same form produced by tectonic metamorphism. A possibility for such a distinction is offered by the fact that the initially formed graphite from organic matter is associated with and partly structurally combined with the decay products of the organic parent material, including species of hydrogen, nitrogen, oxygen and sulfur [9,10]. We postulate that these structural substituents give the initial stabilization to the biogenic rhombohedral graphite and that their gradual loss mediates the progressive hexagonal graphitization. If proven, presence of residual organogenic substituents in the enigmatic oldest rhombohedral graphite could potentially provide the discriminatory evidence.

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Networks of RNA replicators in origin of life

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Introduction: The 'RNA world' hypothesis suggests that RNA initially acted both as an information carrier and a catalyst, functions that were subsequently carried out by DNA and proteins. In such a prebiotic world, catalytic RNA sets or networks could have acted as evolutionary units[1-3]. However it is not immediately clear how such collective systems could evolve as several ingredients are needed to start a Darwinian mode of evolution: reproduction with inheritance, variation and selection. Though many theoretical works explored evolutionary mechanisms with such networks[2-6], there is a lack of empirical studies addressing these questions. In the current project, we are exploiting an experimental system derived from *Azoarcus* Group I intron where ribozymes are able to catalyze the formation of other ribozymes from smaller fragments[7,8]. As the catalytic relationship is directed and specific it allows us to create thousands of different catalytic RNA networks. To explore such a large network space, we have developed a high-throughput experimental set-up by combining droplet-microfluidics[9] with next-generation sequencing where a combinatorial library of RNA networks in droplets can be studied at an unprecedented resolution.

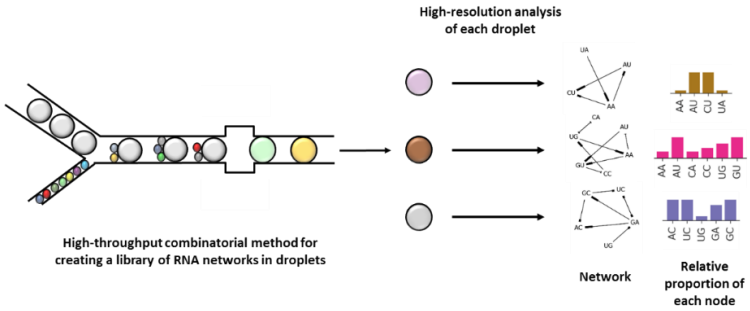

Figure 1 – Schematic representation of a high-throughput method to create a diverse library of RNA networks from the fragments of *Azoarcus* group I intron ribozyme. Using droplet-based microfluidics each of the network from the library can be analyzed at high-resuloution.

Initial analysis suggest that both growth (amount of ribozymes formed) and composition (relative proportion of species or nodes) can be inferred solely from network topology. This will help us in addressing robustness and evolvability of such networks by mapping fitness (at a network or specific node level) on a large scale. Results will also reveal the experimental fitness landscape governing evolution processes with such systems.

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Chenical Evolution Routes to Functional Peptide-Nucleic Acid Chimeras

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One major challenge for scientists keen to understand the origin of life has to do with the pre-LUCA (last universal common ancestor) transition from the chemistry of single molecular families (e.g., RNA, peptides or lipids) into today's DNA-RNA-proteins triad that drives replication and evolution in cells. According to the Central Dogma of biology, the information encoding all living matter is stored in DNA gene sequences and managed by proteins at every level.[1] This synergism is made possible by the ribosome, which translates RNA sequences into proteins. The stunning structural and functional mutualism between nucleic acids and proteins exhibited by the ribosome is a primary guiding inspiration to search for similar synergies within structurally much simpler nucleic-acid-peptide (NA-pep) or nucleobase-peptide chimeras.

In this presentation, we will describe our current effort towards the design, synthesis and structural and functional analysis of a new family of nucleic acid peptide conjugates. Particularly, we have been studied dynamic self-assembly in a prebiotically relevant system consisting of simple peptides amenable to form fibrils and two NA-pep chimeras. The DNA domain of the latter conjugates are complementary to each other, and the peptide domain sequence derived from a family of peptides containing repetitive Glu-Phe dyads previously studied by our group. Such peptides can readily assemble into fibrils effective as catalysts[2] and replicators[3], and even for charge transport.[4] Studies on the putative trajectory leading to self-assembly of peptide fibrils seeded with variable amounts of ssDNA-pep conjugates, or dsNA-pep conjugates, revealed a plethora of different supramolecular structures. Remarkably, we find that dsDNA-pep assemblies (Fig. 1) are more chemically and physically stable than their DNA or peptide alone counterparts, and furthermore that these assemblies are useful for encapsulating small molecules of relevance to prebiotic chemistry, as well as for therapeutically relevant delivery to cells.

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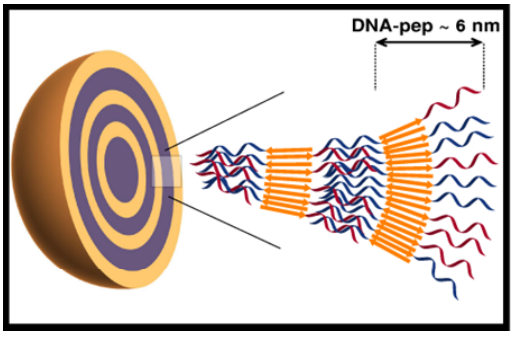

Figure 1 – Nanometric spheres formed via self-assembly of dsDNA-pep conjugates. The layered structure found useful to protect the DNA against thermal and chemical degaradation and for binding small molecules.

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Laboratory Simulated Volcanic Lightning and Prebiotic Synthesis

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Introduction: Analyses of archived aliquots from one of Stanley Miller's classic 1953 experiments that utilized an apparatus configuration wherein a jet of steam was directly injected into an electric discharge (see ***Figure*** below) suggested the potential importance of the synthesis of prebiotic compounds by lightning often associated with volcanic eruptions [**1**]. In 2014, the Munich-based authors above published a paper on the experimental generation of volcanic lightning [**2**], which suggested that the results from Miller's "volcanic" experiment might be directly testable. Contact was rapidly established between San Diego and Munich about doing such a prebiotic synthesis experiment with laboratory simulated volcanic lightning (see ***Figure*** below). In Munich a dedicated fragmentation facility has been built for experimentation involving gas mixtures. Here we report here the preliminary results from experiments using this new facility.

Experimental Conditions and Results: We selected mixtures of gases such as NH_3, N_2, CH_4 and CO_2 to be used in the apparatus and the Munich group collected volcanic ash from Sakurajima volcano (Japan), known for frequent explosive eruptions, which are very often accompanied by volcanic lightning. After using a combination of gases and ash in the laboratory volcanic lightning apparatus, we analyzed the ash for interesting prebiotic compounds. The ash was extracted using water heated over night at 40°C.

Analyses indicated that with NH_3 (in some cases associated with its presence in the gas mixture), as well as simple amino acids such as glycine (electrospray mass spectrometry of OPA/NAC-derivatized amino acids was used for analysis) were synthesized in the experiments as long as there was a reduced gas (either ammonia or methane) present. We hypothesize that in the discharges observed in the experiment, one of the components synthesized was hydrogen cyanide (HCN). It has been know for over a half-century that HCN can react to form HCN polymers that upon hydrolysis yield glycine and lesser amounts of other amino acids [**3, 4, 5**]. We are now carrying out a systematic series of analyses to determine whether essential prebiotic reagents such as hydrogen cyanide, aldehydes/ketones, etc. are made during the laboratory volcanic lightning.

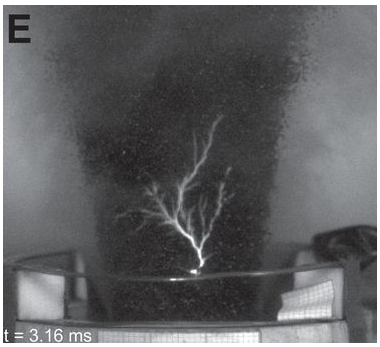

***Figure*: Left, Miller Volcanic Apparatus; Right, Experimental Laboratory Simulated Volcanic Lightning**

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XVIII INTERNATIONAL CONFERENCE
ON THE ORIGIN OF LIFE
San Diego, July 16-21, 2017

ABSTRACT

TETRAHEDRAL CHART OF THE 4 COMMONLY OCCURRING RNA BASES

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The 4 commonly occurring RNA (Ribo Nucleic Acid) bases are: Adenine, Guanine, Cytosine, and Uracil. Adenine and Guanine are purines. Cytosine and Uracil are pyrimidines. In RNA, Adenine normally base pairs with Uracil, and Guanine normally base pairs with Cytosine. The 1-letter symbol for Adenine is A, the 1-letter symbol for Guanine is G, the 1-letter symbol for Cytosine is C, and the 1-letter symbol for Uracil is U.

A Platonic polyhedron is a polyhedron with congruent faces and the same number of faces meeting at each vertex. The 5 platonic polyhedrons are: the Tetrahedron with 4 faces, the Cube with 6 faces, the Octahedron with 8 faces, the Dodecahedron with 12 faces, and the Icosahedron with 20 faces.

Since there are 4 commonly occurring RNA bases and there are 4 faces to a tetrahedron, a useful heuristic device for learning and remembering the chemical structures, the names, and the 1-letter symbol for each RNA bases can be constructed by placing the chemical structure, the name, and the 1-letter symbol for each RNA base on a single face of a tetrahedron.

United States Design Patent Number US D755,287 S, by the author, entitled TETRAHEDRAL CHART OF THE 4 COMMONLY OCCURRING RNA BASES, shows what such a tetrahedron with the chemical structure, the name, and the 1-letter symbol for each RNA bases on each face of such a tetrahedron would look like from front, back, right, left, top, and bottom views. Design Patent US D755,287 S also contains a cut-and-assemble pattern which can be cut out and assembled to make the tetrahedron shown in the design patent.

Although the RNA bases themselves are achiral, the above described RNA base tetrahedron is chiral, existing in two possible enanteriomeric configurations that are mirror images of each other.

Once the tetrahedron is assembled, it can be tossed at random like a 4-sided dice, reading out each face in contact with a flat surface, to generate random RNA base sequences. For example, one such random RNA base sequence that is 100 RNA bases long, which was generated by randomly tossing the RNA tetrahedron is: AGUCGAGG CAGUUCGUACAUAACAGACGUUACCUGUUGGCAUGUCAUUAUAAGUGUG AUUGCGCAAGCACGCGCGUUAGUGGCGGGAAAUAUAUUGACGA.

ABSTRACT

XVIII INTERNATIONAL CONFERENCE
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QUAD AMINO ACIDS

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The 20 commonly occurring alpha amino acids are: Alanine, Arginine, Asparagine, Aspartic Acid, Cysteine, Glutamine, Glutamic Acid, Glycine, Histidine, Isoleucine, Leucine, Lysine, Methionine, Phenylalanine, Proline, Serine, Threonine, Tryptophan,Tyrosine, and Valine. The amino acids, except for Glycine, are all chiral, existing as two enantiomers, L or D, which are mirror images of each other. Such chirality depends on the absolute spatial configuration of the four chemical groups tetrahedrally bonded to the α-carbon of the amino acid. Fischer projections of the L and D amino acids, where the amino and carboxyl groups extend out of the paper, and where the hydrogen and various side groups $R_{1\text{-}20}$ extend into the paper, are shown below:

L Amino Acid $\begin{matrix} R_{1\text{-}20} \\ H_2N{+}CO_2H \\ H \end{matrix}$ D Amino Acid $\begin{matrix} H \\ H_2N{+}CO_2H \\ R_{1\text{-}20} \end{matrix}$

While biological organisms overwhelmingly employ L amino acids, they still make use of D amino acids (see references).

Amino acids are usually thought of as trifunctional reagents which possess an amino group, a carboxyl group, and a side group as the three functional groups. If the remaining hydrogen atom attached to the α-carbon of the amino acid is replaced by a second side group, it would be possible to synthesize quadfunctional amino acids, shown below:

Quad Amino Acid $\begin{matrix} R_{1\text{-}20} \\ H_2N{+}CO_2H \\ R_{1\text{-}20} \end{matrix}$

There are 20 x 20 = 400 possible quad amino acids and they might have potential biological uses.

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Host-parasite oscillation dynamics and evolution in a compartmentalized RNA replication system

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Introduction: The ability of evolution is a prominent characteristic of living things, which produces the present-day complex and sophisticated living world. To understand how such evolutionary ability can appear from a mixture of molecules, we constructed an evolvable system from a reconstituted translation system of *Escherichia coli* and an artificial RNA genome that encodes RNA replicase[1]. In this system, the RNA genome replicate using the replicase translated from itself, and spontaneous mutations are introduced though replication error.

Result: We found that when we repeated the replication process, the RNA genome autonomously evolves according to the Darwinian principle only under a compartmentalized condition, indicating that a cell-like compartment is one of the requirements for evolution in this system. We further analyzed the evolutionary process in detail by using next-generation sequencing technology, and observed that evolution proceeds by repeating two overlapping phases: diversification and domination phases[2]. We also found that a parasitic replicator, which lost the replicase gene but retained recognition sequence for replicase, spontaneously appears in the system. The appearance of such parasitic replicators produced a Lotka-Volterra-like oscillation dynamics only when the system is compartmentalized and caused a large impact on the evolution of the RNA genome, implying that a parasitic replicator might play an important role on host evolution (Figure 1) [3]. We believe that this in vitro system can be a useful experimental model to understand a possible evolutionary scenario for a primitive life-like system to be closer to the present-day living things.

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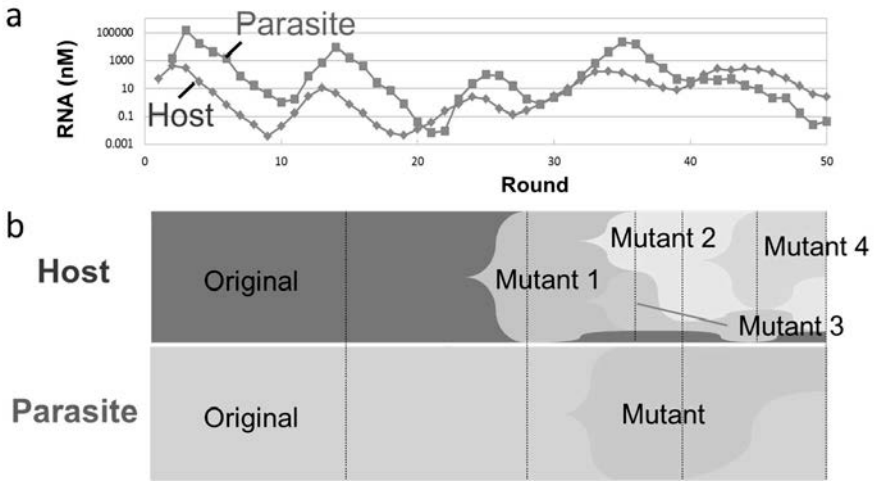

Figure 1 – a) Population dynamics of the artificial RNA genome (host) and parasitic RNA (parasite). The concentrations of both RNA oscillate when they are compartmentalized. b) Sequnece analysis of the host and parasite. Several mutants appeared and dominated the population, which explain the change in the oscillation pattern.

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Effect of Co-solutes on Template-directed Nonenzymatic Copying of RNA

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Introduction: The transition from chemistry to biology resulting in the origin of life still remains an unsolved mystery. A widely accepted hypothesis of the 'RNA world' [1] presumes that RNA played a key role during the emergence and evolution of early life on Earth by acting both as a genetic material, and a replicase that could self-propagate this genetic information. Accurate replication of the encoded information would have played a key role in formation of efficient RNA catalyst. It has been previously shown that the addition of incorrect nucleotides during nonenzymatic replication stalls the process [2]. Furthermore, this initial misincorporation also leads to a cascade of mismatches [3], giving selective advantage to the accurately replicating nucleic acids. However, these studies were carried out without accounting for the presence of any 'background molecules' in the reaction mixture. This chemically simple reaction milieu is not prebiotically realistic as the prebiotic soup would have been a heterogenous solution containing a mixture of many different molecules. Presence of co-solutes and molecular crowding agents is known to affect the kinetics of many contemporary biochemical reaction [4,5]. Hence, it becomes important to analyze the effect of presence of co-solutes on prebiotically relevant nonenzymatic reactions.

Results: In this study, we report the effect of presence of Poly Ethylene Glycol (PEG) and double chain surfactant lipid as co-solutes on nonenzymatic template-directed RNA primer extension reactions using 5'-imidazolides as monomers. It was observed that the rate of primer extension decreased in reactions involving a 'matched' addition of a purine across the cognate template base, in presence of co-solutes.(Fig. 1). We envisage that the diffusion of the potentially stacked purine monomers is possibly reduced in the presence of co-solutes, thus resulting in a decreased rate of extension of the primer. Efforts are ongoing to dissect the underlying cause of this phenomenon using pertinent biophysical techniques.

Furthermore, we also observed that reactions involving the addition of a mismatched monomer across the non-cognate template base, were not notably affected (Fig. 1), resulting in elevated frequency of misincorporations against 'C' and 'U' template bases (Fig. 2). The mutation rate in the presence of co-solutes was found to be higher than what is observed under control reaction conditions. It, therefore, is critical to consider the heterogeneity of the prebiotic soup while studying pertinent enzyme-free reactions. Our results suggest direct implications for efficient replication of functional nucleic acid sequences in a complex prebiotic milieu.

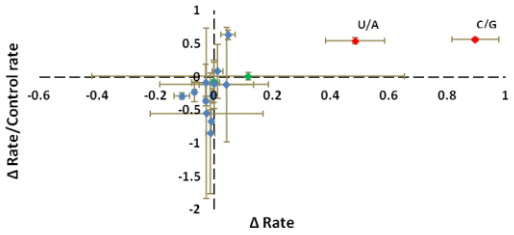

Figure 1- The 'Δ Rate' (rate of control reaction minus the rate of reaction in presence of both the co-solutes) is significantly different from zero for addition of 'G across C' (point C/G) and addition of 'A across U' (point U/A)

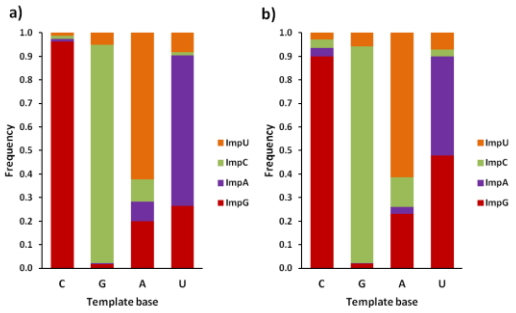

Figure 2 - Incorporation frequencies for addition of cognate and non-cognate bases. a) In the absence of any co-solutes. b) In the presence of lipid and PEG as co-solutes

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Effects of pH and Redox Gradients on Prebiotic Organic Synthesis and the Generation of Free Energy in Simulated Hydrothermal Systems

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Planetary water-rock interfaces generate free energy in the form of redox, pH, and thermal gradients. These disequilibria are particularly focused in hydrothermal systems where reducing, heated vent fluid feeds back into the more oxidizing ocean. The sediments and chimneys precipitated in alkaline hydrothermal vents on the early Earth would have contained reactive iron minerals such as iron (-nickel) sulfides and iron oxyhydroxides (including green rust). These minerals could have promoted carbon fixation and amino acid synthesis, as well as further organic synthesis, and concentrated the products, along with phosphate species, through ad- and ab-sorption. We have developed methods for investigating the effects of geochemical gradients on important prebiotic reactions in these systems, including the formation of simulated hydrothermal precipitates in a gradient (mimicking the electronic / protonic gradients that would be generated across hydrothermal chimney walls) [1]. We have also been able to synthesize hydrothermal minerals over a range of pH / redox states particular to the reactive sedimentary pile at a submarine alkaline vent. It has been shown that simulated hydrothermal minerals can reduce carbon dioxide [2-4] and we observed that the presence of pyruvate in iron-nickel sulfide precipitates increases the electrochemical activity of the chimney/ocean chemical system. These results carry the implication that the generation of organic precursors in hydrothermal sediments and chimneys could be the result of ever increasing mineral-organic feedbacks [5]. We also observed that gradients of pH and redox state affect the synthesis of amino acids from pyruvate [6]; in particular, the oxidation state of the iron minerals affects the yield of amino acid produced. Amino acids may concentrate further on, and within, charged mineral surfaces and be condensed to peptide nests harboring sulfide clusters and phosphate [5,7]. Phosphorus is also readily concentrated into reactive iron hydroxide minerals [8]. However, the suite of amino acids that may be found in a particular mineral system is a combination of what is synthesized there, what is preferentially concentrated / retained there, and what is preserved against degradation. In this way the chemistry of peptides formed in hydrothermal systems would depend on the ad- and absorptive capacity of the ambient minerals. We observed that at alkaline pH (~9) the presence of amino acids affects the absorption of phosphate and phosphite into iron hydroxide minerals. Further work is needed to determine how this depends on pH and redox gradients as well as the forced diffusion of products to a site of contrasting disequilibria. Many of the factors prompting interest in alkaline hydrothermal vents on Earth may also have been present on early Mars, and presently within icy worlds such as Europa or Enceladus. Thus, an understanding of the disequilibria that may have driven prebiotic chemistry in these systems can be put to use in assessing the habitability of other bodies in the Solar System and, eventually, the growing number of promising extra-solar planets.

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Cognition and Learning: A Primary Determinant and Seed of Life

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Introduction: Given the primacy of learning and information processing as a defining feature of the living state, we believe that exploring the emergence of learning in scenarios relevant to the origin of life could yield deep new insights in astrobiology. Despite the fact that life does not violate the laws of thermodynamics, the concentration of information and computational dynamics that are a fundamental characteristic of the biological world, are in sharp contrast to most driven systems, which in general do not spontaneously exhibit behaviour that is reminiscent of an autonomous Maxwell demon (driving gradients of free energy uphill, at the expense of others falling downhill). Thus we would like to propose a new, parallel programme of research in the origin of life field, that explores the emergence of learning in (geo)chemical scenarios relevant to astrobiology.

Context: The study of cognition has traditionally resided within the domains of neurology, artificial intelligence and systems biology. Those fields have made astounding progress in understanding how brains, neural networks, gene regulatory networks, and many other networked systems are capable of storing and processing information, predicting future events, and making decisions. Concepts from learning theory are also being used to enhance and re-write our understanding of evolution [1]. It is now clear that lower level biological systems or subsystems, including gene and protein networks, colonies of simple microorganisms [2] and subsets of cells (e.g. the immune system [3]) are capable of learning. There have also been significant advances in a rather more abstract, but we believe deeply connected realm: stochastic thermodynamics and molecular machines. Theoretical progress in this field now allows the calculation of upper limits for the efficiency with which molecules can make use of a given driving signal or free energy gradient [4,5].

Proposal: We believe that there lies a deep intersect and relationship between all the aforementioned works, and the origin of life. Alongside the search for abiotic synthesis of biomolecules and the exploration of proto-genetic systems, we would like to suggest an additional line of origins enquiry: the emergence of elementary learning systems. We believe that fundamental new insights would be gained from understanding the origin of computation, wherein the outputs of those computations feed back positively on the emergent computational architecture, making it more viable in its environment. The origin of life may well have been concomitant with the origin of cognition: the origin of a system capable of learning but also open-endedly expanding its learning capabilities. To understand that event or events, we must first understand where learning comes from in simple chemical systems, and eventually map that to early Earth conditions and potentially, exoplanetary environments.

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Geobiotropy: the Evolution of Rocks in Symbiosis with Prebiotic Chemistry

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In their interaction with water, minerals inside rocks transform with production of elements and small molecules which intervene in prebiotic syntheses. There is a chemical evolution between the world of rocks and the world of life.

One question arises: Which minerals produced by rocks are signatures for the syntheses of components of life? A contributed answer is proposed: It is based on calculations of thermodynamic functions for elementary equations of carbonation and hydrolysis of Fe(II)Mg- silicates and Fe(II)- monosulfides which compose minerals such as olivine and pyroxenes. The analyses of 4 E-pH redox diagrams, published for corrosion purposes, fulfil the thermodynamic study for anoxic and oxic water. A table is drawn with the minerals which can be signatures of prebiotic synthesis: the geobiotropic minerals.

Several terrains of the solar system are discussed. The minerals in the Tagish Lake meteorite may result from anoxic carbonation and hydrolysis of Fe(II)Mg- silicates and Fe(II)- monosufides. The high T(~350 °C) low pH(3-4) hydrothermal vents of the oceans ridges, may result from anoxic hydrolyses of Fe(II)- monosulfides such as mackinawite, troilite and pyrrhotite. Cases of anoxic and oxic oxydations are discussed for Mars.

A special case of prebiotic synthesis may be observed inside pores of radioactive rocks containing fluids such as H_2, CO_2, N_2 and H_2O and located near uranium radionuclides. Amino acid analytical chemistry, using GC-MS and derivatization methods, is currently under preparation on "bitumen" samples which are observed nearby fluid inclusions of radioactive rocks. Results may be given at the conference. A scenario concerning prebiotic chemistry inside pores containing water, H_2, CO_2, N_2, and located next to radionuclides, is proposed.

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DOI 10.1007/s11084-017-9534-5 (and refs of MP Bassez herein).

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Parallel prebiotic origin of canonical and non-canonical purine nucleosides

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Introduction: Due to its catalytic activity and information storage properties, RNA is believed to have been the key molecule during chemical evolution.[1] Next to the canonical bases, RNA contains more then 120 known modifications, which are critical for regulating diverse biological processes.[2] Without modified nucleosides life as we know it would not be possible. It is an open question of how the essential non-canonical bases evolved that are found today in all three kingdoms of life. It might be possible that some of the most central modifications could have been formed on an early Earth, while others especially the more complex modified nucleosides, might have been the result of biological evolution. Therefore we investigated if there is a chemical pathway that would allow a parallel prebiotic origin of canonical and non-canonical purine nucleosides.

Based on the chemistry reported here, we can conclude that some of the ubiquitously abundant modified RNA purine nucleosides can readily form under conditions compatible with early Earth geochemical models. Their synthesis is possible in parallel to the canonical purine bases by a unified reaction pathway via formamidopyrimidines (FaPys).[3] This shows that these non-canonical nucleosides had a chance to appear together with the canonical ones on the early Earth. Consequently, they would have been part of the prebiotic nucleoside pool and therefore participated in the chemical evolution process that presumable established an RNA world. These non-canonical bases might have been necessary for correct folding of catalytic RNA or facilitating RNA/RNA interactions, giving modified RNA a superior functionality. We assume that the modifications available through our FaPy pathway took over crucial functions and were therefore conserved until today, making them fossils of an early Earth.

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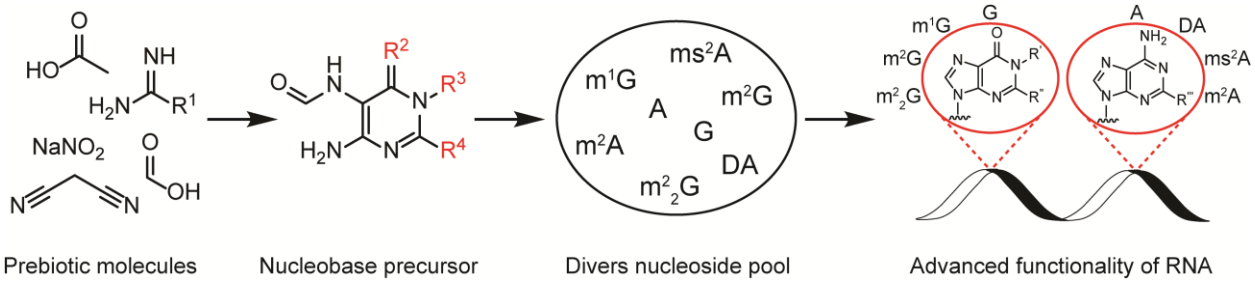

Figure 1 – Scheme of the prebiotic origin of canonical and non-canonical nucleosides. Simple prebiotic molecules can assemble into Formamidopyrimidines (FaPy) as nucleobase precursors. Reaction of the FaPy compounds with ribose provides a divers set of purine nucleosides. From the pool of RNA building blocks, the first RNA polymer must have been assembled. These modified bases might have improved RNAs functionality, leading to a superior RNA molecule that was able to undergo Darwinian evolution.

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Selection for the Spontaneous Appearance of Lifelike Chemistry *in vitro*

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Introduction: Among the most promising theories of life's origin are those that invoke the spontaneous formation of reflexively autocatalytic sets – sets of chemicals in which each chemical is created by at least one reaction in the set and each reaction is catalyzed by other members of the set (or occurs spontaneously)[1]. Such autocatalytic systems could be composed of diverse organic and inorganic components, perhaps including RNA[2-5,7-8]. Previous research has shown that given a sufficiently diverse enough mixture, reflexively autocatalytic sets are highly probable [9]. It has also been proposed that spontaneously emerging reflectively autocatalytic systems can be evolvable if either encapsulated in a membrane[10] or adsorbed onto a mineral surface[11]. We are using a novel class of experiments, modeled after microbial artificial ecosystem selection experiments[12] to evaluate whether evolvable autocatalytic systems can emerge spontaneously in the laboratory.

Research Approach: Mineral particles are incubated in an aqueous soup containing diverse potential building blocks of life and abundant free energy. Each generation we transfer a small aliquot of particles into a new container containing fresh soup and a population of virgin grains. By repeating this over many generations we impose selection for chemical systems that can self-propagate and can be efficiently transferred from generation to generation. Systematic changes over generations, for example in the amount of carbon attaching to grains or the amount of free energy dissipated during a period of incubation, could indicate that systems of chemicals have arisen that can collectively propagate themselves from generation to generation.

Methods: The experiment is conducted under sterile conditions using either iron pyrite or montmorillonite grains and a generation time of 2-3 days. As an additional aid to sterility, vials are autoclaved each generation. The chemical soup we have used includes transition metal ions (as possible catalytysts), ammonium nitrate (as a kinetically-slow source of redox potential energy), and diverse organic monomers including amino acids, sugars, nitrogenous bases, and diverse organic acids.

Currently we are using five analysis methods: (1) Nitrate/Ammonium assays to see if the rate of redox energy changes. (2) Energy dispersive spectroscopy (EDS)/X-ray photoelectron spectroscopy (XPS) to determine the amount of carbon and nitrogen adsorbed onto grains before and after incubation. (3) Assays of total primary amino nitrogen to assess amino acid compositional changes. (4) High performance liquid chromatography (HPLC) to track the formation of peptides and amino acid compositional changes. (5) We hope to soon add an additional assay, based on inclusion of a nonstandard amino acid FRET pair (p-cyanophenylalanine and 7-azatryptophan) to the solution so that FRET signal can be used to detect amino-acid-containing oligomers.

Results: We have completed >45 generations of selection, without evidence of bacterial contamination. Side-by-side comparison of experimental vials with control vials that had not been inoculated from the prior generation has, to date, failed to detect significant changes. We propose continuing this experiment for many additional generations and initiating additional experiments with different reagents and minerals.

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Amino Acid Contents of Meteorite Mineral Separates

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Introduction: Indigenous amino acids have been found indigenous all 8 carbonaceous chondrite groups [1]. However, the abundances, structural, enantiomeric and isotopic compositions of amino acids differ significantly among meteorites of different groups and petrologic types [2, 3]. This suggests that parent-body conditions (thermal or aqueous alteration), mineralogy, and the preservation of amino acids are linked. Previously, elucidating specific relationships between amino acids and mineralogy was not possible because the samples analyzed for amino acids were much larger than the scale at which petrologic heterogeneity is observed (sub mm-scale differences corresponding to sub-mg samples). Recent advances in amino acid measurements [e.g., 4] and application of techniques such as high resolution X-ray diffraction (HR-XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) for mineralogical characterizations allow us to perform coordinated analyses on the scale at which mineral heterogeneity is observed.

Methods: We link amino acid data to mineralogy by performing ultra-performance liquid chromatography with quadrupole-time of flight mass spectrometry (LC-MS) analyses, followed by SEM or HR-XRD analyses on bulk samples (~20mg) and mineral separates (<2mg) from a variety of spatial locations within our meteorite samples.

Results: The matrix material of the Murchison meteorite is comprised primarily of fine-grained phyllosilicates, whereas our non-matrix fraction consists of mostly mafic silicate minerals. Although both matrix and non-matrix fractions contain amino acids, the amino acid abundances of matrix-containing fractions differ markedly from non-matrix fractions (e.g., figure 1).

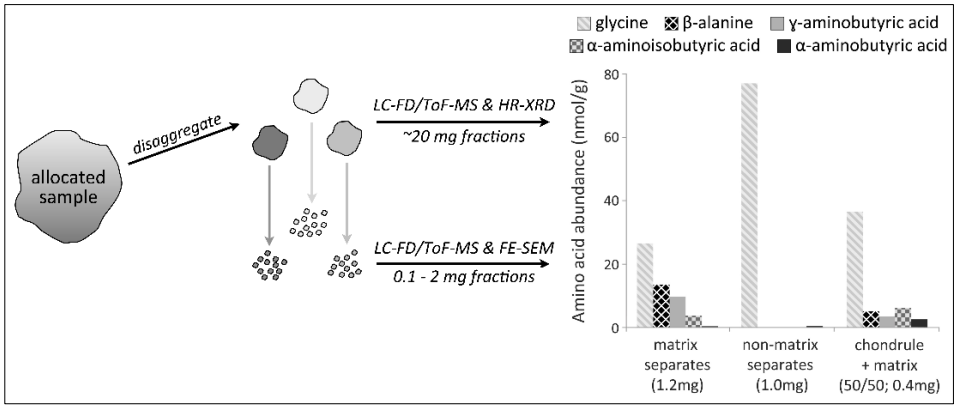

Figure 1. Meteoritic samples are gently disaggregated into ~50mg fractions, which are further sub- divided: one larger fraction (~20mg) for HR-XRD and a dozen mineral separates (e.g., matrix material, non-matrix grains, opaques, etc. of 0.1 to 2 mg) for amino acid analysis by LC-MS and mineralogy characterization by FE-SEM analyses. Results shown are from analyses on mineral separates from the CM2 carbonaceous chondrite, Murchison.

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July 16-21, 2017 at UC San Diego, CA, USA

Spontaneous Phospholipid Membrane Formation by Chemoselective Ligation Reactions

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Introduction: Phospholipid membranes are employed in numerous practical applications such as the study of protein-membrane interactions, drug-delivery, origin-of-life research, and artificial reactors. While the capability of phospholipids to self-assemble into membranes is well characterized, the *de novo* synthesis and formation of membranes from simple precursors is poorly understood. Therefore, one of the major goals of chemical prebiology is the development of simple and robust methods for the preparation of self-assembling non-natural membranes, that will help understand the fundamental structural, dynamical and biochemical features on which nature builds living systems. Here we describe the use of histidine ligation (HL) to form phospholipids *de novo* [1] from water-soluble starting materials – namely a histidine functionalized lysophospholipid and a water soluble fatty acyl thioester (*Fig.* 1). The resulting phospholipids can spontaneously self-assemble into vesicles that can grow to several microns in diameter. Moreover, the orthogonality, the high reaction rate, and the biocompatibility of this approach are key features that make it a powerful tool for the efficient encapsulation of relevant biomolecules, such as proteins. We foresee future applications of HL membrane assembly in understanding of fundamental chemical mechanisms of origin and early evolution of life, especially in relation to membranes. Such approach will also be useful in bottom-up synthetic biology, molecular self-assembly, and biomimetic chemistry research.

As an ongoing work in our group, we have utilized a similar strategy to ligate an amine-functionalized lysolipid and fatty acyl adenylate to generate phospholipid membranes. We hypothesize that such chemistry played an important role in transitioning from primitive fatty acid based membranes to more sophisticated phospholipid based membranes.

References:

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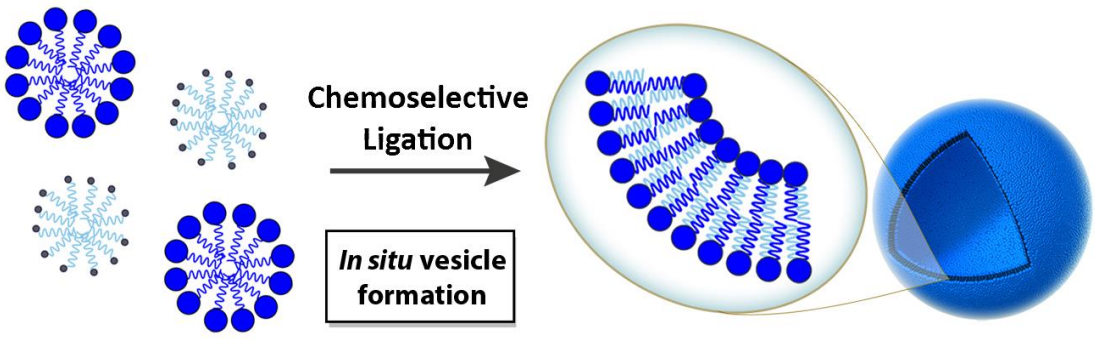

Figure 1 – Formation of membrane forming phospholipids by a chemoselective ligation reaction between non-membrane forming precursors

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Heterogeneity to Homogeneity: Synthesis, base pairing and ligation studies of 4',3'-XyluloNA/RNA and TNA/RNA chimeric sequences

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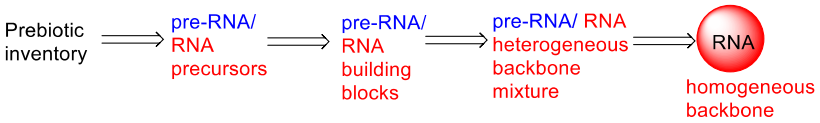

The "RNA world" hypothesis postulates an important role of RNA in the origin of life.[1] However, the difficulties associated with the synthesis of ribonucleoside and its polymerization under potential prebiotic condition[2] led to the assumption that RNA arose from a simpler "pre-RNA" polymer.[3] But this hypothesis raises another question – how did or could the transition from "pre-RNA" to "RNA" happen? [4] The progress from a homogeneous "pre-RNA world" to a homogeneous "RNA world" is contingent upon keeping their respective chemistries spatially separated.[4] However, based on the reality of "clutter" of prebiotic chemistry,[3] we herein present an alternate model which starts, not with homogeneous-backbone systems, but rather with mixtures of heterogeneous-backbones of a chimeric "pre-RNA/RNA".[4]

The formose reaction[5] and glyoxalate scenario[6] suggests the presence of pentulose sugars apart from the pentose sugars, on prebiotic earth. In addition, borate mediated formose reaction demonstrated the formation of threose,[7] and the reaction of glycolaldehyde with cyanamide also led to threose nucleic acid (TNA) and RNA nucleoside precursors[8]. Based on the prebiotic availability of a mixture of sugar precursors, we have synthesized and characterized two model chimeric nucleic acid sequences with sugar-backbone heterogeneity, containing a mixture of (4'→3')-L-xylulose(X^y)-NA with RNA, and (3'→2')-L-threose(T)-NA with RNA. The two chimeric X^yNA-RNA and TNA-RNA systems were found to exhibit unique base-pairing preferences suggesting that heterogeneous-backbone chimeric oligonucleotide systems (e.g. TNA-RNA) may transition to a homogeneous-backbone system (RNA). As a proof-of-principle, heterogeneous chimeric templates were found to mediate the non-enzymatic ligation of homogeneous-backbone oligonucleotides demonstrating a plausible constructive role for backbone-heterogeneity[4] in enabling the handover from chimeric "pre-RNA/RNA world" to a homogeneous "RNA world".

References:

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July 16-21, 2017 at UC San Diego, CA, USA

Adsorption of RNA on Mineral Surfaces and Mineral Precipitates.

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A widely held "RNA first" model proposes that RNA gave organic matter in Earth its first access to Darwinism. Such a model, which requires a mechanism to generate RNA from a prebiotic "soup", must also manage the intrinsic instability of any RNA so formed. Association of RNA with mineral surfaces has been suggested as a possible solution to this problem. However, the prebiotic significance of laboratory experiments that study the interactions between oligomeric RNA and mineral species is difficult to discern. While laboratory-generated samples of synthetic minerals can have controlled compositions, they are often viewed as "unnatural". On the other hand, natural mineral specimens can differ widely depending on their provenance and impurities.

Here, we manage this problem by finding trends in the interaction of RNA with natural mineral specimens, synthetic mineral specimens, and co-precipitated pairs of synthetic minerals. If these trends run in parallel, a persuasive case can be made that those interactions are mineral-specific, rather than simply being examples of large molecules associating with large surfaces of precipitated synthetic minerals, or the consequence of mineral impurities that vary from sample to sample.

Using this approach, we have discovered Periodic Table trends in the binding of oligomeric RNA to alkaline earth carbonate minerals and alkaline earth sulfate minerals. These trends are seen in both natural and synthetic minerals, and are validated by comparison of co-precipitated synthetic minerals.

We also found differential binding of RNA to polymorphic forms of calcium carbonate, and the stabilization of bound RNA on aragonite. Similarly, we found that silicon dioxide (silica, SiO_2), in the form of synthetic opal, adsorbs and stabilizes RNA from aqueous solution more than fully amorphous silica, which in turn adsorbs RNA more than crystalline quartz. Moreover, RNA adsorbed on opal is considerably more stable than the same RNA free in aqueous solution at basic pH.

These results have relevance to the prebiotic concentration and stabilization of RNA in the "Discontinuous Synthesis Model" for the origin of life via an RNA World. Remarkably, the mineral ensemble that we would ideally like for this model is close to that being discovered today by NASA missions to Gale Crater on Mars.

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Developing a Molecular Biology for Alternative Biopolymers in Early Evolution

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One of the more discussed hypotheses for the origin of life is the "RNA first" model. This model postulates that organic molecular systems first gained access to Darwinism through a spontaneous prebiotic formation of RNA molecules that were able to generate replicates, with imperfections, where the imperfections were themselves replicable.

Unfortunately, decades of *in-vitro* evolution attempts at reproducing the events that would have led to such a replicase delivered few, if impressive, results, most of which are highly derived RNA ligases. The fact that it is so difficult to reproduce an RNA species central to the "RNA first" hypothesis suggests that we might be missing something. Thus, many laboratories have sought alternative biopolymers that are both prebiotically accessible, and that also support Darwinism as well or better than standard RNA, managing the rather low intrinsic catalytic ability of RNA as it is today found in terran biology, and the frequently reproduced experimental observation that it is easier to get nucleic acid molecules that catalyze the destruction of RNAs than nucleic acids that catalyze its synthesis.

Here, we report experimental results with such nucleic acid-like biopolymers made from six different building blocks (Artificially Expanded Genetic Alphabet, or AEGIS). These additional nucleotides carry functionality that chemical theory suggests might assist in binding and catalysis, perhaps even catalysis for the synthesis of RNA.

We will describe the development and applications of a molecular biology for this artificial genetic system, including pipelines to synthesize its nucleoside triphosphates and phosphoramidites, procedures to synthesize a oligonucleotides, enzymes that copy the alternative genetic system, and procedures that place the expanded, richer, genetic system under Darwinian selection pressure in the laboratory, with downstream sequencing and analysis to assess the sequelae of laboratory Darwinism.

These results have led to several discoveries. First, additional building blocks appeared to allow the system to adopt macro conformations different from, and additional to, those accessible with standard four letter nucleic acids. Further, it appears that the added information density by added letters provides options for the system to access specific binding confirmations. Further, although quantitative comparison is difficult, preliminary data suggests that the added functionality also allows the system to get tighter and more specific interactions between evolvable biopolymers and a target as it serves both genetic and phenotypic roles.

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Polymer Building Blocks and Dipeptides Stabilize Fatty Acid Vesicles

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A major problem in understanding the origin of cells is explaining how the two essential biological polymers, RNA and protein, became associated with a membrane. The first membranes were probably composed primarily of fatty acids, which spontaneously assemble into bilayers in fresh water. A difficulty with the fatty acids-as-original-membrane hypothesis is that they flocculate in salt water. We propose that building blocks of the two polymers (nucleobases and ribose for RNA and amino acids for protein) bind to fatty acid bilayers, and that this binding increases the formation and stability of membranes [2]. We further suggest that the selection and concentration of compounds and conformational constraints entailed in this process could have facilitated the formation of RNA and protein. This scenario explains how the co-localization of RNA, protein and fatty acid membranes in the first cells could have arisen. We previously showed that RNA bases and ribose do bind to and stabilize vesicles composed of decanoic acid, a prebiotic fatty acid [3]. Here we present evidence that single amino acids and dipeptides also bind to and stabilize such vesicles. (A) SINGLE AMINO ACIDS. Three lines of evidence indicate interaction of single amino acids with decanoic acid vesicles: (1) Four prebiotic amino acids—alanine, glycine, serine and threonine—increased the formation of decanoic acid vesicles, as assessed by the turbidity of the solutions. To confirm that the increases in turbidity were due to more vesicles, we stained membranes with a fluorescent dye and then observed them by fluorescence microscopy. We found that these amino acids increase both the number of vesicles and the density of staining. Four other amino acids—leucine, isoleucine, valine and proline—did not increase turbidity, suggesting that the amino acid sidechains affect interaction with the vesicles. (2) If amino acids interact with fatty acid membranes, they might be expected to mitigate salt-induced flocculation of decanoic acid vesicles, as we found with nucleobases and ribose. We found that two of the amino acids tested, leucine and isoleucine, do substantially reduce flocculation of decanoic acid vesicles by NaCl. (3) Finally, we found that all eight of these amino acids bind to decanoic acid vesicles based on a filtration assay, and that the more hydrophobic ones bind more strongly than the others. (B) DIPEPTIDES. Several dipeptides also increased turbidity, including Ala-Ala, Ala-Gly, Ala-Thr, and Ala-Pro. As with the single amino acids, fluorescence microscopy demonstrated that these dipeptides increase both the number of vesicles and density of staining. Importantly, we found that Ala-Ala and Ala-Gly increase vesicle formation to a greater extent than their unjoined amino acids. Regarding possible mechanisms of interaction, Ala-Ala-NH_2 and Pro-Ala did not increase turbidity, suggesting a free carboxyl group and a primary amine are required. The recruitment of amino acids and peptides by fatty acid vesicles, and stabilization of these vesicles by the recruited compounds, provide an explanation for the co-localization of protein with protocells.

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Thermodynamics of sequence and exploration in prebiotic scenarios

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Using classical and stochastic thermodynamics[1], we study polymers with a sequence (e.g. RNA, peptides) in solution. In the first part, we study (I) closed systems with sequence exchange reactions[2], and (II) open systems with exchange reactions that exchange polymers with reservoirs. We show that these open systems can exhibit exotic behavior. For example, we can obtain increasingly large polymers, by exploiting entropic thermodynamic forces. In the second part, we revisit ligation-fragmentation models of prebiotic RNA and explicitly consider chemical activation. This leads to modified polymer length distributions and general statements about energy and material requirements of such models. More importantly, it introduces a general energy cost for maintenance and sequence exploration. This cost severely limits the emergence of prebiotic functionality (e.g. ribozymes). By accounting for such costs, we can refine prebiotic scenarios.

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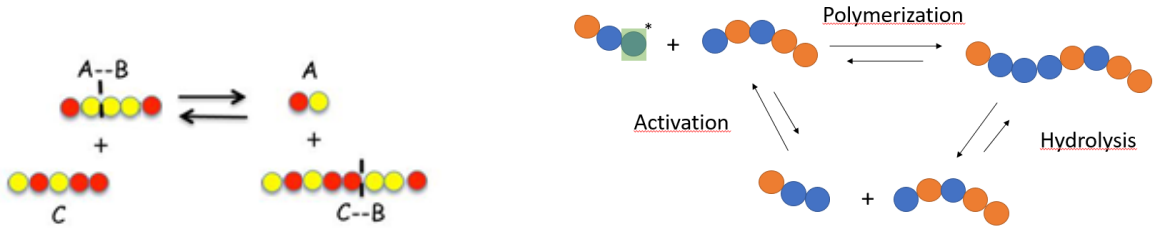

Figure – (left) an example of a (simplified) exchange reaction. (right) a ligation-hydrolysis-activation cycle.

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Model prebiotic iron-sulfur peptides

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Iron-sulfur clusters are indispensable to extant metabolism and are thought to reflect an ancient role in mediating the chemical reactions that led to life. However, there has been no clear proposal for how these inorganic clusters came to occupy such an important position in biology. Here we describe our efforts in delineating a plausible path from short, prebiotically plausible peptides to longer sequences with characteristics similar to modern day ferredoxins. Small molecule thiolates and short peptides can give rise to [2Fe-2S] and [4Fe-4S] clusters in aqueous solution when illuminated with UV light in the presence of iron ions. The resulting iron-sulfur peptides are redox active. Additionally, duplications of iron-sulfur coordinating tripeptides give sequences with cysteinyl ligand spacing similar to contemporary ferredoxins that are better able to stabilize iron-sulfur clusters.

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UV light-driven prebiotic synthesis of iron-sulfur clusters

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Introduction: Iron-sulfur clusters are ancient cofactors that play a fundamental role in metabolism and may have impacted the prebiotic chemistry that led to life.[1] However, it is unclear whether iron-sulfur clusters could have been synthesized on the early Earth. Dissolved iron on prebiotic Earth was predominantly in the reduced ferrous state[2], but ferrous ions alone cannot form iron-sulfur clusters. Similarly, free sulfide may not have been readily available. We have shown that UV light drives the synthesis of [2Fe-2S] and [4Fe-4S] clusters through the photooxidation of ferrous ions and the photolysis of organic thiols. Iron-sulfur clusters coordinate to and are stabilized by a wide range of cysteine containing peptides, and the assembly of iron-sulfur cluster-peptide complexes can take place within model protocells in a process that parallels extant pathways. Our experiments suggest that iron-sulfur clusters may have formed easily on early Earth, facilitating the emergence of an iron-sulfur cluster dependent metabolism.

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July 16-21, 2017 at UC San Diego, CA, USA

Using Reaction Kinetics to Assess Chemistry of Prospective Importance to the Origin of Life

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Determining how the mixture of abiotic chemicals present four billion years ago could have naturally assembled into an autoamplifying network of reactions is a challenge of extraordinary complexity, and it can be difficult to decide where to begin. When evaluating chemical reactions proposed as relevant to the origin of life on Earth, the universal importance of water to life necessitates the consideration of hydrolysis as a deleterious side reaction. This presentation summarizes two key thrusts of research in our group: (i) the influence of simple salts on the rates of coupling and hydrolysis of peptides and (ii) measurements of the rates of thiol–thioester exchange and thioester hydrolysis to assess the feasibility of a Thioester World—a period in early evolution where thioesters may have filled an important role as a kinetically stable, high-energy species like ATP does today.

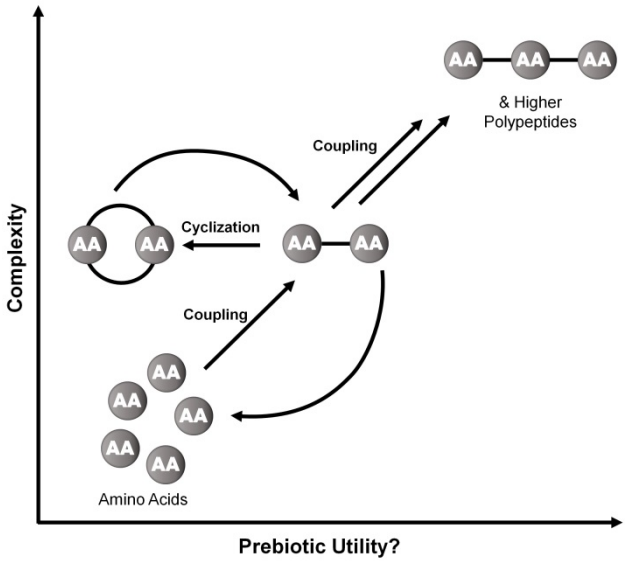

Figure 1 – As amino acids in a system couple to form higher oligomers, the competing rates of hydrolysis and cyclization (into DKPs) must be considered when evaluating the favorability of conditions to the development of complexity.

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The organics on the nucleus of 67P/C-G and how they might have gotten there

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On the comet: In November 2014 the ROSETTA spacecraft successfully deployed its lander Philae to the surface of comet 67P/Churyumov-Gerasimenko[1]. In the first 63 hours after its triple-landing on the comet, the 10 instruments on-board provided a wealth of ground-truth data of the composition and properties of the comet nucleus. Among the instruments, the COmetary Sampling and Composition (COSAC)[2] instrument took a mass spectrum of the gas phase evolved from the dust that the landing kicked up[3]. In this mass spectrum, 16 small organic molecules could be identified, some of which had not previously been identified in comets. They form a family of inter-related species.

In the lab: The more complex molecules identified in the COSAC data are known to form from the smaller ones during high-energy irradiation. A tool which has proven very valuable in elucidating the reaction mechanisms of this high-energy radiation-driven chemistry, is the irradiation of ices with low-energy electrons[4]. Thermal desorption mass spectrometry after irradiation has been used in a number of studies to identify fundamental reaction mechanisms in cometary ice chemistry: Amines will form during electron-irradiation of olefins and ammonia[5,6], alcohols from olefins and water[7], and short amides like formamide from carbon monoxide and ammonia[8].

At the conference: The complex and rich chemistry on the comet and the intricate inter-relations between the substances found on the comet will be presented in detail, as will approaches to a re-evaluation of the COSAC data set based on known ties between certain compounds and data from other instruments aboard Philae/ROSETTA.

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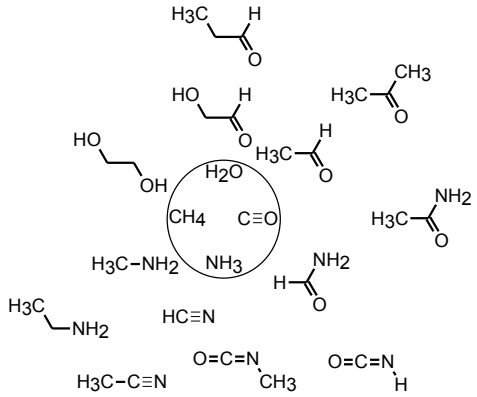

Figure 1 – The 16 molecules that COSCAC identified on the nucleus of comet 67P/Churyumov-Gerasimenko (NH_3 was not unambiguously identified). The molecules are organized from simple in the middle to increasingly complex towards the edge. Many of the complex molecules are known to form from the simpler ones.

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Metabolic Modeling of the Last Universal Common Ancestor

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Background: The origin and diversity of life on earth are intimately linked to metabolic processes. Recent advancements in our understanding of the metabolic capability of early life [1] enables systematic investigations into primordial metabolism. A framework that incorporates geobiochemical, environmental, and metabolic constraints would allow for a more complete understanding of early biological systems.

Approach: Constraint-based modeling of biochemical networks coupled with flux-balance analysis has a long history of contextualizing cellular metabolism [2]. Using recent assessments of early metabolic capabilities [1][3], we construct a metabolic model of a primordial organism that could be representative of the last universal common ancestor (LUCA). A core set of possible metabolic reactions derived from phylogenetic analysis [1] served as a scaffold to build the base metabolic network. Gaps in the base network were filled using a database of candidate reactions and existing modeling algorithms. Geobiochemical phenomena such as hydrothermal vents will be integrated with the model to investigate interactions with the environment.

Significance: A systems biology view of LUCA enables the quantitative evaluation of competing hypotheses concerning the origins of metabolic capabilities. The inclusion of mathematically-defined geobiochemical constraints represents a significant leap forward in systems biology. Ultimately, this model can serve as a framework to investigate the interface between early living systems with geochemical environments.

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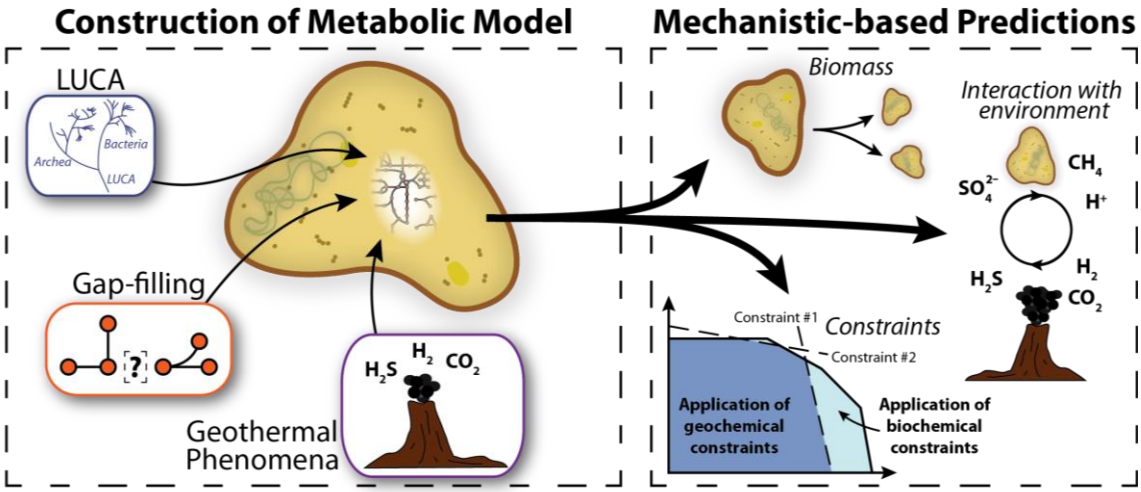

Figure 1 – Conceptual framework for the generation and applications of the metabolic model.

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The Diel Theory of Evolution: Shedding Light/Dark on Abiogenesis

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The possible role of photogenesis in the origin of life has been widely appreciated [1,2]. However, the day/night cycle has been all but ignored [3], which seems surprising considering the importance of circadian clocks in biology and of diel variation in geochemistry [4,5]. The diel theory of evolution raises the rotating earth to the level of primary tinkerer in the evolution of life's chemical complexity [6]. Cycles of solar radiation and darkness must have established a diel rhythm in the primordial soup early in Earth's history. Light-gathering molecules, plentiful in life's molecular arsenal, can be produced from precursors under plausible prebiotic conditions, especially with the aid of UV light [7]. Some chemical reaction cascades require light activation while others are inhibited by solar radiation. The prebiotic soup would have accumulated energy in the form of chemical bonds during the day, and some of that energy would have been available for other reactions in the evening and at night. Thus, as a starting point for experimental work, I suggest the use of cycling, full-spectrum solar radiation—as present on early Earth including UV-C and with a slowly lengthening period—to study the prebiotic chemical milieu.

It is possible that a primordial circadian clock emerged in a broth with a diel rhythm before Darwinian organisms [8,9], but a driving force seems obscure. Rather, organisms may have emerged as a kind of clock and gained separate, endogenous timekeeping as they evolved away from an autocatalytic cycle in the primordial soup. Research showing that metabolism influences endogenous clocks, as much as the other way around, lends support to this idea [e.g. 4].

An autocatalytic photosynthetic system may have been part of a primordial hypercycle that gave rise to life's metabolic complexity, for example, with different parts corresponding to morning, midday, evening, and night [10,11]. Daytime may have been a time for energy storage and synthesis of important precursor molecules. The evening could have been given to polymerization, repair from damage by UV light, and packaging for overnight storage. Nighttime may have been primarily a time to avoid dissolution, for example by proto-viruses, but could have also been an opportunity for primordial recombination. The morning may have been for repair from any overnight degradation and another opportunity for polymerization.

Over time these functions would have shifted within the cycle; for example, it seems likely that early on, most interesting chemistry would have happened by day. Indeed, the transition from daytime to other parts of the cycle may hold some secrets to life's origins; for example, energy storage to last through the night may have driven complex cell form. Packaging information overnight may have also been thermodynamically favorable compared to packaging complex structure, thus providing a driving force for the evolution of the central dogma. Life may have evolved multiple times in this context by short-circuiting or cheating this hypercycle, which may have existed until the great oxygenation event. Earliest life may have been phototrophic, but not necessarily so. Incorporating parts of the autocatalytic machinery may have allowed vesicular components to adopt an organoheterotrophic lifestyle, something like many modern protists.

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Phosphorylation in Urea-Rich Eutectic Solvents

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Introduction: Phosphate is an essential component of DNA, RNA, and a range of metabolic compounds throughout biochemistry. On a prebiotic Earth, phosphate may have been equally valuable, providing nascent prebiotic molecules robust aqueous solubility and relatively thermodyanimcally stable chemical bonds. Nevertheless, the participation of phosphate in the earliest stages of the origin of life has been questioned due to major issues regarding its geochemical availability and chemical reactivity. On a prebiotic Earth, phosphate would have strongly associated with divalent cations in solution (primarily magnesium, iron, and calcium) to form insoluble precipitates that could have prevented phosphate from being incorporated into developing biochemical systems. In addition, the phosphorylation of nucleosides, a dehydration reaction, is thermodynamically unfavorable in aqueous environments. Recent work has focused upon addressing these issues of phosphate availability and reactivity through the utilization of urea-catalyzed phosphorylation (Figure 1) in eutectic solvents [1,2] or in the presence of borate.[3]

Results and Discussion: We are exploring urea-catalyzed phosphorylation in eutectic solvents, including prebiotically plausible eutectic solvents that are rich in urea. In eutectics consisting of urea, ammonium formate, and water (UAFW) high degrees of phosphorylation are observed with ribonucleosides or glycerol when evaporatively heated in the presence of soluble phosphate salts. Additionally, in the presence of $MgSO_4$, water insoluble hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$) can be utilized as a phosphorylation source. Most recently, we have begun to explore additional eutectic solvents that were inspired by the UAFW eutectic system. Some of these solvents are showing significant improvements in phosphorylation of nucleosides, giving phosphorylation yields in excess of 80% under moderate heating.

These results demonstrate the ability of urea-rich eutectics to access urea-catalyzed phosphorylation in a liquid environment, and to mobilize previously sequestered phosphate for these reactions.[2] Overall, this work shows a prebiotic chemical path to phosphorylation of nucleosides that overcomes two of the major barriers to phosphorylation, helping support phosphate as a potential participant in the synthesis of biopolymers during the earliest stages of the origins of life.

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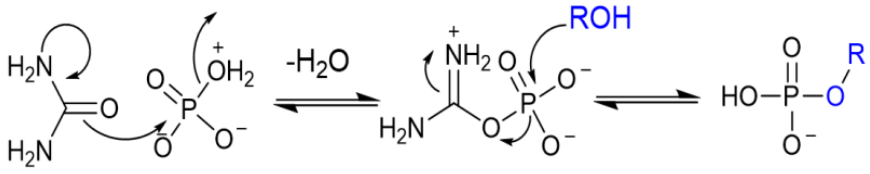

Figure 1 – Proposed mechanism for urea-catalyzed synthesis of phosphate esters. [4]

July 16-21, 2017 at UC San Diego, CA, USA

Chiral Selectivity as a Bridge to Homochirality

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Introduction: In abiotic reactions, equal mixtures of L- and D- amino acid enantiomers are produced unless conditions that favor one enantiomer over the other are present. Understanding how the transition from racemic, abiotic chemistry to homochiral polymers used in proteins occurred is fundamental to our understanding of the origins of life on Earth and the search for signs of life elsewhere, but this transition is still poorly understood. We have begun investigations into whether enantiopure amino acid pools are a necessary condition, or if the polymerization process itself can impart some added degree of stereoselectivity. More specifically, we are exploring the polymerization behavior of chiral amino acids to determine if they show a preference for homochiral or heterochiral polymerization. We are also determining the effects of different amino acid chiral ratios (L > D) to determine at what level of enantiomeric enrichment homochiral peptides become predominant. These data will allow us to evaluate the plausibility of homochiral polymers arising by known abiotic mechanisms.

Methods: We used the prebiotically plausible salt-induced peptide formation (SIPF) reaction [e.g., 1, 2, 3, and references therein] to study the polymerization behavior of a suite of amino acids, with racemic, scalemic, and enantiopure starting mixtures. Peptides were analyzed by ultra-performance liquid chromatography with quadrupole-time of flight mass spectrometry (LC-MS).

Results: Preliminary work demonstrates both chiral and sequence selectivity. Racemic mixtures of alanine and valine show a dipeptide distribution of AA = AV > VA >> VV. As shown in the left panel of figure 1, selectivity is more strongly observed in polymers formed by SIPF; similar experimental runs, using carbodiimide coupling agents do not show this selectivity. The favorability of AA over VV and the mixed dipeptides may be due to the steric differences between alanine and valine.

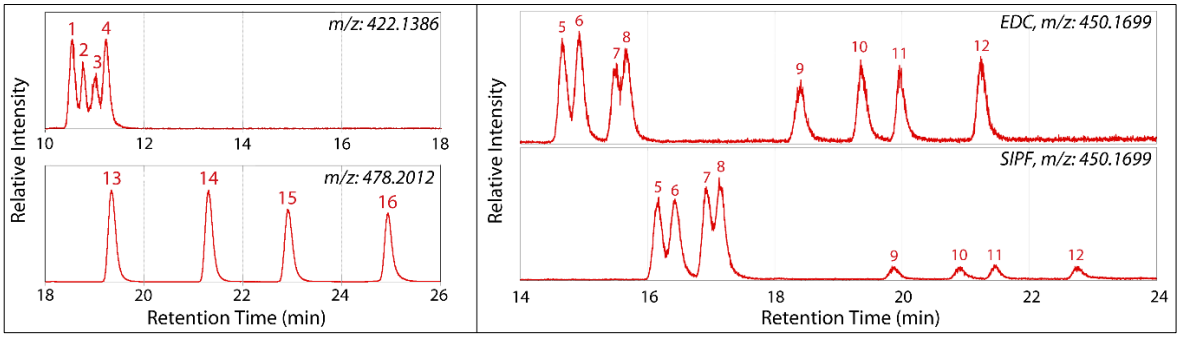

Figure 1. LC-MS extracted ion chromatograms ($M+H^+$) for OPA/NAC derivatives of dipeptides containing alanine and valine. Peak identifications are 1-A_DA_L, 2-A_LA_L, 3-A_LA_D, 4-A_DA_D (m/z=422.1386); 13- VLVL, 14-V_DV_D, 15-V_DV_L, 16-V_LV_D (m/z=478.2012); 5-A_LV_D, 6-A_DV_L,7-A_LV_L, 8-A_DV_D, 9- V_LA_L, 10-V_LA_D, 11-V_DA_D, 12-V_DA_L (m/z=450.1699). The right panel shows the strong preference for AV (peaks 5 – 8) over VA (peaks 9 – 12) in the SIPF reaction (bottom trace) compared with carbodiimide (EDC) coupling which shows no apparent sequence bias.

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A new method to verify of the triplet code based on the interaction of the dipeptide - homologous oligomeric nucleotides under the UV radiation

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In the field of the origin of life, one of the theory suggests that the fraction of organic compound on Earth is from exogenous deliveries via comts or meteorites. While the another theory proposal is that life meteiral formed just on the Earth. However, wherever this matter come from, it must be accompanied with ultraviolet light (UV) radiation[1]. The study of the photo stability of organic matters is an important task. There has been several reports on the destruction rate of amino acids or nucleic acid when irradiated with UV respectively. It's unkown whether there is the synergistic effect between the DNA and the amino acid, both of which are relative to the RNA.

There are many theories about the origin of the genetic code. The most popular theory is that certain amino acid was assigned to a certain triplet on the chain of RNA[2]. Reported methods to confirm genetic code theory focused directly on small molecules by building a reasonable model. They were usually based on the interaction between the amino acid and the corresponding genetic code or anticodon to support their hypothesis[3]. Whereas, RNA chain is transcribed from a DNA chain and the amino is dependent on the sequence of coresponding RNA to synthesis peptide chain. So it's reasonable to believe that there is a relationship between DNA chain and the peptide chain. In order to make clear of the conjecture above, this work designed a research mode based on the interaction between the homology dipeptide and the homology DNA under the UV radiation. Phenylalanine dipeptide (PP) and the single strand poly $(dA)_{20}$ (sspA), poly $(dT)_{20}$ (sspT) or double strand poly $(dA{:}dT)_{20}$ (dspAT) were slected as standard material. The preliminary results (figure 1) showed that when the sspA , sspT or dspAT was added to PP solution, the remain amount increased greatly especially by adding dspAT. It also demonstrated that PP solution adding sspA exhibited more tolerant to UV radiation than that adding sspT. This result corresponds to the fact that the genetic code of phenylalanine is uracil which is complimentary to adenine. Compared with reported method from the perspective of biosynthetic pathways using small molecule mode, this protocol in turn chose the DNA chain and dipeptide to prove the genetic code reflected by the synergistic effect between the oligonucleotide and dipeptide under the UV radiation. The proposed method showed a new insight to research the genetic code.

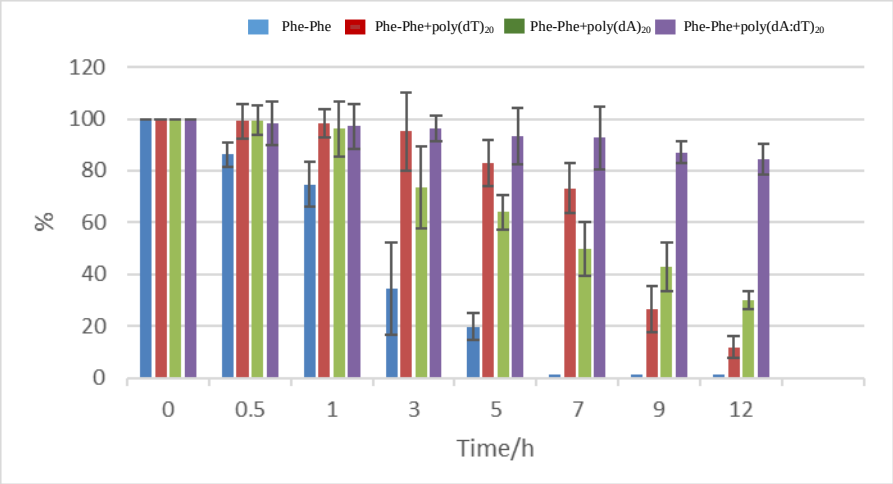

Figure 1. Rate of remaining compounds measured after the samples exposed to UV

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July 16-21, 2017 at UC San Diego, CA, USA

Electrochemistry of early Earth hydrothermal chimneys and simulations of possible prebiotic metabolic pathways

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We present the results of artificial seafloor hydrothermal chimney experiments; chimneys are self-organizing chemical garden precipitates generated from geochemical disequilibria and have been proposed as a possible environment for the origin of life on Earth and on other worlds [1]. Laboratory chimneys were produced using different hydrothermal injection simulants containing sodium sulfide doped with pyruvate, which were injected into a primitive Earth ocean simulant containing a solution of dissolved ferrous iron, nickel, and carbonate [2] (Figure 1). Early Earth anoxic conditions were maintained by continuously purging with argon in the chimney headspace. Electrochemical analysis was performed using custom-made electrodes placed across the chimney wall to analyze the bulk property of surface charge potential at the interface of the chimney / ocean / hydrothermal fluid. We performed *in-situ* electrical properties characterization of the chimney using electrochemical impedance spectroscopy (EIS) and found that when pyruvate was present in the hydrothermal fluid, the electrochemical activity over the entire chimney/ocean chemical system was increased. We postulate that in prebiotic hydrothermal systems, pyruvate or other simple organic acids could serve as key intermediaries to possibly kick-starting metabolic pathways in chimney membranes containing iron-nickel-sulfides as well as other catalytic minerals like iron oxyhydroxides. Further work is needed to investigate whether these chimneys can promote the production of more complex organic products that would be relevant for the emergence of life.

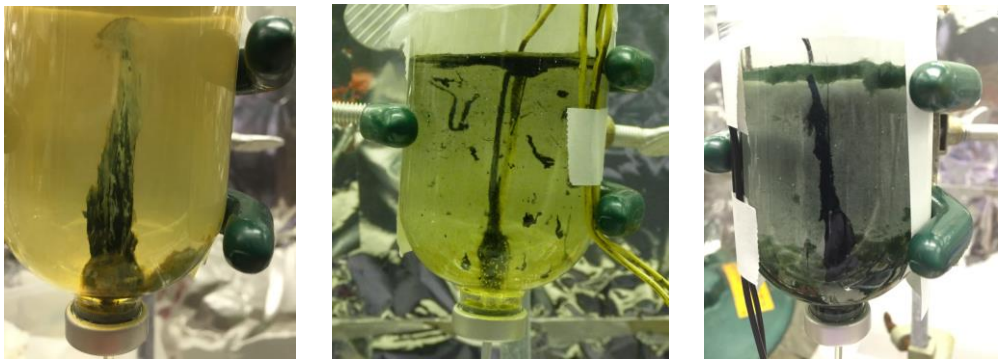

Figure 1: Artificial hydrothermal chimneys

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Mixtures of Hygroscopic Salts and Urea as Prebiotic Media for the Condensation of Amino Acids

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In origin-of-life research, the 'compartmentation problem' entails how the first living systems were able to sequester or protect themselves from their environment and control the volume and moisture content of their enclosures [1]. Here, we describe a model in which mixtures of simple salts and urea are able to absorb limited amounts water from the atmosphere and serve as media to host reactions of prospective importance to the origin of life on Earth. We have quantified the extent of hydration of varous mixtures of salts to form highly saline aqueous solutions as a function of temperature, relative humidity, and composition of the mixture (e.g., identity of the cations and anions present, as well as the concentration of urea). We also present preliminary studies in which a selection of these mixtures are used as alternative environments for the oligomerization of amino acids, which we evaluate by measuring the kinetics of hydrolysis and condensation reactions.

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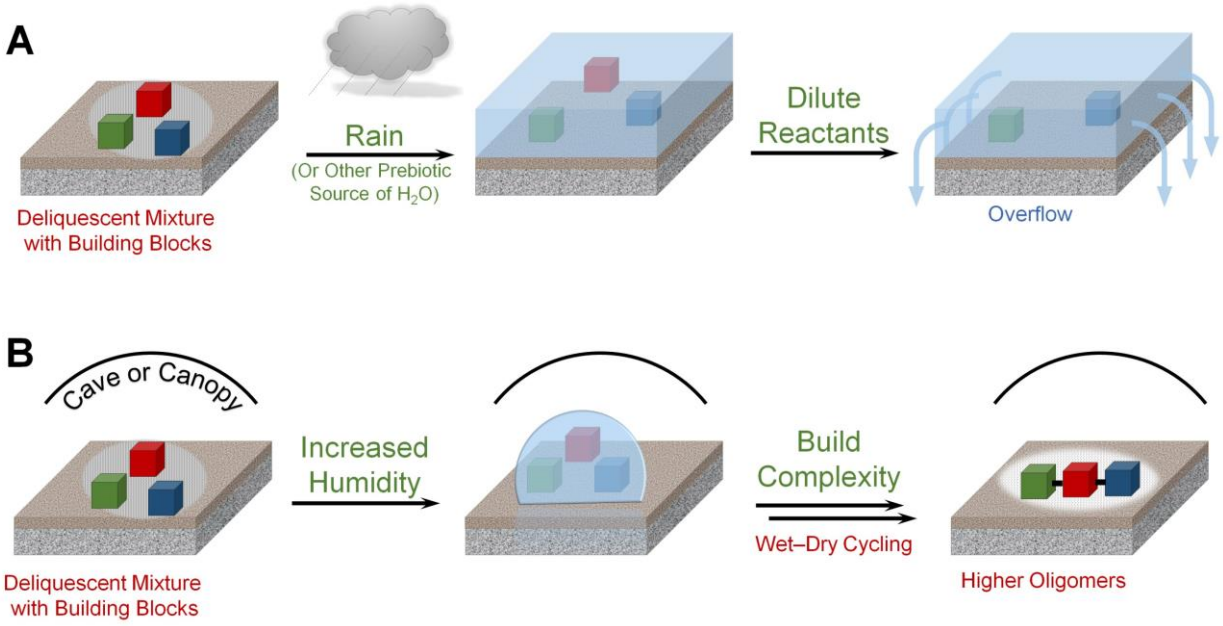

Figure 1 – Typical prebiotic sources of water, such as rain or tides, pose the risk of 'overwatering' a chemical system and limiting reactions such as oligomerization (A). In the proposed system (B) deliquescent mixtures regulate the volume of water in the system and prevent dilution.

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Host Phylogeny and Viral Genome Size suggest that Viruses may be Antique, but not Primitive

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It has been suggested that RNA viruses and viroids are relicts from an ancient RNA/protein World because of their small-genome sizes and their manifold replication strategies[1]. At the other extreme are the giant DNA viruses which have been grouped by some authors into a fourth domain of life[2]. However, the chemical nature of genomes and other biological data like host-cell dependence for replication reveal another explanation for the early evolution of viruses. In the present work, we compared all biological data of viruses such as chemical nature, genome size, segmentation, and host type. We retrieved, organized, compared, and analyzed all biological data of viruses from GenBank, ICTV, and ViralZone platforms up to December, 2016. We found that viruses with larger and smaller genomes mainly infect eukaryotes. DNA viruses have a more genome-size diversity in all three domains of life. RNA-virus genomes can be larger than ssDNA genomes. Some families of RNA viruses can infect phylogenetically-distant hosts. Retroviruses only infect plants and vertebrates (some prokaryotes have retrotransposons, but these are not wrapped in a protein coat). The 96% of viral RNA families infect eukaryotes. The only prokaryotes which are infected by RNA viruses belong to the Proteobacteria which it is phylogenetically-related to eukaryotes. Moreover, most of the segmented and the most of largest genomes (on average) belong to RNA viruses that infect either plants or animals. The chemical nature and sizes of the viral genomes do not reveal any obvious correlation with the phylogenetic history of their hosts. Accordingly, it is somewhat difficult to reconcile the proposal of the putative pre-DNA antiquity of RNA viruses and viroids, with their extraordinary diversity in plant hosts and their apparent absence among the Archaea. This suggests that viruses could be antique, but not primitive.

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July 16-21, 2017 at UC San Diego, CA, USA

Alkaline hydrothermal vents as electrochemical reactors driving an autotrophic origin of life

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Introduction: Hadean alkaline hydrothermal vents have been proposed as electrochemical reactors driving an autotrophic origin of life [1, 2]. Theoretical thermodynamics show that the abiotic synthesis of biomass from H_2 and CO_2 is indeed favoured under these conditions [3]. But CO_2 reduction is kinetically extremely tardy, casting doubt on the feasibility of this mechanism. Given that almost all extant life grows by hydrogenating CO_2, this question is of central importance to the autotrophic origins hypothesis. We are examining the possibility that geochemical proton gradients across inorganic Fe(Ni)S barriers, analogous to autotrophic cells, could have driven CO_2 reduction at the origin of life in alkaline hydrothermal vents.

Here we report the successful reduction of CO_2 to formaldehyde (CH_2O) under simulated alkaline hydrothermal conditions without the aid of organic catalysts, by tapping the free energy of a pH gradient across Fe(Ni)S barriers. We confirm that CH_2O can be transformed under these conditions into biotically relevant sugars via the formose reaction, discovered by Butlerow in 1861. Acetyl phosphate can be synthesised from inorganic phosphate and thioacetic acid, and will phosphorylate organic molecules such as sugars and amino acids, making it a plausible primordial energy currency equivalent to ATP [4]. Following Mellersh & Smith [5], we show that acetyl phosphate can redirect the formose reaction towards biotically relevant sugars such as ribose at high yield. Overall, our results show that alkaline hydrothermal conditions could drive the synthesis of biologically relevant sugars such as ribose from H_2 and CO_2.

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Organic Matter in Extraterrestrial Water-Bearing Salt Crystals

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Introduction: Direct samples of early Solar System fluids are present in two thermally-metamorphosed ordinary chondrite regolith breccias (Monahans (1998) [H5] and Zag [H3-6]), which were found to contain brine-bearing halite (NaCl) crystals that have been added to the regolith of an S-type asteroid following asteroidal metamorphism [1, 2]. The brine-bearing halite grains were proposed to be formed on an icy C-type asteroids (possibly Ceres), and transferred to an S-type asteroid via cryovolcanic event(s) [3]. A unique aspect of these halites is that they contain abundant organic rich solid inclusions hosted within the halites alongside the water inclusions.

Methods: We analyzed in detail the compositions of the organic solids and the amino acid content of the halite crystals with two-step laser desorption/laser ionization mass spectrometry (L^2MS), Confocal Raman Imaging Spectroscopy (CRIS), C,N,O-X-ray absorption near edge structure (XANES), nanoscale secondary ion mass spectrometry (NanoSIMS), and ultra-performance liquid chromatography fluorescence detection and quadrupole time of flight hybrid mass spectrometry (UPLC-FD/QToF-MS).

Results and Discussion: The L^2MS results show signatures of low-mass polyaromatic hydrocarbons (PAHs) indicated by sequences of peaks separated by 14 atomic mass units (amu) due to successive addition of methylene (CH_2) groups to the PAH skeletons [4]. Raman spectra of the µm-sized solid inclusions of the halites indicate the presence of abundant and highly variable organic matter that include a mixture of short-chain aliphatic compounds and macromolecular carbon. C-XANES analysis identified C-rich areas with peaks at 285.0 eV (aromatic C=C) and 286.6 eV (vinyl-keto C=O). However, there is no 1s-σ* exciton peak (291.7 eV) that is indicative of the development of graphene structure [5], which suggests the organics were synthesized cold. NanoSIMS analyses show C-rich and N-rich areas that exhibit similar isotopic values with that of the IOM in the unweathered CR chondrites and less metamorphosed meteorites [6], and are moderately enriched in ^{15}N ($\delta^{15}N$ = 106.1–164.5‰). The total amino acid distribution and abundance of the Zag matrix (~1,940 parts per billion [ppb]) is comparable to other ordinary chondrites (60–3,330 ppb) [7, 8]. While the Zag matrix is γ-ABA and EACA-deficient, the halite is shown to exhibit an opposite trend and is almost depleted in amino acids. The striking difference in the amino acid contents between the halite and matrix indicates their separate synthetic origins.

Conclusion: Abundant, primitive, and highly-diverse ^{15}N-rich organic compounds were detected in brine-water bearing halite crystals that were synthesized on a cryovolcanically-active asteroid. Our study suggests that the asteroidal parent body where the halite precipitated, potentially Ceres, is a host to abundance large variety organic precursors. Insoluble organic matter and amino acids can be synthesized from similar organic precusors under hydrous conditions [9].We envision that similar organic synthetic processes could have occurred on Ceres that synthesized organic solids as well as biologically relevant molecules.

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Physical autocatalysis triggered by a transition metal-catalyzed reaction.

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Introduction: Assuming general consensus that a living organism must possess genetic mechanism, metabolic machinery and a cell membrane,[1] revealing simple structures that meet this criteria will help to understand the orgin of life. Amphiphilic molecules, bearing both hydrophilic and hydrophobic components (Figure 1), represent key intermediates in the origin of life and chemical evolution. They can self-assemble into ordered structures, such as micelles or lipid bilayers, due to their amphiphilic nature. All, micelles, bilayers and vesicles represent primary models for protocell membrane. Moreover modification of these protocell membranes, such in the fatty acylation of peptides and proteins is associated with metabolic regulation processes. Uncovering new autocatalytic pathways, as well as understanding their aggregate dynamics and interaction with other macromolecules, has recently attracted the attention of the scientific community.

Summary: It has been proposed that metals have played a crucial role in the oring of life.[2] We highlight here the importance of merging transition metal-catalyzed reactions and new modes of autoinduction[3] or physical autocatalysis,[4] using simple non-activated molecules, such as alkenes. Our goal is also to uncover new pathways to incorporate important biomolecules (such as sugars, amino acids or small peptides) into these amphiphilic structures, with special interest in autoinductive mechanisms, where the product of the reaction will self-assemble (Figure 1), accelerating the rate of the reaction (ie. by means of the formation of complex dynamic systems, encapsulation or phase transfer catalysis).

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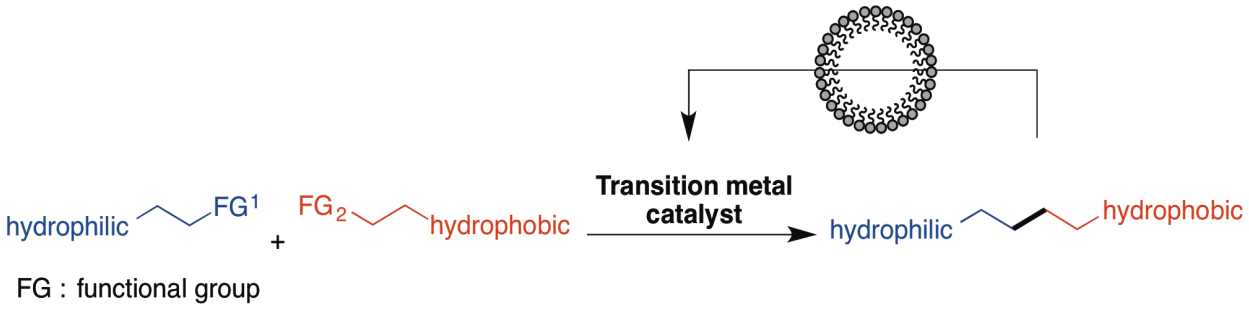

Figure 1 – Schematic summary of the transition metal-catalyzed autocatalytic reaction.

July 16-21, 2017 at UC San Diego, CA, USA

Educating about Origins of Life Research: The Power of Collaborations

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Introduction: The Center for Chemical Evolution is uniquely positioned to pursue high risk, high reward research relating to the Origins of Life field, including in its broader impacts initiatives. There are three major barriers to learning about chemistry and science: they are thought to be too complex, boring or irrelevant, or threatening to personal beliefs. Through partnerships with communicators using a variety of media, the CCE has explored several paths to present scientific concepts and overcome the aforementioned barriers. Over the past 5 years, the CCE has collaborated with Stated Clearly to create short, jargon-free animations that illustrate processes as they are taught. Several million informal and formal learners have been exposed to Origins of Life research through the videos, presented in both English and Spanish. Further efforts are underway to create teaching tools that correspond with education standards so that the animations may be easily incorporated into curriculum materials. Here we share what guides animation development and assessment strategy.

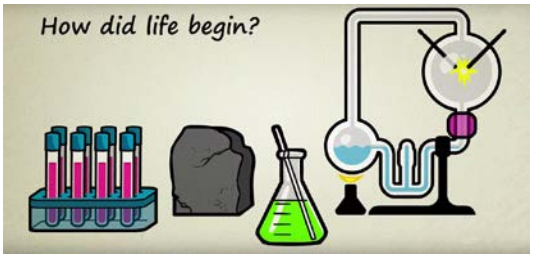

Figure 1 – Image from the animation, "Can Science Explain the Origin of Life?", a collaboration between Stated Clearly and the Center for Chemical Evolution. This animation has been viewed nearly 500,000 times on YouTube.

July 16-21, 2017 at UC San Diego, CA, USA

Enantiomer Excesses in Carbonaceous Meteorites

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r

Introduction: Carbonaceous meteorites are among the oldest objects in the solar system. They provide evidence of organic compounds that were present in the Solar System before the origin of life. Amino acids, purines, pyrimidines and short monocarboxylic acids are some of the classes of prebiotically relevant compounds that have been detected in a variety of carbonaceous meteorites. While the majority of indigenous meteoritic compounds are racemic, i.e., their D/L enantiomer ratios are 50:50 some of the more unusual amino acids contain slightly more of one enantiomer - usually the L. In addition, initial analyses of some meteoritic sugar derivatives (sugar acids) revealed significant enantiomer excesses of the D enantiomers. A question of relevance from such studies is: did extraterrestrial sources aid in the beginning of life's homochirality? This presentation will include updated results of recent analyses of enantiomer ratios of meteoritic compounds as well attempts at laboratory re-creation of such excesses. If the forces that acted on organic compounds (and/or their precursors) in the early Solar System are common, then specific laboratory experiments may indicate whether enantiomer excesses in organic compounds are available for the origin of life in a multitude of planetary systems.

July 16-21, 2017 at UC San Diego, CA, USA

Steering Complex Reaction Networks with Minerals

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Introduction: Modern chemistry approaches to the Origin of Life are typically targeted to exploring the constrained synthesis of prebiotically plausible specific molecules or reaction pathways, or to produce biomolecules. Uncontrolled multicomponent condensation reactions of simple building blocks and the exploration of molecular networks are typically avoided due to the expectation of runaway combinatorial explosion, producing an analytically-intractable, undifferentiated, mess.[1,2] However, these combinatorial explosions can be tamed, and perhaps even controlled, by small changes to the reaction environment – i.e. by the addition of different minerals.

Our recent work has shown that environmental changes (salts, minerals, mixing histories) can programme the condensation of the same amino acids to produce consistently different compound mixtures, with different structural and functional properties.[3] Furthermore, we demonstrated for the first time that simple minerals can program the differentiation of distinct functional ensembles of different molecules from a classic primordial soup model whereby the simple precursor chemicals exhibited to spark discharge conditions.[4] This work therefore shows that the untargeted mixture first approach allows the formation of networks of reactions that generate of diversity from fixed sets of starting materials, and shows that differentiation of product mixtures can occur in the wider environment without the need of biological machinery.

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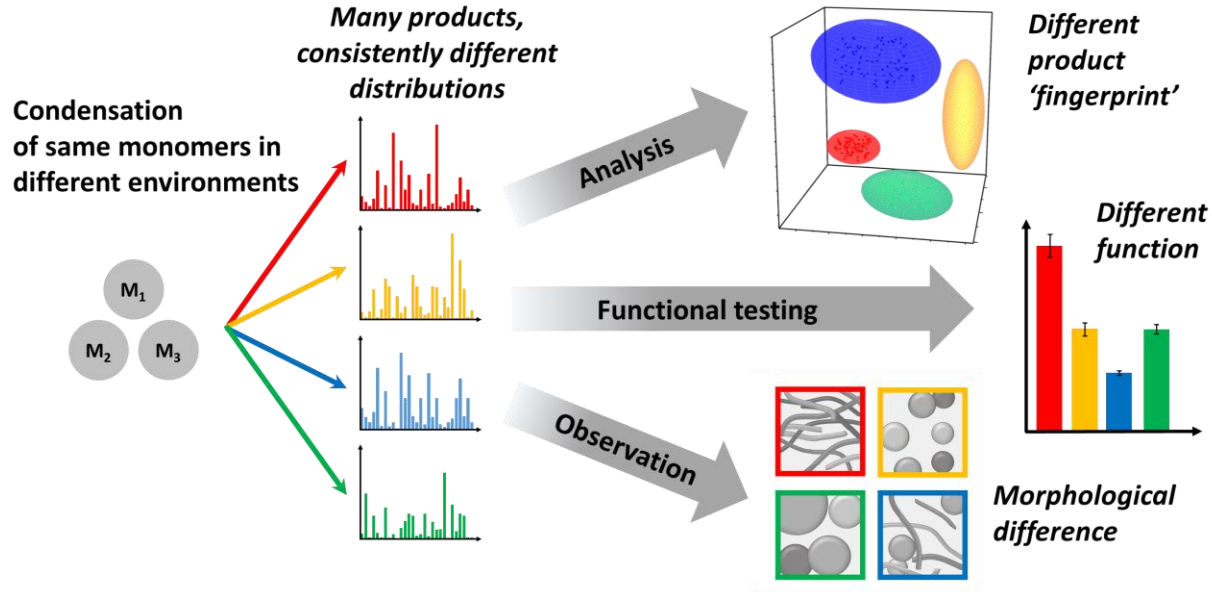

Figure 1 – *Uncontrolled condensation reactions make a mess, but can be steered:* Reactions where polyfunctional building blocks yield combinatorial explosions can be steered by different environmental conditions to give different product distributions with consistently different structural and functional properties.

July 16-21, 2017 at UC San Diego, CA, USA

Comets and Astrobiology, (re)assessment for comet 67P after ROSETTA

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Comets are commonly regarded as objects with a prime astrobiological importance. They are reservoirs of a large amount of material considered as necessary for the origin of life: water and organic molecules. While the measurement of the D/H ratio in the water of comet 67P established in the early stages of the mission that comets such as 67P are probably not a significant source of water on Earth[1], the nature and amount of the volatile organic content of comet 67P is progressively revealed through the complementary measurements of instrument such as ROSINA, COSAC, PTOLEMY[2-4]. The detection of glycine and phosphorous atoms in the atmosphere of the comet have demonstrated the presence of so called "prebiotic" ingredients[5]. However, it takes certainly much more than this to feed the chemical evolution toward the origin of life on a planet.

On the other hand, the COSIMA instrument, analysing the composition of dust particles ejected from the nucleus, has shown that the refractory organic component of those aggregates is found as a macromolecular phase, which bears some similarities with Insoluble Organic Matter detected in carbonaceous chondrites[6]. This organic phase would constitute about half of the mass of the dust particles, hence one of the main form of carbon in the comet.

The form in which carbon has been delivered to the early Earth, and implications for the origin of life, will be discussed with regard to this new inventory of organic matter detected by Rosetta instruments in comet 67P.

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July 16-21, 2017 at UC San Diego, CA, USA

Stability of the D-Ribose-Na^+Montmorillonite and DL-Glyceraldehyde-Na^+Montmorillonite Systems in Aqueous Suspension Under Gamma Radiation Fields at pH 7 and 92°C: Implications in Chemical Evolution

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In chemical evolution, the stability of bio-organic compounds in the surrounding geological environment is as important as their syntheses, especially in the presence of an external energy source (e.g. ionizing radiation, thermal energy, etc.). Therefore, there must be a balance between the synthesis and the decomposition of these molecules to have them for other prebiotic processes[1]. Aldoses, in addition to their biochemical interest as energetic molecules or as structural molecules in biological systems, are also of paramount importance in the context of chemical evolution. The synthesis and preservation of aldoses under prebiotic conditions is a fundamental step for the abiotic formation of the nucleotides that make up the nucleic acids (e.g. RNA where the ribose is the structural aldose)[2]. A more plausible geological scenario should involve the participation of a multiphase system, formed by the presence solids/liquids or liquid/ gases interphases[3, 4]. Several solid surfaces may have been relevant in this context: sulfides, carbonates, and clays. In this work, we highlight the possible role of clay minerals due to their physicochemical properties, their broad geological distribution. The primary objective of this work is focused in studying the stability of two aldoses adsorbed in a clay mineral: D-Ribose-Na^+Montmorillonite and DL-Gliceraldehide-Na^+Montmorillonite suspensions at pH 7 and 92°C under a high radiation field. To this end, the radiolysis of both systems was carried out by exposing them to a different irradiation dose and ratios aldose-clay. The analysis of these systems was performed by UV spectroscopy and liquid chromatography (HPLC) and HPLC-coupled to a mass spectroscopy.

Our results indicate that the aldose-clay systems are relatively stable under irradiation and the radiation-induced or thermal-induced reactions in these systems yield compounds of pre-biological importance.

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Acknowledgments

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Metabolically Coupled Replicator Systems: Overview of an RNA-world model concept of prebiotic evolution on mineral surfaces

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Metabolically Coupled Replicator Systems (MCRS) are a family of models implementing a simple, physico-chemically and ecologically feasible scenario for the first steps of chemical evolution towards life. Evolution in an abiotically produced RNA-population sets in as soon as any one of the RNA molecules become autocatalytic by engaging in template directed self-replication from activated monomers, and starts increasing exponentially. Competition for the finite external supply of monomers ignites selection favouring RNA molecules with catalytic activity helping self-replication by any possible means. One way of providing such autocatalytic help is to become a replicase ribozyme. An additional way is through increasing monomer supply by contributing to monomer synthesis from external resources, i.e., by evolving metabolic enzyme activity. Retroevolution may build up an increasingly autotrophic, cooperating community of metabolic ribozymes running an increasingly complicated and ever more efficient metabolism.

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Magnesium Tolerance and Preferential Selectivity of A Lipid in Binary Lipid Systems: An Evolutionary Approach to Modern Membranes

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Introduction: Early compartmentalization of prebiotic molecules to form protocell membranes is considered an important process for the emergence of life. These protocell membranes are assumed to be composed of single chain amphiphiles (SCAs) due to their prebiotic availability [1]. However, SCA membranes are known to be unstable in the presence of dissolved divalent cations [2, 3], which would have been prevalent on young Earth. Eventually, membranes evolved to more robust phospholipid membranes. Here, we investigated the transition of SCAs to mixed SCA-phospholipid membranes and to phospholipid membranes in the presence of Mg^{2+}. Mg-tolerance of vesicles composed of a SCA, oleic acid (OA) and a phospholipid, palmitoyl-2-oleoylphosphatidylcholine (POPC) was examined. The concentration of magnesium needed to disprupt ~ 100 % of the intact bilayers was defined as the fatal magnesium concentration ($[Mg^{2+}]_{fatal}$). We found that Mg^{2+} acts as an environmental selection pressure for membrane evolution from SCAs to pure phospholipid membranes and the mechansims were identified.

Methods: $[Mg^{2+}]_{fatal}$ for pure OA, pure POPC, and mixed OA-POPC at various stoichiometric ratios (10:1, 5:1, 3:1, and 1:1) in the prescence of Mg^{2+} was determined by different analytical methods namely; fluorescence assay, dynamic light scattering, zeta potential (ζ) measurements, HPLC, and optical microscopy. Quantitative estimation of OA and POPC in the vesicle was achieved by HPLC after the removal of Mg^{2+}-lipid aggregates by filtration through 0.22 μm pore filters.

Results and Discussion: Interestingly, the $[Mg^{2+}]_{fatal}$ increased dramatically with an increase in the POPC content of the vesicle. For instance, $[Mg^{2+}]_{fatal}$ was 3-5 mM for pure OA, ~ 22.5 mM for OA-POPC (10:1), ~ 30 mM for OA-POPC (5:1), and > 40 mM for OA-POPC (1:1) and pure POPC, at 2 mM total lipid concentration. Increasing POPC (zwitterionic) content decreased the relative negative charge density of the vesicles as indicated by the zeta potential measurements, therefore more Mg^{2+} was required to destabilize the vesicles. Further, the relative distribution of OA/POPC in vesicles in the presence of magnesium had significantly decreased in comparison to the original vesicles. Thus, it could be inferred that magnesium preferentially binds to and abstracts OA from the mixed OA-POPC vesicles which results in lower [OA]/[POPC] ratio as compared to the starting bulk ratio. This is the first report on the evolution of fatty acid membranes towards phospholipid-enriched membranes driven by a divalent ion. Increased robustness and greater immunity of SCA-phospholipid vesicles against magnesium may hold implications in assisting Mg^{2+}-poromted processes such as RNA polymerization.

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July 16-21, 2017 at UC San Diego, CA, USA

Oldest Convincing Evidence for Life on Earth Discovered in Archaean Subaerial Hot Springs: Implications for an Origin of Life on Land

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Introduction: New discoveries in the Dresser Formation in the Pilbara of Western Australia reveal that the surrounding North Pole Dome area is not a marine coastline as previously thought but is an ancient volcanic water-filled caldera ringed with hot springs. These rocks have been dated to 3.48Ga making this the oldest pristine piece of the Earth's Paleoarchean crust. Adding to the recently published discovery of Dresser Formation geyserite [1] bedded with well preserved stromatolites (rock textures preserving evidence of microbial activity) the morphologies at the newly discovered "Southern Locality" represent a diverse range of microbial communities thriving within subaerial fresh water hot springs, streams and pools. Preservation visible in the figure below includes: microbial communities within flowing hot water rich in silica; microbial mats ripped up and folded at a shoreline by a storm event; and domical stromatolites buried and preserved by a volcanic ash deposit. Such a robust presence of life on land in the earliest fossil record suggests that life may have originated in or around such hot spring pools. A consensus is building that the chemistry of life favors its origin on land, not in a deep or shallow marine environment [2]. These discoveries add to the weight of evidence in support of a terrestrial origin of life, in which in-falling organic compounds can both be concentrated in pools for reactions to occur and also subject to nonenzymatic polymerization through wet-dry cycling from the hydrothermal system. Polymer-encapsulating protocells cycling through three phases provide a kinetic trap mechanism [3,4] for the chemical evolution of a Woese progenote [5], its evolution into cellular life and a downhill adaptation pathway of early life to the shallow marine setting. The diversity of morphologies observed in Southern Locality rocks suggest that hot springs were dynamic and powerful drivers for life to first arise and then adapt to niches on land and in the sea.

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Figure 1 – Left, stromatolite laminates (red) bedded within barite-length 6cm; Center, edgewise conglomerates produced by rmicrobial mat ripped up by a storm event and; Right,domical stromatolites preserved in volcanic ash.

Hydrogels: Lets thicken the Prebiotic soup

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Introduction: The commonality between gels and cells provides compelling grounds for exploring the relevance of gels in the origin of life. Herein, we draw parallels between the behavior of cytoplasm in contemporary cells and hydrogels. There is need for the exploration of hydrogels in particular, keeping in mind the geological relevance of inorganic species to origins of life[1]. One of the fundamental problems in prebiotic chemistry is the control of water activity in aqueous media (in peptide bond formation, phosphorylation, nucleotide polymerization), which is, thermodynamically, an uphill task.

Our investigation into the importance of inorganic hydrogels began with study of D-ribose. D-ribose ($C_5H_{10}O_5$) is highly important because it is an integral part of DNA and RNA. The half-life of this molecule presents a considerable challenge in studying its role in origins of life. At pH 9 and 60°C, its half-life is about 50 h; in physiological conditions, at pH 7 and 37°C, it would be around 500 h if one extrapolates from the data of [2]. In solution, the D-ribose is in equilibrium with four isomers : α- and β-pyranose (β is the dominant isomer, 83%), and α- and β-furanose.

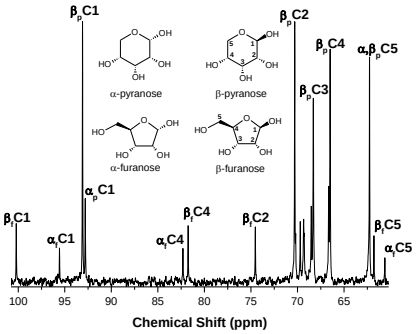

Figure 1 – 13C NMR showing the isomeric forms of ribose in solution.

Here, we present the homogenisation of ribose into hydrogel and the analysis of its diffusion properties in addition to its chemical and thermal stability. About 90% of the mobility of ribose is conserved in the hydrogel environment, which is similar to water, thus analogous to a cell environment. 1H NMR (DOSY sequence) was used for characterising the mobility of ribose in the gel. This environment also has effects on isomerization of D-ribose. We have not observed an evolution in the pyronose/furanose ratio, but have observed a progression of β-forms and a decrease of α-forms. *In situ* NMR and Raman spectroscopy have been used in order to evaluate the thermal behavior of ribose in the gel and in hydrothermal conditions on gels. Preliminary studies show a better thermal stability of the D-sugar in the gel. Hydrogels provide an environment and dynamics that are distinct from those in solution but nevertheless retain fluidity at a slower pace within a confined spatial arrangement. Such hydrogel matrices could also facilitate specific chemical interactions that appear to be necessary for prebiotic chemistry. Investigations on such properties are in progress [3].

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July 16-21, 2017 at UC San Diego, CA, USA

An Origin of Life in Cycling Hot Spring Pools: Emerging Evidence from Chemistry, Geology and Computational Studies

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Introduction: Evidence consistent with an origin of life in a hot spring setting has been accumulating over the past decade. Laboratory and field studies demonstrated that RNA-like polymers and peptides can be synthesized nonenzymatically from their monomers by cycles of hydration and dehydration [1]. Cycling conditions simulate fluctuating fresh water hot spring pools in hydrothermal fields associated with volcanic land masses. Recent investigations of the 3.48Ga Dresser Formation in Western Australia discovered geyserite bedded with well preserved stromatolites [2], suggesting that some of the earliest evidence for life indicates thriving microbial populations in fresh water hot springs on land rather than salty marine conditions. Two independent computational studies used thermodynamic and kinetic analysis to confirm the feasibility that phosphodiester bonds can form spontaneously, using the free energy made available by evaporation that concentrates monomers into thin films on mineral surfaces [3]. Polymers accumulate in a kinetic trap because the rate of ester or peptide bond formation is significantly faster than the rate of hydrolysis. Additional laboratory observations show that such polymers are encapsulated in lipid vesicles during the cycles, forming protocells that can be subjected to combinatorial selection. These results (figure 1) demonstrate the value of interdisciplinary approaches that link chemistry, geology and computational modeling in advancing our understanding of the origin of life as it may have occurred in a cycling hot spring setting on land [4].

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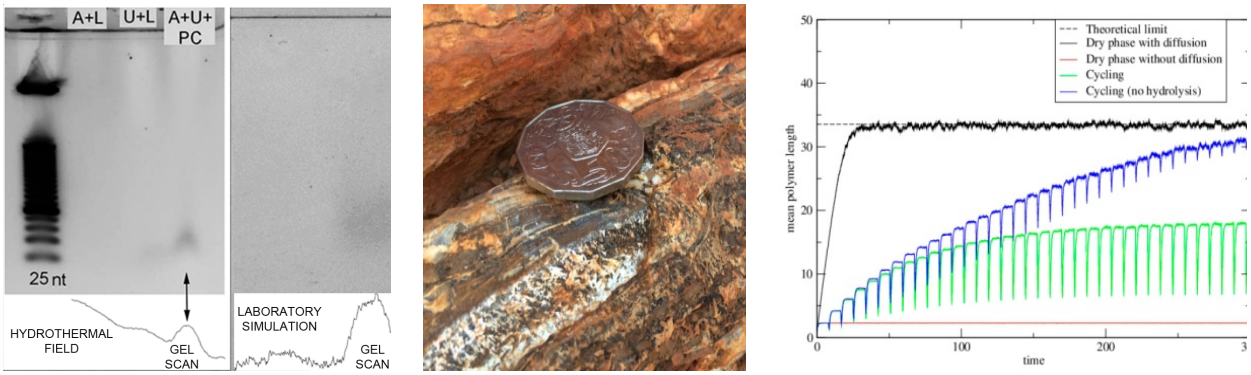

Figure 1 – Left, RNA-like polymers synthesized in a fumarole vent at Bumpass Hell, California and reproduced in the lab through hydration-dehydration cycles in the presence of POPC as an organizing matrix [1]; Center, branching stromatolite (white band) preserved with geyserite in the 3.48Ga Dresser Formation in Western Australia [2] and; Right, computational modeling of kinetic trap where polymer length grows over time through wet-dry cycling with hydrolysis and influx of monomers [3].

Exploring Mars for Evidence of Habitable Environments and Life

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The climate of Mars has been more similar to Earth's climate than to that of any other planet in our Solar System. Still, Mars represents a different example of how planetary environments and processes might affect the presence of life. For example, although Mars also differentiated to form a core, mantle and crust, it evolved mostly if not completely without plate tectonics and it lost most of its early atmosphere. The Martian crust has been more stable than Earth's crust and so it has probably preserved a more complete record of its early history.

Orbital observations revealed that near-surface water was once pervasive. Orbiters acquired evidence of ancient diverse aqueous deposits: layered phyllosilicates, phyllosilicates in intracrater fans, evaporites, deep phyllosilicates, carbonates, intracrater clay-sulfate deposits, Meridiani-type layered deposits, valles-type layered deposits, hydrated silica-bearing deposits, and gypsum plains. These features indicate that early climates were wetter and perhaps also somewhat warmer. The denser atmosphere that sustained liquid water at the surface also provided protection from radiation.

Ancient climates might have favored habitable environments at least in some localities, but since then the Martian surface has been markedly less favorable for life. Dry and oxidizing conditions, together with typically low rates of sedimentation, were not conducive to the preservation of evidence about ancient environments and any life. Candidate sites must be characterized for their potential to preserve evidence of past conditions. Then rovers should explore the most promising sites.

The Mars Exploration Rover (MER) Opportunity revealed sediments that formed in ancient saline lakes whose waters were stirred by ancient winds that also sculptured their salt deposits into sand dunes. Opportunity subsequently explored even older deposits on a crater rim. MER Spirit found evidence that thermal waters, heated perhaps by volcanism or impacts, altered rocks to create sulfate salts and siliceous sinters.

The main objective of the Mars Science Laboratory (MSL) Curiosity rover has been to determine the extent to which Gale crater hosted environments capable of supporting microbial life. The rover has already found stream gravels and sediments that were deposited in an ancient lake. The rover is now traversing to Mt. Sharp, a 5 km-high mound that exhibits layered sedimentary rocks with diverse minerals. These include sulfates and phyllosilicates that formed in the presence of liquid water. This rock sequence was deposited over an extended time period in diverse potentially habitable aqueous environments. Curiosity is poised to characterize a a well-preserved rock record of hundreds of millions of years of habitable environments and profound climate change.

An early hydrological cycle apparently sustained precipitation, streams and lakes. Liquid water participated in rock-weathering reactions, including iron and sulfur oxidation. Volcanism, impacts, groundwater and ice interacted at least locally. Redox chemical energy from volcanism, hydrothermal activity and weathering of crustal materials would have been available for any life. Thus conditions on early Mars could have supported any life, at least locally.

July 16-21, 2017 at UC San Diego, CA, USA

In Situ Synthesis of Lipid Membranes

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Introduction: We have a strong interest in applying covalent coupling reactions to the formation and modification of lipid membranes. We have utilized chemoselective reactions, such as copper-catalyzed triazole formation or the native chemical ligation, to drive the *de novo* synthesis of phospholipid membranes. To interface synthetic membranes with proteins, we have shown that in situ lipid synthesis enables spontaneous incorporation of integral membrane protein. Living organisms carry out the *de novo* synthesis and subsequent remodeling of phospholipid membranes. The development of comparatively dynamic artificial lipid membranes will require simple methods to mimic how native phospholipid membranes are synthesized and remodeled. Using reversible coupling reactions, we have been able to sequentially form and remodel artificial lipid membranes. Interestingly, *in situ* remodeling of phospholipids is capable of controlling micrometer scale changes in vesicle spatial organization, composition and morphology. These studies could shed light and provide important models for the prebiotic emergence of phospholipid based membranes.

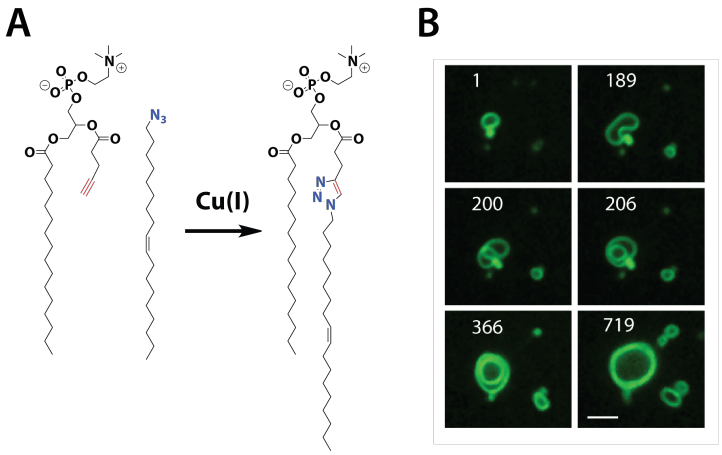

Figure 1 – A) Copper catalyzed azide-alkyne cycloaddition leads to the synthesis of a membrane forming phospholipid from non-membrane forming single-chain precursors. B) Continual phospholipid synthesis can be achieved by utilizing an oligotriazole autocatalyst. The constant production of phospholipids leads to vesicle growth. Numbers indicate elapsed time, in minutes, from start of imaging. Scale bar, 3 microns.

July 16-21, 2017 at UC San Diego, CA, USA

Status of the OSIRIS-REx Sample Return Mission

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Origins, **S**pectral **I**nterpretation, **R**esource **I**dentification, and **S**ecurity–**R**egolith **Ex**plorer (OSIRIS-REx) asteroid sample return mission is the third mission in the New Frontiers program. The spacecraft departed for near-Earth asteroid (101955) Bennu on an Atlas V 411 launch vehicle September 8, 2016 to return samples from near-Earth asteroid Bennu. The spacecraft is on an outbound-cruise trajectory with an Earth-gravity assit in September 2017 which will enable a rendezvous with Bennu in August 2018 (Figure 1). The science instruments on the spacecraft will survey Bennu to measure its physical, geological, and chemical properties, and the team will use these data to select a site on the surface to collect at least 60 g (and as much as 2000 g) of regolith from this primitive object. The team will also analyze the remote-sensing data to perform a detailed study of the sample site for context, assess Bennu's resource potential, refine estimates of its impact probability with Earth, and provide ground-truth data for the extensive astronomical data set collected on this asteroid. The spacecraft will leave Bennu in 2021 and return the sample to the Utah Test and Training Range (UTTR) on September 24, 2023 for global study. Unlike meteorites, the sample will come from a known, well-characterized source and will be collected and transported to Earth to keep it pristine from terrestrial contamination.

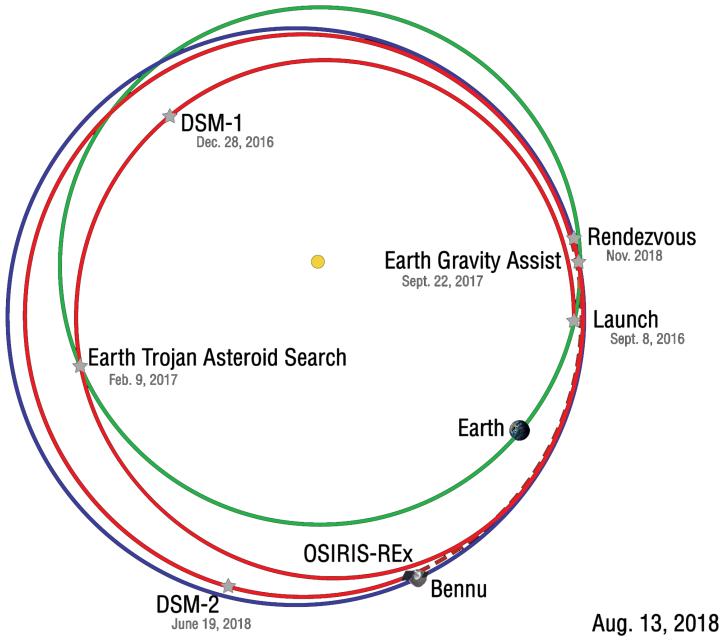

Figure 1 – Orbit diagram of the OSIRIS-REx spacecraft from launch to asteroid arrival, as of the beginning of Approach Phase on August 13, 2018. Included are the spacecraft's positions during Deep Space Maneuver 1 (DSM-1), the Earth Trojan Asteroid Search, the Earth Gravity Assist, Deep Space Maneuver 2 (DSM-2) and the November 2018 rendezvous with Bennu.

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Elucidating signatures of the genetic code with binding assays

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Introduction: What defined specific assignment of amino acids to their cognate codons during the emergence of the genetic code? According to the stereochemical theory, the assignments were established based on affinity interactions between amino acids and their codons/anticodons. In the structure of the modern tRNA molecule, the acceptor stem with the amino acid and the anticodon loop with the anticodon triplet are separated by 6 nm in space, making direct interaction impossible. However, two alternative primal tRNA structures have been proposed that bring together in space the amino acid and the codon determinant [1, 2]. Both structures contain tetraloop-like geometries – simple structures that were recently shown to possess enzymatic activity such as ligation, cleavage, and terminal recombination [3].

In this project, we experimentally study the binding of stable AMP activated amino acid analogs to RNA motifs of AMP-binding aptamers as a testbed or to the above mentioned tetraloop-like structures containing corresponding coding triplets using microscale thermophoresis. We aim to elucidate patterns of anticodon-amino acid correlations for the emergence of the genetic code.

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Dedicated to the Memory of Jim P. Ferris

Role of Minerals in the Formation and Preservation of RNA Oligomers in the Events Leading to the Origin of Life

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Introduction: Montmorillonite, a member of clay minerals with layer structure, catalyses the formation of RNA oligomers containing both 2',5'-linkages and 3',5'-linkages [1]. These synthetic oligomers, formed by montmorillonite catalysis, serve as template for the formation of complementary RNA oligomers [2]. Synthetic oligomers formed by montmorillonite catalysis containing exclusively 2',5'-linkages isolated from the mixture of 2',5'- and 3',5'-linked oligomers by enzymatic hydrolysis also serve as template producing not only 2',5'-linked oligomers, but also 3',5'-linked, i.e., RNA like oligomers [2].

Phyllosilicates, along with calcium carbonate, calcium sulfate, iron oxides and kaolinite have been identified on Martian surface. Biomolecules are constantly delivered onto Martian soil via meteorites, comets and interplanetary dust particles. The amount of organic material delivered to Earth has been calculated to be in the order of 2.4×10^8 g carbon/year [3, 4, 5]. On Earth, these molecules are protected from the harmful effects of radiation by the atmosphere, while on Martian surface they are exposed to the effects of UV and gamma radiation, and the effects of cosmic rays and particles due to thin atmosphere: 7 mbar.

We have irradiated the mixtures of building blocks of RNA and proteins with montmorillonite and other Martian analogue minerals with UV and gamma rays. The dose of UV radiation from a Xenon source received by the samples corresponded to only five days and the dose of gamma radiation from a Co-60 source corresponded to 500,000 years on Martian surface.

Analysis of these UV and gamma irradiated samples demonstrated that in the absence of minerals, the organic molecules were completely decomposed due to the effects of UV and gamma radiation. In the presence of minerals, the survival rate following the UV and gamma irradiation was about 98-99% and 20-10%, respectively [6, 7, 8, 9, 10].

These results clearly demonstrate the role of minerals for the formation and preservation of building blocks of RNA in the events leading to the Origin of Life.

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July 16-21, 2017 at UC San Diego, CA, USA

Continuous processing approaches for prebiotic syntheses of 2-amino-oxazole and subsequent ribo/arabino furanosyl amino-oxazolines

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Introduction: Glycolaldehyde dimer and cyanamide have been postulated to be the first compounds necessary for the formation of DNA/RNA nucleosides. Under mild conditions, these two molecules can react to form 2-amino-oxazole. Upon exposure to (DL)-glyceraldehyde, 2-amino-oxazole can cyclize to form a precursor to (DL)-ribose/deoxyribose, the backbone of DNA and RNA.[1] However, batch/flask conditions do not offer optimized production of 2-amino oxazole and its derivatives. We report a continuous processing approach towards the synthesis of 2-amino-oxazole under ambient temperatures and pressures using water as solvent produces a mean yield of 68%. Higher temperatures and pressures do not appear to impact yields; however, the presence of base such as NaOH or KH_2PO_4 can have a significant effect: in the presence of 0.25 M NaOH yields are optimized to >80%, with the base promoting the essential elimination. Subsequent reaction of 2-amino-oxazole with (DL)-glyceraldehyde in water under continuous processing conditions provides the ribo/arabino furanosyl amino-oxazolines in yields ranging from 29 to 68 %. An enantioselective approach to furanosyl amino-oxazolines and a telescoped approach to these important RNA precursors will be addressed.

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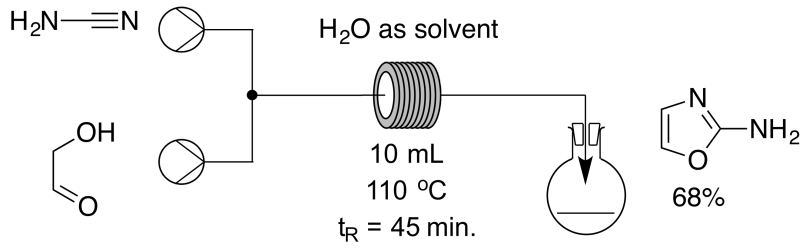

Figure 1 – Continuous processing approach toward the synthesis of 2-amino-oxazole.

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Selection of Amino Acid Chirality Via Weak Interactions in External Fields

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Introduction: An astro-biological model has been developed in which the selective destruction of chiral states in high magnetic fields can create enantiomeric excesses (*ee*s) of about 1 part in 10^6. These excesses may be subsequently auto-catalyzed into the large excesses observed on the earth today. In the present model, atomic nuclei bound in amino acids are destroyed via the weak interaction in stellar environments [1-3]. Nuclei are preferentially oriented in high magnetic fields of certain stellar environments and the molecular interaction couples the nuclear magnetic moment to the chirality through simultaneous orientations of the nuclear magnetic moment in the external field and the molecular electric dipole moment via the Stark Effect. The coupling of atomic nuclei with non-zero magnetic moments to the molecular orbitals via the interaction of the magnetic shielding tensor and the electric dipole moment creates additional energy splittings which depend on the molecular chirality [2]. This effect is exploited in this model to create a chirality-dependent asymmetry in molecular states. An enantiomeric excess is subsequently created via the selective destruction and subsequent amplification of nuclei oriented in strong fields. Possible sites in which this model may exist are proposed.

Results: Initial evaluations of L- and D-alanine indicate that three things are necessary for this model to result in *ee*s sufficient for subsequent autocatalysis to take place. An external electric and magnetic field provide the coupling of the molecular chirality to the nuclear spin. Even modest magnetic fields of ~10 T have been found to be sufficient enough in this model to produce *ee*s on the order of 10^{-6}. The external electric field is produced in the reference frame of the molecule via the motion of the molecular substrate through the magnetic field. Weak interactions then provide an asymmetric mechanism to selectively destroy one chirality over another. It is possible that the combination of strong stellar magnetic fields and destruction of the atomic nuclei in amino acids by a strong neutrino burst in the vicinity of collapsing stars may produce such an effect while still allowing the surrounding environment to survive.

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July 16-21, 2017 at UC San Diego, CA, USA

The Effects of Metal Ions on Reactions of Thioesters in Simulated Prebiotic Environments

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Reactions of Thioesters: The 'Thioester World' model posits that thioesters were a key functional group at some point in the development of life on Earth.[1] We are interested in studying the kinetics of reactions of thioesters, shown in Figure 1, to evaluate their prospective roles in prebiotic chemistry. Previously, we reported kinetics for hydrolysis and thiol-exchange reactions of model thioesters in buffered water.[2] Given that the prebiotic ocean was unlikely to have resembled such a clean system, we have begun to explore the effects of various metals on the hydrolysis, aminolysis, and thiol–thioester exchange reactions of thioesters in more complex aqueous solutions. These solutions include Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+}, and Co^{2+}, all of which are conjectured to have been present in the ancient ocean.[3] The kinetics of the reactions are monitored using ^{1}H NMR spectroscopy.

Analysis of ^{1}H NMR Samples with High Paramagnetic Ion Concentrations: Many prebiotic chemistry models invoke conditions in which reaction mixtures are subjected to wet–dry cycles of hydration (e.g., by rain) and evaporation. The process of evaporation introduces the potential for significantly higher concentrations of metal ions than in the larger prebiotic ocean. When present in substantial concentration, the ions that are paramagnetic (Fe^{2+}, Mn^{2+}, and Co^{2+}) can render NMR spectroscopy impracticable from the broadening of the signals in the spectra. In addition to the study of the kinetics of the hydrolysis, aminolysis, and thiol-thioester exchange reactions, we developed a method that allows the use of ^{1}H NMR spectroscopy to observe prebiotically relevant organic compounds in aqueous solutions containing paramagnetic metal ions.

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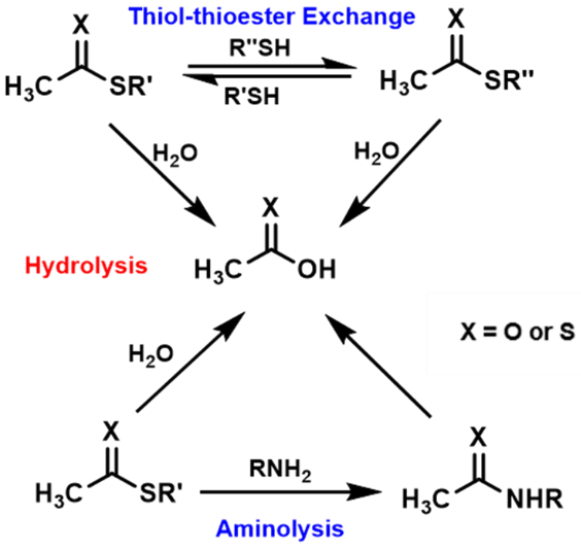

Figure 1. Thiol–thioester exchange, aminolysis, and the competing hydrolysis reaction in water

Glycosylation of Noncanonical Nucleobases in Water: Implications for the Evolution of Early Genetic Polymers

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The prebiotic formation of nucleosides and nucleotides remains a major challenge to the RNA world hypothesis. While model prebiotic syntheses have been reported for the pyrimidine nucleotides[1] and the purine nucleotides[2], yields are low and/or require spatially separated chemical pathways with specific sequential requirements to produce the canonical Watson-Crick base-pairing units. An alternative hypothesis[3] states that RNA is the product of chemical and biological evolution, and that ancestral genetic polymers may have been composed of recognition units similar to the extant set, but with reactivity profiles more amenable to the prebiotic formation of proto-nucleic acid monomers and polymers. For example, the pyrimidines barbituric acid and 2,4,6-triaminopyrimidine (TAP), along with the triazine melamine, react with sugars (including ribose) in water under prebiotically plausible conditions to form glycosides[3a,4]. Furthermore, these glycosides have the propensity to recognize complementary heterocycles in water at the monomer level in a manner analogous to Watson-Crick base pairing; a property not exhibited by the canonical nucleotides[3a,4]. In particular, TAP was found to react with a large variety of pentoses and hexoses to give either *N*- or *C*-substituted glycosides. These results, together with the observation that prebiotically plausible routes to sugars do not produce ribose selectively or in significant yields[5], suggest that prebiotic nucleoside formation would not have been limited to ribose if ancestral RNA (or proto-RNA) utilized TAP or other proto-nucleobases with similar reactivities.

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July 16-21, 2017 at UC San Diego, CA, USA

Redox and pH Gradients Drive Amino Acid Synthesis at Hydrothermal Vents

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Alkaline hydrothermal environments have been proposed as sites for the emergence of metabolism, and thereby life, on the early Earth. In these environments, iron oxyhydroxides (includeing green rust) and sulfides would have comprised hydrothermal sediments and chimney precipitates where alkaline vent fluids interfaced with the early iron-rich ocean [1,2]. These reactive iron minerals could have stoichiometrically, and perhaps catalytically, driven organic chemical reactions such as amino acid synthesis. A step toward such an outcome is through the hydrothermal carbonylation of iron sulfides – a reaction which produces the carboxylic acid, pyruvate [3]. In the presence of metal sulfides and in similar conditions this, and other carbonic acids, can undergo reductive amination to amino acids [4]. We conducted experiments to test if amino acids could also be synthesized from pyruvate in the presence of the redox-sensitive iron oxyhydroxides (precipitated with Cl^- counter ion). Reactions were carried out in an anoxic glove box to simulate early Earth conditions, and the synthesis of alanine was investigated by focusing on the effects of the various gradients likely to be encountered at alkaline submarine hydrothermal vents. These include varying the pH, temperature and also mineral composition. Products were analyzed with ^1H liquid NMR. Our preliminary results showed that while no amino acids were produced at more acidic conditions, high yields of alanine were produced as the pH approached the pK_a of ammonia at ~9.3 and beyond. But it was found that alanine synthesis also depended upon the Fe^{2+}:Fe^{3+} ratios of the iron hydroxide mineral. There was no reaction at all in cases where the iron hydroxide was completely oxidized, whilst only lactate formed in cases where it was completely reduced. Thus, the redox and pH gradients obtaining at the vent must be considered in gauging the likelihood of amino acid synthesis from simple precursors as a first step in assessing the conditions likely to have driven life to emerge on this, and other, wet and rocky worlds.

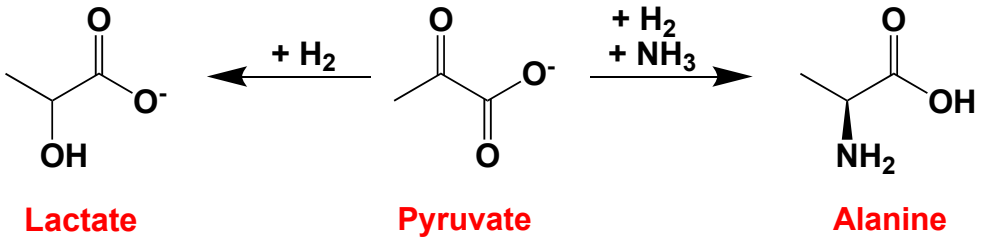

Figure 1 – Reaction of pyruvate reacting with ammonia to produce alanine and/or lactate.

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July 16-21, 2017 at UC San Diego, CA, USA

Prebiotic Peptide (Amide) Bond Synthesis Accelerated by Glycerol and Bicarbonate under Neutral to Alkaline Dry-Down Conditions.

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Introduction: Past studies of prebiotic peptide bond synthesis have generally been carried out in the acidic to neutral pH range [1, 2]. Here we report a new process for peptide bond (amide) synthesis in the neutral to alkaline pH range that involves simple dry-down heating of amino acids in the presence of glycerol and bicarbonate. Glycerol was included in the reaction mixture as a solvent and to provide hydroxyl groups for possible formation of ester intermediates previously implicated in peptide bond synthesis under acidic to neutral conditions [1]. Bicarbonate was added to raise the reaction pH to 8-9.

Results: Our early studies showed that dry-down condensation at 90°C of α-L-alanine in the presence of glycerol and bicarbonate gave high yields of dialanine and cyclic dialanine with a small amount of alanine trimer and tetramer. Both glycerol and bicarbonate were required for peptide bond synthesis. Apparently, the synthesis of long peptides by α-alanine is blocked by efficient intramolecular aminolysis via a 6-membered ring to give the cyclic dimer. In contrast, new HPLC results indicate that oligomerization of the L-2-aminobutyric acid, also an α-amino acid, yields primarily linear oligomers.

Condensation of the β-amino acids (β-alanine and isoserine) under the same conditions produced long linear peptides (9-mer & larger) indicating chain elongation was not blocked by cyclic dimer formation (Fig. 1). Unlike α-L-alanine, β-alanine and isoserine also oligomerized at neutral pH without bicarbonate. Analysis by LC/MS, full spectrum MS, and MS/MS confirmed the synthesis of (a) β-alanine oligomers, and (b) β-alanine +1Da oligomers, a result indicating partial replacement of the terminal amino group of oligomers by an hydroxy group. Oligomerization occurred at 65°C at a much slower rate. Both β-alanine and isoserine are products of model prebiotic synthesis reactions. In addition co-oligomerization of α- and β-amino acids is supported by HPLC analysis that shows additional product peaks not detected in the analysis of the homo-condensation reactions of the two reacting amino acids. The simplicity of this peptide synthesis process suggests that it could have played a role in molecular evolution on the early Earth.

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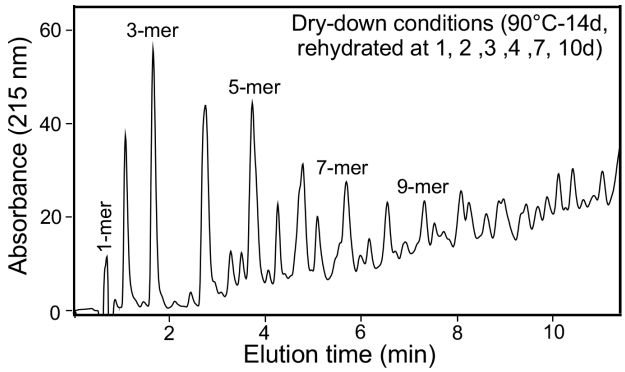

Figure 1. Chromatogram of products of β-alanine dry-down oligomerization promoted by glycerol and bicarbonate.

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Liquid Crystal Self-Assembly of Short RNA/DNA Oligomers as Autocatalytic Pathway for Ribozymes Formation

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Based on a broad experimental exploration of the collective behavior of short DNA and RNA oligomer (oligoNA), we will report recent progresses in the investigation of a pathway by which linear self-assembly and spontaneous Liquid Crystal (LC) ordering might have enhanced the prebiotic formation of long and potentially active RNA polymers. The key features of this auto-catalytic pathway are reported in figure. A hierarchy of base pairing and stacking, linear aggregation, phase separation of sequences and structures, and LC ordering can select oligoNA and guide their polymerization inside compact, ordered yet fluid micro-domains (colored domains inlet picture). Here in, oligoNA are held in end-to-end contact to form chemically discontinuous but physically continuous double strands. Minimal conditions for LC phases to emerge have been recently successfully tested, as DNA 4mer assembling in running-bond type chains [1], and remarkably, mononucleotide triphosphates (dNTPs), which ordering is led by the interplay of Watson-Crick base pairing and chromonic type stacking [2]. LC catalytically promotes non-enzymatic chemical ligation of oligoNA, with more than 10-fold elongation [3, 4]: the LC droplets act as fluid, permeable micro-reactors in which linear oligomers are selected and ligated. Our current investigation is aimed in testing concentration and temperature cycles as promoters of the evolution of a starting random oligoNA-monomer distribution, wherein potentially formed folding sequences would be selected from the LC phase. Lastly, in presence of lipids, hybrid assemblies can form, as vesicles or lamellar phases, stabilized by the tendency for rigid and flexible layers to spatially segregate either in hydrated or dry conditions.

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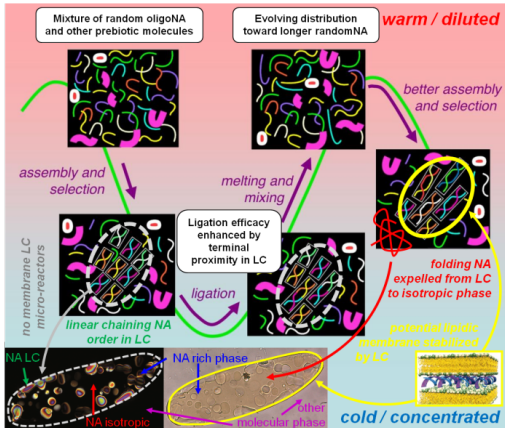

Self-Assembly of Plausible Proto-Peptides

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A primary challenge of origins of life research is to find a plausible prebiotic route for the formation of peptides. Although the synthesis of various amino acids under prebiotic conditions is now generally accepted, their subsequent oligomerization into peptides is more difficult to explain. Recently, a simplified route to the formation of peptides has been reported, which involves subjecting a mixture of hydroxy acids and amino acids, both of which were likely present on the prebiotic Earth, to repetitive wet-cool/dry-hot cycles [1,2]. It has been proposed that the resulting depsipeptides, containing both ester and amide linkages, might have constituted part of the primordial proto-peptides population. We have chemically synthesized short depsipeptides and are now testing if these oligomers possess the characteristics that would have allowed them to be selected by chemical evolution based on self-assembly propensity, stability and functionality. Specifically, we have synthesized a simple depsipeptide library, ranging from dimers to octamers, which contain an *N*-terminal glycolic acid (the hydroxy acid analog of glycine) in order to promote polymerization via ester bond formation.

We have found that applying dry-hot conditions drives oligomerization and we were able to show a structural shift that coincides with polymer growth. We have also found that there is a negative correlation between peptide length and polymerization rate. We will discuss investigations of depsipeptide stability and self-assembly propensity by a variety of spectroscopy- and microscopy-based methods, such as circular dichroism and electron microscopy.

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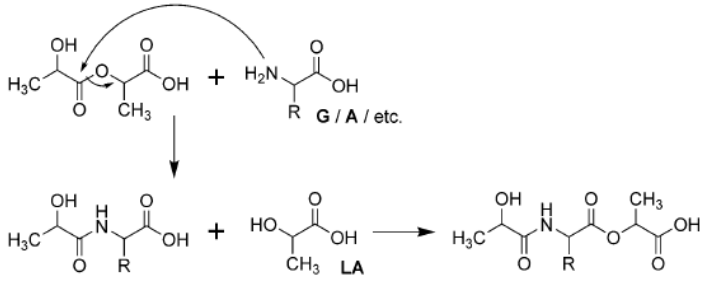

Figure 1 – Proposed reaction scheme for hydroxy acid–mediated peptide bond formation and depsipeptide elongation by ester-amide exchange [1] .

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In vitro RNA-peptide co-evolution system for screening ATP-binding RNP

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Introduction: The advent of biological polymers was a key step for the emergence of life. Modern organisms use proteins to achieve energy harvest and transfer in various ways to sustain structural organization through reproduction of molecules. Whereas "evolvability" of the biological system is maintained by replicable nucleotide polymers that undergo Darwinian evolution. Here Functional RNA-protein complexes (RNPs) represent perhaps the oldest conserved molecular assemblies in cells, such as ribosome carring out transfer of information from RNA to protein.

In order to answer questions regarding the emergence and historical trajectories of the co-evolution of RNA and proteins leading to RNPs, we established an *in vitro* system using a synthetic DNA library consist of both random 60 mer non-coding RNA and a random 42 aa amino acid peptide region. We performed used an mRNA-display method along with in vitro translation system to display both random RNA and random peptides to screen for a potential ATP-binding RNA/peptide/RNP candidates. High-throughput sequencing and bioinformatics analysis of the first round screened RNP library present demonstrated minimal enrichment at the RNA sequence level. with no significant concensus RNA secondary structure. However at the peptide level, the coding region have showed the enrichment of lysine, asparagine, and methionine among the over-represented clusters of coding sequences. Further investigation will involve optimizing the yield of RNA-peptide conjugates during mRNA-display, performing further enrichment on the RNP population, and comparing the results to those of RNA- and peptide-only trajectories.

In Vitro "Evolutionary Arms-Races" between Hosts and Parasites in an Artificial RNA Replication System.

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Abstract: Host-parasite relationships are quite universal in nature, where host organisms are exploited by parasitic organisms, viruses, or transposons. Parasites could have been among the major driving forces in the evolution of life through “evolutionary arms-races” [1], but it is still unclear how universal the arms-race phenomenon is, and how the arms-race influences evolution of their hosts.

In this study, we experimentally investigated the host-parasite evolutionary arms-race using a simple artificial host-parasite system established in our laboratory [2]. This system consists of a reconstituted cell-free translation system and two kinds of RNA, Host and Parasite RNAs, both of which are replicated by an RNA replicase encoded only in Host RNA (Fig.1). In this system, both Host and Parasite RNAs are capable of evolution through mutations introduced by replication errors and natural selection processes. We performed coevolution experiments by encapsulating the Host-Parasite RNA replication system in micrometer-sized water droplets and repeating the process of RNA replication and feeding nutrients (Fig. 2).

We found that

1. The number of Host and Parasite RNAs oscillated and itinerated oscillatory competition phase and coexistent phase during the evolution experiments. (Fig. 3)
2. Novel Parasite RNAs with different sequence lengths emerged in the middle of the evolution experiments.
3. Host RNA evolved faster in the presence of Parasite RNAs than in the absence of them.

These results indicate that evolutionary arms-races between Host and Parasite RNA actually occurred, and that parasites can accelerate the evolution of their hosts.

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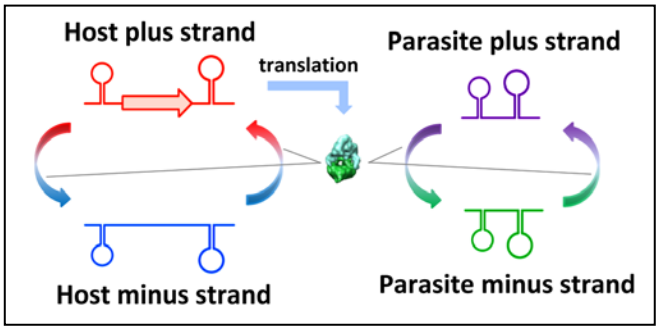

Fig.1 : Host-Parasite RNA replication system

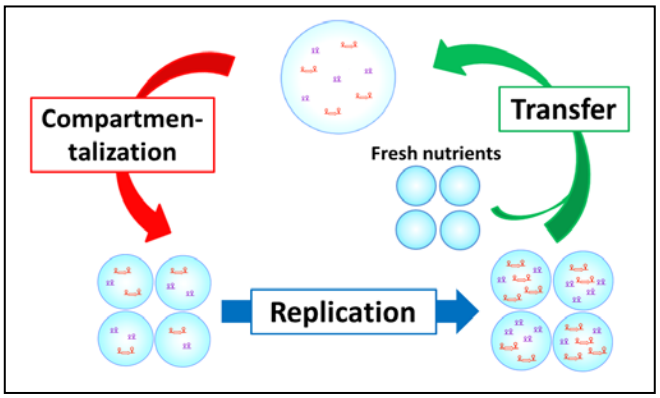

Fig.2 : Schematic of a cycle of coevolution experiment

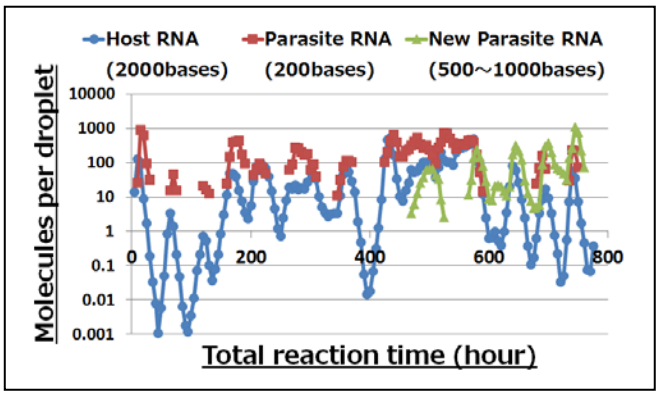

Fig.3 : Population dynamics of Host and Parasite RNA

July 16-21, 2017 at UC San Diego, CA, USA

Amino acid formation by asteroid impacts on ammonia-free oceans

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Introduction: Impacts of extraterrestrial objects on the early Earth have potential to have provided organic compounds and inorganic reductants (e.g., metallic iron and carbon) to the prebiotic Earth[1,2]. Hypervelocity impacts initiate reactions between meteoritic reductants and surrounding materials to form organic compounds. Our previous study, demonstrated the formation of amino acids and nucleobases from iron-bearing meteorite simulants, water, and ammonium bicarbonate[3]. High CO_2 fugacity in the early Earth's atmosphere has been suggested in literature. However, high NH_3 concentrations in the early oceans has not been supported, although low NH_3 concentration is probable[4]. This study shows the results of shock-recovery experiments and flow-reaction experiments simulating post-impact reactions between asteroid minerals, ammonia-free ocean, N_2-CO_2/N_2 atmosphere.

Experiments: Shock-recovery experiments were conducted with a single stage propellant gun at NIMS, providing impact between a stainless steel disc and a container at approximately 0.9 km/s. Starting materials are composed of Fe, Ni, $NaH^{13}CO_3$, N_2, water/NH_3-water. The flow-reaction experiments are conducted at 1000°C with a glass flow line using Fe, Ni, SiO_2, N_2, and H_2O as the starting materials. Products are analyzed with ultra high performance liquid chromatography/tandem mass spectrometry.

Results and Discussion: In the shock-recovery experiments, glycine and β-alanine were formed from Fe, Ni, $NaH^{13}CO_3$, N_2, and ammonia-free water whereas at most 4 additional amino acids including alanine, sarcocine, α-aminobutyric acid, and β-aminoisobutyric acid were formed in experiments with ammonia water. The flow-reaction experiments with ammonia-free starting materials also yielded glycine. These results indicate that formation of amino acids with meteoritic inorganic reductants are possible on the prebiotic Earth. Although the yields of amino acids are lower than products of reaction with ammonia, the present results show a process to form amino acids from an almost infinite source of nitrogen (N_2) and carbon (CO_2) on the prebiotic Earth.

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July 16-21, 2017 at UC San Diego, CA, USA

Pre-LUCA cells: life but not alive

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Introduction: The early evolution of life included a series of transition from non-living matter, through prebiotic organic synthesis, towards the assembly of first evolvable protocells and the Last Universal Common Ancestor of all life (LUCA). Prebiotic chemistry and the simplest, prebiotically plausible stages of protocell evolution have been studied for many years. On the other end of the origin of life timeline, the state and properties of the first live cell, LUCA, have been inferred from phylogenetic analysis and ancient protein reconstitiution. Relatively less effort was focused on the non-living, yet immediately pre-life stages of origins. Our work focuses on that immediately-pre-life stage of evolution. Using liposome bioreactors we create synthetic minimal cells that exhibit some key properties of life without being entirely alive.

Synthetic minimal cells express proteins inside phospholipid liposomes using cell-free protein expression systems and DNA templates. This system represents the latest stage of prebiotic evolution, after the establishment of the Central Dogma. The minimal cells do not undergo spontaneous division, so they're not alive. The cells do not have active homeostasis, but they can maintain a separate internal environment due to relative impermeability of phospholipid membrane. The controllability and modular designeability of cell-free protein expression system and simple phospholipid membranes allow studying major transitions in evolution. They can be used to study heaviliy deoptimised biological processes, and recreate the assembly of basic live cell systems from ancestral components.

In our work, we create synthetic minimal cells expressing complex genetic pathways, with membrane proteins facilitating communication with external environment, and we use combinatorial and programmable fusion to control synthetic cell populations. Together, this creates a comprehensive system to study the advent of cellular processes on the boundary between prebiotic and Darwinian evolution.

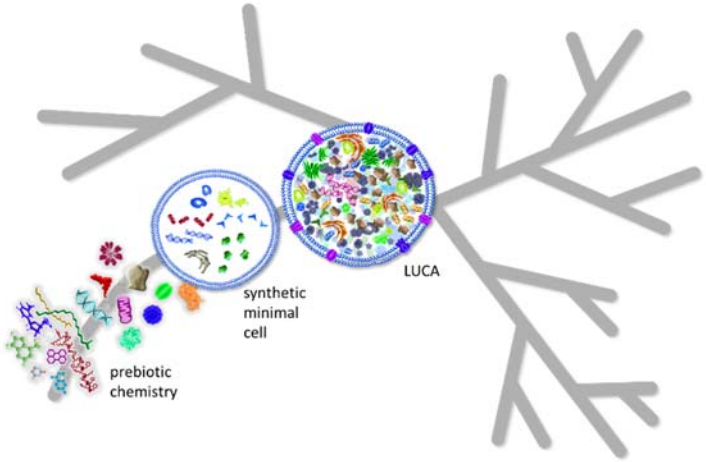

Figure 1 – Synthetic minimal cells are liposome bioreactors mimicking late pre-LUCA stage of prebiotic evolution. The liposome of synthetic minimal cells is made of phospholipids, the cells contain ribosomes, express proteins from DNA, contain membrane channel proteins and maintain some level of homeostasis. The synthetic cells do not spontaneously divide and do not undergo Darwinian evolution.

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Exploring the Role and Reaction Constraints of Malonate within the Context of the "Glyoxylate Scenario"

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Introduction: Malonate has been demonstrated to be the common denominator in the abiotic degradation of numerous organic acids [1]. This inherent stability of malonate and the fact that it is used by current biology in processes like fatty acid biosynthesis [2] suggests an evolutionary persistence. We were interested in whether malonate could have played a role in the "glyoxylate scenario" [3][4], producing prebiotic metabolites for the synthesis of biogenic molecules [5].

Malonate combines cleanly with glyoxylate in an adol addition reaction, one of the most important carbon-carbon bond forming reactions in current biology, at neutral pH (pH = 7) at 50 °C within approximately 24 hours. A key interest of ours, that will be presented, is understanding why clean aldol addition products are observed at neutral pH given malonate's relatively low α-carbon acidity (pK_a = 13-16). Additionally, the reactivity of enolate nucleophiles is expected to increase with increasing pH of the solution, but our preliminary results indicate diminished reaction rates at elevated pH. One hypothesis that is being explored is the formation of a Meldrum's acid-like cyclic acetal intermediate which would be anticipated to drastically reduce the pK_a of the α-carbon on malonate [6], and increase its nucleophilicity at neutral pH (Figure 1a). The potential of Lewis acids to influence the nucleophilicity of malonate in this aldol reaction (Figure 1b) is also being investigated. The presentation will highlight our findings toward better understanding roles and specific reaction constraints of the aldol addition between malonate and glyoxylate within a prebiotic environment.

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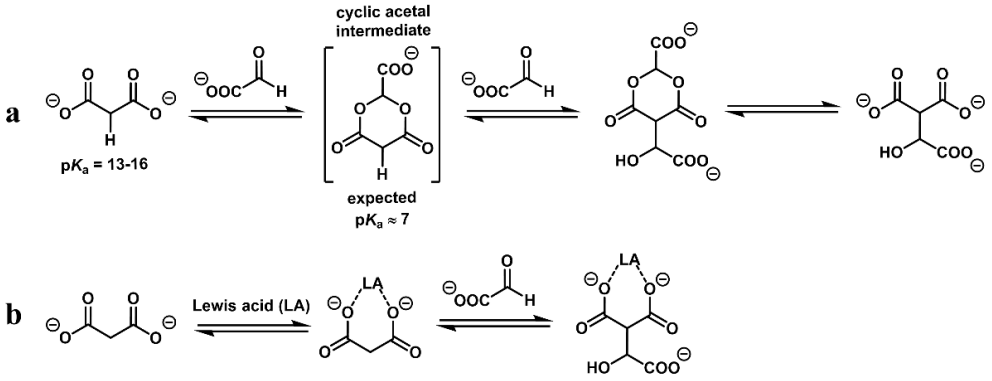

Figure 1 – Possible prebiotically relevant methods that the aldol addition of malonate and glyoxylate might be influenced by (a) formation of a cyclic acetal intermediate or (b) through coordination to a Lewis acid.

Assessment of Secondary Structure in Nucleic Acid Produced in Simulated Prebiotic Conditions

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The earliest forms of life would likely have a protocellular form, with a membrane encapsulating some form of linear charged polymer. These polymers could have enzymatic as well as genetic properties. We can simulate plausible prebiotic conditions in the laboratory to test hypotheses related to this concept. In earlier work we have shown that mononucleotides organized within a multilamellar lipid matrix can produce oligomers in the anhydrous phase of dehydration- rehydration cycles [1]. If mononucleotides are in solution at millimolar concentrations, then oligomers resembling RNA are synthesized and exist in a steady state with their monomers [2]. We have used conventional and novel techniques to demonstrate that secondary structures stabilized by hydrogen bonds may be present in the condensation products produced in dehydration-rehydration cycles that simulate hydrothermal fields that were present on the early Earth. Gel electrophoresis data corroborates the presence of 200-base pair length RNA fragments in products of Hydration-Dehydration experiments. Furthermore, hypochromicity measurements demonstrate a degree of hypochromicity found in single RNA strand of known sequence, as well as results that indicate this is true also for a sample of complementary strands of RNA. Analysis of ionic current signatures of known RNA hairpin molecule as measured using a nanopore detector indicate a significant variability in pattern, different from the signatures produced by DNA hairpin molecules. This informs how we may interpret nanopore data gathered from prebiotic simulations.

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July 16-21, 2017 at UC San Diego, CA, USA

L-Amino Acid Enantiomeric Excesses in Meteorites: Formation Mechanisms and Implications for the Origin of Homochirality

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Introduction: The delivery of organic compounds by carbonaceous meteorites to the early Earth and other planetary bodies could have been an important source of prebiotic compounds required for the emergence of life. However, one major unsolved question is how the homochirality observed in life (*i.e.*, L-amino acids and D-sugars) originated from presumably racemic mixtures in a prebiotic world. Slight to significant L-enantiomeric excess for several indigenous α-dialkyl amino acids were first reported in the Murchison and Murray CM2-type carbonaceous meteorites [1]. Since then L-enantiomeric excesses of up to 21% for the terrestrially rare, non-protein amino acid isovaline have been reported across a wide range of carbonaceous meteorite groups [2], and appear to correlate with the degree of parent body aqueous alteration as inferred from their mineralogy (Fig. 1). Much larger L-excesses of ~45 to 99% have been reported in the Tagish Lake meteorite for the protein amino acids threonine, serine, aspartic and glutamic acids, whereas another common protein amino acid alanine was racemic, suggesting minimal terrestrial contamination of the meteorite [3]. Asymmetric photolytic decomposition of amino acids or their precursors by polarized radiation in the presolar nebula has been proposed as a source of the L-excesses in meteorites, however such large L-excesses would require photodestruction of >99% of the starting materials [4]. We will present the most recent data and discuss plausible amplification mechanisms that could explain the large enantiomeric enrichments observed in meteorites.

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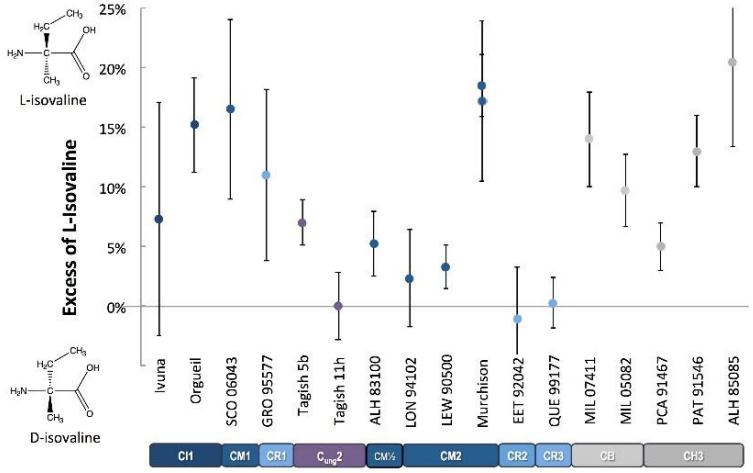

Figure 1 – L-enantiomeric excesses of the non-protein amino acid isovaline found in carbonaceous meteorites range from ~0 to 21%. D-isovaline excesses have not been found in any meteorite to date.

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Restarting over: Alternative evolutionary pathways for terrestrial life on oxygen planets

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Oxgen planets: It is by now well established that the extended protostar to main sequence Kelvin-Helmholtz contraction phase of late M dwarfs induces a runaway greenhouse state in habitable zone planets for 0.1-1.0 Ga. Several earth oceans worth of water may be lost due to the photolysis water in the wet stratosphere of the greenhouse atmosphere and the subsequent XUV induced escape of hydrogen to space [1]. Most of the photolytically produced oxygen will however be retained, building up to several hundreds of bars of abiotic oxygen by the end of the initial greenhouse state [2]. The question is then, generically, whether massive primordial oxygen partial pressures would preempt abiogenesis on otherwise habitable planets.

Alkaline hydrothermal vents: Life may have originated on earth in ultramafic hydrothermal vents acting as natural bioreactors [3]. Alkaline hydrothermal systems could have been nearly continuous in distribution in the Hadean, when the absence of oxygen would have allowed them to act as electrochemical flow reactors in which alkaline fluids saturated with hydrogen mixed within a labyrinth of interconnected micropores with relatively acidic ocean waters rich in carbon dioxide [4]. The restricted geometries provided by the thin inorganic walls, possibly containing catalytic Fe(Ni)S, could have allowed for prebiotic reaction cycles and for the subsequent formation of protocells.

Habitable but lifeless oxygen planets: Black smokers and ultramafic hydrothermal vents will form also on planets with a massive oxygen partial pressure. Spatially confined reducing environments are however not enough for life to arise. It is unlikely that the locally produced prebiotic compounds could live long enough on oxygen planets to allow for subsequent concentration processes and that the restricted pores of the vent towers would be rich in catalytic transition metals. Protocells would need to adapt, in addition, during the limited lifetime of their hosting vent (possibly of only a few Ma) to the high toxicity [5] of the oxygen dissolved in the surrounding seawater. The demise of their birthing thermal vent would otherwise spell out their own fate as well.

Reversing the perspective: M dwarfs systems such as the TRAPPIST-1 system [2] are expected to be rich in small planets, with an incidence rate of about 0.2 for habitable zone planets [6]. The milky way may hence harbor around 200*0.75*0.2=30 billion rocky habitable zone oxygen planets, out of which a small but finite fraction will have retained part of their original water reservoir and hence an ocean. A large number of potentially habitable but otherwise sterile exoplanets may hence offer alternative evolutionary pathways for terrestrial life. It has been suggested in this context [7], that ecospheres of prokaryotes and unicellular eukaryotes may be established on exoplanets by laser-propelled miniaturized interstellar probes (the Genesis project).

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Synthesis of Cyanopolyynes for Photochemical and Spectroscopic Studies

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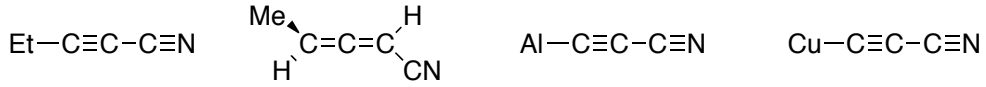
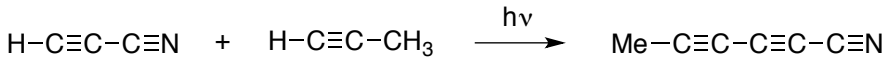
Introduction: Cyanoacetylene is an ubiquitous compound observed in the Interstellar Medium (ISM), comets and the atmosphere of Titan. Derivatives as well as higher homologues are of a great interest to have a better understanding of the syntheses and properties of these 1-alkynyl cyanides in the Universe.

Results: Substituted cyanoacetylenes as well as metallic derivatives and isomers have been synthesized and analyzed by microwave spectroscopy but to date none has been detected in the ISM (Scheme 1).[1]



Scheme 1

To have in hand cyanobutadiyne and the methyl derivative, both compounds detected in the ISM, allowed photochemical studies starting from acetylene or propyne and cyanoacetylene to evidence the formation of such diynes derivatives in the gas and the solid phases (Scheme 2).[2]



Scheme 2

Bromocyanoacetylene (Br-C≡C-CN) has been used to generate C_3N^- and to study the kinetic of decomposition of this anion at room and low temperature, simulating the chemistry of this anion versus several compounds. This study has been extended to C_5N^- starting from BrC_5N recently synthesized in our lab.[2,3]

All these studies give a better knowledge of the chemical behavior of these 1-alkynyl cyanides which is occurring in many places of the Universe.

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July 16-21, 2017 at UC San Diego, CA, USA

A Path to Homochirality on the Primitive Earth: High Temperature Sublimation of Enantioenriched α-Alkylated-α-Amino Acids

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Introduction: In 2011, Viedma et al. observed an increase of the enantiomeric excess (ee) for some α-alkylated-α-amino acids (AAs) quickly sublimed at a very high temperature (500°C).[1] We investigated the possible role played by this phase transition on the Primitive Earth as a path to homochirality.

Results: A racemic α-alkylated AA can be deracemized by co-sublimation with an enantioenriched AA under such harsh conditions. Both AAs have always the same handedness. An unexpected synergistic effect was observed when the complexity of the system was increased by the presence of several racemic AAs (Scheme 1).[2] Such enantioenrichments were also observed for alanine using serine or cysteine which lead after sublimation to alanine and many decomposition products.[3] An increase of enantiomeric excesses was observed using various gas phases (CO_2, N_2, NO,…) and in the 400-560 °C range.

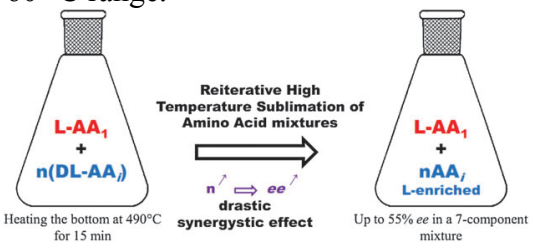

Figure 1. Synergistic effect in the enantioenrichment of high temperature sublimation of mixtures of amino acids

Discussion: In prebiotic chemistry, a relevant property of a compound should be maintained or enhanced when complex mixtures of compounds are involved. Few reactions satisfy this constraint, and many studies have been erroneously associated to the chemistry of the Primitive Earth.

The very simple high temperature sublimation of mixtures of compounds presents a huge potential interest in prebiotic chemistry since any mixture of α-alkylated AAs is thus enantioenriched. The dependence on the nature of the enantioenriched or racemic AAs, their number or the temperature of sublimation is only on the level of the enantioenrichments and the yields. Never a decrease of ees of the main handedness has been observed in such sublimations of more than one AA.

Extension to other initiators or racemates than AAs is currently under progress in our labs.

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The Logic that Emerges from the Self-Referential Genetic Code

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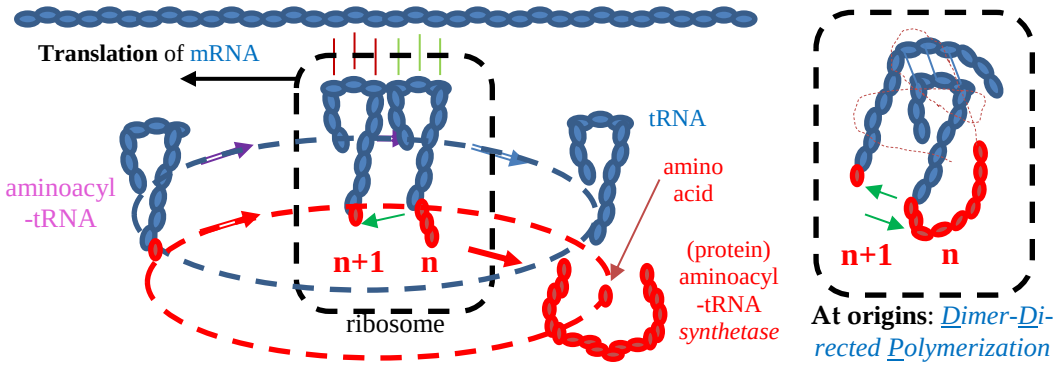

The self-referential model **doi:10.20944/preprints201703.0031.v2** for the formation of the genetic code (in the biochemistry realm) utilizes a logic that mimics the quantum mechanics rationale: the classic realm is generated by processes of decoherence, which disrupt the coherent states that occur in the quantum realm. Another mimicry is the utilization of the pathway 'from disorder to order' in both realms **Quantum Biosystems 2015 6(1):148-159**. I wonder what this coincidence means. Does it suggest mutual theoretical support? Would it mean that our mind is constrained (biased?) to produce similar models for diverse realms of reality? The repetition / similarity in the different realms is reminiscent of the apparent circularity in the adaptive / evolutionary mechanisms and explanations. Adaptation promotes mutual adjustment between the interactants: organisms (in) / environments (out) or genetic memories / proteins. (1) The logic of the living is the metabolic flow that is embedded in the universal and geochemical flows. (2) **At the origins** of the genetic code, there is (proto)tRNA Dimer-Directed Polymerization. The flow is slow because syntheses are bi-directional. Dimers are proto-ribosomes: structures that hold tRNAs together and propitiate the transferase reaction. (proto)tRNAs are complementary-equivalent, superposed, coherent; an anticodon is at the same time codon for the other. Products grow at both (proto)tRNAs. (3) Peptide products that are capable of (proto)tRNA binding and stabilization, without disrupting their activities, establish a self-referential self-stimulatory nucleoprotein production system, at the birth of cells. (4) Decoherence. Separation of the members of dimers was provoked by intromission of the mRNA strings, which may have originated from enchaining of segments of the (proto)tRNAs. (5) **At translation** (better, transliteration)**.** *Ribosome-Directed Polymerization* is directional and the flow is fast. Genetic strings (mRNA) are scanned by laterally associated couples (instead of dimers) of tRNAs that enchain the carried amino acids into proteins. The *synthetase binds* the components together. Elipses indicate recycling of the synthetase substrates, tRNAs and amino acids.

Photochemical synthesis of bioinspired inorganic-organic hybrid protocell-like self-sustaining supramolecular assemblies, "Jeewanu" in a laboratory simulated possible prebiotic atmosphere

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Abstract

Sunlight exposed sterilized aqueous mixture of some inorganic and organic substances shows photochemical formation of self-sustaining biomimetic supramolecular assemblies, "Jeewanu" capable of showing multiplication, growth and metabolic activities (1). The studies using optical and electron microscopy (SCM,TEM, AFM), XRD, EPR, FTIR, LCMS have revealed the presence of various molecules of biological interest viz. amino acids in free as well as in peptide combination, nucleic acid bases as purines as well as pyrimidines, sugars and phospholipids and ferredoxin-like materials in them. These microstructures have been found to show a definite boundary wall and an intricate internal structure. The presence of enzyme-like activities nitrogenase (2) and phosphatase-like activities have been detected in the mixture. Jeewanu have been found to catalyse photoautotrophic processes in the mixture.

In the possible prebiotic atmosphere possibly photosynergistic collaboration of non-linear coherent processes at mesoscopic level led to emergence of biomimetic hybrid supramolecular assemblies similar to Jeewanu capable of showing various functional properties viz. self-organisation and self-sustenance.

a. Keywords : Jeewanu, inorganic-organic hybrid systems, self-organisation, self-sustaining, bioactive, supramolecular assemblies, biomimetic systems, bioinspired

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Structural and Compositional Diversity in Iron-Based Hydrothermal Chimney Simulants Grown with Functionalized Organics

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Background: Serpentinization at moderate temperatures produces an alkaline, reducing fluid that, upon seeping into the ocean, reacts with dissolved metal cations to form porous, tubular precipitates called hydrothermal chimneys [1]. Minerals within a chimney may couple dissipation of the electrochemical gradient between the seawater and vent fluid to organic synthesis [2]. Hydrothermal chimneys have been proposed as a possible environment for origin of life, on account of their similarity to cellular membranes in extant life, which also couple electrochemical gradients to organic synthesis [1-4]. Here, we simulate an iron-rich hydrothermal chimney and show how environmental agents affect its morphology.

Methods and Results: We simulated a hydrothermal chimney by anaerobically injecting sodium hydroxide, with or without organics, into a reservoir of aqueous ferrous and ferric chloride [5]. Tubular precipitates composed of magnetite and iron oxyhydroxides formed where the injection solution interfaced with the reservoir solution. The walls of these structures consisted of concentric layers, each with a crystalline outer surface and a smooth inner surface. Akaganéite gave way to lepidocrocite and then goethite with increasing depth into the chimney wall, perhaps owing to the chloride gradient between the reservoir and injection solutions [6]. Both pyruvate and cysteine weakened the chimney walls and imparted a rounded morphology on all surfaces throughout the chimney. Alanine also weakened the chimney walls, but it imparted a wider range of crystal morphologies, including disks and crossed spines.

Impact: Our results show that ions and organics in the growth environment may impart compositional and morphological gradients on iron-based hydrothermal chimneys. This provides a number of microenvironments throughout a single chimney, each of which may be best suited to catalyze a different reaction within a larger emerging metabolic pathway. The interaction of organics with inorganic motifs in a chimney raises the opportunity for selective concentration of organics and potentially for ligand accelerated autocatalysis, opening the possibility for large-scale organic synthesis [7].

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The Search for Signs of a Second Origin of Life in Ocean Worlds of the Outer Solar System

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Introduction: The question of whether or not we live in a 'biological universe' is, in large part, a question of whether or not the origin of life is easy or hard: Are the conditions for life's origin so unique that life occurs very rarely, or does life arise 'easily' through one – or several – modalities? Arguably the best places to test the 'biology hypothesis' are the ocean worlds of our outer solar system – moons such as Europa and Enceladus [1, 2].

Two specific modalities and locales for the origin of life within ocean worlds are: 1) within hydrothermal systems on active seafloors, and 2) within, or beneath, the ice shells of ocean worlds (regions in which a liquid water and solid ice interface exist). These two options serve as useful points of comparison with respect to life's origin on Earth; were no life to be found on worlds like Europa or Enceladus would such results implicate terrestrial/continental environments (tide pools, hot spring, etc.)? While origins in hydrothermal systems have received considerable attention, less work has been done on origins in ice. Here I detail laboratory experiments relevant to surface and subsurface chemistry on and with Europa and Enceladus, and describe possible pathways for the origin of life as we know it. I will then described the mission concept for the Europa Lander and how that mission could serve to detect and distinguish a second, independant origin of life in our solar system.

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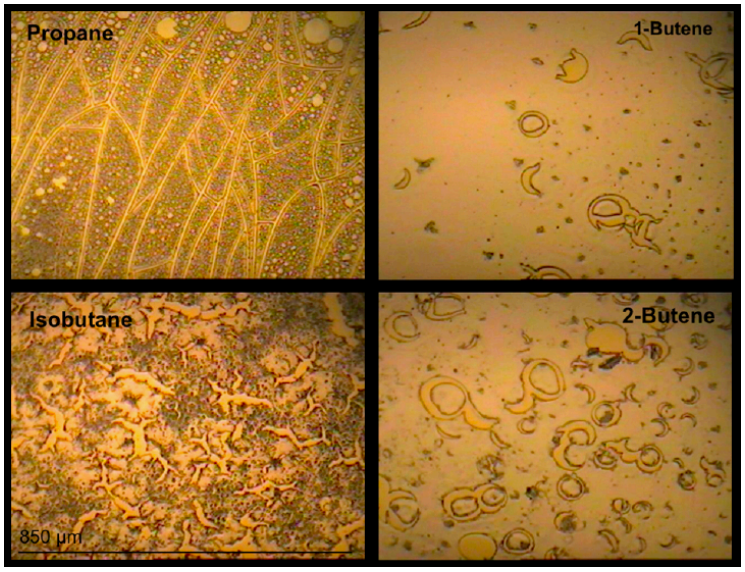

Figure 1 – Residues of electron irriadiated short-chain organics created under cryogenic, vacuum, and irradiation conditions comparable to that of Europa's surface [3].

Between Mica Sheets: Better than Membranes at the Origin of Life?

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Introduction: Organelles without membranes are found in all types of cells and typically contain RNA and protein. RNA and protein are the constituents of ribosomes, one of the most ancient cellular structures. It is reasonable to propose that organelles without membranes preceded protocells and other membrane-bound structures at the origins of life. Such organelles would be well sheltered in the spaces between mica sheets, which have many advantages as a site for the origins of life. [1-3]

Discussion: Lipid bilayer membranes are fragile. Nonetheless they are a popular hypothetical environment for the origins of life. Most subcellular organelles are enclosed in lipid membranes. Some organelles, however, such as the nucleolus, are membrane-less. The nucleolus contains the components of ribosomes and is, physically, a liquid-in-liquid phase separation within the nuclear matrix. [4]

Another problem with a 'membranes-first' model for the origins of life is that membranes around living cells come in 2 basic types: Archaeal membrane lipids have ether linkages; Bacterial and Eukaryotic membrane lipids have ester linkages. [5] If there were membranes before the cellular contents within the membranes were alive, how did there come to be 2 types of membranes surrounding living cells?

The spaces between Muscovite mica sheets provide an enclosure, an environment high in potassium (K) ions, like the intracellular environment of living cells, and anionic crystal lattices with a spacing of 0.5 nm, which is also the distance between anionic phosphate groups in extended single-stranded RNA and DNA. [1] An endless energy source for the origins of life is provided by 'open-and-shut' movements of mica sheets in response to temperature changes and fluid flow. This mechanical energy (work) is arguably the fundamental form of energy in enzymatic reactions, although the obvious form of energy for enzymatic reactions is now chemical energy, typically ATP. In the 'mica world' hypothesis, mechanical energy was used directly for forming chemical bonds, rearranging prebiotic polymers, and blebbing off protocells before a transition to chemical energy such as ATP.

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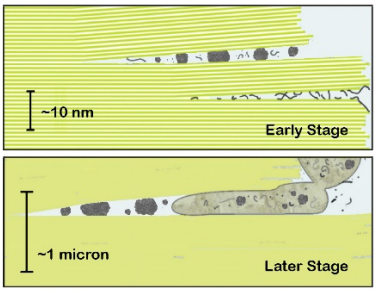

Figure 1 Diagrams of an origin of life between mica sheets under water with membrane-less organelles and other prebiotic structures. Green lines and areas represent green Muscovite mica. Potassium (K) ions in the spaces between sheets (white lines in the Early Stage) hold sheets together. The various gray structures represent extended polymers (linear structures), molecular aggregates and membraneless organelles (gray globules), and protocells (large budding structure in the Later Stage). 10-nm scale bar in the Early Stage is the thickness of 10 mica sheets. 1-micron scale bar in the Later Stage is the thickness of 1000 mica sheets. Adapted from [3].

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Introduction To Astrobiology: A Model For Integrating Research Into an Undergraduate Class

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Introduction: We have developed and taught a course at our college entitled Honors Seminar: Introduction to Astrobiology. This is a course for first or second-year college students suitable for non-science majors. We designed the course to be research-based learning [1-3] using the reverse classroom approach. Students worked in pairs to find answers and critically evaluate their findings. Our strategy was to promote student engagement and creative inquiry, demystifiy the research process, and thereby increase student knowledge and interest. The goals of the course were to discover and understand what comprises astrobiology by qualitatively and quantitatively evaluating data and theories to understand the quest to know if life exists beyond Earth.

The course was co-taught by two instructors, one with expertise in astronomy and the other in biology and chemistry. Each instructor led sessions or activities in his area. As the course evolved, we integrated these different approaches to the study of astrobiology. This approach provided a deeper learning experience. Before class, students had to complete any assigned reading, view assigned videos, and post to the discussion board. During class we discussed what they didn't understand and students completed class activities for the day working in groups. Each week they had two hands on activities – one from each instructor. These often involved analyzing real world databases, e.g., the exoplanet database, Jupiter observational data, or lunar observational data. We also had journal club every week. Each week, one student was assigned to select an article related to astrobiology and make a presentation to the class explaining the article. The other students were expected to read the article and ask questions of the presenter. We had two outside guest speakers in astronomy/astrobiology that talked about their research and engaged in a question answer session with the students. One guest speaker talked with the class via Skype. For some activities (e.g., theories on the origin of life) students had to work in groups and make a class presentation explaining and critically analyzing their presented theory.

Finally students had to work on a semester-long research project. They could work in groups of up to three students. They had to define a a research question, use the scientific method to answer, and write a report on their project. On the last day of class we had poster presentation day (similar to posters at scientific conferences) where each group had to present their research project in poster format to the rest of the class and answer questions. We also had a few co-curricular activities outside the classroom, which were talks, presentations, or activities. There were no exams. Grades were based on student participation, journal club, class activities, and their major research project. The course format was well received even by students that were non-science majors. In fact we were given a standing ovation by the students last year!

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Liquid Crystal Phases of RNA Mononucleoside Triphosphates in Aqueous Solution

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Introduction: Nucleic acid (NA) oligomers as short as 4 base pairs can carry out the self-assembly steps of duplexing, end-to-end aggregation of duplexes, and condensation of aggregates to form columnar liquid crystal phases. In such phases the molecules, self-selected because of their complementarity, create a fluid structural and chemical environment in which oligomer ligation into longer polymers can be strongly promoted [1]. This ligation represents an autocatalytic step in a positive feedback loop in which the liquid crystal structure selects, organizes and polymerizes molecules, thereby enhancing its own stability. Recently it has been shown that Deoxynucleotide Triphosphates (dNTPs) in aqueous solution form duplex base pair stacks that order into columnar liquid crystal phases [2]. Here we investigate the self-assembly behavior of Ribonucleosidal Triphosphates (rNTPs), exploring aqueous mixtures of rATP and rUTP, and of rATP and dTTP, for liquid crystal ordering. The liquid crystal behavior of these mixtures was assayed by polarized light microscopy. These observations showed that mixtures with equimolar concentrations of rATP and dTTP exhibited liquid crystal behavior [Figure 1]. Liquid crystal odering in the rATP and rUTP mixtures has yet to be observed under similar conditions. The observation of columnar phase in the rATP and dTTP mixtures, indicates that they are potential candidates for exploring the effect of liquid crystal ordering on ligation based on pyrophosphate elimination.

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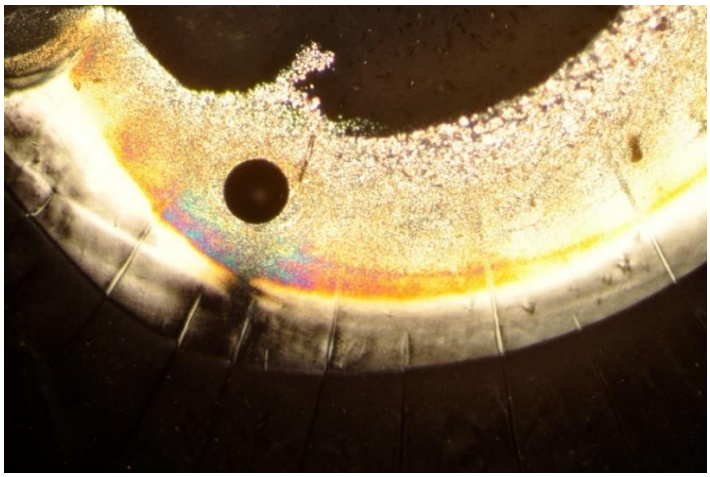

Figure 1 – Polarized Light Microscopy image of RNA Adenosine Trisphosphate (ATP) and Deoxythymidine Triphosphate (dTTP) liquid crystal phases.

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Fuller-Clarke Sphere

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Introduction: The purpose of the Fuller-Clarke Sphere (F-C Sphere) is to provide planetary services analogous to a Dyson Sphere [1] but scaled down to planet size and combined with Arthur C. Clarke's (et.al.) Space Elevator [2] concept. Space Elevators are strategically placed on the planet based on R. Buckminster Fuller's "Great Circles" [3] of a geodesic sphere constructed around the planet using material harvested from the asteroid belt. The F-C Sphere, a Civilization Type ~I.V invention [4], is parked in geostationary orbit and conceived for Planetary Defense from collisions with >~100-m class asteroids (NEOs). It is envisioned as a network of geodesic frames and interconnecting flexible lattice structure nets arrayed within the geo-grid surrounding the planet. In a worst case scenario, the space frame grid is sacrificial - it catches and crumples; collapsing or stretching to absorb the shock of an incoming extinction event asteroid. The F-C Sphere is also principally and globally utilitarian. Given the scale of engineering required, the primary geodesic great circle chords will necessarily be large diameter sections capable of being inhabited and used for planetary circulation; connecting 12 Space Elevator/Space Station vertexes corresponding to the icosahedron vertex point. The natural urbanization at Space Elevator locations will expand the planet's living volume, invoking space ports, transport conduits, energy and resource conveyance, solar collecting or albedo shading, planetary monitoring, communications (without satellites), and orbital station-keeping technology to mention a few. If an NEO approaches on a collision course, internal rail (Hyperloops [5]) shunt inhabitants (commuters around the planet) to safe areas of the 'geo-grid' beyond the crumple zone. Entire inhabited lengths can also jettison off of the great circles or any occupied tributary structural 'spines'. External rail/conveyance systems can provide mobilization of utilities, telescope, or a myriad of space monitoring technology while a rail/conveyance system on the earthward side provides global planetary services and monitoring.

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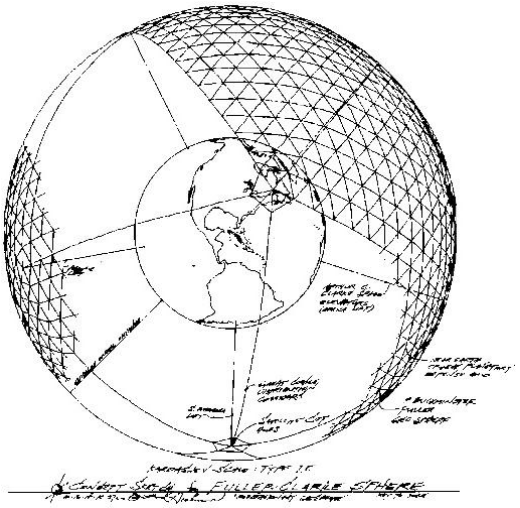

Figure 1 – Schematic Sketch of the **Fuller-Clarke Sphere**

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Functional Interactions Between Early Biopolymers and Primitive Cells

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Introduction: Due to the lack of coded protein synthesis, early life necessarily would have exhibited less-sophisticated catalysts and regulatory molecules in comparison to contemporary life. Despite the extraordinary progress made in the past several decades in employing ribozymes and simple peptides in model primitive proto-biochemical reactions, the range and efficiency of reactions possible using these model prebiotic catalysts is substantially less than that observed using modern protein enzymes synthesized by coded ribosomal synthesis.

Recently, we have demonstrated that compartmentalized biopolymers can exhibit a range of functional behaviors not observed in bulk solution. In a few recent examples, we have observed that the presence of random-sequence RNAs can enable upregulation of ribozyme activity in a growing model protocell [1], a simple dipeptide catalyst, when encapsulated inside a model protocell liposome, can catalyze a chemical reaction enabling growth of catalyst-containing liposomes at the expense of those lacking it, representing a primitive form of Darwinian fitness [2], and that a protein enzyme can perform a chemical transformation on a water-insoluble substrate only when encapsulated inside liposomes [3]. I will present our recent results in such systems, which, taken together, suggest that a wide suite of synthetic and regulatory processes might have been enabled by the interaction of primitive biopolymers and protocell membranes.

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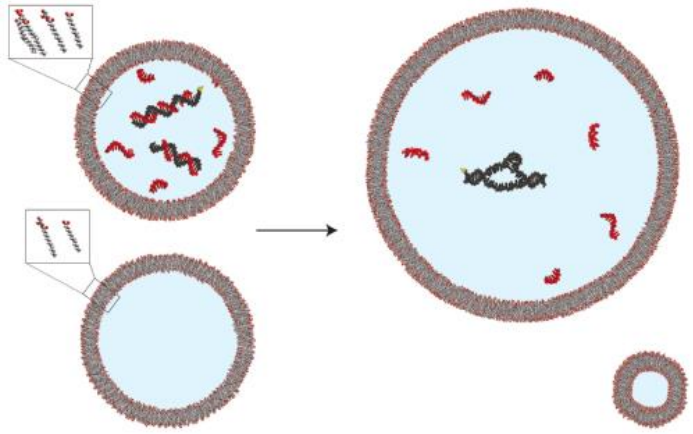

Figure 1 – **Regulation of enzyme activity in model protocells by dissociation of short complementary oligonucleotides.** Mixed fatty acid-glycerol ester-phospholipid vesicles that contain split ribozymes (blue) and high concentrations of short oligonucleotides (red) exhibit no ribozyme activity, due to inhibition by duplex formation between the ribozyme fragments and complementary oligonucleotides (top left). When mixed with vesicles lacking phospholipid (bottom left), the phospholipid-containing vesicles grow at the expense of the phospholipid-lacking vesicles. This growth results in dilution of vesicle contents, inhibitor dissociation, and ribozyme reconstitution (right), increasing catalyst activity in the enlarged vesicles. Figure and caption from [1].

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Amplification of RNA by an RNA Polymerase Ribozyme

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Introduction: In all extant life, genetic information is stored in nucleic acids that are replicated by polymerase proteins. In the hypothesized RNA world, prior to the evolution of genetically-encoded proteins, ancestral organisms contained RNA genes that were replicated by an RNA polymerase ribozyme [1,2]. In an effort toward reconstructing RNA-based life in the laboratory, in vitro evolution was used to improve dramatically the activity and generality of an RNA polymerase ribozyme by selecting variants that can synthesize functional RNA molecules from an RNA template [3]. The improved polymerase ribozyme (fig. 1A) is able to synthesize a variety of complex structured RNAs, including aptamers, ribozymes, and, in low yield, even tRNA. The polymerase can also transcribe, with more modest activity, template RNA into nucleic acid analogs, including threose nucleic acid (TNA). Furthermore, the polymerase can replicate nucleic acids, amplifying short RNA templates by more than 10,000-fold in an RNA-catalyzed form of the polymerase chain reaction (riboPCR, fig. 1B). Thus the two prerequisites of Darwinian life — the replication of genetic information and its conversion into functional molecules — can now be accomplished with RNA in the complete absence of proteins. Currently, polymerases are undergoing in vitro evolution to synthesize complete functional ribozymes within minutes, with the aim of achieving fully autonomous RNA replication of the polymerase itself and other ribozymes of similar complexity. Such a general RNA replicase could, under appropriate conditions, achieve self-sustained Darwinian evolution and would arguably constitute a synthetic form of RNA life.

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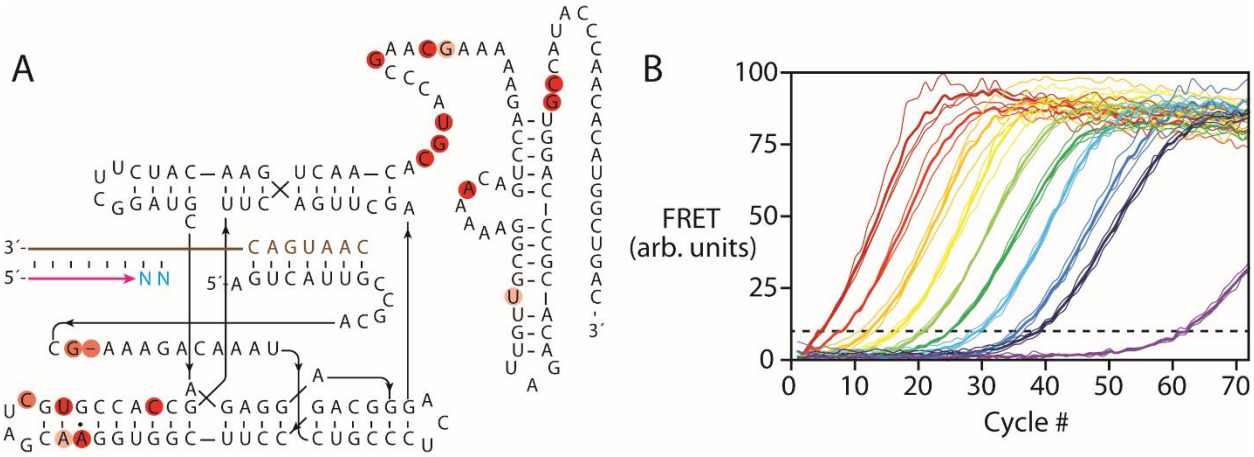

Figure 1 – (A) Sequence and secondary structure of a polymerase ribozyme isolated after 24 rounds of in vitro evolution. Red circles indicate mutations relative to the parental sequence, with color intensity corresponding to the frequency of each mutation in the round 24 population. (B) Real-time riboPCR of a 20-nt template, tracked by FRET between labeled primers in the dsRNA product. Starting template concentration spanned four orders of magnitude, from 10 nM (dark red) to 1 pM (indigo), while primers were at 200 nM.

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RNA-Catalyzed Polymerization and Replication of RNA

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Introduction: According to the RNA world hypothesis, ancestors of extant life stored and expressed genetic information in RNA molecules that were replicated by an RNA polymerase ribozyme. In an effort to reconstruct RNA-based life, *in vitro* evolution was used to improve the activity and generality of an RNA polymerase ribozyme by selecting for variants that can synthesize functional RNA molecules from an RNA template using the four nucleoside 5′-triphosphates (NTPs). The resulting polymerase can synthesize a variety of complex structured RNAs, including aptamers, ribozymes, and tRNA [1]. Furthermore, the polymerase can replicate and amplify short RNA templates in an RNA-catalyzed form of the polymerase chain reaction.

Enhanced RNA polymerase activity: The evolving population of polymerase ribozymes were challenged to synthesize two different RNA aptamers and to copy "difficult" templates that are either purine-rich or contain elements of stable secondary structure. The resulting ribozymes then were challenged to synthesize the hammerhead ribozyme, with selection based on the catalytic function of the synthesized product. This process placed strong selection pressure on the rapid and accurate synthesis of a complex RNA. The current best polymerase ribozyme is able to copy most template sequences, including pairs of complementary sequences. Thus it is able to function as an RNA replicase, achieving the exponential amplification of RNA molecules through repeated cycles of primer annealing, primer extension, and strand separation.

Reverse transcriptase activity: The evolved RNA polymerase ribozyme also has the ability to synthesize DNA molecules from an RNA template using the four dNTPs. This activity would have been crucial for the transition from RNA genomes to DNA genomes during the early history of life on Earth. Although the ribozyme prefers C-rich templates, it is able to incorporate all four dNTPs in good yield and with high fidelity. Further *in vitro* evolution experiments are being carried out to optimize reverse transcriptase activitity, as well as to explore the DNA-templated polymerization of both RNA and DNA.

Self-assembly of ribozyme fragments: The RNA polymerase ribozyme was divided into four fragments that can assemble non-covalently to form a functional enzyme. Two of the divisions have no significant effect on polymerase activity, but the third reduces activity significantly. *In vitro* evolution is being used to devise a better segmentation strategy for the third division to attain full catalytic activity. The aim is to use the non-covalently assembled ribozyme to synthesize each of the four component fragments, as well as their complements, to achieve the RNA-catalyzed exponential amplification of the ribozyme itself. Self-replication and self-sustained evolution of RNA has previously been achieved only in the special case where a ribozyme joins two pre-formed fragments to produce additional copies of itself [2]. Open-ended Darwinian evolution will require that the ribozyme also synthesize the component fragments, which then are either covalently ligated or non-covalently assembled to form a functional replicase ribozyme.

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Necessities for the First Life to Emerge

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Introduction: The origin of life remains unsolved still now, in spite of strenuous efforts of many researchers. On the other hand, all organisms on the Earth inhabit under the fundamental life system composed of gene, genetic code, protein (metabolism). Therefore, the most important point for elucidating the origin of life should be to make clear how the first life system was established [1].

Theoretical Consideration: Then, I propose here the conditions required for emergence of the first life on the primitive Earth, in order of protein, genetic code and gene.

1. Condition for formation of the first protein

Catalytic activity out of many functions of protein is the most essential for life. Therefore, even the first protein must be folded into water-soluble globular structure to exhibit catalytic function in the absence of any genetic function. This means that the first protein must be produced by random joining of amino acids in a protein 0^{th}-order structure or a specific amino acid composition, in which water-soluble globular protein with more flexible structure than extant mature protein can be synthesized by random joining of amino acids at a high probability.

2. Condition for formation of the first genetic code

Genetic code is always used for bridging over between genetic function and protein synthesis. Therefore, the first genetic code must encode a protein 0^{th}-order structure, so that polypeptide chain synthesized under the genetic code can be folded into water-soluble globular structure.

3. Condition for formation of the first gene

Genetic information or base sequence for protein synthesis cannot be designed previously. Therefore, the first gene must be created by random joining of nucleotides under the first genetic code. This means that formation of the first gene would meet with a large difficulty. On the other hand, even the first life could not live with only one gene encoding one protein. This indicates that many homologous genes and entirely new genes must be produced from sense and antisense sequences of the first double-stranded gene, respectively.

Discussion: Water-soluble globular [GADV]-protein, actually aggregate of [GADV]-peptides, can be produced by random joining of [GADV]-amino acids at a high probability, because [GADV]-amino acid composition is one of protein 0^{th}-order structures, which satisfies four conditions (hydrophobicity/hydrophilicity, α-helix, β-sheet and turn/coil formabilities) for formation of water-soluble globular protein [2]. We have previously proposed GNC code encoding [GADV]-amino acids as the first genetic code and $(GNC)_n$ sequence as the first gene [2]. Therefore, polypeptide chain synthesized under the genetic code could be folded into water-soluble globular structure, and various homologous and entirely new genes can be produced from sense and antisense sequences of the first double-stranded $(GNC)_n$ gene after gene duplication, respectively. Based on the above consideration, it is assumed that the first life emerged on the primitive Earth, according to [GADV]-protein world hypothesis or GADV hypothesis [1, 3].

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Protein 0th-order Structure is encoded onto GC-NSF(a) base sequence

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Introduction: We have proposed [GADV]-protein world hypothesis (GADV hypothesis in short) on the origin of life, assuming that life originated from [GADV]-protein world, which was formed by pseudo-replication of [GADV]-protein. [GADV] means four amino acids; glycine [G], alanine [A], aspartic acid [D] and valine [V] [1, 2]. On the other hand, GC-NSF(a) hypothesis for entirely new (EntNew) gene formation in extant microorganisms triggered the discovery of the GADV hypothesis [1-3]. GC-NSF(a) is derived from non-stop frame on antisense strand of GC-rich gene. Therefore, it is quite important for both GC-NSF(a) hypothesis itself and GADV hypothesis to confirm whether EntNew gene is actually created from GC-NSF(a) or not. Oi and Ikehara have obtained direct evidence for the GC-NSF(a) hypothesis, as presented in Poster session in this conference.

Protein 0th-order structure on GC-NSF(a): We discuss on the reason why EntNew gene/protein is easily produced in this presentation, based on protein 0th-order structure or a specific amino acid composition, in which even random joining of amino acids produces water-soluble globular protein with slightly more flexible structure than extant or mature protein at a high probability. The reason is because protein 0th-order structure is written onto GC-NSF(a), as described below.

(1) A large number of different amino acid sequences, at least more than 10^{22}, could be encoded on one antisense strand of a GC-rich gene, because of degeneracy of the genetic code.
(2) Every amino acid sequence encoded by GC-NSF(a) is quite different from that of any previously existing proteins.
(3) One amino acid sequence encoded by a GC-NSF(a) can generate an extraordinary large number (more than 10^{24}) of different protein structures, owing to flexiblity of the protein. This means that a GC-NSF(a) carrying actually one amino acid sequence can encode substantially the large number of protein structures in protein 0th-order structure.
(4) Once a weak catalytic activity for a substrate was detected on a surface of one of the large number of protein structures, the immature protein gradually evolves to a mature enzyme, through introduction of necessary base replacements onto the GC-NSF(a) (Figure 1).
(5) Thus, a catalytic activity necessary to adapt for a new environment can be searched out from the protein 0th-order structure written onto one antisense sequence of a GC-rich gene.

We have considered that life emerged from [GADV]-protein world, which was established by pseudo-replication of [GADV]-protein in one of protein 0th-order structures, [GADV]-amino acids. Thus, the idea, protein 0th-order structure, is indispensable for understanding not only the origin of life but also evolution of fundamental life system composed of gene and protein.

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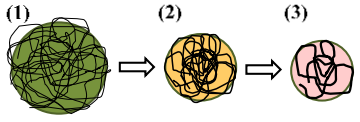

Figure 1. An immature protein (1) with a weak catalytic activity evolves gradually to a mature enzyme (3) with a higher activity and rigid structure through an intermediate (2), as accumulating necessary base replacements onto GC-NSF(a).

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Formation of Outer Shells from Proteinoid Microspheres

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Introduction: Modern organisms are composed of cells for physical compartments. For origins of life, physical compartments are believed to be important. Proteinoids are macromolecules formed by heating a mixture of amino acids, and they have similar composition to proteins[1]. Proteinoids form into microspherical structure in aqueous solutions by heating and cooling[1]. Proteinoid microspheres can form outer shells with increasing pH or thermal gradient[2,3]. Haruna considered that the flow of melted proteinoid molecules formed outer shells[4]. In this study, we elucidated the mechanism of formation of outer shells from proteinoid microspheres with thermal gradient.

Materials and Methods: For this purpose, we examined whether the forced flow of proteinoids formed outer shells from proteinoid microspheres. The heated proteinoid solution was made to flow in the channel that proteinoid microspheres put on. In addition, we made another experiment that the proteinoid solution was kept the temperature constant in thermostatic oven.

Results: When forced flow was given to proteoid microspheres, microspheres began to dissolve and outer shells were formed in about 30 to 60 minutes. Outer shells were not formed when only flow was given, but when only heat (above 40℃) was given, outer shells were formed after 48 hours.

Conclusion: We conclude that formation of outer shells from proteoid microspheres with thermal gradient was caused by dissolution of proteinoid microspheres. Furthermore, we found that the addition of flow promotes the formation of outer shell as compared with heat only.

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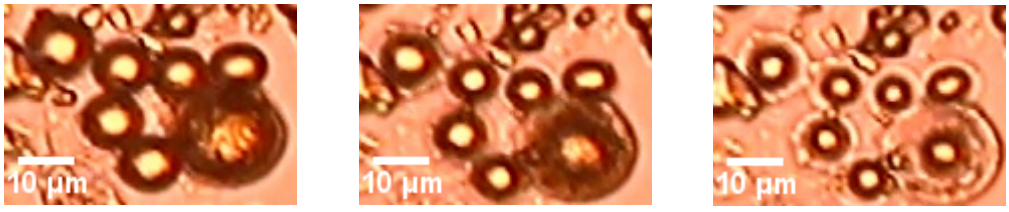

(a) 0min (b) 30min (c) 60min

Figure 1 – Formation of outer shells with forced flow

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Structural analysis of monomeric RNA-dependent polymerases

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Introduction: Due to their role in replication, transcription, and reverse transcription, RNA-dependent RNA polymerases (RdRp) and reverse transcriptases (RT) are key enzymes in the viral biological cycle. Over 20 distinct viral RNA polymerases crystals from the four main RNA viral groups have been obtained. They are characterized by a right hand architecture with three functional subdomains, i.e. fingers, palm and thumb [1]; and a two metal ion mechanism of action. We present here a phylogenetic tree built based on comparisons of RdRps and RTs' tertiary structures.

Material and Methods: Pairwise structural comparisons between the different RdRps and RTs were performed with the Secondary Structure Matching program. A geometric distance measure was then estimated for each of the comparisons using the Structural Alignment Score, which is calculated according to the following formula: (RMSD x 100)/number of aligned residues. The program FITCH, was used to transform the geometric distance into an evolutionary distance

Results*:* The unrooted phylogeny we have constructed using structural comparisons is shown in Fig.1. Single-stranded positive and double-stranded RNA viruses do not form well-defined clades, they are interspersed in different branches, each of them clustering one or two viral families. In the tree shown in Fig. 1, one branch groups ss(-)RNA viruses, i.e., the LaCrosse virus and the Orthomyxoviridae family polymerases. The longest and most distant branch groups together the RTs with the eukaryotic telomerase stemming close to the root of this clade.

Conclusion: In this work we have constructed a tertiary structure-based phylogeny that includes viral RdRps and RTs, as well as an eukaryotic telomerase. All known viral RNA polymerases are homologous monomeric enzymes. It is interesting to note that the tree presented here [1] is not consistent with the Baltimore classification of RNA viruses, suggesting the polyphyly of changes in template organization. The conserved structural similarity of the RdRps palm subdomain with the viral and cellular DNA polymerases is consistent with the hypothesis that it is one of oldest identifiable structural domains present in extant viruses and cells [2].

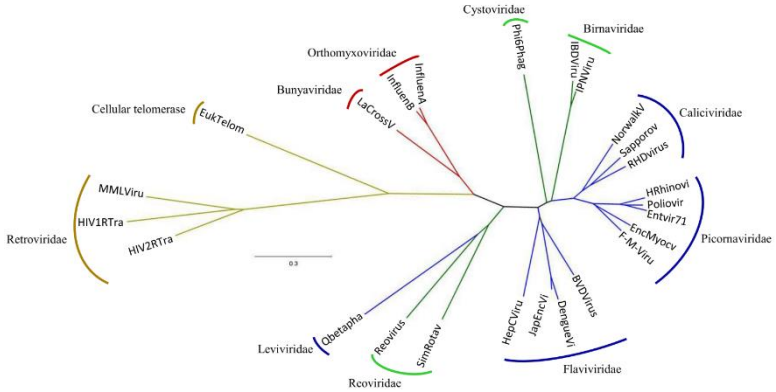

Figure 1. Unrooted dendogram based on the comparisons of RdRps and RTs tertiary structures

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Interaction of Alanine and Aspartic acid with Aluminum, Iron and Zinc Oxides and its Relevance in Chemical Evolution

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Metal oxides are important constituents of earth crust and other planets therefore it is proposed that metal oxides present on earth or in the primeval seas must have catalyzed different biochemical reactions during the course of chemical evolution on primitive earth [1-3]. The present work described interaction of alanine and aspartic acid with aluminum, iron and zinc oxides. Adsorption of amino acids on metal oxides followed Langmuir adsorption model in general in the concentration range 10^{-3} M to 10^{-4} M. Langmuir constants b and Q_o were calculated. Results in present study indicated that adsorption favoured the acidic medium (pH 1.0- 4.0) followed by neutral and finally basic medium. Adsorption of both amino acids on metal oxides follow the order: aluminum oxide > iron oxide > zinc oxide. Aspartic acid was found to be highly adsorbed on all metal oxides in comparison to alanine this may be due to availability of more bonding sites on the aspartic acid. Amino acids are considered to interact with positive charge surface of the metal oxides. The present study suggested that metal oxides might have played a role in stabilization of bioorganic molecules through their surface activity during the course of chemical evolution on primitive earth.

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SELF-ASSEMBLY OF MULTIPLE SMALL RNA FRAGMENTS INTO AN AUTOCATALYTIC PREBIOTIC SYSTEM

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Introduction: The RNA World is the therotical idea that there was a period in the early history of life on Earth when RNA, or something chemically very similar, carried out most of the information processing and metabolic transformations needed for biology to emerge from chemistry. The finding of the catalytic nature of RNA molecules in 1982 by Thomas Cech and Sid Altman demonstrated that RNA could catalyze chemical reactions[1], which supports to the "RNA World" hypothesis. One type of these catalytic RNAs, or ribozymes, is the group I intron, which splices itself out of a nascent transcript using RNA-RNA recombination reactions. Life is based on biopolymers that have the ability to replicate themselves. Ferris *et al.*[2] described the abiotic synthesis of long prebiotic oligomers from activated monomers on catalytic montmorillonite surface. The importance of that study[2] is that it also showed that oligomers with length in the range of 20-30 monomers were abundant than the longer ones under prebiotic conditions. Here, we consider how an autocatalytic self-replicating RNA system may have originated from inactive shorter RNA fragmentsts. In an effort to find out how life emerged from chemistry, it would be useful to be able to demonstrate that even shorter RNA oligomers can form stable catalytically active contiguous ribozymes *in vitro*. This study describes a system that models prebiotic formation of a catalytically active ribozyme by the recombination of inactive RNA oligonucleotides. For a prebiotic system, we use the covalently self-assembling *Azoarcus* tRNA intron, which was previously described[3]. This system entails the self-assembly of *Azoarcus* ribozyme system from two, three or four inactive RNA fragments of about 50 nucleotides each: W, X, Y and Z. Here we show the fragmentation and covalent self-assembly of the *Azoarcus* group I intron from five shorter inactive RNA fragments. Experiments were performed by analyzing the self-assembly of a group I intron from RNA fragments as short as 18 nucleotides. Self-assembly reactions were tested at 48^0C with 25mM Mg^{2+} concentration in aqueous solutions with 2µM RNA. Moreover, these self-assembly reactions are being tested under different hydration and dehydration conditions for a lengthy period of time to analyze how early Earth conditions such as evaporation, and rehydration could affect the replication of an autocatalytic system. Concentrating through evaporation helps the five-piece system to function efficiently when all the fragments come together. This kind of cooperation is potentially important for the emergence of life. Now we are able to show successfully that five small inactive RNA fragments can self-assemble into a catalytically active covalent contiguous ribozyme via RNA-directed recombination. Furthermore, this system illustrates that continuous cycles of hydration-dehydraion enhance the chances that random shorter oligomers will recombine and cooperate well in an autocatalytic system fashion to initial reproduction.

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Hypothesis: ncRNA - cellular activity controller?

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Abstract

Except for DNA viruses, RNAs are widespread in biological systems and are involved in multilaterally adapted systems that control numerous cellular processes, the dimensions of which are still being explored. Principally, there are two broad categories of RNAs, namely coding and non-coding (ncRNA) and this abstract refers to the latter. The ncRNA molecules can form primary structures of approximately 22 nucleotides, as in "guided single stranded microRNAs" (ss(mi)RNA); double stranded miRNA interference segments can exist as a secondary shape; tertiary architectures are common in self-splicing group I and II introns; and, in association with proteins, quaternary structures can be formed eg RNA-induced silencing complex (RISC) and ribosomes. Such structures are multifunctional and are broadly regulatory, being involved in gene regulation as well as interfering with and the processing of both small and large RNAs. Such processing actions are well orchestrated, even to the point of efficient shredding of any unwanted RNAs - for example "used" mRNA within the cell is degraded rapidly (via RISC centres), so as to prevent them from being translated further.

Recent discoveries have also demonstrated that ncRNAs can act as riboswitches (eg glmS ribozymes), whereby they regulate their own activity; and perform genetic control by a metabolite binding mRNA. Furthermore, ncRNAs can act as triggers against invading mobile genetic elements, thereby affording protection against incoming attacks by "parasitic" nucleotide sequences, viruses, transposons, etc. ncRNAs, in addition to ribozymatic activities and carrying genetic codes such as influenza (RNA virus) are significant in that the hallmark of their modular architectural structure implies that structural and possible functional similarities exist among ncRNAs. A unique aspect of ncRNAs is that they are highly conserved and it is thought that they are molecular relics which delineated a 'hypothetical' entity called the "last universal common ancestor" (LUCA), which pre-dated the three domains of life, namely Archaea, Bacteria and Eukarya.

The conserved nature of ncRNAs allows to us to posit that it is highly probable that these molecules still have overall control of cellular activity. This is particularly relevant as there are large number of newly discovered ncRNAs whose functions are still to be explained and validated. During this oral presentation, I will put a case for ncRNAs being involved in the overall control of cellular activity and speculate that this 'cellular activity control' is passed on from one generation to the next.

Fe^{2+} in Prebiotic Non-enzymatic RNA Chemistry and Early Compartmentation

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Iron, one of the most abundant elements on earth, has long been interested for its impact on origin of life. 30 years ago, Wächtershäuser's Iron-sulfur world hypothesis proposed that the catalytic transition metal solid surfaces in hydrothermal vents helped to form the metallo-peptides, which was considered precursors of life. However, in the RNA world hypothesis for abiogenesis, it is not obvious to find the linkage between iron and genetic materials. Inspired by the distinctive role Mg^{2+} plays in modern biology for RNA folding and catalysis, we wonder whether Fe^{2+}, with the same charge and similar ionic radius as Mg^{2+}, could potentially be the ancient RNA cofactor and catalyze non-enzymatic RNA chemistry on anoxic earth. Here, in anaerobic glove box, we study the catalytic effect of Fe^{2+} for non-enzymatic template-directed RNA polymerization and ligation, which are key reactions to achieve the RNA self-replication. We found not only could Fe^{2+} replace Mg^{2+} for these reactions, it also performs much better in near neutral to slightly acidic pH condition and still maintains its catalytic role in low concentration. On this other side, compatibility of Fe^{2+} to fatty acid vesicles is also studied for early cellularization. With the help of citric acid and amino acids as iron chelators, we are able to perform non-enzymatic RNA replication and hammerhead ribozyme self-cleavage inside oleic acid protocells. Our results highly suggest that the abundant Fe^{2+} before great oxygenation event on early earth is closely related to the RNA world and protocell function for origin of life study.

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The total number of possible genetic codes with 64 triplets, 20 amino acids, and one stop signal

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Abstract: The question about the existence of different genetic codes in other regions of the universe is open, as open is the question of the existence of life in other planets of this or other galaxies. If we assume that the four RNA nucleotides C, U, A, G and 20 natural amino acids are the same as in the current standard code, a great number of possible different codes may exist. In this work, we count all the possible genetic codes with some properties in common with the current standard code. In all cases, we assume that there are the 4 RNA nucleotide bases C, U, A, G and 20 amino acids, plus a symbol s with the role of stop signal. We present 3 cases: 1. The subsets A_i of elements of the set $A_S = A \cup \{S\}$, where A denotes the set of 20 amino acids, which have the same number i of coding triplets, being $i \in \{1,2,3,4,5,6\}$, are the same of the current standard code. There are five different kinds of amino acids, according to the numbers of their coding triplets. It is well known that, for every amino acid, and even for the stop signal, the number of coding triplets is equal to 1, 2, 3, 4, or 6. 2. We assume that the subsets A_i of i-coded elements have the same cardinalities of those of the current standard code, that is, the numbers 2, 9, 2, 5 and 3, which conform a partition of the number $21 = 2+9+2+5+3$. 3. In the more general case, we do not assume any restriction about the number of coding triplets for every element of the set A_S. Then, the total number of possible codes will be the total number of surjective functions $F: NNN \to A_S$, from the set NNN, of the 64 triplets, onto the set A_S of the 20 amino acids plus the stop signal. The standard genetic code is, in essence, a surjective function $F: NNN \to A_S$. The fact that this function F is not injective means that the code is degenerated. The calculated numbers permit to calculate the probabilities of having different genetic codes in our universe. Given the recent discovery of several exo-planets which may show conditions for the existence of life, we discuss the present results in terms of how universal may be the universal genetic code.

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Stability of Amphiphilic Systems in Terrestrial Hydrothermal Fields and its Implications for the Origin of Cellular Life

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Introduction: Deciphering how life would have chemically originated continues to be an intriguing mystery. Although the exact sequence of events still remains elusive, a good body of research has narrowed down possible processes that would have been crucial for the transition from chemistry to biology. One pertinent aspect is to understanding the abiogenic origin of polymers on the early Earth. Formation of polymers would have been a fundamental step in the aforementioned transition as most life functions in extant biology are performed by different polymers. Several theories have been put forth in this regard [1, 2]. A theme common to many of these theories suggests that these uphill processes would have been chemically driven in environments that were subjected to repeated cycles of dehydration and rehydration (DH-RH) [3]. Specifically, it is thought to have been driven by condensation of relevant monomers in niches such as prebiotic tidal pools and terrestrial hydrothermal fields [4]. Furthermore, catalytic clay minerals [5], eutectic ice phases [6] and dehydrated lipid matrices [4] have been shown to assist the formation of prebiotically relevant informational molecules [7, 8].

The lipid-assisted synthesis, in particular, has important prebiotic relevance as encapsulation of functional polymers in membranous structures is thought to have been a crucial step in kick-starting evolution of early cellular life [9]. Although extant cellular membranes are predominantly formed from complex lipids, primitive membranes are thought to have formed from simpler amphiphiles like fatty acids and their derivatives [10], whose formation has been shown to occur under specific conditions of pH and temperatures [11]. However, stability of such amphiphilic systems, to repeated cycles of dehydration and rehydration, has not yet been systematically characterized to our knowledge. This is also crucial for evaluating the role of such amphiphilic systems on prebiotically relevant processes, such as the origin of informational polymers under volcanic geothermal conditions.

In this study, the stability of mixed fatty acid vesicles was characterized in DH-RH regimes. Importantly, we also carried out a "realistic" study to evaluate the stability of these systems in hot spring samples that were collected from high altitude regions in Ladakh (India) during the first Spaceward Bound India expedition in Aug 2016. This expedition was undertaken to explore Ladakh; an Astrobiologically relevant site for the study of life under extreme conditions. Our results indicate that the stability of the mixed fatty acid systems varied with repeated cyles of dehydration and rehydration. Importantly, the geochemistry of the hot springs seemed to play a crucial role in determining this stability. In conclusion, our results indicate that the origin of early cellular life would have been, both, niche and geochemical context dependent.

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High Abundance of Borate in Hadean Proto-Arc Environments to form Prebiotic Ribose and Nucleotide?: Geological Constraints from Isua Supra-crustal Belt

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High abundance of borate is necessary to form prebiotic ribose under alkaline conditions [1]. On the other hand, it has been questoned if such borate-rich environments were present on the early Earth, because of uncertainties on (1) availability of boron source rocks, i.e., felsic igneous rocks and (2) mechanism to concentrate borate on the prebiotic Earth.

Proto-arc model has been proposed to explain tectonic evolution of 3.8 to 3.7 Ga Isua Supracrustal Belt, Greenland [2]. Felsic igneous rocks are present at ISB. Those felsic igneous rocks, which were source rocks of boron, were produced by metling of proto-arc materials at depth. Boron in felsic rocks could be extracted by deep fluids and transported further in distance. This model is supported by previous report [3]: boron-bearing fluids, generated around felsic igneous rocks, discharged into oceans as hydrothermal fluids, and precipitating tourmalines in isolated basin on proto-arc of ISB.

In addition, abundant tourmaline crystals are found in metamorphosed sedimentary rocks of ISB in the present study. These geological evidence suggest that 3.8 Ga ocean water already contained appreciable amounts of borate, and borate were enriched in specific basin and/or inside of marine sediments at 3.8 Ga Earth. Early Archean evaporite carbonate was reported from ISB [4]. These carbonate rocks were most likely formed in shallow, partially isolated and alkaline basin. Such basin was formed on platform of proto-arc. Therefore, boron-rich, alkaline and eveportae environments were also present at 3.8 Ga.

Here I propose that environments created by proto-arc were ideal not only for formation of felsic igneous rocks but also for prebiotic ribose and nucleotide formations at Hadean age. In isolated and shallow basin on Hadean proto-arc, evaporation may have helped to concentrate borate and phosphate, probably precipitating lüneburgite ($Mg_3B_2(PO_4)_2(OH)_6 \bullet 8H_2O$). Water in this isolated and shallow basin was alkaline. Lüneburgite further promote phosphorization of nucleoside [5]. Boron-rich and alkaline environments also expected locally at mud volcano and inside ofmarine sediments around proto-arc [6]. Formorse reaction could happen not only at shallow evaporite basin but also in deep marine environments around the Hadean proto-arc. As a result, ribose would have been the major aldopentose in Hadean proto-arc environments followed by formations of ribo-nuculeotiside and ribo-nucleotide by help of lüneburgite.

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July 16-21, 2017 at UC San Diego, CA, USA

Transition to Diversification by Limitation and Competition for Multiple Resources in Catalytic Reaction Networks

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All life, including cells and artificial protocells, must integrate diverse molecules into a single unit in order to reproduce. Despite expected pressure to evolve a simple system with the fastest replication speed, the mechanism by which the use of a great variety of components, and the co-existence of diverse cell-types with different compositions are achieved is as yet unknown.

Here, we show that coexistence of such diverse compositions and cell-types is the result of limitation and competition for a variety of resources, by theoretically studying a cell system with catalytic reaction dynamics that grows by uptake of environmental resources. We find that a transition to diversity occurs both in chemical components and in protocell types, as the resource supply is decreased, when the maximum inflow and consumption of resources are balanced[1]. In addition, we find negative scaling relationship between molecular diversity and resource abundances to achieve the maximum growth speed of the cell[2]. The maximum growth is determined by a trade-off between the utility of diverse resources and the concentration onto fewer components to increase the reaction rate.

Our results indicate that a simple physical principle of competition for a variety of limiting resources can be a strong driving force to diversify intracellular dynamics of a catalytic reaction network and to develop diverse protocell types in a primitive stage of life.

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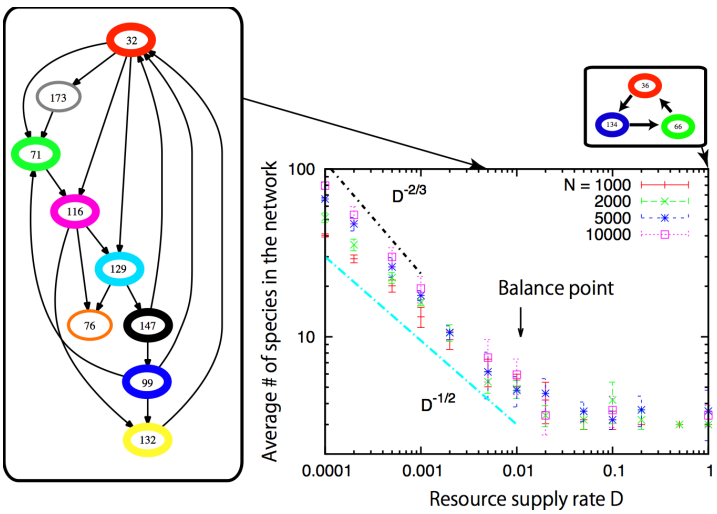

Figure 1 – The average number of species in each cell as a function of resource supply rate D. The diversity, i.e., the number of species in each cell, transits to increase as D is decreased below the balance point. Examples of the catalytic networks formed by molecular species are shown for the values of D indicated by the arrows.

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Influence of Nucleic Acid Intercalators on Model Proto-Nucleotide Supramolecular Assemblies

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The observations that the nucleobases of RNA do not assemble in water as free bases or as mononucleotides presents a significant challenge to the proposal that RNA was the first genetic polymer of life.[1] We are investigating two potential solutions to this problem: 1) that certain prebiotic molecules facilitated nucleic acid polymerization by acting as nanometer-scale surfaces that stabilized base pair formation through non-covalent interactions (the 'molecular midwife' hypothesis), and 2) that RNA has evolved from an ancestral polymer that contained nucleobases that had an intrinsic ability to base pair at the monomer level (the hypothesis RNA is the product of evolution). Previously, small molecules that are known to intercalate between the base pairs of DNA and RNA have been shown to facilitate oligonucleotide polymerization and enhance the stability of duplexes with incompatible backbones,[2-3] results that lend support to the molecular midwife hypothesis. It has also been demonstrated that four plausibly prebiotic heterocycles that are similar in structure to the extant nucleobases of RNA base pair in aqueous solution at the monomer level to form linear supramolecular assemblies,[4-6] results that lend support to the hypothesis that the earliest nucleic acids contained different bases. We are now investigating the potential for known nucleic acids intercalators, as model midwife molecules, to alter the supramolecular structures formed by self-assembling model proto-nucleobases. In the absence of intercalators some of these model proto-nucleobases/nuceotides form assemblies that are microns in length (Fig. 1A). The introduction of cationic intercalators, such a ethidium, to these samples shorten the linear assemblies to discreate fibers of remarkably uniform length (Fig. 1B). In contrast, when purine is added to a solution containing proto-nucleobases/nucleotides that form shorter fibers (Fig. 1C), the assemblies are lengthened and appear to be extremely straight (Fig. 1D). The possible physical underpinnings of these observed phenomena and their potential relevance to the origins of nucleic acids will be discussed.

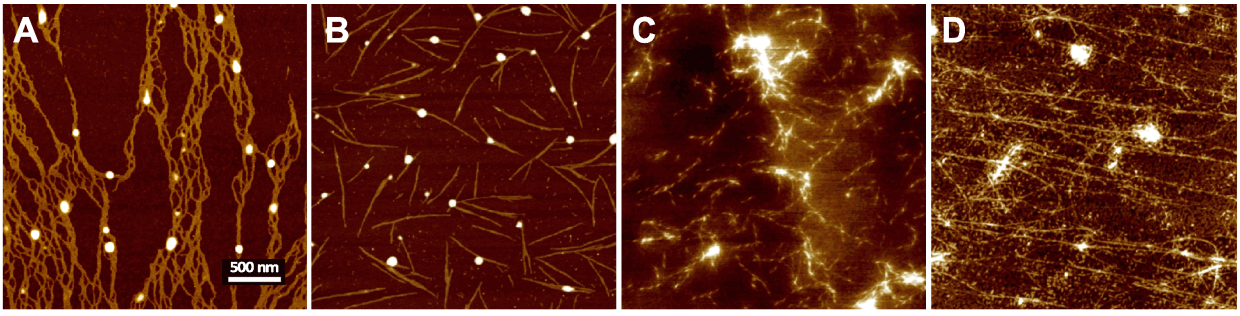

Figure 1 (A) AFM image of 2,4,6-triaminopyrimidine mixed with hexanoic acid-modified cyanuric acid. (B) Sample A after the addition of 1 mM ethidium. (C) AFM image of assemblies formed by melamine-ribosyl-monophosphate and barbituric acid-glucosyl-monophosphate. (D) Sample C after the addition of 50 mM purine.

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Two Gene Hypothesis for the Initiation of Life-like Systems towards the RNA World

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Introduction: In this study, the minimum number of genes for initiation of life-like systems was deduced on the basis of characteristics of RNA molecules and the characteristics of life-like systems [1]. RNA played important roles in the emergence of the first life-like system on primitive Earth since RNA molecules involve both genetic informational and catalytic functions. However, there are several drawbacks regarding the RNA world hypothesis. However, it is necessary to identify what kinds of elemental functions with RNA molecules were essential for the initiation of life-like systems. I have conducted a conceptual analysis of the characteristics of biosystems as a useful approach to deduce a realistic life-like system regarding the definition of life on the basis of comparative analysis of biosystems at different hierarchical levels [2].

Inherent machinery for controlling information and metabolism at different hierarchical levels: Most materials found in life-like systems on the Earth involve the same type molecules for replication, information flow. Although this is true in life-like systems, such as prokaryote, eukaryote, multicellular organisms, social insects, and human societies, these systems can be categorized on what types of inherent machinery for controlling information are present at different hierarchical levels. For instance, the machinery for replication and transformation in eukaryotes is indeed separately carried out inside and outside the nucleus, while prokaryotes do not possess the corresponding mechanism in the cell. The differences among these systems on controlling machinery of bio information was described in detail in the previous paper, and then the machinery for controlling information was named as the central controlling system for information (CCSI) [1]. At the same time, it was shown that these systems possess inherent machinery for controlling inflow/outflow and formation/deformation of energy, material, and information beyond the border of the system. This wide meaning of metabolism machinery is dictated by the CCSI. This was named as the central controlling machinery for the inflow/outflow and formation/deformation of energy, materials and information from environments (CMIO).

Roles and importance of CCSI and CMIO for initiating life-like systems: The characteristics of life-like systems are dependent on the quality of CCSI and CMIO at different hierarchical levels. According to the analysis of relationship between CCSI and CMIO, the requisite that a system possesses both inherent mechanism for CCSI and CMIO would be necessary for initiation of the system as alive beyond the hierarchical level of building blocks. This finding suggests that the establishment of CCSI and CMIO and a linkage between CCSI and CMIO should have been an essential event for emergence of most primitive chemical system resulting a life-like system. For the formation of CCSI, the assumption that the replicase should be essential is deduced on the basis of verification of the RNA world hypothesis. This is equated to that one gene is essential for emergence of CCSI. On the other hand, one gene is also essential for initiation of CMIO as details were discussed [1].

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Mineral-Mediated Chemical Evolution of RNA and Related Molecules Compatible with the Hadean Environments

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RNA world under the Hadean environments: Before the RNA-based or RNA-protein-based life-like systems towards the last universal common ancestor of the present organisms, RNA-like and protein-like molecules should have accumulated by chemical evolution processes from these monomeric materials under the primitive Earth conditions. It is reasonable that different types of naturally-occurring minerals could have played important roles, such as the catalytic formation, selection, and concentration of these biomolecules since these processes should have occurred in aqueous medium or water-rich environments. Extensive studies, such as prebiotic RNA formation in the presence of montmorillonite clay [1,2], have continuously supported experimentally this assumption. Nevertheless, it is also essential to verify whether the Hadean environments were compatible with chemical-physical plausibility of these processes.

Hydrothermal verifications: These chemical evolution experiments have been carried out somewhat or much more mild conditions as comparing with the plausible Hadean environments. We have developed a series of hydrothermal micro-flow reactor systems which enable to analyze chemical evolution processes at temperatures up to 400 ºC, pressures up to 35 MPa within the millisecond to second time scale (0.002 – 200 sec) [3]. On the other hand, a large diversity of the early Earth environments is taken into account. Thus, improvements for in situ monitoring of UV-visible absorption spectra and reactions in the presence of mineral particles were achieved [4,5]. These hydrothermal micro-flow reactor systems are useful for kinetic analysis of the stability and prebiotic formation of nucleotides, RNA, amino acids, peptides, and proteins, and thermodynamic investigation of interaction of biomolecules at high temperatures. By using these systems, we found efficient elongation of alanine peptide from $(Ala)_4$ to $(Ala)_5$ under the hydrothermal conditions, and this is enhanced with carbonate minerals, for instance [5,6]. In addition, we showed a possibility of RNA elongation at temperatures over 100 ºC in the presence of clay mineral [7] and the behavior of a ribozyme [8]. Further improvements of the hydrothermal flow systems are currently investigated [9].

Recently, we focused whether the elongation from $(Ala)_4$ to $(Ala)_5$ occur with or without hydrothermal conditions, and the roles of minerals of clay minerals for this elongation processes.

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Synthesis of Amino Acid Precursors with Organic Solids in Planetesimals with Liquid Water

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Introduction: Amino acids are important ingredients of origin of life, that would have been delivered to Earth by extraterrestrial sources, e.g., comets and asteroids. Amino acids are found in aqueously altered carbonaceous chondrites mainly in the form of precursors that release amino acids upon acid hydrolysis [e.g. 1]. Meanwhile, most of the organic carbon (>70 weight %) in carbonaceous chondrites exists in the form of solvent insoluble organic matter (IOM) with complex macromolecular structures [e.g. 2]. Complex macromolecular organic matter can be produced by either photolysis of interstellar ices [e.g. 3] or aqueous chemistry in planetesimals [e.g. 4]. We focused on the synthesis of amino acids during aqueous alteration, and demonstrated one-pot synthesis of a complex suite of amino acids simultaneously with IOM via hydrothermal experiments simulating the aqueous processing [5].

Experimental: We conducted hydrothermal experiments isothermally at 90°C up to 250°C for 72 hours with a starting solution containing formaldehyde, glycolaldehyde (the simplest condensate of formaldehyde), ammonia, and water with a molar ratio of $C/N/H_2O$ (7.2:0.72:100) and some $Ca(OH)_2$, following our previous method of organic solid synthesis [6]. This starting composition was selected on the basis of the assumption that organic matter in carbonaceous chondrites and comets was formed from a common precursor material that originated in the outer solar system and/or the interstellar medium. We studied the amino acid products by high performance liquid chromatography (HPLC) and ultra performance liquid chromatography with fluorescence detection/quadrupole time-of-flight hybrid mass spectrometry (UPLC-FD/QToF-MS).

Results and Discussion: Amino acid products from hydrothermal experiments after acid hydrolysis include α-, β-, and γ-amino acids up to five carbons, for which relative abundances are similar to those extracted from carbonaceous chondrites [5]. The amino acid abundances are much lower in the nonhydrolyzed fraction than in the acid-hydrolyzed fraction (10 times lower for glycine), which suggests that most of the amino acid experimental products are present as the bound form. The yield of amino acids after acid hydrolysis of our experimental products, ~20 μg of glycine relative to 20 mg of organic solids [6], is consistent with that in the Murchison meteorite, where yields of glycine and IOM are 7 μg/g and 20 mg/g, respectively [7]. Preliminary results from the experiments with the presence of minerals show that both montmorillonite (clay) and olivine enhance the yield of amino acids.

Conclusions: The aqueous chemistry in planetesimals, starting from ubiquitous simple molecules such as formaldehyde and ammonia, can possibly explain the wide variety of organic matter including amino acids and organic solids found in the aqueously altered chondrites.

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Stereoselective Prebiotic Nucleotide Synthesis for Threose Nucleic Acid

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The glycosidic bond formation from sugar and nucleic bases is one of the fundamental problems in prebiotic chemistry for the RNA world hypothesis. However, nucleoside synthesis from sugar and nucleobases has not been successful except the marginal success by Orgel and his coworkers.[1] Recently two studies (Sutherland[2] and Carell[3] groups) showed pyrimidine and purine nucleotide and nucleoside can be synthesized in plausible prebiotic condition. In those syntheses, the nucleobases were formed after their precursors were attached to sugar then converted to ribo-nucleotide or nucleoside.

Threose nucleic acid (TNA) is considered to be one of the plausible prebiotic genetic polymers.[4] In search of the prebiotic pathway of TNA building block (threose nucleoside or nucleotide), the reaction of threose and adenine was investigated. The reaction of threose and adenine gave condensation products in very high yield as an anomeric mixture (more than 70%) but the reaction occurs at the amino-group of the adenine. However the reaction of threose-1,2-cyclic phosphate and adenine provided threose-adenine nucleoside-2'-phosphate stereoselectively (Fig 1). This reaction did not proceed without divalent metal ions (Mg or Ca) which were almost certainly available prebiotically. The prebiotic synthetic pathway of threose-1,2-cyclic phosphate is well known in the literature.[5] The α-hydroxy aldehyde can be phosphorylated by amidotriphosphate in the presence of magnesium chloride. Threose (one of the α-hydroxy aldehydes) can be easily converted to threose-1,2-cyclic phosphate in high yield. Also, threose can be formed by the dimerization of glycolaldehyde under prebiotic plausible condition in high yield.

In this presention, the details of the synthesis of threose-adenine nucleotide and structural proof of the compound will be discussed.

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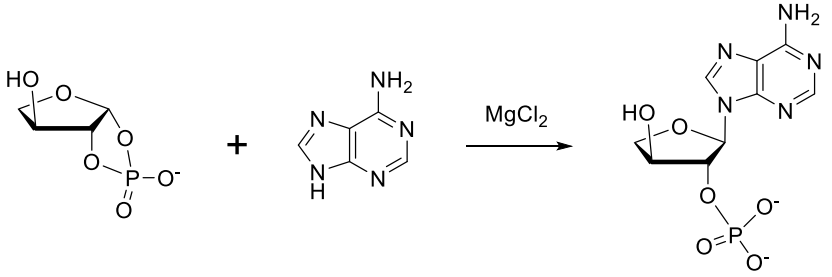

Figure 1 Reaction of threos-1,2-cyclic phosphate and adenine in the presence of magnesium ion provide threose-adenine nucleoside 2'-phosphate

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Improving mRNA-display for *in vitro* RNA-protein co-evolution

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Introduction: Biopolymers such as RNA, proteins and their complexes known as ribonucleoproteins (RNPs) play crucial roles in modern biology, sustaining the evolvability and chemical reactions for life. While the origin and evolution of these biopolymers remain largely elusive, recent advances in synthetic biology have allowed for the synthesis, screening, and evolution of RNA and protein polymers in an *in vitro* setting. Here, mRNA-display represents a powerful and high-throughput approach to probe large sequence spaces for screening functional peptides by the attachment of translated nascent peptide chains to the 3′-termini of their mRNA by employing puromycin (aminoacyl tRNA analog) as the linker. Combined with downstream high-throughput sequencing and recurring amplification/selection, mRNA-display allows for the mapping of trajectories of polymer evolution under specific selective pressures.

Currently, I am optimizing the mRNA-display method towards efficient sampling of primitive functional RNPs from random sets of sequences. One promising strategy for expanding the available sequence spaces is to improve the efficiency of puromycin's ability to enter the A site of the ribosome. Enhancing the efficiency of this key process will allow a greater number of mRNA-peptide conjugates to be synthesized expanding the potential to evolve complex catalytic functions. Considerably many factors can affect puromycin chemistry, i.e., linker design, chemical modification, temperature and pH. I will perform iterative analyses to optimize the covalent linkage of puromycin to the translated nascent peptide, by increasing affinity to the ribosomal A site, as well as covalent reactivity, by mRNA-display protocol optimization and chemical modification of puromycin itself. Expansion of the available sequence space in mRNA- display will not only contribute to understanding the origin of RNA-protein co-evolution, but could also have benefits for biotechnology and medicine. I look forward to discuss the latest results during the meeting.

July 16-21, 2017 at UC San Diego, CA, USA

Roles of Solar Energetic Particles in Production of Bioorganic Compounds in Primitive Earth Atmosphere

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Introduction: A large number of experiments have been conducted to examine possible formation of bioorganic compounds such as amino acids in the primitive Earth atmosphere. Amino acids were easily formed from strongly reducing gas mixtures by spark discharges, ultraviolet light, and other sources. Current models of the early Earth atmosphere were modified to less reducing environments, such as a mixture of CO_2, N_2 and trace amount of reducing carbon species like CH_4 [1]. Simulation experiments suggest, however, that amino acid formation is strongly inhibited under these conditions [2]. We examined the formation of amino acids from such slightly reducing gas mixtures by applying ionizing radiation to simulate the action of galactic and solar energetic particles, though they have been ignored as prebiotic energy sources for their lower energy fluxes [3].

Experimental: Gas mixtures of N_2, CO_2 and CH_4 (total 700 Torr) were introduced to a Pyrex tube together with 5 mL of pure water. The gas mixture was irradiated with 2.5 MeV protons from a Tandem accelerator (Tokyo Tech, Japan). The same composition of gas mixtures were subjected to spark discharges by using a Tesla coil. Each product was acid-hydrolyzed and was subjected to amino acid analysis by HPLC and/or GC/MS.

Results and Discussion: Amino acids were detected when gas mixture with CH_4 molar ratio (r_{CH4}) was as low as 0.5 % was irradiated by energetic protons. The maximum of G-value in production of glycine is reached at r_{CH4}=5%. However, when the same mixture is subject to the irradiation by the spark discharge (accelerated elecrons) or UV irradiation, amino acids were not detected for r_{CH4} lower than 15 %. Considering fluxes of various energies on the primitive Earth [4], energetic protons appear to be an efficient factor to produce N-containing organics than any other conventional energy sources like thundering or solar UV emission irradiated the early Earth atmosphere.

Not only galactic cosmic rays, but also frequent solar energetic particles (SEPs) associated with solar explosive events could have served as energy sources for prebiotic chemistry in the atmosphere of early Earth. Frequent superflares have been observed in young sun-like stars [5], which suggests that high energy SEPs produced during solar magnetic storms could have been efficient in supplying energy for efficient production of HCN and N_2O [6]. Further experimental studies of effects of SEP events on prebiotic chemistry on primitive Earth are in progress.

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Stability of Amino Acid-Related Compounds in Space -Preliminary Results of the Tanpopo Organic Exposure Experiment-

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Introduction: Presence of a wide variety of organic compounds in extraterrestrial bodies such as carbonaceous chondrites suggested that they delivered organic compounds to the primitive Earth in prior to the generation of the terrestrial life. It was suggested that cosmic dusts delivered much more organics to the primitive Earth than meteorites and comets, but presence of bioorganic compounds in cosmic dusts have been unclear, since they have been mostly collected in terrestrial biosphere.

The Tanpopo Mission is the first astrobiology space mission utilizing the exposed facility of JEM, ISS [1]. The mission includes collection of cosmic dusts and space exposure of amino acid-related compounds (free amino acids and their precursors) in order to examine possible delivery of extraterrestrial amino acid-related compounds by cosmic dusts. The mission started in May 2015, and the first sample returned to the Earth in August 2016 after about 1 year's exposure in space. The other samples will retune to the Earth in 2017 and 2018, after 2 or 3 years' space exposure. Here we report the first analytical results of the organic exposure experiment in the Tanpopo Mission.

Experimental: The following five materials were selected for the space exposure: (i) $^{13}C_2$-glycine, (ii) $^{13}C_5$-isovaline, (iii) $^{13}C_3$-hydantoin (a precursor of glycine), (iv) $^{13}C_6$-5-ethyl-5-methylhydantoin (a precursor of isovaline) and (v) products by proton irradiation of a gas mixture of ^{13}CO, NH_3 and H_2O (hereafter abbreviated as *CAW*). CAW is a mixture of complex organic compounds including amino acid precursors [2]. Each material was added to one of dimples on an aluminum plate, dried, and then covered with hexatriacontane. Each plate for space exposure was covered with a SiO_2 or MgF_2 window. The same kind of plates were prepared for (i) dark controls (exposed in space but no light allowed), (ii) cabin controls (stored in the JEM cabin), and (iii) ground controls.

VUV was monitored with an alanine dosimeter [3], and optically stimulated luminescence dosimeter (OSLD) and silver activated phosphate glass dosimeter (RPLD) were used to monitor space radiation. Exposure panels with the aluminum plates and dosimeters were attached to an ExHAM module together with capture panels to collect dusts with ultra-low density silica aerogel [1], and exposed on the Exposed Facility (EF) of Japanese Experimental Module (JEM) of ISS.

The material in each dimple was collected by using small amount of methanol and water. Amino acids were determined by HPLC. Amino acid precursors and CAW were determined after acid-hydrolysis. The materials were also analyzed by GC/MS and LC/MS. Preliminary results will be reported.

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The Discovery of New Meteoritic Amino Acids in the Murchison Meteorite: Implication for New Formation Mechanisms of Meteoritic Amino Acids

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Introduction: Carbonaceous chondrites contain a diverse suite of extraterrestrial amino acids having various structures such as α, β, γ or δ amino-group [1], while terrestrial life uses only α-amino acids. The comprehensive formation pathway that could explain the diversity of meteoritic amino acids remains unclear, even though several mechanisms have been proposed. In this study, we revisited amino acid analysis of the Murchison meteorite and performed the amino acid synthesis experiments simulating the conditions of meteorite parent body to pursue their formation mechanisms, since the distribution of meteoritic amino acids had been influenced by aqueous alteration on the meteorite parent body (e.g. α-aminoisobutyric acid versus β-alanine [2], and L-enantiomeric excess of isovaline [3]).

Materials and Methods: The Murchison meteorite powder were extracted with H_2O at 100 °C for 20 h. The supernatant and the extract residue were subjected to acid hydrolysis with 3M and 6M HCl, respectively. After desalting using an ion exchange column to purify amino acids, both fractions were reacted with isopropanol(iPrOH)/HCl and trifluoroacetic anhydrite (TFAA). The resultant TFA-amino acid-OiPr derivatives were analyzed by GC/MS with a Chirasil-L-Val capillary column. The amino acid synthesis experiments were performed with H_2O/ammonia/formaldehyde/acetaldehyde and/or glycolaldehyde ratio of 1000/10/1/0.1/0.1 (by mol) at 60 °C for 6 days in the presence or absence of olivine powder with the water/mineral ratio of 1/9 (by weight). The reaction products were analyzed by the same procedure as above.

Results and Discussion: Totally 30 amino acids between C_2 and C_6 were identified in the extract of Murchison, in which glycine was the most abundant (up to approximately 3.5 ppm). In addition to the common amino acids such as α-aminoisobutyric acid and isovaline, the nine C_3 and C_4 hydroxy amino acids (isoserine, homoserine, γ-amino-α-hydroxybutyric acid, γ-amino-α-(hydroxymethyl)propionic acid, β-homoserine, β-amino-α-hydroxybutyric acid, α-methylserine, isothreonine and allo-isothreonine) have been newly identified (~20 to ~140 ppb) from the Murchison extract. A new dicarboxy amino acid, β-(aminomethyl)succinic acid, was also detected as a relatively large amount (~90 ppb). The discovery of 10 new amino acids is striking after numerous surveys of meteoritic amino acids since the half century ago.

The simulation experiments yielded various amino acids including the new amino acids with the most abundant of glycine. Moreover, β-(aminomethyl)succinic acid was produced using formaldehyde, acetaldehyde and ammonia in the presence of olivine, but not detected in the absence of olivine. These results indicate that the formose reaction with ammonia in the presence of minerals is an important formation pathway to produce meteoritic amino acids during aqueous alteration on the meteorite parent body.

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Prebiotic Organic Reactions in Water

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Most organic compounds are not water-soluble, but they still can react in water by different mechanisms.

One prominent mechanism is the "on-water", in which the water-insoluble organic compounds are driven towards each other when placed in water by the hydrophobic effects. A proximity of the organic molecules may help orbital alignment of the reactants. As a result, these reactions not only occur but are often faster than those in which the organic materials are soluble in water. In addition, a better stereospecificity is often obtained under the "on-water" conditions [1,2]. Salts, such as amino acids, can modulate the reaction rate [3], which is of prebiotic importance, since amino acids and various inorganic salts were presumably present in the prebiotic soup. If water-insoluble organic compounds are placed in supercritical water, they dissolve, since such water behaves as acetone, which is an excellent solvent for organic compounds. Supercritical water also has acid-base catalytic properties which allows for a variety of otherwise inaccessible reaction pathways [4,5]. Many prebiotic reactions which may occur "on-water" and in supercritical water are also common organic reactions. Many of these were studied as "green" chemical reactions (environmentally friendly, since they occur in water) [5].

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Formation of Initial Cellular Structures Through Thermodynamic Inversion

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According to the author's inversion concept of the origin of life, the transformation of prebiotic microsystems into primary cells proceeded through thermodynamic inversion [1]. Transformation of the kind was related with inversion of the balance **free energy to entropy contributions** from negative to positive. Since this moment, continuous inflow of the 'over-entropy' free energy (as well as information) into the microsystems provided rise of inner energy gradients and formation of primary cellular structures. This process took place in rising hydrothermal fluid, where combination of regular oscillations of pressure/temperature and irreversible fall of their absolute values with approaching to the surface maintained incessant recombination of molecules in the microsystems. Such conditions sustained the initial circulation of free energy and information in randomly synthesized nucleoprotein complexes (Figure 1, A). After the inversion, continuous increase of the 'over-entropy' surplus of free energy and information step by step led to expansion of the circulation and synthesis of the biologically organized (non-random) macromolecules, along with formation of (proto) nucleoid, ribosomes, membrane, and other cellular structures (Figure 1, B).

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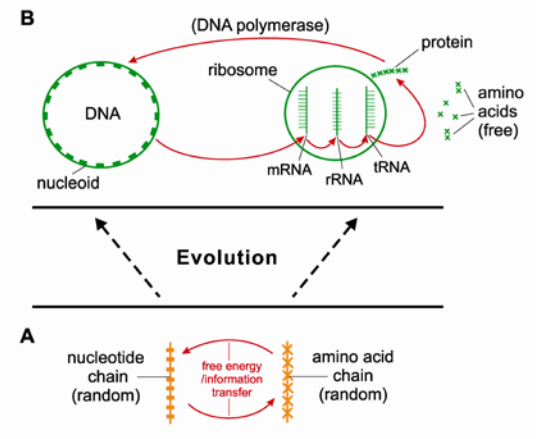

Figure 1 Expansion and divergence of nucleoprotein interaction from a nonequilibrium (oscillating) prebiotic microsystem to a prokaryotic cell through the thermodynamic inversion. Arrows – directions of transfer of information (primarily from left to right) and free energy (primarily from right to left) in course of recombination of nucleoprotein(oid) complexes and their complication. (A) Before the inversion - oscillating prebiotic microsystem: initial interaction (through circulation of free energy and information) between random chains of nucleotides and amino acids (proteinoids); (B) After the inversion – evolved prokaryotic cell: branching of functional nucleotide chains into DNA and RNA, then divergence of RNA sequences into mRNA, rRNA, and tRNA; initiation of proto-ribosomes with the function of organized biosynthesis of proteins on basis of bioinformation contained in DNA and RNA sequences, then transformation of proto-ribosomes into prokaryotic ribosomes; formation of ring double-stranded DNA macromolecule (nucleoid); catalyzing of DNA replication with DNA polymerase.

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In silico ribozyme evolution in a metabolically coupled RNA population

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Background: The RNA World hypothesis offers a plausible bridge from no-life to life on prebiotic Earth, by assuming that RNA, the only known molecule type capable of playing genetic and catalytic roles at the same time, could have been the first evolvable entity on the evolutionary path to the first living cell. We have developed the Metabolically Coupled Replicator System (MCRS), a spatially explicit simulation modelling approach to prebiotic RNA-World evolution on mineral surfaces, in which we incorporate the most important experimental facts and theoretical considerations to comply with recent knowledge on RNA and prebiotic evolution. In this paper the MCRS model framework has been extended in order to investigate the dynamical and evolutionary consequences of adding an important physico-chemical detail, namely explicit replicator structure – nucleotide sequence and 2D folding calculated from thermodynamical criteria – and their possible mutational changes, to the assumptions of a previously less detailed toy model.

Results: For each mutable nucleotide sequence the corresponding 2D folded structure with minimum free energy is calculated, which in turn is used to determine the fitness components (degradation rate, replicability and metabolic enzyme activity) of the replicator. We show that the community of such replicators providing the monomer supply for their own replication by evolving metabolic enzyme activities features an improved propensity for stable coexistence and structural adaptation. These evolutionary advantages are due to the emergent uniformity of metabolic replicator fitnesses imposed on the community by local group selection and attained through replicator trait convergence, i.e., the tendency of replicator lengths, ribozyme activities and population sizes to become similar between the coevolving replicator species that are otherwise both structurally and functionally different.

Conclusions: In the most general terms it is the surprisingly high extra viability of the metabolic replicator system that the present model adds to the MCRS concept of the origin of life. Surface-bound, metabolically coupled RNA replicators tend to evolve different, enzymatically active sites within thermodynamically stable secondary structures, and the system as a whole evolves towards the robust coexistence of a complete set of such ribozymes driving the metabolism producing monomers for their own replication.

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Importance of Sedimentation for Chiral Symmetry Breaking in Far from Equilibrium Peptide Systems

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Introduction: Chiral symmetry breaking in complex far from equilibrium chemical systems with large number of amino acids and large number of similar reactions was considered. It was shown that effective averaging over similar reaction channels results in very weak effective enantioselectivity of forward chemical reactions and that that averaging does not allow most of the known models to result in chiral symmetry breaking during formation of life on Earth. It was shown that such effective averaging does not apply to phase transition during sedimentation process due to high nonlinearity near solubility point.

Models with simple and catalytic synthesis of up to three amino acids, formation of peptides of up to length five, and irreversible sedimentation of insoluble pairs of substances were considered. It was shown that depending on the model and the values of the parameters, chiral symmetry breaking may occur in up to about 10% out of all possible unique insoluble pair combinations even in the absence of any catalytic synthesis. If weak enantioselective catalytic synthesis of amino acids is present, then the number of possible variants, in which chiral symmetry breaking may occur, increases substantially. It was shown that the most interesting catalysts and/or chiral resolving agents have zero or one amino acid of "incorrect" chirality.

An experiment of chiral symmetry breaking was proposed. The experiment consists of a three-step cycle: reversible catalytic synthesis of amino acids, reversible synthesis of peptides, and irreversible sedimentation of insoluble substances.

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Constructing Free Energy Maps of Oligomerization Reactions in Solution

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Introduction: Oligomerization is a key reaction for building complexity in the chemical origins of life. For example, sugars are oligomers of formaldehyde, the nucleobase adenine is a pentamer of HCN, short peptides are oligomers of amino acids, and small RNA molecules are nucleotide oligomers. However, in a complex broth of chemical moieties, would self-oligomerization, co-oligomerization or other chemical reactions dominate? What are the factors that may influence the product distribution as small prebiotic molecules react with each other to form larger molecules? Could such chemical broths generate a proto-metabolic cycle?

What we have done: Our approach to answering these questions is to systematically construct free energy maps for the reactions of prebiotically plausible molecules in solution. A computational protocol was developed based on studying the self-oligomerization of small water-soluble aldehydes [1-2]. We tested our protocol by predicting the equilibrium concentrations of a 1 M solution of glycolaldehyde and found excellent agreement with experimental NMR results [3]. The protocol was subsequently applied to studying the self-oligomerization of CH_2O [4] the co-oligomerization of CH_2O and NH_3 [5], and the reactions of HCN and NH_3 [6]. In all these cases, we calculated the reaction free energies (from first principles) of all potential stable molecules and intermediates, and also transition states connecting stable species. This allowed us to construct a free energy map detailing the thermodynamics and kinetics in systems of molecules with their corresponding oligomers in aqueous solution under standard conditions.

What we are doing: At present, we are investigating if our protocol can be extended to a wider range of systems Current work includes studying the interactions in a CH_2O + HCN + NH_3 H_2O system, co-oligomerization of CH_2O and pyrrole en route to porphyrin rings, and replacement of ester bonds with amide bonds in oligomers of glycolic acid and glycine [7], motivated by the experimental work of Forsyth et al. [8]. While our previous calculations aimed at generating a baseline free energy map for pH 7 and 25^{o}C, we are exploring modifications to our protocol to take into account varying pH, temperature and concentration. This presentation will summarize our recent progress and discuss challenges as we extend our model to a wider range of environments that may have been present in the prebiotic milieu.

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Driving early biochemical reactions by the thermal accumulation of ATP over ADP/AMP?

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Introduction: Life is a non-equilibrium system. The energy required to maintain an organism out of equilibrium is provided by bio-molecules such as ATP. While the synthesis of such energy-rich molecules is nowadays aided by light, this has not been possible in a prebiotic environment. Back then, prebiotic gradients might have enabled a chemical driving of the non-equilibrium. Interestingly, a simple thermal gradient is capable of accumulating ATP over ADP/AMP due to the charge difference. The system delivers a ratiometric excess of ATP utilizing a prebiotically available mechanism and can locally drive biological reactions. With this hypothesis, we can allow previously studied thermal replication and selection systems [1,2] to use ATP as the energy currency of its biochemical reactions. No highly evolved and complex ATP synthase would be necessary for life in its first steps.

Another relevant example is RNA polymerization, which must have been a crucial element at life's early stages but can only operate at sufficient NTP levels. Experimentally, we feed the thermal trap with a close to equilibrium concentration ratio of ATP and ADP. The local accumulation of the energy-rich species is monitored by the fluorescent protein PercevalHR [3].

In conclusion, we propose a system which uses the prebiotically realistic thermal trap to locally shift the equilibrium of ADP and ATP towards an ATP bias and thereby allows biochemical reactions to take off.

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The Robustness of the Urea-Ammonium Formate-Water Mixture as a Prebiotic Solvent

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Introduction:

The dehydration reaction between a phosphate mineral and an organic substance is unfavorable in a water-based environment. On the early Earth it is hypothesized that apatite was the dominant phosphate mineral [1]. Phosphates are poorly soluble and poorly reactive in water under typical (pH ~7) conditions. This is problematic because an efficient process for the synthesis of organophosphates relies on the availability of soluble and/or reactive phosphorus compounds.

Purpose of study:

A semi-aqueous solvent consisting of urea (U), ammonium formate (AF), and water (W) was investigated for the range of fluid-forming conditions potentially available. This solvent was chosen due to the prebiotic nature of the compounds and their prebiotic availability [3,4]. In recent work this semi-aqueous solvent, in the 1:2:4 (U:AF:W) molar ratio, has been shown to create formamide under mild conditions. Furthermore, phosphate minerals are increased in solubility and phosphorylate of nucleosides proceed spontaneously in appreciable quantities [5].

Methods:

The solvent, in varying U:AF molar ratios, were analyzed in a mild environment of an open system heated to 70 °C. The solvents were scanned with H-NMR to determine the composition of fluids present in these solvents over a one week period. Following this study the solvents, in varying molar ratios, were then subjected to wet/dry cycling over a 1 month time frame and again analyzed by H-NMR to determine final compositions.

Significance:

This semi-aqueous solvent has demonstrated robustness through various conditions. Independent of initial molar ratios, the composition of this solvent settles onto a specific final composition in which a four compound milieu of urea, ammonium formate, formamide, and water was created. The one-pot, “warm little pond” origin of life hypothesis was suggested by Charles Darwin in 1871. This work gives credence to this postulate demonstrating that the “pond” may actually be a very robust semi-aqueous solvent composed of simple inorganic compounds that arises spontaneously under a number of geochemical conditions, and enhances solubility of phosphates while simultaneously permitting dehydration reactions.

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Could mineral surfaces have oriented amino acid polymerization towards useful products?

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While it has been shown for a long time that mineral surfaces can promote the formation of oligopeptides from amino acids, [1] little is known on the potential selectivity of this prebiotic pathway: can order emerge through the appearance of non-random amino acids sequences from mixtures of the monomers? Our work is devoted to identifying (biomolecules/minerals) systems that show promising selectivity for condensation reactions.

In a first step toward taking into account the complexity of the "prebiotic soup", we have selected four amino acids in the "short list" of prebiotic chemistry, namely G, A, L, V, D and E[2]. Two couples have been identified that seem to give rise to selective adsorption and/or cooperative adsorption on silicic materials: (V + D) and (L + E) (valine + aspartic acid and leucine + glutamic acid), raising the possibility that they form adducts with a well-defined structure on these minerals. Their thermal reactivity has then been followed upon drying at moderate temperatures, using thermogravimetric analysis, in situ IR and solid-state NMR spectroscopies, and ex situ analysis of organic molecules after desorption (by HPLC and ESI-MS). We observed the formation of several oligomers in conditions where single amino acids only give rise to cyclic dimers. Depending on the heating conditions, and specifically on the water activity, peptides up to hexamers could be formed in a single step. Furthermore, for each chain length, a limited amount of peptides compositions were observed, showing the non-randomness of the process.

In a further step, we compared the reactivity of the selected amino acid couples on different silicic materials. We studied the effect on polymerization of porosity [3], surface defects such as strained cycles and silanols [4], and the presence of transition metal with variable oxidation states ($Fe^{3+/2+}$). To achieve this, we selected silicic materials with well-defined properties, such as pyrogenic and precipitated silicas, mesoporous silica, and clay minerals including montmorillonite and nontronite. Even within this limited set of related materials, very different amino acid reactivities are observed, underlining the importance of a "surface science" approach to questions of prebiotic chemistry.

Our results may provide the missing link between prebiotic syntheses of small molecules such as amino acids, and self-organization phenomena that may come into play once complexity reaches the level of oligopeptides assemblies.

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Metabolic GARD: replicating catalytic network of lipid-anchored metabolites

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Introduction: The Lipid World scenario suggests early compositional replication as an alternative to the templating biopolymers of the RNA World. The graded autocatalysis replication domain (GARD) model is a chemistry-based kinetic formalism of Lipid World that simulates network dynamics within amphiphile-containing compositional assemblies, including lipid vesicles [1]. In GARD, amphiphiles join and leave at rates determined by a mutually catalytic network [2], resulting in homeostatic growth, followed by assembly fission into faithful progeny. GARD computer simulations show stationary states in compositional space termed *composomes*, which preserve their composition across many growth-fission cycles, resembling cell replication [1]. GARD composomes exhibit life-like behaviors such as selection, quasispecies formation and ecology-like population dynamics [3]. This model thus embodies two of the three cornerstones of life's origin: compartmentalization as well as information storage and copying.

Results: A crucial open question is how early prebiotic GARD entities might undergo further molecular complexification, including the appearance of rudimentary metabolism and templating biopolymers. We posit that this could be addressed by an extended GARD model: metabolic GARD or M-GARD. For this, we propose adding metabolic conversions that involve modified amphiphiles, thus preserving the compositional replication forte of basic GARD. M-GARD's chemical reactions take place on both the outer and inner membrane surfaces, as well as within the inner aqueous vesicular volume. M-GARD's metabolic networks employ small molecule catalysis as proposed [2]. This notion draws further support from the experiment-based proposals that present-day low molecular weight cofactors may have been early non-protein catalysts [4,5]. M-GARD assumes the environmental presence of a highly diversity of compounds, some of which capable of generating vesicles. M-GARD's simulated covalent transitions include headgroup modification and clipping. When the latter reactions occur on the inner vesicle surface, they contribute, along with trans-membrane transport, to intra-vesicle metabolism. M-GARD is also capable of simulation photochemically driven and high energy compound-dependent metabolic and transport reactions. Crucially, both the bilayer and lumenal content of the vesicles belong to the same catalytic network, hence are reproduced upon homeostatic growth and fission.

Conclusions: Important dynamic behaviors expected to emerge from M-GARD simulations, particularly when employing high-power supercomputing [6], include: a) Gradual transition from pure heterotrophy to increasing levels of autotrophy. b) Cross-generation gradual increase of homeostatic growth capacity, translated into more effective replication in multi-vesicle GARD reactor simulations with competition [5]; c) Portrayal of open-ended evolution stemming from the metabolic generation of novel compounds, including templating oligomers. .

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Earth Without Life: A Systems Model of a Global Abiotic Nitrogen Cycle

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Introduction: Nitrogen is the major component of Earth's atmosphere and plays important roles in biochemistry [1,2]. Presently, the Earth's surface nitrogen cycle is dominated by biological (including human) fluxes, with abiological fluxes being relatively small. However, prior to advent of biology, all nitrogen cycling would have been abiological, and this cycling would have set the stage for the origin of life.

Model Description: We constructed a kinetic mass-flux model of N cycling, in its various major chemical forms (N_2 and NO_x, NH_x, which stand for oxidized and reduced species, respectively), between the Earth's major reservoirs (atmosphere, oceans, crust, mantle), and including inputs and losses to space, taking into account the rates of fluxes between reservoirs and the total amount of N species which can be accommodated in each, and explore how these fluxes and reservoirs may change over time in the absence of biology. The model topology is shown in Fig. 1.

Flux are estimated from present observed day values and several possible time evolutions, anchored either by geodynamics consideration or rock measurements are modeled.

Discussion: Understanding what controls such a cycle may therefore be used as remote observable for planetary dynamics. We found that the timescales involved in the evolution allow the system to track the steady state closely, and that any long term evolution is due to variations in the steady state due to model parameters. This allows us to map the phase space of possible nitrogen distribution between the different reservoirs, irrespective of potential early transients. We also characterize, all else being constant, how life influences this phase space.

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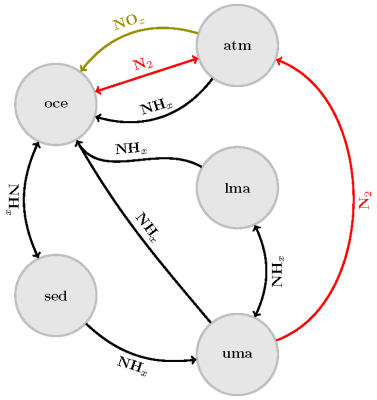

Figure 1 - Coupled model topology showing NO_x, N_2 and NH_x fluxes between Earth's reservoirs. The 'atm', 'oce', 'sed', 'uma' and 'lma' labels stand for atmosphere, oceans, sediments, upper and lower mantle, respectively.

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The Ribosome: A Window in Time

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The ribosome, in analogy with a tree, contains a record of its history, spanning 4 billion years of life on earth. The information contained within ribosomes connects us to the prehistory of biology. Details of ribosomal RNA variation, observed by comparing three-dimensional structures of ribosomes across the tree of life, form the basis of our molecular level model of the origins and evolution of the translational system. We have used information within ribosomes to reconstruct much of the emergence of the universal translational machinery and to understand the evolution of biopolymers. Using a 3D comparative method, we present a molecular-level model for the origin and evolution of the translation system. In this model, the ribosome evolved by accretion, recursively-adding expansion segments, iteratively growing, subsuming, and freezing the ribosomal RNA. The ribosome is also imprinted with a detailed molecular chronology of the origins and early evolution of proteins. When arranged by evolutionary phase of ribosomal evolution, ribosomal protein segments reveal an atomic level history of protein folding. Our models predict that appropriate rRNA fragments have inherited local autonomy of folding and local autonomy of assembly with ribosomal proteins, and that the ribosomal proteins and rRNAs are co-chaperones. We have biochemically and computationally resurrected the ancestral oligomers and polymers predicted by the Accretion Model. We have synthesized the rRNAs described by early steps in the early accretion process and have experimentally explored their properties, focusing on their folding and stabilities. We have measured and computed the thermodynamic stabilities of theses models and experimentally probed their structures. We have also experimentally shown that rRNA can serve as a protein chaperone, aiding in the conversion of random coil peptide oligomers into β-β motifs, which would then collapse to globular domains, supporting previous models in which RNA preceded aboriginal proteins. Our results support a model in which protein folding was an emergent phenomenon of interactions with RNA, and that the evolution of the ribosome was the maturation of the symbiotic relationship between RNA and protein.

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Molecular Cooperation: A Self-less Origin of Life

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Introduction: Molecular cooperation is the obligate dependence of multiple information-bearing molecules on the propagation of the system as a whole. In an RNA world, multiple types of such cooperation would have been possible [1], including simple reaction pathways with more than one informational reactant, polymer strands that interact to form a catalytic whole, cross-catalysis and cyclical-catalysis, a formal autocatalytic set, and perhaps even a hypercycle. I will discuss these various types of molecular cooperation and explore how they differ from "simple" chemistry that may have many reactants but no cooperative component.

Reproduction, replication, and recombination: Living systems are characterized by the propagation and proliferation of informational units as a function of time. Szathmáry [2] introduced a distinction between replicators and reproducers. Here, I will expand on this difference, tie them into prebiotic chemistry, and emphazise that cooperation must have played a key role in the origins of life, rather than being a later evolutionary invention. *Reproduction* is the ability of one molecule to catalyze the production of other, similar molecules. *Replication* is a sub-set of reproduction whereby a template is used to augment the creation of a second molecule from the first, one monomer at a time. *Recombination* is the swapping of large blocks of genetic information, rather than a series of unit-by-unit replication events. We have shown that RNA-dependent RNA recombination can lead to reproduction [3], and that under certain circumstances this type of reproduction can happen cooperatively [4]. Now I will demonstrate that recombination can outperform replication under a variety of common conditions, and conclude that it was far more probable that in life's origin, reproduction occurred via recombination-like chemistry and that replication chemistry was a later biotic invention. The "self" as we know it today, was made possible only after an emergence of a molecular collective. There is clearly increased need to apply the principles of evolution, particularly competition, cooperativity, complexity, and ecology to molecular systems when considering the mechanisms of abiogenesis on the Earth.

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Dynamic Chemical Assembly of Peptide Nucleic Acids

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Introduction: The origin of life was marked by the transformation of simple chemical building blocks into increasingly complex systems. A remarkable example of this was the conversion of prebiotic feedstock molecules into the first informational polymers. Important strides have been made in the laboratory to identify mechanisms by which prebiotic informational polymers could have arisen de novo. Even so, there remains a great need to experimentally demonstrate the non-enzymatic assembly of small building blocks into informational oligomers with functionally competent sequences capable of basic life activities, such as replication. We have developed dynamic peptide nucleic acids (PNA) that efficiently assemble via reversible covalent reactions from simple peptides and nucleobase units. These PNA can undergo dynamic sequence adaptation and template mismatch correction. We demonstrate that, because of their unique structures, the PNA can assemble from relatively simple building blocks via mechanisms that are not available to other PNA or oligonucleotides. In one instance, a tetrapeptide building block is shown to polymerize to give peptides up to >30 residues in length that serve as backbones for the dynamic PNA. Further, we describe the development of a PNA that can reversibly self assemble and undergo dynamic sequence selection, and then spontaneously lock into a given sequence to preserve the contained information content. Our findings highlight an intriguing aspect of dynamic informational oligomers with respect to prebiotic chemistry- the synthesis of their backbones is chemically decoupled from the attachment of nucleobases to the molecule. This greatly simplifies the process of generating lengthy oligomers with specific sequences because the backbone can polymerize in a first step, while the sequence can be selected (reversibly, with the capacity for mismatch repair) in a second step.

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From Astrochemistry to Astrobiology: the importance of cosmic ices for the exogeneous delivery of organic matter onto telluric planets toward the onset of Prebiotic Chemistry

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Introduction: Ices made of simple molecules are ubiquitously detected in the infrared spectra of many astrophysical environments such as molecular clouds [1,2] out of which stars and planetary systems do form, together with many icy debris (asteroids, comets, dust…). Ices may also undergo efficient energetic processing, including ultraviolet irradiation at the turbulent edges of protoplanetary disks [3]. Such icy materials can be straightforwardly simulated in laboratory non-directed experiments in which the photo and thermal evolution of these ices are performed using, in our case, vacuum ultraviolet irradiation, following the classical methods of "matrix isolation techniques" [4]. These laboratory ices may then be used as templates for the astrophysical ones, where a complex radical chemistry develops, leading to the formation of a complex organic matter, soluble (in water and classical organic solvents) and insoluble [5], similar to what is indeed observed in primitive carbonaceous chondritic meteorites and known as SOM and IOM. More specific molecules such as amino acids [6] sugars [7,8] and even nucleobases [9] make these materials particularly attractive for the possible onset of a "true" prebiotic evolution at the surface of a telluric planet if adequate conditions are met (mostly liquid water, organic chemistry, free energy…). Global analytical methods using very high resolution mass spectrometry of the soluble organic residues [10,11] reveal the exreme complexity of these organic materials which parallels the one observed in the Murchison chondrite for example [12] or within the Paris meteorite, as far as specific "biological molecular bricks" are considered [13].

I will replace the importance of extraterrestrial ice evolution toward the making-of the organic matter within the general framework of ***Astrochemistry*** i.e.the chemical evolution of the Galaxy [14] and show, under which conditions and conceprtual considerations, the exogeneous delivery of volatiles and organic matter on telluric planets such as the Earth, as postulated a long time ago [15], should be considered as a serious possibility for the starting-up of a ***Prebiotic Chemistry*** on telluric planets and thus ofimportance for ***Astrobiology.*** A brief presentation of an ongoing new non-directed experiment will be briefly presented.

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The Case for a Gaian Bottleneck: the Biology of Habitability (i.e. the potential non-dominance of abiotic factors in creating circumstellar habitable zones)

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The prerequisites and ingredients for life seem to be abundantly available in the Universe [1]. However, we have yet to find any evidence for extraterrestrial life. A common explanation for this is a low probability for the emergence of life (an emergence bottleneck), notionally due to the intricacies of the molecular recipe. In Chopra and Lineweaver 2016 [2] we present an alternative Gaian bottleneck explanation: If life emerges on a planet, it only rarely evolves quickly enough to regulate greenhouse gases and albedo, thereby maintaining surface temperatures compatible with liquid water and habitability. Such a Gaian bottleneck suggests that (i) extinction is the cosmic default for most life that has ever emerged on the surfaces of wet rocky planets in the Universe and (ii) rocky planets need to be inhabited to remain habitable. In the Gaian bottleneck model, the maintenance of planetary habitability is a property more associated with an unusual and rapid evolution of biological regulation of surface volatiles than with the luminosity and distance to the host star.

The habitability of rocky planets is strongly influenced by the volatile content of the atmosphere (H_2O, CO_2, CH_4, H_2) which controls both albedo and greenhouse warming. However, because of the strength, rapidity and universality of abiotic positive feedbacks, the rapid evolution of the atmosphere, probably within the first billion years as happened for Venus and Mars, can lead to both temperatures too hot for life (runaway greenhouse) and loss of water (runaway loss of hydrogen), that can preclude long term planetary habitability.

The most important data needed to constrain, validate or invalidate the Gaian Bottleneck model will probably come from estimates of the strength of the abiotic negative feedback of the carbonate-silicate cycle [3] in the first billion years of Earth's history when the area of continental crust (and therefore the amount of sub-aerial silicate weathering) was probably negligible.

If negative feedback from silicate weathering is to create a stable circumstellar habitable zone during the first billion years, several conditions need to be fulfilled. Sub-aerial or sub-aqueous silicate weathering [4] needs to be strong enough, to make its negative feedback dominate the positive feedbacks from a runaway greenhouse or a runaway ice-albedo glaciation.

Biotic regulation could provide the necessary level of negative feedback. However, the emergence of metabolisms and ecosystems that could regulate planetary scale greenhouse gases or albedo may be a rare and quirky result of evolution, and therefore present a Gaian bottleneck to the persistence of life on inherently unstable planets.

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Ser-His dipeptide : a potential candidate of the prototype for serine protease

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Introduction: Ser-His is a magical dipeptide which was found to be the smallest functional dipeptide with protease activity[1-3]. In order to explore its protein cleavage spectrum, four differently folded proteins, namely GFP, CyPA, BSA and myoglobin, were treated with Ser-His recently. The resulting digestion products were evaluated with high-resolution mass spectrometry.The cleavage efficiency and cleavage propensity of Ser-His against these protein substrates were calculated at both the primary and secondary sequence levels. The above experiments show that Ser-His cleaves a broad spectrum of substrate proteins of varying secondary structures. Moreover, Ser-His could cleave at all 20 amino acids with different efficiencies according to the substrateprotein, which means that Ser-His has the original digestion function of serine proteases.

We also collected and compared the catalytic sites and cleavage sites of 340 extant serine proteases derived from 17 representative organisms. A consensus motif Ser-[X]-His was identified as the major pattern at the catalytic sites of serine proteases from all of the organismsrepresented except *D. rerio*, which uses Ser-Lys instead. This finding indicates that Ser-His is the core component of the serine protease catalytic site. Moreover, our analysis revealed that the cleavage sites of modern serine proteases have become more specific over the evolutionary history of this family. Excitingly, Prof. Szostak and his co-workers used Ser-His to catalyze the formation of peptide bonds[4]. Thus, Ser-His exhibits microscopic reversibility, similar to modern serine proteases[5].

Another question should be answered is if Ser-His is easy to obtained in prebiotic conditions. At present in our lab, we found that Ser with the activation of phosphorus at N-terminal is more liable to form amide bond with histidine than other ancient amino acids[6], such as Ser, Ala, Pro, Asp. To some extent, it implied Ser and His are perfect couple to form dipeptide among other amino acids.

In summary, to some extent, all above findings indicates that Ser-His is a potentialcandidate of the prototype for serine protease.

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Viscosity-mediated replication of an RNA duplex containing a ribozyme motif

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An important goal in origins of life research is the demonstration of an RNA system that can undergo sustained cycles of replication without the aid of protein enzymes. However, despite decades of research on prebiotic nucleic acid origins and information transfer, the community has yet to accomplish this goal. Previous studies on template-directed RNA synthesis have focused mainly on single-stranded templates and rarely consider the additional challenges associated with multiple rounds of information transfer, such as strand inhibition [1,2]. We will discuss a replication system for gene-length RNA duplexes that is enabled by a viscous solvent (Figure 1). This solvent provides a diffusion-limited environment, which promotes the formation of intramolecular nucleic acid structures, which circumvents the strand inhibition problem [3]. These kinetically trapped single-stranded structures allow the assembly of oligonucleotide substrates on both of the template strands, which can be subsequently ligated. Additionally, we demonstrate that viscous solvents can promote the replication of an RNA duplex containing a hammerhead ribozyme sequence, which is catalytically active in hydrated eutectic solvent conditions. These findings suggest that viscous solvents generated by water evaporation in day/night or seasonal cycles on the prebiotic Earth, could have provided a viable environment for replication of nucleic acid structures with complex intramolecular structures, such as ribozymes.

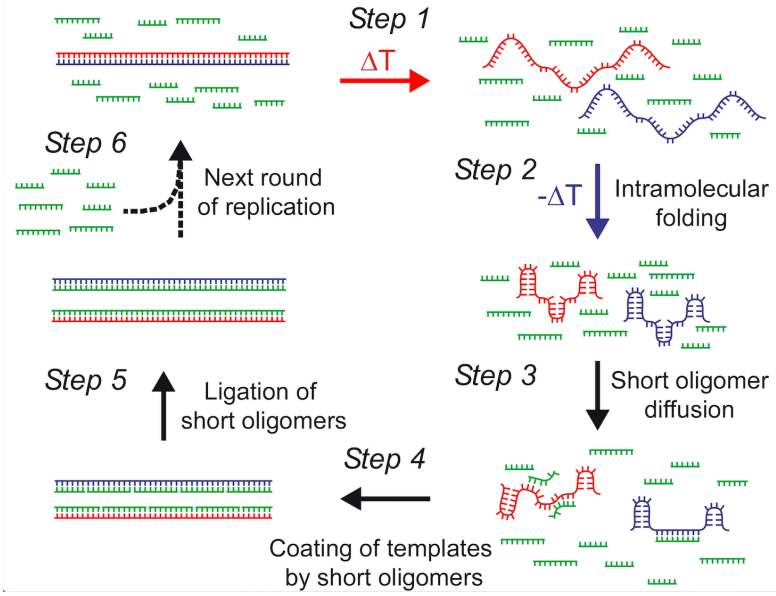

Figure 1 A model process for the prebiotic replication of nucleic acids that circumvents the strand inhibition problem. Adapted from He *et al.*, 2017 [3].

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The initial C isotope ratio for the solar system

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Introduction: Light stable isotope compositions of meteorites, planets, and the Sun constrain how our solar system formed and the nature of the formation environment, with the Sun considered most representative of the bulk starting material. The NASA *Genesis* mission succeeded in measuring O and N isotope ratios in returned solar wind samples [1], [2]. Extrapolation of the solar wind results to the solar photosphere demonstrate that Earth's O and N reservoirs experienced a very different isotopic history than that of the bulk Sun. *Genesis* has not yet reported a C isotope ratio. Here we reanalyze solar photosphere spectral data to determine the C isotope ratio of the sun.

Spectroscopy of the photosphere: CO rovibrational transitions dominate the 2-5 micron spectral window of the photosphere. Shuttle-borne ATMOS FTS data contains thousands of CO fundamental and first-overtone lines, recorded at high signal-to-noise ratio and at high spectral resolution [3], [4]. We used the latest CO dipole moment functions [5] to reduce line strength uncertainties.

Results: Our ^{18}O abundance for the temperature-enhanced photosphere is $\delta^{18}O_{SMOW}$ = -50 ± 11‰, which is the same within errors as the inferred ratio from *Genesis* [1]. Our ^{17}O value is $\delta^{17}O_{SMOW}$ = -65 ± 33‰, which cannot distinguish between the *Genesis* photosphere value and a terrestrial value at the 2-σ level. With good agreement with *Genesis* O isotope results, we now determine a C isotope ratio. We find the photosphere has $\delta^{13}C_{PDB}$ = -48 ± 7‰. Earth mantle carbon is believed to have a mean $\delta^{13}C$ = -5 ‰ [6], implying that bulk terrestrial C is enriched in ^{13}C relative to the Sun by nearly as much as bulk terrestrial O is enriched in ^{18}O. Our results confirm measurements of solar wind in lunar regolith grains [7], and disagree with TiC data from the Isheyevo meteorite which have $\delta^{13}C \sim 0$ ‰ [8].

Implications: Our results demonstrate that bulk Earth, Mars, and asteroids, are enriched in ^{13}C relative to the starting material that formed the solar system. Possible enrichment scenarios, including CO self-shielding in the nebula [9], and inheritance of ^{13}C-rich grains, will be discussed. The key point is that the surficial C on Earth, including ocean carbonates and bicarbonate, is not representative of initial solar system C. The processes that altered the initial C isotope ratio are likely to be common to other solar-mass planetary systems.

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Which Came First, Proteins or Cofactors? Recreating Metabolic Reactions of the Early Earth

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Very little is known about the emergence of metabolic pathways in the early Earth environment. Two prominent theories propose that the first catalytic protein cofactors may have acted as pre-protein catalysts prior to the evolution of protein synthesis, or that metabolic pathways arose from nonprotein catalysts producing chains of reactions with lower rate enhancements than modern proteins [1,2]. However, these theories have not been systematically tested. Examining enzymatic reactions that are considered to be ancient, and determining if the protein cofactor alone can promote proto-enzymatic reactions in an early Earth environment is paramount to testing these hypotheses. We chose Coenzyeme A (CoA), the cofactor central to synthesizing citrate with the enzyme citrate synthase in the citric acid cycle, as a target for beginning such examinations of cofactor activity without its protein enzyme (Figure 1). By monitoring with NMR spectroscopy, we tested whether citrate synthesis from oxaloacetate and acetate, or the acetyl group from acetyl-CoA, could occur in aqueous solutions at pH values relevant to Earth's early oceans and/or hydrothermal fluids (~5-10). We also tested the effect of the presence of dissolved carbon dioxide as bicarbonate, which could act as a carbon source as well as a base to drive reactions under prebiotic ocean conditions. The stability of citrate would also be a factor in prebiotic environments, since it can decay into a variety of products depending on the chemical/geochemical conditions [3]. These results will test the hypothesis that cofactors can promote parts of core metabolic pathways, and could have implications in the search for life on other worlds by offering predictive potential about which environments could have supported such reactions.

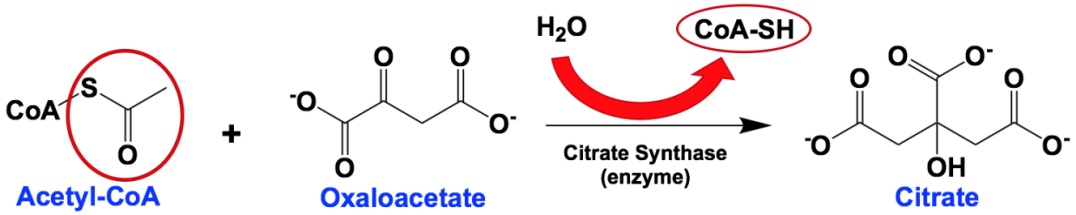

Figure 1: The citrate synthase reaction driven by a protein enzyme and ACoA.

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Non-Enzymatic RNA Backbone Proofreading by Energy-Dissipative Recycling

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Non-enzymatic oligomerization of activated ribonucleotides leads to ribonucleic acid that contains a mixture of 2′,5′- and 3′,5′-phosphodiester linkages, and overcoming this backbone heterogeneity has long been considered one of the greatest limitations to the prebiotic emergence of RNA[1]. We present and experimentally demonstrate a model in which non-enzymatic chemistry progressively converts 2′,5′-linkages to 3′,5′-linkages by iterative degradation and repair. With multiple rounds of this energy-dissipative recycling[2], we show that all 3′,5′-linked duplex RNA can emerge from a backbone heterogeneous mixture, thereby delineating a route that could have driven RNA evolution on the early Earth.

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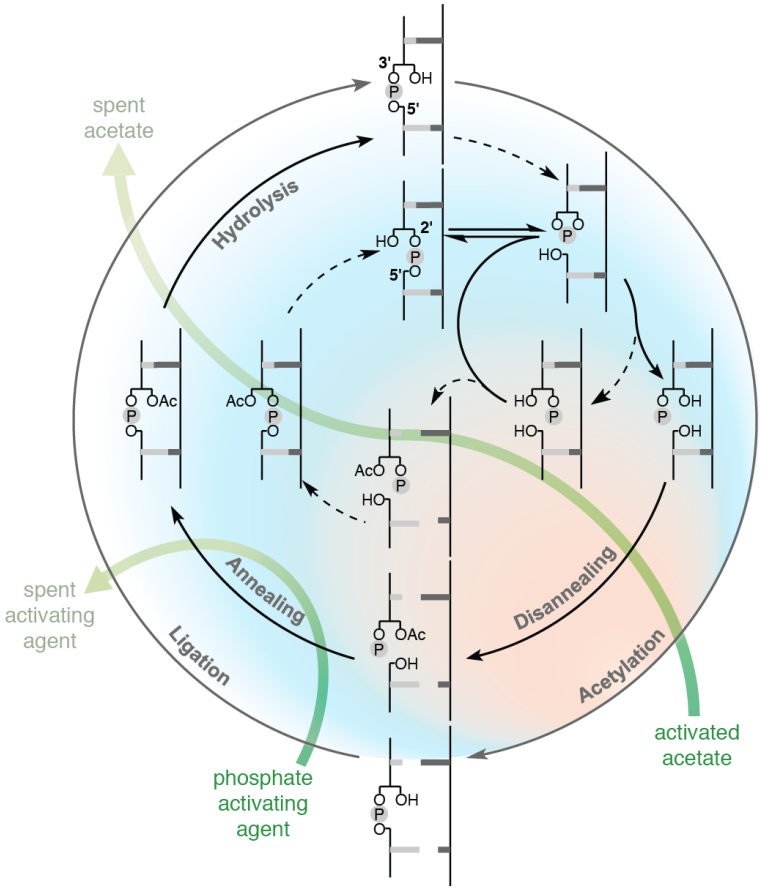

Figure 1 –Proposed model for the recycling of backbone heterogeneous ribonucleic acid. Favored (bold lines) and unfavored (dashed lines) pathways resulting in the conversion of 2′,5′-bonds to 3′,5′-bonds.

The degree of aqueous alteration of carbonaceous chondrites and its influence on the soluble organic content

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Introduction: The soluble organic content of carbonaceous meteorites reflects the chemical reactions that occurred on their parent bodies, solar nebula or interstellar medium [1,2]. Indeed, the degree of aqueous alteration on the parent body of CM chondrites appears to have influenced the distribution and relative abundance of their soluble organic compounds [3-7]. The higher relative abundances of alkylated aromatic hydrocarbons as well as the relative abundances of β-alanine/glycine are related with a higher degree of aqueous alteration on the meteorite parent body of CM chondrites [6]. Furthermore, the more aqueously altered CM chondrites have higher L-enantiomer excess (Lee) values of isovaline [6,8,9]. The Paris meteorite, one of the least aqueously altered CM chondrites analyzed to date could be considered like a point zero in terms of the degree of aqueous alteration [10-15]. The isovaline detected in this meteorite is racemic (corrected D/L = 1.03), indicating that aqueous alteration may be responsible for extending any initial Lee of isovaline [6]. However, aqueous alteration is not responsible for creating an isovaline asymmetry, which may be attributed to other mechanisms. These include e.g. ultraviolet circularly polarized light (UV-CPL) photo-processing of interstellar/circumstellar ices [16-21], equilibrium solid-liquid phase behavior of amino acids in solution [22], or solid-solution phase behavior leading to the formation of conglomerate enantiopure solids during crystallization on the meteorite parent body [23]. While aqueous alteration on the parent body(ies) of carbonaceous chondrites does not explain all their soluble organic content, it is an important player. The analysis of the soluble organic content of carbonaceous meteorites, in particular the very primitive ones helps to build a link between the different contributions from interstellar precursors, solar nebula, and the subsequent incorporation in asteroids.

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July 16-21, 2017 at UC San Diego, CA, USA

Hosting early evolution in heated pores of rock

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Introduction: Life as we know it is a stunningly complex non-equilibrium process, keeping its entropy low against the second law of thermodynamics. Therefore it is straightforward to argue that first living systems had to start in a natural non-equilibrium settings. Recent experiments with non-equilibrium microsystems suggest that geological conditions should be able to drive molecular evolution, i.e. the combined replication and selection of genetic molecules towards ever increasing complexity.

Biochemistry in non-equilibrium settings: As a start, we explored the non-equilibrium setting of natural thermal gradients. Temperature differences across rock fissures accumulate small monomers more than millionfold [1] by thermophoresis and convection [2]. Longer molecules are exponentially better accumulated, hyperexponentially shifting the polymerization equilibrium towards long RNA strands [3]. The same setting implements convective temperature oscillations which overcome template poisoning and yield length-insensitive, exponential replication kinetics [4]. Accumulation and thermally driven replication was demonstrated in the same chamber, driven by the same temperature gradient [5].

Replication and selection for increasing complexity: The replication of long nucleic acid sequences was required for the evolution of biological complexity during the origin of life; however, short sequences are normally better replicators than long ones. Recently, we showed how a common physical environment provides a simple mechanism to reverse this trend and enables long sequences to flourish [6]. On a similar note, the trap is creating gels from oligonucleotides - and sorts them in a phase transition with equal sequence and single base pair discrimination [7]. Replication and trapping of DNA persist over long time in a constant influx of monomers, closely approaching the criteria for an autonomous Darwin process.

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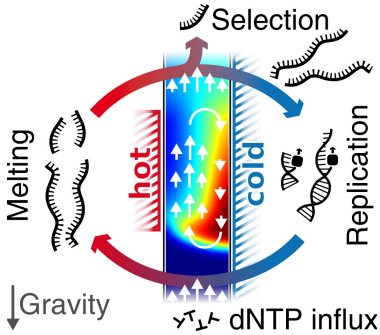

Figure 1 – Local heat flux across pores of rock create an interesting setting for early accumulation, replication and selection.

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Optimal Size for Emergence of Self-replicating Polymer System

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Abstract: Biological systems consists of a variety of polymers that are synthesized from monomers. Here catalysis emerges for a polymer beyond some length, which itself is synthesized by its catalysis. In the problem of the origins of life, it is important to elucidate how such autocatalytic polymerization has emerged and been sustained. The reaction system of self-replicating polymers, as analyzed by stochastic reaction dynamics, has two stable states, one with almost no catalysts and the other with sufficient catalysts to sustain the autocatalytic reaction. The transition from a state without catalyst to that with abundant catalysts is required for the emergence of primordial life, as was discussed by Freeman Dyson in his seminal book [1]. Transition time from the former to the latter gives a measure how autocatalytic polymerization systems is likely to emerge. We investigated such transition time by stochastic reaction dynamics, as a function of the volume of the system.

Transition time between bistable states generally increases with the system size. We find that, however, there is one optimal volume that minimizes the transition time in an autocatalytic polymerization system, which is generally given by the inverse of the catalyst concentration at the unstable fixed-point in the reaction rate dynamics, as estimated from a condition to have a single catalyst molecule. This result suggests that the space volume in a reaction system is an important factor for the origin of life. This is the universal relationship in the field of the origin of life, and is a result from theoretical physics. Also it provides a quantitative prediction for the synthesis of primitive catalytic reaction system for a protocell [2].

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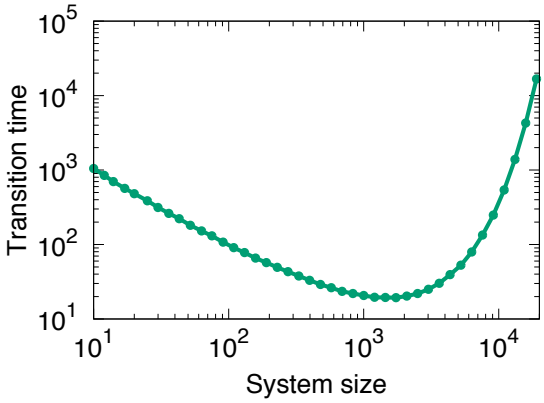

Figure – Transition time from the inactive to active states, plotted as a function of the system size. There is the optimal size that gives the minimum transition time. For each parameter and size, the time is computed as the average over samples of the master equation. Log-log plot.

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From viroids and ribozymes RNA back and forth

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One remaining crucial point in the early life history is to understand how evolution passed from complex prebiotic chemistry to simple biology. Current cellular facts allow us to follow the link from chemical to biochemical metabolites, from the ancient to the modern world. In this context, the "RNA world" hypothesis proposes that early in the evolution of life, the ribozyme was responsible for the storage and transfer of genetic information and for the catalysis of biochemical reactions. Accordingly the hammerhead ribozyme (HHR), the hairpin ribozyme, and the ribozyme contained in hepatitis-δ virus (HDV) belong to a family of endonucleolytic RNAs performing self-cleavage that might occur during replication. Furthermore regarding the ultraconserved occurrence of HHR in several genomes of modern organisms (from mammals to small parasites and elsewhere), these small ribozymes have been regarded as living fossils of a primitive RNA world. On the other hand, the existence of contemporary life in extreme conditions providing habitats for cellular and viral species, encourages us to focus on the activity, persistence and dynamics of RNAs under such conditions. Finally, studying viroids as plausible remains of ancient RNA, we recently demonstrated that viroids replicate in non-specific hosts, emphasizing their adaptability to different environments which enhanced their survival probability over the ages. All these results exemplify ubiquitous features of life, that is the plasticity and efficiency of small RNAs, viroïds and ribozymes, as well as their diversity and adaptability to various extreme conditions. All these traits must have originated in early life to generate novel RNA populations.

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Evolution of Prebiotic Peptides in Amphiphilic Environments

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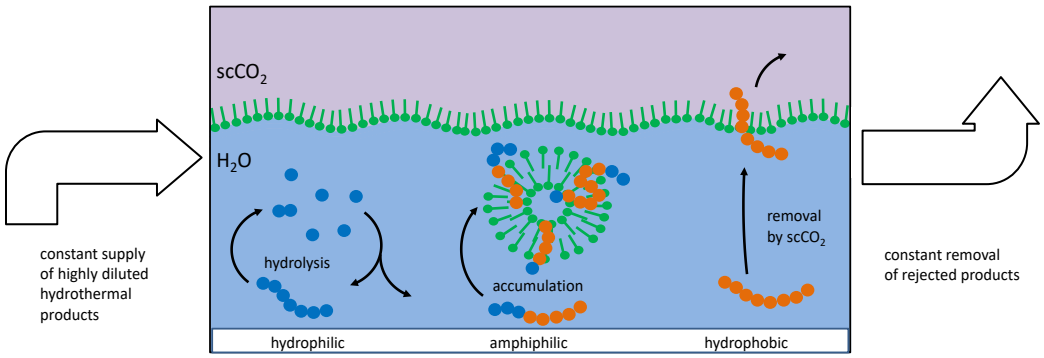
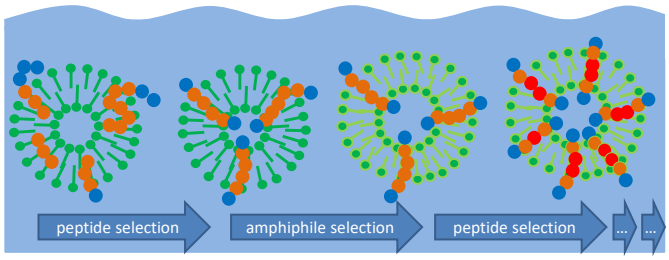
A fundamental problem in many postulated pathways of prebiotic chemistry is the low concentration which is generally expected for interesting reactants in fluid environments. Therefore, a mechanism of selection and accumulation of relevant prebiotic compounds seems to be a crucial condition for further molecular evolution. A very efficient environment for selection and accumulation can be found in the fluid H_2O/$scCO_2$ continuum circulating in tectonic fault zones. Vesicles which form periodically at a depth of approximately 1 km present a selective trap for amphiphilic molecules, especially for peptides composed of hydrophilic and hydrophobic amino acids in a suitable sequence:



Recent experiments which artificially reproduce these conditions have shown that this mechanism leads to an efficient selection and accumulation of amphiphilic peptides, the latter being formed in-situ in the same environment out of a random mixture of amino acids. The experiments are presently continued in order to follow an evolution process of the incorporated peptides as well as of the vesicles as a whole:



Altogether, the described processes lead to peptide-enriched, stabilized, and potentially functionalized vesicles which form a very potent basis for further developments such as a subsequent RNA-based evolution.

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Chiral sugar and amino acid formation in simulated cometary matter inches closer to explaining the emergence of homochiral life

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Abstract: The original appearance of chiral organic molecules in our universe is an essential component of the asymmetric evolution of life on Earth. Simulated cometary ice experiments have indicated that circularly polarised light could be the initial source of life's handedness following prebiotic astrochemical condensation of primordial gases. With advanced analytical techniques, chiral sugar molecules[1,2] including ribose (**Fig.1**), amino acids[3,4] and their molecular precursors produced within these interstellar achiral ice analogues have been detected and are likely to be abundant in interstellar media. These molecular species are considered key prebiotic intermediates in the first steps towards the formation of biomolecular homochirality.

Moreover, enantiomeric excesses have been produced in the cometary ice simulations either by photolytic degradation of racemates[5] or by photochemical synthesis via transfer of *chiral photons*[6]. The significance of these results will be considered with reference to the Rosetta space probe that successfully deposited the Philae Lander on the nucleus of comet 67P/Churyumov-Gerasimenko in November 2014[7]. The analysis of the formation of enantiomer-enriched amino acid and sugar structures within interstellar ices, both simulated and actual, should serve as a means towards furthering understanding the origin of asymmetric prebiotic molecules.

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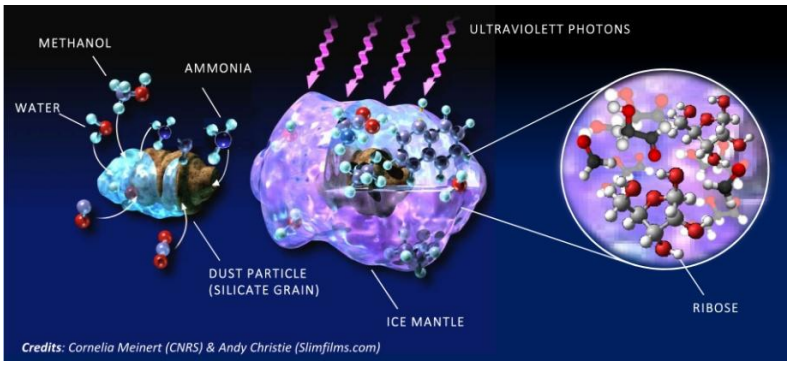

Figure 1 –Ribose forms in the icy mantles of interstellar dust grains from simple precursor molecules (water, methanol, and ammonia) under high energy radiation. Ribose sugars make up the backbone of ribonucleic acid (RNA).

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Effects of Gamma Irradiation in Nucleic Acids Bases Co-adsorbed in a Na-montmorillonite and Fe-montmorillonite: Relevance in Chemical Evolution

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Several authors have been proposed that mineral surfaces had an important role in the study of origin of life, especially in the stage of chemical evolution, due to their ancient origin, wide distribution, adsorption capacity and their physico-chemical properties. Clay minerals can be considered as sites for concentration and catalysis of different reactions, and as protectors of the organic molecules adsorbed into them exposed to an external energy source[1]. The knowledge of the role of clays in the primordial Earth can be extended, studying the behavior of organic compounds, like nucleic acid bases, adsorbed in these minerals, and expose to the action of an energy source[2, 3].

Our aim is to study the role of clays in chemical evolution as a site of concentration of adenine and thymine, to study the effect of co-adsorption in these complementary bases, and as protector agent under γ radiation of adenine-clay system, thymine-clay system, and adenine+thymine-clay system, in simulated primitive Earth conditions. For these purposed bases adsorbed on Fe-montmorillonite and Na-montmorillonite were exposed at different irradiation dose, temperatures, and pH. The bases and radiolytic products were analyzed by UV spectrophotometry, IR spectrometry and High-Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry (HPLC-ESI-MS). Our results show that adenine is adsorbed near 98% at pH acid, but the adsorption of thymine is very low (near 30%). However, when these bases are adsorbed from the same solution, a co-adsorption phenomenon takes places, and there was a significant increment in the adsorption of thymine into the clay. Also, the protection role of the clays toward ionizing radiation was observed, and there was a high recovery of the bases under study.

Our aim is to study the role of clays in chemical evolution as protector agent under γ radiation. We study the co-adsorption of adenine and thymine-clay systems at different irradiation doses, pH to evaluate the adsorption and degree of decomposition

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Computational Exploration of the Chemical Space of Nucleic Acid-Like Compounds

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Introduction: Biological information storage for life as we know it is carried out by the nucleic acids DNA and RNA. However, these may be optimized end-states for life on Earth, or there may be other types of molecules which are similarly capable of carrying out these functions, perhaps used in alien biochemistries or in earlier biochemical states [1]. A number of these have already been synthesized in the lab [2-5], however the set of molecules compatible with this function may be far larger. Understanding this wider "chemical space" may give insights into what makes the biological isomers unique, as well as whether there are other isomers more easily accessed by abiotic chemistry.

Methods: Using graph theory-based structure generation [6], we have exhaustively computed the chemical isomer space of the natural ribosides (compounds of formula $C_5H_9O_4B$, where B is a nucleobase) [7] as well as a much wider range of formulas from C3 to C8, including those also containing N. We further culled these sets to include only likely chemically stable compounds, as well as only compounds containing at least two points of attachment for incorporation into a linear polymer via dehydration reactions or via the attachment of a suitable linker such as phosphate.

Having generated these sets, it is then possible to compute *in silico* some of the chemical properties of these compounds, including their three-dimensional conformations, van der Waals volumes, number of freely rotable bonds and solvent accessible surface areas, among many others. These computations then enable quantitative comparison of the generated structures.

Results: We find there are potentially millions of structural isomers, and many more stereoisomers, of nucleic acid-like compounds over this formula range. However, only a fraction of these are likely able to adopt conformations allowing for complementary strand-recognition. Further compatibility considerations may make the truly nucleic-acid-like set still smaller, though there may also be new strand-recognition motifs which have not been explored yet *in vitro* in these sets.

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Title: Dynamics of Adenosine Monophosphate in Lipid and Salty Environment.

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One of the fundamental questions, which concern the Origin of Life studies, is how the first nucleic acids were synthesized starting from the monomeric constituents, in a prebiotic environment. The question is also highly relevant since it could give additional information to solve the controversy between "Lipid world" and "RNA world" hypotheses[1]. Recent studies reported evidences on a non-enzymatical polymerisation of mononucleotides inserted in confining environments such as lipid multilayers and monovalent salts[2,3,4], pushing toward an "RNA world". The free energy necessary to allow the phosphodiester bond synthesis in such systems is given by Hydrothermal (HD) Cycles of hydration-dehydration at high temperature, conditions which commonly occur in volcanic hydrothermal fields nowadays, and were likely to be ubiquitous on the early Earth environment. Hence life could have been emerged into volcanic "hydrothermal fields", rather than oceanic "hydrothermal vents"[5].

The effects of the confining environments (lipid multilayers and crystal salts) on the mononucleotide (AMP) structure have been recently studied[6,7], and the results showed that the mononucleotides in these systems are forced to lie in a particular "entangled" structure, which may give a higher probability of occurrence of the phosphodiester bond synthesis.

However, what it is still unknown is how both the confining environments and the water affect the mononucleotide mobility itself, giving degrees of freedom to enable the needed molecular rearrangements. To this purpose, we performed Neutron Scattering experiments at the large scale facility "Institut Laue Langevin" in Grenoble, France. Quasi-Elastic (QENS) and Elastic (ENS) data analysis, which gave us insights about the dependence on the hydration level of the AMP dynamics (whose results have been recently published[8]), will be presented, together with new preliminary results on the particular geometry of each hydrogen motions, detected in the pico-to-nanosecond timescales.

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Darwinian Evolution of Mutualistic RNA Replicators with Different Genes

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Introduction: The formation of cooperative relationships between RNA replicators is one of the major transition in early evolution, enabling the expansion of genetic information capacity[1]. A representative model of the cooperative replicators is hypercycle, in which distinct replicators mutually aid each other's replication[2]. Theoretical studies extensively examined the hypercycle and pointed out that the cooperative behavior is susceptible to the emergence of parasitic replicators that provide less or no cooperation[1]. For RNA replicators, parasitic RNAs spontaneously appear with selfish mutations that make the RNAs better templates to be replicated faster by exploiting other cooperative replicators. A possible solution is compartmentalization, which provide parasite-free compartments [1], although there has been no direct evidence. In this study, we experimentally investigated the sustainability of a cooperative RNA replication system that consists of two mutualistic RNA replicators encoding two different genes. We also examined the evolution of the cooperative behaviors through a long-term replication.

Results & Discussion: We combined a reconstituted *E.coli* translation system with two RNA replicators (Rep-RNA and NDK-RNA) encoding different genes: Qβ phage replicase (RNA-dependent RNA polymerase) for Rep-RNA, and *E.coli* NDK (nucleotide diphosphate kinase) for NDK-RNA. The structure of NDK-RNA was modified with 49 mutations so that Qβ phage replicase can replicate it. In this system, NDK is translated from NDK-RNA and synthesizes CTP from CDP in the solution. Then the replicase, translated from Rep-RNA, replicates both NDK-RNA and Rep-RNA with the synthesized CTP. Thus, the RNA replicators are mutualistic.

We repeated the replication reaction in cell-like compartments (water-in-oil emulsion) with nutrients supply via manual fusion-division of compartments. During this cycle, mutations are spontaneously introduced into both the RNAs by replication errors. We found that at high or low RNA concentrations, the cooperative relationship was destructed due to excess parasites generation or dispersion of the two RNAs into different compartments, as previously suggested[3]. On the other hand, in a certain range of total RNA concentrations, both Rep-RNA and NDK-RNA have synchronously and sustainably replicated more than 150 generations (10^{45}-fold replications). The synchronicity of NDK-RNA and Rep-RNA concentrations is surprising because we could not control each concentration independently.

Next, we obtained 32 evolved clones for both the RNAs and analyzed their cooperativities, which we defined as how efficiently proteins expressed from each RNA support the other's replication. In Rep-RNAs, most of the evolved clones showed parasitic behaviors, which provided less or no cooperation. This result is consistent with theoretical predictions that natural selection favors selfish mutations that increase the replication rates of templates but may impair encoded protein functions[1,3]. In contrast, however, we found that most of NDK-RNAs evolved to maintain or increase the cooperativity. This distinctive trait may have stabilized the long-term replication by preventing the spread of parasites that constantly arise from the cooperative RNAs.

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Can Autotrophic Carbon-Fixing Pathways Be Catalyzed Without Enzymes?

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Carbon-fixation pathways used by chemoautotrophs have received much attention as potential prebiotic synthetic pathways that would provide a parsimonious explanation for the organization of biochemistry. The pathways of greatest interest are the reductive tricarboxylic acid (rTCA) cycle,[1-2] the AcCoA pathway (also known as the Wood-Ljungdahl pathway)[1] or even a hypothetical combination of both (Figure 1).[3] However, experimental work to assess the plausibility of these pathways in the absence of enzymes has been limited.[4-7] This presentation will summarize our efforts to identify simple non-enzymatic catalysts for the two pathways and assess productive and parasitic off-cycle reactions.[8]

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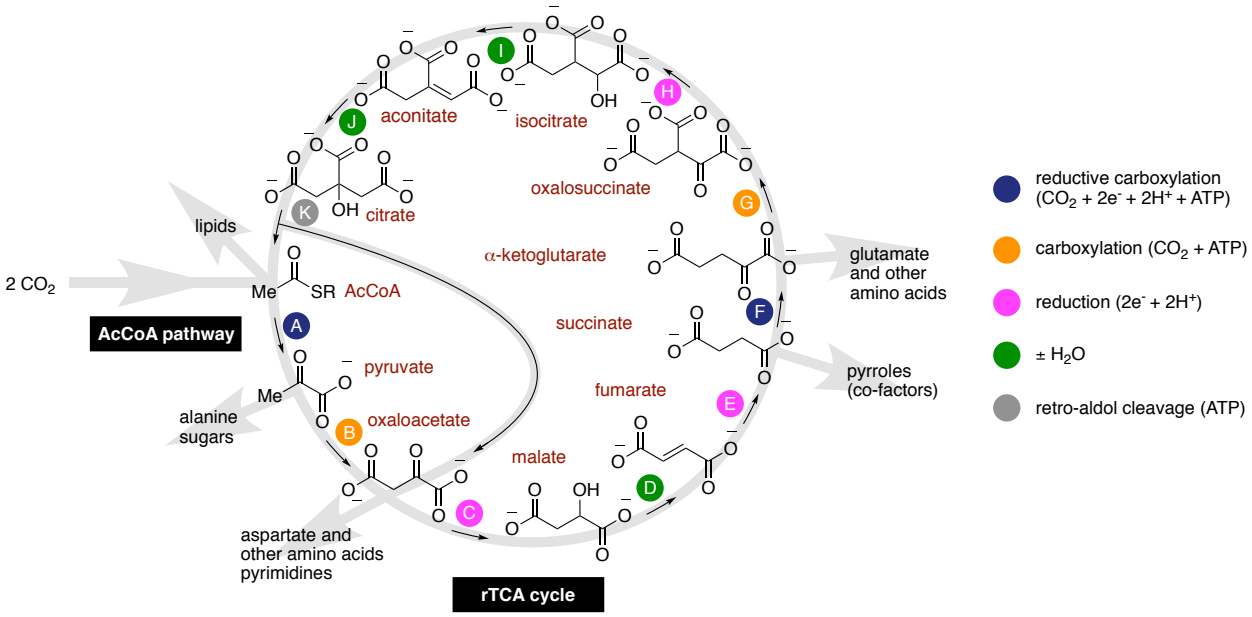

Figure 1 –Hypothetical stabilized autocatalytic network consisting of the AcCoA pathway and the rTCA cycle.

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Thermally Driven Accumulation and Dry-Wet Cycles of Nucleotides

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Introduction: Life has developed in water, but dry steps are essential for many prebiotically plausible syntheses and polymerization processes [1,2]. This posits the question how dry-wet cycles can be combined in a single scenario without diluting reaction products into the ocean.

We found that a nonequilibrium system in form of a temperature gradient across submerged porous rock creates an environment where molecules accumulate both in water and at water-air interfaces [3]. The presence of an interface in the pores results in continuous drying and re-hydration steps of the molecules at the interface. This provides intermediate dry state phases while maintaining high local concentrations of ca. 1000-fold in the aqueous phase. Importantly, even without the interface molecules such as RNA monomers can be concentrated above their limit of solubility, leading to precipitation.

Here, we show the underlying mechanisms for the accumulation process both at the bottom of the pore and at the water-air interface. In both cases a precipitation of diluted molecules can be observed. These mechanisms potentially enable reaction pathways such as the formation, phosphorylation, or polymerization of nucleotides that require aqueous and dry conditions.

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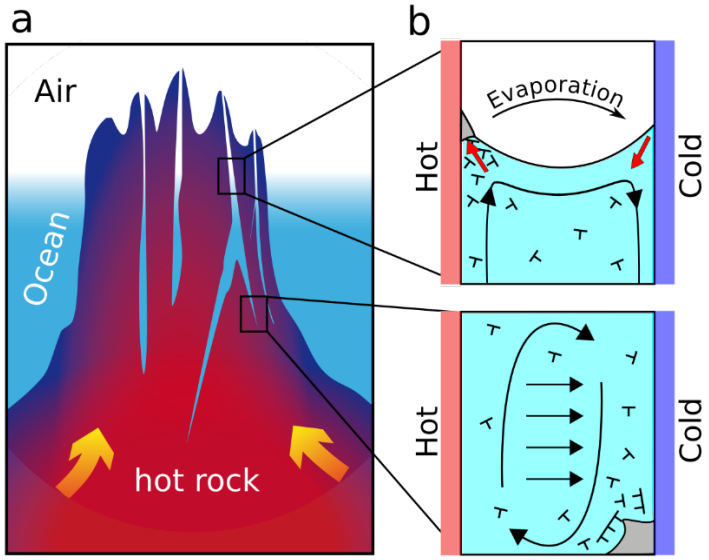

Figure 1 – Accumulation processes in submerged porous rock. a) Hot water emerging from porous rock in e.g. volcanic or steam settings. b) Top: Air-water interfaces formed e.g. by bubbles inside the rock or partial exposure to the atmosphere. The temperature gradient causes convection while simultaneously evaporating water at the hot side and condensing at the cold side. Molecules are thereby strongly accumulated at the hot side of the interface (see arrows), leading to dry phases. Bottom: A combination of convection and thermophoresis results in an accumulation of molecules at the bottom of the pore. Local concentrations can exceed the solubility limit, causing the molecules to precipitate.

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Chirality and Physical Autocatalysis

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Introduction: In an autocatalytic reaction, the product of reaction acts as a catalyst for its own formation, rendering the product a self-replicator.[1] In the case of *physical* autocatalysis, the catalyst is typically a micelle or vesicle composed of amphiphilic species. These structures can catalyse the formation of the amphiphilic product molecules at the interface between organic and aqueous phases (Figure 1).[1] Such self-replicating systems, with their ability to form aggregated, membrane-like structures, have clear relevance in research into the origins of life. For example, the coupled self-replication of these membranous compartments with the self-replication of their contents is required for the design of protocells.[2,3]

The search for asymmetric autocatalysis: In the search for bond-forming (and therefore complexity-inducing) examples of physical autocatalysis the group has been successful.[4,5] For a further increase in complexity we now aim to establish asymmetric variants and examine the role that stereochemistry can play in physical autocatalysis.[6,7] Common to multiple examples of the amplification of chirality is the formation of supramolecular structures, from the aggregation of catalysts in the Soai reaction,[8] to the formation of large supramolecular helical structures.[9] Such aggregates often lead to the emergence of non-linear effects, amplifying chirality from a nearly racemic mixture and offering one mechanistic basis for the emergence of homochirality.[10,11] In examining chirality in the micellar aggregates we form via physical autocatalysis we link, to some extent, two prominent themes on the origins of life – the production of a compartment[2] and the possible requirement for homochirality.[10]

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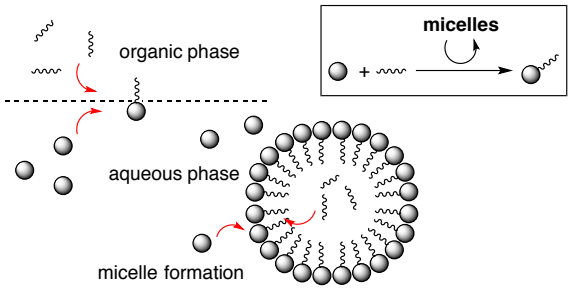

Figure 1 – Physical Autocatalysis: Hydrophobic species in an organic phase and hydrophilic species in an aqueous phase meet slowly at the interface and react to produce an amphiphile. Above a critical concentration, the amphiphiles aggregate into micelle structures. These aggregates allow increased mixing between the phases and therefore an increased rate of reaction; the micelles are self-replicating.

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Exploration of novel subsurface microbial communities within seafloor mantle rocks

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Introduction: Ultramafic rocks in Earth's mantle represent a tremendous reservoir of carbon and reducing power. Mixing of these rocks with overlying seawater due to tectonic uplift causes an exothermic reaction known as 'serpentinization' that also releases hydrogen gas, methane, and small organic molecules.

The H_2 and CH_4-rich environments provided by serpentinization reactions are thought to be analogous to conditions found on the early Earth and perhaps other planets [1][2][3][4]. Much of what we know about the microbial communities living in seafloor serpentinizing environments comes from studies of the Lost City Hydrothermal Field (LCHF) chimney [5][6][7]. However, the chimneys cannot be accurate representatives of the deep, subsurface habitats within the Atlantis Massif where the LCHF is located because they are continuously exposed to oxidized seawater.

During October-December of 2015 the International Ocean Discovery Program Expedition 357 to the Atlantis Massif collected rocks from a subseafloor site of active serpentinization for the first time. This expedition recovered a total of 57 m of rock cores from 17 different drill holes into the Atlantis Massif with the aid of two seabed rock drills remotely operated from the ship. The drill holes were designed to capture rocks that span a range of degrees of serpentinization and varying distances from the LCHF chimneys.

One of the main goals of this drilling project is to generate a survey of the archaea and bacteria in marine serpentinite rocks by comparing the 16S rRNA gene sequences between the recovered cores of various holes with each other, to the background seawater, and to previous studies on carbonate chimneys at LCHF. For reaching this goal, two main questions of ***'Are there unique microbial communities associated with marine serpentinite rocks?'*** and ***'How can we distinguish the endemic microbial communities of subsurface serpentinite rocks from seawater residents?'*** will be addressed. A major challenge of this project is to obtain sufficient high-quality DNA from low-biomass serpentinite rocks for sequencing studies. Customized DNA extraction and purification procedures are currently being optimized for these sample types and to control for and identify contaminating DNA during all stages of sample processing.

Currently, almost nothing is known about the biology of the marine serpentinite subsurface. This research project will produce the first census of the di diversity, genomic content, and metabolic potential of microbes within the serpentinizing rocks collected from the Atlantis Massif.

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SYNTHESIS AND CHARACTERIZATION OF INFORMATIONAL MOLECULES FORMED UNDER PREBIOTIC CONDITIONS

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All processes in extant biology are possible and facilitated by information encoded in polymers. Therefore, the origin of informational molecules had to be a crucial step in the origin of life on Earth. An important molecule in this context is RNA and the RNA World has been hypothesized as a crucial step in the transition from chemistry to biology. However, the RNA molecule is comprised of intra-molecular bonds, which are prone to hydrolysis, especially under the harsh conditions that are thought to have been prevalent on the early Earth [1]. Furthermore, the formation of nucleotides with extant bases, and their subsequent polymerization, have both been problematic, to say the least. Certain environmental niches, such as volcanic geothermal pools, allow the formation of RNA-like polymers, under dehydrating-rehydrating (DH-RH) conditions, by potentially forming kinetic traps [2]. However, the low pH and high temperature conditions that are required for such polymerization to occur also result in the cleavage of the N-glycosidic bond, thereby producing polymers with abasic sites [3]. In the first part of the present study, we set out to characterize the effect of prolonged cycling, under DH-RH conditions, on the stability of resultant molecules and also looked at how they might affect the product distribution. Our observations indicate lower fitness for modern nucleobases under prebiotically relevant conditions. These results are also supported by older experiments wherein formation of nucleosides with extant bases was shown to be difficult.

Alternate bases, on the other hand, have resulted in nucleosides in higher yields, suggesting a viable and prebiotically relevant solution to the longstanding "nucleoside problem" [4]. Towards this extent, we also recently demonstrated the synthesis of a pre-RNA World nucleotide using ribose 5'-monophosphate (rMP) and barbituric acid (BA) as the base analog, under dry-heating conditions [5]. This result was simultaneously also demonstrated by the Hud group thus strengthening the more recently posited pre-RNA World hypothesis [6]. Furthermore, polymerization of the resultant monomer, i.e. the BA-nucleotide, was also observed when we carried out DH-RH cycles at low pH and high temperature. The resulting RNA-like oligomers were shown to have intact bases unlike the reactions that were carried out using canonical nucleotides. Additionally,, incorporation of BA onto preformed sugar-phosphate backbones was also observed when pre-formed rMP oligomers were subjected to heating with BA. Aforementioned studies provide important preliminary evidence that alternate bases could have indeed gotten incorporated into early polymers that may have predated the molecules of an RNA-World. Importantly, these results suggest that BA could have been a putative precursor of modern nucleobases,.Moreover, it also highlights the possibility that the prebiotic soup, which would have contained several types of heterocycles, might have facilitated simultaneous sampling of other potential pre-RNA World heterocycles.

We discuss the selective advantage that such primitive informational polymers could have had under pertinent selection pressures. Importantly, these kinds of processes have implications for shaping the prebiotic landscape that allowed for the emergence of primitive informational polymers of the pre-RNA World(s), prior to the emergence of a putative RNA World.

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Induction of asymmetry in formose reaction

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The autocatalytic transformation of formaldehyde and glycolaldehyde to carbohydrate building blocks, also known as formose reaction, is a cornerstone of prebiotic chemistry. Infact, it has been argued that formaldehyde may be the only one carbon C-, H- and O-containing molecule capable of generating complex organic compounds for the origin of life.[1] Sugars are key components of DNA, RNA and the surfaces of cells, where they perform a wide variety of complex regulatory and communication roles. Recently, sugar molecules including ribose have been detected in interstellar ice analogues suggesting the occurrence of photochemically initiated formose-type reactions,[2] thus demonstrating that carbohydrate can be formed under a wider range of conditions than believed. Even though fomose reaction in general is robust, it has numerous limitations including low yields, absence of chemo- and stereoselectivity. The problem of enantioselectivity has been previously addressed by Bresslow[3] and Pizzarello[4] as they used amino acids and peptides to generate asymmetry in C3 to C5 sugars.

In the present work we investigated influence of diferent chiral species, including amino acids and sugar derivatives, on the enantioseleve outcome of the fomose reaction. These data have been used to gain better understanding of the reaction network. Furthermore, we examined possibility of generating formose rection within prebioticaly relavent systems such as chiral vesicles. Understanding the relationship between key intermediates of the formose reaction may inform the design of an asymmetric autocatalytic reaction.

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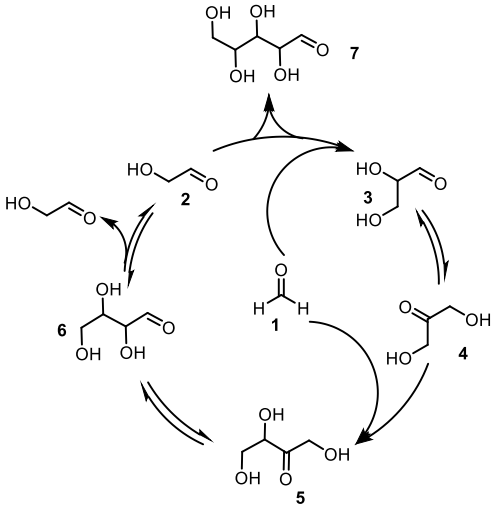

Figure 1 The first stage of formose reaction involves condensation of formaldehyde **1** with glycolaldehyde **2** to yield chiral aldehyde **3**. Aldol condensation of **3** and **2** produces pentoses, while condensation of two molecules of glycolaldehyde **2** results in tetroses **6.** Glyceraldhyde **3** isomerises to dihydroxyacetone **4**. Condesation of **4** with **1** produces erythrulose which in turn can isomerise to **6**.

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Formose reactions with ammonia prevailing for the synthesis of meteoritic soluble organic matter

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Introduction: Chemical evolution of extraterrestrial organic matter has been investigated mainly using carbonaceous meteorites, which are the primitive materials of the solar system. The carbonaceous chondrites contain a few weight % of carbon mainly as organic matter. A wide range of organic compounds including amino acids, carboxylic acids, sugars and nucleobases has been found in the meteorites [1]. The origins and comprehensive formation mechanism(s) of these compounds, however, have not been clarified due to the incomplete understanding of molecular occurrence [2]. The carbonaceous chondrite also contains water mainly as hydrous minerals resulting from aqueous alteration on the meteorite parent bodies. The aqueous activity and minerals could have important roles in chemical evolution in the early solar system. Therefore, further meteorite analyses and simulation experiments are needed to pursue the formation pathways of extraterrestrial organic matter.

Materials and Methods: The Murchison meteorite was extracted with methanol and hot water. The methanol extract was analyzed by high performance liquid chromatography/high resolution mass spectrometry (HPLC/HRMS) using an Orbitrap MS ($m/\Delta m > \sim 100{,}000$). The hot water extract and its extract residue were subjected to acid hydrolysis followed by derivatization to analyze by gas chromatograpy/MS. The simulation experiments were performed using formaldehyde and acetaldehyde with ammonia in aqueous solutions [3, 4]

Results and Discussion: Extensively alkylated N-containing cyclic compounds were revealed in the methanol extract of the Murchison meteorite. More than 600 positive ions were assigned to $C_nH_mN^+$ and $C_nH_mN_2^+$ in elemental compositions, in which saturate- and unsaturate-alkylated pyridines ($C_nH_{2n-5}N$ and $C_nH_{2n-7}N$, respectively) and alkylimidazoles ($C_nH_{2n-2}N_2$) were predominant [3]. In the water extract, totally 30 amino acids between C_2 and C_6 were identified including a new family of nine C_3 and C_4 hydroxy amino acids in addition to the most abundant glycine [4]. The simulation experiments gave various alkylpyridines and alkylimidazoles as well as amino acids including the hydroxy amino acids. Both the N-heterocyclic compounds and the amino acids could be produced from aldehydes and ammonia through aldol condensation and imine formation under an alkaline environment. The presence or absence of minerals affected the compound occurrence in the simulation experiments. Therefore, these results indicate that formose reactions with ammonia in the presence of minerals are an important process to produce meteoritic soluble organic matters including sugars [5] through aqueous alteration on the meteorite parent body. The soluble N-heterocyclic compounds may have a genetic relationship with the meteoritic insoluble organic matter, which also could be produced from aldehydes and ammonia through the similar mechanism proposed by Cody et al. [6]

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July 16-21, 2017 at UC San Diego, CA, USA

Molecular innovation in ciliates with complex genome rearrangements

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Molecular innovation, as the process that produces new functions in an organism, provides a window of opportunity to understand the transitions from non-genic, non-functional material into new genes, functions and structures.

Ciliates, unicellular eukaryotes with two types of nuclei, possess the remarkable ability to rearrange their genomes in processes that involve the selective deletion, ligation and reorganization of genetic information from a sexual genome into a somatic genome. These arrangements can be simple or complex, depending on whether fragments of DNA are joined in the same order in the final product, or whether the rearrangements require translocation or inversion. This type of genomic architecture provides abundant plasticity and increased potential for innovation relative to other eukaryotic lineages.

Molecular innovation profits from the organization of biological information. Most organisms obtain novelty from mechanisms such gene duplication, gene fusions, alternative splicing, or de novo. In ciliates, it can be assumed that all such mechanisms are generally active. Furthermore, it has been shown that alternative DNA processing is able to produce new genes [1], and as such constitutes a ciliate-specific innovation that produces further innovation. This is likely to have contributed greatly to the molecular and functional diversification on stichotrich lineages. We are interested in the evolutionary steps leading to this type of genomic architecture, and the influence it has had on evolutionary innovation.

We undertake phylogenomic analyses of various ciliate species, and explore how the rate of acquisition of new protein-coding genes has accelerated in lineages of ciliates with complex genome rearrangements. Further, we assess genome-wide error rates of the rearrangement process in the model species *Oxytricha trifallax*, aiming to understand how the cellular machinery deals with errors, and how much of those errors could contribute to the conversion of non-coding elements in the genome into new genes.

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A Hot Spring Origin of Life and Early Adaptive Pathway from Woese Progenotes to Marine Stromatolites

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Introduction: Laboratory and volcanic field synthesis of polymers through prebiotically plausible wet-dry cycling [1] combined with the earliest evidence of life on land discovered in 3.48Ga strata of fresh water hot springs in Western Australia [2] suggests an alternative hypothesis [3] to a deep sea origin of life. This hypothesis proposes a complete pathway (figure 1) through: the synthesis of key organic compounds in the solar accretion disk; accumulation and concentration of compounds in pools on land; synthesis and cycling of membraneous protocells encapsulating random sets of polymers; repeated selection of evolving aggregates of protocells yielding a Woese progenote [4]; subsequent distribution of progenotes to varying environments leading to the emergence of living microbial communities; and finally, to global colonization by robust communities of stromatolites so prevalent in the earliest rock record. Malcolm Walter, Martin Van Kranendonk and Tara Djokic of the Australian Centre for Astrobiology, University of New South Wales are acknowledged for their input into this model and visualization.

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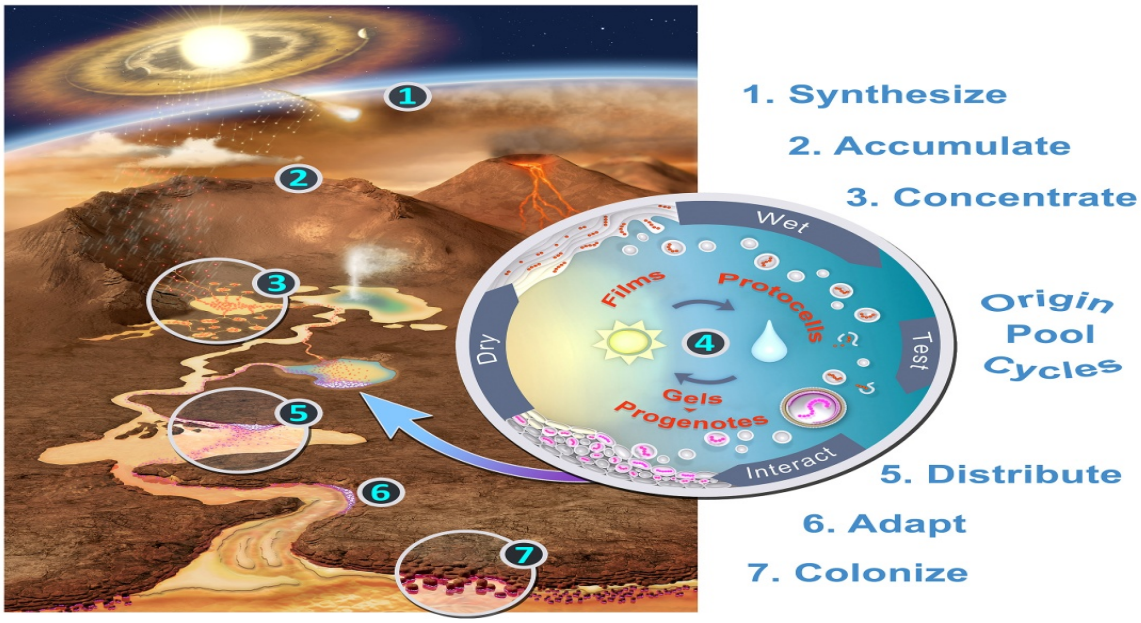

Figure 1 – Visual depiction of a model for a hot spring origin of life in seven stages: 1. synthesis of organic compounds during solar system accretion; 2. accumulation of compounds on land; 3. concentration and chemical reactions; 4. generation and cycling of protocells through three phases; 5. progenote emergence and distribution; 6. transition to cellular life and saline adaptation; and 7. microbial colonization of continental interiors and margins.

July 16-21, 2017 at UC San Diego, CA, USA

Direct Evidence for GC-NSF(a) Hypothesis on Creation of Entirely New Gene/Protein

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Introduction: One of the most fundamental problems, which remains unsolved in the fields of Biochemistry and Molecular Biology, is how entirely new (EntNew) protein or the first family protein was produced which is totally different from any previously exisiting proteins. On the other hand, we have proposed GC-NSF(a) hypothesis on formation of EntNew protein [1, 2]. The hypothesis assumes that EntNew protein was generated from non-stop-frame on antisense strand of, not AT-rich gene, but GC-rich gene (GC-NSF(a)). GC-NSF(a) is codon sequence in the same frame with the corresponding gene on sense strand.

Results and Discussion: It is quite important to get direct evidence that EntNew gene has been actually produced as expected by the hypothesis. For the purpose, every amino acid sequence (AAS) of imaginary protein encoded by GC-NSF(a) of *Pseudomonas aeruginosa* PAO1 genome (GC content=66.6%) was homology-searched against all AASs of extant proteins encoded by the same genome. However, some difficulties were anticipated, when evidence for the hypothesis is searched for, as described below.

(1) Probability of mis-annotation between sense and antisense sequences increases beyond about 60% GC content, because all three stop codons are AT- or AU-rich.
(2) Base sequence of a gene would frequently change without amino acid substitution of a protein encoded by the gene, because of degeneracy of the genetic code, which should induce amino acid substitution in imaginary protein encoded by GC-NSF(a) [3].
(3) Moreover, base sequence of immature EntNew gene would also rapidly change upon development of the immature protein to get a higher catalytic activity and to evolve into mature protein, from just after the gene was newly born.

Nevertheless, it was found that AAS encoded by GC-NSF(a) of *tal* gene encoding transaldolase B has sufficient homology with AAS encoded by *ftsZ* gene encoding cell division protein FtsZ, after the results obtained were cautiously examined and judged whether it is correct evidence or not. In addition, several results supporting for GC-NSF(a) hypothesis were also obtained with 56 bacteria genomes having more than 50% of GC content. Thus, we have concluded that EntNew gene encoding EntNew protein has been generated from GC-NSF(a), according to the GC-NSF(a) hypothesis.

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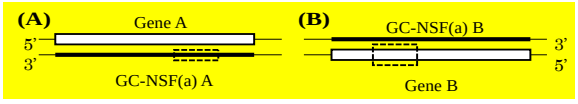

Figure 1. Amino acid sequence (A) of a protein encoded by GC-NSF(a) of a gene A showed sufficient homology with amino acid sequence（B）of an extant protein encoded by another gene B in the same genome. Therefore, it is concluded that (a part of) the gene was created from the GC-NSF(a), according to GC-NSF(a) hypothesis on formation of entirely new protein, which we have proposed.

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Can We Make Life in the Lab? Emergence and Evolution of Self-Replicating Molecules from Dynamic Molecular Networks

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How the immense complexity of living organisms has arisen is one of the most intriguing questions in contemporary science. We have started to explore experimentally how organization and function can emerge from complex molecular networks in aqueous solution [1]. We focus on networks of molecules that can interconvert, to give mixtures that can change their composition in response to external or internal stimuli. Molecular recognition between molecules in such mixtures leads to their mutual stabilization, which drives the synthesis of more of the privileged structures (Figure 1). As the assembly process drives the synthesis of the very molecules that assemble, the resulting materials can be considered to be self-synthesizing. Intriguingly, in this process the assembling molecules are replicating themselves, where replication is driven by self-recognition of these molecules in the dynamic network [2]. The selection rules that dictate which (if any) replicator will emerge from such networks are starting to become clear [3]. We have observed that factors such as mechanical energy [2] and the presence of cosolvents [4] can determine which replicator wins the competition for building blocks. We have also witnessed spontaneous differentiation (a process akin to speciation as it occurs in biology) in a system made from a mixture of two building blocks [5]. When such systems are operated under far-from-equilibrium flow conditions adaptation of the replicators to a changing environment can occur. Thus, the prospect of Darwinian evolution of purely synthetic molecules is tantalizingly close and the prospect of synthesizing life de-novo is becoming increasingly realistic.

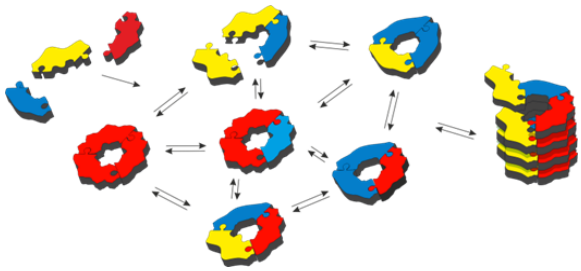

Figure 1 – Molecular recognition between molecules in a dynamic molecular network can lead to self-synthesizing materials, build up from self-replicating molecules.

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A proposal of the Ur-proteome

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Abstract:

We can uncover the plausible Ur-proteome encoded in the RNY chains (where R indicates purine, N means any of the four bases, and Y indicates pyrimidine), that Eigen and Schuster suggested as the first genetic code in the early 70's, based on the logical deduction of the thermodynamic properties of that kind of polyribonucleotide existing in the RNA world.

The evolution of that primeval code has been previously investigated under rigorous mathematical approaches, and it was demonstrated how the current standard genetic code (SGC) can be derived via a dichotomous pathway starting from the RNY code.

Presently, we could find vestiges of the primeval phenotype, corresponding to the RNA genotype, as a collection of peptides constructed from the 8 amino acids (aa) encoded in the 16 RNY triplets. We began by extracting an RNY genome from a contemporary organism and the resulting smaller genome was used as a query in order to obtain a list of ancient proteins encoded by RNY codons, which at first instance was mysteriously heterogeneous.

By looking at the fragments encoded by RNY triplets, it was noteworthy that they are positioned, not in catalytic sites, but in the cofactor binding sites. Some fragments were then extracted, their three-dimensional structure was predicted and, without any additional manipulation, it was startling that such peptides actually bind somehow the now called cofactors, which has been proposed among the early prebiotic molecules nonetheless. It is necessary to recall that currently these fragments contain not only the 8 aa of the ancestral phenotype but they are composed mainly of them in diverse combinations.

Notwithstanding our methodology does not fit into the classic “bottom-up” neither “top-down” approaches, our approach that uses only the 16 RNY triplets as genotype and as phenotype the corresponding 8 aa, an ***Ur-proteome*** can be wrought that consists of a set of primordial peptides that work as ***Cofactor Stabilising Binding Sites (CSBSs)***, i.e. the primitive ***bindome***. It implies that the stabilization of a molecule appeared long before its catalytic use. Indeed, such notion of CSBSs as the first proteins modules in progenotes is not unreliable, and is congruous with several propositions about the primitive forms of life.

Finally, we can state that the ancestral CSBSs constitute the primordia of the peptides that would eventually evolved –likely aided by HGT (thus not purely by Darwinian processes)–, yielding the basic repertoire of LUCA.

Non-Enzymatic Synthesis of Duplex Nucleic Acid

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On prebiotic Earth, environments existed at the interface between land and water characterized by small aqueous pools undergoing evaporation and refilling at elevated temperatures, known as hydrothermal fields. Previous reports have shown that by simulating prebiotic environmental conditions in thermal fields with cyclic dry and wet periods, ampiphilic molecules in the mixture could form fluid lamellar matrices and encapsulate other small molecules [1]. Subsequent report showed that linear charged polymers resulted from these experiments [2]. The lipid matrices work as organizing agents for the condensation of monomers into polymers. The goal for the present study is to evaluate whether the simulated prebiotic environment and the chemical potential made available by cycles of hydration and dehydration is sufficient to drive the synthesis of oligomers resembling DNA, and to demonstrate whether the linear polymers form duplex structures. In order to do so, we expose a mixture containing deoxynucleoside monophosphates and an oligomer template in a lipid suspension to the already established conditions of hydration-dehydration cycles, and analyze using a biological nanopore detector, as well as more conventional tools such as gel electrophoresis.

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An Evaluation of the Prebiotic Plausibility of Depsipeptide Synthesis Under Possible Primitive Conditions

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Introduction: Although numerous reports exist demonstrating the prebiotic synthesis of organic monomers [1-3], the polymerization of such species on the early Earth to form biopolymers important for life remains poorly understood. Recently, the plausible prebiotic condensing reagent cyanamide was shown to polymerize amino acids to generate simple peptides under mimicked primordial conditions [4], but the formation of diketopiperazines, cyclic dipeptides that can limit the availability of amino acid residues for further polymerization chemistry, remained a challenge. More recently, simulated dry-hot/wet-cool environmental cycling has demonstrated the ability to co-polymerize amino acids and alpha-hydroxy acids to generate depsipeptides (containing mixed amide/ester linkages), becoming enriched in amide linkages over time [5], supporting the hypothesis that peptides may have evolved from ester-based precursors. However, these results were obtained using neat standard solutions of a limited number of monomers present at relatively high concentrations. Analyses of primitive simulation experiments suggest prebiotic mixtures are far more complex and produce relatively small quantities of relevant monomers [6]. Ideally, a more robust evaluation of the prebiotic plausibility of depsipeptide synthesis would be executed, entailing the performing of primordial simulation experiments and subjecting the resultant mixtures to mimicked environmental cycling, prior to analysis for depsipeptides.

Methods: Here, we report the development of the first multi-stage analytical platform for the analysis of didepsipeptides in complex mixtures, using ultra performance liquid chromatography, traveling wave ion mobility spectrometry, and high resolution tandem mass spectrometry. Additionally, prebiotic experiments were performed and their resultant solutions were subjected to simulated environmental cycling to constrain the viability that the amino acids and alpha-hydroxy acids formed in-situ could have co-polymerized to yield didepsipeptides.

Results: The results of this investigation provide the first detection of depsipeptides in complex, prebiotic mixtures. Example depsipeptides detected included the glycolic acid-aspartic acid and malic acid-glycine didepsipeptides. Detection of didepsipeptides was further elucidated via acid hydrolysis-, internal standard spiking-, and isotopic labeling experiments.

Implications: The overarching implication of this work is that it provides new insight into the chemical evolution processes that may have been responsible for the synthesis of prebiotic peptides under a variety of possible primordial environments.

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July 16-21, 2017 at UC San Diego, CA, USA

A Roadmap toward Synthetic Protolife

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Abstract: The origin-of-life problem remains one of the major scientific riddles of all time and the difficulties in attempts to synthesize simple protolife reflect yet one additional facet of this long-standing problem. In this lecture it will be argued that a strategy for the synthesis of protolife requires the characterization of the physicochemical state of life's primordial beginnings, not just its material composition. It is through the concept of dynamic kinetic stability (DKS) that key elements of that state can be specified – replicative, dynamic, non-equilibrium and energy- fueled. With the recent dramatic discovery that DKS systems are experimentally accessible and show remarkably different physical and chemical characteristics to regular chemical systems, the door to the possible synthesis of simple protolife now appears to be open. Synthesis of a chemical system able to complexify toward more complex forms – toward life - will need to be initiated with the synthesis of a simple energy-fueled dynamic replicative system activated into the DKS state (Figure 1) [1].

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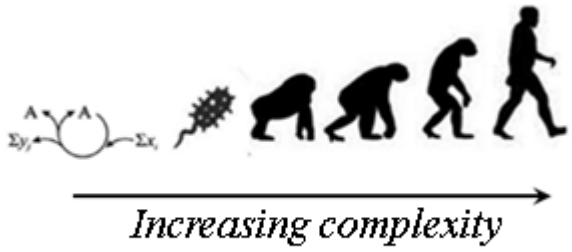

Figure 1 – Schematic representation of the evolutionary process in which a replicative chemical system in the DKS state complexifies toward simple life and then on to more complex life.

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Solubilization and Activation of Phosphorus on the Early Earth

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Introduction: The formation of phosphorylated biomolecules has long been a challenge in prebiotic chemistry due to the poor solubility of phosphate minerals and their minimal reactivity towards organic substrates [1]. In recent times, several new routes have been proposed to overcome these phosphorylation problems, including newly demonstrated phosphorylation by the meteoritic mineral schreibersite in water [2] and phosphorylation promoted by mineral transformation and solubilization within non-aqueous [3] and semi-aqueous [4] solvents. While efficient, these routes require either specific meteoritic minerals, or pools of organic-rich solvents to promote reactions. We report here a new route to enhancing phosphorus reactivity that we propose was active on a wide scale on the the early earth.

Phosphorus Reduction and Solubilization: Phosphate reacts with ferrous iron to form phosphite with a concomitant oxidation of iron. The reaction quotient K is about 0.001 to 0.01, at temperatures less than 200°C. Additionally, with the comparatively high solubility of phosphite relative to phosphate, if water flows through rock where this reaction is occurring, phophosphite will be preferentially extracted, promoting further reduction of phosphate.

This reaction is confirmed by experiments demonstrating reduction of phosphate when heated with ferrous iron. Additionally, analyses of rocks of early Archean age demonstrate a persistent presence of phosphite as a major P constituent. While previously this phosphite was attributed to meteoritic sources [5], a source from oxidation of ferrous iron is also feasible for many of these rocks.

Additionally, we have measured the oxidation rate of phosphite ions, and find the principal route to its oxidation is by reaction of oxygen radicals (OH or OOH) or by biological mediation. Given neither were likely present in abundance on the early earth, phosphite was thus likely a major phosphorus-bearing constituent of Hadean and Archean oceans.

Phosphorus Activation by Oxidation: Phosphite, though kinetically stable, is oxidized by OH and OOH radicals. Both are formed by reaction of peroxide with ferrous iron, via the Fenton reaction. We have demonstrated previously that phosphite is oxidized by these ions and forms phosphate, pyrophosphate, triphosphate, and trimetaphosphate [6]. To this end, the large-scale reduction of phosphate by iron, followed by the iron-mediated oxidation of phosphite, provide a large, steady-state abundance of polyphosphates present at high (disequilibrium) concentrations, ready to promote phosphorylation and setting the stage for the formation of phosphorylated prebiotic compounds.

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July 16-21, 2017 at UC San Diego, CA, USA

Molecular Modeling of RNA Nucleotides under Hydrothermal Prebiotic Conditions

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Introduction: The study of RNA formation and its subsequent accumulation and polymerization in the primitive Earth is one of the key issues related to the RNA World hypothesis. In this regard, many efforts have been dedicated to explore RNA synthesis under different plausible prebiotic conditions, comprising the catalytic function of mineral surfaces, the role of salts or lipid compounds, the exposure to drying/wetting cycles, and so forth [1]. However, one of the main challenges is to achieve the formation of RNA monomers (ribonucleotides) that subsequently polymerized to constitute larger RNA oligomers potentially able to perform more complex chemical processes. In this work, we provide quantitative new insights on the chemical reactions of ribonucleotides synthesis under hydrothermal prebiotic environments, performing *ab initio* molecular dynamics simulations explicitly taking into account water molecules and in presence of a biological pentose phosphate precursor (PRPP). Additionally, we exploit free-energy methods [2,3] in combination with a topological approach developed in our team that accurately tracks the chemical bond network along a reaction path [4]. From this framework, we are able to unveil the mechanism of ribonucleotide synthesis in atomistic detail, as well as to quantitatively assess the thermodynamical properties of this chemical process [5]. In addition, we performed NMR and Mass Spectroscopy experiments to detect the formation of ribonucleotides under hydrothermal conditions, complementing the results obtained from our *in silico* studies and confirming their plausability. Our main finding is that a chemical path from the same precursor of ribonucleotide synthesis in current biological systems is observed in plausible hydrothermal prebiotic conditions (see Figure 1).

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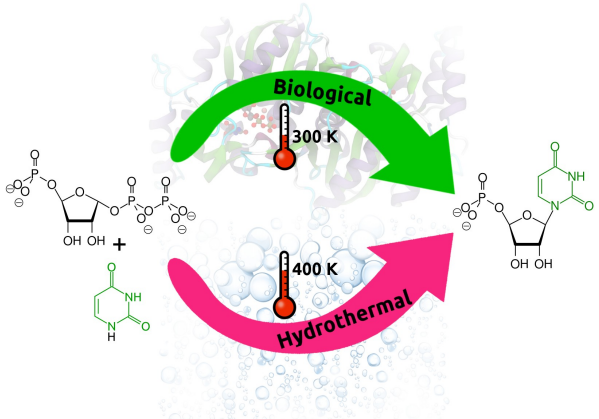

Figure 1 – Ribonucleotide formation from PRPP precursor in current biological systems vs. plausible prebiotic hydrothermal conditions as tested in our simulations and *in situ* NMR experiments. Synthesis in current living forms involves enzyme catalysis by phosphoribosyltransferases.

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Bypassing Evolutionary Roadblocks: Phenotypic Diversity in Isogenic Population Bridges Tradeoff in Evolution of a New Function

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Introduction: A key problem in the development of life on Earth is the origin of novelty. How does evolution achieve the complex diversity of forms and functions we see today, starting from simpler precursors? In particular, how can selection transform one phenotype, optimized to provide a reproductive benefit, into a novel phenotype without sacrificing the original function? One traditional explanation resolving this conflict is a multistage process initiated by gene duplication. One copy preserves the original function, freeing the other to diverge until it finds new function. Cases of this process seem to explain the evolution of some protein families; however, the prevalence of this mechanism throughout evolutionary history is uncertain. It is unclear if both the frequency of spontaneous gene duplication and the availability of productive mutational paths for copied genes are sufficient to account for the incredible diversity of extant life. Instead, we predict that an alternative, more deterministic and repeatable mechanism for evolutionary innovation may play a role.

Key Finding: Recent observations during experimental evolution of a contemporary virus revealed a new mechanism for innovation that does not rely on gene duplication. The virus instead evolved a single copy of the host recognition gene (*J*), that partitions its protein products into populations with different phenotypes: some can carry out the new function, in this case binding to a novel cellular receptor on the bacterial host, and some have improved binding to the original receptor. This new mechanism, termed 'phenotypic stochasticity', relies on natural selection and not the remote chance of gene duplication. The phenotypic stochasticity arose as a side effect of selection favoring a faster reacting host recognition protein. Reaction rates were improved by creating an unstable and disordered protein that can fold into multiple conformations. Because fast reactivity is a property many enzymes experience selection for, it may be a common step on evolutionary paths toward innovation, and may be especially relevant for the earliest forms of simple life, which may have lacked mechanisms for gene duplication and the ability to accommodate expanded genomes.

July 16-21, 2017 at UC San Diego, CA, USA

Exploring the stability of DNA/RNA chimeras by MD simulations: Could early life have utilized mixed DNA/RNA duplexes?

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In the current study we extend previous experimental work [1] on the (in-) stability of heterogeneous chimeric DNA-RNA duplexes by exploring the possible structural basis of experimental observations with Molecular Dynamics Simulations. In this study the DNA duplex $d(CGATTTAGCG)_2$ has been gradually converted into all RNA analog $r(cgauuuagcg)_2$ by two different paths. In Transition I all pyrimidine nucleotides in Strand 1 and then in Strand 2 were sequentially converted from the DNA form to their RNA equivalents followed by the analogous mutation of the puine nucletides. Transition II was generated by the conversion of the purine nucleotides in Strands 1 and 2, followed by the mutation of pyrimidine nucleotides. The changes in the free energies between each step in both transition paths were computed by the Free Energy Perturbation method. The intermediate hetero-duplexes along the Transition I appeared to be substantially less stable (up to 4.5 kcal/mol) than the corresponding homodimers, while along Transition II the intermediates were predicted to have a stability similar to that of the homoduplexes. Although the calculated changes in the thermodynamic stability for some individual species along Transition I and Transition II differ from experimental results, the predicted relative stability of most chiemeric dimers largely agrees with those revealed by experiment.

Our detailed structural analysis of the chimeric structures reveals that Transitions I and II explore different intermediate conformational space, which could be the origin of the observed experimental difference between the stabilities of duplexes along these two transition paths. While during Transition I a B-form helix is gradually converted to an A-form helix, some chimeric intermediates during Transition II occupy states outside of the canonical A/B conformations. Overall, the conformational changes in the systems studied here appear to be driven by the complex energy landscapes that account for the local changes near the mutation sites as well as for the global cooperative processes of backbone helical structure remodeling. The results of this study suggest that a few chimeric systems may be at least as stable as the pure RNA or DNA oligonucleotides of the same composition, while the others may be severely destabilized by the heterogeneity. These results could have important implications regarding the possible participation of chimeric systems in earlier stages of life, and further suggests a mechanism by which these two substantial biopolymers may have been purified and segregated [1].

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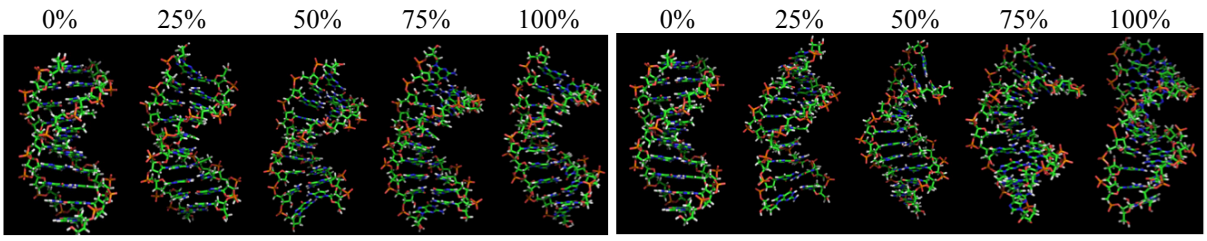

Figure 1. – Snapshots from MD trajectory for the Initial, final and intermediate conformations for Transitions I (left) and II (right) as a fraction of RNA nucleotides added into the system. 0% is all DNA, 100% all RNA.

THE SSU IS FROM MARS, THE LSU IS FROM VENUS. A. S. Petrov[1], Burak Gulen[2], L. D. Williams[1], [1]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, anton.petrov@biologygatech.edu, [2]Department of Chemistry, Technical University of Munich, Munich, Germany, 85748.

We previously described a three dimensional comparative method that allowed temporal ordering of events in the evolution of the large ribosomal subunit (LSU) rRNAs [1]. In these rRNAs, 'insertion fingerprints' are seen to mark sites of known rRNA expansions. A similar accretion model has been developed for the evolution of the SSU [2].

The evolution of the ribosome undergoes via elementary accreation processes that can be grouped into six phases (Fig. 1). In Phases 1 and 2, forming stable catalytically active units; the subunits evolve independently from each and temporal relationships between the subunits are undetermined. In Phase 3, subunit association is initiated, mediated by the recent expansion from minihelix to L-shape tRNA. In Phase 4, the ribosome is a non-coding diffusive ribozyme with proto-mRNA as a positioning cofactor. In Phase 5, the ribosome further expands to an energy-driven, translocating, decoding machine. In Phase 6, the ribosome matures, marking completion of the common core.

Despite similar accretion mechanisms that drive the eveolution of the ribosomal subunits, the SSU and LSU show significant differences in structure, morphology and function:

i. *Domain Structure*. The SSU is dendritic and the LSU is monolithic.

ii. *Flexibility*. The SSU is intrinsically flexible, while the LSU is rigid except on its periphery [3].

iii. *Shape*. The SSU is oblate spheroid and the LSU is hemispheroid

iv. Termini Strand Association and Dissociation. The 3' and 5' termini of the SSU rRNA are dissociated, while the termini of the LSU are associated via base pairing.

v. *The CPK*. A central pseudoknot and the separated strand termini form the ancestral core of the SSU, in comparison to simple stem-loop topology in the core of the LSU.

vi. *Expansions*. Over more recent evolution (*i.e.*, in eukaryotes) the LSU has continued to expand and gain function, while the SSU has undergone far more modest expansion.

Observations inferred from the accretion model suggested that some subunit-specific characteristics arise from singular events that took place early in ribosomal evolution and directed long-term outcomes.

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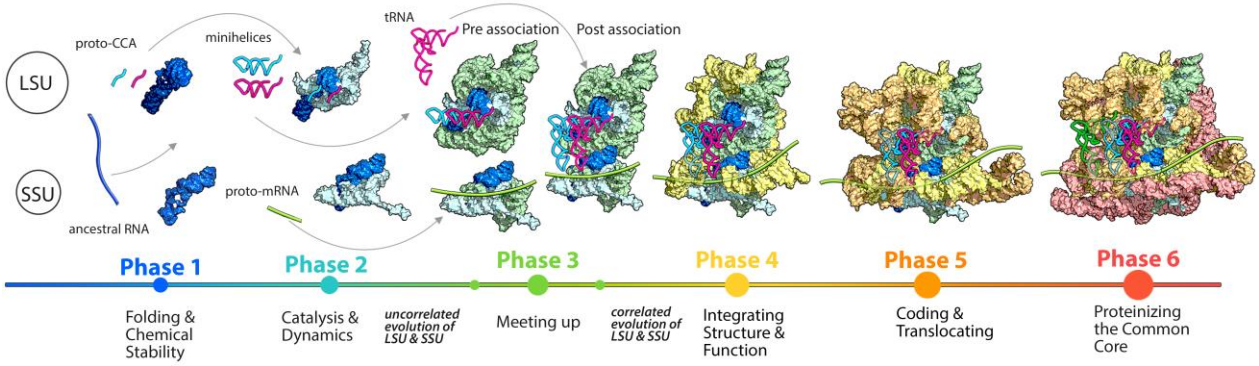

Figure 1. The first six phases of the accretion model of ribosomal evolution [2].

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High-Throughput Kinetic Screening of Non-Enzymatic Metabolic Conversions Driven by Single Amino Acids

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Introduction: Modern metabolism is organized in a set of highly efficient pathways catalyzed by enzymes. However, it is increasingly acknowledged that a variety of spontaneous, non-enzymatic reactions occur concomitantly with enzyme functions, recalling the relics of an ancestral remote network governed by very rudimentary activities. What were the structural and kinetic properties of those systems and how could they have progressed towards more efficient biological networks?

Results: In this work we explore the combined catalytic potential of single amino acids and metals on intermediates of central carbon metabolism. We make use of quantitative metabolomics techniques in enzyme-free *in vitro* assays to reconstruct the reactivity landscape and kinetics of what are regarded as some ancestral pathways. An unbiased high-throughput screening for catalytic individual amino acids was performed on more than 200 possible reactions among sugars from glycolysis and pentose phosphate pathway. Cysteine turned out to be a prominent enhancer of several interconversions between sugar phosphates. Moreover, these effects were further improved by metal ions, in particular iron (II). We provide structural and dynamical evidences (based on NMR and LC/MS data, respectively) of complementarity between these molecules. Through this illustrative example we would like to highlight the benefits of a metal-amino acid alliance and show some specificity/efficiency issues during the first evolutionary steps towards enzyme catalysis.

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Permeability-Driven Selection in a Semi-Empirical Protocell Model: The Roots of Prebiotic 'Systems' Evolution

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Introduction: The origin-of-life problem has traditionally been conceived as the chemical challenge to find the type of molecule and reaction dynamics that could have started a process of Darwinian evolution. However, in addition to molecular kinetics and evolutionary dynamics, other physical and chemical constraints (like compartmentalization, differential diffusion, selective transport, osmotic forces, energetic couplings) could have been crucial for the functional integration and intrinsic stability of intermediate systems between chemistry and biology. These less acknowledged mechanisms of interaction might have made the initial pathways to prebiotic *systems* evolution more intricate, but were surely essential for sustaining far-from-equilibrium chemical dynamics and as a source of innovative behavior.

Results: Here we explore a protocellular scenario in which some of those additional factors are addressed, demonstrating their 'system-level' implications. In particular, an experimental study on the permeability of prebiotic vesicle membranes composed of binary lipid mixtures allows us to construct a semi-empirical model in which protocells are able to reproduce and undergo an evolutionary process based on their coupling with an internal chemistry that supports lipid synthesis. We show how differential permeability linked to changes in the membrane composition could become a property with selective value in those systems, modulating proto-metabolic activity and protocell division time. Thus, the endogenous production of membrane components is proposed as an early prebiotic breakthrough, key in the development of protocellular populations with increasing dynamic robustness and adaptive potential.

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Chiral molecules in space and their likely passage to planetary bodies as recorded by meteorites

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The findings in carbonaceous meteorites of organic compounds having both a lineage to interstellar environments and identical counterparts in the biosphere have revealed very deep roots for the chemical evolution that preceded life. The most intriguing and debated similarity between these abiotic compounds and terrestrial biomolecules has been the detection in meteorites of several chiral compounds showing enantiomeric excesses of configurations matching those of biomolecules, e.g., L-, for amino acids[1] and D-, for sugars[2]. We searched Murchison meteorite extracts for propylene oxide (PO), the only chiral molecule discovered so far outside solar environments[3], and detected its possible derivative. This compound is also chiral, displays a mass profile and chromatographic separation very similar to those of the oxide and, upon acid hydrolysis, produces propylene glycol (PG), the expected water alteration product of PO. Both PO and PG were detected in Murchison with variable enantiomeric excesses (*ee*) averaging ~ 10% and to have the (R)(+) configuration, i.e., of the same optical isomer as for sugars in the biosphere and sugar derivatives in meteorites. The hydrolysates of meteoritic PO also contained several PG homologous compounds as well as polymeric materials with δD of *+235 and +65* respectively, suggesting the possibility of a yet unknown compositional complexity in meteorites. If the occurrence of *ee* in PO or other interstellar molecules cannot be ascertained with current spectroscopic methodologies, our data would allow to imply it

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Sequence Duplication as an Evolutionary Mechanism in Functional RNAs

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Introduction: RNA plays a central role in contemporary biology, and is thought to have been even more important during the origin and early evolution of life. The "RNA World" hypothesis posits that RNAs preceded protein enzymes and DNA as catalysts and carriers of genetic information, respectively [1]. Understanding the adaptive mechanisms available to RNA is therefore useful when attempting to reconstruct the early evolutionary history of life. Sequence duplication is a primary driver of molecular evolution in proteins, with many modern proteins exhibiting repetitive architectures [2], but the role of duplication events in RNA evolution is less well understood. Our study uses *in vitro* evolution to explore the ways in which duplication of a functional RNA sequence affects the range of secondary structures and associated functions available to the RNA through evolution.

Methods: We designed two experimental RNA constructs, the first containing a single sequence for an ATP-binding aptamer [3] and the second containing two tandem copies of the aptamer sequence. We then generated mutagenized populations from each via error-prone PCR of the DNA templates followed by transcription. Using affinity chromatography, we first selected for RNA molecules in each population capable of binding to ATP, and subsequently selected for molecules capable of binding both ATP and GTP simultaneously. After several rounds of selection, RNA populations exhibiting the desired binding affinities were reverse-transcribed and sequenced using high-throughput sequencing, and their sequences analyzed using RNA secondary structure-prediction software.

Results and Conclusions: Preliminary secondary structure predictions generated for the total range of possible point mutants suggest that aptamer formation will be disrupted in 76.4% (91 of 119) of point mutants for the single-aptamer construct, but only 48.5% (116 of 239) of double-aptamer point mutants will exhibit disruption of both aptamers. Results from the ATP-binding selection appear consistent with these predictions, as a larger proportion of the mutagenized double-aptamer population retains ATP-binding activity than is observed for the mutagenized single-aptamer population. Additionally, both single and double-aptamer mutagenized populations were observed to increase in their ability to bind both ATP and GTP columns over the course of the selection process, but it appears that dual-affinity binding is more pronounced in the mutagenized double-aptamer population. These findings suggest that duplication of a functional sequence can facilitate the evolution of novel functions in RNA while retaining historical functions.

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Impact of Molecular Crowding on in vitro Ribozyme Evolution

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Abstract: The cellular environments in which RNA functions in contemporary biology are characterized by extensive macromolecular crowding which is a feature likely shared by protocellular life and by the environments of prebiotic synthesis from which life emerged. Molecular crowding encompasses a complex set of effects such as excluded volume effects through steric hindrance, modulation of chemical interactions, and alteration of structure and activity of water. The excluded volume effects are thought to favor compact molecular states and foster improved native state folding of biopolymers. Moreover, crowding can have varying impacts on reaction rates, by increasing them or decreasing them depending on the dominant catalytic mechanism. Despite the importance of crowding, this environmental parameter has not been explored through in vitro evolution.

We investigated the impact of molecular crowding on the evolution of ligase ribozymes. We evolved populations of ligase ribozymes in dilute and crowded buffered solutions. After 5 rounds of evolution, populations were randomly mutagenized. The desired level of mutagenesis was confirmed by a decrease in population activity. The mutagenized populations were evolved for an additional three rounds in dilute buffer, 20% Dextran 6000, or 20% PEG 8000. These populations were sequenced through high throughput sequencing. We find that populations evolved in dilute solutions have the highest levels of activity, which is inhibited by PEG. Populations evolved in PEG are indiscriminant with respect to crowding. Among the most abundant sequences, all have a preference for a particular environment. Populations evolved in dilute solution and in the presence of dextran are largely composed of a shared set of sequences and secondary structures, whereas populations evolved in PEG are dominated by a single ribozyme.

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Modular Growth and Structural Remodeling in Early RNA Evolution

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Abstract: RNA molecules are widely believed to be early, if not the earliest, genetic and catalytic molecules. The earliest evolving RNAs are expected to be limited in length, with RNAs increasing in length over time. Combined phylogenetic and structural evidence suggests that complex modern RNA structures evolved from simple shared structures that evolved in the context of much shorter RNAs. Understanding the role of RNA in both the origin and evolution of life therefore requires an understanding of evolution as a function of polymer length. One way of conceptualizing this is with fitness landscapes. On these landscapes each genotype has a value of fitness, and the evolution of a phenotype to reach a fitness peak occurs through consecutive mutations. If a landscape consists of isolated peaks, then evolutionary optimization is possible only through recombination or alterations to the landscape. Alternatively, if the landscape contains large networks of near-neutral mutations, large volumes of genotypic space are crossed without marked effect on fitness, eventually resulting in more deterministic outcomes to the evolutionary process. The connectivity of fitness landscapes, and therefore the potential for optimizing fitness, is predicted to depend heavily on polymer length.

By combining exhaustive mapping of fitness landscapes for short RNAs with structure guided mapping for long RNAs, we investigated the RNA fitness landscapes as a function of polymer length. We evolved populations of ligase ribozymes of two lengths, one population with 20 fully random nucleotides (20N population) and one with 80 fully random nucleotides (80N population). We evaluated the evolved populations by way of combining high throughput sequencing data with comparative sequence and structure analysis. We examined the connectivity of fitness landscapes within both the 20N and 80N populations and found evidence for extensive neutral networks that include evolutionary paths connecting distinct secondary structures through a continuous series of active intermediates. We also observed that the optimal structures evolved within the short 20N ribozyme populations are present as modular components of the ribozymes evolved in the longer 80N populations. On the basis of the outcome of these evolution experiments, we assayed a range of structures of increasing length and complexity in which the longer RNAs preserve the functional structures of the shorter RNAs. Catalytic activity increases with these increasingly complex structures. This result demonstrates that the preservation of preexisting structures during the addition of new structural modules can be used to build upon the evolutionary success of shorter polymers. This is consistent with models according to which this evolutionary mechanism is responsible for modern ribosomal structures. Finally, we observed that the 80N ribozymes that utilize the structures present in the shorter ribozymes are less fit than other structurally unrelated 80N ribozymes. This result, along with evidence for evolutionary paths between distinct secondary structures, indicates that optimization of function for longer RNAs may lead to global structural rearrangements that erase evidence of the ancestral structure. The potential for such structural rearrangement complicates attempts to reconstruct ancestral RNAs based on extant structures. Understanding how polymer length impacts fitness landscapes provides both insight into early evolutionary processes in general and provides guidance to the interpretation of specific features of the molecular record preserved in modern RNA structures.

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Probing the Mechanism of Self-Reproducing Micelles

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Introduction: Surfactants are widely agreed to have played an important role in the emergence of life on Earth. Surfactant aggregates such as micelles and vesicles can catalyse reactions, compartmentalise and concentrate reagents, and self-reproduce.[1] These physical and chemical processes could have played a key role in the transformation of non-living matter to the first cellular forms of life. A key mechanism for the self-reproduction of surfactant aggregates is physical autocatalysis (Fig. 1). Here a micelle or vesicle catalyses the formation of more surfactant molecules in a biphasic system by facilitating the mixing of the two phases and in doing so drives its own reproduction.[2]

A novel autocatalytic reaction: The range of reactions currently known to proceed via physical autocatalysis is very limited and examples where physical autocatalysis is driven by bond forming transformations are even more scarce.[3] Reactions where molecular complexity increases by forming new bonds must have played an important role in prebiotic synthesis. The work presented here describes a novel physical autocatalytic reaction where new bonds are formed via a copper-catalysed azide-alkyne cycloaddition. We discuss in-depth mechanistic studies of this system and the scope and the limitations of the reaction.

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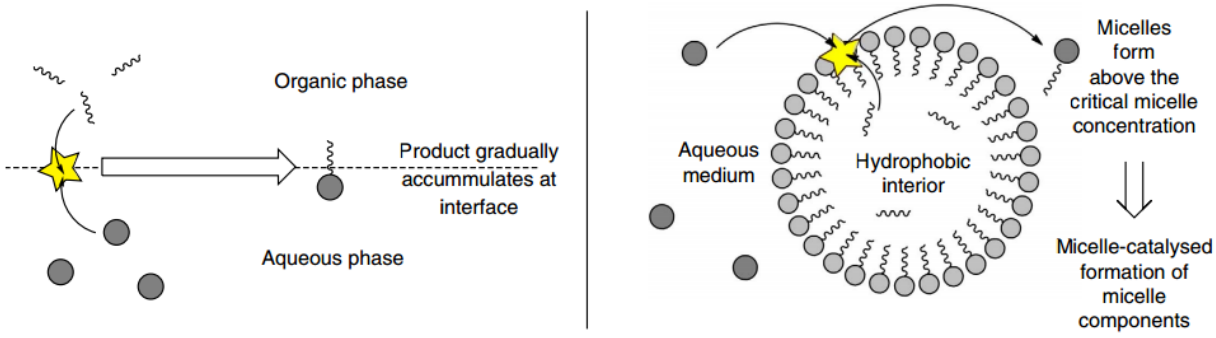

Figure 1 – Schematic representation of physical autocatalysis.[3] Left: Surfactant is slowly generated at the interface during a lag period. Right: The surfactants aggregate once the critical micelle concentration is reached and the resulting micelle starts to catalyse the reaction.

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Prebiotic Synthesis: Selection Overcoming Clutter

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Introduction: Living organisms are highly complex chemical systems that exploit a small constellation of universally conserved metabolites. The chemical unity of these metabolites provides compelling evidence that a simple set of predisposed reactions predicated the appearance of life on Earth.[1-5]

Prebiotic Selection from Complex Mixtures: Non-enzymatic syntheses of both nucleic acids and amino acids are essential to elucidating the origins of life, however overcoming the "*clutter wrought by prebiotic chemistry*"[1] to select the specific palette of metabolites exploited by life is widely cited as the chief obstacle to understanding the origins of life. Now, through the application of a systems chemical analysis of canonical nucleotide and proteinogenic amino acid syntheses, we have discovered that 2-aminothiazole–a hybrid product of prebiotic nucleotide and amino acid syntheses–delivers unprecedented efficiency and selectivity in directing prebiotic synthesis of the canonical metabolites essential for life from complex mixtures.[2] Our results emphasize the importance of holistic systems analysis.

Divergent Purine and Pyrimidine Nucleotide Synthesis: Although remarkable progress has been made toward understanding prebiotic nucleotide synthesis, to date all syntheses account separately for the pyrimidine and purine ribonucleotides.[3] Here, we present a novel divergent synthesis of pyrimidine and purine nucleotides from a common prebiotic precursor.[4] The generational and constitutional relationship between pyrimidine and 8-oxo-purine nucleotides suggests that 8-oxo-purine ribonucleotides may have played a significant role in early evolution.[4]

Triose Glycolysis and Nature's Highest-Engery Phosphate: Triose glycolysis is one of the most-central and highly conserved pathways in metabolism. We present a novel α-phosphorylation controlled reaction network that gives access to glyceric acid 2-phosphate, glyceric acid 3-phosphate, phosphoenol pyruvate, pyruvate, and phosphoserine.[5] The results presented demonstrate that mild, prebiotically plausible conditions can efficiently furnish all of the key components of a core metabolic pathway that is central to energy transduction, as well as amino acid, sugar, nucleotide, and lipid biosyntheses.[5]

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Fitness in the RNA World

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Life probably progressed through a primitive form based on RNA, in which RNA acted as both a genetic material and a catalyst for biochemistry. Understanding the evolution of RNA is therefore central to understanding the origin of life. Evolution can be thought of as a random walk through the space of all possible sequences. The function of fitness in sequence space is known as the 'fitness landscape.' If the fitness landscape were known, evolution could be accurately modeled as diffusion on the landscape with a tendency to drift upward due to natural selection. The fitness landscape is difficult to interrogate due to the vast size of sequence space. However, with high-throughput sequencing, we are able to map fitness landscapes for short but functional sequences of RNA, thus gaining a comprehensive 'birds-eye view' of the fitness landscape and discovering viable evolutionary pathways. One implication of our findings so far is that the ability of natural selection to optimize function across sequence space would be frustrated by the topology of the landscape, which consists of isolated islands of functional sequences. We are also studying the probability distribution of fitness and catalytic activity by analyzing the *in vitro* evolution of longer RNA sequences. This analysis reveals a log-normal distribution of rate constants, suggesting a mechanism for the emergence of function as the multiplicative result of many independent contributions. I will discuss implications of this research on understanding the probability of emergence of functional RNA and the role of chance and the repeatability of evolution in the RNA World.

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Estimating Ribozyme Kinetics from Analysis of *in Vitro* Selection

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Ribozymes and other biological reagents generated through in vitro selection have become important tools in medicine and the life sciences; but as selection methodology advances, our understanding of the evolutionary dynamics involved lags far behind. Selections often fail, require additional rounds to converge on a candidate sequence, or simply behave erratically. Existing theory does little to predict such difficulties or offer solutions, relying on distribution parameters and assumptions never tested in a selection environment. By combining selection theory with observations of real-world evolving molecular populations, it should be possible a mathematical description of the actual dynamics involved in a ribozyme selection. Here, we demonstrate several statistical techniques and that show promise in analyzing the ideality, scope of evolution, and fitness landscape present in a selection for a triphosphorylation ribozyme. Using new methodology, we find evidence for novel models of stochastic effects during in vitro selection, as well as of an initial distribution of chemical activity in random molecular space. The magnitude of such distributions is consistent with existing difficulties in selection design, suggesting that stochastic effects play a significant role in complicating selections, and suggesting selection parameters for optimizing future similar selection. Our results also show some correlation between estimated fitness and measured ribozyme activity, suggesting a viable alternative to the heuristic methods typically used to interpret high-throughput selection data, with further significance to many types of in vivo selection.

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Coenzymes, viruses and the RNA world

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The results of a detailed bioinformatic search for ribonucleotidyl coenzyme biosynthetic sequences in DNA- and RNA viral genomes are presented. No RNA viral genome sequence appears to encode for sequences involved in coenzyme biosynthesis. In both single- and double-stranded DNA viruses a diverse array of coenzyme biosynthetic genes has been identified, but none of the viral genomes examined here encodes for a complete pathway. Although our conclusions may be constrained by the unexplored diversity of viral genomes and the biases in the construction of viral genome databases, our results do not support the possibility that RNA viruses are direct holdovers from an ancient RNA/protein world. Extrapolation of our results to evolutionary epochs prior to the emergence of DNA genomes suggest that during those early stages living entities may have depended on discontinuous genetic systems consisting of multiple small-size RNA sequences.

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A Prebiotic Pyruvate Reaction Network that Leads to a Continuous Production of Metabolic Compounds: Evidence from Carbonaceous Chondrites?

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At the heart of central carbon metabolism lies pyruvate, a small keto-acid that is generated from glycolysis and used as the carbon source for the construction of lipids, amino acids, gluconeogenesis and the citric acid cycle [1]. How did this small organic come to occupy a vital position in extant biochemistry? One hypothesis is that pyruvate naturally exhibited the chemistry that facilited its incorporation into a proto-metabolism. Previous investigations on the chemistry of pyruvate have demonstrated its versatility and scenarios for the prebiotic synthesis of pyruvate or closely related compounds have also been recently reported [2–7]. The detection of pyruvate and related citric acid cycle compounds in carbonaceous chondrites has also provided strong evidence for its prebiotic relevance [8]. In attempts to understand the survival of these sensitive compounds in uncontrolled meteoritic environments, we have found that pyruvate can serve as a single-source reactant and continuously generate even labile compounds such as oxaloacetate. The production of these metabolites appear to result from facile isomerization, hydration, fragmentation, and decarboxylation reactions of subsequent pyruvate aldol-type polymers. Importantly, compounds such as oxaloacetate and other (larger) products replenish the starting material as they readily degrade to pyruvate. We have searched meteorite samples to find additional evidence of this reaction network that took place before the origin of life. Additional results from these studies, proposed mechanistic pathways, and implications for prebiotic chemistry will be presented.

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Nitrogen Heterocycles in Miller-Urey Spark-Discharge Mixtures: Using Chemical Trends to Elucidate Plausible pre-RNAs on the Early Earth

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Introduction: Although it is thought that RNA preceeded DNA as the first genetic material, the prebiotic synthesis of RNA has yet to be demonstrated [1]. The difficulty in RNA synthesis under prebiotic conditions has led to the opinion that RNA may have been preceeded by a simpler genetic molecule (i.e., a pre-RNA) [2]. Numerous studies have synthesized potential pre-RNAs in the lab, but the synthesis of their monomers and their subsequent polymerization remains unresolved [3]. A more tenable approach to identify plausible pre-RNAs may be to determine the chemical fate of nitrogen heterocycles in a prebiotic environment. Nitrogen heterocycles are of particular interest because they may have been available on the early Earth and are the means by which DNA, RNA, and by extension, likely any pre-RNA, can store information [4-6].

Methodology: The reactivity of 53 nitrogen heterocycles was explored in mixtures produced from a Miller-Urey spark-discharge apparatus. Spark-discharge experiments were carried out in the presence of water (pH 8) under two 1 bar atmospheres: (1) a reducing atmosphere of 40% N_2, 10% CO_2, 25% H_2, and 25% CH_4 and (2) a neutral atmosphere of 50% N_2 and 50% CO_2. The resulting mixture was incubated with a single heterocycle at 80°C and analyzed using a high resolution linear ion trap orbitrap hybrid mass spectrometer with a direct analysis in real-time ion source. Adducts and their mechanism of synthesis were confirmed by incubating heterocycles in solutions of plausible reactants and analyzing via MSMS and nuclear magnetic resonance.

Results: The most common products appeared to be due to reactions between nitrogen heterocycles and cyanoacetylene, glycolonitrile, acrylonitrile, cyanide and their hydrolysis products. Interestingly, each of these reactants are known to spontaneously polymerize in solution, and may therefore represent the first step towards building some type of pre-RNA structure.

When heterocycles are incubated with acrylic acid and glycolonitrile they yield propanoic acid (R-CH_2CH_2COOH) and acetamide (R-CH_2CONH_2) adducts. Eventually the acetamide adduct will hydrolyze to form acetic acid. Heterocycles with acetic acid adducts have been proposed as the heterocycle unit for the pre-RNA, Peptide Nucleic Acid (PNA). PNA is a polymer with a N-(2-aminoethyl)glycine (AEG) backbone. Given that AEG has been identified in spark-discharge mixtures [7], our results demonstrate the one-pot synthesis for the components of PNA under prebiotic conditions. Ongoing work includes an effort to determine whether heterocycles with acetamide and propanoic acid adducts can attach to AEG to form a PNA monomer.

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Early Earth Environments for an Emerging RNA World – More Widespread than Previously Thought?

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The RNA World hypothesis offers a solution to the unlikely scenario for the co-evolution of DNA and proteins during the emergence of life. In order to realize an RNA World, however, there must be a polymerization pathway for abiotically synthesized, monomeric nucleotides to form the necessary, catalytic RNA oligomers. It is well established that select, activated montmorillonite clay samples can catalyze RNA oligomerization at ambient pressure, however, it is critically important to explore these and other pathways in the context of plausible, prebiotic geochemical and mineralogical environments on early Earth. In the present work, we broadened the search for oligomerization pathways to include not only a montmorillonite clay, but also nontronite, lizardite (a serpentinization product), and anorthite, which are likely to have been produced under the bulk chemical conditions of prebiotic Earth; sulfur-rich pyrrhotite and black smokers, which would have been abundant at the ocean floor; and calcite, which is a common mineral that was likely widespread on early Earth. The reactions were performed with imidazole-activated 5'-adenosine monophosphate under ambient, 5 kbar, and 10 kbar pressure. Matrix Assisted Laser Desorption Ionization-Time-of-Flight Mass Spectrometry (MALDI-TOF MS) was used to characterize the reaction products. Reactions using montmorillonite clay typically yielded linear oligomers of 10 or more nucleotides up to 5 kbar, and shorter oligomers at 10 kbar. Carbonates and carbonate-bearing phases, on the other hand, yielded longer oligomers as pressures increased. Nontronite, pyrrhotite and the black smoker chimney sample also yielded oligomer lengths that exceeded mineral-free control experiments, but the results did not vary with pressure. While the mechanisms of these reactions are not yet understood, the important discovery that co-varying mineralogy and experimental parameters such as pressure can lead to catalytic activity in samples previously thought to be non-catalytic suggests that geologically-relevant environments that could support an RNA World on early Earth may have been much more widespread than previously thought.

THE QUESTIONABLE PROSPECT OF DEEP SEA ALKALINE VENTS AS ORIGIN SITES

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Introduction and Background: With presumed parallels to present-day bioenergy management, accounts over the past two decades have presented deep sea alkaline vents as sites for the start of life [1]. They posit that pH gradients of 6-10 across inorganic membranes provoke the conversion of phosphate to pyrophosphate, which then through its subsequent exergonic reversion to phosphate activates endergonic oligomerizations of neighboring nucleotides and amino acids.

Discussion: It is argued here that the flawed application of a number of kinetic and thermochemical factors challenge the viability of the proposition. The shortcomings include the absence of evidence supporting the existence of such membranes [2] and the apparent disregard of the prohibitive hydrolytic instability of oligonucleotides [3] which at vent temperatures and pHs should undergo full and exhaustive hydrolysis over characteristic times of hours. The accounts moreover describe the application of software tools that employ aqueous data bases and are designed unambiguously for aqueous geochemical modeling to support the notion of a hydrophobic and ostensibly nonaqueous membrane medium. Perhaps the most significant failure of the proposition is its violation of the second law of thermodynamics. The breakdown derives from the fact that while exergonic, pyrophosphate hydrolysis is anti-entropic at vent pHs. Its pairing with the negative reaction entropy of nucleotide oligomerization then dictates that the summed enthalpic yield of the pair boost the entropy of the medium sufficiently to effect second law noncompliance. The assigned intricate and multifarious catalytic features of the proposed medium, however, including phosphate confinement and peristaltic activity along narrow channels, are far too highly anti-entropic to be balanced by the modest enthalpic yields of assisted oligomerization, and compliance with the second law becomes unattainable.

Conclusion: Vent environments are highly corrosive and obstruct the spontaneous formation of both pyrophosphate and oligonucleotides; they are both kinetically and thermodynamically excluded from a role in life's beginnings. Fundamental perspectives dictate that an origins site include both an acidic rather than an alkaline medium and a means of shifting the Gibbs energies of the oligomerization reactions from end- to exergonic values while concurrently avoiding second law noncompliance. Those requirements are met in the evaporating pools within naturally occurring hydrothermal fields; that setting both shifts the oligomerization Gibbs energies through a swing in the properties of the aqueous medium from near ideal to highly crowded and nonideal [4], and provides a suitable second law offset arising from the highly entropy-positive evaporation of water.

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Elucidating the evolution of metallo-β-lactamases through ancestral gene reconstruction

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Introduction: Proteins are the core of an organism's survival and adaptation, therefore understanding their evolutionary history is critical to knowing their ability to survive [1]. Enzymes, a type of protein, are the catalysts for biochemical reactions and the crux for all cellular processes. The metallo-β-lactamases are a family of enzymes that hydrolyse the commonly prescribed β-lactam antibiotics, rendering them ineffective [2]. The evolutionary history and origins of this family of enzymes is unknown due to the low sequence homology in the clade [3]. I created an ancestral library of the metallo-β-lactamase BcII to understand the evolution of this enzyme and how it may affect antibiotic resistance and disease pathogenesis. I accomplished this by reconstructing ancestral sequences at nodes along the metallo-β-lactamase phylogeny and producing the corresponding recombinant proteins. I determined the phenotype of these enzymes, through their catalytic efficiency with nitrocefin, their zinc content and estimated binding affinities, to illuminate the evolutionary history of this enzyme. From the reconstructions I was able to determine that all six zinc binding residues are conserved. The homology modelling of the 4 ancestral states shows that the metallo-β-lactamase structure evolved before the node where the B1 B2 subclasses join on the metallo-β-lactamase phylogeny. This indicates that the origin of the zinc binding residues and the structure requires delving into the metallo hydrolase super family. From this I have not only created a complete phylogeny differing from those previously published, but I have also shown that while the stability has increased in the extant state of the enzyme, activity has not. While this still requires further experimental verification, this study brings the field one step closer to understanding the origins and evolution of metallo-β-lactamases.

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Protocell Self Assembly As Predicted by Mineral Surface Chemistry

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Introduction: The enclosure of functional biomolecules in a lipid bilayer membrane was an important process for the emergence of life on Earth. Single chain amphiphiles (SCAs) are considered for model protocell membranes because of their prebiotic availability and ability to self assemble. The effect of minerals in enhancing the rate of formation of SCA vesicles was reported in a seminal work [1]. However, no relationship with chemical properties of the minerals was identified and the reason for catalysis without direct contact remained unexplained. The aims of the present study were to re-examine the potential effects of minerals on the initial self-assembly of vesicles as model protocell membranes and their survival after formation, and to identify mineral-specific trends.

Methods: Decanoic acid (DA, pH 7, HEPES) and decanoic acid/decanol (DA/DOH = 2:1, pH 8.1, bicine) were used for this study. Komatiite and tonalite rocks, representing early oceanic and continental crusts; secondary minerals (oxides, oxyhydroxides, carbonates, sulfides, aluminosilicate) formed from weathering komatite and tonalite were also used. Vesicle formation was monitored by fluorescence and absorbance spectroscopies and dynamic light scattering. Mineral-vesicle interactions were visualized by optical microscopy and cryo-TEM.

Results and Discussion: The critical vesicle concentration (CVC), apparently increased only in the presence of positively-charged minerals at ≥ 1 mg.mL^{-1} loadings because of lipid adsorption and settling of the lipid-mineral aggregates [2]. Above the CVC, initial vesicle formation rates were promoted in the presence of all minerals and were shown, for the frist time, to depend on the isoelectric point (IEP) of the minerals, which itself depends quantitatively on mineral chemistry, structure and interfacial hydration [3]. Initial rates were faster on more positively-charged minerals [2]. Membrane permeability remained unaffected by minerals once vesicles were formed. The initial rate-accelerating effect was ascribed to rapid lipid adsorption on mineral surfaces [2]. These adsorbed lipid islands serve as a matrix [4] for further lipid attachment and its rapid transformation to vesicles compared to a control system without minerals. Modified Deraguin-Landau-Verwey-Overbeek (DLVO) theory indicates that the electrostatic effect of the mineral's surface charge was effective even up to ~ 15 nm distance from the surface through 2-3 stacked lipid bilayers [5]. Our work confirms the original findings [1] and goes further in establishing the relationship of vesicle self-assembly to mineral IEP, and providing a theoretical basis for the catalytic effect without direct contact with the mineral surface [2, 5]. Both the thermodynamics and the kinetics of membrane self-assembly showed dependence on fundamental properties of minerals. The structure-activity relationships identified here between membrane self-assembly processes and the physical-chemical properties of minerals may help predict the plausible survival of protocell membranes in proximity of other minerals, which may have been present on early Earth and other rocky planets such as Mars.

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From quantum computational physics to the origins of life

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Computational approaches are nowadays a full, self-standing branch of chemistry, both for their quantum-based ("*ab initio*") accuracy, and for its multiscale extent. In prebiotic chemistry, however, due to the instrinsic complexity of the chemical problems, *ab initio* atomistic simulations have so far had a limited impact, with the exception of a few relevant studies, including the elucidation of the chemical interactions between biomolecules with surfaces, such as ice and minerals, or the simulation of the effect of the pressure/temperature shock waves induced by meteorite impacts in the early Earth. Surprisingly, even the celebrated Miller experiments, which historically reported on the spontaneous formation of amino-acids from a mixture of simple molecules reacting under an electric discharge, have never been studied at the quantum atomistic level.

Here we set the general problem of chemical networks within new topology-based concepts, using search algorithms and social network data analysis. This allows a very efficient definition of reaction coordinates even in the complex chemical environments which are typical of likely prebiotic scenarii. We thus report on the first *ab initio* computer simulations, based on quantum physics and a fully atomistic approach, of Miller-like experiments in the condensed phase. Our study [1] shows that glycine spontaneously form from mixtures of simple molecules once an electric field is switched on. We identify formic acid and formamide [2] as key intermediate products of the early steps of the Miller reactions, and the crucible of formation of complex biological molecules, as confirmed by our recent experimental and theoretical study on high-energy chemistry of formamide [3]. From a broader chemical perspective, we show that formamide plays the role of hub of a complex reaction network in both the gas and the condensed phase [4]. We are now going on a larger scale, studying the atomistic mechanisms of RNA nucleotides synthesis in fully realistic prebiotic solution environments [5]. All these results pave the way to novel computational approaches in the research of the chemical origins of life.

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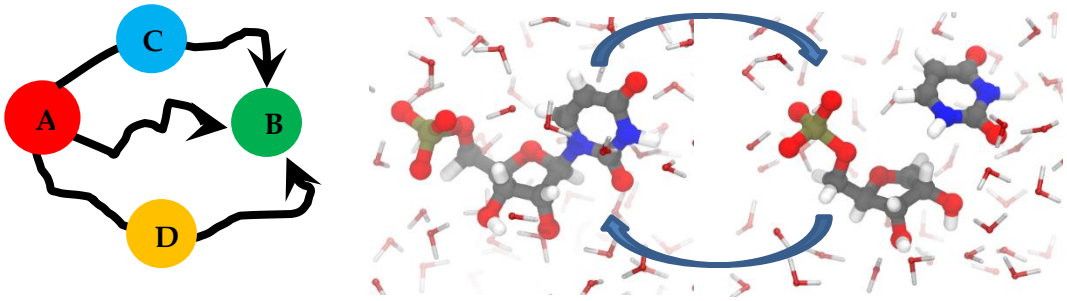

Figure 1 – Left, pictorial representation of the reaction paths connecting A and B, with possible C or D intermediates. Right, example of a fully quantum atomistic simulation of the A-to-B degradation/synthesis reaction between one uridine mono-phosphate nucleotide and one uracil plus a phosphoribose, in explicit water solution.

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Synthesis and characterization of a putative pre-RNA World ribonucleoside precursor

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Introduction: Nonenzymatic oligomerization of RNA molecules from non-activated monomers, such as AMP and GMP has been shown to occur under volcanic geothermal conditions. [1] This process is however prone to issues mainly due to the propensity of these monomers to undergo depurination when subjected to polymerization under high temperature and low pH conditions prevalent in a volcanic geothermal system. This has further lend credence to a prevailing hypothesis that RNA must have been predated by prebiotically more plausible and stable oligomers made of 'alternate' monomers, which might have formed with relative ease on the early Earth. In this regard, our lab has reported the formation of a Barbituric acid (BA) containing ribonucleotide using ribose monophosphate (rMP) and barbituric acid as the starting materials; [2] a result that was also demonstrated in a simultaneous study conducted by the Hud group. [3] In this study, it was shown that dehydration and rehydration of ribose monophosphate (rMP) and barbituric acid at low pH resulted in the formation of both C- and N-glycoside analogs. Furthermore, it was observed that this product mixture also resulted in oligomerization under acidic condition in which the traditional N-glycosides of purines tend to lose their informational moiety. Therefore, the C- and/or N-glycoside analogs of BA could potentially serve as pre-RNA World candidates for understanding the abiotic oligomerization of RNA like polymers that might have populated such worlds.

In the aforementioned oligomerization it was observed that all possible isomers of the BA nucleotide were formed in the reaction (i.e. α/β anomers of both the C-and N-glycoside). Additionally, the yield of the above reaction was such that the isolation of the desired monomer in substantial quantity was limiting. Therefore, in order to have a suitable starting material to, both, characterize the oligomerization reaction and to demonstrate information transfer potential with extant RNA, chemical synthesis of a BA containing nucleoside is highly desirable. In the present study we report a chemical synthesis scheme for BA containing ribonucleoside (N- and C-linked glycoside) analogs. To achieve this, we have synthesized the ribose donor in a few steps with just D-ribose sugar using sophisticated protection and activation chemistry.[4] Subsequent synthesis of BA ribonucleoside will be accomplished by performing glycosylation reaction between the ribose donor and BA, followed by a deprotection step. The resultant product will be used to systematically characterize the oligomerization of the C-and N-glycosides of BA under pertinent prebiotic reaction conditions. Eventually, we also aim to study information transfer capability from such an oligomer with the molecules of a putative RNA World.

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Design of Novel Asymmetric Autocatalytic Systems

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Introduction: The origin of chemical asymmetry in life is unknown, with asymmetric autocatalysis a prevalent concept put forward to explain this.[1][2] Despite this asymmetric autocatalytic reactions are rare, the Soai reaction being the only conclusive example, in which the chiral products which increase in enantiopurity over time.[3]

Nonlinear effects in asymmetric catalysis: Here we discuss the design novel asymmetric autocatalytic reactions, based on modes of catalysis distinct from the Soai reaction, which share common principles. Essential to asymmetric autocatalysis is the notion of minor enantiomer inactivation, leading to nonlinear effects. Based on early work by Frank, Blackmond describes how monomeric autocatalysts would not be expected to enantioenrich without some suppression of the catalytic activity of the minor enantiomer.[4][5] In the case of Soai's system nonlinear effects arise from catalytically active dimers and higher aggregates.[6]

It is generally acknowledged there is little direct prebiotic relevance to the Soai reaction, due to the highly specific conditions required. In contrast, organocatalysis, in which organic small molecules aid the production of others, often shows relatively low air and water sensitivity, important considerations in prebiotic chemistry and many asymmetric transformations are known.[7][8] Although many systems displaying nonlinear effects have been found, the interactions causing these effects are often poorly understood and examples in the field of organocatalysis are rare.[9] Here we discuss investigation into nonlinear effects in known organocatalytic reactions. The results of this will inform the design of potential autocatalytic systems.

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Archean Fluid Inclusion of Hydrothermal Quartz Minerals - Archives of Prebiotic Chemistry on Early Earth?

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The composition of fluid inclusions in minerals such as quartz which have grown in the hydrothermal environment of continental crust during the Archean period might provide important information about the first organic molecules formed by hydrothermal synthesis.

We present evidence for organic compounds which were preserved in fluid inclusions of Archean quartz minerals from Western Australia. Samples from a quartz dyke north of Jack Hills and >3 Ga old quartz pebbles from a conglomerate of the Jack Hills in Western Australia (a region where the oldest zircons, with an age of more than 4.3 Ga, were found) were analyzed.

With comprehensive two-dimensional gas chromatographic analysis a variety of organic compounds were found which unambiguously show that simple and even more complex prebiotic organic molecules have been formed by hydrothermal processes. Depending on the chemical composition, all compounds determined, except for those containing nitrogen, can be assigned to four classes: aliphatic hydrocarbons, halocarbons, alcohols, and aldehydes.

Stable-isotope analysis results for CH_4 clearly indicate that the CH_4 found in the inclusions of Australian quartz samples was formed from abiotic precursors such as carbon dioxide or elemental carbon and makes a biogenic (e.g. from microbes) or thermogenic origin (decomposition of organic matter) highly unlikely. Obviously, the liquid phase in the continental Archean crust provided an interesting choice of functional organic molecules. We conclude that these organic substances could have made an important contribution to prebiotic chemistry which might eventually have led to the formation of the first living cell.

The first prebiotic chemistry and the formation of protocells could have occurred in the hydrothermal environment of tectonic fault zones in the upper continental crust, and could undergo complex reactions in a two-phase environment formed by hot water and supercritical carbon dioxide.

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The composition of comets – overview of 30 years of investigations

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The study of comets is important for understanding the origin of our solar system and as such ultimately for identifying the prerequisites for the development of life. As comets are considered remnants of the early solar system formation and spent most of their lifetime at temperatures below 50 K, their chemical composition, particularly in view to organic compounds, is very important for understanding whether the complex organics, from which life might have developed, were formed from simpler molecules on the surface of the primitive Earth or were supplied as ready by impacting comets. The latter would mean that such complex molecules were already present 4.6 billion years ago. Also the intimate mixture between minerals and organic molecules is an essential aspect for the origin of life. Different grain surfaces provide different catalytic properties, and can locally lead to a decrease of entropy on the expense of the entropy elsewhere in the closed system of multigrain dust.

The first major breakthrough in identifying the organic composition of a comet nucleus dates back to 1986, when three spacecraft (VEGA 1&2 and Giotto) passed through the inner coma of comet Halley and obtained in-situ measurements of its gas and dust composition. A number of small organic molecules, known to be present in the interstellar medium were detected in the gas coma, and the presence of organic macromolecules was discovered in the comet dust. About 10 years later (1996-1997) the apparition of the extraordinary bright comet Hale-Bopp in combination with the availability of new sophisticated observing facilities at sub-mm wavelengths, led to a quantum leap in our understanding of the evolution of the gas coma composition as a function of heliocentric distance. In 2006, after another decade, the Stardust mission returned a sample of dust particles collected in the coma of comet Wild-2 which permitted the detailed analysis of the returned material in laboratories available on the Earth; and in 2016, again about 10 years later, the Rosetta mission concluded its 2-year rendezvous-mission with comet Churyumov-Gerasimenko. In these 30 years of comet compositional investigations important progress was made in identifying the composition and chemistry of comets. An overview will be given of the most important milestones with special emphasis to organic material.

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Searching for Signs of Life on Exoplanets

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The search for life in other planetary systems is a relatively new but exciting endeavor. Thousands of exoplanets are known to orbit nearby stars and small rocky planets are established to be common. The ambitious goal of identifying a habitable or inhabited exoplanet is within reach. But how likely are we to succeed? We need to first discover a pool of planets in their host star's "extended" habitable zone and, second, use the James Webb Space Telescope to provide evidence of atmospheric biosignature gases. A biosignature gas is defined as one that is produced by life and accumulates in an atmosphere to detectable levels. Any kind of ab initio approach to predicting what biosignature gases might be is so challenging that nearly all work done to date basically follows the "We know what Earth life produces, so how would the signature of these products appear if transplanted to another, slightly different, Earth-like planet" (Earth-like refers to a planet with about the same size and mass as Earth, with oceans and continents, a thin N_2-CO_2-O_2 atmosphere, and a similar radiation environment). Gases studied in this context include oxygen, the otherwise unexplained simultaneous presence of gases out of thermodynamic equilibrium (specifically methane with oxygen), methyl halides, sulfur compounds, and others. For successful detections, transiting exoplanets require fortuitous alignments and this near-term approach is therefore only the first step in a long journey. The next step is sophisticated starlight suppression techniques for large ground-and space-based based telescopes to observe small exoplanets directly. Assuming that we can identify some of the above "biosignatures" in an exoplanet atmosphere, what are the implications for origin of life's research?

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Exploring the Evolutionary Accident Hypothesis: Are Extant Protein Folds the Fittest or the Luckiest?

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Introduction: Considering the range of functions proteins perform, it is surprising they fold into a relatively small set of structures or "folds" that facilitate such function. One explanation is that only a minority were fit enough to emerge from Darwinian selection during the early evolution of life. Alternatively, perhaps only a fraction of all possible folds were trialed [1]. Understanding proto-catalyst selection will aid understanding of the origins and early evolution of life.

To investigate which explanation is correct, we study a protein evolved *in vitro* to bind ATP by Jack Szostak (Fig. 1) [2]. This protein adopts a fold which is absent from nature [3]. We are testing whether this fold would have possessed the capability to evolve that would have been essential to survive natural selection on early Earth. Folds that couldn't improve their fitness and evolve to perform new functions would have been replaced by rivals that could.

To determine whether the fold is evolvable, we are attempting to change the function of the protein by rationally redesigning to bind GTP. Two design strategies in the region of the nucleobase have been implemented to provide hydrogen bonding partners for the ligand i) an insertion ii) a MET to ASN mutation. Redesigns are being studied computationally at Ames Research Center including free energy of binding calculations. Binding affinities of promising redesigns are to be validated by experimental collaborators at FortéBio using Super Streptavidin Biosensors.

If the fold is found to be non-evolvable, this may suggest that many structures were trialed, but the majority were pruned on the basis of their evolvability [1]. Alternatively, if the fold is demonstrated to be evolvable, it would be difficult to explain its absence from nature without considering the possibility that the fold simply wasn't sampled on early Earth. This would not only further our understanding of the origins of life on Earth but also suggest a common phenomenon of proto-catalyst evolution.

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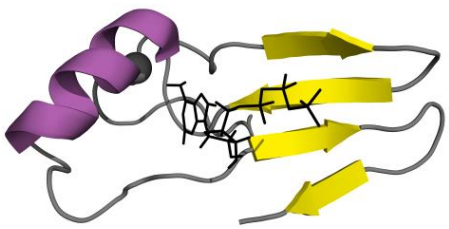

Figure 1: The novel fold of an ATP-binding protein evolved via mRNA display.

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LIQUID CRYSTAL FORMATION BY BASE-PAIRING AND DUPLEX STACKING OF MONONUCLEOSIDE TRIPHOSPHATES IN AQUEOUS SOLUTION

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Introduction: Nucleic acid (NA) oligomers as short as 4 base pairs can carry out the self-assembly steps of duplexing, end-to-end aggregation of duplexes, and condensation of aggregates to form columnar liquid crystal phases. In such phases the molecules, self-selected because of their complementarity, create a fluid structural and chemical environment in which oligomer ligation into longer polymers can be strongly promoted [1]. This ligation represents an autocatalytic step in a positive feedback loop in which the liquid crystal structure selects, organizes and polymerizes molecules, thereby enhancing its own stability. Such a scenario has been proposed as a mechanism for the appearance of sequence-directed assembly in early life, and for providing polymer feedstock to the RNA world [2]. However, starting from even few-base oligomers is problematical, because such families of molecules are already highly selected. Any realistic scenario must start from pools of simpler and more diverse molecular species. In this paper we demonstrate that mixtures of single nucleobase species in aqueous solution can order into liquid crystal phases in which the key elements of base-pairing of nucleosides, columnar stacking of base-pairs, and of complementarity-dependent selection are operative. We observe for the first time duplex columnar liquid crystal order in aqueous solution of dATP/dTTP and dGTP/dCTP at high concentrations (~700mg/mL) and low temperature (5°C) [Figure 1]. Liquid crystal phases were not observed in mixtures containing only individual triphophates and were observed in mixtures containing all four dNTPs. These observations set the stage for exploration of ligation reactions involving formation of natural phophodiester bonds by pyrophosphate elimination.

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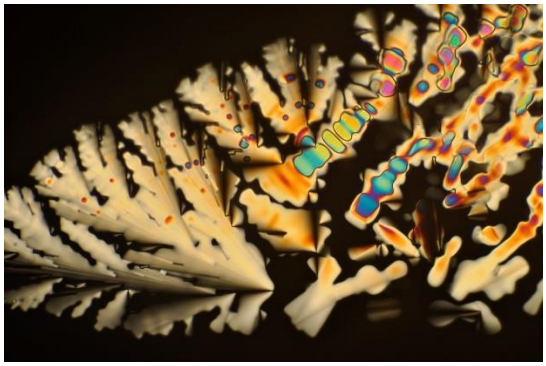

Figure 1- Polarized light microscopic image of dATP/dTTP aqueous mixture columnar fan textures.

Additional Information: This work supported by NSF Biomaterials Grant DMR-1611272, NSFMRSEC Grant DMR-1420736, ALS Beamline 7.3.3 is supported by U.S. DoE under contract No. DE-AC02-05CH11231

July 16-21, 2017 at UC San Diego, CA, USA

Intricate behavior of 4-base nanoDNA sequences: an intersection between condensed matter and RNA world

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Introduction: nanoDNA are short sequence DNA oligomers having ~20 or fewer A, T, G or C nucleotide bases, that can form liquid crystal phases if they have the appropriate combination of complementarity, hydrophobic end-stacking, and/or sticky-end hydrogen bonding (G sticking to C or A to T) when dissolved in water [1]. nanoDNAs are of interest in an origins-of-life context because their LC phases can effectively catalyze DNA autoligation and create longer sequences from shorter ones in the absence of protein catalysis [2]. As a bridge between ligation mediated by intermediate length nanoDNA oligomers and LC formed from single-base monomers [3], we pursue a general characterization of the self-assembly and phase behavior of particularly short 4 base DNA sequences, including GCCG, GTAC, and ATTA, as a function of both concentration and temperature. GCCG, which assembles into Watson-Crick duplexes by 2X2 sticky-end base pairing, and which also forms G-quartets, exhibits coexisting LC [Figure 1], crystalline and glassy phases. Watson-Crick duplexes appear to dominate in fresh GCCG mixtures, but tend to settle into a more complicated crystal structure over time. The crystal structure is a network of sites on a square lattice where sets of four GCCG molecules come together to form an H-bonded quartet. At especially high concentrations, GCCG exhibits a reentrant isotropic phase which we interpret as a glassy G-quartet mediated structure.

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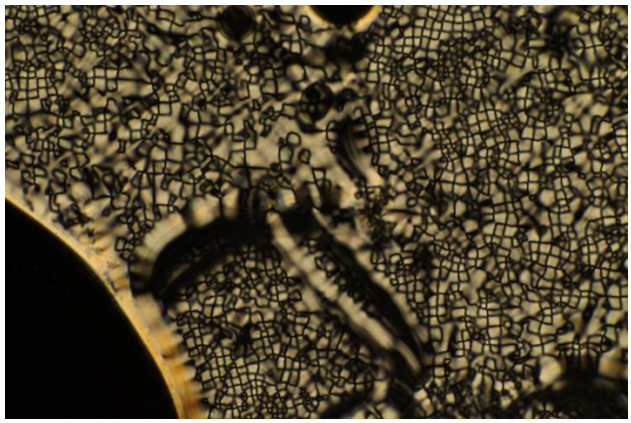

Figure 1 – Polarized light microscope image of GCCG aqueous mixture chloesteric LC phase with parabolic focal conic defect structure.

Additional Information: This work supported by NSF Biomaterials Grant DMR-1207606, NSF MRSEC Grant DMR-1420736. ALS Beamline 7.3.3 is supported by U.S. DoE under contract No. DE-AC02-05CH11231.

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Increasing the Relative Production of Ribose Under Mild Prebiotic Conditions

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During the abiotic stage of the early earth, meteorites were delivering abundant and diverse organic compounds to our planet and there was also (likely) indigenous production. Among these compounds were sugars. Since discovering the importance of ribose in biology scientists have wondered how this apparently labile compound came to biological prominence: was ribose synthesized in sufficient relative quantities (compared to other sugars) to form a polymer such as RNA? For example in the classical formose reaction, the most cited prebiotic reaction for producing sugars, ribose is usually a minor component [1]. Prebiotic chemists have strived to answer this question by various experimental methods. For example, the Benner group has shown a preferential synthesis of ribose in the presence of borate minerals [2]. Also, Geoffrey Zubay, using lead as a catalyst in the production of sugars, suspected that ribose was a primary product among resulting aldopentoses [3]. We addressed the question of prebiotic ribose abundance by manipulating various parameters in formose-type reactions. We used known meteoritic (i.e., prebiotic) minerals such as Na^{+}, Ca^{2+}, and Mg^{2+}, anions, and photolysis at multiple wavelengths. The resulting compounds were analyzed as their (+)butyl/trifluoroacetyl derivatives by gas chromatography–mass spectrometry. In preliminary experiments we find the abundance of ribose can be significantly increased relative to other sugars (Fig. 1). We can vary this relative abundance depending on reaction parameters. Details of these methods and further results will be presented.

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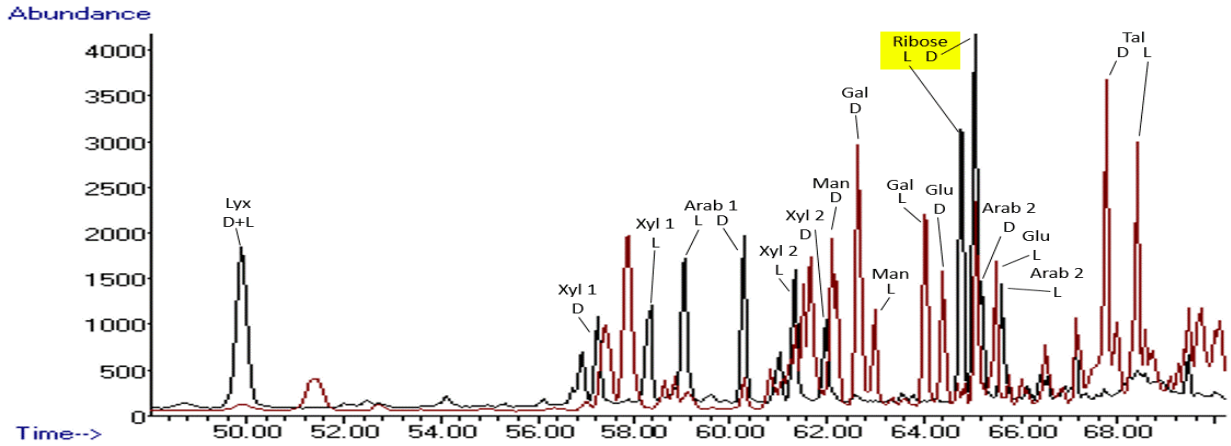

Figure 1 – Isotope (^{13}C) labeled 5C and 6C sugars from a formose-type reaction. The abundance of ribose is significantly increased compared to that in classic formose reactions, as well as other reactions we have performed (not shown) with different initial reaction parameters. (Ribose is racemic as shown by area integration).

Lyx=Lyxose, Xyl=Xylose, Arab=Arabinose, Man=Mannose, Gal=Galactose, Glu=Glucose, Tal=Talose; Numbers refer to different diasteriomers of a given compound.

July 16-21, 2017 at UC San Diego, CA, USA

Protolife Membrane Composition

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Introduction: A simpler membrane than those of current cells was likely present as a protective envelope for protolife. Using the same primordial conditions as have been demonstrated to form polypeptides, an amphiphilic substance comprised of only two precursor compounds likely present on primordial Earth can be formed by a condensation reaction [1]. Amphoteric lipoamino acids are readily synthesized in up to 50% yield when various amino acids and fatty acids are reacted under several different conditions: by heating in an inert atmosphere or by wet/dry cycling in inert atmosphere or even in air, particularly in the presence of a range of salts, minerals or clays. Similarly, when lauric (dodecanoic) acid was reacted with the dipeptide glycylglycine, a yield of 10% of lauroylglycylglycine was formed. Similar compounds in combination with cationic surfactants have been shown to form vesicles [2], to form micelles in dilute aqueous solutions and to form both hexagonal and cubic crystalline bilayer phases at higher concentrations [3,4]. Since lipoamino acids and lipopeptides lack glycerin, they avoid a prebiotic problem of early selection between the different chiralities found in archaeal compared to bacterial membrane lipids [5]. Also, since they do not contain phosphate, the need for early abstraction of phosphate from the environment is forestalled. Cells of current life forms lend credence to the early presence of these compounds: 1) lipopeptides and lipoamino acids are found in cells of both Bacteria and Eukarya [6,7]; 2) a lipopeptide has been found to replace membrane phospholipids in Bacteria raised in phosphate-depleted environments [8]; and 3) lipoamino acids and lipopeptides are synthesized by cells by means of non-ribosomal peptide synthetases [9], precluding the potential early need for RNA. Presence of amino acids and peptides at the surfaces of two-dimensional membranes would have provided catalytic surfaces on which various chemical reactions could have occurred. These results demonstrate that lipoamino acids and lipopeptides would have likely formed alongside peptides under the same prebiotic conditions, would have been likely components of a prebiotic membrane, and could have provided a variety of chemically active residues for chemical evolution.

Reaction Example:

$$CH_3(CH_2)_{10}COOH + NH_2CH(CH_3)COOH \rightarrow CH_3(CH_2)_{10}CONHCH(CH_3)COOH + H_2O$$

Figure 1 - Lauric acid + Alanine → Lauroylalanine + Water

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July 16-21, 2017 at UC San Diego, CA, USA

Automated oligopeptide formation under simple programmable conditions

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Introduction: Biopolymer formation (including nucleic acids and proteins) is one of the most relevant process towards origin of life. However, polymeric reactions include condensation processes which are thermodynamically constrained in an aqueous environment. Traditionally, in the case of peptides, many high-yielding reactions have been developed, but these are complex and use activated amino-acid precursors or heterogeneous supports [1].

Prebiotic chemistry has usually investigated the formation of life's precursors and their polymerization under very specific conditions. In contrast, we have explored the effect of several parameters at once on a model oligomerization reaction. We used a high-throughput automated platform – the 'abiotic peptide synthesiser' (APS) – that allowed us to run several reactions in parallel and automatically vary both the input and process variables. Herein, we show peptide bond formation from hydration/de-hydration cycles of unactivated amino acids, achieving yields of up to 50%, in which the majority of products are longer oligomers ($n \geq 3$) [2].

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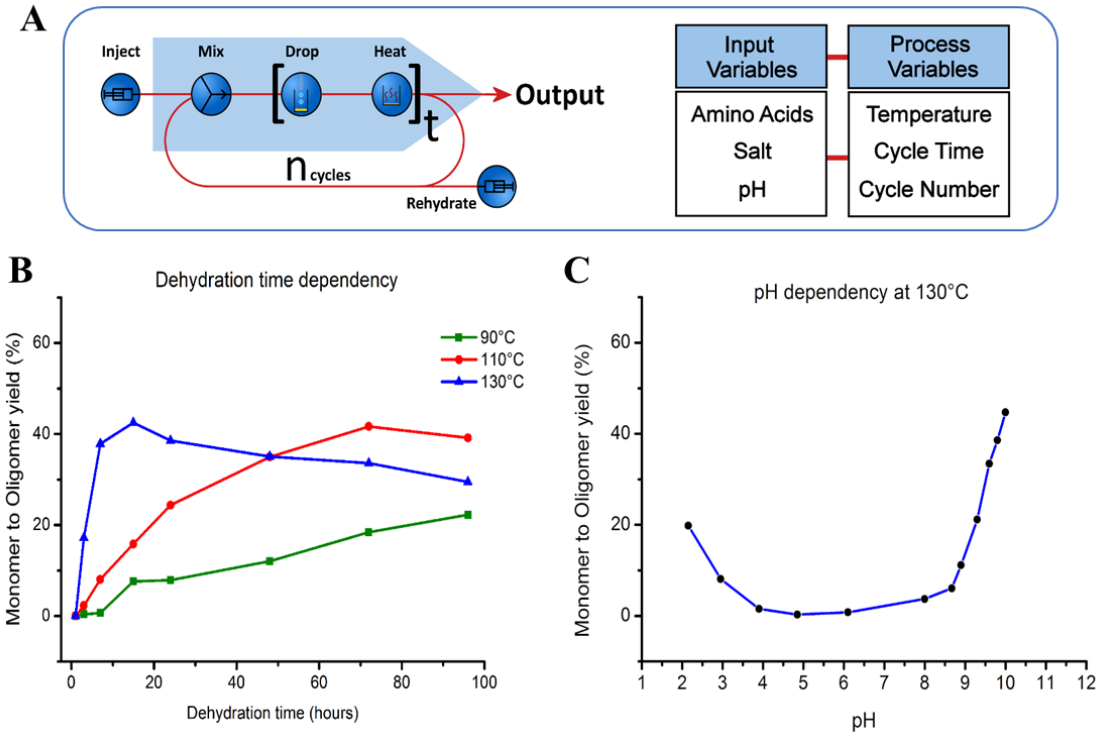

Figure 1 – **A.** Process flow diagram for the 'Abiotic Peptide Synthesiser' (APS) system. Reaction outcome is controlled by selection of input variables and process variables. **B.** Graph showing glycine oligomer yield from a single cycle as a function of dehydration time. **C.** Graph showing glycine oligomer yield from a single cycle as a function of pH (at 130ºC for 24 h).

July 16-21, 2017 at UC San Diego, CA, USA

Can a reaction's environment program its outcome, and does it matter?

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Chemists go to great lengths to avoid making complex mixtures:[1] because they expect molecules of interest to be so dilute as to result in non-functional systems ('tar') [2,3] and because they are expected to be 'analytically intractable'.[4,5] This is often especially true in Origins research,[6] where the taming of combinatorial explosion in 'uncontrolled' condensation reactions of bio-monomers or their analogues is an important open question. Controlling chemical complexity generated in condensation reactions is enormously challenging, and currently only achieved using strategies such as protecting group chemistry to produce single defined products.[1]

Our group has been exploring the complexity generated by 'uncontrolled' condensation reactions of polyvalent monomers, which most chemists eschew. We are interested in how it can be tamed by the recursive interaction with environments, and how complex ensembles of products may have consistently defined structural and functional properties (even if their composition is not comprehensively understood).[7] This is a 'systems' approach to reaction complexity (set out Figure 1), in contrast to planned organic syntheses/disconnections. As model systems, we have studied the condensation of both simple pure building blocks[8] and complex mixtures of the kind produced by prebiotic monomer syntheses.[4, 6] We have used analytical approaches more common to Systems Biology to take a new approach to the synthesis of functional macromolecules, and are combining these with inspection of structure and function. In this contribution I will present our latest results,[6] demonstrating the impact of an environments ability to steer product distribution in complex reaction systems, leading to real and reproducible effects in the realms of structure and function.

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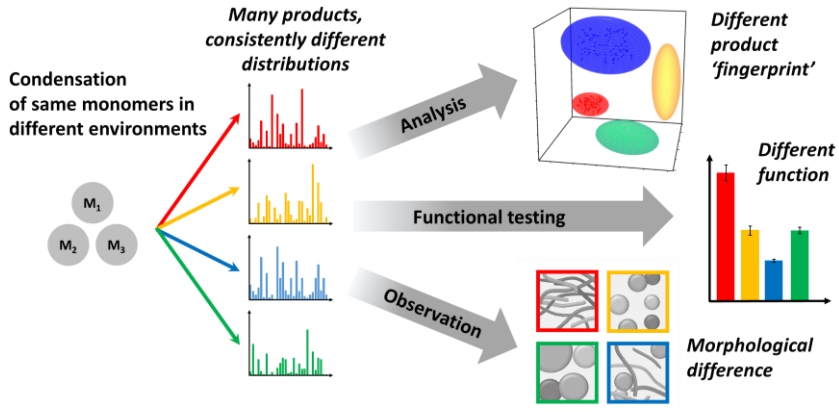

Figure 1 – Center figures and captions after the text of the abstract.

July 16-21, 2017 at UC San Diego, CA, USA

Lanthanide Cofactors for Triphosphorylation Ribozymes

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The RNA world hypothesis describes an early stage in the evolution of life in which RNA would have served as genome and the only genome-encoded catalyst. RNA world organisms would have required an energy source for the thermodynamically unfavorable polymerization of RNA. We previously showed that trimetaphosphate (Tmp), a prebiotically plausible energy source, can be used by ribozymes to triphosphorylate RNA 5'-hydroxyl groups, thereby generating chemically activated RNA 5'-phosphates that contain the thermodynamic driving force for RNA polymerization [1]. Analogous 5'-triphosphates could be seen as the precursors for ATP, the energy currency in every known form of life.

To test whether different metal ion cofactors could be used by triphosphorylation ribozymes we performed an in vitro selection in the absence of Mg^{2+} and in the presence of the lanthanide Yb^{3+}. Lanthanides are promising cofactors for triphosphorylation reactions because they activate Tmp for nucleophilic attack, modulated by the lanthanide's coordination status [2]. While the lanthanide's prebiotic relevance is debatable (they are highly enriched in pegmatitites [3] but these minerals may be hard to mobilize) these experiments explore the chemical space accessible to RNA-catalyzed RNA triphosphorylation.

After eight rounds of selection from a pool with 150 randomized nucleotides several active ribozymes were recovered. Interestingly, different sequence clusters displayed very different responses to changes in pH and ion concentrations. This suggests that these lanthanide-using ribozymes employ different catalytic strategies.

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July 16-21, 2017 at UC San Diego, CA, USA

The Nonenzymatic Copying of RNA Templates

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The copying of short RNA templates without enzymes is likely to have been an important aspect of genetic replication in primitive cells, prior to the evolution of RNA replicase ribozymes. As part of our broader studies of the origins of cellular life, we have therefore been pursuing laboratory studies of nonenzymatic RNA replication. We have recently used both thermodynamic and kinetic studies to demonstrate an important catalytic role for activated downstream nucleotides in the addition of an activated monomer to a primer. We subsequently showed that this catalytic effect was due to the formation of a covalent imidazolium-bridged dinucleotide intermediate in primer-extension. Structural studies suggest that this intermediate binds to the template by Watson-Crick base-pairing, and in the bound state is preorganized for reaction with the primer 3'-hydroxyl. Subsequent mechanistic studies then led to the identification of 2-aminoimidazole as a superior nucleotide activating moiety. Remarkably, our investigations into the potentially prebiotic synthesis of 2-aminoimidazole show that it can be synthesized together with the nucleotide precursor 2-aminooxazole. In addition, we have found that replacing the canonical U monomer with the prebiotically accessible sulfur-substituted nucleotide 2-thio-U allows for faster and more accurate template copying. The combination of 2-thio-U with 2-aminoimidazole activated monomers and activated helper trinucleotides enables the rapid and accurate copying of short mixed sequence templates. Taken together, these advances suggest that the nonenzymatic copying of short RNA templates may have been possible on the early Earth.

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Simple non-coded peptides enhance RNA polymerase ribozyme function

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Introduction: Protein synthesis in modern biology depends on multiple elaborate machineries (eg. ribosomes, mRNA, tRNA, etc.). However, at the early stage of the evolution of life the translation system must have emerged as a much simpler system (or just one small ribozyme). Therefore, the peptides synthesized at that time were probably simple non-coded peptides. It is still elusive how such simple peptides could be functional without specific sequences encoded by the genetic code. To answer this question we tested if simple non-coded peptides have any benefit on function and survival of an RNA polymerase ribozyme (RPR) [1].

Experiments: RPRs have been developed and engineered in several laboratories as modern-day models of RNA replicase in the RNA world [2–5]. However, They require high concentration of Mg^{2+} (200 mM) to perform RNA synthesis efficiently [6,7]. This is problematic because the ribozyme itself is unstable in high Mg^{2+} condition [8]. Here, we describe oligo-lysine and its analogues stimulate RPR function in low Mg^{2+} condition by promoting docking between RPR and substrate RNAs (primer and template) [1]. Furthermore, oligo-lysine could accelerate in vitro evolution of RPR in low Mg^{2+} conditions. The newly engineered RPR could perform RNA synthesis at near physiological Mg^{2+} concentration in the presence of oligo-lysine (Fig 1).

Discussion: Considering RNA has strong negative charges, positively charged peptides like oligo-lysine probably enhanced interaction between RNA molecules in the RNA world. Therefore, such simple peptides could have enhanced functional networks among ribozymes and helped the life in the RNA world to evolve into more complicated cellular systems.

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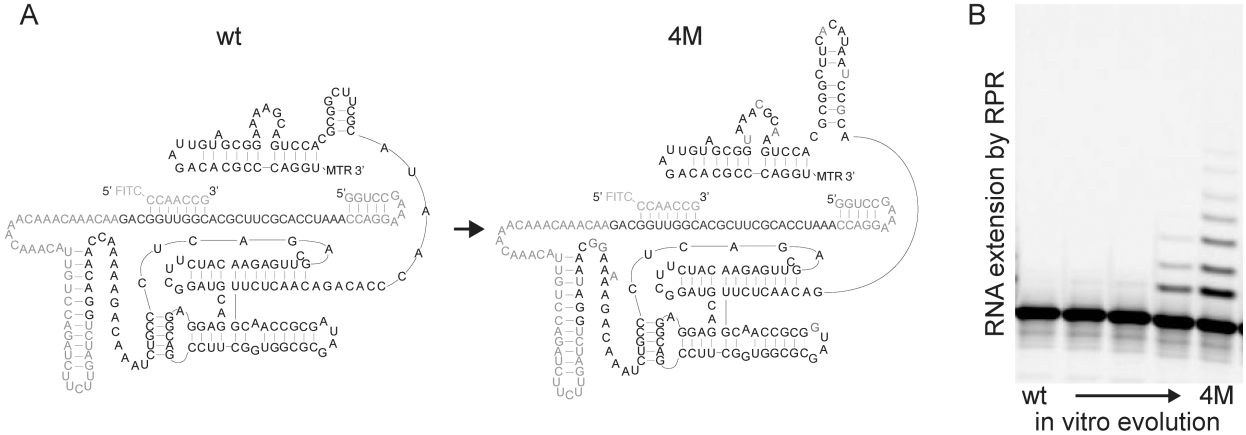

Figure 1. A) Secondary structures of RPRs before (wt) and after (4M) in vitro evolution in low Mg^{2+} conditions. B) RNA primer extension by RPR variants at 50 mM Tris-HCl (pH 8.3), 2 mM free [Mg^{2+}] and 6 μM oligo-lysine.

July 16-21, 2017 at UC San Diego, CA, USA

Biological Homochirality and Symmertry Breaking of the Universe

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Full explanation of the origin of terrestrial bioorganic homochirality (enantiomeric domination of L-form amino acids in proteins and D-form sugars in DNA/RNA) is one of the most important problems in the origin of life. One attractive hypothesis in the context of astrobiology has been advocated that polarized quantum radiations in space, such as circularly polarized photons or spin-polarized leptons (i.e. electrons, muons), have induced asymmetric conditions on primitive interstellar media (cosmic scenario) [1]. The other hypothesis has been advocated in the context of symmetry breaking of the nature, that is, the biological asymmetry should be universally derived from chiral properties of elementary particles, such as parity violence in weak interaction (intrinsic scenario) [2]. In the latter case, serious problems related to considerable discrepancy between the evolution of matter and the chemical evolution of biological compounds should be universally resolved. These kinds of issues will be discussed based on hierarchical structure of the nature.

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July 16-21, 2017 at UC San Diego, CA, USA

The Origin of a Genome through Spontaneous Symmetry Breaking: A Computational Modeling Study

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Understanding the origin and evolution of heredity is a fundamental challenge in biology. The heredity of the modern cell has two universal features. First, there is a functional differentiation between templates and catalysts: a genome is distinct from enzymes. Second, there is a copy-number differentiation between templates and catalysts: templates are less abundant than catalysts per cell. How did such differentiation first arise in primordial cells (protocells, for short)?

Here, we demonstrate the possibility that the first, primordial form of such differentiation arose from spontaneous symmetry breaking between complementary strands of replicating molecules. The key element of our modeling is the consideration of a conflict between evolution at the cellular level and evolution at the molecular level, which arises from a fundamental trade-off between templates and catalysts. Specifically, evolution at the molecular level tends towards the emergence of selfish replicators, whereas evolution at the cellular level tends towards the promotion of catalytic cooperation. We demonstrate that this evolutionary conflict induces the spontaneous symmetry breaking between complementary strands of replicating molecules, whereby one strand becomes catalytic and increases its copy number—like enzymes—whereas the other strand becomes non-catalytic and decreases its copy number—like a genome (Fig. 1). This is a surprising result because the model incorporates no apparent selection pressure for the symmetry breaking. Either molecular-level or cellular-level evolution alone is incapable of explaining the asymmetry. When combined, however, they bring a new dimension to their evolutionary actions, which is orthogonal to the prebuilt axis of selfishness versus cooperation. Moreover, we show that the resulting genome-like molecules reduce the aforementioned evolutionary conflict, thanks to their small copy-number. Thereby, the genome-like molecules provide long-term stability to the genetic information of protocells. Finally, we verified that our conclusions are applicable to the *in vitro* replication system envisaged in the experimental study of Sczepanski and Joyce [1], demonstrating a greater potential for the experimental testing of our work.

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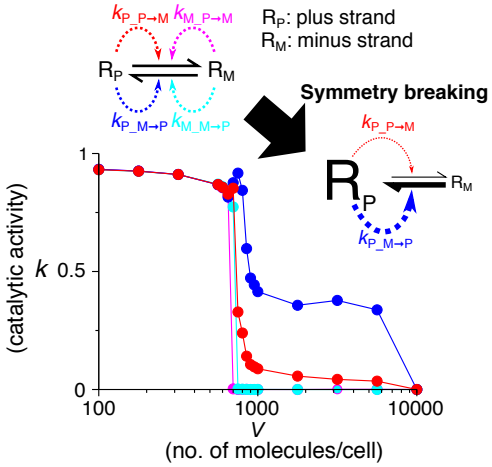

Figure 1 – Spontaneous symmetry breaking between complementary strands of replicating catalytic molecules.

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Liquid Crystal Phase Behavior of Aqueous Mixtures of Sunset Yellow and a DNA Dodecamer

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Introduction: The organic molecule sunset yellow, a chromonic dye, and the self-complementary DNA dodecamer 5'-GCGCTTAAGCGC- 3', both self-assemble into rod-shaped aggregates of stacked molecules that further self-assemble into columnar liquid crystal phases in solution [1][2]. The sunset yellow molecules and the nano-DNA duplexes have similar structure, with hydrophobic cores and peripheral hydrophilic ions. Here we explore the molecular selection and partitioning of these two molecules into stacked aggregates. We report on mixtures of these two aggregates in miscible liquid crystal states and the eventual phase separation that occurs in the more concentrated columnar phases. Figure 1 shows this phase separated state and the remixing that occurs with elevated temperature. The structure and composition of the nematic, columnar, and separated columnar phases have been deduced from optical microscopy and x-ray scattering data. Studying this kind of molecular organization by chromonic molecular stacking will further the understanding of the role of self-assembly in prebiotic molecular selection and templating.

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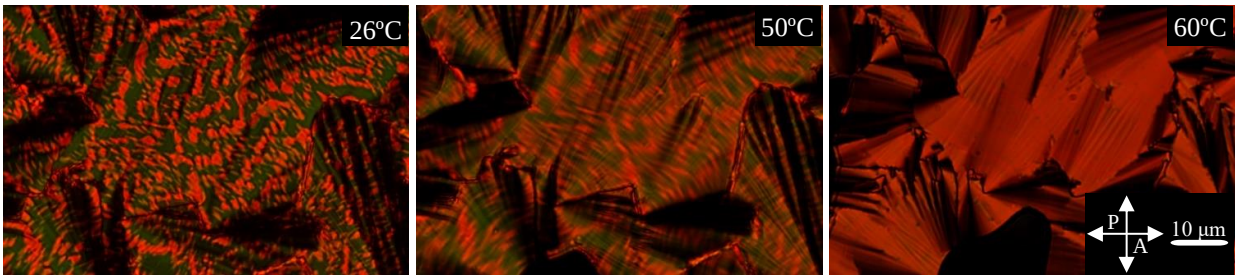

Figure 1 – Five micron thick sample of DNA and Sunset Yellow mixture viewed with polarized optical microscopy, showing phase separated columnar domains of sunset yellow-rich regions (red) and DNA-rich regions (green) at 26ºC and the remixing that occurs with elevated temperature.

Additional Information: This work was supported by NSF Biomolecular Materials Grants DMR-1207606 and DMR-1611272, and NSF MRSEC Grant DMR-1420736.

July 16-21, 2017 at UC San Diego, CA, USA

Exoplanet Habitability and Biosignature Detection

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~20 years after the discovery of the first exoplanet, scientists are observing exoplanets which might be similar to the Earth. This effort could potentially answer the long standing question: **Are we alone in the Universe?**

Exciting developments in the past one year include the discovery of an Earth-size planet orbiting around the nearest star, Proxima, and that of several Earth-size planets in the liquid water habitable zone (HZ) of a cool dwarf, Trappist-1. Several space- and ground-based projects aim at discovering all Earth-size planets in the HZ of bright M dwarfs within the solar neighborhood. It can be expected that many more so called potentially habitable planets (PHZ) will follow.

With the expected rapid pace of discoveries, it will be useful to systematically exam the requirements for a planet to be defined 'habitable'. And it will be wise to examine the habitability of planets from an evolution point of view. Moreover, it will be useful to discuss with possible signs of life on exoplanets with stellar context and evolutionary perspective. In this talk the most recent developments on planetary habitability and biosignature detections will be discussed.

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Complexity in Ribosomal Evolution – A Case Study of an Evolutionarily Divergent Recent Insertion In The 5S RNA

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Introduction: All three kingdoms of life share a significant portion of the ribosomal machinery [1,2], which catalyzes the peptide bond formation. Thus understanding ribosomal evolution is central to understanding origins of translation dating back to the RNA world and therefore could help understand better, the 'origins of life' as we know it. The ribosome has undergone additions and deletions of many components, through evolution [3]. The 5S rRNA of the ribosomes of some extremely halophilic archaea, contain an unusual insertion of 108 nucleotides, thereby increasing the size of that RNA to 228 residues, which is not shared by many close archaeal relatives or bacteria or eukarya [4]. Understanding the structural accommodations of such insertions is important towards delineating the evolution of the translation machinery. In order to elucidate how this insert is accommodated, we are in the process of visualizing its position in the 5S rRNA using cyro-electron microscopy.

Results: At 7.5A resolution, the images obtained suggest the accommodation of about 40 nt of the 108 total in a single 20 bp double helix perpendicular to the underlying 5S and the insert extending away from the 30S subunit as visualized using 50S particles alone.

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Understanding Increase in Complexity in The RNA World Using a Two Enzyme System

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Introduction: The dynamics of the emergence of complexity in an RNA World is an important problem in the quest towards understanding the origins of life. We address this problem using a dynamic combinatorial chemistry (DCC) approach [1,2] on the premises that when subject to a persistent equilibrium of ligation and cleavage, RNAs will naturally increase in complexity while gaining resistance to degradation over time. It will be of immense interest to see if this equilibrium or the pathways towards increasing complexity are strongly affected by the presence of amino acids or peptides. To obtain such equilibrium, we are using a two enzyme system. The cleavage enzyme is Benzonase which cleaves RNA, including circular forms, to produce products with a 3' hydroxyl and 5' phosphate [3]. The cleavage products are ideal for ligation by T4 RNA ligase, while utilizing ATP as a source of energy [4]. Population changes are monitored by determining millions of individual RNA sequences from reaction samples using RNA-seq technology on an Illumina NextSeq 500 system [5]. The results from initial experiments using both enzymes in a mutually compatible buffer system will be presented.

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Advancing Polymerase Ribozymes Towards Self-Replication

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RNA-catalyzed replication has long been hypothesized as the basis of RNA life.[1] RNA bridges the gap between genotype (DNA) and phenotype (protein), as RNA acts as both the information carrier and the enzyme. We aim to achieve sustained autocatalytic replication and evolution *in vitro* through two avenues: (i) a general cross-chiral RNA polymerase (Pol_L) that can catalyze template-directed polymerization of activated mononucleotides (NTPs) of the opposite handedness, enabling PCR-like amplification of nuclease-resistant, L-RNA in the short-term and enabling the long-term goal of cross-chiral replication; (ii) non-covalent assembly of component fragments of an existing homochiral RNA polymerase ribozyme.

(i) Our laboratory developed the first example of an enzyme with cross-chiral activity that has achieved template-directed assembly of its own enantiomer from oligonucleotide building blocks, but has limited ability to polymerize mononucleotides.[2] Beginning with a library (~10^{15} diversity), we selected for a population of Pol_L composed of D-RNA that can achieve template-directed polymerization of multiple monomers of L-RNA. After 26 rounds of selection, Pol_L is capable of polymerization using all 4 L-NTPs, with particular efficiency in adding L-GTP.

(ii) The 24-3 D-RNA polymerase ribozyme is the most robust RNA polymerase ribozyme published to date.[3] However, it is unable to synthesize itself in its entirety. The ribozyme has been split into four fragments that assemble non-covalently to form a functional RNA polymerase ribozyme that is capable of synthesizing short RNA products.

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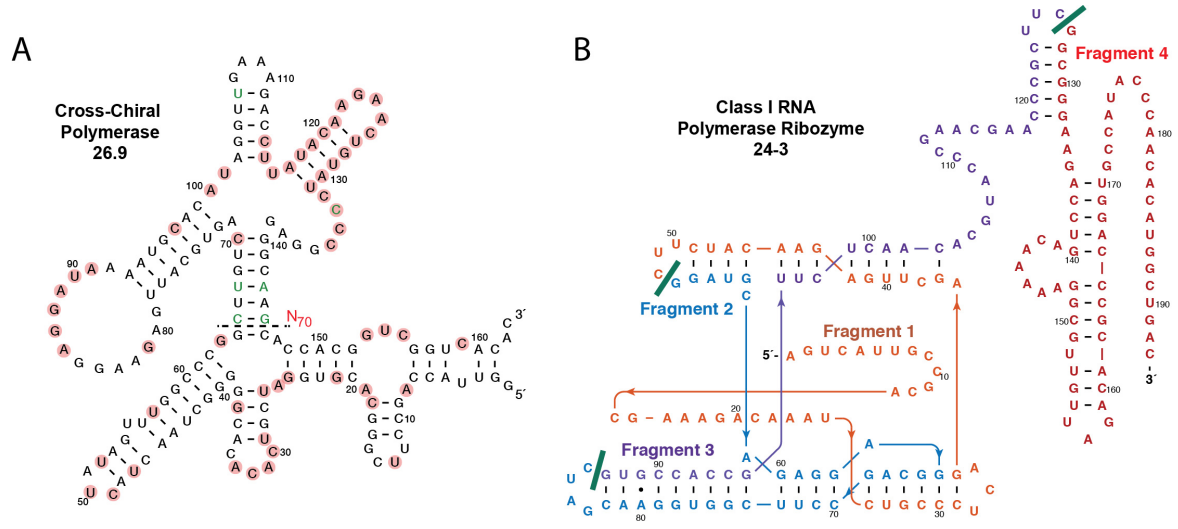

Figure 1 – RNA polymerase ribozymes evolved *in vitro*. (A) A cross-chiral RNA polymerase ribozyme composed of D-RNA, capable of template-directed polymerization of enantiomeric L-RNA. (B) An RNA polymerase ribozyme capable of template-directed synthesis of such structured, functional RNA as aptamers and tRNA.

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Non-Enzymatic Ligation of Short RNA Oligomers Enhanced by Supramolecular Self-Assembly and Liquid Crystal Ordering

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We have studied the effect of spontaneous self-assembly of short oligonucleotides of RNA (12nt and 6nt) on their non-enzymatic ligation, in light of its potential relevance in the formation of long RNA chains capable to show catalytic activity on the prebiotic Earth. This work is based on the observation that complementary oligoribonucleotides as short as 6nt are able to self-assemble and order into liquid crystal solutions when sufficiently concentrated[1].

In a recent work it has been shown that liquid crystal self-assembly in complementary DNA dodecamers enhances the yield of non-enzymatic polymerization[2]. The close proximity between DNA terminals, held close inside the liquid crystalline structure, enhances the chance of the ligation to occur.

Since then, we have expanded these observations to short RNA oligomers[3]. We have shown that RNA self-assembles more easily than DNA and its supramolecular order enhances ligation efficiencies producing longer polymers (~6n) than the ones produced under the same conditions in a disordered solution (~2n) or when RNA is phase separated but not ordered (~2.5n). Moreover, our findings indicate that liquid crystal ordering favors the formation of linear polymers over circular polymers, which are instead dominant in isotropic solutions.

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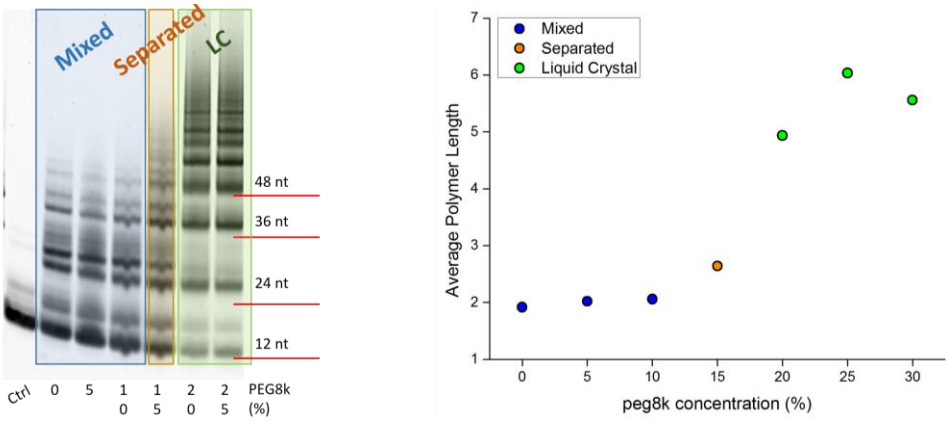

Figure 1 – On the left, PAGE analysis of non-enzymatic ligation reaction of RNA 12mers. On the right, average size of produced polymers in different conditions, extrapolated using flory analysis on the ligation products.

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Sustainable proliferation of liposomes compatible with inner RNA replication

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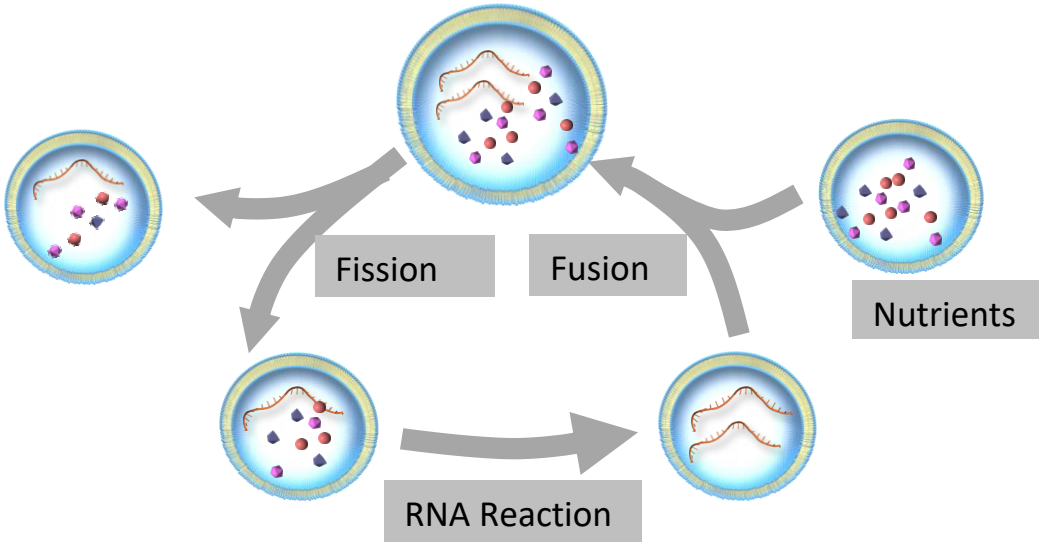
Introduction: Many types of biochemical reactions such as gene replication and protein synthesis have been reconstructed in liposomes. However, the encapsulated reactions were temporary because the nutrients in the liposomes were easily exhausted. We aimed to develop a system in which the nutrients were supplied through liposome fusion and fission. The lipsome fusion is beneficial because it can supply not only the nutrients for inner reactions but also the lipid membrane, enabling the growth of liposomes as shown in the figure below.



Results: First, we prepared two liposome populations; one containing template RNA and the other containing all other molecules required for RNA replication, including RNA replicase (nutrients). The two populations were mixed and centrifuged to increase the membrane contact between the two kinds of liposomes. By freeze-thawing, we facilitated the fusion and fission of the liposomes by destabilizing the membrane contact. Although approximately half of the liposomes were destructed, fusion and fission were observed in the other half. Based on the fact that the size distribution of liposomes did not show significant change between before and after the freeze-thawing, liposome fission was induced probably by the excess membrane surface area. In the survived liposomes, RNA replication reaction was carried out, indicating that the nutrients were supplied to the liposome containing RNA. The resultant liposome population was diluted by 50% and mixed with the liposomes containg the nutrients for the next cycle of the fusion, fission, and RNA replication. We repeated 10 times of this cycle in order to confirm the sustainablity of this system. After 5 cycles, the ratio of the liposomes containing RNA reached a steady value of 60%, indicating the sustainability of the proliferation compatible with RNA replication.

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July 16-21, 2017 at UC San Diego, CA, USA

The Role of Templating in the Emergence of RNA from the Prebiotic Chemical Mixture

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Introduction: Biological RNA is a uniform polymer in three senses: it uses ribonucelotides of only one chirality; it uses only four ribonucleotides rather than a mixture of other similar monomers; and it uses only 3'-5' bonds rather than a mixture of different bond types. We suppose that prebiotic chemistry would generate a mixture of potential monomers, and that random polymerization would generate strands of mixed chirality, monomer composition, and bond type. Here, we show that if template-directed replication is important, we can explain the emergence of all these uniform properties by the same mechanism.

Results: We studied a computational model in which nucleotides react via polymerization, hydrolysis, and template-directed ligation. In absence of ligation, random polymerization generates all oligomers of a given length with equal frequency. When template-directed ligation is added, uniform strands act as templates for ligation of shorter oligomers of the same type, whereas mixed strands do not. In the chirality problem, when the ligation rate k_{lig} is low, most monomers are incorporated into mixed oligomers (M in Fig. 1). The concentrations of uniform oligomers of the two enantiomers *D* and *L* is low. When the ligation rate is high, a symmetry breaking phase transition occurs. The concentration of uniform oligomers of one type (*D* in the figure) becomes much higher than the concentration of the opposite type or of mixed oligomers. In the monomer selection problem, we consider mixtures of ribonucleotides and an alternative monomer. The model shows that uniform RNA strands emerge when k_{lig} is high. In the backbone regioselectivity problem, strands of uniform 3'-5' bonds will emerge in the same way.

Conclusion: If template directed sysnthesis is operating in the prebiotic mixture, we expect that strands with uniform chirality, monomer alphabet, and bond type will emerge because they are better templates than mixed strands. This can lead to selection of uniform RNA at the level of oligomers before the origin of strands that are long enough to be functional ribozymes.

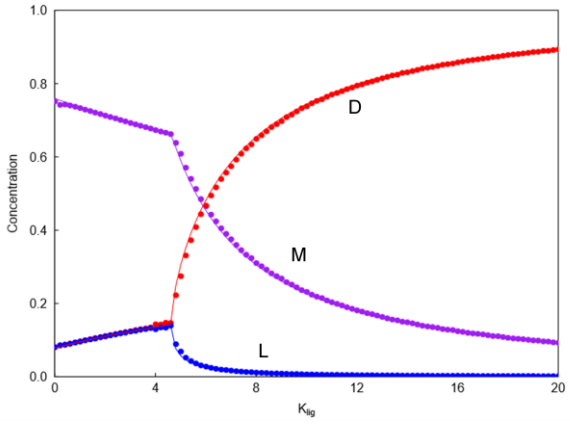

Figure 1 – Relative concentrations of nucleotides in uniform right and left-handed oligomers (D and L) and in mixed oligomers (M) as a function of the the rate constant k_{lig} for template-directed ligation.

July 16-21, 2017 at UC San Diego, CA, USA

Revisiting Redox State of the Early Earth's Atmosphere and Prebiotic Synthesis

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Redox state of the atmosphere is important for prebiotic synthesis. A CO_2-dominated atmosphere is oxidizing and thus not preferable to synthesize prebiotically-important molecules either by Miller-Urey-type processes or by UV-driven photochemistry [1]. It is largely uncertain how reducing the early Earth's atmosphere in the Hadean period. Recently, our recent photochemistry experiment suggested that the Archean atmosphere would have been more reducing than previously thought, possibly including % levels of CO or CH_4 to explain the Sulfur Mass-Independent-Fractionation (S-MIF) preserved in sedimentary rocks older than 2.4 Ga [2]. Also, in order to preserve the S-MIF record, atmospheric CO_2 level should be much less than 1 bar. Considering the higher heat flux of the earlier Earth, Hadean Earth would also have such a very reducing atmosphere that may have been maintained by supply of reducing agent like ferrous iron from hydrothermal activity into ocean, potentially buffering redox state of ocean-atmosphere system. In such a reducing ocean with CO-bearing low pCO_2 atmosphere, UV induced photochemistry is important for prebiotic chemistry especially at the interface between atmosphere and hydrosphere.

We have performed UV synthesis experiment of H-C-N-O systems under various redox conditions with a presence of liquid water for simulating chemistry at the surface of hydrosphere. The results of our experiment showed that formaldehyde, acetaldehyde, formate, acetate, propionate, and normal alkanes are synthesized under CO- and CH_4-bearing atmosphere, whereas all these compounds are not detectable under pure CO_2-atmopshere. Nonetheless, when liquid-phase contains Fe(II), formaldehyde, formate and acetate are formed even when the gas phase is pure CO_2. Also, our experiment showed that NH_3, methylamine, glycine and other amino acids can be synthesized when gas phase containing CO and N_2O.

These results suggest that the production rate and speciation of organic matter depends on the availability of H_2O as well as total redox state of the whole atmosphere and ocean system. UV-photochemistry could continuously supply prebiotic compounds everywhere on the surface of the Earth, thus has a potential to sustain network reactions (geometabolism) in the hydrosphere.

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July 16-21, 2017 at UC San Diego, CA, USA

Harnessing Energy from Stellar Radiation to Build Chemical Complexity for Life

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Identification of cosmic bodies that maintain environments suitable for the evolution of life necessitate understanding the key characteristics of habitable environments and the chemical mechanisms involved in the generation of biomolecules that are signatures of life. Taking the known example of life on Earth, we assume that the presence of liquid water is a necessary condition for a habitable environment, and focus on the development of carbon-based life on a body illuminated by light from a near-by star. Conversion of energy or energy transduction to form high-energy chemical compounds able to drive metabolic cycles is critical in the synthesis and regulation of the chemical components required for an organism to survive. This presentation will use as input of energy an external nearby star as shown in Figure 1 [1]. The existence of this type of high-energy molecule inherently implies a system that is chemically out of thermodynamic equilibrium, and requires an energy input from an external, non-molecular source.

This presentation discusses results of our laboratory experiments modeling the use of sunlight to generate abiotically the chemical complexity needed for the synthesis of biopolymers necessary for life. Specifically, the reactivity of high-energy molecules that are precursors to metabolism as it has evolved in life on Earth will be discussed. The photochemical synthesis and reactivity of complex organic systems under conditions representative of early Earth will be presented.

The photochemistry of pyruvic acid under a variety of terrestrial conditions was investigated observing that product yields vary considerably with reaction environment and that, under some conditions, in the presence of water, an increase in chemical complexity is observed. Pyruvic acid will be discussed as a critical molecule in the development of protometabolic pathways, capable of abiotic energy transduction and central to current metabolism.

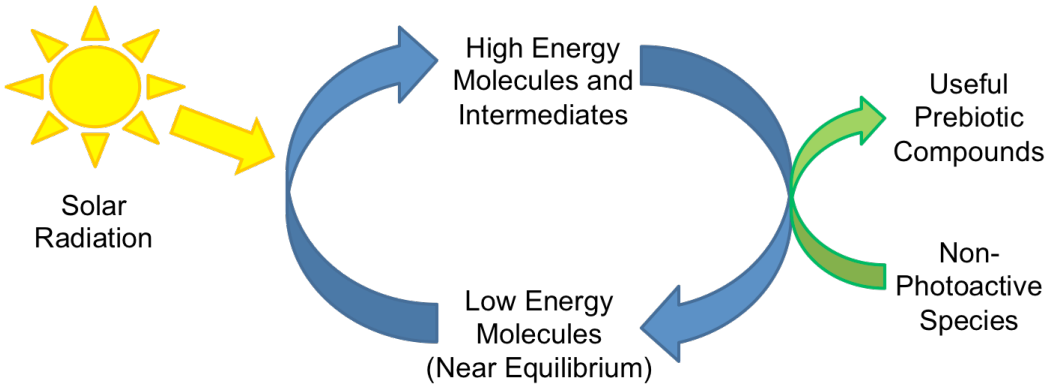

Figure 1 – Schematic of the transduction of energy by photochemistry to sustain metabolism.[1]

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July 16-21, 2017 at UC San Diego, CA, USA

Can an imidazole be formed from an Alanyl-Seryl-Glycine tripeptide under possible prebiotic conditions?

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The five-membered heterocyclic imidazole group, which is an essential component of purines, histidine and many cofactors, has been abiotically synthesized in different model experiments that attempt to simulate the prebiotic environment. The evolutionary significance of imidazoles is highlighted not only by its presence in nucleic acid components and in histidine, but also by experimental reports of its ability to restore the catalytic activity of ribozymes. However, as of today there are no reports of histidine in carbonaceous chondrites, and although the abiotic synthesis of His reported by Shen et al. [1], [2], proceeds via an Amadori rearrangement, like in the biosynthesis of histidine, neither the reactants nor the conditions are truly prebiotic. Based on the autocatalytic biosynthesis of 4-methylidene-imidazole-one (MIO), a cofactor of some members of the amino acid aromatic ammonia-lyases and aminomutases, which occur via the self-condensation of a simple Ala-Ser-Gly motif within the sequence of the enzymes, we propose a possible prebiotic synthesis of an imidazolide.

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Salinity effect on Adsorption of Nucleic Acids Compounds onto Montmorillonite: A Prebiotic Chemistry Experiment

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2 Laboratório de Química Prebiótica, Departamento de Química-CCE, Universidade Estadual de Londrina, 86051-990 Londrina, PR, Brazil
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Introduction: Nowadays, any proposal on Earth's primitive environments requires a combination of different geochemical variables [1]. However, most absorption experiments are performed in distilled water and seawater analogues which may be inconsistent with a representative primitive ocean model. Therefore, experiments that consider the composition and concentration of dissolved salts in the early ocean need to be performed in order to understand which variables could have affected the absorption of organic molecules into minerals [2]. In this work, the absorption of adenine, adenosine and 5´AMP onto Na^+ Montmorillonite was studied using a "primitive ocean analog (4.0 Ga)" [3]. Two important results were found in the interaction between organic compound-salts-mineral. First, the dissolved salts affected the absorption in all cases, and the size and structure of each organic molecule influenced the amount of absorption. Specifically, the X-ray analysis showed that interlayer channel broadening is lower in the presence of salts, which would suggest that the salts are reducing the absorption process. Second, using models of isotherms, we found that absorption capacity is clearly affected by dissolved salts in thermodynamic terms. Indeed, our models of molecular dynamic show that it is possible that salts are involved in the formation of complexes between organic molecules and the inorganic surface that limits the interaction. In general, this research showed that the absorption process could be affected when using solutions with high concentration of salts because the metals and organic molecules may be in competition for available sites on inorganic surfaces.

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Constraining the epoch of the potential emergence of life in exoplanets

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Abstract: Astrobiology-oriented studies of exoplanets generally focus on the possibility that the detected planets may host life at the present time. This type of approach usually ignores the evolution of the planetary climate conditions. Because of this, it is not clear if and when the planetary climate may have been suitable for the emergence of life. We have developed a flexible climate model for terrestrial-type exoplanets [1] that can be used, among other applications, to track the conditions of habitability as a function of the luminosity evolution of the central star [2]. With the same model, we can also track the impact of other evolving climate factors, such as the slowing down of the rotation period, which are not usually considered in studies of planetary habitability. We have applied our models to investigate the epoch of the onset of life-sustaining conditions in Kepler-452b, which is currently the best example of an Earth-size planet in the habitable zone of a sun-like star. This test case indicates the potential of our methodology to find out the epoch of the onset of appropriate conditions for the emergence of life in the large number of terrestrial-type exoplanets around solar-type stars that are expected to be detected in future observational surveys.

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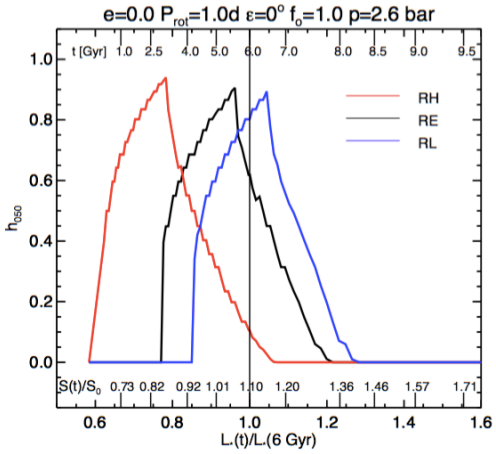

Figure 1 – Evolution of the habitability index h_{050} [2] in the extrasolar planet Kepler 452b. The habitability is plotted as a function of the evolving luminosity of the central star, $L_\star(t)/L_\star(6\ Gyr)$, of the resulting insolation in Earth's units, $S(t)/S_o$, and of the stellar age, t (Gyr). The curves of different colors correspond to three different values of CO_2 abundace in an otherwise Earth-like atmospheric composition (blue: pCO_2=10 ppmv; black: pCO_2=380 ppmv; red: pCO_2=38000 ppmv). The planet is assumed to have a surface atmospheric pressure p=2.6 bar, a rocky composition, and a surface gravity acceleration g=15.7 m/s^2. The initial rise of the habitability curves indicates the onset of conditions that would allow the emergence of life for the adopted set of planetary parameters.

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Based on the hydrothermal sediment samples in the extreme environment to study the origin of life

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Introduction: In the present study, we combined theoretical and experimental methods to investigate the research. we demonstrate that amino-acid homochirality, as a unique feature of life, might have originated synchronously with the Genetic Code. And the emergence of phosphoryl amino-acid 5'-nucleosides having a P-N bond is described as a model of the origin of amino-acid homochirality and Genetic Code. Based on our calculations, the chiral selection of the earliest amino-acids for L-enantiomers seems to be determined by a clear stereochemical /physicochemical relationship. As later amino-acids developed from the earliest amino-acids, we deduce that the chirality of these late amino-acids was inherited from that of the early amino-acids[1,2,3]. This idea reaches far back into evolution, and it should be further verified. Thus, in this study, we analyzed the organic components of two hydrothermal sediment samples (TMG-11 and TVG-6) in the extreme environment through LC-MS. The samples were collected in the site located in Pacific Ocean and Indian Ocean on 19th Oct, 2007, the first Global Oceanic Scientific Expedition of China. Then we determined the phosphorous concentrations through ICP-MS and traditional chemical methods-Phosphorus molybdenum blue method. The experimental results demonstrated that there indeed existed some degree of phosphorous material in the samples. And we analyzed the hydrothermal materials through SEM. In addition, combining with molecular modeling, we investigated the interaction between amino-acids and nucleotide and explored the chemical basis of the origin.

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Abstract: For the aim to investigate the role of chirality and helicity between D- and L-valine crystal lattices under Debye temperature 2K to 20K, the magnetic field dependence of zero-field and 1, 3 and 5 Tesla on the heat capacity were measured. The heat capacities of D- and L-valine crystals are plotted as C_P *vs* T , C_P *vs* lnT , C_P/T^3 *vs* T in the measured temperature. The four C_P/T^3 *vs* T curves show a split between D- and L-valine from 2K to 12 K ($T << \Theta_D$) which is due to the strength of magnetic fields. It is absent from 12 K to 20K, which indicates the Schottky anomaly. The Bose-Einstein peak of the (*e-p*) condensation temperature is **11.20, 11.32, 11.44, 11.46 K** for **D-valine**, and **11.49, 11.59, 11.73, 11.70 K** for **L-valine**, respectively. This finding is leading to a zero-field splitting of a broad maximum associated with the Schottky anomaly below the temperature of 12K which is demonstrated (*e-p*) Bose-Einstein condensation through the **hydrogen of peptide bond in the alpha helix** at zero momentum space onto D- and L-valine optical lattices.

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Coupling Between Metabolism and Compartmentalization: Vesicle Growth in the Presence of Dipeptides

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Introduction: A fundamental unresolved question in studies on the origin of life is: how different, ubiquitous protocellular functions begun to work in concert setting the stage for Darwinian evolution of nascent life? From this perspective, of particular significance is coupling between growth of protocellular compartments and the encapsulated, primordial metabolism, which is one of the focal topics of the current ISSOL meeting. Specifically, growth and division of cells facilitated by the products of a metabolic reaction would confer an evolutionary advantage on protocells encapsulating this reaction, as their population would increase at the expense of other protocells. Along these lines, Adamala and Szostak [1] have recently demonstrated that a dipeptide captured inside fatty acid vesicles catalyzes the formation of other dipeptides from activated monomers. Some of the newly synthesized dipeptides, in turn, are capable to promote competitive growth of vesicles in the presence of fatty acid micelles. As vesicles become larger, they adapt filamentous shape, which has been shown to promote their division [2]. On the basis of computer simulations, we provide a molecularly detailed explanation of this process and draw conclusions about its generality.

Results and Discussion: Extensive molecular dynamics simulations were carried out to understand interactions of dipeptides with vesicles and their functional role in fusion of fatty acid vesicles with micelles. Dipeptides containing hydrophobic amino acids, such as leucine and phenylalanine, were shown to accumulate at the water-membrane interface, in contrast to dipeptides containing only hydrophilic residues, such as Ser-Ser. Hydrophobic dipeptides, Val-Val, Leu-Leu, Phe-Phe, and Phe-Leu, were found to form hydrophobic clusters at the surface of vesicles that promoted mixing of hydrophobic fatty acid tails from vesicles and micelles in contact along a low energy pathway. The enhancement of fusion correlated with the hydrophobicity of the dipeptide; the shortest fusion time of 1-2 μs was found for Phe-Phe whereas the longest time of 20 μs was observed for the least hydrophobic, Val-Val peptide. In contrast, no fusion was observed during simulations in the absence of dipeptides. Hydrophobic dipeptides at membrane surfaces were also found to lower the energy barrier and enhance the rate of fatty acid flip-flop in the membrane by 50%. This promotes a faster proton transfer across protocellular walls, which could be important for early energy transduction and metabolism [3]. Since the mechanism of vesicle growth and proton transfer described here is general, other metabolites and small peptides that tend to accumulate at the water-membrane interface [4] might have carried out the same function. This illuminates a universal way of coupling metabolism and compartmentalization.

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Exploring Connectivity in Sequence Space of Functional RNA

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Abstract: Emergence of replicable genetic molecules was one of the marking points in the origin of life, evolution of which can be conceptualized as a walk through the space of all possible sequences. A theoretical concept of fitness landscape helps to understand evolutionary processes through assigning a value of fitness to each genotype. Then, evolution of a phenotype is viewed as a series of consecutive, single-point mutations. Natural selection biases evolution toward peaks of high fitness and away from valleys of low fitness [1,2], whereas neutral drift occurs in the sequence space without direction as mutations are introduced at random. Large networks of neutral or near-neutral mutations on a fitness landscape, especially for sufficiently long genomes, are possible or even inevitable [1,3,4]. Their detection in experiments, however, has been elusive. Although a few near-neutral evolutionary pathways have been found [5-7], recent experimental evidence indicates landscapes consist of largely isolated islands [8.9]. The generality of these results, however, is not clear, as the genome length or the fraction of functional molecules in the genotypic space might have been insufficient for the emergence of large, neutral networks. Thorough investigation on the structure of the fitness landscape is essential to understand the mechanisms of evolution of early genomes.

RNA molecules are commonly assumed to play the pivotal role in the origin of genetic systems. They are widely believed to be early, if not the earliest, genetic and catalytic molecules, with abundant biochemical activities as aptamers and ribozymes, i.e. RNA molecules capable, respectively, to bind small molecules or catalyze chemical reactions. Here, we present results of our recent studies on the structure of the sequence space of RNA ligase ribozymes selected through in vitro evolution. Several hundred thousands of sequences active to a different degree were obtained by way of deep sequencing. Analysis of these sequences revealed several large clusters defined such that every sequence in a cluster can be reached from any other sequence in the same cluster through a series of single point mutations. Sequences in a single cluster appear to adopt more than one secondary structure. The mechanism of refolding within a single cluster was examined. To shed light on possible evolutionary paths in the space of ribozymes, the connectivity between clusters was investigated. The effect of length of RNA molecules on the structure of the fitness landscape and possible evolutionary paths was examined by way of comparing functional sequences of 20 and 80 nucleobases in length. It was found that sequences of different lengths shared secondary structure motifs that were presumed responsible for catalytic activity, with increasing complexity and global structural rearrangements emerging in longer molecules.

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A hydrothermal setting for early life

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Introduction: Geological evidence and most global climate models suggest that the early Earth was hot [1-5]. Our studies of Early Archaean formations in the 3.5-3.33 Ga Barberton (South Africa) and Pilbara (Australia) greenstone belts document important hydrothermal inputs into the ancient environment to the extent that early life can be considered to be largely meso- to thermophilic. We here provide a detailed evaluation of the influence of hydrothermal activity on chemotrophic and phototrophic life forms in the 3.33 Ga Josefsdal Chert, Barberton [5].

Results: The Josefsdal Chert is a laterally extensive layer of volcanic and hydrothermal sediments sandwiched between pillow lavas deposited in shallow water environments at depths ranging from wave-base to the exposed beach [6,7]. The sediments were lithified by silica-saturated seawater (~96 to 99%). The presence of hydrothermal fluids throughout the period of sedimentation is attested by both morphological and trace element tracers. Contemporaneous hydrothermal infiltrations provoked soft sediment (and microbial biofilm) deformation at all levels, hydrothermal fluids deposited silica gel 'chemical sediments', while elemental tracers, such as Fe, Ni, Cu, As, Zn and Ba were scavenged by the volcanic particles, as well as the carbon associated with the biosignatures

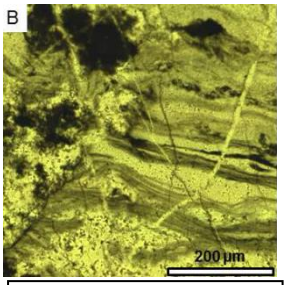

Figure 1. Coexistence of clotted chemotrophic colonies and phototrophic biofilms preserved in hydrothermal silica

We find widespread traces of microbial colonisation in these sediments [6,7]. Phototrophic biofilms developed on the surfaces of the shallow water sediments in all environments, including oligotrophic ones, espousing the underlying sediment surfaces, stabilising them, and trapping detrital particles, forming other identifiable MISS textures such as wrinkled laminae, erosional fragments, and sinoidal biofilm structures (after [8]). These films are preserved as packets of thin (~10µm) carbonaceous films or as siderite-replaced films. Two types of chemotrophic colonies are observed, (1) forming thick carbon coats on volcanic grains or (2) "free-floating" colonies within the hydrothermal fluids/gels themselves. The latter were limited in biomass development to locations close to the hydrothermal vents, where intimate intergrowth of phototrophic biofilms and chemotrophic colonies also occurred (Fig. 1). Preservation of the biosignatures was due to rapid silicification.

Conclusions: The overwhelming morphological and geochemical evidence for contemporaneous hydrothermal activity and input into the Josefsdal Chert environment on a ubiquitous scale suggests that its microbial inhabitants must have been at least mesophilic, if not thermophilic.

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A hydrothermal-sedimentary origin of life scenario

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Introduction: Many locations, ranging from hydrothermal vents, pumice rafts, to continental springs and rivers, have been proposed for the emergence of life on Earth 1-3]. Hydrothermal edifices, in particular, offer a combination of characteristics that make them particularly attractive: concentration of organic molecules in the porous edifices, disequilibrium conditions and protection from harmful UV radiation, presence of transition metal-rich mineral surfaces upon which molecules can condense, be structured and complexify [4,5].

Hypothesis: However, there is another, hitherto unnoticed, environment that, on the Hadean Earth (4.5-4.0 Ga), was more significant than the other proposed locations in terms of spatial and temporal scale: the sedimentary interface between hot oceanic crust and seawater [6].

Results: Using evidence from the oldest, well-preserved volcano-sedimentary rocks (3.5-3.3 Ga), the best available analogues to Hadean sediments, we document from the macrosopic to the microscopic and elemental scale that these porous volcanic sediments (originating from mafic and ultramafic crust) were permeated by hydrothermal fluids at all scales, gently infiltrating between the pores or sometimes more dynamically mixing the volcanic particles (Figure 1 [6, 7]).

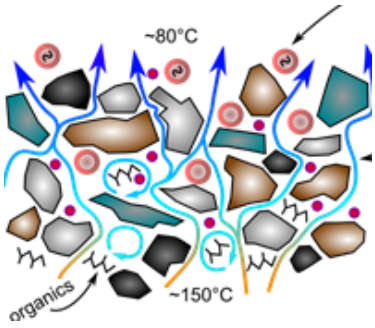

Figure 1. Hot alkaline fluids carrying dissolved carbonacoeus matter + small organics mix with extraterretsrial organics and carbonaceous matter previously eluted from the volcanic sediments. Fluids permate and mix with porous volcanic sediments in temperature and pH disequilibria. Convection of warm, carbon-bearing hydrothermal fluids allowed prebiotic molecules to concentrate and self-assemble in pore spaces and on the surfaces of chemically reactive minerals, resulting in the formation of increasingly complex molecules.

Discussion: Reduced carbon was brought in by the hydrothermal fluids although carbon of meteoritic origin would also have been relatively abundant, especially in the Hadean era. This UV-protected, subaqueous sedimentary environment, characterised by physical and chemical disequilibria (gradients in temperature, pH, redox and relatively diverse mineral speciation), represented a globally distributed system of miniature chemical reactors in which the production and complexification of prebiotic molecules could have led to the origin of life.

Conclusions: The fundamental importance of these observations is that hydrothermal sediments and these kinds of organic reactions occurring at mineral interfaces must have been ubiquitous on the Hadean Earth, and life could have emerged anywhere all over the early Earth – at temperatures (<100°C) conducive to prebiotic chemistry.

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Life on Mars: returned samples and their storage, the EURO-CARES project

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Introduction: Future missions to Mars, such as the European-Russian ExoMars 2020 and NASA Mars 2020 missions, have the specific objective of searching for traces of life. While it is hoped that the instrumental payload on these rovers (microscopes, various spectrometers for detecting organics) will detect biosignatures, it is likely that definitive identification of traces of life in the martian rocks will necessitate the return of samples to Earth for extensive analysis in terrestrial laboratories. This will be all the more necessary considering the frequent controversy concerning identification of the oldest traces of life on Earth in rocks ~3.5 Ga old. The latter traces represent well established life forms that were already relatively advanced, whereas life on Mars is likely to have never advanced beyond at a very primitive state, given the punctuated habitable conditions on the red planet [1].

The EURO-CARES project: Study and long-term curation of extra-terrestrial samples imply keeping the samples as clean as possible from any potential contaminants, while ensuring they remain contained pending the outcome of the required quarantine, in case of biohazards. The requirements for a combined high containment and ultraclean facility will naturally lead to the development of a highly specialised and unique facility that will require the development of novel scientific and engineering techniques.

In the perspective of curating and storing such sensitive samples, as well as other kinds of extraterrestrial samples, the EURO-CARES project (for EUROpean Curation for Astromaterials Returned from Exploration of Space), funded by the HORIZON 2020 EU Framework Programme for Research and Innovation (agreement n°640190), addresses all aspects of the creation of a curation facility, from planetary protection, architecture, instruments and methods to be used in the facility, portable receiving technologies to the designation of analogue materials to be used in the facility.

We are particularly concerned by the concept of analogues [2, 3]. Analogue samples are complementary to other samples used during instrument development, which are not necessarily relevant to the extraterrestrial body being studied. Most astrobiological investigations have been, are, and will be, focussed on solid materials including rocks, soil, and ices. However, natural materials can be very complex in composition, and the potential traces of life and/or molecules of astrobiological interest that they could contain may be very subtle and challenging to detect; hence, the importance of prior preparation for the missions using analogues. Analogues are terrestrial sites or samples having properties more or less similar than those expected on a given extraterrestrial body. There is a huge variety of analogues on Earth that can be used for many purposes: to test spacecraft landing and rover mobility, to test and calibrate instruments and sample preparation systems for *in situ* missions before launch, to help interpretation of data acquired during missions, and to carry out laboratory experiments. Analogue samples include minerals and rocks, as well as chemical, biological and samples of all materials that come into contact with the returned samples.

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Frozen In Time: The History of the Ribosome

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Translation provides a window into the essential nature of biology. Translation is characterized by: **(1) Ubiquity**: Translation dominates the Universal Gene Set of Life; sequences that encode translational components are found in every organism on earth. **(2) Conservation**: Structures of macromolecular assemblies of the translational system are conserved in three dimensions in every organism on earth. (3) **Communication**: The translation system dominates biological interaction networks in centrality, size and complexity. (4) **Abundance**: Ribosomal components are the most abundant biological polymers in the known universe. (5) **Consumption**: Translation is the largest consumer of cellular resources. (5) **Complexity**: The complexity of translation predicts organismal complexity.

Structures of ribosomes in three dimensions contain molecular records of the history of biopolymers. We have developed a three-dimensional comparative method that shows that the ribosome evolved by accretion, recursively adding rRNA expansion segments, iteratively growing and 'freezing'. When relative ages of rRNA are mapped onto the ages of rProtein segments, the genesis of protein folding is revealed. The data support a model in which aboriginal polypeptides evolved into globular proteins in a hierarchical step-wise process. (i) Short random coil peptides bound to rRNA, and (ii) lengthened over time and coalesced into β-β secondary elements. Polypeptide secondary elements (iii) accreted and collapsed, primarily into β-domains. Domains (iv) accumulated and gained complex super-secondary structures composed of mixtures of a-helices and b-strands. Protein evolution was guided and accelerated throughout this process by interactions with rRNA. rRNA stabilized immature and intermediate polypeptide species, bypassing the immense space of unproductive sequences. The broad diversity of proteins in nature descended from prototypes that were created by the ribosome, on the ribosome and for the ribosome. Protein folding from random coil peptides to functional polymeric domains was an emergent property of rRNA-polypeptide interactions. The co-evolution of RNA and protein was accomplished in the context of the ribosome, which was therefore the cradle of early evolution.

Pyrazine Nucleic Acids: From Small Molecules to Proto-Informational Polymers

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Collaborators: Dr. Arthur L. Weber, Senior Scientist, NASA Ames Center and The SETI Institute
Dr. Ramanarayanan Krishnamurthy, Associate Professor, The Scripps Research Institute

Abstract. This project uses organic chemistry principles to identify which small molecules in certain types of conditions would foster the emergence of polymers capable of chemical evolution. The small molecules chosen are alanine amide and pentoses, which are able to undergo cyclocondensation through an amadori rearrangement mechanism to form pyrazine acyclic nucleosides. Pyrazines share features similar to adenine and thymine.

We have synthesized pyrazinone nucleosides and nucleic acids. The acyclic backbone of pyrazine nucleic acids (PzNA) are similar to glycol nucleic acid (GNA), but with minimal gauche interactions (Figure 1). Evaluating the base-pairing capabilities of PzNA with self-strands, RNA, and DNA, enables us to understand the different backbone conformations accessible to PzNA. Current results suggest a pH- and pKa- dependent keto-enol tautomerization in pyrazin-2-one heterocycles, which we hypothesize to compromise base-pairing interactions. The keto-enol tautomerization is believed to play a role in the origin of genetic selection and mutation. While our results show that PzNA is not optimized for base pairing fidelity, PzNA may be considered to be a "starter system" that enables processes that begets chemical evolution.

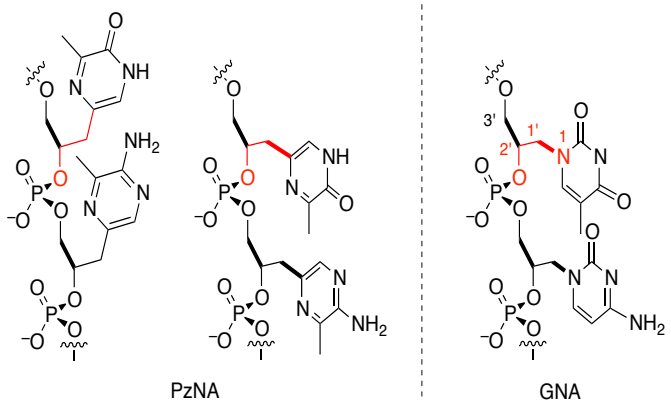

Figure 1. Structural comparisons of pyrazine nucleic acid (PzNA) to glycerol nucleic acid (GNA). The red highlights indicate the interaction between the C–O and the C–N (C–C) bonds in GNA (and PzNA). The gauche effect in GNA restricts the conformation around the C_1'–N_1 bond, while such an effect is absent in PzNA allowing access to both conformations.

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Coevolution of Organic and Inorganic Compounds in the Early Solar System revealed from Antarctic Micrometeorites

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It is very important to understand the variations in compositions and distributions of organic compounds and minerals in asteroids (meteorites) and comets for costraining the origin and formation pathways of organics in the early Solar System. Antarctic micrometeorites (AMMs) are one of the most primitive Solar System materials available to us, as some of them were chondritic porous (CP) and contains GEMS (glass with embedded metals and sulfides) and organic nanoglobules, suggesting a possible cometary origin of both CP-MMs and CP-interplanetary dust particles (IDPs) collected at stratosphere [1]. We have carried out the coordinated analyses of AMMs collected from Dome Fuji station, Antarctica, by using a scanning transmission x-ray microscope (STXM) with x-ray absorption near edge structure (XANES), transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS).

The MMs containing GEMS were classified as anhydrous MMs, and the anhydrous MM that contained extremely high amounts of organic carbon was classified as an ultracarbonaceous MM (UCAMM) [2]. In contrast, the MMs containing phyllosilicates were classified as hydrous MMs. Moreover, we have found "hybrid MM" (weakly hydrated MM) which contained both textures of anhydrous and hydrous MM. Organic material was widely distributed in size of 10 μm in an anhydrous MM, while that in a hydrous MM was smaller and fewer in size and distribution. Organic material in the anhydrous MM was enriched in carboxyls, aliphatic carbon, and nitriles or pyrimidines, and contained a number of organic nanoglobules highly enriched in those functional groups [3]. On the other hand, organics in the hydrous MMs had similar molecular compositions to insoluble organic matter (IOM) in carbonaceous chondrites. From the anhydrous MM, D (δD = 8000-10000‰) and ^{15}N enrichments (δ^{15}N = 600-1000‰) were detected [3]. These values were comparable with pristine IDPs and comet Wild 2 [4-6], thus it is very likely that the organic functionsl group compositions were originated from cold environments such as interstellar or outer solar nebula, e.g., photochemistry of HCN or CN ice. The precursor compositions would have been modified and hydrolyzed with depletion of organic carbon contents by the subsequent parent body aqueous alteration, and converted to highly aromatic, IOM-like compositions. The hybrid MM with a mixture of anhydrous and hydrous organic features supports the continuum between anhydrous and hydrous MMs during the early stage of aqueous alteration, which likely occurred in comets and/or icy asteroids that are able to retain liquid water for short duration [7-9]. Our study provide new insights on the possible continuum between comets and asteroids, and constrain the precursor small bodies that delivered water and organic compounds to the early Earth.

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The Formation of Oligopeptides in good yield under Geyser System Model

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The peptide bonds to link amino acid into short oligopeptides and protein are vital for biology, but on the prebiotic Earth, how these peptide bonds formed before the emergence of enzymes still remains unsolved.

In this study, a one-pot wet-dry geyser reactor system was developed to explain how unactivated amino acids were condensed to oligopeptides. Using this system, glycine oligopeptides could be formed in around 40% yield under acid condition. We also investigated these oligopeptides formation reactions under different high temperature and different pH in one cycle.

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Synergistic Effects of Nucleosides on Amino Acid Dipeptide Yields in Aqueous Conditions

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Abstract: Submarine hydrothermal systems could be the sites for the origin of life on earth.[1,2] Since then, researchers' interested in studying the chemical origin of life have dramatically increased in aqueous solutions. It was found that amino acids can form dipeptide in the presence of the trimetaphosphate (P_3m) aqueous solution.[3] However, how do the nucleotides activate amino acids to produce the dipeptides? We focus on the relationship between the nucleoside and efficiency for amino acid peptide formation to dissect the origin of genetic code from modern ribosome system. Our previous study showed that the dipeptide yield was dependent on the type of nucleosides. In this paper, our concern is the synergistic effect of codon and anticodon (A/U, C/G) on the forming peptide of amino acid. The detailed experimental strategy is showed as Figure 1 a. To take the peptide formation of phenylalanine (Phe) as an example, the preliminary experimental results reveal that the synergistic effect of the A/U, anticodon/condon of Phe, could be more promoted the formation of Phe-Phe dipeptide than C/G (Figure 1 b, 1 c). The above results imply that there are some synergistic effects of nucleosides on dipeptide yields, which might give novel view to understand the genetic code origin.

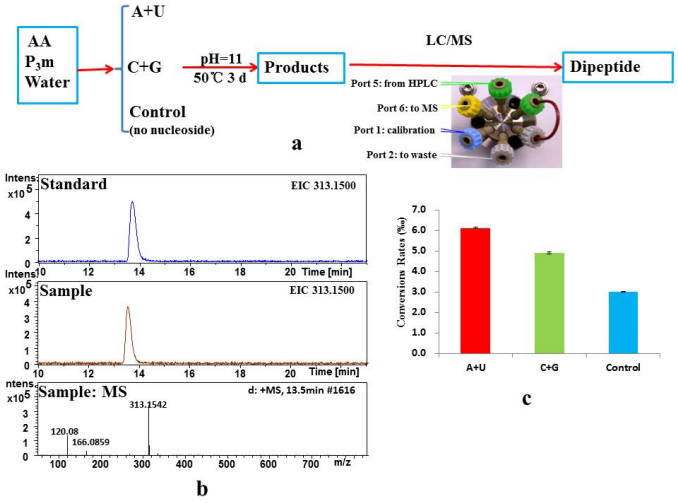

Figure 1 Reaction and analysis of Phe-Phe product

a: Synthesis of Phe-Phe; b: HPLC-ESI-MS/MS spectra of Phe-Phe product and Standard; c: Yields of the Phe-Phe dipeptide

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Acknowledgements

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July 16-21, 2017 at UC San Diego, CA, USA

Growth of proto-peptides by continuous feeding of monomers

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The formation of polypeptides on the early Earth is a long-standing problem in the field of prebiotic chemistry. Although it is generally accepted that amino acids were present on the prebiotic Earth [1,2], a plausible mechanism to form long chain polypeptides is still ellusive. Because of high activation energies and formation of side-products, direct peptide bond formation is slow unless elevated temperatures or chemical activating agents are used. Our previous work has described a simple system composed of hydroxy acids and amino acids that is capable of forming peptide bonds under mild conditions [3]. Hydroxy acids form metastable oligoesters in the oscillating (hot-dry/cool-wet) environment and transform into mixed copolymers via the ester-amide exchange reaction. Further analysis of kinetic and activation parameters showed that the ester-mediated pathway enables the amide bond formation by providing a route with lower activation energies [4].

We further interrogated the ability of the ester-mediated reaction, identifying a strategy that enables the formation long chain polymers with peptide backbones. This reaction behaves similarly to chain-growth living polymerization: new monomers add to one end of chains step-by-step without termination. Unreacted monomers were fed to the dry mixture every cycle by an automated "day-night" machine. The feeding composition was found to affect the oligomer distribution. Longer oligomers can be produced more efficiently when only amino acids are fed because of a smaller number of active oligomer chains. This work provides a comprehensive study of the ester-mediated reaction to synthesize amide bonds. This simple reaction is shown to be a robust pathway to synthesize long chain depsipeptides in mild conditions.

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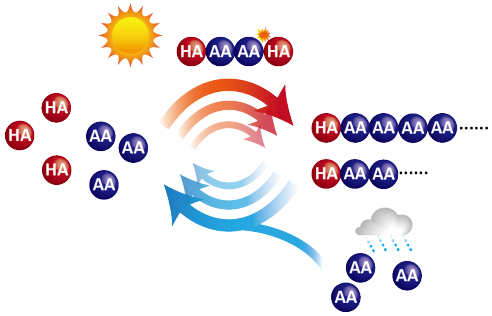

Figure 1 – Production of long chain depsipeptides by continuous feeding during the environmental cycling.

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Co-origin of Oligopeptide/Oligonucleotide/Membrane with an N-phosphoryl Amino Acid Model in Origin of Life

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Introduction: In recent years, a new viewpoint has been concerned in origin of life that is focused on forming high-yield products, contrast with giving thousands of compounds in low yields. In other words, selectivity and efficiency are focused instead of diversity and complexity[1]. Lacking of enzymes, **high-selectivity reactions may be more favorable for initial life in prebiotic chemistry**.

Phosphorus compounds are active in transport processes and information conservation; energy conversion and transfer, membrane structures and signal transmission. Meanwhile, more evidence indicates that phosphorylation may also play in a centre role in the origin of life[2]. Since Miller experiment revealed the high possibility of bioactive molecules converted from inorganic molecules, Different kinds of amino acids, nucleotides and membrane precursors have been considered to be possibly exist in prebiotic period[3]. Herein, we are determined to establish a new model for the co-origin theory[4], which phosphorylation manifests significantly indispensable in origin of life.

Polyphosphates were found to be approached in prebiotic period. In recent years, focused on trimetaphosphate (P_3m), our group has successfully synthesized various essential life molecules, including ATP, oligopeptides, and membrane precursors.(Figure 1A) This reaction system provides the diversity of phosphonic derivatives. On the other side, unsatisfactory selectivity seems deficiency for primal lives. With this in hand, we proposed an *N*-phosphoryl amino acid model for deeply studying the importance of phosphorylation in life process[5]. In this article, we demonstrated a green and efficient pathway for the synthsis of phosphatidylserine (PS)[6] and Ser-His, an original molecule evolutionary model of modern protease[7] (Figure 1B). Notably, histidine shows reputably activity in this peptide reaction competing against other amino acids. We owe to selfcatalysis of Ser-His[8], which might suggest the origin of protease.

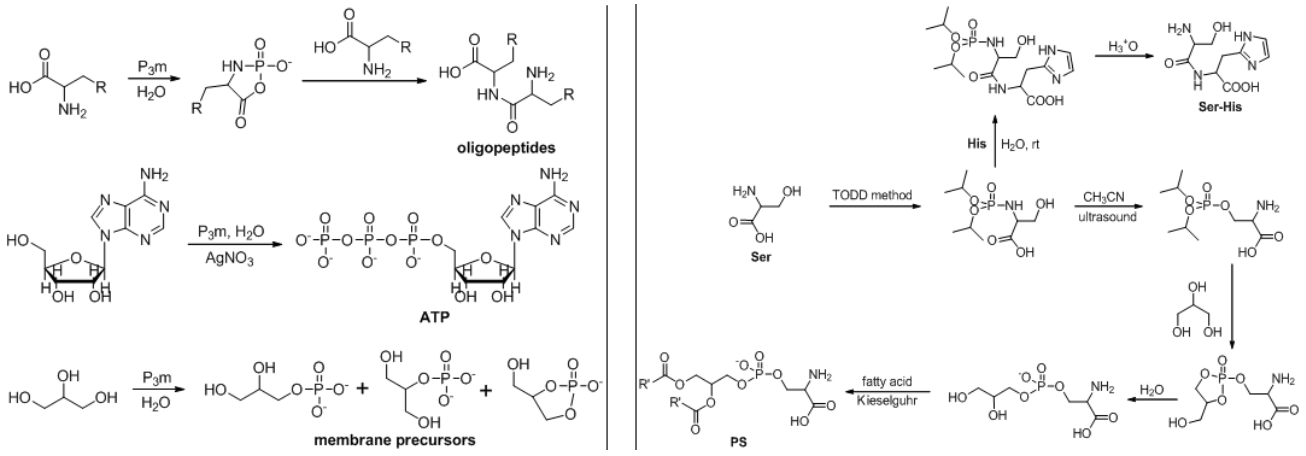

Figure 1 (A) Bioactive molecules treated by trimetaphosphate (B) *N*-DIPP-Ser-mediated formation of PS and Ser-His

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Information Analysis is used to Determine the Identity Elements of the Operational tRNA Code

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Introduction: The correct implementation of the genetic code involves a complex machinery of biological pathways. At the core of such a process lies the transfer RNA (tRNA), a key molecule responsible of the translation process. To sustain such convoluted process, the tRNA holds two genetic codes. The anticodon code designed to read the messenger RNA, and a second genetic code known as the operational code [1], which is commonly mapped [2] to the acceptor stem of the tRNA. This second genetic code directs the correct identification of each tRNA by its cognate aminoacyl-tRNA synthetase (aaRS) by stereochemical means. The problem of deciphering this recognition code and identifying the sites along the tRNA structure involved is known as "the identity problem". In this work, the information theory is used to analyze $\sim 53{,}000$ sequences of tRNA genes of the 20 amino acids to determine the specific sites of the tRNA structure participating in the positive recognition of their respective aaRSs. The variation of information $VI(X,Y)$, is a measure of information distance and it is given by: $VI(X,Y) = H(X) + H(Y) - 2I(X,Y)$, where $H(X)$ is the Shannon's entropy and $I(X,Y)$ is mutual information. A list of sets of sites is provided for each tRNA isoacceptor. According to this measure, the sites which are nearby to the anticodon, bridge the information of the anticodon to the rest of the structure, thereby these sites are the ones involved in the second genetic code. The list provides for each tRNA a set of sites that were modified with complete synchronicity among all samples, i.e., these sets comprise the identity elements for each tRNA associated to each amino acid. Previously undetected identity elements are reported.

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Assessing the Abundances of Sugar Molecules on Comet Nuclei

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Introduction: Recent detections of the biologically relevant compounds glycolaldehyde (GLA) and ethylene glycol (EG) on comets [e.g., 1,2] warrants investigations as to how abundant they are on the comet nuclei and how these molecules may survive impact onto a habitable planet or moon. The presence and availability of these molecules in hospitable pre-biotic environments may be important for understanding the origin of life as we know it.

Previous experiments have assessed the survivability and production of these sugar molecules under impact conditions [3]. The results, together with published values of observed production rates of water, GLA, and EG [e.g., 1] on a few Oort-Cloud comets (e.g., C/1995 O1 Hale-Bopp, C/2012 F6 Lemmon, C/2013 R1 Lovejoy 2013, and C/2014 Lovejoy 2014) have allowed us to estimate the amounts of GLA and EG that could have been delivered via cometary impact. Even with a high degree of uncertainty in comet diameters and volumes, we have determined that extremely large amounts of these molecules could have survived the impact of a single comet.

Compiled cometary data [4] have been used to estimate total amounts of delivered GLA and impact-produced EG that may have been available on habitable planets or moons, especially during the era of late heavy bombardment (~4.2 to ~3.7 billion years ago; 5,6,7) when life may have been developing on Earth [e.g., 8,9].

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The Model for Genetic Code Origin Study Based on the Dipeptide Yields Variation with the nucleosides

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Introduction: Genetic code origin is one of the most essential issues of origin of life. How the "primitive code" derived from the very beginning? The genetic code recognition system in modern ribosome is a very complicated system and it is not easy to touch the core of the problem.

Some previous reports have focused on potential importance of weak direct interactions between amino acids and triplet codon nucleotides[1,2]. In order to uncover the possible origin of the genetic code, the influence of nucleotide on peptide synthesis should also be considered. Therefore, we build up a simplified chemical model for the origin of genetic code studies. This system consists of phosphorous compounds, amino acids and nucleosides. From aqueous phase to organic phase, six representative amino acids (Phe, Trp, Tyr, Val, Leu and His) were tested in this chemical model. It was found that the "translation products" dipeptide yields for each of the five amino acids (Phe, Trp, Tyr, Val and Leu) showed some positive correlation with their 2nd position on their codon/anticodon nucleosides, respectively. For some amino acids, such as Val and Leu, the 1st position of the triplet code also provides some profound effect. That means the codon/anticodon nucleosides of the 2nd and 1st position both have the helpful effect on the translation products, but the 2nd position is more important.

The chemical model we raised here is the first model that can be used in experimental tests, and could be considered as the core of the genetic code translation mechanism. It may provide some new strategies to understand the origin of genetic code that confounded people for years.

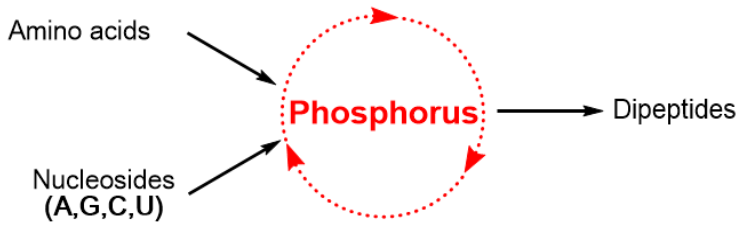

Figure 1. Chemical model for the origin of genetic code studies

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