



COST Action CA17120  
**CHEMOBRIONICS**  
Program & Abstracts

30/80 MEETING  
alkaline vents 30th  
Mike Russell's 80th

March 11-13, 2019  
Granada Science Park  
Spain



# Monday, March 11, 2019

8:00	Registration
8:50	Opening
9:00	<a href="#">Russell</a> ( <i>plenary lecture</i> ) - Prospecting for life and the unearthing of green rust
10:00	<a href="#">Ponce</a> - Synergies of technology developments in space exploration, climate change and emergence for life research
10:20	<a href="#">Nakamura</a> - Regulating reaction selectivity of electricity-driven prebiotic chemistry
10:40	Coffee + discussions + posters
11:10	<a href="#">Preiner</a> - The role of hydrogen activation in early metabolism
11:30	<a href="#">Milner-White</a> - Protein 3D structure and the origin of life
11:50	<a href="#">Muñoz-Santiburcio</a> - Nanoconfined water at inorganic pores: implications for prebiotic chemistry in hydrothermal vents
12:10	<a href="#">McGlynn</a> - Oxidative thioesterification
12:30	<a href="#">Xavier</a> - Autocatalytic networks in ancient bacterial and archaeal metabolism
12:50	<a href="#">Schusztler</a> - Macroscale precipitation kinetics: Towards complex precipitate structure design
13:10	<a href="#">Rongy</a> - How to make an $A + B \rightarrow C$ reaction oscillate through the coupling between Marangoni and buoyancy-driven flows
13:30 -15:30	Lunch ( <i>Vía Láctea restaurant</i> )
14:45	<b>Working group 4</b> discussion session
15:30	<a href="#">Sainz-Díaz</a> - Interactions of organics with confined mineral surfaces
15:50	<a href="#">Bartlett</a> - What are the necessary conditions for free energy conversion and learning?
16:10	<b>Management committee meeting (part 1)</b>
17:00	Coffee + discussions + posters
17:30- 18:40	<b>Management committee meeting (part 2)</b>

## Tuesday, March 12, 2019

- 9:00 [Nitschke](#) (keynote lecture) - Can the mineral fougurite mediate the step from strictly exergonic chemistry to a free energy converting precursor of bioenergetics?
- 9:30 [Lane](#) - The origins of growth and heredity in alkaline hydrothermal vents
- 9:50 [Trolard](#) - Contribution of soil science to knowledge on the green rust fougurite
- 10:10 [Chadwick](#) - Methanotrophy: looking backward

10:30 Coffee + discussions + posters

- 11:00 [Hochlaf](#) - Multi-scale investigations of the interaction of small molecules with surfaces
- 11:20 [Horvath](#) - Modeling of precipitation reactions
- 12:00 [Kirin](#) - Development of new catalysts and new materials using self-assembly of metallated oligoamides
- 12:00 [Sojo](#) - A few lessons learned trying to fix CO<sub>2</sub> in alkaline vent conditions
- 12:20 [Camprubí-Casas](#) - An origins simulator - Did vectorial electrochemistry power the emergence of life?
- 12:40 [Shock](#) - Evolution as energy minimization
- 13:00 [Cooper](#) - Development of a minimal photosystem for hydrogen production in inorganic chemical cells

13:20- Lunch

16:00 (*Vía Láctea restaurant*)

14:45 **Working group 1** followed by **working group 3** discussion sessions

- 16:00 [De Wit](#) - Flow control of reaction fronts in radial injection
- 16:20 [Speetjens](#) - Flow-controlled engineering of scalar transport in fluids
- 16:40 [Toth](#) - Flow-driven crystallization

17:00 Coffee + discussions + posters

- 17:30 [Roca-Sanjuán](#) - On the origin of the chemical structure of DNA nucleobases: Photochemical selection
- 17:50 [Wong](#) - Nitrogen oxides in early earth's atmosphere as electron acceptors for life's emergence

21:00 Mike's Birthday Party  
(*María de la O restaurant*)

## Wednesday, March 13

- 9:00 [Martin](#) (keynote lecture) - Alkali, carbon, native metal and a pathway
- 9:30 [Allen](#) - On the constant internal environment of nascent living cells: Redox homeostasis in the emergence of life
- 9:50 [Cardoso](#) - Fluid mechanics at the origin of life
- 10:10 [Puigmarti-Luis](#) - Chemistry in flow: Bioinspired conditions for chemistry and materials synthesis

10:30 Coffee + discussions + posters

- 11:00 [Cejkova](#) - Pattern forming droplet systems
- 11:20 [Denkov](#) - Self-shaping droplets: from spheres to platelets with flagella
- 11:40 [González](#) - A new mathematics at the origin of life, from numeration systems to the genetic code
- 12:00 [Jensen](#) - Soft-matter interactions enable mechanosensitive intercellular transport
- 12:20 [Jordan](#) - The first cell membranes at the origin of life in alkaline hydrothermal vents
- 12:40 [Szymczak](#) - The agate osmotic pump? The fingerprints of flow and deposition in agate structures
- 13:00 [Bristol](#) - From Carnot to Clausius-Boltzmann and back: rethinking the foundations of thermodynamics with applications to origin of life research

13:20- Lunch

15:30 (*Vía Láctea restaurant*)

14:45 **Working group 2** discussion session

- 15:30 [Menez](#) - New classes of abiotic organic compounds highlighted in the oceanic crust: implications for rock-powered life
- 15:50 [Biesheuvel](#) - Metal corrosion: a self-organizing precipitation process of economic relevance
- 16:20 [Birkedal](#) - Chemical gardens from the gel/liquid interface
- 16:40 [Szilagyi](#) - Atomic-scale description of Fe-S cluster nests in peptide maquettes

17:00 Coffee + discussions + posters

- 17:30 [Beckett](#) - Mineral nano-engines: The work they might do
- 17:50 [Cartwright](#) - Warm little ponds or warm little pores?

18:10- Wrap up session - round table discussion  
19:00

# POSTERS

**Altair** - Application of alkaline vent theory in deep natural radioactive environments scenarios

**Aytemiz** - Clathrate hydrates: Theory and experiment

**Balci** - Solvation of strong acid molecules (HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>) on/in water clusters

**Baymann** - Electron bifurcation locally augments redox-disequilibria

**Duval** - Fougérite, the key mineral to understand bioenergetics mechanisms at the origin of life?

**Escamilla-Roa** - Abiotic production of Martian carbonates from self-assembly tubular structures

**Griesshaber** - Formation of biopolymer membranes in biological hard tissues and biomimetic analogues

**Grubisic** - Computational study of bio- and nano-systems: chemical, spectroscopic, and conformational aspects

**Gutiérrez Ariza** - Fluid dynamics in chemical garden formation

**Ioannou** - Spontaneous formation of iron-sulphur clusters under alkaline conditions

**Koyun** - Self-organisation of carbonaceous core-shell particles in bitumen

**Kuhlenbeck** - A well-ordered thin film model system for iron sulfide catalysis

**Mikac** - Different morphologies of nanostructured silicon for various applications

**Neubeck** - Sulfur chemistry paved the way for evolution of antioxidants

**Osmanbegovic & Louhi-Kultanen** - Influence of various solutes on formation of ice layer

**Pérez del Valle** - Compressibility of 2m1 muscovite-phlogopite solid-solution

**Pisapia** - Catalytic role of serpentinite paragenesis for the in situ abiotic synthesis of amino acids: a way towards metalloenzymes?

**Rammu** - Stability and morphology of mixed amphiphile vesicles under hydrothermal vent conditions

**Rocha** - Planar chemical gardens and submarine methane hydrate deposits: spider-leg growth

**Sánchez** - Coarse-grained computer modeling of nanomaterials: approaches to bridge the scales

**Schmahl** - Patterns of biocrystal packing in modern carbonate biological hard tissues

**Seifried** - Nucleation and morphology of ices

**Spanoudaki** - Growth of chemical gardens within the co-flow of two reactants in a microfluidic device

# ABSTRACTS

## On the constant internal environment of nascent living cells. Redox homeostasis in the emergence of life

**John Allen**

*University College London, UK*

Two fundamental properties of life as we recognize it are homeostasis and vectorial redox chemistry. It is suggested that redox homeostasis originated in the iron sulphide vesicles that were proposed by Michael J. Russell to have formed the geochemical incubators of the first living cells. Possible mechanisms securing redox homeostasis are discussed. The transition to free-living cells depended on the proto-cells' ability to maintain a proton motive force for energy conversion, providing for active transport.

The persistence of regulatory circuits maintaining intracellular redox state is outlined. The origin of oxygenic photosynthesis may have resulted from failure of a redox switch that selected between different anoxygenic photochemical reaction centres. Any exoplanet with detectable free oxygen is likely to have made these transitions.

## Application of alkaline vent theory in deep natural radioactive environments scenarios

**Thiago Altair**

*University of São Paulo, Brazil*

In natural radioactive environments, water radiolysis can produce a chemical diversity besides the products of biological importance, such as  $H_2$ . Although the proposal of radioactive decay as an alternative source of energy for living systems has existed for more than thirty years, this hypothesis gained strength after the recent discovery of a peculiar ecosystem in a gold mine in South Africa, whose existence is dependent on chemical species produced by water radiolysis. In this work, we calculate the chemical disequilibrium generated locally by water radiolysis and analyse the possible contribution of this disequilibrium for the emergence of life, having as reference the alkaline hydrothermal vent (AHV) theory. Overall, we described the possible free-energy conversion mechanism that could be a requisite for emergence of life in a widely present scenario in wet planets.

## Solvation of Strong Acid Molecules ( $HNO_3$ , $HCl$ , $H_2SO_4$ ) on/in water clusters

**F. Mine Balcı<sup>1)</sup> and Nevin Uras-Aytemiz<sup>2)</sup>**

*1) Süleyman Demirel University, Faculty of Arts and Sciences Department of Chemistry, Isparta, Turkey, 2) Bandırma Onyedi Eylül University, Faculty of Engineering and Natural Sciences Department of Engineering Basic Sciences, Bandırma-Balıkesir Turkey*

$HNO_3$ ,  $HCl$  and  $H_2SO_4$  play an important role in atmospheric processes. These molecules take place in heterogeneous reactions, which cause ozone depletion in the atmosphere. Most of these reactions have occurred at the Polar Stratospheric Clouds (PSC), which is on the Stratosphere layer of the atmosphere [1,2].

The topic is about interaction of  $HNO_3$ ,  $HCl$  and  $H_2SO_4$  molecules on/in hydrogen-bonded water clusters. Furthermore, the interactions of more than two strong acid molecules ( $H_2SO_4/HNO_3$  or

HNO<sub>3</sub>/HCl) on water molecules have been considered [3-5]. The main tool for this study is Gaussian 09 package program[6]. The non-covalent interactions (NCI) [7] and atoms in molecules (AIM) [8] theories were applied to the clusters in order to get additional insight of the nature of the interactions. The results will be discussed in terms of structures, energetic, topologic and spectroscopic perspectives.

[1] Molina, M. J.; Tso, T.-L.; Molina, L. T.; Wang, F. C.-Y. *Science* 238, 1253, 1987.

[2] Lowe, D. and MacKenzie, A.R. *JASTP*, 70 (1), 13–40, 2008.

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[4] Balci, F. M. and Uras-Aytemiz, N. *J. Phys. Chem. A*, 115, 5943-5954, 2011.

[5] Balci, F. M. and Uras-Aytemiz, N. *J. Mol. Graph. Model.* 80, 272–281, 2018.

[6] Gaussian 09, Revision E.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2016.

[7] Contreras-García, J.; Johnson, E.R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D.N.; Yang, W. NCIPLLOT: a program for plotting non-covalent interaction regions, *J. Chem. Theory Comput.* 7, 625–632, 2011.

[8] Todd A. Keith, AIMAll (Version 13.02.26), TK Gristmill Software, Overland Park KS, USA, 2012 (aim.tkgristmill.com).

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## What are the necessary conditions for free energy conversion and learning?

**Stuart Bartlett**

*California Institute of Technology/University of Southampton, USA*

As well as dissipating environmental free energy gradients, a fundamental distinguishing feature of life is the myriad mechanisms by which it incorporates, stores, processes, and exploits information. In this talk I will outline arguments for seeking information processing in early life and how hydrothermal vents may provide relevant niches for primordial learning.

## Electron bifurcation locally augments redox-disequilibrium

**Frauke Baymann**

*CNRS, France*

Electron bifurcation is known to play an important role in bioenergetics since the work of Peter Mitchell in the 1970s. The enzyme he described – the Rieske/cytb complex (alias Complex III in mitochondria, bc1 complex in purple bacteria and b6f complex in cyanobacteria, plants and algae) has ever since been characterized in detail to understand the molecular bases of quinone-based electron bifurcation.

In recent years flavine-based electron bifurcation has been discovered. In contrast to quinone-based electron bi-furcation which is known for a single enzyme family only, flavine-based electron bifurcation is now recognized as an obligate or a facultative step of the reaction mechanism of many different enzymes.

We will present the thermodynamics of electron bifurcation and suggest that such reactions – based on transition metal ions that undergo two-electron conversions such as Mo or W – occurred early on and may have played a role in the emergence of life.

## Mineral Nano-engines: The work they might do

**Patrick Beckett**

*UC Davis, USA*

Some proponents of the Alkaline Vent Theory for life's emergence maintain that specific chemical and general thermodynamic considerations are what distinguish alkaline vents as the most likely place for life to have emerged on Earth. As Nick Lane has written, "life transcends chemistry". Russell et al. maintain that life's specialized transduction mechanisms (i.e. molecular motors) together with the appropriate environmental energy resources are what enable this transcendence. If one simultaneously takes the view that the nano-scale structures found in cells are a necessary, defining feature of life and that appropriate geochemical environments these structures can couple to must be available for life to emerge, then classical thermodynamics cannot adequately describe such systems.

Another thermodynamic framework consistent with, but other than, classical thermodynamics must be used. In this talk I will provide a brief overview of such a framework, called stochastic thermodynamics. Stochastic thermodynamics has been developed in recent decades to translate concepts from classical thermodynamics, such as work and entropy, to individual molecular systems driven arbitrarily far from equilibrium. I will introduce the Jarzynski Equality and Crook's Fluctuation Theorem to demonstrate how the arrow of time and dissipation relate to the work required to drive nano-scale systems between different free energy states. The relationship between stochastic thermodynamics and information processes at the nano-scale will also be introduced, briefly. Equipped with this general framework, I will then provide examples of how stochastic thermodynamics might be applied to minerals that are stochastically driven by the environment in the context of alkaline vents. I will argue that this framework provides a natural, intuitive entry point for the emergence of information in mineral systems, and that minimum energetic bounds for information processes one might hypothesize for such mineral systems can be established.

## Metal corrosion: a self-organizing precipitation process of economic relevance

**Maarten Biesheuvel**

*Wetsus, European Centre of Excellence for Sustainable Water Technology, The Netherlands*

We briefly describe our project to use ion transport theory to model the process of metal corrosion. Unlike in a traditional electrochemical cell, here the two electrodes (anode and cathode) do not even exist at time zero, but develop during the process, move and transform. We briefly outline our mathematical approach, and future plans. We also discuss the topic of microbial corrosion.

## Chemical Gardens from the gel/liquid interface

**Henrik Birkedal**

*Aarhus University, Denmark*

Chemical gardens are obtained from a gel/liquid interface inspired by bone biomineralization. A gelatin gel loaded with metal ions ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ) was overlaid by a high pH solution of phosphate or carbonate. Centimeter-long tubular outgrowths were obtained. The tubular crystallography and the impact of the metal ions on gel properties will be discussed.

## From Carnot to Clausius-Boltzmann and Back: Rethinking the Foundations of Thermodynamics with Applications to Origin of Life Research

**Terry Bristol**

*Portland State University, Institute for Science, Engineering and Public Policy, USA*

Atkins: "There were two paths to thermodynamics". Carnot focused on the nature of engines. Boltzmann on atoms. "Thermodynamics still has both aspects." Carnot's engineering thermodynamics is the more general framework subsuming Boltzmann's formulations as limited, idealizing special cases. For Carnot, work, the 'effect' of the engine, is the net product of a cyclic process.

## An origins simulator - Did vectorial electrochemistry power the emergence of life?

**Eloi Camprubí-Casas**

*Origins Center, Utrecht University, The Netherlands, [e.camprubicasas@uu.nl](mailto:e.camprubicasas@uu.nl)*

Hadean alkaline hydrothermal vents have been proposed as electrochemical reactors driving an autotrophic origin of life (Russell et al., 1988, Whicher et al., 2018). Theoretical thermodynamics show that the abiotic synthesis of biomass from H<sub>2</sub> and CO<sub>2</sub> is indeed favoured under these conditions (Amend & McCollom, 2009). But CO<sub>2</sub> reduction is kinetically extremely tardy, casting doubt on the feasibility of this mechanism. Given that almost all extant life grows by hydrogenating CO<sub>2</sub>, this question is of central importance to the autotrophic origins hypothesis. Within the newly created Origins Center I am examining the possibility that geochemical proton gradients across inorganic Fe(Ni)S barriers, analogous to putatively ancient autotrophic cells, could have driven CO<sub>2</sub> reduction at the origin of life in alkaline hydrothermal vents.

Under these conditions the non-enzymatic synthesis of organics has been successfully reported (Herschy et al., 2014) but has proven difficult to reproduce systematically, most probably due to the high stochasticity inherent to large-scale simulators. A microfluidics approach is optimal at increasing the control exerted over the experimental variables (pH gradient, temperature, mineral crystallinity, etc.). My aim is to explore whether abiotic reactions analogous to those of the acetyl CoA pathway and reverse incomplete Krebs cycle could be catalyzed by Fe(Ni)S minerals tapping into a natural pH gradient. These theoretically predicted pathways (Camprubi et al., 2017) could proceed via Fischer-Tropsch-type hydrogenations and Koch-type carbonylations, which usually occur at much harsher conditions, thanks to the pH-mediated reduction potential modulation.

## Fluid mechanics at the origin of life

**Silvana Cardoso**

*University of Cambridge, UK*

We study chemical-garden growth in a Hele-Shaw cell as an analogue of submarine hydrothermal vents. The interaction of fluid flow and chemical precipitation is analysed and modelled. We show how semi-permeable membranes formed in chemical gardens are efficient nano-scale pumps that promote flow and mixing of dissolved chemicals. We explore the implications of our findings for the origin of life on the seabed.

## Warm little ponds or warm little pores?

**Julyan Cartwright**

*CSIC and Universidad de Granada, Spain*

Where did life begin? Darwin famously speculated in private about a “warm little pond”. Indeed that is one theory today. But were the oceans, rather than ponds, the cradle of life? Of course, Darwin could know nothing of the hydrothermal vents on the ocean floors, discovered only in the late 1970s. The existence of another class of vent emitting warm, rather than hot, mineral-laden water at alkaline, rather than acid, pH was predicted thirty years ago by my friend Mike Russell as the possible birthplace of life. A decade later such vents were found, beginning with the Lost City Hydrothermal Field discovered in 2000. Recent work of my colleague Silvana Cardoso and her student Yang Ding demonstrates that hydrothermal vents can function better than warm little ponds in terms of providing an environment in which complex chemistry can occur via cycles of condensation reactions. In this view, life began from intrinsic cycles of concentration in chemical nanoreactors in the pores within membranes of alkaline hydrothermal vents; geological instances of chemical gardens. We suggest that life incubated at Russell’s vents within these warm little pores.

## Pattern forming droplet systems

**Jitka Cejkova**

*University of Chemistry and Technology Prague, Czech Republic*

We focus on the organic system based on a decanol droplet placed in a solution of alkaline decanoate. In this system in both presence and absence of salt intriguing pattern formation is observed. We will discuss the similarities between purely inorganic chemical gardens and the structures in our system.

## Methanotrophy: looking backward

**Grayson Chadwick**

*California Institute of Technology, USA*

The reduction of CO<sub>2</sub> through the Wood-Ljungdahl pathway supports autotrophic growth in both methanogenic archaea and acetogenic bacteria and is thought to be one of the most ancient metabolic pathways. The central C1 carbon handling metabolism is shared between all known CO<sub>2</sub> reducing methanogens with little variation. In the last two decades methanotrophic archaea have been discovered and described from marine and freshwater environments, where a complete reversal of the methanogenic pathway appears to be possible, oxidizing methane to CO<sub>2</sub> and reducing an ever increasing list of electron acceptors. When the methane producing and methane consuming versions of this metabolism appeared on earth is important for our understanding the global carbon cycle throughout the history of life on earth, as well as our understanding for the emergence of life as both processes have been hypothesized to be the ancestral metabolism. Recent genomic sequencing efforts of methanotrophic and methanogenic archaea from many different environments has expanded our understanding of the intertwined evolutionary history of methanogenesis and methanotrophy and helps shed light on how one can evolve into the other. Here I summarize recent developments in our rapidly changing understanding of methane metabolism in the extant archaea, and what, if anything, can be said about these metabolisms looking backwards through time.

## Development of a Minimal Photosystem for Hydrogen Production in Inorganic Chemical Cells

**Geoff Cooper**

*School of Chemistry, University of Glasgow, UK*

Inorganic chemical cells (iCHELLs) are compartment structures consisting of polyoxometalates (POMs) and cations, offering structured and confined reaction spaces bounded by membranes. We have constructed a system capable of efficient anisotropic and hierarchical photo-induced electron transfer across the iCHELL membrane. Mimicking photosynthesis, our system uses proton gradients between the compartment and the bulk to drive efficient conversion of light into chemical energy, producing hydrogen upon irradiation. This illustrates the power of the iCHELL approach for catalysis, where the structure, compartmentalisation and variation in possible components could be utilised to approach a wide range of reactions.

## Flow control of reaction fronts in radial injection

**Anne De Wit**

*Université libre de Bruxelles, Belgium*

The dynamics of  $A + B \rightarrow C$  fronts is analyzed theoretically and experimentally in the presence of passive advection when A is injected radially into B at a constant inlet flow rate  $Q$ . We show that the radial injection allows to control the properties of the front like the position of the reaction zone and the amount of product produced per unit of time.

## Fougerite, the key mineral to understand bioenergetics mechanisms at the origin of life?

**Simon Duval**

*CNRS, France*

Research on biological energy conversion has shown that the catalytic centres of the implicated enzymes are clusters of transition metals which strongly resemble certain minerals prompting the hypothesis that the emergence of life on our planet may have been initiated by mineral-borne metals. Our project proposes a first experimental test of this hypothesis via comparison of the catalytic properties of di-iron hydrolases and in particular soluble methane monooxygenase to those of the structurally affine mineral fougerite. Our approach represents a radical departure from the traditional research on prebiotic synthesis of organic molecules towards the investigation of a thermodynamically more sensible emergence of life from metabolic reaction networks harboured and performed by minerals.

## Abiotic production of Martian carbonates from self-assembly tubular structures

**Elizabeth Escamilla-Roa,<sup>1</sup> María-Paz Zorzano,<sup>2,1</sup> and Javier Martin-Torres<sup>1,3</sup>**

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Carbonates on Mars have been detected in several Martian meteorites, by remote sensing from orbiting spacecraft, as well as in-situ by different rovers such as Spirit, which identified

outcrops with 16-30 wt. % carbonate minerals in Gusev Crater [1]. On the other hand, the Mariner 6 and 7 missions also detected hydrated minerals as Mg carbonate (hydromagnesite)  $Mg_5(CO_3)_4(OH)_2 \cdot 4OH$ . The presence of carbonates on Mars is still not understood [2]. There are studies that indicate that carbonates like [siderite](#) ( $FeCO_3$ ) can only precipitate at [pH](#)'s greater than 5 [3]. The presence of carbonates on Mars may also be interesting as a biomarker for microorganisms activity [4]. Silicates are common minerals particularly in soils and sediments on Earth and Mars. Natural silicates can be formed by self-organizing reaction-precipitation processes [5], through which, tubular structures may appear. These forms have great importance in the formation of micrometer-scale fibers, biomineralized shells, mineral deposits in caverns and hydrothermal vents on the ocean floor [6]. The tubular structures can also be considered as plausible marker for the ancient presence of water on Mars or other environments [7]. Additionally, the presence of sulfates on Mars has also been confirmed [8]. The aim of this study is to simulate the formation of self-assembling tubular carbonate structures through reaction-precipitation processes of silicate in alkaline conditions with several plausible Martian  $CaCl_2$  and sulfates such as, basanite ( $CaSO_4 \cdot 1/2H_2O$ ), kieserite ( $MgSO_4 \cdot H_2O$ ) and jarosite ( $KFe^{+3}(SO_4)_2(OH)_6$ , under the presence of  $CO_2$  (about 400 ppm under ambient Earth conditions). These experiments suggest that carbonate can appear from the abiotic precipitation of solutions that may have existed on Mars.

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## A new mathematics for the origin of life, from numerations systems to the genetic code

**Diego L. Gonzalez**

*CNR/IMM Bologna Section*

*University of Bologna, Department of Statistical Sciences*

**Simone Giannerini**

*University of Bologna, Department of Statistical Sciences*

**Greta Goracci**

*University of Bologna, Department of Statistical Sciences*

The genetic code is the most universal trait of life; as such, its peculiarities are a source of invaluable information for understanding the origin of life. One of the more puzzling of these peculiarities is represented by the degeneracy of the code. Amino acids are represented by more than one codon giving origin to an apparently bizarre degeneracy distribution.

Can we describe the degeneracy distribution from a mathematical point of view?

We introduce a new mathematical approach based on non-univocal representation systems of integer numbers; the model allows to describe exactly the degeneracy distributions of both the Nuclear and the Mitochondrial variants of the genetic code (see Gonzalez 2004, and Gonzalez et al 2016 for a review). The model uncovers new symmetry properties of the genetic code that have been used to find universal correlations in coding sequences of DNA (Gonzalez et al, 2006, 2008). Surprisingly, the model has also profound implications from the point of view of the origin and evolution of the genetic code (Gonzalez et al, 2009, 2019). In particular, we found a putative ancestor of the LUCA code (Last Universal Common Ancestor) that possesses the same degeneracy distribution of the extant Vertebrate Mitochondrial genetic code. This pre-early code is based upon a special set of 64 four-base codons, i.e., tesseræ (from the greek {tessera} = four), and a set of ancient symmetric adaptors with anti-codons of the same length. Within the same framework it is possible to explain in detail all the evolutionary transitions implied by our theory, mainly the transition to extant codes of three-base codons without incurring into the Crick informational catastrophe.

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## Computational study of bio- and nano-systems: chemical, spectroscopic, and conformational aspects

**Sonja Grubisic**

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The popular AMBER-based force-field (FF) has been developed for the simulations of the  $\alpha$ ,  $\alpha$  dialkylated peptides with cyclic and linear side chains. Manuscripts summarizing these results have been published [1-3]. New atom types have been included, and relevant parameters have been fitted based on geometries, vibrational frequencies and potential energy surfaces computed at the DFT level, both in vacuo and in different solvents. Particular interest is devoted to the spin labeled peptides which contain other  $\alpha$ -tetra-substituted non-natural amino acids such as paramagnetic amino acid 2,2,6,6-tetramethyl-N-oxy-4-amino-4-carboxylic acid, TOAC, used as spin label in biologically important protein studies. The residue is stable under ordinary conditions and can provide access to useful conformational information

through well-established magneto-structural relationships. The modified force field has been employed in the context of an integrated approach, that combines enhanced-sampling molecular dynamics (MD) and quantum computations with experimental measurements, for the investigation of environmental and nanosecond time scale motions on the spectroscopic data (EPR, NMR) of nitroxide spin probes [4]. MD plays a fundamental role in characterizing protein disordered states that are emerging as crucial actors in many biological processes. The parameterization is not limited to only the NO moiety; rather, the aim is to provide at the force-field level an accurate description of the whole structure of the nitroxide probes (TOAC, MTSSL-methane thiosulfonate), their solvent interactions, and possibly covalent bonds between nitroxide probes and diamagnetic species, which are relevant to the situation of site-directed spin labeling (SDSL) methods. Molecular dynamics simulations based on a newly developed amber force field for  $\alpha$ -aminoisobutyric acid (Aib) have been also used to identify the arrangement of two enantiomers of Aib-containing peptides into stereocomplex molecular structure.

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## Fluid dynamics in chemical garden formation

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Chemical gardens are an example of self-organizing systems formed in out-of-equilibrium conditions. When soluble metal salts are added to aqueous solution containing anions complex biomimetic structures are formed. These structures, despite their chemical diversity, have one common feature: the spontaneous formation of a semipermeable membrane. This membrane shows a selective transport of ions and molecules producing a concentration gradient providing energy for possible prebiotic reactions. These structures offer confined spaces where the interaction with organic molecules can be available.

Similar systems can be found in nature, such as, at the hydrothermal vents on the ocean floor that can be very interesting because of their possible role in the origin of life. These structures, although larger, and more complex than in the laboratory chemical gardens, exhibit mechanisms of formation that can be similar.

Hence, the study of chemical garden can be interesting, and more specifically the hydrodynamics that define their shapes by acting as a guide for the precipitation reaction. In this preliminary work we show some first results of the visualization of this fluid dynamics via Schlieren optics, a method proven especially useful to study non-homogeneous media in a non-intrusive way.

# Multi-scale investigations of the interaction of small molecules with surfaces

**Majdi Hochlaf**

*U. Paris-Est, Lab. Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, France*

I will present first principles investigations of the spectroscopy and dynamics of small and medium-sized molecules interacting with macromolecular systems. These systems can be either a cavity of a crystalline or amorphous porous material, or a gas-liquid model interface. This represents a groundbreaking topic in atmospheric chemistry and heterogeneous catalysis, with important environmental and industrial applications such as gas sequestration and separation. The complexes between small and macro molecular species still represent, however, complicated molecular systems since their interactions, at the microscopic level, are not yet fully understood. In addition, some of the processes they are involved in are not known in sufficient details. Recent experimental studies showed that electronic and nuclear motions within these entities may lead to complex features. Our work helped to interpret these phenomena and to propose a predictive model. Hence, we will discuss the effects occurring when a small molecule is approaching the cavity of a porous material or a gas-liquid interface. Specifically, we will show the importance of considering the quantum nature of the atomic nuclei together with the possible cross-talk between nuclear and electronic degrees of freedom such as those taking place between the inter and intra low frequency modes and the intermonomer potential. We all also show that the outputs of these computations are of outstanding importance for modeling and engineering applications of confinements and solvation. For illustration diverse examples will be presented [1-10].

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## Modeling of precipitate reactions

**Dezső Horváth, Ádám Kaló, Gábor Pótári, Ágota Tóth**

*University of Szeged, Hungary*

Two scenarios are addressed in flow-driven precipitation processes. A precipitation reaction can be driven by a gravity current that spreads on the bottom as a denser fluid is injected into an initially stagnant liquid. Supersaturation and nucleation are restricted to location where the two liquids come into contact, hence the flow pattern governs the spatial distribution of the final product. We quantitatively characterize the flow associated with the gravity current and distinguish three zones where the coupling of transport processes with reaction can take place depending on the time scales. A scaling law associated with the region of Rayleigh–Taylor instability behind the tip of the gravity current is also identified. The spatial distribution and growth of precipitate particles are also modeled in a microfluidic device where good agreements with experimental observations are found.

## Spontaneous formation of iron-sulphur clusters under alkaline conditions

**Ioannis Ioannou**

*University College London, Uk*

Iron–sulphur clusters are one of the most ancient and ubiquitous components of life. These modular clusters facilitate electron transfer via redox reactions, and as such they are integral parts of the respiratory and photosynthetic electron transfer chains within all living organisms. Moreover, they are present in numerous redox enzymes involved in carbon, oxygen and hydrogen metabolism, such as hydrogenases and ferredoxins that are believed to be amongst the earliest proteins formed during the origin of life. Thus, this dependence of life on iron-sulphur clusters likely stems from the ancient chemistry from which cellular life emerged. Existing methods for the formation of iron-sulphur clusters include the use of excess amounts of organic ligands as well as strictly controlled reaction conditions, and it is unclear whether such synthesis mechanisms could have occurred in prebiotic earth. Other theories place the formation of iron-sulphur clusters in environments that could be proven prohibitive for life. On the contrary, alkaline hydrothermal vents since their discovery have been proposed as a friendly environment for the birthplace of life. It is believed that they could have provided not only the necessary elements for life to emerge, but also the appropriate conditions. In our work, we investigate the possibility of the formation of iron-sulphur clusters under anoxic and alkaline conditions in the presence of simple organic ligands. Our first results indicate that the addition of small amounts of ferric chloride ( $\text{FeCl}_3$ ) and sodium sulphide ( $\text{Na}_2\text{S}$ ) in an anoxic, alkaline solution similar to the conditions of deep sea alkaline hydrothermal vents containing low mM concentrations of organic ligands, leads to the direct formation of iron-sulphur clusters.

## Soft-matter interactions enable mechanosensitive intercellular transport

**Kaare H. Jensen**

*Technical University of Denmark, Denmark*

Intercellular channels strongly impact essential processes from morphogenesis to disease resilience in plants and fungi, yet it is unknown if transport is actively regulated. Here we show that elastic deformations of cell-cell pores can enable intricate control of intercellular transport processes.

## The first cell membranes at the origin of life in alkaline hydrothermal vents

**Sean Jordan**

*University College London, UK*

Vesicles formed from single chain amphiphiles (SCAs) such as fatty acids could have played an important role in the origin of life on Earth. These bilayer membranes not only form compartments that concentrate organics, but could hypothetically drive growth through vectorial chemistry in geological ion gradients. Incorporation of FeS minerals into these membranes could have allowed these geological gradients to be harnessed and utilised to catalyse organic chemical reactions. One major criticism of the deep sea alkaline hydrothermal vent hypothesis for the origin of life is that the chemical environment would not allow vesicle formation. It has been argued that the high temperatures, extremes of pH, high salinity, and presence of divalent cations would completely disrupt their development. But these arguments are based on laboratory investigations involving simple models of one, two, or three SCAs, even though Fischer-Tropsch Type (FTT) synthesis under hydrothermal conditions has produced a wide range of fatty acids and alcohols including an abundance of compounds with chain lengths of C10-C15. Here we show that mixtures of six to twelve fatty acids and alcohols can form vesicles in aqueous solutions ranging from pH 7 to 12. Similarly, these solutions will produce vesicles at alkaline pH in the presence of modern seawater concentrations of NaCl, Mg<sup>2+</sup>, and Ca<sup>2+</sup>. Addition of two simple isoprenoid molecules further improves their stability. These vesicles form most readily at temperatures of ~70°C, and require strongly alkaline conditions to self-assemble. We have also investigated the formation of simple FeS clusters coordinated by a single amino acid, cysteine. These mixtures form 4Fe4S clusters similar to those found in the active centres of many enzymes in modern living organisms and may represent their abiotic precursors. Incorporation of these clusters into the simple SCA membranes may bring us one step closer to understanding how proton gradients in alkaline hydrothermal vent systems could have been harnessed at the origin of life.

## Self-organisation of Carbonaceous Core-shell Particles in Bitumen

**Ayse Koyun, Hinrich Grothe**

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Exploring the bitumen character on a molecular level and investigating its ageing behaviour is vital and necessary, as it shapes its macroscopic characteristics. Therefore, additional clues to predict its long-time performance on the streets could be gained. A comparison between laboratory aged bitumen samples with different ageing states gives clues whether and how the ageing influences the core-shell particles, which are situated on the bitumen surface.

Since ageing, which is mainly caused by sunlight in the atmosphere (photo oxidation of bitumen with reactive oxygen species (ROS)), is taking place on the first nanolayers of bitumen, the dynamics of the surface have been studied, which includes the formation and reformation of the core-shell particles on the surface. The changes with aging were observed with Atomic Force Microscopy (AFM), which is capable to picture the topography at a sub-micrometre level and Fluorescence Microscopy, which allows tracking respective molecular changes. It was found, that the size and amount of core-shell particles on the surface is not only determined by the ageing state, but also depends on the cooling rate of the specimen, which has been studied here in more detail.

This study presents the visualization of the bitumen surface at various ageing states, provides a deeper insight on the core-shell particles within the microstructure (asphaltene micelles), and will allow clues concerning the mechanical properties and the aging behaviour of bitumen at a macroscopic level.

## A well-ordered thin film model system for iron sulfide catalysis

**Helmut Kuhlenbeck**

Fritz Haber Institute, Germany

A thin well-ordered iron sulfide layer was grown on Au(111) to be used as a catalytic model system for CO<sub>2</sub> activation and other reactions. The film has a metal-deficient NiAs structure with a reconstructed sulfur-terminated surface. As-grown layers and reduced layers are inactive with respect to CO<sub>2</sub> activation, but reduced layers can be activated by gold. Details will be presented on the poster.

## The origins of growth and heredity in alkaline hydrothermal vents

**Nick Lane**

University College London, UK

Alkaline hydrothermal vents could have fostered the origin of biochemistry under anoxic Hadean conditions<sup>1</sup>. Computational modelling indicates that geologically sustained proton gradients in alkaline hydrothermal vents could drive carbon and energy metabolism in early cells, so long as their membranes were leaky to protons, enabling the passive clearance of protons by hydrothermal flux<sup>2</sup>. Bilayers composed of single-chain amphiphiles (SCA) such as fatty acids meet these requirements<sup>3</sup>. In principle, proton flux across SCA membranes could facilitate CO<sub>2</sub> reduction by H<sub>2</sub> using Fe(Ni)S catalysts in an analogous fashion to the Ech (Energy-converting hydrogenase) of some methanogens<sup>4</sup>, as the mid-point reduction potentials are pH sensitive<sup>3,5</sup>. Microfluidic work shows that steep pH gradients across Fe(Ni)S barriers can be formed by laminar flow, but evidence for CO<sub>2</sub> reduction by H<sub>2</sub> is equivocal. If some organics were formed this way, thermodynamics indicates that the main products ought to be amino acids and fatty acids<sup>6</sup>. Modelling predicts that positive feedbacks between amino acids, FeS minerals and simple SCA membranes could drive protocell growth through a form of membrane heredity<sup>7</sup>. Experimental testing of these predictions shows that vesicles formed from SCAs are robust under oceanic alkaline hydrothermal conditions<sup>8</sup>. Several types of FeS cluster can be produced under these conditions by chelation with single amino acids, notably cysteine<sup>9</sup>. Ongoing work is addressing whether such clusters can associate with the membrane and reduce CO<sub>2</sub> through vectorial chemistry.

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## Prebiotic catalysis on metal sulfides for the origin of life

**Yamei Li**

*Earth-Life Science Institute, Tokyo Institute of Technology, Japan*

Transition metal sulfides have been proposed as key players in prebiotic organic synthesis. Here we will introduce our work on nitrogen conversion catalyzed by an enzyme mimetic sulfide catalyst. Further, we will propose a method to rationally screen prebiotic sulfide catalyst from the mineralogy database based on advanced theories on electrocatalysis.

## Alkali, carbon, native metal and a pathway

**Bill Martin**

*University of Düsseldorf, Germany*

In 1999 I saw origins in images of RNA. Then I met Mike. Today I see origins as rock–water–carbon interactions during serpentinization in hydrothermal vents, reactions that generate hydrogen, native metals and reduced carbon. In 2019, my PhD students can reenact the core exergonic reactions of ancestral microbial physiology using H<sub>2</sub>, native metals, CO<sub>2</sub> and water in my lab. Progress. Thanks Mike.

## Oxidative thioesterification

**Shawn McGlynn**

*Earth Life Science Institute, Japan*

I will discuss oxidative and reductive thioesterification in the context of early metabolism.

## New classes of abiotic organic compounds highlighted in the oceanic crust: implications for rock-powered life

**Benedicte Menez**

*Institut de Physique du Globe de Paris, France*

Recent evidences for the presence of diverse abiotic organic compounds in serpentinites are presented. It includes amino acids (Ménez et al. ( Nature 564, 59-63) and condensed carbonaceous matter (Sforna et al. (2018) Nat Commun, 9, 5049) shown to form during the hydrothermal alteration of the oceanic crust. Consequences for microbial life strategies in the deep biosphere are addressed.

## Different morphologies of nanostructured silicon for various applications

**L. Mikac, H. Gebavi, M. Raić, N. Baran, M. Gotić, M. Ivanda**

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Materials research has generated countless advances in areas such as electronics, information technologies, transportation, biomedicine, energy storage as well as nanotechnologies. Our research unit New Functional Materials (NFM) is devoted to the synthesis, characterization, simulation and development of new functional materials for support and implementation of

high-tech industries. A combination of the chemical and physical approaches is aimed to accelerate the discoveries of new functional materials through innovations in synthesis, measurements, modelling and applications.

The sensor based on nanostructured Si is related to the low-level concentration detection of specific molecules by surface-enhanced Raman scattering (SERS) [1-3]. Development of such sensor is motivated by the needs of food industry which is searching for simple and reliable method of detection of hazardous species in food [4]. The main advantage of the SERS technique is rapid analysis, minimal sample preparation time, and the ability to analyze the matter in all aggregate states. In our group SERS sensor is developed using porous Si and Si nanowires as templates for silver deposition [5, 6].

Porous Si is an interesting material in sensing applications due to its large specific surface area, and compatibility with modern semiconductor production processes. Research in functionalization of the porous surface is ongoing in an effort to produce a variety of sensors, increase their sensitivity, and selectivity to gases including hydrogen, ammonia, and nitrous oxides [7].

The most widely used anode is graphite whose lithiated compounds have stable phases up to the  $\text{LiC}_6$  stoichiometry corresponding to a theoretical specific capacity of 372 mAh g<sup>-1</sup>. In contrast, Si has a very high theoretical capacity of 4200 mAh g<sup>-1</sup> and can intercalate 4.4 Li into Si at high temperature to form  $\text{Li}_{15}\text{Si}_4$ . Silicon also features a working potential around 0.4 V vs. Li<sup>+</sup>/Li which is safer than operating potential of graphite (0.05 V vs. Li<sup>+</sup>/Li). Although Si owns all of these advantages, Si based anodes suffer from huge volume expansion upon cycling ( $\approx$  400%) causing electrode fracture and electrical isolation during repeated cycling. Continuous volume changes cause the breaking-reformation of the solid electrolyte interphase (SEI) film which leads to consumption of lithium-ions and electrolyte. Exhaustion of the electrolyte causes the degradation of conductivity and induces fast capacity loss. There are two common strategies to avoid this problem: combining Si with different kind of carbon materials (amorphous carbon, conductive carbon black, carbon nanotubes, graphene) or designing nanoscale silicon with different structures. The porous structure provides a large space to accommodate volume expansion and large surface area for Li-ion transport from electrolyte to Si. Porous Si particles are prepared by electrochemical etching and planetary ball milling.

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## Nanoconfined water at inorganic pores: implications for prebiotic chemistry in hydrothermal vents

**Daniel Muñoz-Santiburcio**

*CIC nanoGUNE, Spain*

Hydrothermal vents offer a very rich network of nanometric channels which are filled by water. When confined to such nanoscale spaces, the properties of water change dramatically with respect to those in the bulk regime, which has a profound impact in the chemistry taking place therein. Here, I will present a global view of a series of studies on nanoconfined water within mackinawite FeS sheets at extreme conditions, describing several different processes of extreme importance for prebiotic chemistry: from the transport of H<sup>+</sup> [1] and OH<sup>-</sup> [2] to water self-dissociation [3] and to peptide synthesis and hydrolysis [4]. Finally, I will also present recent results regarding nanoconfined water within graphene sheets [5] that show the different possible regimes of water in bidimensional confinement.

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## Regulating Reaction Selectivity of Electricity-Driven Prebiotic Chemistry

**Ryuhei Nakamura**

*Earth-Life Science Institute (ELSI), Tokyo Institute of technology, Japan*

In this presentation, first I will present the electronic and protonic functions of natural hydrothermal vent minerals. This is followed by the investigation of electricity-driven prebiotic CO<sub>2</sub> reduction and nitrate/nitrite reduction. Finally, I will discuss how to control the reaction selectivity of electricity-driven prebiotic chemistry based on the electron and proton transfer theory.

## Sulfur chemistry paved the way for evolution of antioxidants

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The first organisms on the young Earth, just 1-1.5 billion year old, were likely chemolithoautotrophic anaerobes, thriving in an anoxic world rich in water, CO<sub>2</sub> and N<sub>2</sub>. Until the accumulation of O<sub>2</sub> in the atmosphere, it is generally assumed that life was exempted from the oxidative stress that reactive oxygen species (ROS) impose on hydrocarbon-based life. Therefore, it is somewhat perplexing to note that life on the early Earth already carried antioxidants. The task of metabolic enzymes such as superoxide dismutase enzymes (SOD), catalase (CAT) and peroxiredoxins (PRDX) is to remove all forms of ROS, including H<sub>2</sub>O<sub>2</sub>. Yet, they have been found in all domains of life and are considered to be of primitive origin. Phylogenetic investigations have suggested the presence of these enzymes in the Last Universal

Common Ancestor (LUCA), far predating the Great Oxygenation Event (GOE) sometime between 2.3–2.7 billion years ago, thought to be due to the appearance of oxygen producing microorganisms and a need to respond to the appearance of Reactive Oxygen Species (ROS). There are different approaches to account for the development of antioxidants well before the introduction of oxygen by microbial activity: (1) that there might be a non-biological source of ROS that pre-dates the oxygenic microbial activity and (2) that sulfur, the homologue of oxygen, might play a role. Here we address (2) by comparing the relevant sulfur and oxygen chemistry.

We hypothesize that Reactive Sulfur Species (RSS) may have been the trigger for the evolution of antioxidants and that the ROS antioxidants started out as “anti-sulfur” enzymes developed to cope with, and take advantage of, the RSS extensively that were abundantly present on the early Earth.

## Can the mineral fougérite mediate the step from strictly exergonic chemistry to a free energy converting precursor of bioenergetics?

**Wolfgang Nitschke**

*CNRS, France*

In a brief overview of the history of origin of life research, I will try and convey the notion that it is free energy converting processes rather than prebiotic synthesis of organics that we have to elucidate to understand how life may have emerged. Respective mechanisms in extant life will then be scrutinized to single out specific free energy converters which may have existed prebiotically and hence are promising candidates for having driven the emergence of the dissipative structure called life. This approach suggests the mineral fougérite as a particularly interesting candidate. I will describe the properties of fougérite and lay out possible future avenues for testing bio-relevant catalytic and free energy converting reactions performed by this mineral.

## Compressibility of 2m1 muscovite-phlogopite solid-solution

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Layer silicates are minerals with confined nanospaces and can behave as inorganic membranes with high absorption properties for organic molecules. Then, they can have an important role in the first steps of the prebiotic chemistry and the Origin of the Life. Muscovite

(Ms) and Phlogopite (Phl) belong to the 2:1 dioctahedral and trioctahedral layer silicates, respectively, and are the end members of Ms-Phl solid solution (SS). In this work, this SS was studied in the 2M1 polytype and modelled by substitution of three Mg<sup>3+</sup> in the Phl octahedral sites by two Al<sup>3+</sup> and one vacancy, and computationally examined at DFT level as a function of pressure (P) to 9 GPa. Cell parameters as a function of P and composition, and bulk moduli as a function of the composition agrees with the existing experimental results and show either linear or quadratic trends. The mixing Gibbs free energy (G<sub>mix</sub>) can be approximated, calculated and fitted to quartic polynomial functions as a function of composition. From the minima and saddle points of the G<sub>mix</sub> an approximated solvus can be calculated. At low P, a gap of solubility is found, however, at high P and T, an increasing of the crystalline solubility is found.

## Synergies of technology developments in space exploration, climate change and emergence for life research

**Adrian Ponce**

*Jet Propulsion Laboratory, USA*

What do Russell's model for the emergence for life, the fight against climate change, and the endeavor to become a multi-planetary society, have in common? Life hydrogenates CO<sub>2</sub>, and in the alkaline hydrothermal vent model for life's emergence, the prebiotic version of this chemistry begins in the deep subsurface. There, carbonic acid-laden waters of the Hadean ocean react with rock at elevated temperatures to produce molecular hydrogen, formate and methane, which are circulated back into the Fe, Ni and Mo-bearing ocean via alkaline hydrothermal vents. Here the spontaneous precipitation of transition metal-bearing minerals, such as green rust (fougerite), produce catalytic membranes that separate the two fluids to generate steep pH and redox gradients across them. The resultant chemical potential is sufficient to drive organic complexification toward an autocatalytic, autotrophic metabolism thought to be the pathway to denitrifying methanotrophic acetogenesis. To elucidate plausible, though falsifiable, mechanisms that are consistent with this model, new experimental and theoretical approaches are needed to advance our understanding. Inspiration for such advances may come from other fields that aim to hydrogenate CO<sub>2</sub>, such as electrochemical CO<sub>2</sub> scavenging in the production of fuels and chemicals, as well as *in situ* resource utilization (ISRU) of the Martian atmosphere as we endeavor to become a multi-planetary society. Detailed understanding of candidate mechanisms is key, and the advancement of experimental/theoretical means to enable this may be driven by industries where significant commercial potential exists. Those advancements are contributing valuable tools for the better understanding of the seemingly intractable issues facing research into the emergence of life. Towards this end, this presentation will review some recent developments in electrochemical approaches to hydrogenate CO<sub>2</sub> in the fight against climate change and for ISRU in Mars exploration.

## The role of hydrogen activation in early metabolism

**Martina Preiner**

*Heinrich-Heine-University, Germany*

The probably most ancient CO<sub>2</sub> fixing metabolic pathway is – simply put – the catalyzed reaction between H<sub>2</sub> and CO<sub>2</sub>, the product of which is an activated acetyl group. We are investigating the possible transition between geochemical H<sub>2</sub>/CO<sub>2</sub> redox reactions to biochemical reactions in the so-called Wood-Ljungdal pathway and thereby showing the crucial role of H<sub>2</sub> activation via transition metals.

## Chemistry in flow: Bioinspired conditions for chemistry and materials synthesis

**Josep Puigmarti-Luis**

*ETH Zurich, Switzerland*

Chemists and material scientists frequently study functional self-assembled structures at the global minimum of Gibbs energy (thermodynamic control). Recently, however, there is a major interest to develop new methods that could potentially convey an increased control of self-assembly processes in time and space (kinetic control). Here, I will show how microfluidics can advantageously be used.

## Stability and morphology of mixed amphiphile vesicles under hydrothermal vent conditions

**Hanadi Rammu**

*Centre for Life's Origins and Evolution at the Department of Genetics, Evolution and Environment, University College London, London, United Kingdom*

Evidence points to a chemotrophic and autotrophic origin of life in hydrothermal vents. The complexity of phospholipids in modern day membranes suggests that the composition of the Last Universal Common Ancestor must have been simpler. A proposed composition for protocell membranes includes single chain amphiphiles (SCA), such as fatty acids. These can spontaneously self-assemble into vesicles (liposome-like compartments) when in solution and above a 'critical bilayer concentration'. A major criticism of the alkaline hydrothermal vent hypothesis argues against a marine environment for the origin of life due to the high temperatures, strongly alkaline pH, ocean salinity and divalent cations that disrupt vesicle self-assembly. But these arguments are based on vesicles formed from 2-3 SCAs. Here we show that by using mixtures of prebiotically plausible C<sub>10</sub> – C<sub>15</sub> fatty acids and 1-alkanols, alkaline hydrothermal conditions favour the self-assembly of vesicles in aqueous solution between pH 6.5 to >12 and in 600 mM NaCl, 50 mM Mg<sup>2+</sup> and 10 mM Ca<sup>2+</sup>, and greater stability is conferred by adding C<sub>10</sub> isoprenoids.

## On the Origin of the Chemical Structures of DNA nucleobases: Photochemical Selection

**Daniel Roca-Sanjuán**

*Institut de Ciència Molecular, Universitat de València, P. O. Box 22085, València 46071, Spain*

Natural selection is a fundamental aspect for Life evolution according to Darwin's theory. In the context of the chemical building blocks of Life, a similar concept can be postulated, the "photochemical selection". It is based on several spectroscopy experiments and molecular modeling simulations aimed to determine the response of the DNA constituents to UV-Vis light, and it affirms that the chemical structure of DNA nucleobases, which are the most sensible molecules to UV-Vis radiation, might had been selected in early stages of Earth in the presence of intense UV irradiation. Thus, canonical DNA bases have intrinsic mechanisms for a fast dissipation of the energy provided by the UV irradiation. Contrarily, modifications of the chemical structure of the DNA bases give rise to molecules which retain the UV light and therefore they are prone to reactivity with other molecules from the environment destroying the molecule itself. DNA integrity could only occur for the stable molecules against UV light.

In this contribution, we shall show the main findings obtained on the photochemical properties of thymine, adenine, cytosine and guanine by using quantum chemistry, which allow to comprehend the “photochemical selection” of the nucleobases <sup>[1–4]</sup>.

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## Planar chemical gardens and submarine methane hydrate deposits: spider-leg growth

**Luis Rocha**

*University of Cambridge, UK*

A novel type of gas escape structure has been identified under the Congo continental slope seafloor, called “Spider Structures”. These structures consist of a large sub-circular depression from which various furrows protrude, each of them with high methane venting activity. The growth of these structures is studied with analogue laboratory experiments, consisting of planar chemical garden filaments formed in a Hele-Shaw cell, with sodium silicate acting as the host solution and cobalt chloride, copper sulphate or manganese chloride being used as the injected solutions. The precipitate filaments are modelled considering the mechanism of formation and spreading of solid at their tip. The model has good agreement with the experimental results and is shown to be applicable to the submarine spider structures, revealing that the flow of methane in these occurs in the cracks of the sediment. Additionally, the Spider Structures are found to grow with a self-organized dispersion mechanism with a dispersion coefficient as high as  $10^{-4} \text{ m}^2 \text{ s}^{-1}$ , thus enhancing physical and chemical exchanges.

## Dynamics of interacting fronts in a simple $A + B \rightarrow C$ reaction-diffusion model

**Laurence Rongy**

*Université libre de Bruxelles (ULB), Belgium*

Pattern interaction has so far been restricted to systems with relatively complex reaction schemes that lead to rich spatio-temporal dynamics. We show that a simple second-order chemical reaction is capable of generating similar complex phenomena, such as attractive or repulsive interaction modes between the localized reaction zones (or fronts). The complexity in the pattern dynamics emerges here due to finite-size effects which are reflected by an appropriate choice of initial conditions and could play a role in the control strategy of periodic precipitation patterns.

# PROSPECTING FOR LIFE AND THE UNEARTHING OF GREEN RUST

**Michael Russell**

*NASA Interim Employment Program*

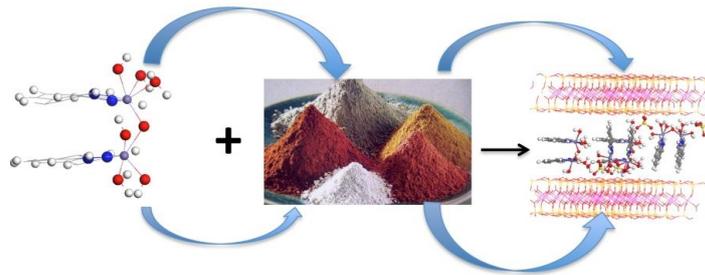
“When we are young, the words are scattered all around us. As they are assembled by experience, so are we, sentence by sentence, until the story takes shape,” So said Louise Erdrich in her “Plague of Doves”. First words for me were absorbed from books with titles like ‘Ungava Bay’, ‘Coral Island’ and ‘The Call of the Wild’. From these my course was set, I would be an ‘explorer’, or so I thought! That plan did not work out so well. Needing a job after leaving school, I found one in a factory as a ‘Works Chemist Improver’, testing nickel catalysts for the hydrogenation of phenol to cyclohexanol, taking in along the way, Sabatier’s principle. At night school I amassed enough exams to study geology with chemistry and physics at Queen Mary College. Armed thus I travelled to the Solomon Islands where geology is a ‘happening’ – earthquakes, volcanoes and hot springs! – with the added opportunity of prospecting for Fe, Cu and gold! Next was Canada to spend time at the Sullivan mine, sunk into a giant stratiform Pb-Zn-sulfide orebody thought to have been precipitated from submarine hot acidic springs about 1.5 billion years ago. At last I reached northern British Columbia and the Yukon, prospecting, amongst other metals, for Fe, Ag and Mo. Thence to Ireland researching what I also took to be 340 million-year-old ‘exhalative’ (i.e. hot spring-related) Pb-Zn orebodies. The exhalative theory was given a boost by the discovery, in 1979, of 350°C metal-bearing acidic waters issuing from Black Smoker chimneys in the Pacific. The discovery sent us searching—successfully we thought—for fossil examples of such chimneys in the Irish mines. But because these chimneys measured just a few cm in height compared to the metric size of the active chimneys, our reports were met with some derision. So it was a relief to realize, inspired by my young son’s experiments, that our chimneys were doing the same job, albeit more slowly than the very hot ones, and were generated as chemical gardens, a finding that put us on the road to thinking about the emergence of life. After all, we knew as geologists, there were no organic molecules on the early Earth, and that to make life’s particular organic molecules from scratch would require an inorganic membrane. And what better than a membrane comprising Fe minerals dosed with Ni in our chimneys to mediate the ‘hydrogenation’ of CO<sub>2</sub> – life’s job anyway. Indeed, such a membrane would also keep the two fluids, with their contrasting redox and pH characters, from direct mixing, just as biological membranes do to this day. At the same time, my field research amongst ancient ocean floor basalts and associated ultra-mafic rocks, contributed to the Alps from Tethys Ocean, indicated that alkaline waters bearing hydrogen and methane were a result of the ubiquitous process of serpentinization; a process that must have operated in all ocean floors over all time. Thus we could predict, as foundational to the Alkaline Hydrothermal Vent theory, the nature of the Lost City hydrothermal field ten years before its discovery in the North Atlantic in 2000. Lost City comprises a number of carbonate and brucite (Mg(OH)<sub>2</sub>) chimneys tens of metres high that continually issue alkaline, 90°C hydrothermal spring waters. We had surmised that Ni-enriched FeS chimneys would have precipitated at comparable alkaline springs issuing into a metal-rich carbonic ocean on the very early Earth (inducing membrane potentials comparable to those capable of succoring all life, and thereby, sufficient to drive life into being). However, our laboratory precipitates also revealed the oxyhydroxide mineral fougérite (or green rust, [Fe<sub>11</sub>Fe<sub>12</sub>(OH)<sub>12</sub>][CO<sub>3</sub>•3H<sub>2</sub>O]), the likely precursor to the magnetite (Fe<sub>3</sub>O<sub>4</sub>) now comprising the Archean Banded Iron Formations. We now look upon green rust, supported by sulfides, dosed with Ni and Mo and converting the hydrothermal H<sub>2</sub> to electrons and protons, as the pliable organizational seed of all life. But recent experiments indicate that the hydrogenation of CO<sub>2</sub> is too simple an idea. Instead, redox (electron) bifurcation from H<sub>2</sub> is required to step up potentials sufficiently to drive the endergonic processes needed for life to onset from C1 compounds, and that this was likely mediated by a Mo-complex such as [FeO(OH)(MoS<sub>4</sub>)<sub>2</sub>]<sup>3-</sup>, H-bonded in the interlayers of green rust in processes that transcend chemistry.

## Interactions of organics with confined mineral surfaces

**C. Ignacio Sainz-Díaz**

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The interaction of molecules on mineral crystal surfaces is interesting for understanding some natural phenomena related with crystal growth, biomineralization, mineral stability, prebiotic chemistry, and also for many applications, such as, catalysis, weathering effects, mineral transformations, environment, agriculture, pharmaceuticals, etc. The surface reactivity is especially different in confined spaces. The first step for any prebiotic chemical reaction with organics is the adsorption on a mineral surface. Some minerals provide confined spaces, where could be possible chemobronic scenarios for the first chemical reactions forming the initial complex molecules necessary for the origin of the Life. These interactions can happen in terrestrial and extraterrestrial mineral surfaces. Several examples of confined mineral surfaces will be showed, such as, silicates, chemical gardens, and clay minerals. These interactions have been studied at atomic scale by means of theoretical calculations by using force-fields based on empirical interatomic potentials and quantum mechanical calculations. Some adsorption systems will be showed, such as, small molecules, aminoacids, carboxylic acids, metal-organometal complexes, proteins, etc. Most of these adsorptions are energetically favorable on minerals formed in the prebiotic earth crust after the formation of the hydrosphere and may have played an important role in the process of chemical evolution.



## Coarse-grained computer modeling of nanomaterials: approaches to bridge the scales

**Pedro A. Sanchez**

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Chemobronics systems are a paradigmatic example of materials with intricate macroscopic morphologies that emerge from a complex interplay of interactions governing their synthesis processes. The broad range of lengths and time scales involved in such processes makes unfeasible their appropriate modeling by means of a unique approach. In one hand, first principles approaches only provide atomic and molecular force fields that can be used to study the microstructure and short time dynamics in fully atomistic computer simulations. On the other hand, continuum approaches can model macroscopic properties and long time dynamics, as long as some meaningful connection with the microscopic properties can be established. Mesoscopic approaches are aimed at bridging the scales between microscopic and macroscopic models, on the basis of coarse-grained representations of the microscopic properties.

In this contribution I present an overview on cutting-edge techniques developed for the coarse-grained computer modeling of complex materials, focused on those with relevance for chemobronics systems. This includes methods for determination of coarse-grain effective force fields from atomistic simulation data, efficient calculations of long range electrostatic and magnetostatic interactions and hydrodynamics.

## Nucleation and Morphology of Ices

**Teresa M. Seifried, Philipp Baloh, Fabian Weiss, Hinrich Grothe**

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For the Earth's climate system ice clouds are of major importance. On the one hand they can act as a cooling factor by reflecting parts of the solar radiation, and on the other hand they can cause warming by absorbing solar radiation and by trapping the outgoing blackbody radiation. These effects are not well understood for making exact predictions about the overall radiation balance of the Earth. In fact, clouds and aerosol particles are known as one of the largest uncertainties of the radiation balance in the report of the International Panel on Climate Change IPCC.

Here, water-oil emulsions were used to mimic cloud droplets and their freezing behavior. Aqueous droplets containing citric acid as a model compound for carboxylic acids in cirrus clouds. Different concentrations of citric acid were prepared and observed using the following methods: a) X-Ray Diffraction for the phase composition, b) Environmental Scanning Electron Microscopy (ESEM) for the morphologies of the samples, c) Raman Spectroscopy for the chemical compositions of the droplets.

Citric acid alters the freezing behavior of water in a way that Cubic Ice  $I_c$  (i.e. stacking faults in the hexagonal ice structure  $I_h$ ) crystallizes.  $I_c$  occurs at elevated citric acid concentrations at the expense of  $I_h$ . At very high concentrations the droplets do not crystallize and stay amorphous. This is interesting as it was not expected that  $I_c$  can form under these conditions. Similar experiments were also carried out with malonic, succinic, glutaric, and tartaric acid. Even though none of these carboxylic acids occur in the atmosphere in relevant amounts, predictions for the influence of carboxylic acids in general can be derived.

## Macroscale precipitation kinetics: Towards complex precipitate structure design

**Gabor Schuszter**

*University of Szeged, Hungary*

Coupling of transport processes and chemistry is essential in dynamic systems. To fine-tune precipitate structures, kinetic investigation must be performed. Characteristic time scale changes from milliseconds to hours. We elaborated experimental methods for the kinetic study of fast and slow reactions. The applicability is illustrated via injection experiments.

## Evolution as Energy Minimization

**Everett L. Shock and Grayson Boyer**

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One hypothesis linking evolution with energy is that the equivalent result, cheaper, prevails. Likewise, combined changes in power demand and power supply that maintain the relation: supply > demand are driven to proceed. Testing these hypotheses may be possible by tracking paths through an economy of minimized costs via Gibbs energy minimizations of biomolecular compositions. Our tests are conducted in hydrothermal ecosystems that are microbially dominated and variable on small scales that can be profitably sampled. Initial efforts used metagenomic data to inventory all proteins in several microbial communities from settings with defined geochemical compositions, because we were able to estimate independently standard Gibbs energies of formation of proteins from their elements (Dick & Shock, 2011; PLoS ONE, 6, e22782; Dick & Shock, 2013, PLoS ONE, 8, e72395). Results showed that 1) the relative

thermodynamic stabilities of molecules from each class of proteins depend predominantly on temperature and oxidation state, with the higher temperature homologs also more reduced, and that 2) using average protein compositions at the phylum level allowed predictions of relative abundances through Gibbs energy minimization that align with measured community structure. Carrying this analysis forward was made possible by direct mass spectrometric analysis of membrane lipid extracts from hydrothermal microbial communities. Results based on harvesting intact polar lipids again show correlations of molecular bulk composition with the temperatures and redox states of sample locations. Once again, an independent means of estimating standard Gibbs energies of lipid molecules from their elements allows minimization of Gibbs energies for lipid assemblages representing microbial communities. Results confirm that each lipid assemblage is most energetically fit at its multidimensional geochemical location. What was inferred for proteins decoded from metagenome reads is supported by direct analysis of lipids extracted from samples. Biomolecules have to work well as cheaply as possible, and evolution will see to it that this result is attained robustly.

## A few lessons learned trying to fix CO<sub>2</sub> in alkaline vent conditions

**Victor Sojo**

*Institute for Advanced Study, Berlin, Germany*

The alkaline-vent theory predicts the spontaneous pH-driven reduction of CO<sub>2</sub> in the ocean with H<sub>2</sub> from the vent, catalysed by Fe(Ni)S clusters precipitated at the interface. Using microfluidic reactors at ambient pressure, we set out to test this prediction. We were unable to detect reduced carbon products under a number of conditions. We suggest that high-pressure reactors may be a necessity.

## Flow-controlled engineering of scalar transport in fluids

**Michel Speetjens**

*Eindhoven University of Technology, The Netherlands*

The flow field is key to scalar transport (chemical species, heat) in fluids and admits manipulation via an appropriate flow forcing. Hence properly engineered flows (in principle) enable practical application of the physical phenomenon key to chemobrionics, i.e. the formation of solid structures in fluids by precipitation, which has great potential for materials technology. Enhancement of scalar transport in fluids engineering often relies on reorientations of a laminar base flow by e.g. cyclic repositioning of impellers or systematic activation of moving boundary segments. Reorientation generally follows a fixed protocol (typically periodic in space or time) designed to accomplish chaotic advection (i.e. the rapid global dispersion of fluid parcels). However, whether this approach (particularly in the context of synthesized precipitation) indeed yields optimal scalar transport due to the non-trivial interplay of the fluid motion with molecular diffusion and chemical reactions is unclear. The present study explores an alternative approach: pro-active reorientation based directly on the state of the scalar field and aiming at accomplishment of a predefined (heterogeneous) state. The latter capability is especially important for synthesized precipitation, since it may enable systematic realization of certain morphologies. The control strategy concerns step-wise activation of the specific reorientation that gives optimal scalar transport for a certain time horizon. Key enabler is a compact model for efficient prediction of the scalar evolution based on its spectral decomposition in the base flow. The control strategy is investigated for a representative problem: enhanced heating of a cold fluid in a 2D domain by an unsteady flow driven by step-wise activation of moving boundary segments. This reveals that pro-active reorientation can substantially accelerate the heating compared to the conventional approach of time-periodic activation designed for chaos and thus demonstrates its potential for attaining optimal scalar

transport in reoriented flows. First studies on accomplishment of predefined heterogeneous states by this control strategy are in progress.

## The agate osmotic pump? The fingerprints of flow and deposition in agate structures

**Piotr Szymczak and Bartłomiej Rosa**

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Agates are banded forms of the microcrystalline quartz, formed by the deposition of layers of silica filling voids in volcanic vesicles. Due to the large difference in molar concentration of silica in aqueous and solid phase, a large volume of silica solution is required to produce a single agate amygdale. How is this solution supplied to the amygdale and - even more importantly - what is the mechanism of its continuous replenishment during the deposition process? A clue to these questions can be found in the presence of 'infiltration channels' - bulbous structures at the edge of the amygdale, which show characteristic thinning of the agate banding. It has been hypothesized that these structures are the remnants of the original flow paths supplying the silica-rich solution [1] to the interior of the amygdale. We test this hypothesis by the numerical simulations of the coupled fluid flow—precipitation kinetics model and show how the dynamics of the precipitation process can be linked with the final shape of the infiltration channel. We also comment on the implication that these results have on the possible mechanisms of agate formation

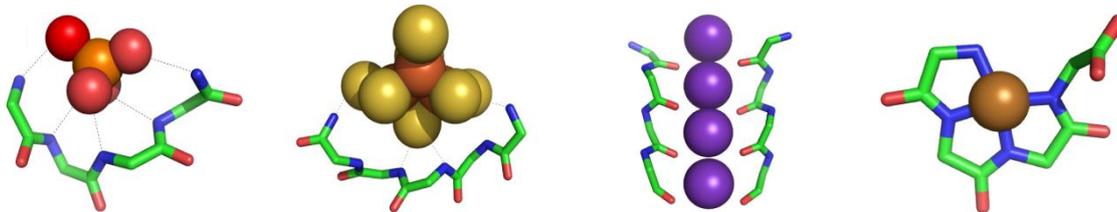
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## Protein 3D structures at the origin of life

**James Milner-White**

*Glasgow University, UK*

Proteins are relatively easy to synthesize, compared to nucleic acids and it is likely that there existed a stage prior to the RNA world which can be called the protein world. Some of the 3D peptide structures in these proteins have, we argue, been conserved since then and may constitute the oldest biological relics in existence. We focus on 3D peptide motifs consisting of up to 8 or so amino acid residues. The best known of these is the "nest", a 3 to 7 residue protein motif, which has the special function of binding anionic or  $\delta^-$  groups of atoms<sup>1,2,7</sup>. Ten percent of amino acids in typical proteins belong to a nest so it is a common motif. A 5-residue nest is found as part of the well known P-loop that is a recurring feature of many ATP or GTP-binding proteins and it has the function of binding the phosphate part of these ligands. A synthetic hexapeptide, ser-gly-ala-gly-lys-thr, designed to resemble the P-loop, has been shown to bind inorganic phosphate<sup>8</sup>. Another type of nest binds iron-sulphur centres. A range of other simple motifs<sup>5</sup> occur with various intriguing 3D structures; others bind cations or form channels that transport potassium ions ; another type forms coloured heme-like structures with certain metals. Amyloid peptides will also be discussed<sup>4</sup>. It now seems<sup>3,5</sup> that the earliest polypeptides, far from being functionless stretches, were functionally rich, and had many of the properties that might be expected to encourage and stabilize simple life forms in the hydrothermal vents of ocean depths.



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## Atomic-Scale Description of Fe-S Cluster Nests in Peptide Maquettes

**Robert K. Szilagyi, Becky Hanscam, Luke McHale, Amanda Galambas, Valérie Copie, Joan B. Broderick, and Eric M. Shepard**

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The presentation will summarize our insights gained from a combined computational and experimental study of small peptide interaction with Fe-S clusters under physiologically relevant conditions. As the result of a spontaneous self-assembly process, short 8 – 16-mer peptides were demonstrated to house a [4Fe-4S] cluster, and thus provide a synthetic platform to create [4Fe-4S] maquettes. The maquettes can be used as biomimetic compounds of prosthetic groups of metalloproteins and metalloenzymes, such as bacterial ferredoxins, high-potential iron-proteins, and small molecule (H<sub>2</sub>, N<sub>2</sub>, CO/CO<sub>2</sub>) activating metalloenzymes. We focused in on [4Fe-4S] maquettes using peptides of general primary structure of Cx<sub>2</sub>Cx<sub>2</sub>C and Cx<sub>3</sub>Cx<sub>2</sub>C. These cysteine rich motifs correspond to bacterial ferredoxin metalloproteins and radical S-adenosylmethionine metalloenzymes, that both harbor redox active [4Fe-4S] clusters. Under our experimental conditions, Cx<sub>2</sub>Cx<sub>2</sub>C and Cx<sub>3</sub>Cx<sub>2</sub>C peptides were determined to coordinate high levels of [4Fe-4S]<sup>2+</sup> clusters, ranging between (80% – 100%). The maquette-[4Fe-4S]<sup>2+</sup> clusters are redox active, as they can be reduced to the [4Fe-4S]<sup>+</sup> state; however, this is not a simple

one-electron process, since the cluster decomposition and reassembly process results in 7–17% reduced cluster yields. Due to the non-crystalline state of the [4Fe-4S] maquettes, we utilized molecular dynamics calculations powered by empirical force fields for peptides and spectroscopically validated density functional theory for the cluster bound states in order to correlate maquette stability and redox chemistry with molecular structure. Together, our results provide the first atomic-scale description of Fe-S cluster coordination in maquettes.

Financial support for the research from NSF Chemistry of Life Processes program (Grant # 1609557) is greatly appreciated.

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## Flow-driven crystallization

### Agota Toth

*University of Szeged, Hungary*

The presence of concentration gradients maintained by flow may yield products significantly different from those prepared in simple continuously stirred batch reactors. It can also lead to the enrichment of the thermodynamically unstable crystalline form or may be used to select the required polymorph which is essential for construction or pharmaceutical industry.

## Contribution of soil science to knowledges on the green rust fougérite

### Fabienne Trolard<sup>1</sup>, Guilhem Bourrié<sup>2</sup>

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Since 1905[1], green rusts were depicted in soils, particularly soils in which moderate reductive conditions occurred, i.e. hydromorphic soils. Thus, only with a reasoning of the chemistry of iron, this author predicts that the typical blue-green color of this soil is due to a ferrous-ferric compound. Subsequently, the characteristic blue-green color of this compound was used as the universal criterion for recognition in the World Reference Base, the WRB [2]. In parallel, the chemist Chardon in the field of corrosion of steels experimentally obtained green rust as early as in 1935 and Bernal et al. in 1959 [3] proposed structures that are still valid today.

The discovery of green rust fougérite in soils of Fougère's forest [4] and the establishment of its mineralogical structure, its thermodynamic properties and its environmental conditions of occurrence and reactivity are the result of a multidisciplinary approach. Thus, it was necessary to:

- propose new sampling and sample conditioning protocols,
- preserve in all circumstances (field, laboratory, measurements in the instruments) the initial oxidation-reduction conditions,
- implement all the means of investigation of the solid: Mössbauer (in lab and *in situ*), Raman, XAS, MEB, XR diffraction,
- synthesize the mineral to establish references for structure and thermodynamic properties,

- acquire data, particularly with *in situ* sensors, on both the soil solution, with specific protocols, and the solid to be able to study the solid-solution interactions and to model them.

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## Clathrate hydrates: Theory and experiment

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Clathrate hydrates (called also as gas hydrates) are solid inclusion compounds consisting of an ice like network of host water molecules link through hydrogen bonding. Unlike the ice structure, the arrangements of water molecules create cavities (host lattice) that can enclose a large variety of small gas molecules ( $< 10 \text{ \AA}$ , guests). Recently, we have developed a new all-vapor aerosol methodology, a routine sub-second time scale has been achieved for the formation of clathrate hydrates (CHs) at low temperatures (80–220 K) and pressures.1-4 The rates observed for such formations are possible due to routine molecular-level premixing of hydrate components within the vapor phase and “catalyst”.1-6 In this communication, I will review the catalytic action of the molecules in terms of FTIR spectroscopy and ab initio molecular dynamics studies.

## Nitrogen Oxides in Early Earth's Atmosphere as Electron Acceptors for Life's Emergence

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Using a combination of general circulation models and photochemical models, we quantify the NO<sub>x</sub> production in the Hadean Earth's atmosphere. NO<sub>x</sub> is a critical component in some emergence-of-life scenarios: atmospherically generated nitrate (NO<sub>3</sub><sup>-</sup>) is the most attractive high-potential electron acceptors for driving the highly endergonic reactions at the entry points to autotrophic metabolism.

## Autocatalytic Networks in Ancient Bacterial and Archaeal Metabolism

**Joana. C. Xavier**

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Life is a self-sustained, autocatalytic, set of reactions. How did biological networks emerge from geochemistry? Here we model that emergence in vent-like settings, applying algorithms of autocatalysis to 5994 prokaryotic reactions and looking closer at autocatalysis in an acetogen and a methanogen. These overlap in a connected graph of 172 reactions that point to an early autotrophic metabolism.

# Self-shaping droplets: from spheres to platelets with flagella

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Recently we reported a conceptually new bottom-up approach where phase transitions in oil droplets transform them into micrometer-sized, fluid objects with complex shapes, such as regular polyhedra, platelets shaped as hexagons, triangles, squares, toroids, and others [1,2]. Many of these shapes spontaneously form micrometer and sub-micrometer in diameter fibers, which resemble in shape the flagella of the living cells, Fig. 1. Experimentally, the system is realized as the oily drops are dispersed in appropriate long-chain surfactant solutions and are slowly cooled down to a temperature range around the freezing point of the oil [1,2]. Under these conditions, molecular multilayers of intermediate plastic phases are formed at the oil-water interface, which are able to deform the drop surface and to self-assemble into long fibres [2]. The observed shapes resemble closely some of the microorganisms observed in nature, e.g. the microalgae diatoms, which hints to a general (non-chemistry specific) mechanism of shaping [3]. The concept of “tensegrity” (tensorial integrity) was invoked to explain these results [3] and a theoretical model was developed on this basis [4]. We show that these systems appear as a convenient toolbox for studying the mechanisms of morphogenesis (structure and shape genesis) in nature from minimal in composition and structure molecular components.



**Fig. 1:** Examples of spontaneously formed oil droplets with flagella, obtained via cooling of (left)  $C_{15}$ -in-water and (right)  $C_{16}$ -in-water emulsions, stabilized by  $C_{16}EO_{20}$  nonionic surfactant (Brij 58) [1,2].

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# Formation of biopolymer membranes in biological hard tissues and biomimetic analogues

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Structural materials secreted by multicellular organisms are hierarchically organized composites that have unique combinations of strength and toughness. These materials consist of two material classes behaving as matrix and as reinforcement: the matrix consists of biopolymers and the reinforcement of minerals. The fabric of biopolymer matrices is developed either as membranes or/and a network of fibrils. Matrices in carbonate biological structural materials are composites consisting of  $\beta$ -chitin fibres and proteins. It was demonstrated that many biopolymers have structural characteristics of liquid crystals (1). Based on this notion, it was suggested that biopolymer matrices in mollusk nacre form via a liquid-crystallization, hence, a self-assembly processes (2, 3).

Crystallization in hydrogel-mineral aggregates is often used to study mineralization in biological environments (4). Hydrogels are porous networks of polymers. The pores can be filled with an aqueous solution whose composition can easily be varied. At aggregate formation the mineral fills the porous network of the gel, and, similar to biopolymer matrices that become occluded within the biocrystals, the gel matrix becomes intercalated into the growing biomimetic composite crystal. These characteristics render crystallization experiments with hydrogels as ideal systems to explore parameters that might be involved in the incorporation of organic matrices into biocrystals and help to understand how characteristics of this incorporation influence the structuring and hierarchical organization of the inorganic component.

Some structural characteristics of carbonate biological hard tissues can be reproduced by biomimetic hydrogel-carbonate composite aggregates, such as phase selectivity, mesocrystallinity and a hierarchical assembly of both, the mineral as well as the hydrogel. Furthermore, even though, at composite aggregate formation and growth some co-alignments of hydrogel fibres take place, in contrast to cholesteric liquid phases, hydrogel organization lacks any intrinsic structural order. Hence, the directing influence on mineral organization will largely be different to that of biopolymer matrices in carbonate biological hard tissues.

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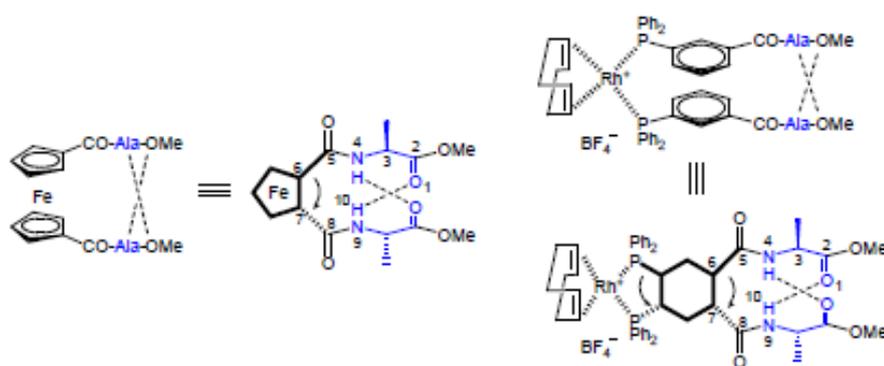
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# Development of new catalysts and new materials using self-assembly of metallated oligoamides

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In recent years, metallated oligoamides like 1,*n*'-disubstituted ferrocenes attract considerable attention.<sup>[1]</sup> Out of the wide variety of possible artificial self-assembled structures in 1,*n*'-disubstituted ferrocene amides, only a few are actually described in the literature. In particular, self-assembled structures with one or two inter-strand hydrogen bonds are known, that resemble artificial  $\gamma$ - or  $\beta$ -turns, respectively, where L-amino acids specifically induce P-helical chirality of the central metallocene. We and others have developed selective supramolecular catalysts inspired by these specific structures.<sup>[2]</sup> In this presentation, new catalysts and other systems based on the same self-assembled structural motifs will be presented.<sup>[3]</sup>



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# Influence of various solutes on formation of ice layer

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Key words: freeze layer crystallization, purification, crystallization kinetics, organic solutes

Melt crystallization is a separation technique used for ultra-purification of organic compounds up to level of purities of 99.99 % (Beckmann 2013). Specific case of melt crystallization is freeze layer crystallization, which is formation of crystal layer on subcooled surface in crystallizer from the melts or mother liquid (Mehdi 2016). In present study the freeze layer crystallization was applied as a purification and separation method for various aqueous solutions where water as solvent was crystallized. Ice layers were formed on cold finger inside jacketed crystallizer with controlled temperature. The main objective of the study is to investigate the crystallization kinetics and purification efficiency obtained by layer crystallization as function of various solutes presents in aqueous solutions. Organic solutes, sucrose and ionic liquids, were chosen based on novel application of freeze crystallization as purification and concentration technique of viscous industrial solutions.

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# Catalytic role of serpentinite paragenesis for the in situ abiotic synthesis of amino acids: a way towards metalloenzymes?

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Serpentinization processes are known to generate favourable conditions for abiotic organic synthesis. Yet, identifying the pathways leading to the production of complex organic molecules is a challenging problem that has critical implications for prebiotic chemistry, the origin of life and the functioning of modern rock-hosted life. This potential for abiotic synthesis was confirmed by the analysis of hydrothermal vent fluids, as well as laboratory and thermodynamic modelling, but remains underexplored in deep natural rocks. In order to further investigate serpentinizing environments as a critical venue for prebiotic chemistry and life activity, we applied a correlative microscopy approach, including SEM/TEM, Tof-SIMS imaging and Synchrotron-based Deep-UV fluorescence and Fourier Transform Infrared microspectroscopies supported by chemometrics analysis [1].

This approach was applied to serpentinized peridotites from the Atlantis massif (30°N, Mid-Atlantic ridge; IODP Expeditions 304/305) to track organic compounds at the pore level in rocks. We highlighted for the first time the *in situ* abiotic synthesis of amino acids in the hydrating oceanic crust [2]. They were found associated with submicrometric sulfides, altogether trapped within the nanoporosity of a highly reactive iron-rich saponite clay, which would have catalyzed Friedel-Crafts type reactions and thus promoted amino acids formation during a low-temperature alteration stage of the rocks. The co-localization of amino acids with such minerals showing structural similarities with the active sites of metalloenzymes likely present in LUCA would be consistent with the hydrothermal hypothesis of the origin of life, in which pioneer metabolisms may have mimicked the formation of organic compounds catalyzed by transition metals.

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# Growth of chemical gardens within the co-flow of two reactants in a microfluidic device

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## Abstract

Chemical gardens offer a unique opportunity to design tailored precipitation structures in far-from-equilibrium conditions [1]. However, when they grow in a 3D container from the dissolution of a crystal seed, they feature complex and erratic morphologies due to the interplay between osmotic, buoyancy, and reaction–diffusion processes. Various strategies, such as injection growth [2], the quasi-2D growth in the Hele-Shaw cell [3] and the membrane growth in microfluidic devices [4] have been proposed to control the growth of chemical gardens and produce materials with a given macroscopic morphology which could be used to perform specialized tasks, such as catalytic reactions, separation processes, or chemical sensing.

Here, we propose to control the growth of chemical gardens using a microfluidic device with a co-flow geometry. This experimental setup allows to control the relative speed at which the two reactants ( $\text{CoCl}_2$  and  $\text{Na}_2\text{SiO}_3$ ) meet to react by tuning the flow rate in each capillary and their inner diameters. For given capillary diameters, we show that varying the flow rates affects the macroscopic morphology and composition of the chemical gardens produced.

For large values of flow rates of both reactants, we observe the formation of regularly spaced membranes on the surface of the precipitate structure. The distance  $\lambda$  between two successive membranes can be controlled by varying the flow rates and decreases when flow rate in the inner capillary increases. Finally, we characterized the composition of the chemical gardens using powder X-Ray Diffraction and Energy Dispersive using X-rays, and their microscopic morphology using Scanning Electron Microscopy.

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## Time Displacement / Chemobrionic Garden

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*Time Displacement / Chemobrionic Garden*

Video documentation of generative sound installation

*In crystals we have pure evidence of the existence of a formative life principle, and although in spite of everything we cannot understand the life of crystals – it is still a living being.*

— Nikola Tesla, 1900

Time Displacement – Chemobrionic Garden explores a relationship between hydrothermal chemistry, the passage of time, and the evolution of sound. The project consists of several small chemical garden formations in a water glass (sodium metasilicate) solution, to provide a culturological insight into research on chemical processes and the origin of life. The chemical reactions are monitored by cameras to detect changes in colour and shape by means of microcontrollers. The changes affect the code for live sound generation, and slowly alter the generative drone composition in the gallery space. The slow changes in sound evade the scale of human perception.

**Production:** Projekt Atol Institute and Ljudmila, Art and Science Laboratory, 2016

**Photo credit:** Katra Petriček / Aksioma Archive

