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Geochemical modeling of the solution-minerals equilibria in alkaline hydrothermal vents from Lost City and pH control

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2021 COST ACTION



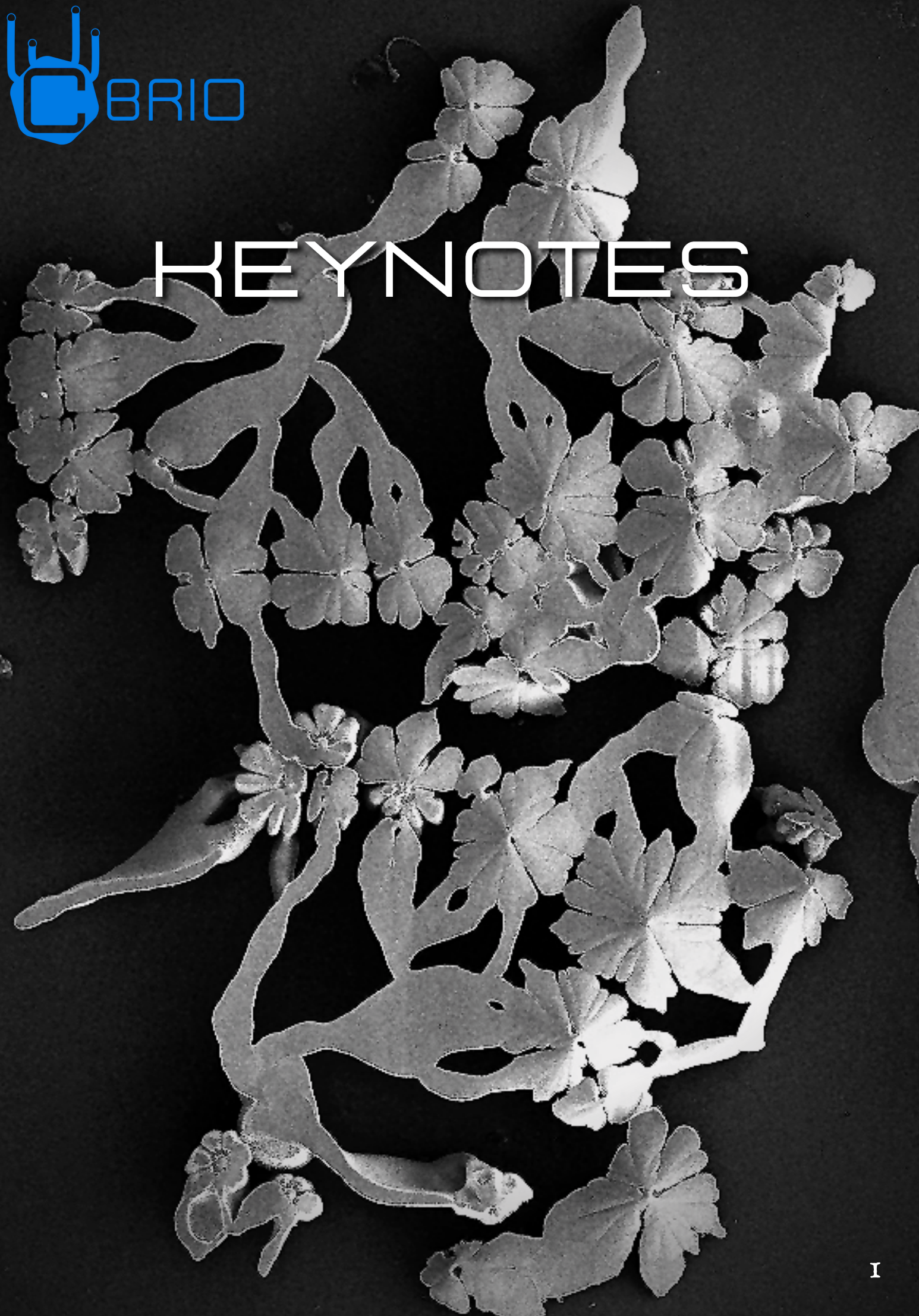
CHEMOBRIONICS

BOOK OF ABSTRACTS





KEYNOTES



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Biological self-organization in synthetic cells

All of biological research is done on a single sample: that of modern, terrestrial life. In the quest to engineer synthetic living systems, we seek to expand that sample size, enabling investigation of general properties of life in the lineage agnostic, synthetic organisms.

Synthetic minimal cells are liposomal bioreactors that have some, but not all properties of live cells. Creating artificial living systems allows us to diversify the chassis of biological studies, and provides novel opportunities for bioengineering. We can begin to answer questions about healthy and diseased natural cells, and ask new questions about the limits of biology. Engineering synthetic cells with fundamentally different physical and chemical properties, we can compare behaviors and begin drawing broad conclusions about basic rules of biological life.

Synthetic cells are fully defined and engineerable, enabling studies of natural processes with level of detail unavailable in complex and messy live cell. In synthetic system, there is less noise from underlying endogenous processes of cells, and no limitations of survivability. Synthetic cells provide new chassis for biological studies, for broadening understanding of our own type of biology, and for investigating alternatives to the single known life form.

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Formation of carbon-sulfur biomorphs and implications for the search of life

The rock record of early Earth contains numerous examples of microscopic organic filaments and spheres, commonly interpreted as fossil microorganisms. Microfossils are among the oldest traces of life on our planet, making their correct identification crucial to our understanding of early evolution. Yet, spherical and filamentous microscopic objects composed of organic carbon and element sulfur can form in the abiogenic reaction of sulfide with organic compounds. These objects, called carbon-sulfur biomorphs, spontaneously form by self-assembly under geochemical conditions relevant to sulfidic Precambrian environments. Furthermore, they adopt a diversity of morphologies that closely mimic a number of microfossil examples from the ancient rock record (Figure 1).

Here, I will present results on the formation conditions of the C-S biomorphs and preservation potential in rocks. I will also propose some hypotheses regarding their self-assembly mechanism, and possible implications on biosignature research on early Earth and other planets.

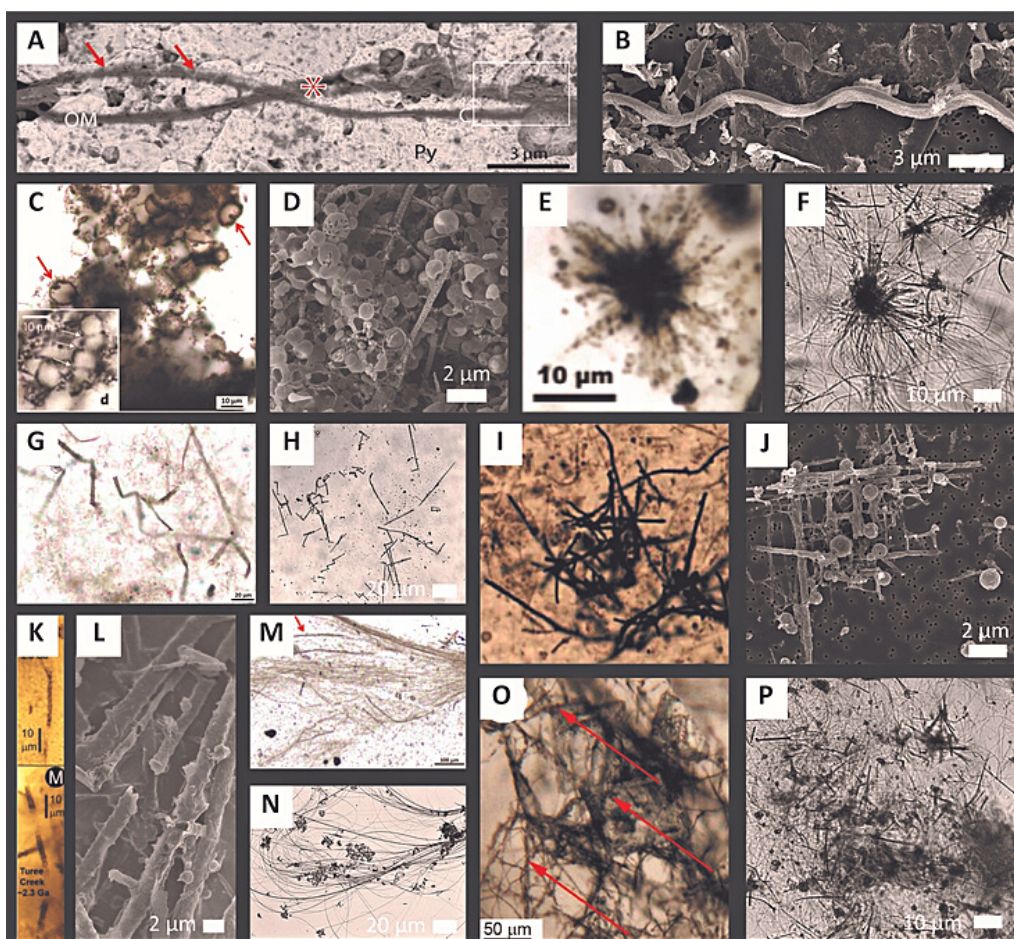


Figure 1: Side-by-side comparison of Precambrian putative organic microfossils and carbon-sulfur synthesized in the laboratory (Nims et al., *Geology*, 2021, doi.org/10.1130/G48152.1)

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The motion of life-like crystals: From pushing obstacles during active precipitation to self-moving tubes

Biomorphs are polycrystalline assemblies composed of metal carbonates and silica. They form smoothly-curved life-like shapes such as sheets, helices, funnels, and corals each composed of thousands of coaligned crystalline nanorods. Micrometer-sized posts composed of the photoresist epoxy SU-8 were photolithographed onto glass substrates and placed into the biomorph forming solution. These posts induced a new morphology reminiscent of fibrous, hair-like bundles that typically initiated along the perimeter of the cylindrical SU-8 material. Scanning electron microscopy reveals that the hairs are composed of many thin strands coaligned along the direction of growth that expand through continuous fractal-like branching or abrupt splitting events. Biomorphs also formed on the glass substrate; however, following the collision with SU-8 obstacles the growth transformed into fibrous hairs and ultimately detached the posts from the glass.

Creating self-moving objects often requires advanced production techniques as exemplified by catalytic, gas-forming microrockets. Conversely, the self-organization of precipitate tubes in chemical gardens are formed by simply injecting metal salts into silicate solutions. When using manganese salts for the initial reaction conditions, this method generates hollow, cylindrical objects rich in catalytic manganese oxide that also feature a partially insulating outer layer of inert silica. In dilute H₂O₂ solution, these structures undergo self-propulsion by ejecting streams of oxygen bubbles. Each emission event pushes the tube forward by 1-2 tube radii. The ejection frequency depends linearly on the peroxide concentration as quantified by acoustic measurements of bursting bubbles.

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On the challenges of energy coupled reactions: recent work on thio-esters, phosphate esters, and two pot electrochemistry.

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Chemobrionics and the search for life on Mars

It is often acknowledged that the search for life on Mars might produce false positive results, particularly via detections of objects, patterns or substances that resemble the products of life in some way but are not biogenic. Here, I discuss some of the known processes that could have generated “false biosignatures” on early Mars (compiled by McMahon and Cosmidis for J. Geol. Soc., in revision). I suggest that strategies for assessing candidate biosignatures on Mars could be improved by new knowledge on the physics and chemistry of abiotic self-organization in geological systems, requiring the contribution of colleagues and methods across several disciplines, particularly including the chemobrionics community. Chemists, physicists and materials scientists have long been interested in symmetry-breaking, self-assembly, and the emergence of complex structures and materials in far-from-equilibrium conditions. There is a vast literature on the numerical and experimental interrogation of these processes and the analytical characterisation of their products. This existing expertise now needs to be translated into a geological and astrobiological context by focusing on the minerals, fluids, and pressure-temperature conditions present on Mars today and in the geological past. Ideally, multiple high-resolution analytical techniques should be used to facilitate in-depth comparison with candidate biosignatures based on rich, multi-scale, multi-proxy datasets combining morphological, textural, and compositional information. As a case study, I will present recent work on enigmatic mineral filaments discovered in Jurassic calcite veins from Liguria, Italy (McMahon, et al., 2021, *Geobiology* 19, 473-488). Although the origins of these filaments are still not known with certainty, quantitative comparisons with experimental chemical gardens, particularly those produced from polymetallic mineral salts (by P. Knoll and O. Steinbock), are highly suggestive. I will also discuss the special case of agates and the remarkable inclusions they contain. Finally, I will share some preliminary results from ongoing experiments on the chemical alteration of Mars-analogue minerals.

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Self-organizing matter for functional materials

Shaping, sculpting, and forging customizable compounds into arbitrary forms has the potential to revolutionize technologies for advanced functional materials. Current self-assembly strategies allow impressive levels of control over either shape or chemical composition, but not both, as self-assembly inherently entangles shape and composition. Inspired by natural and biologically controlled mineralization processes, we here achieve independent control over shape and composition by performing chemical conversion reactions on nanocrystals which were first self-assembled in nanocomposites with programmable microscopic shapes. We show that these conversion reactions are surprisingly materials agnostic, allowing a large diversity of chemical pathways, and develop conversion pathways yielding a wide selection of shape-controlled compositions ranging from perovskites to transition metal chalcogenides. Previously unimaginable customization of shape and composition is now achievable for assembling advanced functional components using bioinspired mineralization strategies.

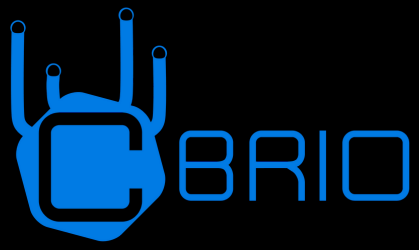
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Periodic Precipitation of Nanoparticles in Gradient-free Media

Many natural and synthetic processes involving mineral precipitation develop periodic structures composed of nanoparticles. The mechanisms involved typically involve spatial concentration gradients and reaction-diffusion processes. Here we discuss the periodic precipitation of calcium phosphate nanoparticles in a stirred, batch reactor driven by an enzyme-catalyzed reaction, the decomposition of urea by urease. Internal pH changes caused by competing reactions – production of ammonia and removal of phosphate – resulted in periodic changes in supersaturation and nucleation of nanoparticles. A simple model involving the biocatalytic reaction network coupled with burst nucleation of nanoparticles above a critical supersaturation reproduced key features of the experiments. These findings may provide insight to the self-organization of nanoparticles in biomineralization.



TALKS



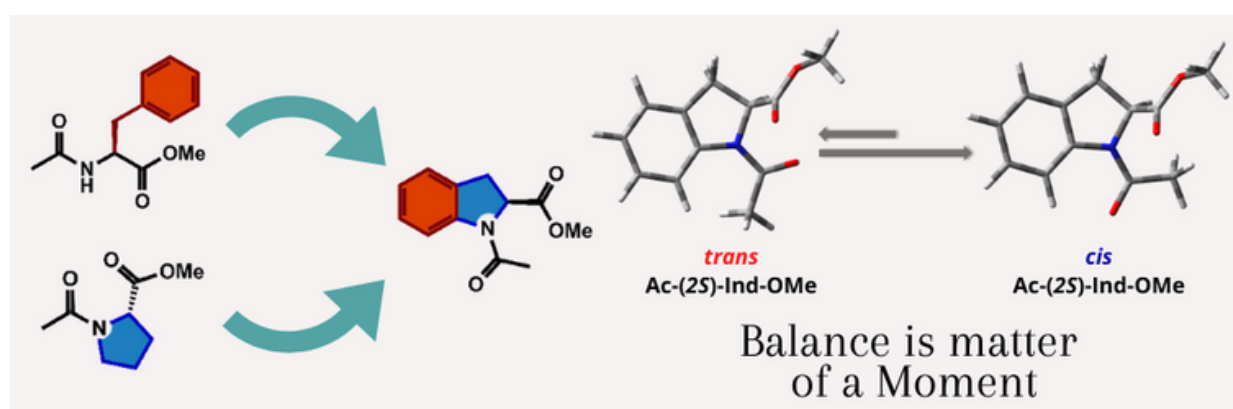
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A proline mimetic for the design of new stable secondary structures

A thorough experimental and computational study on the conformational properties of (S)-indoline-2-carboxylic acid derivatives has been conducted. Methyl (S)-1-acetylimdoline-2-carboxylate, both a mimetic of proline and phenylalanine, shows a remarkable tendency toward the cis amide isomer when dissolved in polar solvents. This behavior is opposite to the general preference of proline for the trans isomer, making indoline-2-carboxylic acid a good candidate for the design of different secondary structures and new materials(1).



The deep comprehension of the conformational properties of simple molecular scaffolds can bring to the design and synthesis of new and stable secondary structures. In the context of Chemobrionics Cost Action, I am interested in the application of this knowledge for the development of well-structured oligomers and their aggregation in solid state. Moreover, in the self-assembly of amphiphilic molecules derived by peptide mimetics which can allow the synthesis on demand of different soft-materials (micelles, vesicles, membranes, etc.).

1. J. Org. Chem., 2021, 86(12), 7946-7954

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Self-organized growth of titanium dioxide nanotube arrays

Thanks to having remarkable features in photocatalysis, dye-sensitized solar cells, and biomedical devices, titanium dioxide is an excessively studied compound in materials science. In 1999, the first reports exhibited the possibility to develop ordered arrays of TiO₂ nanotubes by a basic but optimized electrochemical anodization of a titanium metal foils. Anodic titania nanotubes grown on titanium by a simple anodization in various types of fluoride containing electrolytes have attracted scientific and technological interest in the past decade. This study gives a short summary about this self organizing phenomenon of TiO₂ nanotube structures with varying geometries such as arrays, hexagonal cavities and distinct tubes. Specifically, the question of “what are the driving forces that lead to the impressive self-ordering during the development of anodic oxides in various forms” will be addressed. Why are tubes and pores formed and what are the key parameters controlling these arrangement?

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Light-controlled nucleation and shaping of self-assembling nanocomposites

Controlling self-assembly of nanocomposites is a fundamental challenge with exciting implications for next-generation advanced functional materials. Precursors for composites can be generated photochemically, but limited insight in the underlying processes have hindered precise hands-on guidance. Here we demonstrate light-controlled nucleation and growth of self-assembling composites according to precise user-defined designs. We induce photochemical carbonate generation to steer the precipitation of nanocomposites of barium carbonate nanocrystals and amorphous silica (BaCO₃/SiO₂). By optimizing surface free energies, and reaction and diffusion rates, we induce nucleation following micrometer-defined light patterns. We sculpt the contours and individual features of the growing composite by optimizing the ratio between carbonate generation, precipitation and diffusion rate. Moreover, based on these insights we draw lines of nanocomposites over millimeters with micrometer precision using dynamic light patterns. These results open previously unimaginable opportunities for light-directed self-assembly of functional composites.

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Formation and characterization of amino acids-iron-silicate chemical gardens in flow conditions

The precipitation of arginine and tryptophan amino acids, iron(II) chloride and sodium silicate has been produced experimentally under out of equilibrium flow conditions, generating tubular materials, which have been obtained following the phenomenon of chemical gardens. The surfaces of these minerals with the amino acids could be a scenario for the first prebiotic chemistry related to the origin of the life. Therefore, the formation of these iron(II)-silicate inorganic precipitates in presence of amino acids has been investigated to study how arginine and tryptophan interact or affect to the growth of iron-silicate chemical gardens. The generated tubular structures (Figure 1) have been characterized by different techniques such as X-ray diffraction, Fourier transform infrared spectroscopy and elemental analysis. The results demonstrated the presence of the amino acid in the structure of the chemical gardens. Specifically, the highest concentration of the amino acids in the chemical gardens was obtained when the amino acids were initially placed in the tablet together with the iron(II) chloride. Then, this work showed that arginine and tryptophan amino acids can interact and form part of the structures of iron-silicate chemical gardens.



Figure 1. Photographs of chemical gardens formed with arginine (a) and tryptophan (b).

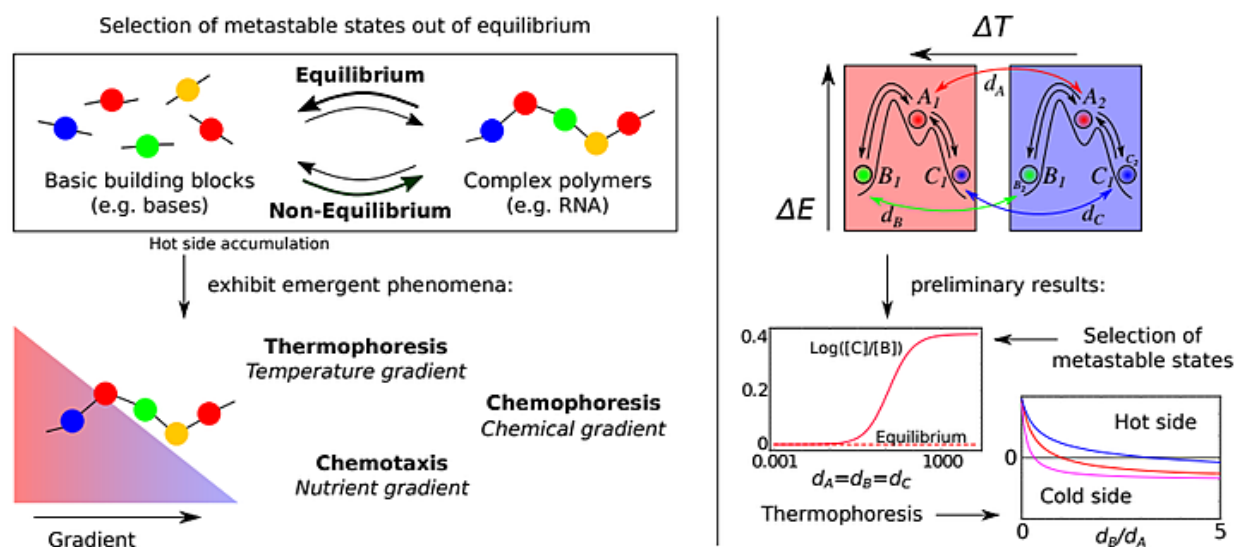
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Selection of chemical states out-of-equilibrium driven by dissipative phenomena

Life has most likely originated as a consequence of processes taking place in non-equilibrium conditions (e.g. in the proximity of deep-sea thermal vents) selecting states of matter that would have been otherwise unfavorable at equilibrium. External sources, and the subsequent thermodynamic necessity of dissipating heat, might have driven pre-biotic molecules against their equilibrium fate. In a simple chemical network, the presence of a thermal gradient selects states participating in faster reactions and contributing the most to the dissipation rate. The furanose conundrum potentially finds a solution within this picture. Furanose is boosted beyond the limits set by equilibrium thermodynamics, exhibiting maximum selection at optimal dissipation, as gauged by the temperature gradient and energy barriers for isomerization. This predicted optimum is compatible with temperature drops found in hydrothermal vents. A byproduct of our approach is that as the complexity of the chemical network increases, the velocity of reaction paths leading to a given state determines its selection, giving rise to non-trivial localization phenomena in state space. Selection of states can also appear in different non-equilibrium processes, as thermophoresis and chemotaxis, potentially providing a further grasp on the role of dissipative phenomena in driving the emergence of complexity at the dawn of life.



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Structure drives dynamics: controlling chemical communication in arrays of diffusively coupled micro-oscillators via compartmentalization properties

Networks of diffusively coupled inorganic oscillators, confined in nano- and micro-compartments, represent a powerful tool for studying collective behaviors observed in biological systems. By taking advantage of a microfluidic technique, we study the dynamics of arrays of diffusively-coupled Belousov-Zhabotinsky (BZ) oscillators encapsulated in water-in-oil single emulsions and in water/oil/water (w/o/w) double emulsions (DEs). In single emulsions new synchronization patterns are controlled by modulating the structural and chemical properties of the phospholipid-based membranes confining the BZ microoscillators. Changes are induced by introducing specific dopants that do not alter the basic backbone of the phospholipid bilayer but modify the membrane lamellarity or react with the chemical messengers. A transition from 2-period clusters (showing 1:a resonance, being a the ratio between the two characteristic oscillating periods in the array) to 1-period antiphase synchronization is observed by decreasing the membrane lamellarity. Unsynchronized oscillations are found when the dopant interferes with chemical communication. In the presence of multi-compartmentalized shells, after an initial induction period, all the oscillators pulsate in phase with halved period with respect to the native one. The experimental dynamics are interpreted within a unique kinetic framework based on the Field, Körös and Noyes (FKN) model, including mass-exchange terms to modulate the coupling strength among successive oscillators.

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Brinicles: Sea-ice tubular precipitates

Brinicles are little-studied tubular ice precipitates which form beneath the sea ice during metamorphic processes of the ice pack. Gravity-driven drainage of super-cooled brine causes freezing of the surrounding sea-water and further growth of the brinicle. Within the scope of a COST STSM, brinicles have been grown and studied in laboratory conditions.

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Formation and growth of lithium phosphate chemical garden

We show that chemical garden^(1,2) can be developed from an alkaline metal precipitate. A flow-driven setup has been used to study the formation of lithium phosphate garden. By injecting sodium phosphate solution into lithium chloride solution a liquid jet appears, on which precipitate grows. The hydrothermal vent-like structure continuously builds upward until a maximum height is reached and the vertical growth stops while the tube diameter still increases. The analysis of the growth profiles has revealed a linear volume growth rate with respect to the injection rate. The expansion in diameter, localized at the tip of the structure, scales with a power law suggesting that the phenomenon is controlled by diffusion and convection.

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High resolution nanoscale chemical analysis of bitumen surface microstructures

Surface microstructures of bitumen are key sites in atmospheric photo-oxidation leading to changes in the mechanical properties and finally resulting in cracking and rutting of the material. Investigations at the nanoscale remain challenging. Conventional combination of optical microscopy and spectroscopy cannot resolve the submicrostructures due to the Abbe restriction. For the first time, we report here respective surface domains, namely catana, peri and para phases, correlated to distinct molecules using combinations of atomic force microscopy with infrared spectroscopy and with correlative time of flight –secondary ion mass spectrometry. Chemical heterogeneities on the surface lead to selective oxidation due to their varying susceptibility to photo-oxidation. It was found, that highly oxidized compounds, are preferentially situated in the para phase, which are mainly asphaltenes, emphasising their high oxidizability. This is an impressive example how chemical visualization allows elucidation of the submicrostructures and explains their response to reactive oxygen species from the atmosphere.

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Pharaoh's serpents revisited, fluid dynamics in confined spaces

Described for the first time in 1821 by Wöhler, the Pharaoh's serpent is a spectacular reaction in which the combustion of mercury(II) thiocyanate gives place to the formation of a serpent-shaped branched solid among other gas products.

The beauty and huge volume of this interesting resulting solid, obtained even with a small amount of reactant, used to make this experiment a perfect toy model for chemistry class demonstrations until its toxicity was discovered.

Despite this early interest as a commercial chemical toy, little research has been done about this phenomena in the past 200 years. In this work we aim at extending the existing chemical characterization of the product material via SEM and microfocus X-ray diffraction, as well as offering a new point of view on the physical aspects of the reaction. We recorded the growth of several of these "serpents" under a Schlieren setup to shed light at the fluid dynamics involved in the formation of the solid and applied μ CT techniques to further explore its structure.

As well as confirming recent results from Miller, T.S(1) regarding chemical characterization, we observed flow and explosions of gas during the formation of the branches, specially those growing downwards; and internal galleries, much larger in size than the intrinsic pores of the material that suggest a tubular growth guided by this hot flow.

We also discussed the similarities this phenomenon shares with another utterly interesting and famous set of reactions, chemical gardens, as its formation, under specific conditions, also exhibits this tubular growth driven by fluid jets so characteristic of the latter.

1. Miller, T. S., d'Aleo, A., Suter, T., Aliev, A. E., Sella, A., & McMillan, P. F. (2017). Pharaoh's serpents: new insights into a classic carbon nitride material. *Zeitschrift für anorganische und allgemeine Chemie*, 643(24), 1572-1580.

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Toward the design of new metal-organic frameworks for CO₂ and H₂O adsorption

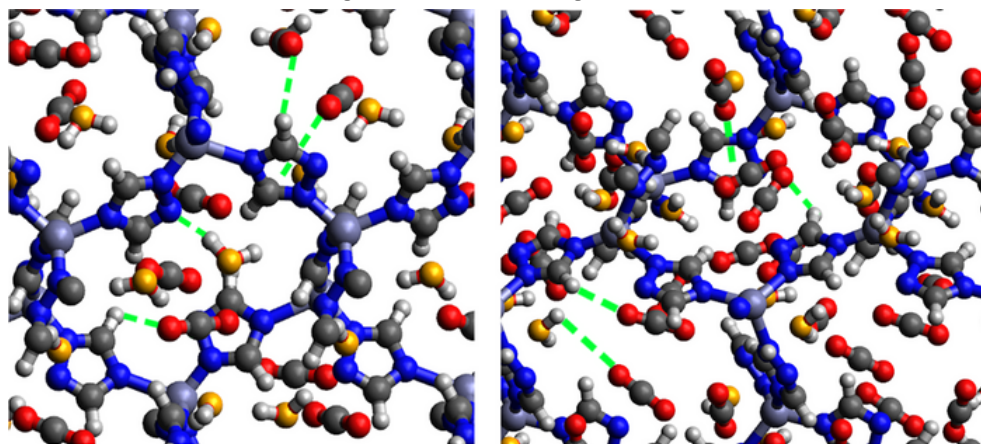


Figure 1: GCMC adsorption sites of CO₂ molecules inside the pores of ZTF in the presence of H₂O near the nitrogen atom of the triazole subunits (left). GCMC adsorption sites of CO₂ molecules inside the pores of ZTF in the presence of H₂O near the Zn site (right). Non-bonded interactions are highlighted. For better clarity, we artificially colored the O atoms of CO₂ in red and that of H₂O in yellow.

In the search for future good adsorbents for CO₂ capture, a nitrogen-rich triazole-type metal-organic (MOF) framework is proposed based on rational design and theoretical molecular simulations. The structure of the proposed MOF, named Zinc Triazolate based Framework (ZTF), is obtained by replacing the amine-organic linker of MAF-66 with a triazole, and its structural parameters are deduced. We used grand-canonical Monte Carlo (GCMC) simulations based on generic classical force fields to correctly predict the adsorption isotherms of CO₂ and H₂O. For water adsorption in MAF-66 and ZTF, simulations revealed that the strong hydrogen bonding interactions of water with the N atoms of the triazole rings of the frameworks are the main driving forces for the strong water uptake by adsorption. We also show that the proposed ZTF porous material exhibits an exceptionally high CO₂ absorption capacity at low pressure, better than MAF-66. In addition, the nature of the interactions between CO₂ and the MAF-66 and ZTF surface cavities has been examined at the microscopic level as can be seen in Figure 1. This figure shows that the interactions occur at two different sites, consisting of Lewis acid - Lewis base interactions and hydrogen bonds, as well as obvious electrostatic interactions. In addition, we have studied the influence of the presence of H₂O molecules on the adsorption of CO₂ on ZTF MOF. The GCMC simulations reveal that the addition of H₂O molecules leads to an increase in the adsorption of CO₂ at very low pressure, but a reduction in this adsorption at higher pressures. More details can be found in Ref. 1.

We thank the COST Action CA17120 Chemobrionics (CBrio) of the European Community for support. This work was supported by two STSM Grants from COST Action CA17120.

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Controlled formation of chemical gardens toward the fabrication of chemobronic materials

Chemobronic systems typically result in the formation of self-assembling abiotic macro-, micro- and nano- material architectures. Chemical gardens are a classical example of a chemobronic system characterised by the spontaneous formation of colourful hollow tubular precipitates following the introduction of metal salt seeds to reservoirs of anionic solution. From a technological perspective, chemobronic processes may hold great promise for the creation of novel, compositionally diverse and ultimately, useful materials and devices. Challenges remain in controlling these reactions at a scalable manner and processing the resulting structures without breakage or loss of alignment. In this work, chemical gardens are grown from a hydrogel-solution interface housed within a customisable synthesis vessel. This platform was adapted with inlet and outlet channels such that reactant solution can be displaced. We demonstrate that systematic displacement of reactant solution with deionised water affords a means to cease chemical garden formation and purify the self-assembled tubular microstructures. Furthermore, displacement of purification media with a polymer phase provides a viable route for fabricating heterogeneous composite materials that incorporate chemobronic components. Analysis of a chemobronic composite by micro-computed tomography (μ -CT) and scanning electron microscopy (SEM) revealed aligned, high-aspect ratio channels running through an otherwise dense polymer matrix. This work sets a precedent for utilising chemobronic principles to create technological relevant constructs, paving the way for the development of novel materials in a variety of application areas, such as regenerative medicine, catalysis and microfluidics.

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Materials grown from the gel/liquid interfaces

Chemobrionics has become an interdisciplinary and modern terminology of chemical gardens. In this talk, we present an emerging class of chemobrionics – the structures grown from the gel/liquid interfaces by using examples of two novel structures, i.e. the (copper-sulfide)/carrageenan cloud and calcium-phosphate tubes. In our system, an upper solution is the “liquid” and a lower carrageenan-based hydrogel is the “gel”. Several parameters including pH, concentration of salts and carrageenan, temperature, time of both phases that influence the growth of the structures have been examined. The structure, composition, properties of the structures was characterized using X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). While the calcium-phosphate tubes possess an intrinsically artistic beauty, the electrical conductivity of the (copper-sulfide)/carrageenan nanocomposite was, for the first time, exploited to be used as a sensor of relative humidity and temperature.

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Self-organized patterning on the soft tubules

Spatial gradients yield self-organized patterns in systems far from equilibrium. Here, we study the organized structures when an acidic solution of chitosan with various molecular weights is injected into a pool of sodium hydroxide solution. The compressive stress generates the surface instabilities on the boundary-aided tubules^(1,2). Wrinkling and folding patterns are monitored by varying the flow rates and the container's orientation. The characteristic properties of the tubes support the physical features of the organized patterns. Furthermore, in the presence of metal salts, the hierarchy of patterns: large-scale buckling and Liesegang-like micropatterning of precipitations have been explored. The flow-driven conditions provide a simple framework for designing pattern formations and control over the structures.

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JERZY MASELKO

The law of chemical self-creation. Transition from nonliving to living matter.

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Tautomeric and conformational switching in a new versatile N-rich heterocycle ligand

A new N-rich triazolo-triazole derivative, 4-methyl-7-(pyrazin-2-yl)-2H-[1,2,4]triazolo[3,2-c][1,2,4]triazole (C₈H₇N₇), bearing a pyrazine residue at 7-position of the triazolo-triazole bicycle was synthesized, and its acid-base and metal coordination properties were evaluated in solution. The results showed amphoteric behaviour and the formation of stable complexes with Cu(II) and Zn(II) in pH intervals in which the ligand is neutral or deprotonated. Computational studies were performed to evaluate the stability of the different tautomers or conformers of the ligand, and the proton position in the neutral and acidic forms. The solid-state isolation of the different tautomers of a chemical compound can be a challenging problem. Tautomers are considered as "living molecules" because of the equilibrium they undergo and the relative amounts of different forms in solution can be altered by physical or chemical factors (temperature, solvent, pH, metal ions, etc..) through the laws of chemical equilibrium(1). In many cases, tautomers with an energy very close to the most stable one cannot be isolated (elusive tautomers). The calculated energy of the 3H tautomer for similar studied triazolo-triazole systems is greater than for the 2H tautomer by only 1 kcal mol⁻¹ or less(2). Despite this the 3H-tautomer should be considered elusive, because it has not been observed in the solid state for any of the pure triazolo-triazole compounds studied. For this reason, we show a successful and reliable way to isolate elusive tautomers by metal complexation.

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Tungstate chemical gardens

Tungstate phases, with formula MWO_4 (being M divalent cation, e.g. Co, Zn, Cu, Mg...), are interesting materials, which have a great potential for the industry (e.g. electrode material for supercapacitators or microwave dielectric ceramics), and mainly as photocatalyst for water oxidation. In view of the interest of these materials for the industry, tungstate anion was chosen to grow chemical gardens using different cations, in particular Co^{2+} (which was first described in Pimentel et al., 2020), Cu^{2+} and Zn^{2+} . The growth of tungstate chemical gardens was carried out using a 1M Na_2WO_4 solution and pellets of $CoCl_2$, $ZnCl_2$ and $Cu(NO_3)_2$.

In all three cases, the chemical gardens grew as balloon-like structures, which floats only when small pellets were used. These balloon-like structures also developed tubes of different shape and size depending on the cation used, as can be seen in Fig. 1. Interestingly, the colors of the membranes formed varied along the time, which indicates the ageing of the precipitates formed. However, only the final membrane, i.e. after the ageing process, could be extracted from the solution without breaking it, which leads to the mixing of the outer and inner solution and the precipitation of a different phase. In the case of tungstate chemical gardens grew using the cobalt pellet, the initial reddish membrane seems to be composed by $Co_2(OH)_3Cl$, which turned violet along the time. Such a violet phase seems to be an amorphous phase composed by cobalt and tungstate. The chemical garden grew using the zinc pellet is colorless at the beginning and turns whitish with time, although the membrane seems to be composed, along all the experiment, by an amorphous phase of zinc and tungstate. When the copper pellet was used, the membrane turns from bluish to turquoise, which is formed by two different phases: $Cu_4(NO_3)_2(OH)_6$ and an unknown crystalline phase.

As this is an ongoing project, the results presented here are preliminary. Future work for this research will include: i) try to determine the unknown phase crystallized using the copper pellet; ii) determine the composition of the initial membrane of these chemical gardens; iii) study the inverse tungstate chemical gardens, i.e. using the Na_2WO_4 as pellet (this has also be initiated); iv) use other cations to grow new chemical gardens, in particular, Ca^{2+} and Fe^{2+}/Mn^{2+} to try to synthesize scheelite and wolframite chemical gardens, respectively; and v) use molybdate anion to try to synthesize powellite chemical gardens, which belongs to the scheelite group, and other molybdate chemical gardens.

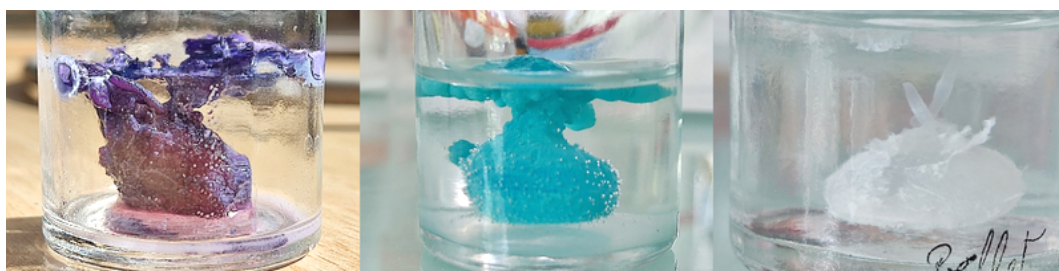


Fig. 1: Tungstate chemical gardens using pellets of Co (left), Cu (center) and Zn (right).

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Metabolism first - why chemobrionics is key to life

Living matter, as a minimum⁽¹⁾, is composed of (i) a metabolism that transforms energy to support the involved reactions e.g., to generate building, (ii) an informational system with inheritable information that at least in part controls the metabolism and (iii) a container that co-localizes the metabolism and the informational system. Further, the system exists in (iv) an environment that provides resources and free energy as well as absorbs waste.

Landauer's principle⁽²⁻⁴⁾ states that an ability to copy and evolve information costs free energy. Therefore, free energy must be a prerequisite for replications to occur, and thus the existence of a metabolism is prerequisite as a converter of available free energy into the work needed in replication. As chemobrionics⁽⁵⁾ explores simple self-organizing processes, some of these processes could act as a "metabolic motor" for an information replication process.

Information in modern life usually refers to sequential information (e.g., in DNA and RNA or proteins), while compositional information⁽⁶⁾ (e.g., the composition of an aggregate) is a less restrictive form of information that can also be replicated. We show how compositional information can be coupled to a metabolism experimentally as well as in simulation in the context of a minimal living protocell⁽⁷⁻⁹⁾.

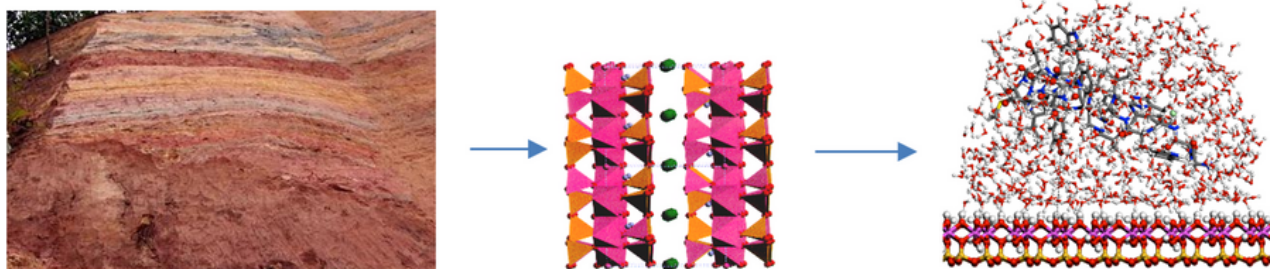
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Adsorption of organics on confined mineral surfaces in prebiotic chemistry.

The first stage of any prebiotic chemical reaction with organics can be the adsorption on a mineral surface. Besides, the interaction of molecules on mineral surfaces is critical for understanding some natural phenomena related with crystal growth, biomineralization, mineral stability, weathering effects, prebiotic chemistry, and also for many applications, such as, catalysis, biomedicine, environment, agriculture, pharmaceuticals, etc. The behavior of molecules and surface reactivity is especially different in confined spaces. Some minerals provide confined spaces, where possible chemobronic scenarios could exist for the first chemical reactions forming the initial complex molecules that were necessary for the precursors of the origin of the Life. These interactions can happen in terrestrial and extraterrestrial mineral surfaces. Several examples of confined mineral nanosurfaces 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 interactions with minerals will be showed involving small molecules, aminoacids, carboxylic acids, metal-organo-metal complexes, proteins, etc. Most of these adsorptions are energetically favorable on minerals formed in the prebiotic earth crust and may have played an important role in the process of chemical evolution in the prebiotic stage and the origin of the Life.



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Are rusticles deep-sea chemical gardens?

Vertical tube-shaped iron-oxide accumulations, named rusticles, obtained from the wrecks of the HMAS Sydney II and the HSK Kormoran at 2480 m ocean depth were chemically analysed along with surrounding seawater. Rusticles consisted of a porous aggregation of iron oxides and high levels of toxic metals and metalloids. Their growth rate is approximately 1 cm per year, predominantly over the areas of the hulls that remained underwater during their service years. A connection between the quality of antifouling paints and rusticle growth and composition was found. A mechanism explaining the formation of rusticles is proposed based on corrosion of carbon steel in deep-seawater, water chemistry, surface complexation of iron oxides and chemical garden formation mechanisms. This study provides a complete rationalization of the process of rusticle formation and deep-water corrosion that is applicable to the long-term integrity of offshore infrastructure. <https://doi.org/10.1002/maco.202112289>

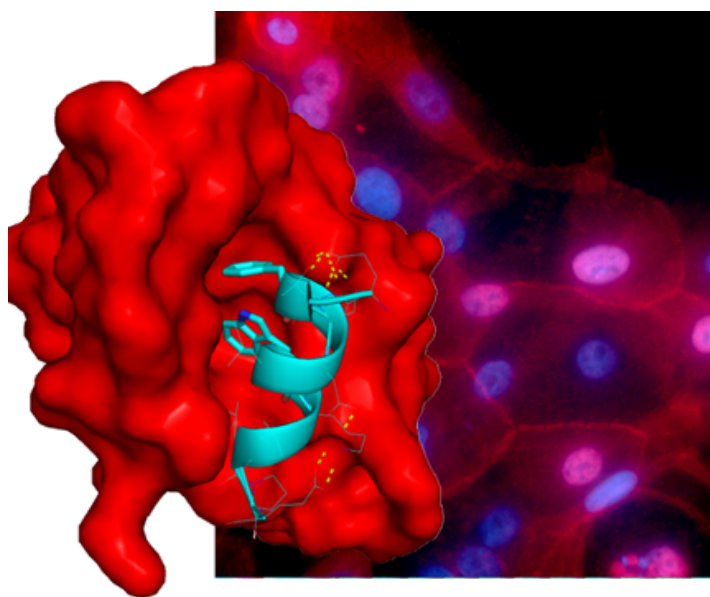
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Computational study of electronic structure and intermolecular interactions of peptides as prebiotic systems

In prebiotic Earth conditions, amino acids and peptides could be the first molecules responsible of the initial stages in the Origin of Life scenario. On the other hand, it is known that cells with new adaptive capacities due to accumulation of mutations are entropically more favored and multiply and survive better; this behavior is observed in cancer cells perhaps that is why cancer is the second cause of death worldwide, leading to the high mortality rate. The knowledge of molecules, such as peptides and proteins involved in tumor processes, allows identifying therapeutic targets to develop new drugs. Computational chemistry allows us to explore and analyze molecules that might have been present in prebiotic stages on Earth at the atomic level. The aim was to evaluate and analyze the stability, the physicochemical properties and chemical reactivity of p53-derived peptides with cytotoxic effect on breast cancer, using quantum-chemical descriptors: chemical hardness, ionization potential, electrophilicity index, atomic charges, and molecular orbitals at the DFT-B3LYP level in an aqueous solution, and its intermolecular interactions by molecular docking. The results showed that hydrophobic amino acids improve the cytotoxic effect. Peptides with three mutations are less stable than peptides with two mutations, hence, a more stable peptide does not necessarily imply a high therapeutic effect. Residues: F19, W22, W23 and their respective atomic charges of nitrogen atoms, as well as its hydrogens of the amide groups of these amino acids, are determinants for the interactions. All these features contribute to the stability and chemical reactivity and consequently, to the binding affinity of p53-derivative peptides with MDM2 protein.



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Electrochemical growth of chemical gardens

The far-from equilibrium precipitation reaction of chemical gardens can lead to the formation of biomimetic and complex structures providing a new route for the rational architectural design of functional materials. Inspired by recent developments in the field of chemical gardens, we put forward a new scientific question: "Is it possible to create an electrochemical garden?" By implementing state-of-the-art electrochemical techniques and using the phenomenon of metal corrosion, we sculpture self-organized structures on a zinc disc-electrode surface by a mechanism similar to that of chemical gardens. A deeper search in the formation mechanism reveals that ion-selective membranes are the driving force for the growth of an electrochemical garden. At last, electrochemical instabilities, introduced under proper conditions, result in the emergence of current oscillations in the region where electrochemical gardens were discovered. Current oscillations sculpture the electrode surface with a variety of self-organized precipitate structures.

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Wormholing the rocks - insights from 4d tomography

Dissolution of porous media introduces a positive feedback between fluid transport and chemical reactions at mineral surfaces leading to the formation of pronounced wormhole-like channels. While the impact of flow rate and reaction rate on the shapes of the wormholes is now well understood, much less is known about the dynamics of their propagation. In this study we capture the evolution of wormholes and their effects on flow patterns by in-situ X-ray microCT imaging of dissolving limestone cores. 4D tomography allows us in particular to correlate the permeability changes in a dissolving core with the advancement of the tip position of the wormhole. Surprisingly, we find that the relation between the two is highly nonlinear, with extensive periods of relatively fast growth of the wormhole which is nevertheless not reflected in any significant change in the overall permeability. We hypothesize that this is caused by the presence of highly cemented regions in the core which act as permeability barriers for the flow. The presence of such regions is confirmed by a detailed analysis of the pore geometry based on the tomographic data. The results demonstrate that the analysis of the wormhole dynamics in 4d tomography can be used to probe the internal structure of the rock.

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Geochemical modeling of solution-mineral interactions in alkaline hydrothermal vents from Lost City

Data were acquired in situ on the fluids emitted by the alkaline hydrothermal vents of Lost City hydrothermal field (on the medio-Atlantic ridge). These data demonstrate the reducing nature of this environment, close to the lower limit of stability of water at high pressure and temperature. Equilibrium with amakinite, the rare ferrous analogue of brucite, is more likely than equilibrium with brucite. This allows for computing pH values in situ close to 8 and thus mildly alkaline, while pH measured on boat board are larger than 10. At Lost City environment geochemical modeling suggests that secondary oxidation lead to a possible control of iron by a chloride-green rust fougérite.

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Investigation of Vaterite Growth under Controlled Constant Composition Conditions

Observations of complex, non-equilibrium morphologies and polycrystallinity of calcium carbonate can be explained within the classical crystallization theory, via kinetic roughening and interface instability induced at high thermodynamic driving forces. To investigate the effects of solution supersaturation and temperature on morphology development of vaterite crystals, seeded growth experiments at a constant composition setup is utilized in this work. Spherulitic vaterite particles were used as seeds for crystal growth experiments in aqueous solutions at a supersaturation range of $S_{\text{vaterite}}=1.5-5$ and at temperature values between 10-60°C. The constant composition conditions were fulfilled by automated titrant addition to compensate for ion consumption, changing ionic strength and alkalinity in the reaction media. The overall growth rate, growth rate constant and the apparent growth order were calculated by using the titration curves. The overall growth rate constant increased with increasing supersaturation and higher temperature, while the growth order decreased from 2.11 to 1.40 as temperature increased from 10°C to 40°C. The new layers of growth developed from the equator of the seed vaterite particles, indicating the anisotropy of the inner structure of the vaterite spherulites. The effects of temperature and supersaturation on the growth morphology were decoupled in a matrix of experiments. At 10°C, the subunit size of the new growing layer was smaller at high S ($S_{\text{vaterite}}=5$) than at low S ($S_{\text{vaterite}}=1.5$), which was consistent with the results of a phase field modelling(1) and our previous findings(2). High supersaturation gives rise to high rate of the growth front nucleation, leading to a high extent of non-crystalline branching, small grain size and compact morphology. By fixing the supersaturation at low value ($S_{\text{vaterite}}=1.5$) and allowing for 50 w% growth, with increasing temperature from 10°C to 40°C, the shape of the subunits changed from long and thin needle-like to short and thick rectangular. When particles were grown to higher extents (200 w% or higher), at low supersaturation ($S_{\text{vaterite}}=1.5-2.5$), the subunit size increased drastically and produced a morphology with hexagonal plates stacked perpendicularly from equator to poles. On the contrary, at high supersaturation ($S_{\text{vaterite}}=5$), the subunit size did not show a significant change due to high rates of growth front nucleation. Our results demonstrate the strong correlation of particle morphology with thermodynamic driving force for growth, which is elucidated within the framework of classical crystal growth theory.

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Organic-to-inorganic transition of chemical gardens

In the emerging field of chemobrionics, spatiotemporal chemical structures construct in far-from-equilibrium systems. In our experiments, when the pre-gel alginate solution is injected into the calcium salt solution, the sol-gel transition develops the budding and tubular hydrogel morphologies. Furthermore, the inorganic tribasic phosphate and organic alginate compounds are reacted with calcium ions competitively, and balloon-type structure forms at higher concentration of phosphate ions. The gelation process, electrochemical potential, and X-ray micro-CT characterizations yield the comparison of transition between the pure organic and inorganic-organic peculiarities. This precise control of the structures and material properties can be used in designing new functional materials.

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An inverse problem in network growth

Nature offers us a wide range of visually similar, branched, self-organised structures – river networks, erosion patterns, blood vessels or leaf venation. Deciphering rules governing the growth of such systems is often hard, and requires the consideration of specific processes governing the extension and splitting of the tips of the network. However, the geometry of the structure itself buries information about its past configuration which is inherently linked to the growth dynamics. We thus formulate an inverse problem - can the growth dynamics be inferred from the analysis of the final geometrical shape?

In our study we focus on growth of thin fingers in a harmonic field, with a growth rate and direction determined by the field gradient at the tips of the fingers. We approach the problems numerically, developing tools to simulate the growth and to extract growth laws of the network based on the final pattern. The latter method is validated against synthetic data and then used to analyse the natural networks.

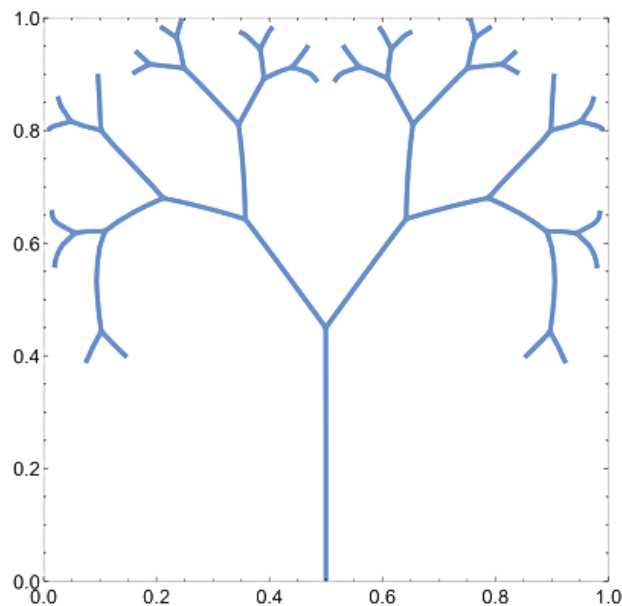


Fig 1. An example of growth simulation. Network grows in a box with zero field boundary condition on the bottom and reflective boundary condition on other walls of the box. Inside the box, Poisson equation for field describing the growth is solved.

POSTERS



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Self-assembled structures from solid cadmium(II) acetate in thiol/ethanol solutions: A novel type of organic chemical garden

Cadmium(II) acetate in tablet form, immersed in ethanol solutions with a high concentration of heptanethiol (30–80 mM), was able to develop self-assembled sail-shaped structures. The solution in which the self-assembled structure is formed is totally organic (both solute and solvent), thus representing a unique case among organic Chemical Gardens. The constituting material for this new Chemical Garden (CG) is made of a single phase, namely a cadmium heptanethiolate with a microcrystalline structure consisting of a central cluster $[Cd_nSn]$. The morphological and structural features were studied using different techniques (SEM-EDS, elemental analysis, ATR-FTIR, ^{113}Cd MAS NMR, XRPD). A crystalline cell for the Cd(II) heptanethiolate cluster was obtained that completely differs from that of the solid phase precipitated by mixing an ethanol solution of Cd(II) acetate with heptanethiol. It follows that the conditions under which the formation of Cd(II) heptanethiolate occurs (slowly from solid, quickly from solution) play a critical role in determining the nature and structure of the precipitating phase.

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Evaluation of chemobionic structures using different types of reactants

Chemobionics are biomimetic complex structures that have different morphology, chemical composition and microstructure depending on the reactants, growth methods and environmental conditions. In this study, chemobionic structures composed of different reactants including calcium (Ca^{2+}), magnesium (Mg^{2+}), zinc (Zn^{2+}) and chromium (Cr^{3+}) salts and silicate (SiO_3^{2-}) and carbonate (CO_3^{2-}) anions were formed with the use of injection method and their growth pattern were evaluated. In addition, the microstructures of some chemobionics that could be removed from the reaction vessel were studied using scanning electron microscopy (SEM). Different growth regimes (jetting, budding) were observed which are highly dependent on the type of constituents. At the zinc chloride experiments, a large unstructured transparent envelope formed in a short time, it was dragged up with the fluid jet and accumulated at the air-liquid interface. Among the metal salts, chemobionics grown from chromium salt had more resistant membrane structure, and so, they were removed from the reaction vessel more easily without rupture. In this experiment, a straight green tube of about 1.0 mm in diameter formed in a jetting growth regime. Calcium chloride salt created wider white tubular structure that grew as a cluster with several narrow tubes at the top surface of this cluster. Unlike other metals, chemobionic structures generated in magnesium chloride experiments showed quite different morphologies in silicate and carbonate solutions. In silicate solution, a narrow transparent tube was observed along the vessel as a result of budding growth in which several nucleation were seen at random locations of structure. When the anion solution was replaced by carbonate, a wider cluster-like chemobionic was formed instead of a long tube and the verticality of the structure grown with carbonate solution was smaller than in silicate case. Obtained micrographs from SEM analysis shows that the textures of chemobionics are clearly different for the different reactants and these microstructures are highly consistent with the literature. These differences in growth regime and morphologies could be due to the variations of reactivity, solubility and density of reactants.

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The role of amorphous and crystalline domains involved in the self-assembly of biomimetic compounds and their time-frames evolution monitored by dynamic light scattering and nanogravimetry techniques

The self-organized of nano-micro chemistry structure and bio structures enclosed in the definition of chemobiotic compounds has opened always a debate about the amorphous/crystalline nature of bio-fragments with some peculiar differences on their assembly and related energy balance(1). Also, if it is well known that concomitant variables play a role on the final geometries, remain however crucial its packaging assemblies of repeat units in a time frame-by-frame regime, realized as an evolving performance of chemistry gradients. In particular biomimetic structure which seem to arise from seeds agent or induced by densities change to define complex membrane spontaneously, evolve to a major energy stability plan of system(2). Then some hypothesis on energy involved can be formulated. In order to follow the primary step which evolved spontaneously to colloids and their tubular shape, the optical and thermal analysis techniques, such as dynamic light scattering and thermal analysis, were performed on some bio-samples. The experimental phases were performed in real time monitoring the phase change starting from reference samples, perfectly clear, to nano-micro phases to study their stable structure by DSC and TGA analysis. Furthermore, our work will be focused to correlate the dynamic light scattering analysis(3) with the nanogravimetry analysis(4) in order to quantify crucial instant before the micro structure spherulitic assembly. Data expected will be to consolidate the knowledge on the time frames evolution in a medium solvent oriented to a regime of colloid state.

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Detection of glyphosate by surface-enhanced Raman spectroscopy.

Glyphosate is one of the most commonly used pesticides on global basis. It is used for the control of weed growth but it is proven that it can persist in the environment. There are numerous studies indicating the harmful effects of glyphosate on human health(1). In this work glyphosate is detected by surface-enhanced Raman scattering (SERS). SERS has proven to be an effective technique for detection of various analytes in low concentration(2). The SERS substrates used for detection of glyphosate water solution were silver and gold nanoparticles (NPs). The calculated mean particle size from TEM analysis for the Ag NPs was about 32 and 72 nm, while Au NPs had an approximate diameter of 27 nm. The synthesized NPs were quite stable in aqueous media and had zeta potential -34.9 (Ag NPs) and -12.9 mV (Au NPs). Samples were analysed using 532, 633 and 785 laser excitations. SERS spectra quite varied when Ag or Au NPs were used. For example, at 532 nm excitation with Ag NPs two prominent SERS glyphosate peaks are at 771 cm^{-1} and 1052 cm^{-1} . Using Au NPs and 633 nm excitation, the most prominent peaks are at 1024 cm^{-1} and at 1313 cm^{-1} . Au colloidal solution and 785 nm excitation resulted in spectra where the most pronounced peak is at 1012 cm^{-1} . The results suggest different ways of glyphosate absorption to the Au and Ag NPs which is dependent on the pH of the solution. The lowest limit of detection of 100 nM was obtained with silver NPs using 532 nm laser excitation.

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Experimental and theoretical studies on the intercalation of organics into the Mg₂Al and Zn₂Al layered double hydroxides

Double Layered Hydroxides (LDH) are layered minerals that provide nanoconfined spaces in the interlayer space being a possible scenario for adsorption of organics in the prebiotic chemistry. Besides, these minerals have been extensively investigated in recent years due to its promising applications in areas such as nanodeposits for drugs delivery, catalysis, and as components in optical, electrical and magnetic devices. The most widely studied LDHs contain both divalent and trivalent metal cations, a generic formula for these LDHs may be written as $[M^{2+}_1-xM^{3+}_x(OH)_2][An^-]_x/n \cdot yH_2O$, where M^{2+} may be Mg^{2+} , Zn^{2+} , or Ni^{2+} and M^{3+} can be Al^{3+} , Ga^{3+} , Fe^{3+} , or Mn^{3+} . A^{n-} is a non-framework charge compensating inorganic or organic anion, e.g. CO_3^{2-} , Cl^- , SO_4^{2-} , RCO_2^- . In this work, ionic form of the non-steroidal anti-inflammatory drug naproxen (NAP) was intercalated by ion exchange reaction from pristine Layered Double Hydroxide (LDH) materials with $Mg_2Al(OH)_6-Cl$ and $Zn_2Al(OH)_6-Cl$ compositions. Then, atomic modelling calculations were performed at quantum mechanical level based on Density Functional Theory and classical force fields based on empirical interatomic potentials for the sodium naproxen salt and for the first time for the LDH-NAP systems. Calculations revealed that NAP anions assume different dispositions when in the NaNAP crystal or when intercalated into LDH. Infrared wavenumbers calculations agreed with the experimental results and supported bands attribution.

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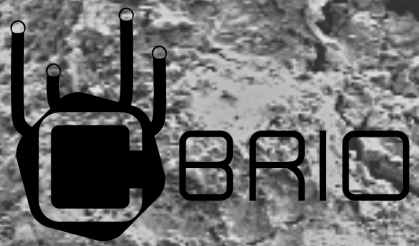
Rheological properties of rotator and crystalline phases of alkanes

The simplest organic molecules, alkanes, with intermediate chain lengths ca. 16-50 C-atoms, are known to crystallize by passing through intermediate phases called rotator phases, *R*. These phases are observed between the fully ordered crystalline phases and the isotropic liquid phase(1). The molecules in *R* phases possess long-range positional order, while preserving certain mobility to rotate around their long axis. This results in a complex visco-plastic rheological behavior which plays a key role for processes observed in living and non-living nature, for example in disperse systems, lubricants and for the mechanisms of cuticle self-healing layers in plants and insects(2).

Data for the rheological properties of such peculiar materials below their melting point, T_m , however, are missing due to specific difficulties in the rheological experiments. In the current study we developed a procedure allowing us to distinguish the phase transitions between the separate *R* phases and between crystalline and rotator phases using rheological measurements. The experiments were performed with alkanes with chain length between 17 and 30 C-atoms and with several alkane mixtures.

The obtained results show that the storage and loss moduli of the *R* phase are ca. 10-times lower than those of respective *C* phase. We found that the rheological properties of the *C* phases depend mainly on the subcooling below the crystallization temperature, while the *R* phases become softer with the increase of the alkane chain length. These results were explained assuming that the rheological properties of the crystal phases are determined mainly by the sliding of the ordered crystalline domains with respect to one another, while in the *R* phases we have multiple defects (kinks) in the molecular structure whose number increase with the alkane length which soften the structure. The proposed methodology and the obtained results serve as a solid basis for further rheological studies of this important class of technological systems.

1. D. Cholakova, N. Denkov. Adv. Colloid Interface Sci. 2019, 269, 7-42.
2. N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova, S. K. Smoukov. Nature 2015, 528, 392-395.
3. D. Cholakova, K. Tsvetkova, S. Tcholakova, N. Denkov, manuscript under review.



VIDEOS

MATHIS LEEMANN

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Mathis Leemann, Saniya Ustun, Jan Havlík, and Jitka Čejková

If you have a garden and a library, you have everything you need

The title of our 5-min length audio-visual chemobrionics related project is a quotation by Cicero. It was chosen with the aim to show, that in the same way as Roman garden was designed for thinking, philosophizing and discourse, the chemical gardens can also open the door to philosophical questions such as what is life and how it originated. Our video focuses on showing the beauty of silicate chemical garden that are made from cobalt, copper, iron, calcium, nickel and a mixture of metal salts which have never been presented. The viewer will be puzzled by the hypnotic slow growth of the structures and the manifold of colors they can produce. Tiny aerial air bubbles, flowing inner solutions, thick and alienlike structures changing colors will let the audience perplexed, dreamy, wondering why nature is presenting such delightful sight. Furthermore, extracts of Doktor Faustus by Thomas Mann, The Origin of Life by John Desmond Bernal and Mechanism of life by Stéphane Leduc are added to deepen the experience. The inspiration for this audio background was taken from Julyan Cartwright's works focused on the chemical gardens, their history and mentions in the literature.

SANIYA USTUN

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Saniya Ustun, Mathis Leemann, Jan Havlík, and Jitka Čejková

How to create a chemical garden

Our educative video "How to create a chemical garden" is aiming at high school students and other people interested in chemistry. It presents step-by-step guideline on how to grow a chemical garden at home or in a lab, including safety instructions, all the materials and methods needed. The tutorial also includes a full explanation of working principles and a detailed description of the chemical garden growth mechanism. The video takes 3 minutes, so it is long enough to explain the important details and on the other side short enough to keep the attention of the audience. At this moment the video and its subtitles is in English, however the other language mutations are planned and all of them will be published on YouTube channel of Chemobrionics COST Action.

IVAN VALENT

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Táňa Sebechlebská and Ivan Valent

Modelling ion transport to charged surfaces: Dynamics of electric double layer formation

Ion transport plays an important role in many self-organization processes such as crystal growth, periodic precipitation, formation of colloid particles, biological morphogenesis, and many others. The ionic flows are driven by gradient in both chemical and electric potentials and the resulting behavior is usually complex showing nonlinearities in time and space. We have developed computational tools for modelling time-dependent electrodiffusion processes based on the first principles using the Poisson-Nernst equations coupled with the Poisson equation (PNP theory). As an example, we demonstrate application of such numerical approach to model dynamics of an electric double layer (EDL) formation at a surface subject to a sudden charge injection. Both the Gouy-Chapman (GC) and Gouy-Chapman-Stern (GCS) models of EDL were examined. The results are illustrated by Figure 1.

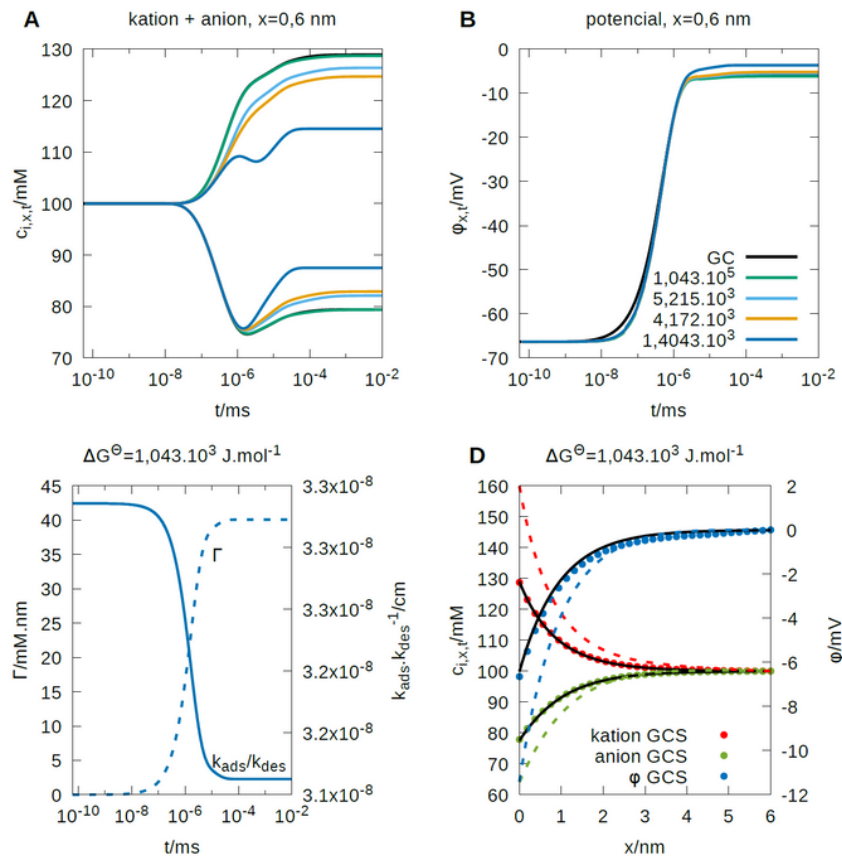


Figure 1. Evolution of EDL after coulostatic injection ($-8,54 \text{ mC m}^{-2}$) for various desolvation energies of the cation. A: concentrations of cations (upper lines) and anions; B: electric potential; C: surface concentration of cations (dashed line); D: spatial profiles of ion concentrations and electric potential in the steady state (dashed lines for the GC model).

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