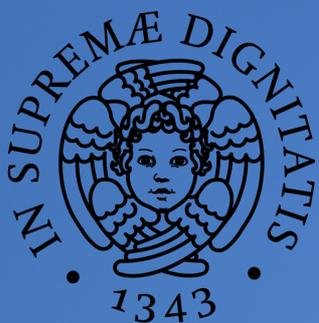




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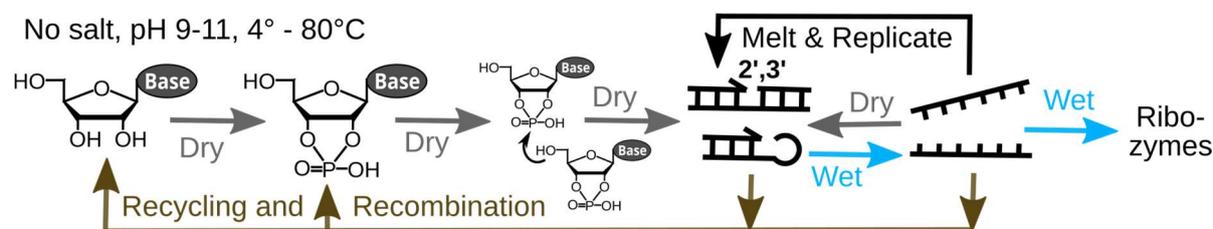
Dew RNA world: starting evolution from the solid state

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Understanding the emergence of life means to recreate a physico-chemical system that is capable of open ended Darwinian evolution. The more simple it is and the less special compounds and conditions it require, the more probably it can occur. We will discuss experiments that imply a fundamentally simplified RNA world that starts from the solid state. We revisited polymerization and templated ligation of RNA from nucleotides with 2',3' cyclic phosphates. They oligomerized under alkaline conditions at pH 9-11 without catalysts or added salts, reaching 10 mers in a day, both in the 'dry' state or in the wet-dry cycling at a heated air-water interface¹. At high temperatures, the oligomers were dominated by G, but cold and dry conditions, achieved in the planet simulator of McMaster University, yielded random sequences of GC or GCAU. The yield for oligonucleotides which contain still a functional 2'3'-phosphate peaks between 4°C and 25°C. Under similar conditions, phosphorylation from Trimetaphosphate and templated ligation was observed under such "dry" conditions. We envisage therefore a one pot reaction from nucleosides to the replication of oligomers. The separation of strands would be provided by the condensation of salt-free dew droplets which also dissolve new feeding nucleosides from the solid state, triggering another cycle of phosphorylation, polymerization and templated ligation in the "dry" state. A likely driving for this mechanism would be the day night cycles. We are searching for short RNA sequences to enhance this replication by ligation in the dry state, leading to a much simplified RNA world to trigger self-amplified biological evolution of functional sequences. In deeper layers of the porous rock, we envisage that air-water interfaces drive more sophisticated Ribozymes. We shown that CO₂-water interfaces can drive the replication towards sequence lengths of up to 1300 mers, overcoming the tyranny of the shortest by the length selective accumulation under evaporation-based capillary flow². The long strands separate under the pH and salt cycling provided by the Hadean atmosphere of CO₂. While the replication was still implemented by a polymerase to enhance kinetics, preliminary results show a similar strand separation for Ribozymes under elevated Mg²⁺ concentrations.



¹ doi:10.26434/chemrxiv-2022-zwh2t (2022)

² Nature Physics doi.org/10.1038/s41567-022-01516-z (2022)

3D Presentation: ESA's space mission Rosetta-Philae - the detection of organic molecules on a cometary nucleus

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ESA's Rosetta mission had made spectators from all over the world dream: On 12 November 2014, the Rosetta mission posed the little robot Philae on the nucleus of comet 67P/Churyumov-Gerasimenko. The Rosetta Space Probe collected information about the composition of the comet nucleus and the origin of the Solar System.³ Rosetta is the first probe to place itself in orbit around the comet and to place a lander on the surface of a cometary nucleus. After 10 years of travel, the separation of the Philae lander from the Rosetta orbiter was carried out on November 12, 2014. Twenty minutes after Philae's landing and bouncing on the cometary nucleus, the COSAC instrument successfully performed the first chemical analysis of cometary surface material that cannot be analyzed from the Earth. 16 organic molecules were identified in the cometary sample by using COSAC's MS-only mode.⁴ The first results of the analysis of the cometary nucleus surface by the COSAC instrument will be presented along with a new interpretation of the data.⁵ These in situ cometary results will be interpreted in relation to laboratory experiments that allow for the simulation of cometary ices showing amino acids,⁶ aldehydes⁷ and ribose⁸ as produced in form of simulated cometary ices in the laboratory.⁹

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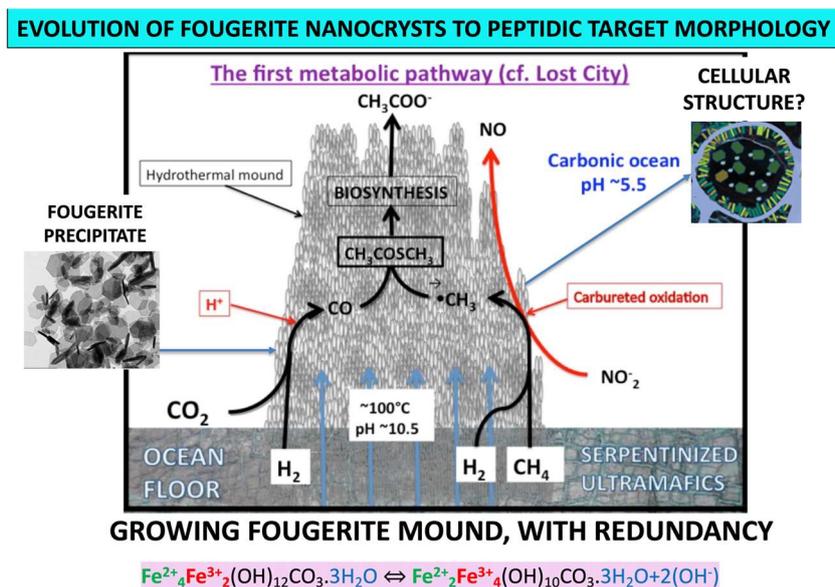
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Fougerite makes manifest the link between inanimate and animate matter

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A submarine mound comprising spontaneously precipitated nanometric fougerite (green rust) with subordinate FeS separating alkaline $H_2 > CH_4 > HS$ -bearing hydrothermal fluids from iron-bearing carbonic ocean, provides both the appropriate disequilibria and the electro-chemomechanical means to convert those disequilibria to an ordered metabolism [1-3]. Naturally selected for “least action” fougerite, with its bilaterally active redox-sensitive structures that also limit degrees of freedom, is capable of dynamic agency, so filling the divide between the material and the living world – a mineral entity “trying to do things” [4-7]. It is the “truly minimal agent” that has the ability and unpredictability to exploit the steepest gradients and put them to work [8,9]. It also heralds the emergence of complex sentient beings with capabilities beyond those of mere particles [10-12]. The synthesis and output of the first organic polymers in fougerite’s interlayers had the effect of breaking the routine of simply generating more and more fougerite at the submarine alkaline mound, thus forcing the system toward a new target morphology – an attractor state [13], one that approximates a homeostatic cell while retaining the agencies of fougerite’s interior surfaces (Figure) [14]. We hold this to be an early stage on the path to Life as “a combined metabolic-inheritance system that becomes embedded in its own time” [15].



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Precipitation patterns and reaction fronts in radial geometries

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Motivated to understand how mineralisation reactions can transform CO₂ dissolved in water into solid carbonate precipitates in the framework of Carbon Capture and Sequestration (CCS) techniques, we study both experimentally and theoretically the properties of calcium carbonate precipitates in radial flow conditions. We find that the amount and spatial distribution of the solid phase depends on the injection flow rate and concentrations. To understand the properties in advection conditions of the related $A+B \rightarrow C$ fronts, we derive the temporal scalings of the evolution of the front position, reaction rate, width of the reactive zone and amount of product formed. We further discuss how the radial geometry of injection can change the properties of chemical fronts with regard to the rectilinear case.

Earth's First Bioreactors: The Origin of Cells Meets Bioengineering

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Cells are the most complex systems known at the nanoscale, but they were not designed or built from scratch by engineers. That was a task of Nature, which makes Bioengineering a very special kind of engineering. In the last decades, bioengineering has mostly focused on a reductionist approach, deconstructing cells to engineer their parts (e.g. genetic engineering and protein engineering) or building de novo systems that imitate life and its parts (e.g. biomimetics and synthetic biology). There must exist, however, more general principles of Bioengineering that will be vital in the long road of research towards the origin of the first cells. In my work I have identified some of these as communication and cooperation in complex systems, (self-)organization, maintainability and integrity, efficient energy use, among others. In this talk I will give a general perspective of how we can transition from a paradigm of chemical retrosynthesis focused on the individual parts of a cell to one where we look at how they function together. This perspective will be supported by examples from my own work that include i) the study of very early life (e.g. the last universal and bacterial common ancestors), ii) the prediction of early autocatalytic metabolic networks, iii) the study of energy efficiency in early metabolic networks, and finally iv) what makes hydrothermal vents the geochemical setting that aligns best with the predicted, dynamic and necessary physical-chemical niche for the origin of cells.

Towards Understanding Self-Assembly Behavior of a Fungal Hydrophobin (RodA) at Air/Water Interfaces through Comparative Molecular Dynamics (MD) Analysis

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Hydrophobins (HFB) are small, secreted, cysteine rich proteins of filamentous fungi. With large hydrophobic patches on the protein surface, hydrophobins take part in various extracellular processes in the life cycle of fungi. These multi-functional proteins are assembled into simple amphipathic layers or rodlet-like structures on the surface of the conidia or at hydrophilic/hydrophobic interfaces. But, the mechanism behind the layer formation and their conformational states in water/air-water interfaces are not fully elucidated yet. An opportunistic human pathogen, *Aspergillus fumigatus* is known to express a diversity of HFBs. RodA is the main HFB coating the fungal structures. RodA was shown to aid in invasion by masking lectins on the spore surface from detection by the immune system. Moreover, the fibrillar structures of the HFB rodlets are highly similar to amyloidogenic proteins which play a key role in neural and metabolic disorders. Understanding the self-assembly behavior of these proteins may shed light into the protein aggregation mechanisms leading to various life processes as well as human disorders. Therefore, these findings encourage us to study the behavior of HFBs at the interfacial environments and monitoring self-assembly of RodA monomeric structures at the molecular level. In previous studies, it was hypothesized that different loop regions between conserved cysteine residues play a key role in self-assembly and formation of fibrillary structures on the conidia surface. In this study, MD simulations of 4 monomeric RodA HFBs of *A. fumigatus* in solution, at air/water interface were conducted using NAMD and initial steps of aggregation patterns of biomolecules both in solution and at air-water interface and key interactions play a role in assemblies were determined by trajectory analyses. Varied initial orientations of 4 monomers were generated and tested to understand the effect of the initial interacting regions of monomers on the stability of the HFB assemblies in both environments.

How Molecular Forces and Rotating Planets Create Life

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Origins research has been reconceptualized as a problem in colloidal chemistry and chemical engineering; the reconceptualization provides fresh insights into what life is and how and where life emerged during the Archaean eon.

At a molecular level, non-covalent molecular forces ensure the colloidal stability of growing and dividing prokaryotic cells, crowded with closely interacting biomacromolecules. The key molecular forces are hydrogen bonding (hydration, the hydrophobic effect), screened electrostatic forces and “hard-core” repulsions; their commensuration clarifies physicochemical conditions necessary to create the living state of matter. These forces, together with biochemical reactions, control the spatiotemporal sequences of cytoplasmic, sol-gel transitions during the cell cycle—the metabolic and genetic processes of being alive. Colloidal theory predicts that gelled (concentrated) biomacromolecules are separated by ion-conducting channels regulated by biochemical “tagging” reactions, such as phosphorylations, methylations and many others. To be alive, the Last Universal Common Ancestors had a similar level of colloidal and molecular sophistication already about 3.5 billion years ago.

At a macroscopic (chemical engineering level), the rotating Earth can be viewed as a chemical reactor, where multicomponent and multiphase chemistry took place in the atmosphere, hydrosphere and lithosphere. When proto-organic molecules with the CHONSP atoms accumulated in intertidal zones, their huge variety became simplified by cyclic phase separations (self-purifications) in colloidal, briny sediments rich in potassium and magnesium ions (cf. the Usiglio sequence of marine evaporites). These ions, not coded for in organismal genomes, participated in the evolution of proto-proteins and proto-RNAs, which are known to functionally depend on magnesium and potassium ions. Thus, proto-biomacromolecular evolution took place within geochemical, colloidal microspaces of briny sediments patterned by wet-and-dry tidal cycles, from which the first life cycles of prokaryotic-like organisms emerged “on the fly.” The persistent, stoking action of the tidal energies is the agent—the creator of first life. The molecular and macroscopic processes have been arranged as a jigsaw puzzle of eight evolutionary stages, connected by the crowding transition—when molecular forces between crowded biomacromolecules become commensurate. The jigsaw puzzle of life’s emergence suggests a number of experiments with multicomponent, concentrated compositions using cyclically driven chemical processes (their cyclic character echoes in today’s PCR processes of the amplification of DNA segments). The jigsaw puzzle also explains the physicochemical origin of eukaryotic cells in the first three billion years of the Earth’s chemical and microbial evolution.

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The effect of the presence of amino acids on the precipitation of inorganic chemical-garden membranes: Biomineralization at the origin of life

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The formation of iron(II)-silicate chemical gardens in presence of the amino acids arginine and tryptophan has been investigated to study how the amino acids affect the growth of iron (II)-silicate chemical gardens. With different techniques, of X-ray diffraction, Fourier transform infrared spectroscopy, elemental analysis and scanning electron microscopy, we analysed the inorganic precipitates formed. The results demonstrated the presence of the amino acid in the structure of these chemical gardens. Specifically, the higher 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. The presence of amino acids alters the surface during the formation of iron silicate chemical gardens. The amino acids do not precipitate as crystalline solids but as an amorphous phase or isolated molecules. We have detected that the amino acids adsorb chemically to the iron cations of the chemical garden surfaces by hydrogen bonds and coordination complex with the carboxylate groups.

This work shows that if life first incubated within mineral membranes, for example within hydrothermal vents on the ocean floor of the early Earth, the hypothesis of a biological takeover of the self-assembled mineral structures with the incorporation of molecules of prebiotic chemistry such as amino acids is feasible. The first proto-cells could have manipulated the mineral membranes that formed their compartments in order to control their metabolism. This biomineralization process would have been the beginning of evolution, and with it, of biology.

Dichotomic Classes and Entropy Optimization in Coding Sequences

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In this work we investigate the existence of universal optimizations in coding sequences. Usually, these take the form of correlations between nucleotides that are observed in many organisms and that might be related to error correction and energy optimization. We address the problem in terms of a mathematical model of the genetic code introduced in Gonzalez(2008) and further studied in Gonzalez et al.(2008, 2009, 2016), Giannerini et al.(2012). This new paradigm leads to the definition of dichotomic classes that can be seen as nonlinear functions of the information contained in a dinucleotide. Such classes represent precise biochemical interactions and are used as a binary coding scheme for DNA sequences. We study the entropy structure of dichotomic classes derived from coding sequences under different probabilistic assumptions on the underlying process. The theoretical derivations are tested by using the new probabilistic results of Giannerini and Goracci (2018) on the small sample asymptotics for the entropy measures used. The results indicate that the paradigms of information/communication theory are essential for the understanding of the organization of genetic information.

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Giant Vesicles as Tunable Reactors for a Bottom-up approach to Artificial Cells

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Cells are the most amazing chemical laboratories developed over billions of years of natural evolution. Even the simplest biological cells are able to maintain and organise thousands of parallel processes structured in chemical networks and accomplish complex tasks essential for life, such as metabolism, maintaining homeostasis, growth, self-division, self-replication, and adapting and responding to environmental stimuli. In order to master processes of increasing complexity, chemists are taking inspiration from nature to shift from a reductionist towards a systemic approach for designing new research protocols and achieving technological and scientific goals. Therefore, fast-growing disciplines, such as synthetic biology and systems chemistry, are creating and engineering artificial and synthetic systems able to reproduce life functions based on bottom-up approaches.¹⁰ This new view showed to be very successful for the design of nano- and micro-objects (particles, micelles, vesicles, etc.) and their applications (e.g., smart materials, targeted drug delivery, biocompatible devices, etc.).¹¹ Moreover, a systems chemistry approach to cell imitation is thought to be a valuable contribution to understanding fundamental open questions in the origin of life studies.¹² Giant vesicles (GVs), i.e., water-in-water compartments defined by an amphiphilic bilayer made of phospholipids (liposomes), fatty acids, synthetic polymers (polymersomes) or their combinations (hybrid vesicles), are becoming the most used model for studying artificial cells.¹³ Here we present an overview of the methods used for the encapsulation of the chemicals into the GVs and we describe the dynamical features of a few model systems able to accomplish complex tasks, such as cell-cell communication, self-division, mineralization and membrane deformations.

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The $\text{Fe}(\text{OH})_2$ Amakinite – $\text{Mg}(\text{OH})_2$ Brucite – $\text{Fe}(\text{OH})_3$ system : thermodynamic data, experimental evidence and implication for fougérite formation by direct co-precipitation or by secondary oxidation in solid phase

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Fougérite, the natural mineral of the green rusts group, incorporates Fe(II), Fe(III) and Mg(II) in a brucitic layer, defining thus a ternary solid solution. The Fe(II) end member is known as amakinite, in strongly reducing conditions, present in iron meteorites but can be oxidized by water. Field data from hydrothermal events in Lost City suggest that amakinite may form in conditions similar to those that could have favoured life's emergence in Hadean ocean and be later oxidized into fougérite. However, experimental data obtained at laboratory show that direct precipitation of Mg and Fe(II) hydroxides leads to separate precipitation of the pure end members, while Fe(III) hydroxide in a brucitic structure is unstable and remain virtual. This paper presents a set of thermodynamic data for the three end members and discusses the conditions of formation of fougérite on the basis of the reaction scheme of polymerization of Fe(II) in solution, using the partial charge model by Jolivet and the differences of Allred-Rochow electronegativities of the metals.

Controlling self-assembly by chemical fuels

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Looking at nature, we see that living materials with biological functionality, such as the actin or microtubule (MT) cytoskeletal network, achieve dynamics as well as supramolecular structures with the same protein building blocks. In other words, the components can assemble, but also react (i.e., tubulin is also an enzyme that hydrolyses guanosine triphosphate GTP), which in turn affects the assemblies. In this way, living systems use chemical fuels (e.g., GTP) and self-assembly to create a built-in chemomechanical interaction. Moreover, such networks operate in sustained out-of-equilibrium states at the onset of oscillations,¹⁻³ which results in rapid response and adaptivity. Here, we present our recent⁴⁻⁶ reaction cycles in solution and gels, where interesting new behaviors were found, such as supramolecular size oscillations, traveling polymerization, or transient disassembly. We hope such reaction cycles form the basis of new life-like materials where material properties are fuel (and waste) dependent.

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Iron (III) chloride chemical gardens over carbon steel: electrochemistry and mineralogical composition

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This presentation gathers all the results from the experiments carried out to prove/disprove the rusticle formation hypothesis proposed in the paper “Deep-sea corrosion rusticles from iron-hulled shipwrecks”. It includes electrochemical and mineralogical analyses of the chemical gardens and a comparison with the naturally formed ones. DOI: 10.1002/maco.202112289

The role of self-assembly of biomimetic compounds compared to polymer amorphous and crystalline phase by dynamic light scattering, DSC and TGA techniques

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The self-organization of nano-micro chemistry structure and bio-structures attributed to the definition of chemo compounds has recently opened a debut about the amorphous / crystalline nature of bio-fragments with some peculiar differences on their assembly strategies and related energy balance¹. 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 step-by-step regime, realized as outcome of an evolving performance of chemistry gradients. In particular biomimetic structure which seem to arise from seeds agent or from induced density changes to define complex membrane spontaneously, evolve to a major energy stability plan of the system². Then some hypothesis on packaging exchange energies involved in the assembly steps can be formulated. In order to follow the primary step which evolved spontaneously to colloids and then to 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 solution by related light scattering during significant 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 analysis³ with the nano gravimetry analysis⁴ in order to quantify crucial instant before the micro structure of spherulitic assembly. Data expected will be able to consolidate the knowledge fundamental on a restrict field where the time frames evolution in a medium solvent are oriented to a regime of colloid state.

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Vacancy Defect and Its Aggregates with Bjerrum Defects in s-I and s-II type Clathrate Hydrates

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" Clathrate hydrates are cage-like structures of water molecules that host guest gas molecules. The particular hydrate structure formed depends on the size and chemical interactions of the guests that react with water/ice to form the hydrate. Two most common ones that are a subject of this study are structure I (sI) and structure II (sII). We will present a density-function theory (DFT) study of vacancy defect and its complexes with Bjerrum defects in terms of structure, energetics and dynamics. These defects are believed to be important for the formation of these structures and transport of guest gas molecules through the cages of host water."

The mysterious force called osmosis

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In physical chemistry, the flow of solvent (water) across a semi-permeable layer (membrane) to locations of high concentrations of dissolved species (solutes, such as ions) is called osmosis. The osmotic pressure is seen as the force that develops when solvent flows (for instance against gravity) and builds up a hydrostatic pressure.

But why does water do this? From overall thermodynamic energy analysis, we know that for the system as a whole it will do this, as the total energy goes down (the concentration of solutes becomes more equalized out). But how does an individual water molecule ‘know’ how to do this? What force acts on it?

The analogy with a gas, such as that it is because molecules ricochet against outer walls, does not work, because ions in water don’t have ballistic motions where they would bounce again and again against the outer walls. An explanation that describes the water as molecules that like ions distribute over slots and diffuse to lower concentration (activity), is not reasonable; the phenomenon should also exist (in theory) when the water is continuum fluid, without a molecular character. Or in other words, the molecular character cannot be part of an explanation. There are several papers –often by emeriti professors– that try to make sense of the phenomenon, but the papers often lead to more questions than answers.

I will explain that besides the above statement of overall thermodynamics, we know two things: apparently water flows because of hydrostatic pressure gradients and osmotic pressure gradients (and frictions with walls and solutes); osmotic pressure is a direct measure of solute concentration, and at membrane outer interfaces we have mechanical equilibrium. These elements together provide a comprehensive and successful framework to describe osmosis, to predict it quantitatively. However, it does not answer the question as to why the water molecules act in this way, what is the local force that they are subjected to.

GCMC studies of adsorption of sulfur dioxide and hydrogen sulfide by metal organic frameworks

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The advances in using metal organic frameworks (MOFs) as adsorbent materials for CO₂ capture have been already investigated owing to their favorable properties such as their large surface area, permanent porosity and tunable pore size/functionality. In search for low carbon future and good adsorbents for CO₂ capture, a nitrogen-rich triazole-type metal-organic framework (named ZTF), is proposed on the basis of rational design and theoretical molecular simulations. The structure of proposed MOF is constructed by modifying MAF-66, where the amine-organic linker is replaced by a triazole. We used grand-canonical Monte Carlo (GCMC) simulations based on generic classical force fields to predict correctly the adsorption isotherms of CO₂ with and without the presence of water at different temperatures. We show that the proposed porous material exhibits exceptional high CO₂ uptake capacity at low pressure, better than MAF-66.1 In addition, we have studied by using GCMC simulations the capture of highly toxic gases as SO₂ and H₂S by ZTF and MAF-66. 2 Results show high capacity of investigated MOFs for SO₂ and H₂S adsorption. The nature of the interactions between H₂S/SO₂ with the pore surface cavities was examined at the microscopic level. SO₂ is adsorbed to the pore surface by two types of hydrogen bonds, either between O of SO₂ with the closest H of the triazole 5-membered ring or between O of SO₂ with the hydrogen of the amino group. These interactions depend on the orientation of SO₂ inside the pore. Finally, the calculations demonstrated that the principal interactions between H₂S and pores were found at the nitrogens of material by a relatively strong hydrogen bonds.

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Self-organization of micro-structures on a bitumen surface

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Exploring the bitumen character on a molecular level and investigating its self-organisation on micro and nanoscale level 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 detailed characterization with atomic force coupled infrared spectroscopy, time-of-flight mass spectrometry, and fluorescence microscopy gives clues about the composition of core-shell particles, which are situated on the bitumen surface. The self-organisation of bitumen core shell particles was investigated because of its chemical convenience. It opens up as a model substance to understand the crucial mechanisms of core-shell formation. This study presents the visualization of the bitumen surface with various microscopic and spectroscopic techniques up to nanoscale lateral resolution, 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.

Dissolution in the flow: shapes and patterns

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We analyze the evolving shapes of the objects dissolved by a reactive flow. To understand the shape dynamics, we combine microfluidic experiments, numerical simulations and analytical calculations. The experiments use gypsum cylinders (10 mm radius, 0.5 mm thick) cast from rehydrated CaSO_4 hemihydrate. The numerical simulations use a finite-volume discretization of the reactive-transport equations with a mesh that conforms to the evolving shape of the mineral. Finally, the analytical approach is developed using conformal mapping techniques. The asymmetry introduced by the flow causes the initially cylindrical sample to take on a shape resembling one half of a figure eight, with the tip pointing in the downstream direction. The simulations give a near perfect match to the experimental size and shape. We quantify the evolution of the volume of the grain and its surface area, as well as its overall shape as the function of the Peclet number. Next we discuss the differences between the geometric surface area and the reactive surface area of a dissolving object and explore a potential use of these results to upscale the reactive transport problem.

Biom mineralization at the origins of life

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“Alkaline hydrothermal vents have become a candidate setting for the origins of life on earth. These structures have important key features, such as temperature, redox and pH gradients that could drive chemical reactions and thus early metabolism. In addition, the availability of inorganic minerals could serve as catalysts, and the presence of a complex network of inorganic compartments could have concentrated key molecules and served as primitive compartments. We investigated a new set of interactions between inorganic structures and organic alcohols. The long chain alcohol we chose to test for these interactions was 1-decanol. We experimented with decanol in the formation of chemical gardens that have long been used as experimental proxies for hydrothermal vents. The integration of the alcohol within these chemical gardens produced a range of new emergent structures at both microscopic and macroscopic scales. We show how self-generating inorganic structures can be influenced by the presence of organic substances and we then postulate about the role of such structures in origin of life scenarios.”

A study on calcium-phosphate gardens grown from the interface of a κ -carrageenan-based hydrogel and interrelated liquid

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In the present work, two chemobronic systems with tubular structures grown from a hydrogel/liquid interface were investigated: a calcium-based hydrogel with a phosphate counterion solution (Ca-gel) and a phosphate-based hydrogel with a calcium counterion solution (P-gel). Knowledge about the system parameters, such as pH, was acquired and have confirmed steeper gradients of these in the Ca-gel system that lead to longer tubular structures. The tubular structures were kept in counterion solution for 1, 7, 14 or 28 days and then were characterized with different techniques. Analyses revealed that the tubular structures contained hydroxyapatite phase for the Ca-gel system and calcite-mixed hydroxyapatite phases for the P-gel system. In addition, the Ca-gel tubes contained some amounts of κ -carrageenan, originating from the hydrogels, within their structure.

Hydrogen induced blister cracking of pipe steels in sour aqueous environments potential approach as chemical garden

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The chemistry of chemical garden may be related to the setting of Portland cement, the formation of hydrothermal vents, and during the corrosion of steel surfaces on which insoluble tubes can be formed. Hydrogen embrittlement also known as hydrogen assisted cracking or hydrogen-induced cracking, describes the embrittlement of a metal by hydrogen. In steels, diffusible hydrogen atoms come from water and are typically introduced by reduction of H^+ or H_2O to neutral atomic H in a wet electrochemical process. Our work was focused on a possible practical application of chemical gardens, namely to metal corrosion in sour aqueous environments, in which corrosion products on the metal surface may be colloidal in character and corrosion tubes can form on the surface of rusting iron or steel. The experimental trials consist of exposing unstressed test low carbon steel specimens to a standard test solution (NACE TM0284 Solution A) of sodium chloride, acetic acid (NaCl, CH_3COOH) solution saturated with H_2S at ambient temperature and pressure. Hydrogen embrittlement is a complex process involving a number of distinct contributing micro-mechanisms, not all of which need to be present. The mechanisms include the formation of brittle hydrides, the creation of voids that can lead to high-pressure bubbles, enhanced decohesion at internal surfaces and localised plasticity at crack tips that assist in the propagation of cracks. There is a great variety of mechanisms that have been proposed and investigated as to the cause of brittleness once diffusible hydrogen has been dissolved into the metal. The presence of sulfides tends to increase the amount of atomic hydrogen available. This reaction is brought about by the presence of HS^- ion which exists in equilibrium with the H_2S .

It follows, therefore, that the harmful influence of diffusible hydrogen can be mitigated by preventing its entry into steel or by rendering it immobile once it penetrates the material.

Bubble-driven Action Painting: Chemical Gardens' Potential for a New Conception of Multi-Agential Expression

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What happens if you dare to conceive chemical gardens as 'paintings in action'? This contribution aims at interpreting scientific research approaches on chemical gardens through the lens of the endeavours that can be found in artistic practices. The artists (in discussion) implicitly or explicitly thematize alchemical aspects of the colours in chemical gardens in order to move toward a new kind of dynamic, multi-agential concept of painting or imagery. First, the involved substances are appreciated in their potential for being a colour equipped with more agency than normal, capable of co-creating configurations with humans bridging several orders of scale. Reinterpreting chemobronic literature, I distil several 'drives' inherent in the combination of the materials that produce ongoing events. These drives are interpreted as painterly gestures to finally arrive at some specifics of such an expression where the artists are more the ones to curate or orchestrate the processes.

Circular Dichroism Imaging (CDi) for probing chiral solids

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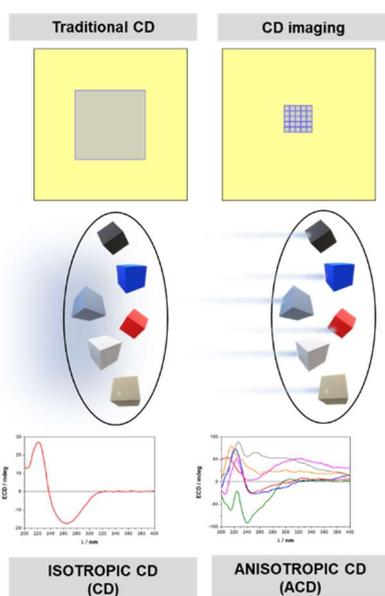
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Circular Dichroism (CD) is used for elucidating chirality because of its extremely high sensitivity for monitoring and characterizing even the smallest structural changes of molecules both in solution and in solid-state. The current CD instrument layout results that a broad light beam is passing through the sample. For this reason, any recorded spectrum by



using a regular CD instrument is close to isotropic one and represents an average of chiroptical properties of a quite large area ca. 1 cm². It triggers serious consequences, which limit in the end the use of CD spectroscopy on some grounds.

Using the concept of electronic circular dichroism imaging (CDi) developed thanks to highly collimated synchrotron radiation, we were able to get for the first time insight into the spatial arrangement of our model microcrystalline solid. By exploring with the spatial resolution of ~0.1 mm randomly formed domains, we noticed that anisotropic CDi (ACD) spectra might be very different from the emergent CD spectrum recorded using a traditional instrument (reflecting the isotropic ECD spectrum). The analysis of data disclosed that the observed isotropic solid-phase ECD spectrum is directly

governed by the anisotropy of oriented crystals.[1] This introduces a new quality for solid-state ECD measurements and opens up appealing chapter for probing and mapping chiral solids and materials, including in particular chiral active pharmaceutical ingredients (APIs).

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Dynamic self-assembly to synchrony of active gel

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“Active soft materials exhibit various dynamics ranging from pulsating behavior to self-assembly. In our experiments, the ethanol-infused chitosan bead self-propels continuously and intermittently. The shape of the active gel deforms into a circular to asymmetric shape, and further fission occurs by increasing the ethanol or decreasing the chitosan amount. Interestingly, the attractive and repulsive interaction of multiple gadolinium-polymer gel beads aggregates them in distinct order, and their self-assembly generates oscillatory activity in various synchronous modes.”

Light-controlling nucleation and growth of metal carbonate crystals using resonant near-infrared laser heating

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Spatiotemporal control over crystal nucleation and growth is of fundamental interest for understanding how organisms assemble high-performance biominerals, and promises new manufacturing routes for functional materials. Many methods have been developed towards static or global control, however gaining simultaneously dynamic and local control over crystallization remains challenging. In this work, near-infrared (NIR) light locally heats water to induce crystallization of retrograde soluble compounds with spatiotemporal control. Using a custom-build optical setup, the NIR light intensity is modulated to start, steer, and stop crystallization of single crystals of calcium carbonate with micrometer precision. Tailoring the crystallization conditions enables polymorph control to position vaterite, aragonite, and calcite, and straightforward extension of these principles towards other compounds is demonstrated by patterning barium-, strontium-, and calcium carbonate crystals according to user-defined micrometer patterns. Since many important compounds exhibit retrograde solubility behavior, NIR-induced heating opens unprecedented opportunities for light-controlled crystallization with precise spatiotemporal control.

From Incohesive Precipitation to Cohesive Chemical Garden Walls

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Chemical gardens form tubes from far-from-equilibrium dynamics which occurs when a metal salt (mainly transition metals) is introduced into an alkaline solution (e.g., silicates, sulphates, and carbonates). The final product has a diameter ranging from one micron to one centimeter and lengths of up to several decimeters long. The wall of these hollow structures is composed of thousands of precipitates bound together to form a cohesive semipermeable membrane. The growth of the chemical garden wall occurs at the wake of the front between the metal salt and alkaline solution and a discernible particle-rich liquid can be seen to precede the tube walls. Understanding the cause for this transition from flowing precipitates into the solid, bound material can inform future methods for carbon, capture, and sequestration (CCS). For example, creating a precipitate wall can help trap injected CO₂-rich liquids in CCS injection sites; however, these more solid structures can also prevent mixing and further desired mineralization of carbonate products. Here, we explore the precipitation of magnesium and calcium minerals from the injection of sodium bicarbonate into a Hele-Shaw cell filled with either MgCl₂ or CaCl₂. Depending on the experimental parameters, the magnesium-based experiments form a loose precipitate or stable walls that break and expand with continual injection. For the same experimental conditions, the calcium system never forms a cohesive wall and only small precipitate material forms which creates radial stripes during the continued injection of NaHCO₃. Furthermore, the high concentration and high injection rate regimes forms high amounts of gas trapped in the solution during and after injection.

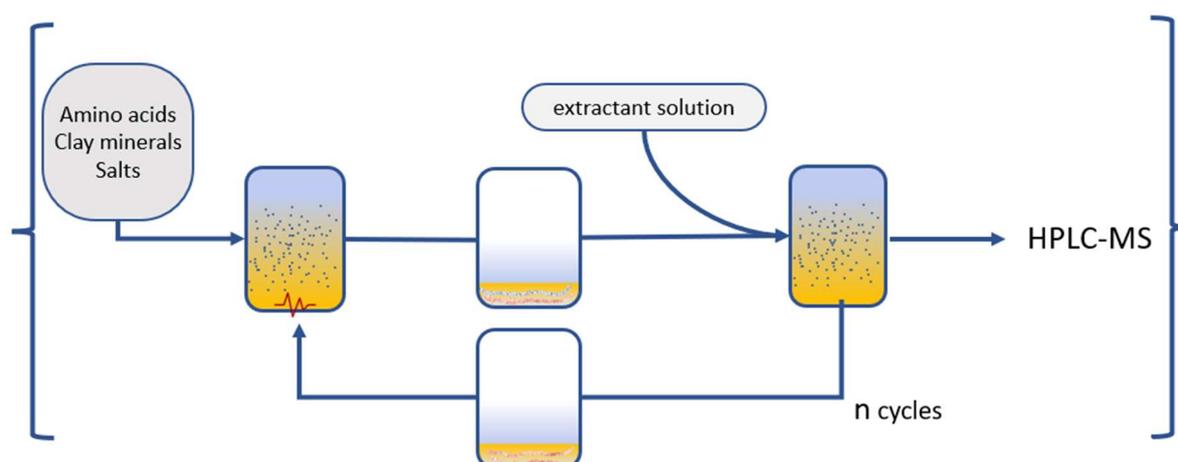
Selection and catalysis of amino acids by clay minerals

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"There is a wide variety of approaches to how the origin of life occurred, plausibly it was in a 'prebiotic soup' containing the building blocks which influenced by the soup bowl i.e., the mineral environment. Clays and clay minerals are pointed out as precursors of the early life due to their catalyst and ability to accumulate a wide range of different molecules.¹⁴ A lot of work has already been done investigating the capacity of minerals to store and catalyse varied types of biomolecules, but here we present a review about its role in the diversification and differentiation of the products throughout recursive cycle feed-dried experiments (Figure 1) containing mixtures of clay minerals and amino acids. The aim is to search and identify its role in the complexification, selection and ordering in complex mixtures".



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Continuum models of ion transport

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Ion transport is involved in many electrochemical, technological and biological processes such as crystal growth, periodic precipitation, formation of colloid particles, morphogenesis and other self-organization processes. Developments in computer power and numerical algorithms allow for the use of continuum electrodiffusion models capable of solving a full set of time-dependent Nernst-Planck and Poisson equations (the NPP or PNP theory). We illustrate applicability of this approach on several examples including models of ion transport in a simple membrane channel^{15,16} and models allowing to simulate the dynamics of electric double layer formation.¹⁷

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Energetics and metabolism of the Last Universal Common Ancestor

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Life is organized as a series of chemical reactions forming a metabolic network. The underlying reactions at the origin of metabolism before the emergence of life itself had to be energetically far from equilibrium to occur spontaneously, setting up the cornerstone for a highly efficient metabolism. Potentially, this process began 4 million years ago with geochemical processes in the Earth's crust in serpentinizing systems, namely hydrothermal vents¹⁸.

The autotrophic metabolism of the last universal common ancestor (Luca) is characterized by conceiving a biosynthetic core network comprising more than 400 metabolic reactions necessary to synthesize amino acids, bases and cofactors from hydrogen (H₂), carbon dioxide (CO₂) and ammonia (NH₃), as well as hydrogen sulfide (H₂S) and phosphate¹⁹. These components were potentially already available in hydrothermal vent on the early Earth. Thermodynamic investigations of these reactions under hydrothermal conditions reveal that 95–97 % are exergonic ($\Delta G \leq \text{kJ}\cdot\text{mol}^{-1}$), therefore energy releasing and running spontaneously. Over three-third of the core reactions obtain their energy not from hydrolysis of triphosphates but instead are thermodynamically driven by energy from involved carbon bonds²⁰.

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Structure and growth of mineral dendrites

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Mineral dendrites are an example of pattern which form in rocks when they are infiltrated by the hydrothermal, manganese-bearing fluids. As these fluids mix with the oxygenated fluid within the rock pores, manganese oxide precipitates, forming the intricate patterns. Several models of this process have been proposed, which vary in complexity. One model assumes precipitation of manganese oxides directly on the surface of the growing dendrite, which then elongate. Another model involves an initial growth of small nanoparticles of manganese oxide, which then aggregate into larger structures.

We study this process using lattice-Boltzmann method to track the evolving concentrations of all of the species involved in reaction. Next, we analyze the dependence of the morphology of the resulting patterns on the physical parameters characterizing the reaction and growth, such as the concentrations of the initial solutions, reaction rates, nucleation thresholds or surface energy of the dendrites.

The impact of reaction rate on the formation of flow-driven confined precipitate patterns

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The production of solid materials via chemical reactions is abundant both in nature and in industrial processes. Precipitation reactions coupled with transport phenomena lead to enhanced product properties not observed in the traditional well-stirred systems. In here we present flow-driven pattern formation upon radial injection in a confined geometry for various chemical systems to show how reaction kinetics modifies the emerging precipitate patterns. It is found that chemically similar elements, such as alkaline earth or transition metals react on very different time scale under the same experimental conditions and thus can produce significantly different patterns.

Spatial precipitate separation enhanced by complex formation

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The separation and extraction of inorganic precipitates with similar solubility products is a challenging task in chemical technology. A computational fluid dynamics study of a precipitation reaction is presented using an open Helle-Shaw reactor. Cobalt(II) oxalate and copper(II) oxalate have solubilities within an order of magnitude and their precipitation occur simultaneously, thus this system is used for validation. A general model has been constructed where two metal ions compete for one common anion. Several parameters have been varied to identify the key factors responsible for the spatial separation of the precipitate, and the extent of segregation is quantified with two new descriptors. With this model we are capable not only of determining the driving force behind the separation, but also adjusting parameters in order to extract the desired precipitate.

Formation of Concomitant Nanomorphologies of Self-Aligned Anodic Titania Nanotube Arrays: Chaotic Nanowires and Nanobamboos

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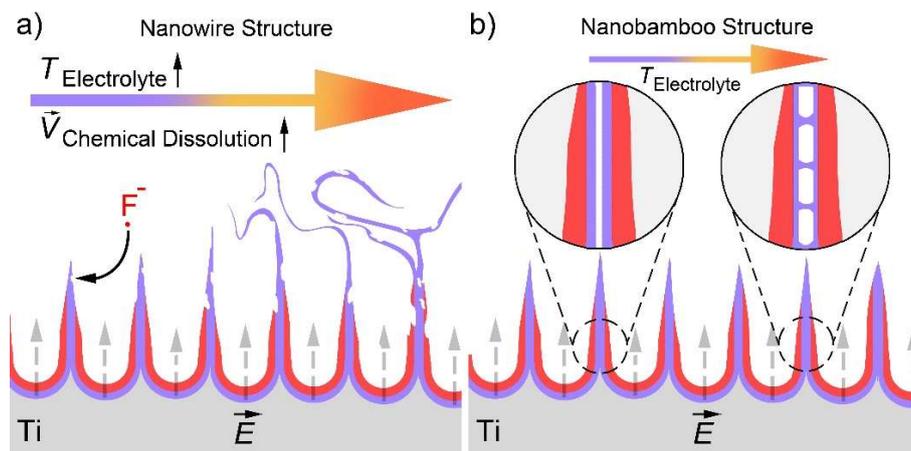


Figure 1. Formation of chaotic titania nanowire surfaces (a) and intertubular nanobamboo structures (b) during electrochemically fabricated titanium dioxide nanotube arrays.

Until early 21st century, although the most of the explanatory studies of the self-organizing ceramic nanomaterials, such as nanotubes, nanobullets, nanomembranes, and their growth mechanism had been well-known; their concomitant nanomorphologies, such as nanobamboos, chaotic nanowire sub-surfaces and core/shell structures, have not been investigated for an engineering purpose to develop more complex systems. Thanks to monitoring and characterization technologies, we learned their resulting nanofeatures with their incoming potential in use. Today, one of the practical method to fabricate aligned ceramic nanomaterials on metal surfaces is electrochemical anodic oxidation. From photon-catchers in solar cells to biocompatible implant surface modifications, titanium dioxide nanotube arrays have been used in various technologies. This study gives short summary about formation mechanism and conditions of emerging nanomorphologies coming after self-aligned titanium dioxide nanotubes.

Didactic activities about the ‘Chemical gardens’ for kids and school students during covid-19 pandemic at the University of Pisa

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In the frame of two courses of chemistry education for future chemistry teachers (Course of Chemistry) and future primary school teachers (Course of Primary School Science Education) at the University of Pisa, several activities concerning ‘chemical gardens’ were planned by undergraduate students during the academic year 2019-2020. Chemical gardens are indeed very fascinating examples of complex chemical reactions, and from the educational point of view they can be used, first, to engage students and, second, to introduce some key-concepts in chemistry, such as ‘heterogeneous and homogeneous mixtures’, solutions, chemical substances and chemical transformations. With respect to previous academic years, the covid-19 pandemic strongly affected the teaching and learning modalities of the chemistry education courses and it was the occasion to introduce students to the use of digital tools for educational purposes. In this context, several interactive activities,²¹ such as an online platform dedicated to kids and primary school classes, as well as videos and other digital materials^{22,23,24} were prepared and presented during online Open Days organized by the Department of Chemistry at the University of Pisa.²⁵

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To What Inanimate Matter Are We Most Closely Related and Does the Origin of Life Harbor Meaning

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“The question concerning the meaning of life is important, but it immediately confronts the present authors with insurmountable obstacles from a philosophical standpoint, as it would require us to define not only what we hold to be life, but what we hold to be meaning in addition, requiring us to do both in a properly researched context. We unconditionally surrender to that challenge. Instead, we offer a vernacular, armchair approach to life’s origin and meaning, with some layman’s thoughts on the meaning of origins as viewed from the biologist’s standpoint. One can observe that biologists generally approach the concept of biological meaning in the context of evolution. This is the basis for the broad resonance behind Dobzhansky’s appraisal that “Nothing in biology makes sense except in the light of evolution”. Biologists try to understand living things in the historical context of how they arose, without giving much thought to the definition of what life or living things are, which for a biologist is usually not an interesting question in the practical context of daily dealings with organisms. Do humans generally understand life’s meaning in the context of history? If we consider the problem of life’s origin, the question of what constitutes a living thing becomes somewhat more acute for the biologist, though not more answerable, because it is inescapable that there was a time when there were no organisms on Earth, followed by a time when there were, the latter time having persisted in continuity to the present. This raises the question of where, in that transition, chemicals on Earth became alive, requiring, in turn, a set of premises for how life arose in order to conceptualize the problem in relation to organisms we know today, including ourselves, which brings us to the point of this paper: In the same way that cultural narratives for origins always start with a setting, scientific narratives for origins also always start with a setting, a place on Earth or elsewhere where we can imagine what happened for the sake of structuring both the problem and the narrative for its solution. This raises the question of whether scientific origins settings convey meaning to humans in that they suggest to us from what kind of place and what kinds of chemicals we are descended, that is, to which inanimate things we are most closely related.”

The constant rate of LGT across geological time as far back as genomes go

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The top down approach to early evolution starts with the study of comparative physiology, the analysis of prokaryotic genomes. A factor that complicates the study of early evolution, in particular very early evolution near LUCA, is lateral gene transfer, LGT. Although it is clear that LGT occurs today, it is not known whether it occurred in the past as well, and if the rate was similar to what we observe today. To analyze and quantify the influence of lateral gene transfer on genome evolution in prokaryotes, prokaryotic gene clusters were examined with respect to shared gene differences per genome pair in relation to the sequence divergence of 36 highly conserved genes, mostly ribosomal proteins, also known as the phylogenetic core. Across diverse bacterial phyla a very similar gene flux rate relative to amino acid substitutions in the core can be observed. For an average bacterial genome comprising roughly 3000 genes, the rate of flux for ancestrally shared genes is roughly 5 gene differences per amino acid substitution in the core. Across archaeal phyla, the flux rate is slightly lower at 4 gene differences per amino acid substitution in the phylogenetic core. The results indicate that the rate of LGT relative to amino acid substitutions in the core has been surprisingly constant both across lineages and throughout geological time. This in turn indicates that the study of early evolution from a phylogeny perspective will always be hampered by the workings of LGT.

Light-controllable shape transition and pore opening in cell-sized vesicular systems

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The development of stimuli-responsive biomimetic artificial compartments is of high relevance in the research field of bottom-up synthetic biology. Mimicking real cell behaviour, such entities can undergo modification of biophysical properties of the membrane under a physical (e.g. light) or chemical (e.g., pH) environmental clue. From one side, the ability to control cell shape transitions and morphology is of crucial importance to understand how fundamental life properties like replication or communication have emerged in primordial cells, in the absence of complex biomolecular machineries. While, from a practical point of view, these systems are emerging as promising biomedical therapeutic tools capable of entrapping and releasing small drugs under specific triggers. Among the possible strategies, the insertion of photoswitchable lipids in liposome membrane results successful in affecting the bilayer order and dynamics thus enabling manipulation of membrane stability²⁶, stiffness²⁷, fluidity²⁸, domain formations²⁹, permeability³⁰ and modification of lipid and membranes signaling functions³¹, using light. In this framework, phospholipid giant unilamellar vesicles (GUVs, diameter > 1 μm) are the most suitable cell-model systems to study morphological changes and compartmentalized biochemical reaction via direct observation in real time. Here, GUVs were synthesized using a mixture of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine and a photosensitive azobenzene-derivative amphiphilic molecule which undergoes photoisomerization upon irradiation with UV-A and blue light. Photoswitchable lipid vesicles revealed a wide range of UV-induced shape changes including prolate, pear shaping, budding transitions, pearling, tethering, pore opening and bursting. Furthermore, the artificial photosensitive vesicles showed changes in the membrane permeability towards small water soluble compounds upon photoisomerization. For this reason we envisage their application as drug delivery tools. As proof-of-concept study, the photocontrollable release of doxorubicin, a widely used anticancer drug with fluorescent properties, has been further investigated. Once the release mechanism is optimized, the future perspective is to transfer our system to smaller liposome scale (100 nm), relevant for *in vivo* applications.

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Polymeric chemical gardens

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Chemical gardens are one of the most fascinating chemical classes. Well-known chemical gardens are obtained from clumps of metal crystal salts immersed in water glass, forming coral-like hollow structures. Though this process of creation of chemical gardens is well-known for centuries, only recently a scientific attention is dedicated to it, but there is still a very little data about polymeric chemical gardens. In our work we have tried to form polymer chemical gardens by injecting different biopolymer solutions into different cationic liquids. The behavior of injected biopolymer solution was assessed, and it was concluded that many parameters, such as concentration of solutions, the size of needle and quivette, injection rate etc., affect the shape of obtained polymeric chemical garden. This is just the beginning of the research, and the mechanisms that describe these processes are yet to be explained. A further investigation of this subject could lead to development of biocompatible materials with potential biomedical application.

Self-assembly of lysozyme on cellulose nanocrystals for sustainable antibacterial materials

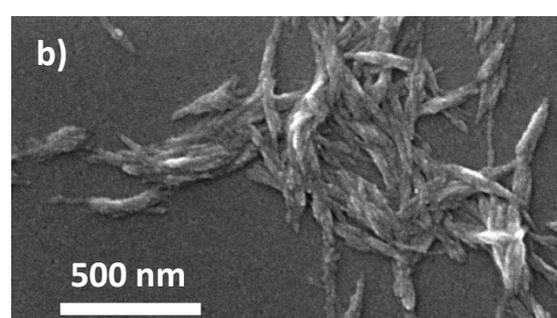
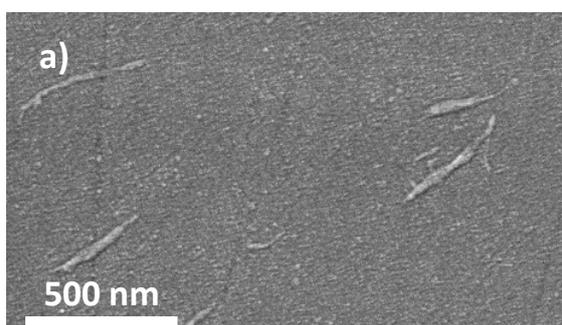
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Nanostructured materials represent promising substrates for the immobilization of biocatalysts and for their activation. Cellulose nanocrystals (CNCs), accessible from waste and/or renewable sources, are sustainable and biodegradable, show high specific surface area for anchoring a high number of enzymatic units, and high thermal and mechanical stability. In this communication, we present a holistic enzyme-based approach both to the fabrication of CNCs from cotton linters and to antibacterial materials by enzymes immobilization onto sustainable CNCs. The antibacterial property is a highly desired feature of water-dispersible materials, since CNCs composites may find application in the field of sustainable coating paper and textile. First, we describe the use of endoglucanase from *Aspergillus niger* for the enzymatic hydrolysis of Avicel. This approach is greener if compared to hydrolysis carried out by mineral acids and successfully yields neutral CNCs. Then, we describe enzyme self-assembly, performed between the lysozyme from chicken egg white and neutral or negatively charged sulfated cellulose nanocrystals. The lysozyme displays interesting protection properties against the proliferation of *Candida albicans*, *Aspergillus niger*, *Staphylococcus aureus*, and *Escherichia coli*. Self-assembly of lysozyme on nanocrystals can be conducted by incubating lysozyme and nanocrystals at room temperature in a pH 8.0 buffer. The reaction can be performed under mild conditions in an orbital shaker. The wash solutions and the self-assembled samples are analyzed using the BCA (bicinchoninic acid) colorimetric assay. The immobilization reaction of the enzyme on the biodegradable substrate produces interesting biohybrid systems, which exhibit preserved enzymatic activity and potential application as antibacterial material.



Electro-magnetic influence on BZ assemblages of ferroin loaded Dowex beads

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Our experimental work is focused on the occurrence and influence of travelling waves inside catalyst loaded Dowex beads. The catalyst is ferroin. Three types of Dowex beads are used, specifically 50W-X8, 50W-X4 and 50W-X8, with mesh sizes from 16 to 100. We use two types of interface in between user and Dowex bead assemblages inside the glass tank reactor filled with catalyst free BZ solution. The first interface is created using potentiostat and its working electrode. The second interface is created using electromagnet.

When negative electric potential is introduced on working electrode inside the catalyst-free BZ solution, it locally generates activator according to reaction: $\text{BrO}_3^- + 2e^- + 3\text{H}^+ \rightarrow \text{HBrO}_2 + \text{H}_2\text{O}$. When positive electric potential is introduced on working electrode, it attracts Br⁻ ions, the inhibitor, locally.

When magnetic field is on, in range (0-330mT), it influences the period of oscillations of all beads inside the field, non-locally.

We report pulses, travelling waves and dampened oscillation in reaction to electric field using assemblages of Dowex 50W-X8 with mesh size 50-100 and equimolar mixture of malonic acid and 1,4 cyclohexanedione as a substrate, working for over 19 hours

We report travelling waves with period in between pulses below 1 second in reaction to magnetic field using assemblages of Dowex 50W-X8 with mesh size 16-50 and malonic acid as a substrate working for 6 hours.

Dowex 50W-X8 beads with solution of malonic acid and 1,4 cyclohexanedione seem to be proper candidate for chemical computing device with electro-magnetic interface, working for a day.

Mechanistic and kinetic analysis of CO₂ reduction in the context of abiogenesis

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Alkaline hydrothermal vents produce H₂ from reactions of iron containing minerals with water during serpentinization. This has been a source of energy in early anaerobic ecosystems in the Earth's crust and because of that, such systems are of high interest for the research in Origin of Life. In the chemical evolution group in the Institute of Molecular Evolution at the Heinrich Heine University in Düsseldorf we work on how organic material and metabolic pathways could have come to be on the early Earth, with a special focus on the environment of H₂ producing hydrothermal vents. We simulate the chemical reactions of these hydrothermal vents with the help of metal catalysts, which act as the precursors of enzymes used by life in metabolism and analyse the products of these reactions. Using a pressurized reactor, the conditions of alkaline hydrothermal vents are simulated. A H₂/CO₂ mixture reacts in water in the presence of a metal catalyst. The alkaline conditions of serpentinizing vents are simulated by adding KOH to the H₂O. The main resulting products are acetate, formate, and pyruvate. This presents a potential abiotic precursor to the acetyl-CoA pathway, which is used by anaerobic bacteria and archaea for biosynthesis and is the most ancient route of CO₂ fixation used by life. The above reaction has been tested and published at conditions of 100°C and 16 hours reaction time (Preiner et.al. 2020, <https://doi.org/10.1101/682955>), however a factor analysis of the influence of reaction time and temperature on the system and its products was still missing, which I would like to present in a poster at Chembrionics.

Synthesis of Hard Materials in Soft Vesicles: ZIF-8 precipitation in Giant Unilamellar Vesicles

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The control of the synthesis and assembly of hard micro- and nano-materials composed from inorganic and/or organic compounds have received considerable attention in the last decades.³² For this purpose, researchers use many templates and structure-directing agents such as vesicles, micelles, liquid crystals, emulsion droplets and lipid nanotubes.

Among different types of templates, vesicles, that are water-in-water compartments stabilized by amphiphilic molecules self-assembled into bilayers, present unique structures that can simultaneously supply different microenvironments for the growth and assembly of hard materials: the inner chamber of vesicles, the outer surface of the vesicles, and the space between bilayers.³³

The aim of our research is to employ Giant Unilamellar Vesicles (GUVs) as template for Metal–Organic Frameworks (MOFs) synthesis. MOFs are an important class of crystalline nano-porous materials with great potential for a wide range of industrial applications, for example, catalysis, gas storage and drug delivery.³⁴

Among the several types of MOFs, we will focus on Zeolitic Imidazolate Frameworks 8 (ZIF-8). That consists of Zn²⁺ ions linked to the N atoms of deprotonated 2-methyl imidazole to form neutral porous frameworks. We have chosen ZIF-8 because its formation in liquid phase has been extensively studied in the literature and it has unique physical and chemical properties such as thermal stability and great surface area.

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Influence of radial advection on properties of autocatalytic fronts

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Properties of reaction-diffusion-advection autocatalytic fronts have been studied both experimentally and theoretically in radial geometries. We have analyzed the influence of the ratio of the reactant concentrations and flow rate on the temporal evolution of the front position in polar axisymmetric systems. At early times advection is the main transport process, dominating over reaction. In the long-time asymptotic limit, we obtain the same behavior as in the rectilinear case – i.e., the autocatalytic front travels at the constant reaction-diffusion velocity. We verify these findings experimentally using the chlorite-tetrathionate reaction.

Modular and convergent synthesis of a new class of amphiphilic molecules for the formation of self-assembled materials

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Amphiphilic glycopeptoids (Fig 1) are formed by two main parts: a sugar, which represents the polar head, and a peptoid, which constitutes the apolar tail. Peptoids are N-substituted glycines which act as mimetic peptides with an efficient cell membrane penetration by diffusion and a better resistance to protease enzymes. Moreover, the easy modular synthesis and access to a broad variety of primary amines allow for the synthesis of large libraries of amphiphilic molecules. The libraries of peptoids can be coupled to a broad variety of sugar-based polar heads.

Although systematic studies on the self-assembly ability of amphiphilic glycopeptoids (Fig 1) are not reported in literature, studies on amphiphilic polypeptoids with a non-saccharide base have shown how this class of compounds is highly promising in the context of self-assembly. Each self-assembly geometry is related to the surfactant molecular structure.

The main goal of the project is the development of a simple, fast and versatile synthetic approach which allows the preparation of a great variety of amphiphilic molecules.

A deep physico-chemical study of self-assembly properties of these molecules will help to understand the correlation between molecular structure and macromolecular aggregation geometry.

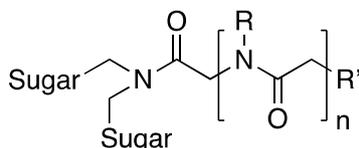


Fig 1: amphiphilic glycopeptoid generic structure

A microfluidic labyrinth self-assembled by a chemical garden

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"Mazes and labyrinths - sometimes defined as a maze with only a single path - have been of great interest in microfluidics. A number of chemical-, physical- and biological-based maze solving techniques have been reported in recent years: chemical waves, chemotactic droplets, Marangoni flow or the nematode *Caenorhabditis elegans*, have been investigated. On the other hand, self-assembled mazes have been reported in slow drainage of a granular-fluid system in two-dimensional confinement. And maze structures have been noted to self-organize by wrinkling. Here we report on a chemical garden system that self-assembles a microfluidic maze."

Hyaluronic acid based chemical gardens

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Organic chemical gardens of hyaluronic acid based hydrogels can be developed via injection of alkaline solution of hyaluronic acid into acidic solution of Iron(III) chloride. Variation of injection rate as well as iron ions concentrations have resulted in different morphology of physically crosslinked hyaluronic acid based hydrogels – from fibers to globular ones at higher injection rates. This investigation has served as an initial step for further investigation of different self-assembly structures which can explain the processes in living organisms.

Pellet-grown chemical gardens in horizontal confined geometry

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Chemical gardens are self-assembled precipitate structures created by the formation of semi-permeable membranes. They emerge from the complex interaction between convective flow, osmosis, diffusion, and precipitation chemistry. In this study, we examine the dynamics of chemical gardens grown from pellet in horizontal Hele-Shaw cells at greater details. The use of Hele-Shaw cells makes the chemical gardens grown within quasi-2D, so that it is easier to visualise and analyse them. Chemical garden explosion, where the precipitate membrane undergoes explosive rupturing at reproducible times since experimental onsets, was a phenomenon previously reported for chemical gardens grown from cobalt chloride pellets and sodium silicate solution in Hele-Shaw cells. Here, it has been studied further and shown to also occur in chemical gardens made from manganese chloride and sodium silicate. In our next steps, we will analyse the patterns of the chemical garden structures qualitatively and quantitatively. To visualise the convective and osmotic flow behaviour in these chemical gardens, we plan to then conducted experiments under schlieren optics.