

Chemobionics: From Self-Assembled Material Architectures to the Origin of Life

Abstract Self-organizing precipitation processes, such as chemical gardens forming biomimetic micro- and nanotubular forms, have the potential to show us new fundamental science to explore, quantify, and understand nonequilibrium physicochemical systems, and shed light on the conditions for life's emergence. The physics and chemistry of these phenomena, due to the assembly of material architectures under a flux of ions, and their exploitation in applications, have recently been termed chemobionics. Advances in understanding in this area require a combination of expertise in physics, chemistry, mathematical modeling, biology, and nanoengineering, as well as in complex systems and nonlinear and materials sciences, giving rise to this new synergistic discipline of chemobionics.

Silvana S. S. Cardoso

University of Cambridge
Department of Chemical
Engineering and Biotechnology
sssc1@cam.ac.uk

Julyan H. E. Cartwright

Universidad de Granada CSIC
Instituto Andaluz de Ciencias
de la Tierra
Instituto Carlos I de Física
Teórica y Computacional
julyan.cartwright@csic.es

Jitka Čejková

University of Chemistry and Technology
Prague
Department of Chemical Engineering

Leroy Cronin

University of Glasgow
School of Chemistry

Anne De Wit

Université Libre de Bruxelles (ULB)
Nonlinear Physical Chemistry Unit

Simone Giannerini

Università di Bologna
Dipartimento di Scienze Statistiche
“Paolo Fortunati”

Dezső Horváth

University of Szeged
Department of Applied and
Environmental Chemistry

Alírio Rodrigues

University of Porto
Department of Chemical Engineering

Michael J. Russell

Università degli Studi di Torino
Dipartimento di Chimica

C. Ignacio Sainz-Díaz

Universidad de Granada CSIC
Instituto Andaluz de Ciencias de la Tierra

Ágota Tóth

University of Szeged
Department of Physical Chemistry
and Materials Science

Keywords

Chemical garden, chemobionics, origin of life,
biomimetics, submarine alkaline vent theory

I Introduction

Chemobionics [3] is a newly emerging field of fundamental nonlinear and complex systems science that intersects with physics, chemistry, biology, and materials science, and involves the study of biomimetic materials as complex systems based on self-organized structures involving semipermeable membranes and amorphous as well as polycrystalline solids. “Chemobionics”—from “chemo” and Greek “brucin” (to grow or enlarge, in this case meaning to grow owing to osmotic pressure)—encompasses the classical chemical gardens as shown in Figure 1, but the field goes far beyond this centuries-old experiment. Several factors are working in unison to make a concerted research effort in this field both relevant and timely. It is today commonly accepted that self-assembly is an excellent way to form complex structures in an evolving series of small steps [4, 13, 19]. Indeed, it is the foundation for much of modern nanoscience. Yet nature applies not only self-assembly, but also self-organization, which allows the stepwise building of complex patterns ultimately from simple building blocks (e.g., [23]). Harnessing such methods for scientific and technological applications is thus extremely promising, but it is currently hampered by incomplete understanding of the underlying fundamental phenomena.

The same challenges are encountered by those seeking to comprehend how these physical and chemical processes may have taken part in the emergence of life on this planet and elsewhere in the universe, as these same chemobionic systems are found at oceanic hydrothermal vents [5], and the hypothesis that life may have incubated within them over 4 billion years ago in the transition from geophysical and geochemical mechanisms to biology is today one of the most promising theories for the emergence of life on Earth [8, 39].

Research related to these biomimetic nanotubular or microtubular systems is developing very fast, and much work is appearing from individual research groups, both in Europe and worldwide, related to the self-organized chemical-garden phenomenon. However, the efforts of these research groups have been scattered, researchers working independently without cohesion. This impedes the making of a strong research effort in this area that will both advance fundamental science and enable the future exploitation of advances in chemobionics by other fields. Chemobionics requires a transdisciplinary approach rather than conventional, more narrowly defined research projects. The more limited approach has further hampered advances in the area in that research has been artificially divided along the traditional lines of physics, chemistry, biology, and so on. This has been detrimental because the distinction between these fields is blurred in the area of chemobionics, where, as is generally the case with nonlinear and complex systems, more holistic approaches are required.



Figure 1. Plantlike structures: a classical chemical-garden experiment.

A new European-wide chemobionics network, founded by us and funded by COST (European Cooperation in Science and Technology), addresses this need. This network, scheduled to run from 2018–2022, links nationally funded research projects and aims to be an essential facilitator for world-class European chemobionics research that will enable large-scale concerted European-scale research efforts. Additionally, and very importantly, the network will greatly improve the training of early-stage researchers through short-term scientific missions to groups working in different areas. This will not only train early-stage researchers in transdisciplinary research but also allow them to gain experience in diverse approaches to research group organization, management, and communication. Thus, the network will be an essential component both in European research itself and in rearing the European researchers of the future. We are also organizing networking workshops as well as chemical-garden demonstrations, exhibitions, and art–science installations that will involve researchers early in their careers, giving them an opportunity not only to develop research synergies, but also to advocate for science.

2 The State of the Art

Over the past four centuries, the surprising precipitation structures known as chemical (or crystal, silica, silicate) gardens have fascinated people, as well as being the basis of different philosophical and scientific theories, an inspiration for literature, and motivation for many experiments. Classic chemical gardens are hollow precipitation structures that form when a metal salt seed is deposited in an aqueous solution that contains anions such as silicate, phosphate, carbonate, oxalate, or sulfide (Figure 2). The seed releases metal ions in the solution that precipitate with the anions in the external solution, forming a gelatinous colloidal membrane that surrounds the seed [12]. There is an obvious visual similarity between the precipitated structures in chemical gardens (Figure 1) and a variety of biological forms, including those of plants, fungi, and insects. In addition, in a way, the process of chemical-garden formation from an inorganic seed in a reactive solution resembles the growth of plants from a seed in water or in soil.

These biomimetic structures and processes have led researchers to ask themselves: Do chemical gardens and biological structures share similar formation processes? Can these inorganic structures teach us about biological morphogenesis, or is the similarity just accidental? Are they related to the origin of life? And, if the precipitation is affected by chemical and environmental parameters, can the process of building complex structures be organized as biology does, to produce self-organized precipitates as useful materials? Could a synthetic biology system be developed, using genetic material, to initiate, control, or manipulate a chemical garden?

There are many other reaction systems that can form similar chemical gardens, and many details of their formation process are specific to the particular system, but the main universal aspect is the formation of some kind of semipermeable precipitation membrane, across which pronounced concentration gradients can be formed and maintained, resulting in osmotic and buoyancy forces [12, 37, 42] (Figure 3). Obviously, chemical gardens are not the only pattern-forming system in chemistry.

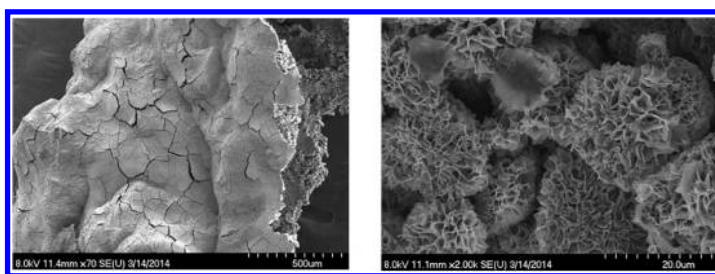


Figure 2. SEM images of the outer (left) and inner (right) surfaces of a copper phosphate tube show that the inner side has high surface area, suggesting it could be a good catalyst, while the outer is smooth.



Figure 3. CoCl_2 pellet reacting with 1.5 M Na_2SiO_3 in a 2D experiment in a vertical Hele-Shaw cell shows fluid-flow effects of buoyancy and osmosis.

Liesegang rings, for example, are another pattern-forming system studied for a long time that involves chemical precipitation. However, Liesegang rings do not involve semipermeable membranes and, thus are a very different phenomenon. Chemical gardens and related structures (Figure 4) are found in laboratory chemistry, ranging from silicates [20, 22, 44] to polyoxometalates [16, 35], in applications ranging from corrosion products [6] to hydration of Portland cement [10], and in natural environments ranging from hydrothermal vents in the depths of the ocean to brinicles under sea ice [11, 15, 32, 45].

The structures formed in chemical-garden experiments can be very complex. Experimental and theoretical studies of chemical-garden systems have accelerated since the end of the 20th century with developments in nonlinear dynamics, the study of complex systems, the understanding of the formation of patterns in chemical and physical systems [25], and the development of more advanced experimental and analytical techniques [40]. Many aspects of chemical-garden systems, such as their electrochemical [21] and magnetic properties [41, 43], have been recently characterized. It has been observed that in some systems self-assembling chemical engines may appear spontaneously [18]. A greater understanding of the process of forming chemical gardens in recent decades has also enabled researchers to begin to control it [36], deliberately fabricating structures using advanced precipitation techniques that have many potential uses in the science and technology of materials, especially at the nano scale. On the one hand, chemical gardens show us that complex structures do not have to be of biotic origin and emphasize the dangers of using morphology as a sign of biological origin, and on the other hand, they suggest a possible way to achieve a protocol from an abiotic beginning. We now know that the discovery of a biomimetic form is not a direct indication of the existence of life, because it can be produced by organic matter, such as living organisms, or by abiotic phenomena, such as chemical gardens. However, modern research shows that chemical gardens in hydrothermal vents on the sea floor are a plausible path for the origin of life on earth [27].

The scientific and technological importance of chemical-garden systems goes far beyond the first experiments that saw their visual similarity to plant growth. Chemical-garden-type systems now encompass a multitude of self-organized processes involving the formation of a semipermeable membrane that creates persistent macroscopic structures from the interaction of precipitation reactions and solidification processes with diffusion and fluid motion [26].

The challenge remains to elucidate the growth processes to understand and apply science for the benefit of various applications. Chemobronic processes are diverse and apply to many disciplines; specific systems and properties are studied in, among others, geology, planetary science, astrobiology,

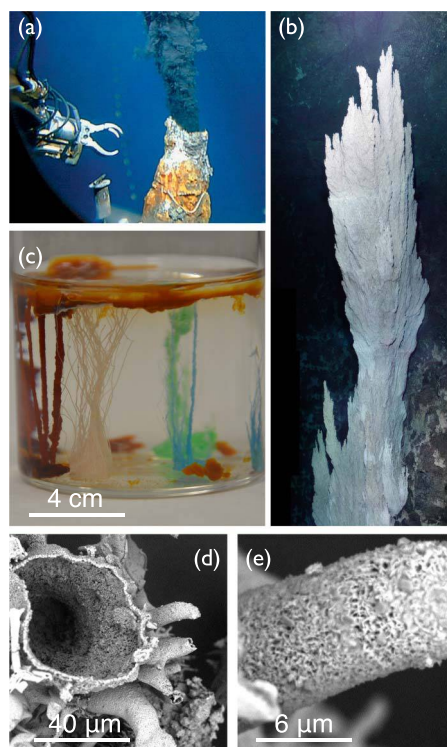


Figure 4. Tubular structures are found at all scales in laboratory and natural chemical gardens [9], ranging from micrometers to tens of meters in size. (a) Black smoker chimney and (b) Lost City alkaline hydrothermal vent. These tubular structures are several meters tall. (c) Laboratory chemical garden. (d, e) Electron microscope views of a single chemical garden tube.

biology, material science, and catalysis. Researchers in these disciplines usually do not communicate with each other, and there is no general knowledge that these phenomena are very interrelated.

3 Self-Assembled Material Architectures and their Possible Technological Applications

The current commitment to chemobrionics is at the level of fundamental scientific research. The research that is being carried out in this very active field today lies close to the heart of complex systems and nonlinear science. There are large, active scientific communities in physics and chemistry that that will be alive to further developments in this field. Moreover, the question of how life began in the universe is perhaps the greatest challenge of complex systems and their self-assembly and self-organization. The linking together of research with the field of chemobrionics certainly spurs efforts towards putting together the pieces of this question, an answer to which would surely reverberate beyond science [7, 38, 48].

From a technological perspective, chemobrionics can be used to learn about physico-chemical systems that in some ways mimic biological systems and, if these systems are mastered, may lead to the development of new self-assembling technologies that could operate from nanometer to meter scales (Figure 5). The richness and complexity of these chemical motors and chemical batteries, to name two already foreseen developments, and the fact that they emerge from simple, mostly two-component chemical systems, indicate that their formation is an intrinsic physical property of the specific chemical systems. By simply changing concentrations or reactants and other experimental

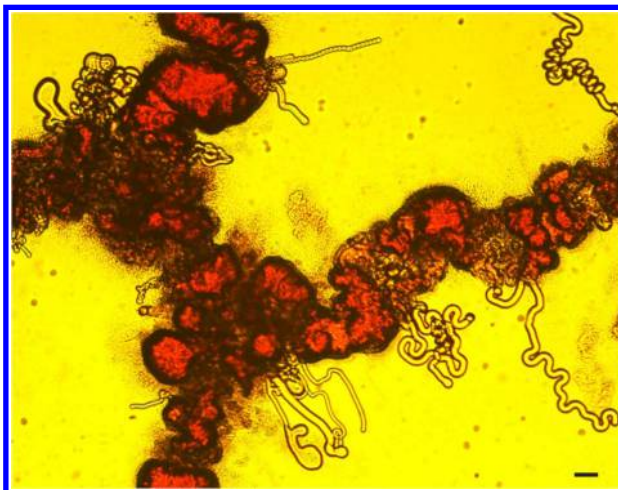


Figure 5. Decanol droplets placed in an aqueous solution of alkaline sodium decanoate form filamentary structures. The formation and growth of these structures morphologically resemble the formation and growth of tubular structures in traditional chemical gardens. Initial conditions: glass slide with a diameter 10 mm, 77.2 μl of 10 mM decanoate solution, 0.6 μl of decanol, 0.5 μl of 6.5 M NaCl. Image taken at time 1 hour after beginning of experiment. The scale bar corresponds to 100 μm [14].

parameters we may arrive at a collection or library of these chemical “engines” [3]. And by expanding on the self-assembling nature of these out-of-equilibrium chemical systems, we may eventually be able to form larger functioning structures. One of the main challenges is to control the morphology, size, and thickness of these structures. Related to this, another important challenge and a great technological development opportunity is the application of micro- or nano-probes to analyze the chemical compositions of internal and external fluids, micro electrical potentials, fluid dynamics, and thickness of layers.

In overcoming these hurdles, a great research opportunity can be opened to produce homogeneous and tailored micro- and nanotubes for industrial applications. However, for these last opportunities to become possible, it will be necessary to overcome another challenge, namely, to optimize these structures in order to improve their plasticity and mechanical strength. We highlight some of the possible technological applications of chemobrionics:

- **Organic and bio-materials:** It is a challenge to extend chemical gardens to organic and mixed inorganic–organic chemobrionic systems [33]. This can open a great opportunity to create nanostructures for bio-materials that have high biocompatibility with living cells and tissues. Chemical gardens may also be worth considering with regard to selective adsorption–desorption processes of interest, for example, for the slow release of drugs [1].
- **Medicine:** Hughes et al. [24] have employed chemobrionic structures as self-assemblages of calcium phosphate tubes to form cellular scaffolds for hard-tissue engineering. That bone-marrow-derived mesenchymal stem cells bind to these tubular structures is particularly promising for bone regeneration operations.
- **Electrochemistry:** The electrochemical properties of self-assembling chemobrionic membranes are poorly understood, and further studies of these phenomena in laboratory experiments will help us understand the larger-scale energy generation that occurs in natural chemical-garden systems. During their formation, chemical gardens produce an electric potential across their interfacial membrane [2], which has a clear technological application to fuel cell technology [31].

- **Catalysis and adsorption:** Chemical gardens are formed by controlled crystal growth at an interface, not unlike electroplating material onto a surface or growing thin solid films. Taking into account that chemical-garden micro- or nanotubes can have reactive internal surfaces with chemical and adsorption properties, these structures will be useful in applications such as nanocatalysts and nanosupports for catalysts.
- **Gas adsorption:** The porosity and the large surface area of these tubes could be advantageous for selective adsorption–desorption of gaseous pollutants and gas exchange processes. For these potential applications, other challenges need to be overcome, such as the necessary mechanical properties, plasticity, and morphology control.
- **Microfluidics and controlled branching and tubular networks:** If we can control branching in chemical-garden tubes, we can construct tubular microfluidic networks for fluid processing, mixing, and so on. Important advances have already been achieved in this respect in recent years [46], but more remains to be done.
- **Sensors and filtration:** Semipermeable membrane materials are of compelling interest for many applications, and chemical gardens have already been shown to possess semipermeable properties. Choice of starting components, or incorporation of functional molecules, in these soft materials could open new avenues in hybrid membrane research for small-molecule sensing or water recycling.
- **Chemical motors:** Chemical motors may be defined as structures that move using chemical reactions to produce the required energy. In chemical gardens the motors first self-construct spontaneously, and then they may move in many different modes. Examples of the motion include linear translation, rotation [28], periodic rupturing [17, 34], periodic buoyancy oscillations, periodic waving or stretching of the entire structure, and periodic ejection of complex tubes [29].
- **Back to cement:** The application of chemical-garden ideas to understanding the hydration of Portland cement has lain mostly dormant since a burst of activity from the 1970s to the 1990s. With the fresh insights and new analytical techniques available today, determined researchers could make a large contribution to this subfield with obviously high industrial impact.
- **Complex materials:** A possible outcome of experiments where one reactant solution is injected into the other one at given concentrations is to be able to control the composition and structures of the precipitates and crystals formed. For instance, layered or complex materials could be synthesized upon successive injection of solutions of different composition. This provides a route to the design and growth of complex materials.

Thus a significant number of potential applications and fields can benefit from chemobionics research, and the perspective and insight gained from a better understanding of chemobionics can provide new perspectives and also new bridges between currently disconnected areas of scientific and technological interest.

4 The Origin of Life

The *submarine alkaline vent theory* (SAVT) for the emergence of life on Earth, now 30 years old, has reached the stage where it provides a clear path forward in emergence-of-life research involving transdisciplinary approaches to the problem [13, 47].

That theory now leads research on the emergence of life, as evidenced by references to it made in many recent books and by the rapid growth in citations. It is predicated on the unique proposal that chemical (i.e., proton and electron) disequilibrium on the early Earth (acting as a battery) was at a

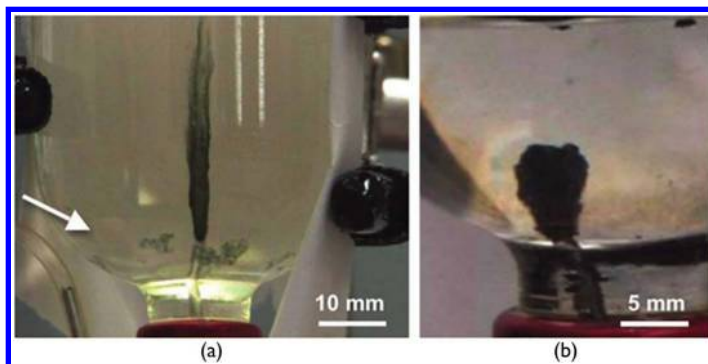


Figure 6. Chemical gardens and the origin of life. Simulacrum of the Hadean Ocean containing 10 mM ferrous iron. (a) When injection rate is rapid, a chimney grows to ≈ 35 mm in 8 min before the top spalls off and settles (white arrow). (b) Geodic growth is favored when injection rate is slow [30].

potential approaching 1 volt. Built on empirical evidence—for example, the rapid reduction of nitrate (the likely first high-potential electron acceptor) to ammonia and the amination of pyruvate to the amino acid alanine—the SAVT predicts that the 50 or so hydrous interlayers of green rust, clamped between layered pliable redox-active iron oxyhydroxide boundaries dosed with Ni, Co, and Mo and supported by iron sulfides, provide the potential to: (i) reduce CO_2 to formate, (ii) differentiate and specialize functions such as proton-pumping and thereby generate, through a conversion engine, a far out-of-equilibrium PPI:Pi ratio of 10^{10} , early life's main power source, (iii) enable electron bifurcation, bequeathing life a molybdenum-mediated step-up transformer to drive strongly endergonic reactions and thus provide the organic framework molecules required for metabolism, (iv) oxidize hydrogen and methane with nitric oxide to methyl groups to react with formate, and thereby (v) produce the acetic acid, the target molecule of all metabolism, and pyruvate, (vi) polymerize these to heterochiral peptides to protect the evolving system at its various scales—all in all, resulting in the germination and first flowering of the organic evolutionary tree as it emerges from the hydroponically fertilized green rust seed. A further research direction, still at its very early stages, is to investigate how green rust could begin to act as a digital information system to control particular amino acid (and peptide) output from aminations of carboxylic acids. The above geochemical and biochemical steps must interface with biophysical and geophysical steps that involve the self-assembly of semipermeable mineral membranes across which chemiosmosis operates. Submarine alkaline hydrothermal vents are thus natural chemical gardens (Figure 6).

We hope that ongoing research will outline, and/or provide, stringent experimental evidence to indicate the success, partial success, or failure of the SAVT—in its present form involving pliable, redox-active, yet resilient iron hydroxide boundaries of green rust, considered to have provided the organizational seed to all life—thereby disinterring the roots of the evolutionary tree that have lain hidden for the last 160 years.

5 A Network to Coordinate Research

An initial workshop on chemical gardens and chemobionics was organized at the Lorentz Center, Leiden, in 2012, and proved a great success. The new COST network on chemobionics is a natural successor to that workshop.

The aim of this COST Action is to link research groups throughout Europe and beyond to stimulate new, innovative, and high-impact interdisciplinary scientific research on chemobionics. The objective is to build bridges between the various communities to allow understanding and controlling

physical, chemical, and biological properties of self-organized complex precipitation processes. This integrated fundamental knowledge will be shared with research groups focusing on specific applications, as well as with groups involved in the popularization of science and those at the interface between science and the arts.

The objective of this network is to coordinate the expertise of research groups throughout Europe and beyond to stimulate new, innovative, collaborative, and high-impact transdisciplinary scientific research on understanding the nonlinear dynamics of these far-from-equilibrium complex systems, the formation of biomimetic microtubular and nanotubular forms, and the interactions with other systems, including nanomaterial applications, new routes to the development of synthetic and artificial biologies, and thermodynamical implications related to the origin of life on Earth. We have discussed the wide range of systems that can be considered chemical gardens or to which the concepts, ideas, and methods developed for chemical gardens can be applied.

The identified objectives will help in generating new bridges with related systems to enhance the potential of this field. This Action will also stimulate the coordination of laboratory facilities, including the co-use of equipment and processing software. The combination of these coordination Actions in expertise, laboratory facilities, and applications will stimulate faster growth of the field of chemobionics and its impact on society.

Particular research coordination objectives are:

1. To understand the relationship between the experimental conditions and morphology of these structures formed out of equilibrium.
2. To combine different instrumental and analytical techniques to characterize these structures in terms of the chemical compositions and the gradients of chemical compositions and crystallinity.
3. To understand the fluid dynamics during the formation of chemical gardens and biomimetic nanomaterials.
4. To understand the interactions between metallic oxide–hydroxide layers in the formation of tubular forms at the atomic scale.
5. To understand the thermodynamics in the interactions of the internal surfaces of these materials with water and organic molecules.
6. To construct a protocol for flow-controlled synthesis of a solid material.
7. To explore the role of chemobionics for the emergence of life at hydrothermal vents.
8. To promote dissemination and science–art crossover activities related to chemical gardens.

Our wish is that the coordination of research through this network should lead to the development of new areas of fundamental scientific inquiry through sharing the knowledge and enhancing the research abilities of the participants. In particular the network is coordinating research that will have significant impacts on important contemporary issues. On the side of fundamental science and artificial life research, new knowledge about the origin of life here on Earth and in the universe fulfills one of the most basic human desires: to understand where we came from, and whether we are alone in the universe. On the technological side, there is the impact of the formation of new functional materials. While in the short term this is fundamental science, the knowledge derived and disseminated under this Action will have strong socioeconomic impacts in the long term. It is clear that an enhanced ability for the development of new materials, with applications in diverse areas such as energy technologies or information and communications technology, will be very helpful in the long term.

Acknowledgments

This work was supported by COST Action CA17120.

References

1. Angelis, G., Zayed, D. N., Karioti, A., Lazari, D., Kanata, E., Sklaviadis, T., & Pampalakis, G. (2019). A closed chemobiontic system as a biochemical delivery platform. *Chemistry—a European Journal*, *25*(56), 12916–12919.
2. Barge, L. M., Abedian, Y., Russell, M. J., Doloboff, I. J., Cartwright, J. H. E., Kidd, R. D., & Kanik, I. (2015). From chemical gardens to fuel cells: Generation of electrical potential and current across self-assembling iron mineral membranes. *Angewandte Chemie International Edition*, *54*(28), 8184–8187.
3. Barge, L. M., Cardoso, S. S. S., Cartwright, J. H. E., Cooper, G. J. T., Cronin, L., De Wit, A., Doloboff, I. J., Escribano, B., Goldstein, R. E., Haudin, F., Jones, D. E. H., Mackay, A. L., Maselko, J., Pagano, J. J., Pantaleone, J., Russell, M. J., Sainz-Díaz, C. I., Steinbock, O., Stone, D. A., Tanimoto, Y., & Thomas, N. L. (2015). From chemical gardens to chemobionics. *Chemical Reviews*, *115*(16), 8652–8703.
4. Branscomb, E., & Russell, M. J. (2017). Why Frankenstein theories for the emergence of life ('warm little ponds,' 'prebiotic soups,' 'energized assemblages of building blocks,' ...) cannot in principle be correct. Presented at the 2017 NASA Astrobiological Institute Principal Investigators Meeting, University of Illinois, Urbana-Champaign, IL.
5. Branscomb, E., & Russell, M. J. (2019). Why the submarine alkaline vent is the most reasonable explanation for the emergence of life. *BioEssays*, *41*(1), 1800208.
6. Brau, F., Haudin, F., Thouvenel-Romans, S., De Wit, A., Steinbock, O., Cardoso, S. S. S., & Cartwright, J. H. E. (2018). Filament dynamics in confined chemical gardens and in filiform corrosion. *Physical Chemistry Chemical Physics*, *20*(2), 784–793.
7. Burcar, B. T., Barge, L. M., Trail, D., Watson, E. B., Russell, M. J., & McGown, L. B. (2015). RNA oligomerization in laboratory analogues of alkaline hydrothermal vent systems. *Astrobiology*, *15*(7), 509–522.
8. Camprubí, E., de Leeuw, J. W., House, C. H., Raulin, F., Russell, M. J., Spang, A., Tirumalai, M. R., & Westall, F. (2019). The emergence of life. *Space Science Reviews*, *215*(8), 56.
9. Cardoso, S. S. S., & Cartwright, J. H. E. (2017). On the differing growth mechanisms of black-smoker and Lost City-type hydrothermal vents. *Proceedings of the Royal Society A*, *473*, 20170387.
10. Cardoso, S. S. S., Cartwright, J. H. E., Steinbock, O., Stone, D. A., & Thomas, N. L. (2017). Cement nanotubes: On chemical gardens and cement. *Structural Chemistry*, *28*(1), 33–37.
11. Cartwright, J. H. E., Escribano, B., Sainz-Díaz, C. I., & Tuvall, I. (2013). Brinicles as a case of inverse chemical gardens. *Langmuir*, *29*(25), 7655–7660.
12. Cartwright, J. H. E., García-Ruiz, J. M., Novella, M. L., & Otálora, F. (2002). Formation of chemical gardens. *Journal of Colloid and Interface Science*, *256*(2), 351–359.
13. Cartwright, J. H. E., & Russell, M. J. (2019). The origin of life: The submarine alkaline vent theory at 30. *Interface Focus*, *9*(6), 20190104.
14. Čejková, J., Štěpánek, F., & Hanczyc, M. M. (2016). Evaporation-induced pattern formation of decanol droplets. *Langmuir*, *32*(19), 4800–4805.
15. Coatman, R. D., Thomas, N. L., & Double, D. D. (1980). Studies of the growth of "silicate gardens" and related phenomena. *Journal of Materials Science*, *15*(8), 2017–2026.
16. Cooper, G. J. T., Bowman, R. W., Magennis, E. P., Fernandez-Trillo, F., Alexander, C., Padgett, M. J., & Cronin, L. (2012). Directed assembly of inorganic polyoxometalate-based micrometer-scale tubular architectures by using optical control. *Angewandte Chemie International Edition*, *51*(51), 12754–12758.
17. Ding, Y., Gutiérrez-Ariza, C. M., Sainz-Díaz, C. I., Cartwright, J. H. E., & Cardoso, S. S. S. (2019). Exploding chemical gardens: A phase-change clock reaction. *Angewandte Chemie International Edition*, *58*(19), 6207–6213.
18. Duval, S., Baymann, F., Schoep-Cothenet, B., Trolard, F., Bourrié, G., Grauby, O., Branscomb, E., Russell, M. J., & Nitschke, W. (2019). Fougérite: The not so simple progenitor of the first cells. *Interface Focus*, *9*(6), 20190063.
19. Endres, R. G. (2017). Entropy production selects nonequilibrium states in multistable systems. *Scientific Reports*, *7*(1), 14437.
20. Glaab, F., García-Ruiz, J. M., Kunz, W., & Kellermeier, M. (2016). Diffusion and precipitation processes in iron-based silica gardens. *Physical Chemistry Chemical Physics*, *18*(36), 24850–24858.

21. Glaab, F., Kellermeier, M., Kunz, W., Morallon, E., & García-Ruiz, J. M. (2012). Formation and evolution of chemical gradients and potential differences across self-assembling inorganic membranes. *Angewandte Chemie International Edition*, *124*(18), 4393–4397.
22. Haudin, F., Cartwright, J. H. E., Brau, F., & De Wit, A. (2014). Spiral precipitation patterns in confined chemical gardens. *Proceedings of the National Academy of Sciences of the USA*, *111*(49), 17363–17367.
23. Herrmann, J., Li, P.-N., Jabbarpour, F., Chan, A. C. K., Rajkovic, I., Matsui, T., Shapiro, L., Smit, J., Weiss, T. M., Murphy, M. E. P., & Wakatsuki, S. (2020). A bacterial surface layer protein exploits multistep crystallization for rapid self-assembly. *Proceedings of the National Academy of Sciences of the USA*, *117*(1), 388–394.
24. Hughes, E. A. B., Chipara, M., Hall, T. J., Williams, R. L., & Grover, L. M. (2020). Chemobionic structures in tissue engineering: Self-assembling calcium phosphate tubes as cellular scaffolds. *Biomaterials Science*, *8*, 812–822.
25. Hussein, A., Maselko, J., & Pantaleone, J. T. (2016). Growing a chemical garden at the air–fluid interface. *Langmuir*, *32*(3), 706–711.
26. Kaminker, V., Maselko, J., & Pantaleone, J. (2014). The dynamics of open precipitation tubes. *Journal of Chemical Physics*, *140*(24), 244901.
27. Martin, W., Baross, J., Kelley, D., & Russell, M. J. (2008). Hydrothermal vents and the origin of life. *Nature Reviews Microbiology*, *6*(11), 805–814.
28. Maselko, J., Borisova, P., Carnahan, M., Dreyer, E., Devon, R., Schmoll, M., & Douthat, D. (2005). Spontaneous formation of chemical motors in simple inorganic systems. *Journal of Materials Science*, *40*(17), 4671–4673.
29. Maselko, J., & Pantaleone, J. (2019). Universal chemical machine: Continuous increase of complexity and chemical evolution. *Journal of Systems Chemistry*, *7*, 38–51.
30. Mielke, R. E., Russell, M. J., Wilson, P. R., McGlynn, S. E., Coleman, M., Kidd, R., & Kanik, I. (2010). Design, fabrication, and test of a hydrothermal reactor for origin-of-life experiments. *Astrobiology*, *10*, 799–810.
31. Nakanishi, K., Cooper, G. J. T., Points, L. J., Bloor, L. G., Ohba, M., & Cronin, L. (2018). Development of a minimal photosystem for hydrogen production in inorganic chemical cells. *Angewandte Chemie International Edition*, *57*(40), 13066–13070.
32. Neves, J., Grugel, R. N., Sheetz, B., & Radlinska, A. (2019). *Experimental investigation of cement hydration in gravity-free environment* (Technical Report). NASA.
33. Pampalakis, G. (2016). The generation of an organic inverted chemical garden. *Chemistry—a European Journal*, *22*(20), 6779–6782.
34. Pantaleone, J., Tóth, A., Horváth, D., RoseFigura, L., Morgan, W., & Maselko, J. (2009). Pressure oscillations in a chemical garden. *Physical Review E*, *79*(5), 056221.
35. Points, L. J., Cooper, G. J. T., Dolbecq, A., Mialane, P., & Cronin, L. (2016). An all-inorganic polyoxometalate–polyoxocation chemical garden. *Chemical Communications*, *52*(9), 1911–1914.
36. Pópit-Tóth, E., Schuszter, G., Horváth, D., & Tóth, A. (2018). Peristalticity-driven banded chemical garden. *Journal of Chemical Physics*, *148*(18), 184701.
37. Rauscher, E., Schuszter, G., Bohner, B., Tóth, A., & Horváth, D. (2018). Osmotic contribution to the flow-driven tube formation of copper–phosphate and copper–silicate chemical gardens. *Physical Chemistry Chemical Physics*, *20*(8), 5766–5770.
38. Russell, M. (2006). First life: Billions of years ago, deep under the ocean, the pores and pockets in minerals that surrounded warm, alkaline springs catalyzed the beginning of life. *American Scientist*, *94*(1), 32–39.
39. Russell, M. J., & Hall, A. J. (1997). The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *Journal of the Geological Society of London*, *154*(3), 377–402.
40. Schuszter, G., Brau, F., & De Wit, A. (2016). Calcium carbonate mineralization in a confined geometry. *Environmental Science and Technology Letters*, *3*(4), 156–159.
41. Stone, D. A., & Goldstein, R. E. (2004). Tubular precipitation and redox gradients on a bubbling template. *Proceedings of the National Academy of Sciences of the USA*, *101*(32), 11537–11541.

42. Stone, D. A., Lewellyn, B., Baygents, J. C., & Goldstein, R. E. (2005). Precipitative growth templated by a fluid jet. *Langmuir*, *21*(24), 10916–10919.
43. Takács, D., Schuszter, G., Sebők, D., Kukovecz, A., Horváth, D., & Tóth, A. (2019). Magnetic-field-manipulated growth of flow-driven precipitate membrane tubes. *Chemistry—a European Journal*, *25*(65), 14826–14833.
44. Thouvenel-Romans, S., & Steinbock, O. (2003). Oscillatory growth of silica tubes in chemical gardens. *Journal of the American Chemical Society*, *125*(14), 4338–4341.
45. Vance, S. D., Barge, L. M., Cardoso, S. S. S., & Cartwright, J. H. E. (2019). Self-assembling ice membranes on Europa: Brinicle properties, field examples, and possible energetic systems in icy ocean worlds. *Astrobiology*, *19*(5), 685–695.
46. Wang, Q., Bentley, M., & Steinbock, O. (2017). Self-organization of layered inorganic membranes in microfluidic devices. *Journal of Physical Chemistry C*, *121*, 14120–14127.
47. Wang, Q., & Steinbock, O. (2020). Materials synthesis and catalysis in microfluidic devices: Prebiotic chemistry in mineral membranes. *ChemCatChem*, *12*(1), 63–74.
48. Zhao, W., & Sakurai, K. (2017). Realtime observation of diffusing elements in a chemical garden. *ACS Omega*, *2*(8), 4363–4369.

This article has been cited by:

1. Qingpu Wang, Franco M. Zanotto, Oliver Steinbock. 2020. Precipitate Patterns in a Hele-Shaw Cell with Small Sinusoidal Height Variations. *The Journal of Physical Chemistry C* **124**:39, 21617-21624. [[Crossref](#)]
2. Pawan Kumar, Dezső Horváth, Ágota Tóth. 2020. Bio-inspired flow-driven chitosan chemical gardens. *Soft Matter* **29**. . [[Crossref](#)]