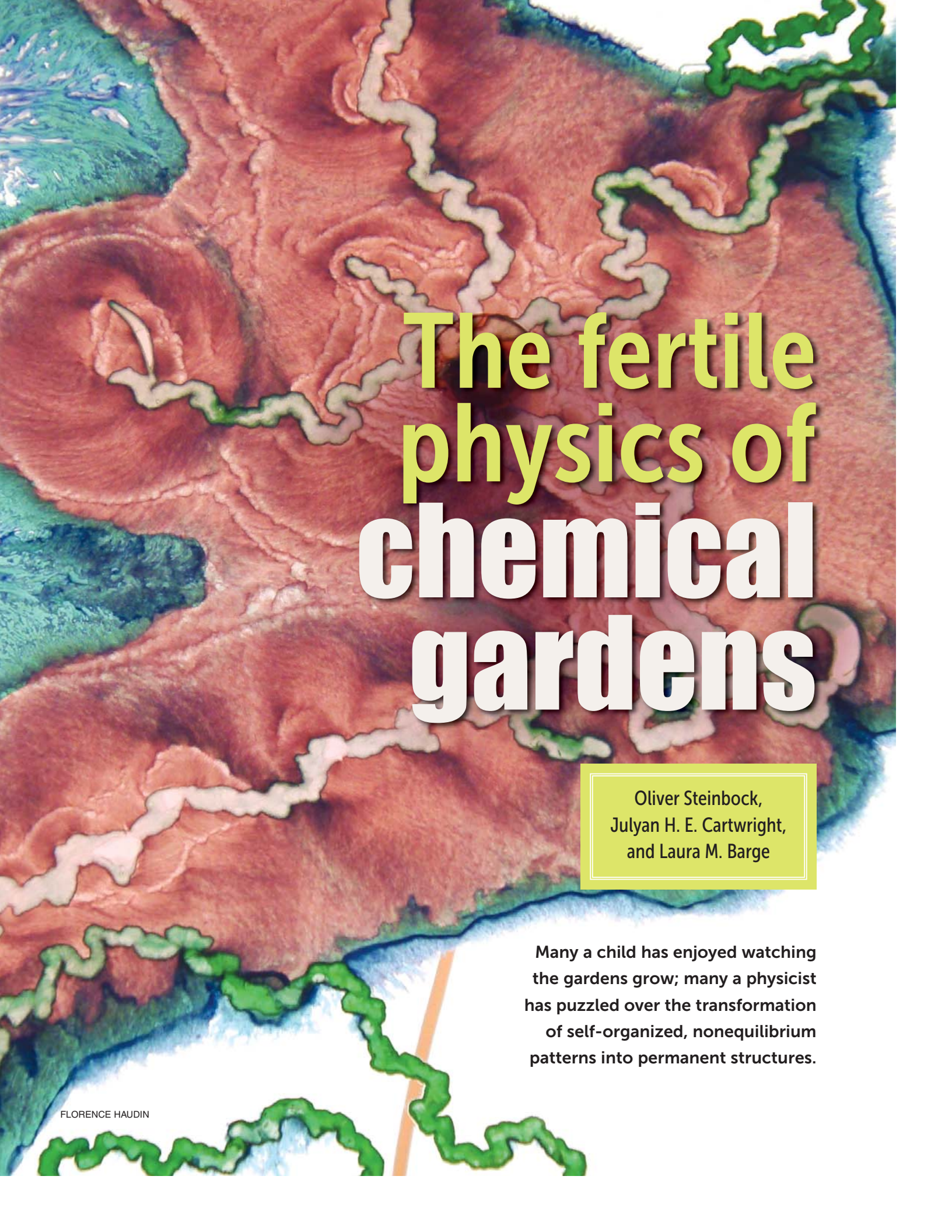


An abstract, colorful artwork depicting the intricate, branching, and swirling patterns of chemical gardens. The colors range from deep reds and oranges to bright greens and blues, creating a complex, organic texture. The patterns resemble a network of veins or a microscopic view of a growing organism.

The fertile physics of chemical gardens

Oliver Steinbock,
Julyan H. E. Cartwright,
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Many a child has enjoyed watching the gardens grow; many a physicist has puzzled over the transformation of self-organized, nonequilibrium patterns into permanent structures.



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“I shall never forget the sight. The vessel of crystallization was three-quarters full . . . and from the sandy bottom there strove upwards a grotesque little landscape of variously colored growths: a confused vegetation of blue, green, and brown shoots.”

That is how a character in German novelist and Nobel laureate Thomas Mann’s *Doctor Faustus* described the colorful mineral structures that he observed spontaneously growing from crystals placed into solution—an experiment that many readers may remember from their childhood chemistry kits or from classroom demonstrations. (See the cover of this issue.) But those experiments are not just toys: Many related systems are found in nature, technology, and the laboratory. First described in 1646 by Johann Glauber, “chemical gardens” are one of chemistry’s oldest fascinations, attracting even the curiosity of Isaac Newton.¹

Though not alive, chemical gardens do exhibit certain characteristics, including self-organization and the formation of membranes, reminiscent of biological systems. Indeed, in the 19th and early 20th centuries the self-assembling structures were thought to reveal insights into the mechanism of life emerging from an inorganic setting.

Today the chemical and molecular aspects of those systems are well understood, and the research focus has shifted to the physics of chemical gardens. The aim is to quantitatively explain basic features such as the growth speed and radius selection in the gardens. Bigger-picture questions are also being addressed that link chemical gardens to a larger class of self-organizing systems far from thermodynamic equilibrium. In that spirit, researchers are investigating macroscopic growth patterns and dynamical complexities such as relaxation oscillations in the system pressure that can lead to twitching and shape changes.

The physical approach reveals perplexing scaling laws and attracts researchers with backgrounds in nonlinear dynamics, pattern formation, self-assembly, and fluid dynamics. Materials scientists could learn potentially important

lessons as chemical gardens create macroscopic complexity and hierarchical nano-to-macro architectures. There is even the possibility of making device-like tubes from molecular processes in a new field of study that has been termed chemobionics. Finally, by studying chemical gardens that form in geological settings, researchers are again focusing on their role in the origins of life on Earth.

How does your garden grow?

Kits for growing a chemical garden are available at many toy and hobby stores, but making your own is simple (see box 1). It involves placing a seed crystal of a metal salt into a silicate or similar solution. A precipitate structure then sprouts from the seed and begins to grow; it often reaches the height of a typical test tube in just 10–20 minutes. Within the first seconds, the dissolving salt generates a thin membrane of colloidal metal hydroxide particles that aggregate around the seed (figure 1). The membrane expands and ruptures again and again under osmotic pressure,² each time releasing a buoyant jet of salt solution that immediately reprecipitates additional inorganic membrane as it reacts with the reservoir solution. Thus the structure continues to grow from that self-organized osmotic pump until the seed particle at the base is fully dissolved. For some background on osmosis, see box 2. The chemical garden itself can take many forms, from bulbs to hairs to plume-like structures. In the simplest case, it consists of just a hollow tube of precipitate, which forms around the jet of salt solution and extends the reactant-delivering conduit upward.

The precipitate membrane continues to form only as long as the interior solution of the dissolving salt continues to flow into the reservoir solution—that is, for as long as the far-from-equilibrium chemical contrast persists between exterior and interior solutions. Once equilibrium is reached, the resulting tubes and structures remain. Sometimes fragile or prone to oxidation, the structures can nevertheless be

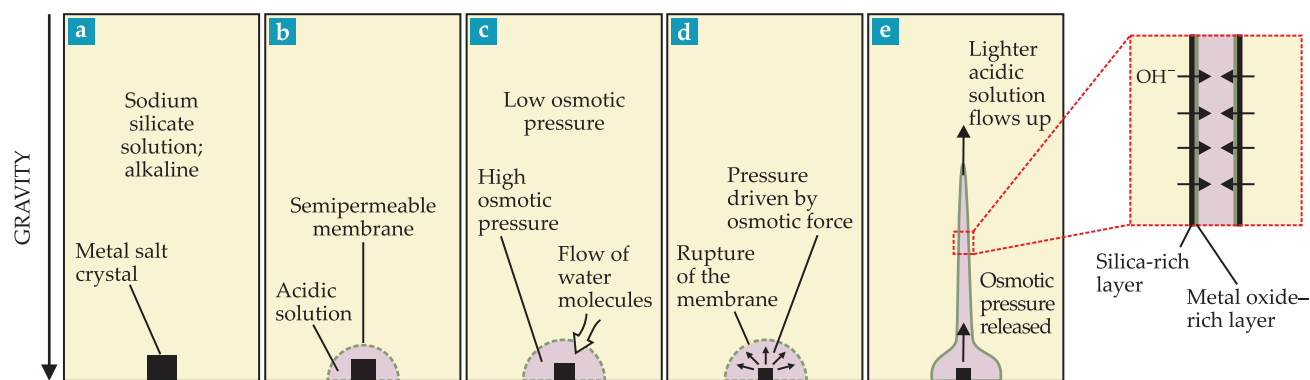


FIGURE 1. HOW A CHEMICAL GARDEN GROWS. (a) A metal salt crystal at the bottom of a container with an appropriate alkaline solution begins to dissolve. (b) A thin membrane of metal hydroxide particles forms almost instantly, creating a small acidic compartment. (c) The membrane allows water molecules and hydroxide ions (OH^-) to flow inward through osmosis, which increases the interior pressure and (d) eventually ruptures the membrane. (e) As the buoyant metal–acid solution rises, the membrane immediately self-heals and a stem forms. The inset shows some details of the often fragile tube.

analyzed with the usual array of materials characterization techniques: x-ray diffraction, electron microscopy, and various forms of optical spectroscopy, to name a few. The work has led to an unprecedented understanding of the formation process, which we now know involves self-organization even at the microscale. In a typical case, the hollow membranous tube of precipitate is about 1 mm across, with 10- μm -thick layered walls consisting of an outer layer of amorphous silica and an inner layer rich in polycrystalline metal hydroxide or oxide (figure 1e, inset).

The chemical garden phenomenon is not limited to silicate

systems. Chemical gardens can form from a wide range of seed chemicals—for example, salts of iron, cobalt, nickel, copper, or calcium—and in many different reservoir solutions, such as carbonate, phosphate, hydroxide, or borate, that can precipitate with the seed cation. Chemical garden systems do not even have to be strictly inorganic. Recently, the zoo of tube-forming chemicals has been further extended by Lee Cronin's group at the University of Glasgow and their colleagues, who grew self-assembling polyoxometalate tubes in which the other key player is an organic anion.³ The diverse chemical inventory that can lead to the formation of self-organized chemical garden

structures clearly suggests universal principles that are more rooted in physics than in chemistry. We must understand the relevant physics not only to control the growth of chemical gardens but also to harness the many possible applications of self-assembling inorganic tubes that can incorporate diverse materials.

The quest to simplify

The multitude and variety of tube structures that form in a typical chemical garden experiment are definitely fascinating and entertaining. But the variety hinders efforts to make reproducible and systematic measurements of key physical quantities such as the tubes' morphologies, radii, and growth speeds. To enable more rigor, many studies now replace readily available seed particles with more controlled reagent reservoirs. One common technique is to use pressed seed pellets, which offer the advantage of reproducible sizes, shapes, and weights.

Alternatively, the seed reagent solution can be loaded into well-defined polymer beads that, in addition to offering the obvious control over size and reagent load, provide access to rather small size scales. One of our groups (the Steinbock lab) has grown mi-

BOX 1. DO-IT-YOURSELF CHEMICAL GARDENING

Ingredients

1. Test tube or beaker.
2. Sodium silicate solution, also called water glass. You can buy it ready-made, usually as a 40% solution, or make your own by dissolving solid $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ in water.
3. Metal salt crystals, such as ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), calcium chloride (CaCl_2), copper sulfate (CuSO_4), or nickel chloride (NiCl_2).

Instructions

1. Fill the test tube or beaker with sodium silicate solution mixed with water. You can vary the ratio; a 40% sodium silicate solution could be mixed with water in a 2:1 ratio. Mix well.
2. Drop a few millimeter-sized particles of the metal salt into the solution; tap so that the salt settles to the bottom.
3. Watch your chemical gardens grow! Tubes form within a few minutes and can grow to heights of more than 10 cm. The color of the resulting tubes often corresponds to the respective metal hydroxide. For example, FeCl_2 yields brown or green growths; CaCl_2 , white; CuSO_4 , blue; and NiCl_2 , green. Different salts in the same solution result in a multicolored chemical garden.
4. Always use proper chemical safety procedures and dispose of the gardens as chemical waste.

The image shows chemical garden tubes grown with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ crystals in sodium silicate solution mixed with water.



IVIRIA DOLOBOFF

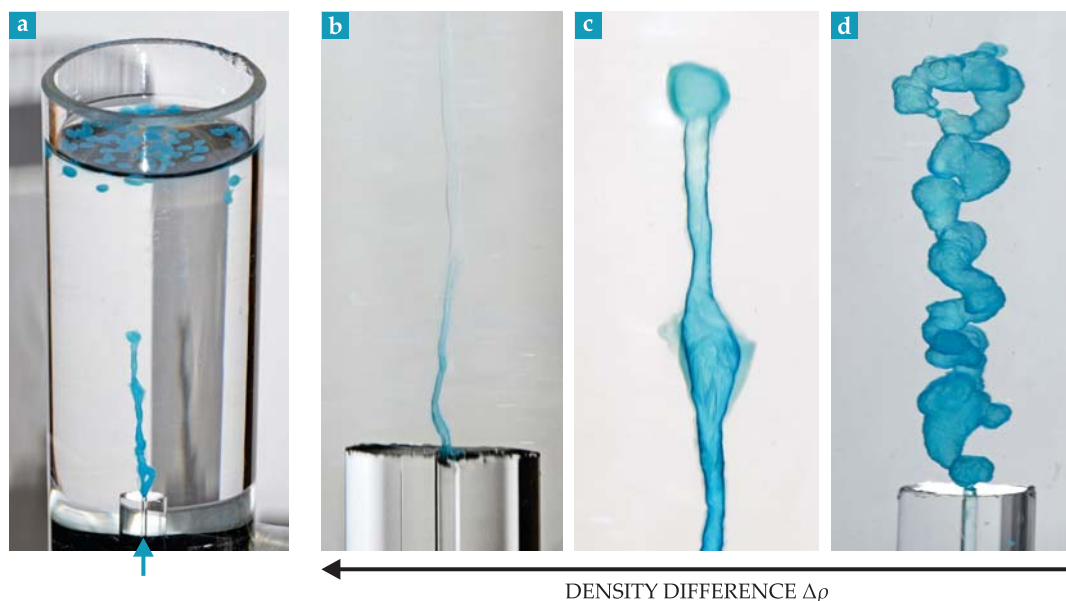


FIGURE 2. FLOW-CONTROLLED CHEMICAL GARDENS. (a) A metal salt solution (blue) is injected steadily through the bottom of a reservoir holding sodium silicate solution. The tube morphology is determined by the density difference $\Delta\rho$ between the outer and inner solutions and varies from (b) smooth jetting tubes, to (c) oscillatory popping structures in which the upper nodule is pinched off and drifts away, to (d) budding tubes that continually expand. Short movies of these processes accompany the online version of this article.

crogardens with metal-ion-loaded microbeads as the seeds. Those experiments created shells and protruding tubular structures with radii as small as $3\text{ }\mu\text{m}$ —smaller than the size of a human red blood cell. In microfluidics and biomedical applications, such thin tubes must usually be produced by expensive lithographic techniques and are somewhat limited in their three-dimensional routing and materials repertoire. Another intriguing observation in these microgarden systems, by a team with Jerzy Maselko and James Pantaleone at the University of Alaska Anchorage, is that the self-assembling tubes extending out of the bead can propel the bead into motion, if the growth point of the tube is pinned to a stationary substrate—for example, using impurities or gas bubbles on a glass slide.⁴ That is an example of a system in which isothermal chemical reactions create directed large-scale motion through spontaneous symmetry breaking.

Control is key

A much more precise level of control over chemical garden systems is available by using a seed solution—rather than a seed particle—that is injected directly into a large reservoir of the other reactant.⁵ Such injection delivery is typically performed in the upward direction, at constant rates, using a needle or small tube. Downward-directed injection is also possible if the seed solution is denser than the reservoir solution; so is horizontal injection if buoyancy is excluded. Injection experiments usually form one single tube, and, perhaps more important, the initial concentrations, densities, and viscosities of the reacting exterior and interior solutions are precisely known.

One of the first advances from such studies was the identi-

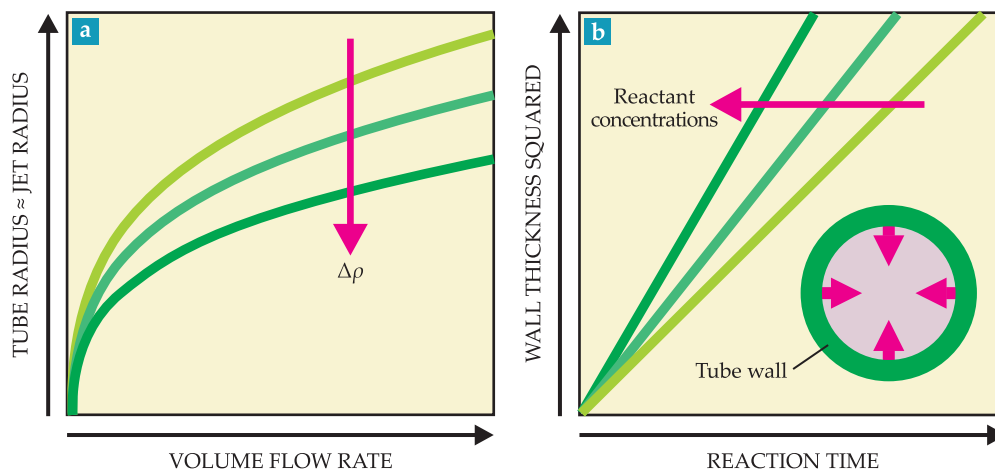
fication of distinct growth regimes in chemical garden formation (figure 2). If the injected interior solution is highly buoyant, open-tube growth occurs around an ascending fluid jet. At some lower density difference $\Delta\rho$, jetting growth gives way to an oscillatory mode in which the tube is capped by an expanding membrane envelope that periodically detaches from the extending stalk, similar to an expanding and popping balloon. At even lower buoyancy, the balloon no longer pops off but breaches locally to nucleate a new bud, and a cactus-like, hollow chain of nodules eventually forms. An enormous variety of precipitate morphologies and physical behaviors is observed in the $\Delta\rho$ parameter space, and a classical seed-crystal system might contain any or all of them in a single experiment.

Popping and budding tubes are essentially closed structures that separate the two solutions by an intervening membrane. How can the solutions react and the structure grow if the reaction partners are separated? Clearly, the membranes are at least somewhat porous and permeable. But they are also a self-healing material. If fresh and thin, the elastic membrane can stretch and reconstitute itself in a continuous fashion; if older and thicker, it ruptures, but the breach is almost instantly sealed as the two reactive solutions come into direct contact and form new wall material. That rupturing process is also responsible for crack patterns that are sometimes observed on the exterior surface of chemical gardens. Those patterns can be quite spectacular and are reminiscent of polygonal crack patterns in drying soil (see the article by Lucas Goehring and Stephen Morris, *PHYSICS TODAY*, November 2014, page 39). But in at least some chemical systems, the cracks have outward protruding ridges that result from the reactive sealing events.

Open jetting tubes are a different story. The first surprise is that the solid-forming reaction typically works itself up the ascending jet. The speed v of the wall's climb is a key feature of the system dynamics but has not been well studied. Only this year Bruno Batista and one of us (Steinbock) showed that for certain conditions the vertical-tube growth speed can obey the power law dependence $v \propto Q^{3/2}$, where Q is the fluid injection rate. The intriguing exponent of $3/2$ is a great target for future quantitative modeling efforts, but to date its origin is

FIGURE 3. JETTING TUBES CAN BE EXPLAINED QUANTITATIVELY.

(a) A jetting tube's outer radius (50–500 μm) is determined by the radius of the buoyant reactant jet and depends on the injection rate and on the density difference $\Delta\rho$ between the outer and inner solutions. **(b)** Once the tube wall has formed, it thickens strictly inward, in the direction of the metal solution. These dynamics are typically diffusion controlled, obey a square-root law, and accelerate with increasing reactant concentrations.



unknown. Similar mysteries surround the minimal amount of reactants needed to induce tube growth. Below the relatively high density threshold of about 0.1 mol/L, open-tube growth fails; only hydrodynamic plumes of free colloidal particles are seen. Clearly, particle aggregation and assembly are crucial to the tube's vertical growth.

Additional control over tube formation can be accomplished by using gas bubbles to direct or shape tube growth.⁶ In conventional gardens, bubbles sometimes occur accidentally; air trapped on the seed particle's rough surface during placement into the reservoir solution can drag the precipitate vertically upward as it forms. But by using a gas syringe, one can intentionally introduce a bubble into the solution stream of the injection and pin the bubble to the upper growth rim of the forming tube. That simple intervention generates extremely linear tubes thanks to the high buoyancy of the bubble. Although the bubble is pinned to the gel-like rim of the tube, there

seems to be a large enough gap for new material to form at the reactive solution interface; the gap can even spin, creating helical patterns or a thick rim on the tube surface.

Getting quantitative

For both high-buoyancy bubble-guided tubes and closed structures grown in the low-buoyancy budding regime, the volume increase of the chemical garden structure is essentially identical to the volume rate $Q = dV/dt$ of the injected solution. Accordingly, the tube radius R is connected to the vertical growth velocity v by volume conservation: $\pi R^2 v = Q$. Experiments that control the speed of the bubble (for example, by attaching it to a rod that moves upward at constant speed) hence select a particular tube radius. For experiments in which the ascent of the bubble is not controlled but is limited only by its pinning to the tube, the situation is more complicated. However, the tube radius appears to be about 80–90% of the bubble radius, and

for a given bubble size and pump rate, a particular growth velocity is selected by the underlying volume conservation.

A breakthrough in the quantitative description of open tubes occurred with the realization that the outer radius R of the jetting tubes increases monotonically with the injection rate Q (see figure 3a). The experimental data are well described by the radius of the corresponding nonreactive jet. The problem of radius selection is thus reduced to a comparably simple fluid dynamics analysis⁷ that must consider the fluid flow around the injected jet as well as backflow near the vessel wall. The equation describing that situation is reminiscent of the Hagen–Poiseuille law $Q \propto R^4$, but it involves an important logarithmic correction term. Regardless of the details, at least one quantitative aspect of chemical garden growth is now pleasingly described by an analytical expression that involves no free parameters if strict symmetries are assumed.

BOX 2. OSMOSIS

The physical process of osmosis involves a molecular flow between two fluids, generally to alter a molecule's concentration in one of the fluids. Today's understanding of osmotic pressure and membrane processes arose in the late 19th and early 20th centuries to a great extent from studies by physicists including Lord Rayleigh, Josiah Willard Gibbs, and Walther Nernst, who used data from chemical gardens.

Osmotic pressure is produced by the force induced when some molecules in a fluid are able to cross a pore-containing region that is a barrier for other molecules due to their size, charge, or other relevant property. Some of the solute molecules rebound from the pore entrance and subsequently, through collisions, transfer part of their momentum to neighboring

solvent molecules. A similar process happens at the pore exit. A difference in the concentrations of solute between the entrance and exit creates the osmotic force. A boundary region of that sort is often termed a semipermeable membrane. The semiempirical Kedem–Katchalsky equations are widely used for modeling transport in physical, chemical, and biological membranes and in other porous media, both in the laboratory and in geology. Work involving kinetic theory, fluid mechanics, and thermodynamics performed by Silvana Cardoso's group at Cambridge University has derived from first principles the equations governing osmosis in a porous medium, which contain the Kedem–Katchalsky equations as one limit.¹⁴ The first-principles understanding allows researchers to investigate how osmosis and fluid dynamics come together in chemical gardens.

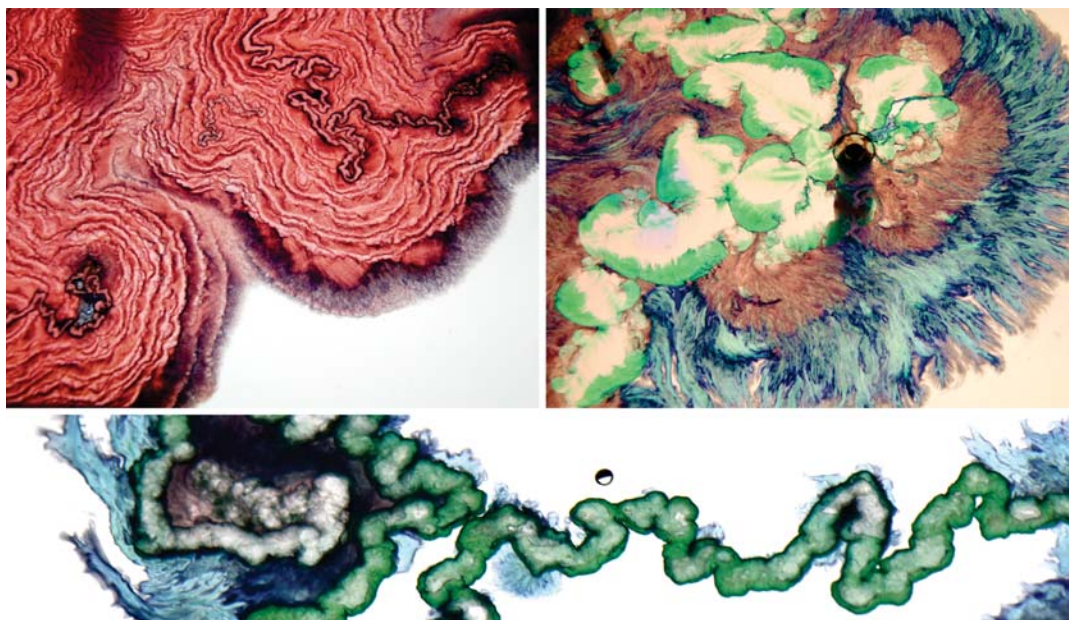


FIGURE 4. HELE-SHAW CELLS reveal the “innards” of chemical gardens. In these experiments by Anne De Wit and her colleagues, cobalt solution was injected into a thin layer of clear silicate solution confined between two horizontal plexiglass plates.⁹ Each image is a few centimeters across. The green channel structure in the lower panel is reminiscent of three-dimensional tubes, but the system also reveals a wealth of unexpected features. More recent studies further simplified the experimental conditions by creating a linear membrane wall in the laminar flow through a microfluidic device. (Images courtesy of Florence Haudin.)

Once we consider the slower, secondary thickening of the tube wall, the physical rule of hydrodynamics ends and reaction–diffusion processes again become important. The first surprise is that the radial growth is unidirectional, typically inward (see figure 3b). Measurements of the temporal dynamics of radial tube growth revealed square-root dependencies that are indicative of a diffusion-controlled process. The unidirectionality of that growth has been attributed to the generic behavior of product formation in reaction–diffusion systems and to the electrically charged character of the thickening, microporous tube wall.

A network of possibilities

A wealth of interesting materials science can be performed or rediscovered in chemical garden tubes. Beyond the basic desire to characterize the composition of the wall, researchers are also motivated by the possibility of producing microfluidic networks with controlled self-assembling tubes. For instance, the Cronin group has grown tubes that are tightly guided by local convection currents that are directed with computer-controlled holographic heating patterns. Among their demonstrations are branching and fusing tubes that create structures reminiscent of microfluidic networks.³ Others have examined the materials features of the tube walls themselves. Versatile composition- and treatment-dependent applications are being found in areas like catalysis and chemical sensing.¹ For example, tubes can be made of catalytic aluminosilicates, and it is possible to use

the tube wall as a platform for trapping various injected components ranging from CdSe/ZnS quantum dots to polymer beads and even biological cells. The wall material can also be transformed after the actual growth process; in a recent study, heating the tubes to 900 °C produced devices such as silica-supported, photocatalytically active ZnO tubes. Beyond chemical changes, heating can also induce a transition from amorphous to crystalline materials that, surprisingly, often leaves the macroscopic tube structure intact.¹

The self-organization of chemical garden formation is a non-equilibrium situation fueled by steep concentration gradients that in most other scenarios would quickly dissipate. That fundamental characteristic is shared with living systems that have mastered the art of controlling and utilizing such far-from-equilibrium conditions for materials synthesis and other engineering feats. Chemical-garden tube walls also feature interesting bimodal pore size distributions that allow ions and molecular species to be exchanged across a wall. That dynamic exchange of species is reminiscent of biological membranes.

The surfaces of the precipitate can have an intrinsic charge, and chemical garden walls exhibit compositional and sometimes redox (reduction–oxidation) gradients that reflect the interface between the initial reacting solutions. During a chemical garden experiment’s far-from-equilibrium phase—while the interior solution is still being injected or the seed crystal is still dissolving—the gradients across the membrane can give rise to a membrane potential not unlike the potentials generated across biological membranes. The potential and corresponding current are easily measured with a multimeter. Combined with modeling the Nernst redox potentials of the exterior and interior solutions, those measurements can quantify the electrochemical disequilibrium in a particular system, which allows researchers to draw an analogy to very low power batteries or fuel cells. The battery-like aspects of laboratory chemical gardens were recently demonstrated by two of us (Barge and Cartwright) and colleagues at NASA’s Jet Propulsion Laboratory (JPL): Several chemical garden experiments linked

together electrically in series could light a small LED device.⁸ In certain reaction systems, the fuel-cell analogy is enhanced by the catalytic properties of the tube or precipitate wall; for example, a tube of redox-active material could both generate an electric potential from ion gradients and drive reduction or oxidation of some other component in the surrounding solution. Such possibilities naturally lead one to consider materials applications like using chemical-garden precipitates as electrode materials or electrocatalysts, and they can also help with understanding similar phenomena in natural systems.

Injecting solution rather than using seed particles has been an important step toward controlled and quantifiable studies of chemical gardens. Other simplifications have also been pursued to control the precipitation process. For instance, the reaction can be carried out in Hele-Shaw cells that confine the entire system to a thin, flat layer of solution into which the second reactant

is injected at a constant rate (see figure 4). The resulting structures are essentially flattened versions of the conventional chemical gardens but reveal some novel features that either do not exist or are hidden in three dimensions.⁹ (See also *PHYSICS TODAY*, January 2015, page 14.) On one hand, if the injected reactant is of low concentration, the observed patterns are reminiscent of viscous fingers in reaction-free systems; on the other, for low silicate concentrations, an initially circular disk forms and eventually develops hair-like structures that grow with a characteristic wavelength radially outwards. At high injected-reactant concentrations, filaments form that are similar to the usual 3D chemical garden structures or tubes. The filaments are elongated channels that compartmentalize the flat liquid layer, just like a 3D chemical-garden tube divides the liquid volume into exterior and interior reactant pools.

It is thus likely that the thin walls defining the channels in the Hele-Shaw cell are close chemical and physical analogues to the regular tube wall. The Hele-Shaw system shows various intriguing phenomena, of which the most striking is the logarithmic spiral segments that form across a wide range of parameters. The spiral growth can be explained with a simple geometric model that depends on how the curvature of an expanding bubble of one reacting solution in the other varies with time. Structures in the Hele-Shaw experiments are phenomenologically similar to patterns observed in other self-organizing

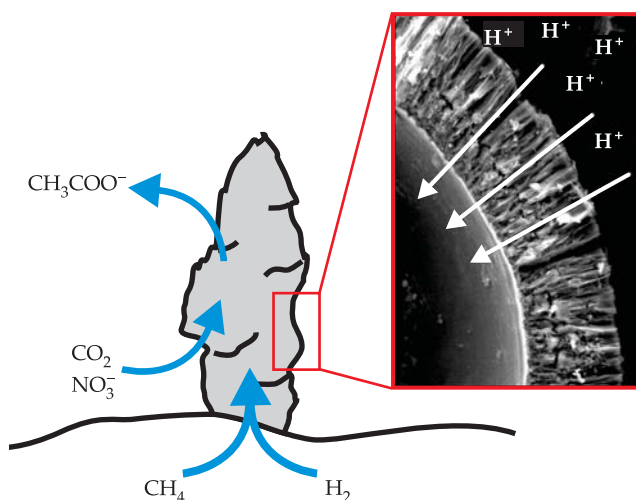


FIGURE 5. HYDROTHERMAL VENTS as chemical gardens for the origin of life. The schematic represents an ancient hydrothermal mound precipitated on the early Earth sea floor. Water–rock reactions in the ocean crust produce a reduced alkaline hydrothermal solution that feeds into an acidic carbonic ocean. At the interface of ocean and hydrothermal fluids, an inorganic semipermeable chimney membrane—a geological chemical garden—forms. The wall of the chemical garden is spanned by two types of steep chemical disequilibria: redox gradients, defined by electron acceptors such as nitrate and carbon dioxide in the ocean and electron-donating fuels hydrogen and methane in the hydrothermal fluid, and a pH gradient between acidic ocean and alkaline hydrothermal effluent that provides a proton motive force. Acetate is the waste product. Within the porous chimney wall, redox and pH transmembrane gradients could couple to biosynthesis reactions by free-energy-converting mechanisms and possibly drive an emergence of metabolism. (Figure adapted from reference 10.)

systems and remind us that chemical gardens belong to the realm of nonlinear physics.

Origin of life

There are many variations on the classical chemical garden experiment, but they all feature chemically contrasting solutions that form a self-assembling inorganic precipitate membrane at their interface. Similar processes can occur in natural geological settings. An example that is potentially of great scientific importance is hydrothermal-vent-driven chimneys on the ocean floor (see figure 5). Hydrothermal chimneys were discovered in the 1970s in “black smoker” vents on the volcanically active mid-ocean ridge. The vents release an influx of superheated, mineral-rich, acidic fluid into the cold seawater through fissures in the ocean crust. The various pH, chemical, and thermal gradients between the vent fluid and seawater lead to the precipitation of minerals at the fluid inlet point, where they form a hollow chimney through which the hydrothermal fluid continues to flow.

Precipitate particles also billow out from the vent plume as “smoke” and are later deposited in hydrothermal sediments.

A gentler, cooler type of hydrothermal vent can also form away from the mid-ocean ridge; it is driven simply by the chemical interaction of seawater with the olivine (an iron–magnesium silicate) in the ocean crust. In those alkaline vents—such as the stunning Lost City hydrothermal field, discovered in 2000 in the mid-Atlantic ocean—the water–rock chemistry produces a high pH, reducing vent fluid rich in dissolved minerals. The precipitated chimneys of the Lost City can be tens of meters tall. Alkaline hydrothermal vents produce organic molecules, have moderate temperatures, host chemical conditions hospitable for biochemistry, generate energy in the form of electron donors hydrogen and methane, and would have been common on early Earth. It is therefore not surprising that alkaline vents have been proposed as “flow-through chemical reactors” that could have driven the emergence of life.¹⁰

Today’s sea-floor vent systems generate life-facilitating energy in the form of electron-rich fuels, and the chemical-garden-like properties of hydrothermal chimneys are at the heart of the vents’ relevance for life’s origin on primordial Earth. Many of the features that we have discussed from laboratory studies are also common to hydrothermal chimneys. Those features include porous and permeable inorganic membranes, the presence of catalytic minerals in the tube walls, and

the abilities of the walls to incorporate other components, to generate electrical energy, and possibly to drive redox reactions. In black smoker systems, where chimneys are typically composed of metal sulfide minerals, the chimney wall is electrically conductive and can act as a redox catalyst.¹¹ And in porous alkaline vent chimneys, organics produced by water–rock reactions become concentrated by gradients within the pores.¹²

Laboratory chemical garden experiments have simulated properties of hydrothermal chimneys in different natural environments, including early Earth and other planets with water–rock interfaces. At JPL, researchers from the NASA Astrobiology Institute's Icy Worlds team experimentally showed that in the iron-rich seas of Earth when life emerged, chimneys at alkaline vents would likely have incorporated particularly reactive mixed-valence iron hydroxide and iron sulfide minerals, as well as trace components of nickel, molybdenum, and other elements that could have helped drive life-like metabolic reactions—powered by the ion, proton, and electron gradients between the vent fluid and the seawater.¹⁰ But still, many of the essential proposed functions of a hydrothermal chemical garden for prebiotic chemistry—such as the ability to harness geochemical disequilibria and, particularly, the transition to a more life-like model of disequilibrium conversion by molecular engine enzymes¹³—will require a new physical understanding of those nonlinear systems and new laboratory techniques that allow us to simplify the system and isolate individual variables.

Chemical gardens nimbly transform nonequilibrium patterns into permanent lasting structures. That process makes them an ideal model for a new type of technology in which macroscopic objects and devices are not engineered by extrusion molding or similar approaches but rather are organically grown by spatially self-controlling or programmed chemical reactions. It will be interesting to see how far the range of accessed shapes and hierarchical architectures can expand beyond the complex but nonetheless limited range of structures in chemical garden systems.

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