

Complexity from precipitation reactions

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A key challenge for modern molecular sciences is to bridge the gap between the nanoscopic world and macroscopic devices. The underlying question is whether one can control chemical reactions to produce directly macroscopic complexity, hierarchical order, and ultimately entirely new types of materials. If viewed as a form of complicated chemistry, biology unambiguously answers this question with a resounding “yes” and, furthermore, demonstrates the powerful potential of this approach. However, this fundamental reassurance does not provide significant help in developing nonbiological model systems and leaves us with seemingly insurmountable hurdles. The PNAS article by Haudin et al. (1) is an important step to overcome some of these hurdles, as it provides just such an experimental model.

The work by Haudin et al. (1) follows up on hints that can be found in some of chemistry’s earliest literature. In 1664, Johann Glauber described reactions producing “philosophical trees, both pleasant to the eye and of good use” (2). Today, these structures are known as chemical or silica “gardens” and are common demonstration experiments in school and introductory college classes. A chemical garden is typically grown by placing a macroscopic salt particle into a sodium silicate solution (3). The dissolution of the “seed” particle causes the formation of insoluble metal hydroxide that forms colloidal particles, and subsequently surrounds the seed with an inorganic membrane. The system—now compartmentalized by this thin membrane—is subject to osmotic pressure, which drives an inflow of water and subsequently ruptures the membrane (4). From this site, a jet of buoyant salt solution, sustained by the osmotic pump action near the base, rises upwards and templates the growth of a hollow inorganic tube.

These precipitation tubes can be several centimeters long and have typical diameters of a few millimeters that, under controlled conditions, can be reduced to about 1 μm (5) (Fig. 1). The wall structure often consists of amorphous silica near the outside surface and amorphous or polycrystalline metal hydroxides/oxides toward the inner surface.

Tube formation occurs for a wide range of metal salts (excluding compounds of the alkali metals) and numerous anions, such as the aforementioned silicate, carbonate, phosphate, borate, and sulfide, with the latter ones generating different (silica-free) wall compositions. Seemingly related microtubes can also form from complex polyoxometalates (6), whereas hollow cones and other hierarchical microstructures result from the CO_2 -induced coprecipitation of barium carbonate and silica (7). Recent studies also draw links to large, hollow ice tubes (brinicles) underneath sea ice (8).

Haudin et al. (1) address the formation of this class of tubular micro- and macrostructures from a fresh and original perspective. Following earlier advances in method development (9), the authors inject salt solution (CoCl_2) at constant pump rates into a large reservoir of silicate solution. Their simple but innovative idea was to perform this experiment under quasi-2D conditions in a horizontal Hele-Shaw cell, which consists of two closely spaced, parallel plates with a central injection site. Such set-ups have been frequently used for the study of “viscous fingering” patterns that occur when a less-viscous fluid is injected, displacing a more viscous one. Because of mathematical similarities, the latter experiments are of importance to fluid flow in porous media and relate to the efficacy of oil recovery from oilfields.

The experiments by Haudin et al. reveal numerous patterns that the authors term flowers, lobes, filaments, and worms (1). All of these fascinating structures emanate from the central injection site and divide the shallow layer into two compartments containing either cobalt solution or silicate solution. Depending on the used reactant concentrations, the boundary between these two domains ranges from sharp and wall-like to broad and diffuse. The latter structures are reminiscent of reactive displacement patterns first reported by Nagatsu et al. (10), who studied the formation of $\text{KFe}[\text{Fe}(\text{CN})_6]$ (a blue precipitate) in Hele-Shaw cells. The sharp, solid walls can trace the shapes of logarithmic spirals over distance of several centimeters. These striking and beautiful

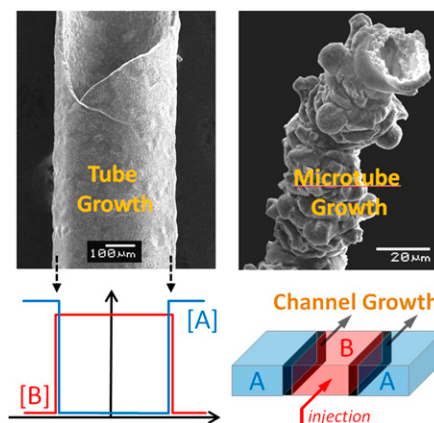


Fig. 1. Scanning electron micrographs (Upper) of hollow precipitation tubes formed in sodium silicate solution. The thin, cylindrical wall forms at the interface of an outer silicate solution (A) and a flow-driven metal salt solution (B, Left). Using Hele-Shaw cells, the 2D analogs of such tubes can form channel-like structures with self-extending walls (Right).

patterns are formed when a product front breaks and new precipitate formed at the breach begins to move the existing “solid line” outwards. A geometric theory is presented to describe the resulting rotational motion and the formation of the observed spirals.

The filament-like structures that occur at high reactant concentrations are seemingly the closest analog to the 3D hollow tubes in conventional chemical gardens (Fig. 1). The length-extending growth occurs at the end distant from the central injection site. Accordingly, these thin channels are self-extending conduits that deliver reactant solution over steadily increasing distances. Applications of this growth process could include the production of microfluidic devices in which the channel walls consist of a broad range of compounds. In this context, one can envision wall materials that perform specialized tasks, such as catalytic reactions, separation processes, and chemical sensing. For such applications, it will be important to establish precise control over the channel width and the global channel pattern. Such protocols have indeed been developed for 3D polyoxometalate tubes by

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Cronin and colleagues, who used a computer-controlled laser-based system to generate tailored convection patterns (6). It will be interesting to see whether these methods can be transferred to the system of Haudin et al. (1).

A crucial feature of chemical gardens is that the wall forms in the presence of very steep concentration gradients that are non-transient because of their existence in a steadily moving reaction zone (i.e., the upper rim of the tube or the end of the channel). Another advantage of the quasi-2D conditions is that this wall is oriented perpendicular to the flat plates of the Hele-Shaw cell. This orientation exposes the interior structure of the wall in a way that will greatly assist future efforts to characterize the wall's chemical structure and its slow thickening dynamics. Both of these features are difficult to study for 3D tubes, as only the outer surface is exposed for in situ characterization. Accordingly, most earlier studies have relied on the materials characterization of the fully formed and often dried tube. For example, Roszol and Steinbock showed that the radial growth of the tube wall is unidirectional (typically in the inward direction) and that the wall width typically increases according to a square-root law (as expected for diffusion-controlled processes) (11). Such experiments can now be performed during wall growth by simply monitoring the wall thickening with a video camera. Other in situ characterization techniques, such as micro-Raman spectroscopy, discussed in the report by Haudin et al. (1), can be expected to deepen our understanding of these complex materials.

As outlined in this commentary, the lessons to be learned from the growth

dynamics of chemical gardens will provide an interesting model for the study of materials synthesis under nonequilibrium conditions. However, the relevance of this system extends

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much further, as life on Earth might have started in very similar materials. As proposed by Russell et al. and others, hydrothermal vents—or more precisely the cooler, off-axis alkaline vents—constituted an ideal hatchery for prebiotic chemistry and early forms of life-like systems (12). These chimney-like structures formed

when mineral-rich water (containing also other species such as CO, H₂, and CH₄) surged into the anaerobic Hadean ocean. Their precipitation walls offered a phelotra of micro- and macropores that created cell-like spatial confinement without the presence of lipids. Moreover, the structures consisted of various minerals, including sulfides and oxides of metal ions, such as iron and nickel. These geochemical catalysts might have jump-started the production of compounds that subsequently modified the reactivity of the pore surfaces in a biocatalytically relevant fashion. Finally, the wall structures were exposed to steep and extremely long-lived concentration gradients that are reminiscent of modern transmembrane gradients in living cells. The work by Haudin et al. (1) has the potential to assist in the experimental analysis of these questions by providing simple, microfluidic geometries for the more direct characterization of inorganic membrane systems that seem relevant to this intriguing origins-of-life hypothesis.

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