Polka-Dot Chemistry and Zebra Stripes

Scientists claim first sighting of elusive Turing structures in chemical landscapes

By IVAN AMATO

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Pinwheel pattern depicts a spiral arm rotating within a gel hosting reactions of malonic acid, potassium bromide and potassium bromate. Scientists created the image by superimposing a spiral arm's position at 2-minute intervals. Though its shape remains constant, the arm's location changes, ruling it out as a Turing pattern.

Imagine a field of grass punctuated by blazing patches. As fast as each patch burns, new grass miraculously grows back, only to succumb again to the flames. Each fiery patch emits a continuous spray of mist to adjacent regions, protecting those areas from incineration. The result: a stable patchwork of burning and protected regions, whose specific pattern depends both on the fires' strength and on the direction and rate of the moisture dispersing from flaming patches.

"It's a little weird," admits Patrick De Kepper, a physical chemist at Bordeaux University in France. Yet his botanic metaphor characterizes the bizarre patterns – called Turing structures – that he thinks he's witnessed in a mixture of continuously reacting chemicals.

Indeed, the chemical facts appear stranger than metaphoric fiction. He and his Bordeaux co-workers have focused their attentions on carefully controlled reactions involving chlorite, iodide and malonic acid. Stripes and dots develop within clear or sometimes yellow regions where concentrations of iodide are low; darker, blue-gray patches form where concentrations of iodide are high. These patterns the scientists observed forming within the reaction systems have persisted – without moving – for as long as 20 hours.

As De Kepper's burning-grass metaphor might suggest, this stable, chemical quilt emerges from a continuous interplay between the initial chemical reactants and their own reaction-inhibiting products, as those products diffuse into surrounding areas. In chemical terms, the blue-gray patches represent "reduced" areas – regions populated with iodide molecules that have gained an electron; the clear or yellow areas signal the "oxidized" patches that donated those electrons.

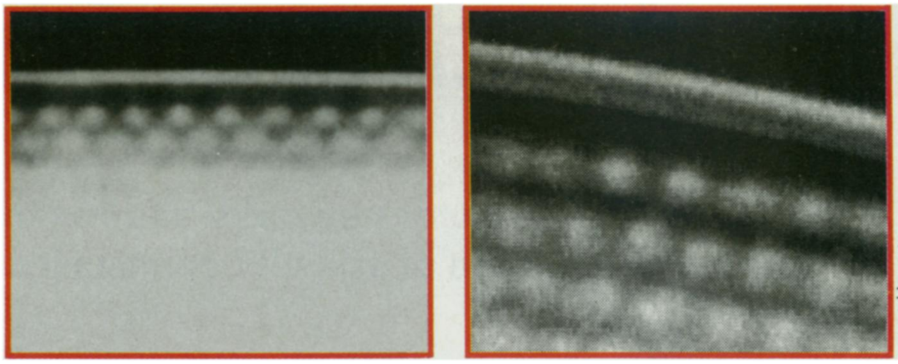
The brow-wrinkler here stems from an unmet expectation: that chemicals in a reaction will eventually disperse uniformly throughout a reaction vessel, just as a drop of red food dye will quickly disperse evenly throughout a glass of water, producing a uniformly pink liquid. The spontaneous emergence of stable chemical patterns in the Bordeaux experiments is akin to that drop of red dye breaking into tiny droplets that align themselves into neat stationary rows and columns.

Despite the conceptual appeal of Turing structures to theorists, "there has been a growing skepticism about their reality in the physical world," the Bordeaux team writes in the June 11 PHYSICAL REVIEW LETTERS. De Kepper recalls, for instance, informally sharing these remarkable new observations with some other scientists, who responded as though he had claimed to have captured a unicorn. They had come to assume Turing structures filled only the minds of theorists and never the glassware of laboratories, he says.

Though scientists have hunted these structures for nearly 40 years, observes chemist Irving R. Epstein of Brandeis University in Waltham, Mass., the Bordeaux investigators "have what appears to be the first real instance of a Turing pattern." Others, such as physicist Harry L. Swinney of the University of Texas at Austin, warn that appearances can deceive, and that some uncertainty lingers. But even critics agree that De Kepper's group has bagged an impressive chemical trophy, whatever it is.

The first suggestion that reaction and diffusion processes might lead to stable chemical patterns surfaced in 1952, when the late Alan Turing, a British mathematician, proposed these hypothetical phenomena to explain the genesis of such biological patterns as a zebra's stripes. Though most biologists have all but ignored Turing's conjecture, Turing struc-

These inauspicious dots and lines, resulting from reactions of malonic acid, potassium iodide and potassium chlorite in gels, may represent the first sightings of Turing patterns — stable chemical patterns long envisioned by theorists. Photo at left shows dots spaced at about 0.2 mm in a small gel strip. At right, similar patterns emerge within a ring-shaped gel.



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tures have intrigued chemical theorists and have been the object of pursuit of experimentalists. Yet like the fabled unicorn or the Loch Ness Monster, the imagined structures have remained well hidden. Until now, De Kepper says.

Technical obstacles placed Turing structures virtually beyond experimental reach for more than three decades. Until the late 1980s, for example, scientists investigating closely related chemical systems performed their experiments in "closed" reactors, such as beakers or petri dishes. Most of these researchers studied Belousov-Zhabotinsky reactions, which oscillate between stable states — often marked by different colors — or generate spirals, moving wave fronts and other dynamic spatial and temporal patterns (SN: 7/1/89, p.6). Closed reactors suffice for transient patterns, which eventually disappear as their chemical ingredients reach equilibrium and become uniformly distributed throughout a solution, like the drops of dye in the water.

To prevent equilibrium, Swinney and his co-workers developed more complex open reactors. In these, fresh reactants continuously diffuse into the reaction zone, preventing the chemical equilibrium that closed systems always develop. By forcing both the reaction and diffusion processes to occur within an inert, porous gel such as polyacrylamide, Swinney's team calmed the convective mixing, stirring and other pattern-killing movements that plague both open and closed reactors.

De Kepper's open reactor consists of an inert, matchstick-sized gel strip flanked on each side by a constantly refreshed, pH-controlled chemical reservoir. One reservoir contains chlorite, the other malonic acid. The two contain equal amounts of iodide. This sets the stage.

After roughly three hours, each reactant's diffusion across the porous gel's 3-millimeter width will have established a steady gradient. The chlorite, iodide and malonic acid react within the gel, and equilibrium never occurs because the researchers constantly replenish the reservoirs with more of the starting reactants. A starch-like molecule laced throughout the gel signals the develop-

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ment of oxidized or reduced regions by turning yellow or a subtle blue-gray, respectively.

Initially, a series of yellow and dark stripes forms within the gel, parallel to its long dimension. But when the researchers restrict the concentration of malonic acid to a specific, narrow range, "the rows give way to lines of dots," De Kepper says. These reflect the spontaneous emergence of local concentration differences – like stationary microdroplets of dye – in the gel. The distance between adjacent dots in a line spans about 0.2 mm, or about half the width of a typed period. Other reactors, which differ only in their size and shape, yield similar polka-dot patterns.

The two-dimensional arrangement of dots that De Kepper has observed developing in his reactors resembles a well-known crystallographic arrangement that theorists previously had predicted might appear in nonequilibrium chemical systems. The Bordeaux team has failed so far to document the pattern's exact structure in the gel's thin third dimension, but De Kepper says he continues working on it.

To support their claim that these chemical polka dots constitute a genuine Turing structure, the researchers note that the lines of dots form spontaneously, and stay in place once they form. Moreover, the size of the spots and their positioning do not depend on the specific dimensions or geometry of the gel – nor does the gel have textural regularities that might explain the phenomenon. Finally, these patterns seem to match what theory predicts for these conditions.

Still, their case for having observed Turing structures needs strengthening, says Swinney, who often collaborates with De Kepper and has seen related patterns in his own lab. "I have some reservations about whether they have observed Turing structures," he says. The Bordeaux researchers haven't actually witnessed a clear chemically induced transition from lines – which De Kepper admits might form from physical processes at the gel-reservoir borders – to the dots, which require a more exotic explanation. Without actually observing the transitions, Swinney cautions, the Bordeaux scientists cannot rule out the possibility that the dots represent some nonchemical artifact of the experiment's design.

"What makes their experiment particularly interesting, though, is that it comes the closest to having a pattern emerging from a uniform concentration of chemicals," he notes. In June, he traveled to Bordeaux to help design experimental tactics for observing the controversial line-to-dot transitions.

"The whole business of chemical patterns is a very exciting one these days," Swinney says. Since about 1987, he and co-workers have observed temporarily stable chemical waves traveling around a ring of gel. Like the blades of a pinwheel in the wind, the waves change location but not shape, in this open reactor. But the pattern's movement disqualifies it as a Turing structure. In a series of papers coming out later this year, Swinney and his colleagues describe a variety of these Turing-like patterns in open reactors.

Indeed, De Kepper says, "There's a whole new world of chemical structures awaiting discovery." His finding of apparent Turing structures bolsters Turing's original conjecture that such chemical phenomena may play an organizing role in biological form and function.

One possible biochemical role, De Kepper speculates, might be a chemical switch to turn genes on and off as an organism develops from a single cell into a highly differentiated and organized community of cells. "This [genetic orchestration] might be set by patterns of chemical concentrations in the cell environment," he adds. But conjectures like these will remain merely nice ideas, he notes, until bench scientists sort out a lot more basic Turing-structure chemistry. □