Reports

Scroll-Shaped Waves of Chemical Activity in Three Dimensions

Abstract. *Ferric ions catalyze the oxidation of malonate by bromate in acid solution, sometimes at a spatially uniform, steady rate, but sometimes in a self-regenerating three-dimensional wave which resembles a rotating scroll, often with its axis closed in a ring. In cross section perpendicular to the axis, one sees an involute spiral emerging from a thin cylindrical core. This "dissipative structure" organizes reaction stages periodically in space and time everywhere except along its rotation axis, which may therefore be a thermodynamically unique locus.*

Detonation of a spatially homogeneous explosive results in propagation of a wave of chemical activity, behind which the reaction is complete. Reactions are also known in which each passing wave of activity leaves the reagent only a little closer to exhaustion. In such media many waves may propagate in succession, separated by a minimum interval. This feature of the gas-phase oxidation of phosphorus attracted Rayleigh's (*1*) attention as long ago as 1921. More recently and more conveniently, in a reagent first prepared by Zaikin and Zhabotinsky (*2*), waves of chemical activity propagate through a motionless liquid at room temperature. These waves are seen by color changes due to the local oxidation-reduction potential of metal ions present in catalytic amounts. In a variety of recipes (*2–5*), the metal ion (or ion complex) catalyzes the oxidative decarboxylation of an aliphatic acid by bromate in acid aqueous solution. Several groups have investigated the reaction kinetics involved (*6*).

My purpose here is to discuss the wave geometry (*7–10*) in three dimensions, setting into perspective previous reports (*5, 8, 9*) which were restricted to two-dimensional organization in the periodic steady state. Figure 1 shows a layer of reagent (*5*) 1.5 mm deep at 25°C, printed at actual size. The dark regions are orange (ferrous phenanthroline) and the light regions are blue (ferric phenanthroline). The blue waves are propagating through the motionless reagent at about 6 mm/min. It is essential to realize that these waves are really propagating, like action potentials in nerve membrane, through this excitable medium. Any wave can be blocked by a barrier. They are not due to spatial phase gradients of a limit cycle oscillation, such as described in (*9, 10*). Until triggered by an encroaching blue wave, the reagent remains orange. All these waves are emerging at nearly equal intervals in time (± 10 percent) from 19 distinct sources, most of which are not points, but arcs of curves up to 15 mm long. The waves emerge from some sources, for example, A to E, as parallel closed rings about a distance λ_0 apart, but from others, for example F to H, as single spirals with the same pitch, λ_0. A sufficiently elongated spiral source like F often decays into a more symmetric spiral source; A and H decayed in this way before this picture was taken. Similarly, a sufficiently elongated ring source like A or B often decays into two or more less elongated ring sources or a pair of counter-rotating spirals like I, or both. If we define parity as the number of clockwise spirals minus the number of counterclockwise spirals, it is conserved in every decay, except at the edge of the dish, where a spiral can vanish.

Elongated spiral and ring sources continually shorten toward greater symmetry; notice in Fig. 1 that wave spacing is about one-sixth greater in the direction of the long axis than at right angles to elongated sources because such sources contract lengthwise between emissions. Just before achieving perfect symmetry, ring sources abruptly vanish, as in Fig. 1, J to L. Thereafter, the expanding central disk remains quiescent (unless a spontaneously oscillating version of the reagent is used). In contrast, spiral sources persist after contracting to a point, as in H and I. The final pattern then consists exclusively of involute spirals, all rotating at close to the same period, and so partitioning the dish into polygonal domains bounded by lines of cusps. These are the "reverberators" of Zaikin and Zhabotinsky (*2, 3*). This eventual periodic steady state in two dimensions was the subject of a previous report [(*5*) and its cover photo].

The nature of the elongated sources is betrayed by their period: in striking contrast to the ring waves emitted from heterogeneous nuclei (*2*), all elongated sources emit waves at the same interval (± 10 percent) as the involute spiral (*5*). I believe that all three are views of a scroll-shaped three-dimensional wave, seen in projection as it

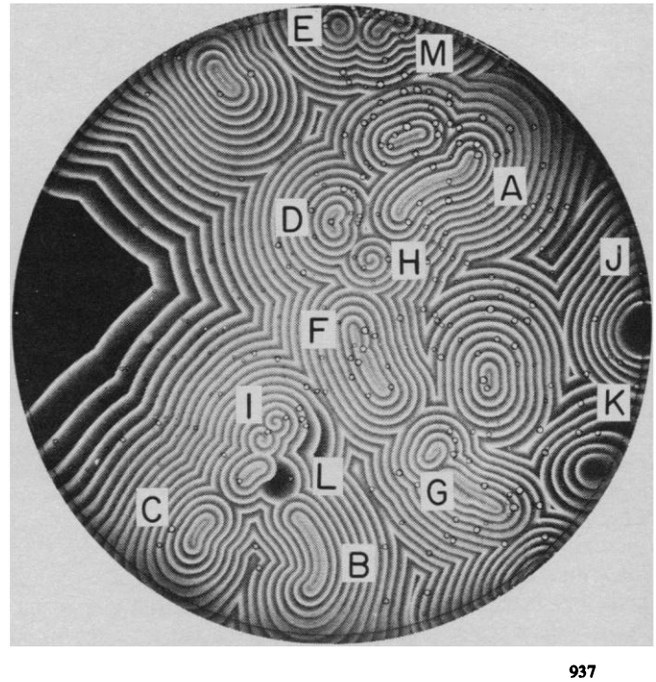

Fig. 1. Liquid layer of reagent (*5*) 1.5 mm deep at 25°C, shown at actual size. After spontaneous development of pacemaker waves in concentric rings, and several minutes before this picture was taken, the fluid was briefly and gently sheared to create crossed concentration gradients. My contention is that the waves seen here in projection all emerged from scroll axes (some of them curved) lying at various angles to the interfaces. The small circles are CO_2 bubbles.

lies at various angles in the reagent. If a wave like Fig. 2a lay at any angle other than 90° to the interfaces, as in Fig. 2b, then in projection perpendicular to the interfaces it would be seen as an elongated source of waves, all connected in a single spiral. In contrast, if the scroll axis curves around to encounter the same interface twice, then it will emit waves between parallel interfaces in distinct elongated rings, as often as the scroll rotates (Fig. 2c). In either case, if the scroll axis is sufficiently long, then its gradual bending (perhaps in part due to convection currents) may result in an arc vanishing through one interface. The remaining segments then constitute distinct ring sources (if the segment begins and ends on the same interface) or spiral sources (if the segment crosses from one interface to the other) without change of collective parity.

In liquid layers thicker than the layer in Fig. 1, it is not uncommon to see ringlike sources emitting ring-shaped waves alternately inward and outward at close to this same minimum period. These seem to be scrolls in which the axis closes in a ring, making a "vortex ring" of chemical activity. All other scroll waves may be regarded as bits and pieces of scroll ring truncated by the interfaces.

In favorable lighting and so forth, it is sometimes possible to see the scroll waves directly by stereomicroscopy, for example, at M in Fig. 1. This has the advantage that the wave is seen in motion in three dimensions, but interpretation is difficult, at best, because all colors are seen in projection—through differently colored layers in the most interesting cases—and the least mechanical or thermal disturbance wrecks the wave patterns.

A less direct check on these interpretations was attempted: if the "variety of less stable forms" (*5*) shown in Fig. 1 derive from scroll waves, then these elongated sources should never be seen in a reagent too shallow to accommodate the scroll wave's core. The core may be defined roughly as a cylinder of circumference λ_0 surrounding the scroll axis. To accommodate a core λ_0/π wide, the scroll axis would have to tilt more than 45° from the horizontal in a layer shallower than $\lambda_0/2\pi \cong \lambda_0/4.4$. The horizontal elongation of the sources would therefore be less than this, and thus negligible, whereas it could be arbitrarily great in layers deeper than λ_0/π. When I used the reagent of (*5*), with $\lambda_0 = 1.3$ mm, and sandwiched it between parallel Plexiglas plates held 0.02 to 2 mm apart by calibrated ball bearings, I found no elongated sources in layers less than 0.3 mm deep. Using a less acid reagent with $\lambda_0 = 2.2$ mm (*11*), I found no elongated sources in layers less than 0.6 mm deep. But in deeper layers they were easy to create (by rolling one plate several millimeters across the other), with longevity proportional to the depth.

Waves propagate equally well in the homogeneous, porous, and relatively inert matrix provided by a Millipore filter. Elongated ring sources are never found in a single 1/7-mm thickness of Millipore (with $\lambda_0 = 1.6$ mm at 20°C), nor in a double thickness of Millipore, but they do appear in a stack of three or more clinging together by the surface tension of reagent between them, as expected in view of the core diameter. Thus, a further test is to try three-dimensional reconstruction of scroll waves from serial section: waves propagating through stacked Millipores can be examined in cross section (as though microtomed) by inducing waves from suitable initial conditions, letting them develop for several minutes (at least ten scroll rotations), then plunging and dispersing the stack into cold 3 percent perchloric acid. All wave patterns are fixed within about 1 second by the cold, the dilution of all inorganic ions, and formation of the insoluble ferrous phenanthroline perchlorate complex. Restacked in their original alignments, these filters reveal a diversity of wave patterns. Most of them can be described as bits and pieces of scroll waves such as Fig. 2, a to c. Occasionally a complete scroll ring is found, such as Fig. 2c, connected to its mirror image.

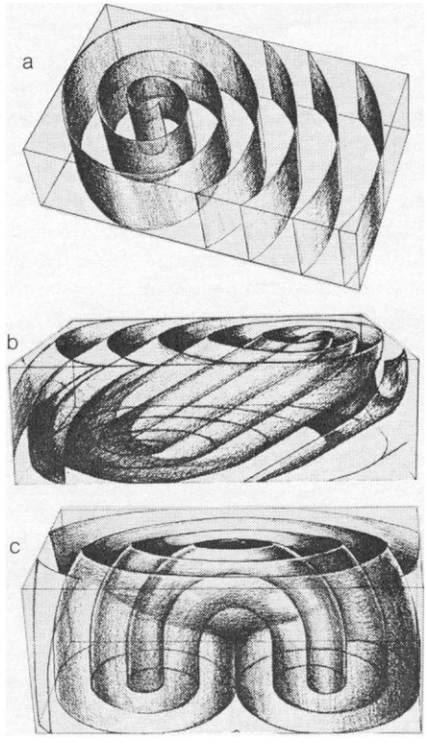

Fig. 2. The wave forms of Fig. 1 are idealized here in three dimensions in an attempt to exhibit the blue wave fronts (half of the Fe^{2+} isoconcentration surfaces) as originating from segments of a scroll wave which continually propagates out into a thin horizontal layer of excitable reagent. (a) Involute spiral (Fig. 1, H and I); (b) elongated spiral, shown as emerging from a tilted scroll (Fig. 1F); (c) source of elongated ring waves, shown as a U-shaped scroll wave (Fig. 1, A to E). The wave forms of Fig. 1 correspond not to the intercepts of these waves with top or bottom interfaces (although those, and intermediate levels as well, can be seen in peeling open a Millipore stack), but to vertical projections completely through these waves. Structures such as Fig. 1F are therefore replaced in Millipore sections by deformed spirals such as those drawn on the top and bottom faces of (b).

The scroll axis may be a thermodynamically unique locus if, as symmetry considerations suggest, it is held at relatively time-independent concentrations by diffusion from the involute wave uniformly rotating around it. These concentrations would not be the same as in the locally attracting homogeneous steady state approached in the most orange part of the cycle. Nor need they equal the time-averaged concentrations in the blue-orange cycle going on everywhere else. Consequently, along this threadlike axis snaking through the liquid, such thermodynamic parameters as temperature and free-energy dissipation may differ from their time-averaged values elsewhere (*11*).

To me, the fascination of the scroll wave and the reason for detailed analysis of its core are that it provides a self-sustainingly periodic solution to kinetic schemes which, in the absence of opportunity for spatial differentiation, are only transiently excitable from a locally stable equilibrium. The core of the scroll wave is a "dissipative structure" (*12*), uniformly and rigidly rotating about a chemically quiescent axis in three-dimensional space. The quiescent orange solution and the scroll wave solution are two alternative, but locally stable, modes of spatial and temporal organization of this series of reactions. A transient disturbance exceeding a minimum threshold can flip the sys-

tem into or out of either mode. These facts reinforce the impression, gathered by watching solitary waves collide and vanish rather than pass through each other, that these phenomena are essentially nonlinear. They could not have been discovered [although the periodicity and symmetries of wave trains can be described (*8*)] by linear mathematical models. In (*11*) an analysis is offered (together with experimental details) which attempts to rationalize these nonlinear features in terms of modification of a nonoscillatory and fundamentally nonlinear excitable kinetics by diffusion.

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11. A. Winfree, in *Science and Humanism: Partners in Human Progress*, H. Mel, Ed. (Aharon Katchalsky Memorial Symposium, Univ. of California Press, Berkeley, in press); *Sci. Amer.*, in press; in *Lecture Notes in Biomathematics*, P. van den Driessche, Ed. (Springer-Verlag, in press). Realization of a stationary scroll axis may require better-controlled experimental conditions than I have yet contrived. The disintegration of elongated λ_0-spiral sources and λ_0-ring sources into shorter segments of the same total parity shows that the scroll axis slowly drifts or writhes about. Even when nearly perpendicular to both interfaces, in thin liquid layers or in a Millipore, it may move about: microscopic observation shows that the interior tip of the involute spiral wave does not propagate quite in circles around a stationary center, but rather meanders in loops of length of the order of λ_0 throughout a core region of diameter about λ_0/π. Thus, no volume element escapes excitation to blue from the orange quiescent state within the span of a few rotations. I do not know whether this symmetry-breaking instability of the scroll axis is due to the interaction of reaction and diffusion, or to local inhomogeneities of temperature, Millipore density, and so forth.
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13. W. T. Moore at Purdue suggested the use of Millipore filters. E. Blackwell, Purdue Audio-Visual Center, drew Fig. 2. This report is dedicated to the memory of Aharon Katchalsky.

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Origin of the Mesoamerican 260-Day Calendar

Abstract. *The sacred 260-day Mesoamerican calendar probably originated near a latitude of 15°N, where there is a 260-day interval between transits of the zenithal sun. Archeological and faunal evidence favors an origin in the Pacific lowlands rather than in the highlands near Copán, Honduras, although Copán, which is located at the 15th parallel of latitude, later became the principal Mayan astronomical center.*

Although civilized peoples in all parts of the world, including Mesoamerica, developed calendars based on the length of the tropical year (365 days), in Mesoamerica a second calendar 260 days in length came into being. Variously known as the *tzolkin* or *tonalámatl*, this 260-day count served as a sacred almanac or ritual calendar for all peoples of Mesoamerica and has continued in use in some of the more isolated regions of southern Mexico and Guatemala to the present day (*1*, p. 55). The 260-day cycle was the most important measure of time among all Mesoamerican civilizations, for not only did it guide the daily rituals of the people but it also formed the basis for other measures of time of great astronomical and religious significance (*2*, p. 265). For example, a double *tzolkin* (520 days) equates almost exactly with three eclipse half-years (519.93 days) and therefore provided a means for predicting solar eclipses (*3*, p. 149). Furthermore, because each day had its own name and number, a period of 52 years would elapse before the 260-day almanac would come back into phase with the 365-day calendar. This period of 52 years has been called the calendar round, or "Aztec century" (*tonalpohualli*), and was responsible for the fatalistic belief among Mesoamerican peoples that history repeated itself on a cyclical basis.

Despite the central importance of the 260-day calendar in the life, art, and science of pre-Columbian Mesoamerica, no satisfactory explanation has yet been advanced as to how and where this original contribution to time-keeping began. In 1966, Coe (*1*, p. 55) stated: "How such a period of time ever came into being remains an enigma. . . ." Other investigators have debated the locational origins of this unique Mesoamerican calendar. Kidder (*4*) favors a highland origin, but Thompson (*5*) cites an observation by Gadow that "several of the fauna which serve as day-names and day-glyphs . . . are foreign to the Mexican plateau and, one might add, to the highlands of Guatemala." Satterthwaite (*6*) writes that Caso finds the earliest evidence of the sacred round count at Monte Albán in Oaxaca, whereas Vaillant (*7*) states that the 52-year cycle seemingly stems from the Mixteca Puebla area. Robertson (*8*) likewise sees no reason to question colonial accounts of Mixtec origins for the 260-day calendar. Moreno (*9*), on the other hand, assumes the calendar to be of Mayan origin but concedes that an Olmec origin "may turn out to be more feasible"; yet he concludes by suggesting the Yucatan Peninsula as its birthplace. Coe (*1*, p. 60) disagrees, arguing that the "Mayan" calendar had reached pretty much its final form "by the first century B.C. among peoples who were under powerful Olmec influence and who may not even have been Maya. From them, writing and the calendar were spread along the Pacific coast of Guatemala and into the Maya highlands, eventually reaching the developing states of the Petén forests." It is thus apparent that there is little agreement as to when, where, or how the sacred almanac came into being or which people was responsible for its creation.

Although structures assumed to have been observatories have been identified at such sites as Monte Albán and Chichén Itzá, the Mayan center at Copán, Honduras (Fig. 1), is generally recognized as having been of paramount importance in pre-Columbian astronomical studies (*1*, p. 161; *2*, pp. 323 and 325; *3*, p. 70; *10*). It is my contention that Copán attained its distinction as the single most important center for astronomical studies in the New World because it was the only place within the Classic (lowland) Mayan realm where the sacred 260-day calendar could be calibrated. Because of Copán's preeminence in astronomy, there is a strong temptation to ascribe the origins of the *tzolkin* to this place—a temptation which I feel impelled to resist on historical grounds. On the contrary, rather than arguing in favor of Copán as the birthplace of the calendar round, I would propose just the reverse, namely, that the calendar round was responsible for the founding of Copán.