assess statistically the likelihood of detection of pre-Clovis sites besides Meadowcroft, given a reasonable model of population movements from Alaska to Meadowcroft; the abundance of Clovis evidence; and the relative archaeological 'visibilities' of Clovis sites and putative Meadowcroft-like pre-Clovis sites. Such calculations, along with further scrutiny of Meadowcroft's dating and further efforts to locate other pre-Clovis sites, will eventually provide convincing evidence for who were the first Americans. ☐

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Chemical physics

Reactions with directed motion

Richard M. Noyes

THE Belousov–Zhabotinskii (BZ) reaction probably exhibits the richest phenomenology of any known non-living collection of chemicals. Whenever we think we know at least the list of qualitative behaviour patterns in space-time, something new is added to the compendium. Such an addition is the report of Noszticzius *et al.* on page 619 of this issue[1], showing that a train of chemical waves can be made to travel unidirectionally around a ring almost indefinitely somewhat as an induced electrical current can flow around a superconducting coil.

The BZ system involves the oxidation of an organic substrate by acidic bromate, often catalysed by an oxidation–reduction couple, such as Mn(II)–Mn(III) or Ce(III)–Ce(IV), based on a 1-equivalent change (see ref. 2 for a recent review). Over wide ranges of composition, the state of such a system can be characterized as oxidized or reduced, depending on the potential of a platinum electrode or on the colour of a redox indicator. Reduced states have much larger concentrations of bromide ions than do oxidized states.

In some stirred solutions, an oxidized or a reduced state is repeatedly converted suddenly to the other type by 'relaxation oscillations'. In other stirred solutions, a persistent state can be 'excitable'; perturbation beyond a sharply defined threshold will initiate an excursion of several orders of magnitude in the concentration of bromide ion. Temporary and permanent bistability, oscillations induced by silver ions, bursting, amplified fluctuations and deterministic chaos are terms that have evolved to designate some of the more exotic phenomena in open and closed stirred systems.

Fig. 1 Rotating spiral trigger waves in a thin layer of BZ solution. Note that where the waves meet, there is no interference pattern. (Courtesy of Arthur T. Winfree, from ref. 6.)

If a closed system is unstirred, wave phenomena may be generated. Undoubtedly the most dramatic such behaviour is the 'trigger wave', studied in great detail by Winfree[3], which consists of a narrow band of oxidized state moving through a medium of marginally stable, but excitable, reduced state. At the leading edge of the band, diffusion depletes the local concentration of bromide and triggers an autocatalytic excursion that temporarily converts the reduced state to an oxidized one. By the time that local region has returned to a reduced state with enhanced bromide concentration, the oxidized region has moved on. A trigger wave moves unidirectionally into a reduced region by destroying bromide ions in front of it and leaving a greater bromide concentration behind. The greater the bromide concentration in front of the wave, the slower it travels: a sufficiently great concentration can stop the wave entirely.

When trigger waves meet, they annihilate each other without diffraction effects. Figure 1 shows two spiral waves twisting in opposite directions and disappearing where they meet. Winfree has generated still more complex three-dimensional patterns and has suggested analogies to arrythmias in cardiac arrest.

Until now, studies of trigger waves have been conducted in closed systems. Noszticzius *et al.*[1] in this issue report the development of a clever ring system in which reducing chemicals are replenished by diffusion from the centre and oxidizing chemicals from the outside. They also use temporary concentration gradients to block waves travelling in one direction, either clockwise or counterclockwise. They thus select waves that are free to circulate around the ring indefinitely in only one direction. Figure 3 (*c* and *d*) on page 620 shows that the waves travel faster near the outside of the ring where the medium is more oxidizing, and that the waves disappear as one moves toward the more reducing medium in the centre. These observations are consistent with those previously reported by Winfree.

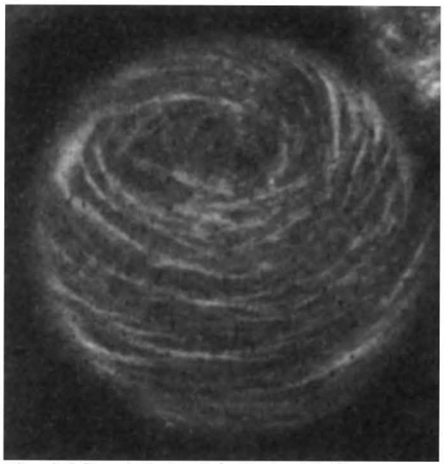

Fig. 2 Microtubules labelled with fluorescent antibodies in a fertilized sea urchin egg. (Courtesy of Patricia Harris, from ref. 4.)

Such directed behaviour is reminiscent of chemical streaming found in biological systems. All the wave phenomena observed in the BZ reaction so far, however, are based on the coupling of understood chemical reactions with diffusion of species in less than micromolar concentrations. The BZ system has not yet demonstrated directed motion of macroscopic amounts of material such as are sometimes seen in living cells.

Figure 2 shows a spiral arrangement of microtubules in a fertilized sea urchin egg[4]. These microtubules are apparently responsible for the rotation of the peripheral cytoplasm with relation to the inner region of the cell[5]. Other dramatic examples of movements within cells include the migration of pigment granules in chromatophores of fish scales; actin-based streaming of cytoplasm of certain algal cells; microtubule-dependent movement of chromosomes at mitosis; and transport of vesicles along the length of nerve axons. If bodies big enough to be seen in a microscope move unidirectionally through a viscous fluid, they must be acted on by directed forces of a kind that Newton could have understood. The chemical mechanisms of some of these biological processes are only just beginning to be elucidated. ☐

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