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Letters

Pattern Formation and Self-Organization in a Simple Precipitation System

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Various types of pattern formation and self-organization phenomena can be observed in biological, chemical, and geochemical systems due to the interaction of reaction with diffusion. The appearance of static precipitation patterns was reported first by Liesegang in 1896. Traveling waves and dynamically changing patterns can also exist in reaction−diffusion systems: the Belousov−Zhabotinsky reaction provides a classical example for these phenomena. Until now, no experimental evidence had been found for the presence of such dynamical patterns in precipitation systems. Pattern formation phenomena, as a result of precipitation front coupling with traveling waves, are investigated in a new simple reaction−diffusion system that is based on the precipitation and complex formation of aluminum hydroxide. A unique kind of self-organization, the spontaneous appearance of traveling waves, and spiral formation inside a precipitation front is reported. The newly designed system is a simple one (we need just two inorganic reactants, and the experimental setup is simple), in which dynamically changing pattern formation can be observed. This work could show a new perspective in precipitation pattern formation and geochemical self-organization.

Self-organization and spontaneous pattern formation in reaction−diffusion (RD) systems have a great and highly increasing relevance in the natural and life sciences.[1−3] Over the past decades, various self-organization phenomena have been reported: precipitation patterns,[4−8] self-oscillatory systems,[9] traveling waves,[10] and Turing patterns.[11−13] The existence of stable and stationary patterns in RD systems was predicted by Turing in 1952, yet the experimental evidence had been waited on for a long time,[11] while in 1990, De Kepper presented a CIMA reaction in an open system[12] with substantially different diffusion coefficients of the activator and inhibitor species.

The Belousov−Zhabotinsky (BZ) system serves as a classical and extensively studied example of self-oscillatory systems and the spatial pattern formation in homogeneous RD systems,[10] respectively. Conditions for the presence of such patterns have been studied both experimentally and theoretically. These results

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were involved for a systematic design of oscillatory systems[9,14−17] and chemical waves in excitable systems: for example, the control of traveling waves during the catalytic oxidation of carbon monoxide using a focused laser beam[18,19] or global delayed feedback.[20] Target patterns (e.g., spiral waves) can also be observed in this heterogeneous medium, despite the essential differences from the classical BZ systems. In biological systems, calcium waves are known to increase the efficiency and specificity of gene expression[21] and also have importance in intracellular signaling.[22] The mathematical models describing the evolution of excitation waves have the same core: a self-accelerating step and a negative feedback have to be present.[23]

In other RD systems, precipitation patterns can emerge, where the diffusion of two, usually inorganic, species are coupled with their reaction.[4−8,24] The existence of such patterns is usually explained by the instability of colloidal substances arising from the reactants.[4,25] The classical patterns are static and stationary in the sense that the formed precipitation objects (bands, rings, or more complex ones) stay at the given position. Instead of static ones, dynamically changing precipitation patterns can be formed if the complex formation of precipitate is possible; for example, in a classical Liesegang experimental setup, a precipitation front can move through the reaction domain.[26−29]

Pattern formation phenomena as a result of precipitation front coupling with traveling waves are investigated in a new simple RD system that is based on the precipitation and complex formation of aluminum hydroxide. A unique kind of self-organization, the spontaneous appearance of traveling waves and spiral formation inside a precipitation front, is reported. We can observe a coexistence of moving precipitation patterns with traveling waves (perpendicular to the diffusion flux vector of the invading electrolyte) inside the precipitate, using a rather simple experimental setup. Until now, no experimental evidence had been found for the presence of such patterns in precipitation systems.

An agarose gel contained $AlCl_3$ (inner electrolyte) of given concentration was prepared as follows. Agarose (Reanal) was dissolved in distilled water in such a way that it produced a 1% solution, which was heated to 70−80 °C and stirred until it became crystal clear. The solution was then mixed with the given amount of $AlCl_3$*$6H_2O$ (Reanal) to obtain a prescribed concentration of the inner electrolyte. After that, the solution was poured into a Petri dish, which was held firmly horizontally to obtain a uniformly thick gel. We used NaOH in all experiments as an outer electrolyte with a concentration of 2.50 M. After the completion of the gelation process (1 h), the outer electrolyte was directly placed on the gel surface, and the pattern formation was monitored in transmitted light.

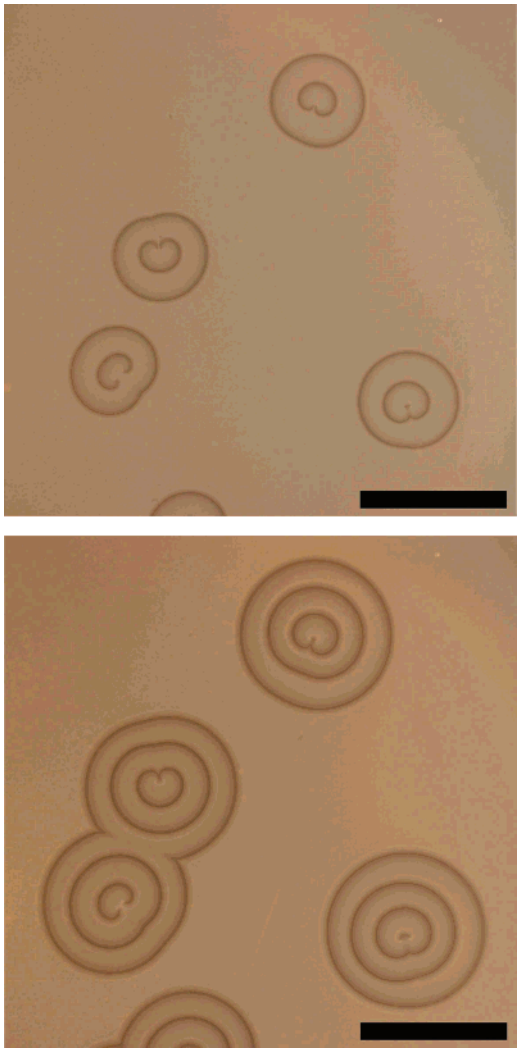

Figure 1. Evolution of double spirals in the aluminum hydroxide precipitate (top view). Initial conditions: agarose gel containing $[Al^{3+}] = 0.29$ M with a thickness of 6.4 mm in a Petri dish (d = 14 cm); outer electrolyte (50 cm^3, [NaOH] = 2.50 M) was placed on top of the gel surface. The pictures were taken at t and $t + 390$ s, respectively. The scale bar represents 1 cm.

The phenomenon reported here incorporates both traveling waves as being in excitable systems and precipitation patterns (as precipitation fronts, Liesegang phenomenon). $AlCl_3$ as an inert electrolyte is uniformly distributed in agarose gel, and the outer electrolyte diffuses into the gel, producing the precipitate $Al(OH)_3$. Precipitate formation is preferred at the interface of the electrolytes (gel surface); at the same time, the excess of the outer electrolyte behind the front reacts with precipitate by complex formation (redissolution). In such a way, a sinking precipitation layer evolves in the gel driven by diffusion with a decreasing velocity. The precipitation process and complex formation produced a sharp thin aluminum hydroxide layer by the following reactions:[30]

$$Al^{3+}(aq) + 3\,H_2O \leftrightarrow Al(OH)_3(s) + 3\,H^+(aq) \quad (1)$$

$$Al(OH)_3(s) + H_2O \leftrightarrow [Al(OH)_4]^-(aq) + H^+(aq) \quad (2)$$

A few minutes after the initialization, a well-defined self-organization can be observed in the precipitate. Figures 1 and

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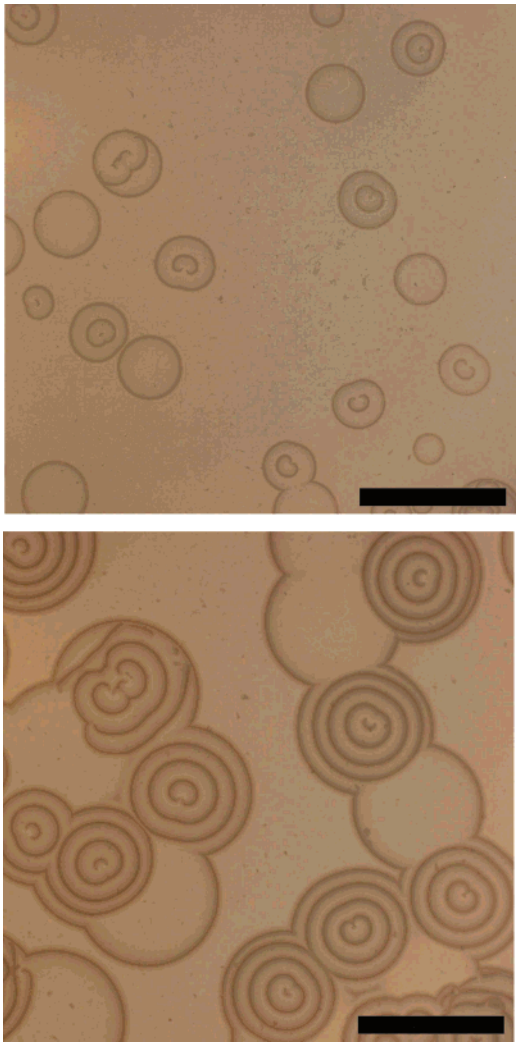

Figure 2. Self-organization in the aluminum hydroxide precipitation surface (top view). Initial conditions were the same as those in Figure 1, except the agarose gel containing $[Al^{3+}] = 0.30$ M was used. The pictures were taken at t and $t + 390$ s, respectively. The scale bar represents 1 cm.

2 show spontaneous double spiral formation (see Supporting Information). The spatiotemporal pattern evolution consists of two components:

1. The sinking precipitation layer, which is parallel to the gel surface and orthogonal to the observation direction (top view), travels through the gelled medium due to precipitation and complex formation.

2. Self-organization occurs inside the whole width of the thin precipitation disk (∼50−200 μm). At the beginning of the experiment, we observe double spiral formation resulting in cardioid patterns without any external perturbation. The number of double spirals increases in time, showing saturation kinetics and generating more and more traveling waves. Afterward, the wave velocity decreases, and, as it reaches zero (after a few hours), the pattern freezes. The "excitability" of the system increases at the beginning of the experiment (the formation of double spirals), has a maximum in time and decreases until the pattern freezes. The initial excitability of the system can be controlled by the $AlCl_3$ concentration. In the case of low initial excitability ($[AlCl_3] = 0.280$ M), the double spirals may turn into a single circular traveling wave, as the tips of the double spiral cannot produce the new spiral cores. At high initial excitability ($[AlCl_3] = 0.320$ M), the whole disk is filled with

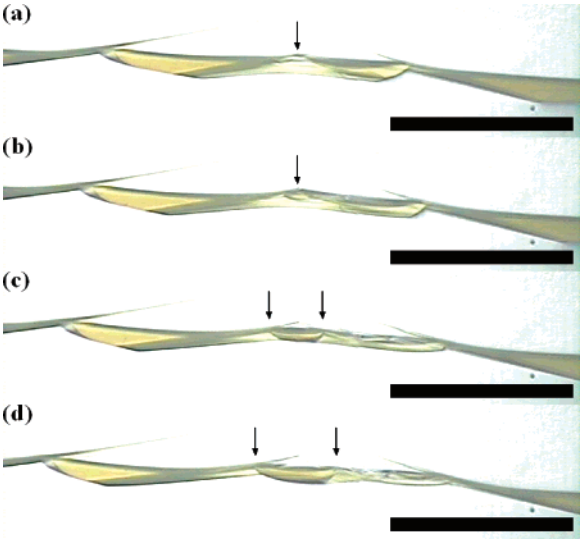

Figure 3. Traveling precipitation wave formation from the active center (side view). The agarose gel sheet contained $[Al^{3+}] = 0.30$ M with a thickness of 1 mm. The outer electrolyte ([NaOH] = 2.50 M) was contacted to the thin vertical side of the gel sheet. The darker and lighter areas represent colloidal and solid precipitate, respectively. The pictures were taken by optical microscope, and the time step was 30 s. The scale bar represents 1 mm.

active double spirals. Increasing the initial concentration of the inner electrolyte further, the well-defined self-organization vanishes. The velocity of spiral evolution (∼1 cm h^{-1}) is approximately one order higher than that of the motion of the precipitation layer (∼0.1 cm h^{-1}): the time scale of the evolution of the precipitation layer differs substantially from that of the self-organization.

Such self-organization exists in a small range of $[Al^{3+}]$ (0.28−0.34 M) at a fixed concentration of the outer electrolyte (2.50 M NaOH). Increasing the Al^{3+} concentration results in an increase in the physical quantities related to the excitability: the number of active double spiral centers and the average wavenumber (Figures 1 and 2).

Experiments in the thin (1 mm) gel sheets were also performed to investigate the dynamics of wave formation and traveling (perpendicular to the observations above; side view). After the start of the experiment, a thin precipitation layer formed. The dynamic of the pattern formation has two governing forces: the production of solid and macroscopic precipitation surfaces inside the precipitation layer (which are represented by edges in a two-dimensional cross-section) and the evolution of precipitation fronts along these ones (Figures 3 and 4). One can detect dark regions (traveling waves) observing this phenomenon from above (Figures 1 and 2) using transmitted light, where the precipitation fronts travel along the edges. These dark regions correspond to a very thin (∼30 μm), but solid precipitate. White regions (Figures 1 and 2) correspond to thicker precipitation layers. Figures 3 and 4 show the active center and wave annihilation inside the precipitation layer (see Supporting Information), respectively. The composite of the precipitation layer can be inhomogeneous, as shown in Figures 3 and 4: lighter and darker parts are precipitate particles of smaller and larger size distributions, respectively.

This type of pattern formation could be general in precipitation systems. The problems arising in the experiments are twofold: the characteristic size and the observability of these structures. Similar patterns have been seen on a microscopic scale by reacting copper chloride (inner electrolyte) with sodium hydroxide or potassium hydroxide (outer electrolyte). The formation of such structures only becomes evident when the copper hydroxide is

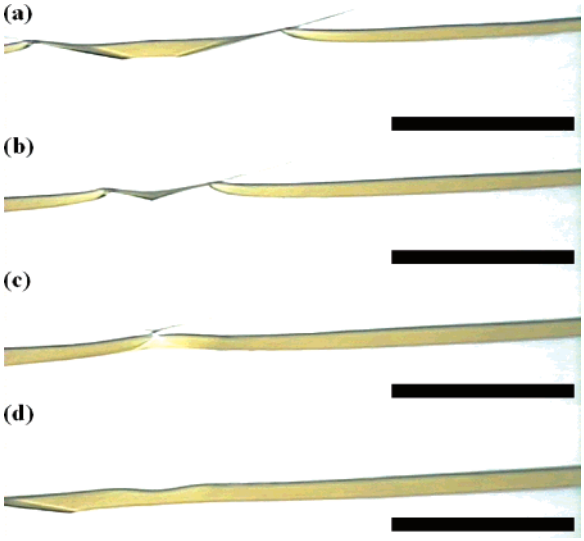

Figure 4. Wave annihilation inside the precipitation layer (side view). The agarose gel sheet contained $[Al^{3+}] = 0.30$ M with a thickness of 1 mm. The outer electrolyte ([NaOH] = 2.50 M) was contacted to the thin vertical side of the gel sheet. The darker and lighter areas represent colloidal and solid precipitate, respectively. The pictures were taken by optical microscope, and the time step was 70 s. The scale bar represents 1 mm.

oxidized further, and, at this stage, the pattern is already permanent.[31,32] In $CuCl_2/K_3[Fe(CN)_6]$ (outer/inner electrolytes), another interesting phenomenon can occur: locally, only one circular front is formed, and these fronts annihilate to produce a Voronoi diagram-based pattern.[33]

All experimental results suggest that some reactive intermediate species should exist in precipitation systems. These may produce precipitate and take part in an autocatalytic process coupled to a negative feedback producing the dynamic phenomenon observed. Here the complex formation of precipitate plays an important role only in the transparency of the pattern and cannot affect the mechanism of spiral and target pattern formation.

We have found a simpler system (containing originally two inorganic components) in which a new self-organization appears. The formation of an active center and the annihilation of traveling waves have been observed in the study of several seashell patterns.[34] An activator−inhibitor-type model has been developed to describe this phenomenon.[34] Our finding may also be important to understand more deeply geochemical self-organization,[35] applying a never before used approach. Interestingly, this dynamic pattern formation phenomenon could have been observed before the BZ system was reported.

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Supporting Information Available: Video 1: This movie shows the evolution of double spirals in the $Al(OH)_3$ precipitate from the top. An agarose gel contains 0.29 M $AlCl_3$, and the outer electrolyte ([NaOH] = 2.50 M) was placed onto the gel surface. The self-organization was recorded over a time period of 50 min. The size of the domain is 5.25 × 3.50 cm. Video 2: This side-view movie shows the evolution of the $Al(OH)_3$ precipitation layer (traveling wave formation from the active center; $[Al^{3+}] = 0.30$ M, [NaOH] = 2.50 M). The phenomenon was recorded over a time period of 17 min. The size of the domain is 3.20 × 2.40 mm. Video 3: This side-view movie shows the evolution of the $Al(OH)_3$ precipitation layer (annihilation of traveling waves; $[Al^{3+}] = 0.30$ M, [NaOH] = 2.50 M). The phenomenon was recorded over a time period of 10 min. The size of the domain is 3.20 × 2.40 mm. This material is available free of charge via the Internet at http://pubs.acs.org.

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