Bifurcation of the Ostwald-Liesegang supersaturation−nucleation−depletion cycle *

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ABSTRACT


A new formulation of the Ostwald supersaturation−nucleation−depletion cycle is adopted to model precipitate banding in rocks. In a special limiting case, the system is shown to support a propagating steady deposition pulse. The limit of existence is determined analytically for a simple model analogue of a pyrite/goethite system. Using numerical simulations, an unsteady pulse of mineral deposition is obtained and is shown to develop a variety of patterns with an appropriate change in the system parameters—apparently showing that the steady pulse obtained analytically is unstable. The domains of existence of unsteady pulse, undulatory patterns and discrete bands are determined.

I. THE OSTWALD SUPERSATURATION-NUCLEATION-DEPLETION CYCLE

Over the past two decades a great deal of interest has been generated in spontaneous pattern formation of the Turing (1952) reaction/diffusion type. As clarified by the Brussels group (Glansdorff and Prigogine, 1971), this mechanism of pattern formation requires a constant supply of free energy to sustain macroscopic order, i.e. the patterns are strictly nonequilibrium structures. However, evidence of a great many patterning phenomena in rocks indicates that there must be other scenarios for self-organization that can freeze in patterns long after they were formed and free energy is no longer being expended. In fact, some geological patterns have existed for millions of years. The process of order preservation must itself be an intimate part of or act simultaneously with pattern generation—the latter being a less probable coincidence.

One mechanism appropriate for biological and many geological conditions seems to be involved in the various precipitate self-patternning effects (Liesegang, 1913, 1986; Hedges and Myers, 1926; Stern, 1954, 1967). Here we study a mechanism of macroscopic precipitate pattern self-organization.

Runge and Liesegang and later investigators demonstrated that the interdiffusion of two coprecipitates can lead to the formation of banded patterns in one dimension, ring-shaped localization of precipitate in two dimensions and corkscrew patterns in three dimensions (Liesegang, 1913, 1986; Hedges and Myers, 1926; Stern, 1954, 1967). Since there need not be any precipitate in these systems before the interdiffusion process started, it was conjectured by Ostwald (1925) that the mechanism of band formation involved a sequence of supersaturation, nucleation and de-
Fig. 1. Ostwald supersaturation–nucleation–depletion cycle. (a) X and Y concentration profiles and A dissolution front. The flow-driven aqueous species X (of velocity v) reacts with precipitate A to form aqueous species Y causing the motion of an A dissolution front (of velocity u). (b) Evolution of the profile of the XY concentration product. When XY exceeds the nucleation threshold \( Q_n \), a first B precipitate band is formed. Immediately after precipitation takes place, the system is depleted in X and Y, subsequently XY increases gradually until supersaturation builds up and exceeds again the nucleation threshold causing the formation of a second band etc. (c) Banded B deposition profile.

Prager (1956) took the Ostwald concept and formulated it as a mathematical model by postulating an infinitesimally discrete zone of nucleation at a point where nucleation is triggered by locally exceeding a critical supersaturation. The Prager model and later modifications give banding, but suffer from the fact that the bands have zero width and that the handling of the band as a boundary condition on the conservation equations for the coprecipitates is introduced in a somewhat unnatural way.

In this paper we formulate the Ostwald cycle using a model suggested by geological applications (Ortoleva, 1984). That some repetitively banded mineral distributions in rocks could be accounted for by the Liesegang banding process was proposed by Liesegang himself (1913). Indeed it is clear that interest in the physico-chemical basis of the self-organization of macroscopic patterns dates back at least to the time of Liesegang (the latter part of the 19th century).

The model developed has a number of novel features. It was set forth for a geological problem wherein a flow of reactive water is imposed on a porous rock. The basic nucleation model holds equally well for the case where the two coprecipitates both diffuse and flow is absent—the more familiar Liesegang experiment. From the theoretical standpoint, the present model is quite interesting because it allows for a number of exact results and self-consistent approximation schemes. The model also seems to allow for the possibility of banding to appear as a Hopf bifurcation (Marsden and McCracken, 1976) from a planar, steady deposition front. Hence models of this type may be used to map Liesegang phenomena onto a problem in more standard bifurcation theory.

II. MODELING A FLOW-DRIVEN OSTWALD-LIESEGANG CYCLE

We now consider a simple model of an oxidative pyrite (mineral A) dissolution front and the associated banded precipitation of
goethite (mineral B). An influx of a solution containing a solute X is imposed into an inert porous matrix containing grains of a solid A that reacts irreversibly with X via:

\[ mX + nA \rightarrow qY + \cdots \]  \hspace{1cm} (II.1)

where \( m, n, q \) are stoichiometric coefficients and the dots represent possible inert products of the \( X-A \) reaction other than \( Y \). The next step in the mechanism to be studied here is the nucleation and growth of a second solid \( B \) according to:

\[ xX + yY \rightarrow bB \]  \hspace{1cm} (11.2)

with stoichiometry \( x, y, b \). This two-step process is an analogue of the oxidative dissolution of pyrite to produce a deposition of an iron oxide mineral such as goethite. This “redox front” process is observed in the field to be accompanied by a banded deposition of the \( B \)-analogue behind a front of the \( A \)-analogue.

Let \( X \) and \( Y \) indicate concentrations per pore fluid volume and \( \phi \) be the fraction of the volume of the medium that is pore fluid. We take \( X \) to evolve via:

\[ \frac{\partial X}{\partial t} = \phi D_A \nabla^2 X - \frac{\partial}{\partial t} \left( \phi \nabla (\vec{u} X) \right) + \frac{m}{n} \rho_A \frac{\partial \phi_A}{\partial t} - \frac{x}{b} \rho_B \frac{\partial \phi_B}{\partial t} \]  \hspace{1cm} (II.3)

and similarly for \( Y' \); \( \rho_A \) and \( \rho_B \) are the solid molar densities and \( \phi_A \) and \( \phi_B \) are the volume fractions of the medium that is \( A \) or \( B \). The velocity of the flow, \( \vec{v} \), is taken to be constant. In obtaining eq. II.3 (and its \( Y \)-analogue) we neglect variations \( \phi \) and in the diffusion coefficients \( D_X \) and \( D_Y \) caused by the mineral dissolution and precipitation reactions.

To bring out some of the natural parameters in the problem, we introduce scaled quantities. Let a bar over a variable be its typical value. Then we make the following definitions:

\[ X = \bar{X} X', \quad Y = \bar{Y} Y', \quad \epsilon = \phi \bar{X}/\rho_A, \quad \xi = \rho_B/\rho_A, \quad D_Y = D_X D, \quad \bar{r}^2 = D_X \bar{t}, \]  \hspace{1cm} (II.4)

\[ t = \bar{t} t', \quad \vec{r} = \bar{r} \vec{r}', \quad \vec{v} = \frac{\vec{r}}{t} \vec{v}' \]

With this (II.3) becomes:

\[ \frac{\partial X'}{\partial t'} = \nabla'^2 X' - \vec{v}' \cdot (\vec{u}' X') + \frac{1}{\epsilon} \frac{m}{n} \frac{\partial \phi_A}{\partial t'} - \frac{x}{b} \frac{\partial \phi_B}{\partial t'} \]  \hspace{1cm} (II.5)

and similarly for \( Y' \). To complete the description we need equations for \( \phi_A \) and \( \phi_B \).

Let \( n_A \) be the number density of \( A \) grains and \( L_A^3 \) be their volume; then \( \phi_A = n_A L_A^3 \). Assuming the dissolution of \( A \) via \( X \) proceeds by a mass action, surface kinetic limited rate law, we have:

\[ \frac{\partial L_A^3}{\partial t} = -k L_A^2 X^m \]  \hspace{1cm} (II.6)

for rate constant \( k \). Using the defining relation between \( \phi_A, n_A \) and \( L_A \) this yields, assuming \( n_A \) to be constant:

\[ \frac{\partial \phi_A}{\partial t} = -\gamma \phi_A^{2/3} X^m \]  \hspace{1cm} (II.7)

where:

\[ \gamma = k \bar{t} \bar{X}^m n_A^{1/3} \]  \hspace{1cm} (II.8)

Next assume that \( B \) is produced as a thin coating on the pre-existing grains of other inert minerals in the medium. Then if \( \tau \) is the \( B \) coating thickness we get:

\[ \frac{\partial \tau}{\partial t} = g ( X^x Y^y - Q ) \]  \hspace{1cm} (II.9)

Again we assume mass action kinetics; \( Q \) is the equilibrium constant for \( B \). The factor \( g \) accounts for nucleation barriers. Our model introduces a supersaturation value of \( Q \) denoted \( Q_n \). With this \( g \) is taken to have the form

\[ g = \begin{cases} 0, & X^x Y^y < Q_n, \quad \tau = 0 \\ g_0, & \text{otherwise} \end{cases} \]  \hspace{1cm} (II.10)

for a growth constant \( g_0 \). This nucleation law allows for growth to start even when there is no \( B \) (i.e. \( \tau = 0 \)) as long as the critical supersaturation is exceeded.

Let \( \Sigma \) be the surface area of the inert grains (on which \( B \) precipitates) per unit rock volume. For simplicity we assume \( \tau \) always
remains small so that the \( B \) grain coating surface that is in contact with the pore fluid, remains constant at the value \( Z \). Then \( \phi_B = n_B \Sigma \tau \) and we have:

\[
\frac{\partial \phi_B}{\partial t} = i \Sigma n_B g( X^X Y^Y, \tau)[ X^X Y^Y - Q ] \tag{II.11}
\]

Collecting the above results and dropping all primes, we get the following model:

\[
\frac{\partial X}{\partial t} = \nabla^2 X - \nabla \cdot (X\vec{v}) + \frac{m}{n\epsilon} \frac{\partial \phi_A}{\partial t} - \frac{\omega}{\epsilon} \frac{\partial \tau}{\partial t} \tag{II.12}
\]

\[
\frac{\partial Y}{\partial t} = D \nabla^2 Y - \nabla \cdot (Y\vec{v}) - q \frac{\partial \phi_A}{\partial t} - \frac{\gamma \omega}{\chi \epsilon} \frac{\partial \tau}{\partial t} \tag{II.13}
\]

\[
\frac{\partial \phi_A}{\partial t} = -\gamma \phi_A^{2/3} X^m \tag{II.14}
\]

\[
\frac{\partial \tau}{\partial t} = \epsilon \Gamma \Theta(X^X Y^Y, \tau)[ X^X Y^Y - 1] \tag{II.15}
\]

where:

\[
\omega = n_B \xi \Sigma / b
\]

\[
X^{x+y} = Q \tag{II.16}
\]

\[
\Gamma = \frac{\tau g_0 Q}{\gamma \epsilon}
\]

\[
\Theta = \frac{g_0 Q}{\tau} - \frac{\gamma \omega}{\chi \epsilon}
\]

In the developments of this study we consider the limit \( \epsilon \to 0 \) keeping \( \Gamma \) constant. This implies that solid \( A \) has a high molar density relative to \( X^\phi \) (a typical situation geologically would be for \( \epsilon \) to be \( 10^{-3} \) to \( 10^{-9} \) or smaller) and that the precipitation rate coefficient of \( B \) is small (so that \( g_0 Q / \epsilon \) is of order one for small \( \epsilon \)).

III. SOLID DENSITY ASYMPTOTICS

Solid density asymptotics may be used to approximate the above problem in the \( \epsilon \to 0 \) limit (Ortoleva et al., 1987a). Because \( \epsilon \) is small, the time to dissolve an \( A \) grain is long. Thus we define a new time \( t^* \) such that \( t = t^*/\epsilon \) so that the time to dissolve an \( A \) grain is on the time scale of order unity as \( \epsilon \to 0 \). Transforming the above equations for \( X, Y, \phi_A \) and \( \tau \) to this new time and taking \( \epsilon \to 0 \), we obtain (dropping the * on \( t \)):

\[
\nabla^2 X - \nabla \cdot (\vec{v} X) - \omega \frac{\partial \tau}{\partial t} = 0 \tag{III.1}
\]

\[
D \nabla^2 Y - \nabla \cdot (\vec{v} Y) - \frac{\gamma \omega}{\chi} \frac{\partial \tau}{\partial t} = 0 \tag{III.2}
\]

\[
\frac{\partial \tau}{\partial t} = \Gamma \Theta(X^X Y^Y, \tau)[ X^X Y^Y - 1] \tag{III.3}
\]

In the present dimensionless concentration variables, \( \Theta \) may be written:

\[
\Theta = \begin{cases} 0, & X^X Y^Y < \eta, \tau = 0 \\ 1, & \text{otherwise} \end{cases} \quad \eta = Q n / Q \tag{III.4}
\]

In the \( \epsilon \to 0 \) limit, \( \phi_A \) jumps from zero to its initial value \( \phi_A^0 \) at a surface we denote \( S(\vec{r}, t) \) = 0. With this, eq. III.1 operates in the domain \( S < 0 \) where \( A \) has been dissolved via eq. II.1. In the zone \( S > 0 \), \( \phi_A = \phi_A^0 \) and \( X \) vanishes. In eq. III.4 \( \eta \) is the factor by which \( X^X Y^Y \) must exceed its \( B \)-equilibrium value (\( Q \) in dimensional quantities and one in the present scaled variables) to attain nucleation.

Purely kinematic considerations may be used to show that the \( A \)-dissolution interface evolves according to the dynamics:

\[
\frac{\partial S}{\partial t} + u | \nabla S | = 0 \tag{III.5}
\]

where \( u \) is the normal advancement velocity for the interface (Chadam and Ortoleva, 1986). At the dissolution interface one may use solid density asymptotics to derive the boundary conditions for \( X \) and \( Y \) at \( S = 0 \) (Ortoleva et al., 1987b). One finds:

- \( X \) and \( Y \) continuous
- \( \phi_A \) jumps from 0 to \( \phi_A^0 \)
- \( D \vec{n} \cdot \left[ \nabla Y \right]_{10} - \left. \nabla Y \right|_{0-} = - q u \left( \phi_A^0 \right) \)

where \( \vec{n} (= \nabla S / | \nabla S |) \) is the unit normal to the advancing \( \phi_A \) jump surface and \( 0^+ \) and \( 0^- \) imply evaluation at \( S = \pm 0^+ \), \( 0^+ \) being a positive infinitesimal. The description is completed by supplying the initial data \( S(\vec{r}, 0), \phi_A(\vec{r}, 0), \phi_A(\vec{r}, 0) = \phi_A^0 \) and \( \tau(\vec{r}, 0) \) and the boundary data for \( X \) and \( Y \).
IV. PLANAR CONSTANT VELOCITY SOLUTIONS

A. Formulation

A fundamental solution of the above problem is a constant velocity and profile entity that advances into the unaltered region where \( \phi_A = \phi_A^0 \) (henceforth a constant) and \( \tau = 0 \). We assume \( \bar{v} \) is constant along the positive \( r \) direction so that the \( A-B \) disturbance advances in the positive \( r \) direction also. Changing to a moving coordinate \( \xi \) fixed to the wave of speed \( \bar{u} \) (so that \( \xi = r - \bar{u}t \)) and locating the \( \phi_A \) discontinuity at \( \xi = 0 \) we have:

\[
[X' - \bar{u}X + \omega \bar{u} \tau]' = 0, \xi < 0; \quad X = 0, \xi > 0
\]  
(IV.1)

\[
[DY' - \bar{u}Y + \frac{\omega y \bar{u}}{X} \tau]' = 0
\]  
(IV.2)

where a prime indicates a \( \xi \) derivative. For the planar problem we take \( S = \xi; \) the boundary conditions at \( \xi = 0 \) are given by eq. III.6 and become:

\[
X(0^-) = 0
\]  
(IV.4)

\[
Y(0^-) = Y(0^+)
\]  
(IV.5)

\[
-X'(0^-) = m \bar{u} \phi_A^0
\]  
(IV.6)

\[
D[Y'(0^+) - Y'(0^-)] = -q \bar{u} \phi_A^0
\]  
(IV.7)

to the above equations we add the boundary data fixing the concentrations at the inlet (assumed far upstream from the front):

\[
X(-\infty) = X_M
\]  
(IV.8)

\[
Y(-\infty) = Y_M
\]  
(IV.9)

for \( \xi > 0, \) \( X \) vanishes and \( Y(\infty) \) is to be determined.

Because \( X \) vanishes at \( \xi = 0 \) and the nucleation of \( B \) requires \( \chi' \chi > \eta, \) it is clear that, if nucleation takes place at all, the leading edge of \( B \) nucleation occurs at a value of \( \xi, \) denoted \( \xi_n, \) located near and to the left of the origin as in Fig. 2. By definition \( \xi_n \) is determined by the condition:

\[
X' \chi(\xi_n) Y' \chi(\xi_n) = \eta
\]  
(IV.10)

Whether or not a \( \xi_n \) exists depends on the values of \( X_M, Y_M \) and the other parameters of the problem. A central goal of the present calculation is to determine the domain of parameters for which a steady \( B \)-pulse solution exists.

Consider a solution which is steady and has \( \tau \) non-zero continuously over an interval as follows. The spatial region where \( \tau \) is non-zero starts from \( \xi_n \) and extends to some finite value \( \xi_d \) if the inlet is undersaturated with respect to \( B \) as in Fig. 2. More precisely:

\[
\tau \neq 0 \quad \text{for } \xi_d < \xi < \xi_n \quad X_M \chi Y_M < 1 \quad (IV.11)
\]

The qualitative form of the steady deposition pulse is indicated in Fig. 2.

B. Reformulation

Because the left end of the \( B \) deposit is bathed in undersaturated fluids, there is a finite zone in which \( B \) exists; hence \( \tau(-\infty) = 0. \) Thus the conserved quantities in brackets in eqs. IV.1, 2 can be evaluated at \(-\infty\) to yield:

\[
X' - \bar{u}X + \omega \bar{u} \tau = -v X_M
\]  
(IV.12)

\[
DY' - \bar{u}Y + \frac{y \omega \bar{u}}{X} \tau = -v Y_M
\]  
(IV.13)

These equations may be solved in the various domains \((\xi < \xi_d, \xi_d < \xi < \xi_n, \xi_n < \xi < 0 \) and \( \xi > 0 \) and matched at the boundaries of each domain to insure continuity of \( X \) and \( Y \) and their derivatives (except at \( \xi = 0 \) where the
derivative jump conditions (eq. IV.6, 7, apply).

The entire problem may be reduced to an equation for an auxiliary quantity \( Z \) defined as follows. Let:

\[
\alpha = e^{-v \xi} \quad \text{(IV.14)}
\]

\[
Z(\alpha) = \int_{\alpha_n}^{\alpha} d\alpha' \tau(\alpha') \quad \text{(IV.15)}
\]

where \( \alpha_n = -v \xi_n \) (and similarly for \( \alpha_d \)).

The calculation proceeds by finding \( X(\alpha) \) and \( Y(\alpha) \) in terms of \( Z(\alpha) \) and then putting the results in the \( \tau \)-equation (IV.3), obtaining an equation for \( Z(\alpha) \).

Rather than give the general case, we take \( D = x = y = 1, \ Y_m = 0 \) for simplicity. Thus we obtain:

\[
\begin{align*}
X(\alpha) &= \frac{\omega u Z - vX_M(1 - \alpha)}{v \alpha} \quad \text{(IV.16)} \\
Y(\alpha) &= \frac{\omega u Z + vX_M}{v \alpha} \quad \text{(IV.17)}
\end{align*}
\]

The resulting equation for \( Z(\alpha) \) is:

\[
\alpha^3 Z'' = \Lambda \left\{ Z^2 + X_M \alpha Z + X_M^2 (\alpha - 1) - \alpha^2 \right\} \quad \text{(IV.18)}
\]

\[\Lambda = \omega \Gamma/v^2 \quad \text{(IV.19)}\]

This equation must be solved subject to:

\[
\begin{align*}
\tau(\alpha_n) &= Z'(\alpha_n) = 0 \\
\tau(\alpha_d) &= Z'(\alpha_d) = 0 \\
\tau(\alpha) &= Z'(\alpha) < \infty \quad \text{for} \ \alpha_n < \alpha < \alpha_d
\end{align*}
\] (IV.20)

Furthermore, evaluating \( X(\alpha) \) and \( Y(\alpha) \) at the nucleation point \( \alpha_n \) subject to:

\[
Z(\alpha_n) = Z'(\alpha_n) = 0 \quad \text{IV.21)
\]

and inserting those values in the boundary condition \( X(\alpha_n)Y(\alpha_n) = \eta \), we obtain the relation:

\[
\frac{\alpha_n^2}{(\alpha_n - 1)} = \frac{X_M^2}{\eta} \quad \text{IV.22)}
\]

that yields \( \alpha_n \) in terms of \( X_M \) and \( \eta \). The range of parameters \( X_M, \eta, v, \Lambda \) for which these conditions (IV.20–22) are attained, is the range of conditions for which the steady deposition pulse solution suggested in Fig. 2 exists.

In Fig. 3 the dependence of \( \alpha_n \) on \( \eta/X_M^2 \) is shown. Note that there are multiple solutions. Recalling that \( \alpha = \exp(-v \xi) \) and that \( v \xi \) is the distance that the leading edge of the precipitate zone lags behind the \( A \) front, we see that the (+)-branch corresponds to a pulse lagging further behind than the (−)-branch. However, the physically allowed nucleation point is that closest to the \( A \) dissolution front. Hence the (+)-branch is unphysical.

C. Limit of existence of steady-state solutions

The \( Z \) equation (IV.18) was simulated in the computer for a set of model parameters, using different values of the inlet concentration \( X_M \) such that \( X_M > 4 \eta \). It is found that for a given value of \( X_M \), there exists a critical value \( \Lambda_c \) of the parameter \( \Lambda \), above which no steady-state solution exists. Numerically, this corresponds to a situation where the third condition in eq. IV.20 fails to be satisfied, i.e. \( \tau( = Z') \) never goes to zero for \( \alpha > \alpha_n \). Fig. 4a shows the shape of the steady-state pulse solution for \( B \) deposition obtained at three different \( X_M \) values, and at \( \Lambda = 1 \) for each
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Fig. 4. (a) Steady-state B deposition pulses obtained numerically as solutions of the Z–α equation (IV.19) at different $X_M$ values and at $\Lambda = 1$. 1: $X_M = 2.10$; 2: $X_M = 2.15$; 3: $X_M = 2.20$. (b) $\Lambda$–$X_M$ diagram showing the limit of existence of steady-state solutions. No steady-state solution exists above this curve ($\Lambda = \Lambda_c$). The dashed line shows the critical $X_M$ value ($= [4\eta/\gamma]^1/2$) as obtained from eq. IV.23, here for the case $\eta = 1.1$.

case. The curve in Fig. 4b shows the limit of existence of steady-state solutions determined numerically as above. We now turn to the question of the stability of these solutions.

V. UNSTEADY DEPOSITION—THE TRANSITION TO LIESEGANG BANDING

We now present results on unsteady deposition via numerical simulations. The calculations were carried out on the following set of equations in one spatial dimension using the program REACTRAN (Ortoleva et al., 1987a; Haskin et al., 1988; Chen et al., 1990):

$$\frac{\partial X}{\partial t} = \phi D_X \nabla^2 X - \phi \nabla \cdot (X \nabla) + \rho_A n_A \frac{\partial}{\partial t} \left( \frac{4}{3} \pi R_A^3 \right) - \rho_B n_B \frac{\partial}{\partial t} \left( \frac{4}{3} \pi R_B^3 \right) \tag{V.1}$$

$$\frac{\partial Y}{\partial t} = \phi D_Y \nabla^2 Y - \phi \nabla \cdot (Y \nabla) - \rho_A n_A \frac{\partial}{\partial t} \left( \frac{4}{3} \pi R_A^3 \right) - \rho_B n_B \frac{\partial}{\partial t} \left( \frac{4}{3} \pi R_B^3 \right) \tag{V.2}$$

$$\frac{\partial R_A}{\partial t} = -k_A (K_X - Y) \tag{V.3}$$

$$\frac{\partial R_B}{\partial t} = k_B (XY - K_B) \tag{V.4}$$

Note that for $k_A \to \infty$ this reduces to the model (III.1–3) for the special choices $y = x = m = n = q = b = 1$. Thus the large $k_A$ results are directly comparable with the calculations of the previous section.

Simulations were carried out for the case where the critical nucleation supersaturation ratio $\eta$ was 1.1. From equation IV.22 we must have $X_M^2 > 4\eta$ for deposition of B when $k_A$ is large. The cases studied here are $X_M = 2.10, 2.15$ and 2.20. Fig. 5 shows the B deposition profile for the case where $X_M = 2.10$. In going from frame (a) to (e), we see the effect of increasing the parameter $\Lambda$ (0.040, 0.200, 0.215, 0.400 and 1.00, respectively) on the shape of the B deposition profile at the indicated time. Fig. 5(a) ($\Lambda = 0.05$) shows an unsteady B pulse moving behind the A front and characterized by randomly and irregularly forming shoulders as time advances. At $\Lambda = 0.2$, the pulse starts developing a “wiggle structure” with maxima and minima (Fig. 6(b)). The intensity of the spatial undulation in the pulse profile is increased as $\Lambda$ increases.
to 0.215 as shown in frame (c) of Fig. 5. Note that over this \( \Lambda \) range (0.2–0.215), the wiggle is extremely sensitive to a small increase in \( \Lambda \). This explains the abrupt decrease in the observed minimum in going from frame (b) to (c). At higher \( \Lambda \) values, a transition to the formation of discrete bands is observed (Fig. 5, (d) and (e)) such that \( B \)-free zones separate bands of \( B \) deposition. At a later time, the \( B \) deposition profile of Fig. 5 (e) \((\Lambda = 1.0)\) evolves into a pattern where discrete bands with precipitate free zones are well defined (Fig. 6(a)). In Fig. 6(b) \( \Lambda \) is increased to 5.0

Fig. 5. Results of the numerical simulations of eqs. V.1–4, for the following set of parameters suggested by geological data: \( \rho_A = \rho_B = 0.25 M \), \( n_A = n_B = 1.0 \times 10^2 \) grains/cm\(^3\); radius of grain on which \( B \) nucleates \( R_B = 0.7 \) mm; \( D_2 = D_3 = 10^{-7} \) cm\(^2\) s\(^{-1}\); flow velocity \( v = 10^{-7} \) cm s\(^{-1}\); system length 3 cm; \( \phi = 0.1 \); \( X_M = \rho M = 2.10 \times 10^{-6} \) M; \( Y_M = 0 \); \( k_A = 5.0 \times 10^{-4} \) cm \(^{-1}\) M\(^{-1}\) s\(^{-1}\); \( K_A = 100 \); \( K_B = 10^{-12} \) M\(^2\). The figure shows \( B \) deposition profiles at \( t = 4.5 \times 10^{12} \) s for values of the rate coefficient \( k_B \) as follows: (a) \( 3.25 \times 10^{-4} \) cm \(^{-2}\) M\(^{-2}\) s\(^{-1}\); (b) \( 1.30 \times 10^{-3} \) cm \(^{-2}\) s\(^{-1}\); (c) \( 1.40 \times 10^{-3} \) cm \(^{-2}\) s\(^{-1}\); (d) \( 2.60 \times 10^{-3} \) cm \(^{-2}\) s\(^{-1}\); (e) \( 6.50 \times 10^{-3} \) cm \(^{-2}\) s\(^{-1}\). Note the transition from unstable pulse (a) to wiggle structure (b–c) to discrete banding (d–e) as \( k_B \) increases.

Fig. 6. \( B \) deposition profiles at \( t = 7.5 \times 10^{12} \) s. (a) \( k_B = 6.50 \times 10^{-3} \) cm \(^{-2}\) s\(^{-1}\); (b) \( 3.25 \times 10^{-2} \) cm \(^{-2}\) s\(^{-1}\). (All other parameters are the same as in Fig. 5.) Alternating precipitate and precipitate-free zones are observed.
and as a result all the precipitate-free zones are well developed.

Fig. 7 shows the time evolution of a "wiggle structure". At an early stage, we see that as time advances, the bump which lags farthest behind the \( A \) front loses structure and is dissolved out while the one close to the front grows and gains structure (frames (c)–(e)). At later times the wiggle has less intense extrema and maintains an irregular structure.

Note that the shape of the pulse obtained from the numerical analysis at low \( \Lambda \) values suggests that the steady pulse obtained analytically is unstable. Fig. 8 shows the different
domains in the $A - X_M$ plane where unsteady pulse, wiggle structure or discrete banding solutions are obtained. Note that at lower inlet concentrations $X_M$, the transition to banding takes place at smaller values of the parameter $A$. This suggests that the pulse is more stable for larger $X_M$ and perhaps accounts for the fact that $\alpha_n$ is in better agreement with the analytical value as $X_M$ increases (Table 1).

The phase diagram in Fig. 8 reveals the richness in structure of the Liesegang banding problem. Finally, it should be noted that the numerical simulations were carried out for a case where the $A$ dissolution front has a finite width, while in the analytical study, the $A$ profile experiences a discontinuity, because $k_A \to \infty$.

VI. FURTHER DEVELOPMENTS

Having demonstrated that the above nucleation model sustains a number of interesting patterning phenomena, it is worthwhile to consider further possible developments. Natural directions that suggest themselves include a linear stability analysis of the steady planar deposition $B$ pulse to the formation of undulatory phenomena and for the possibility of morphological instability (Ortoleva et al., 1987b) that would indicate the onset of complex two- and three-dimensional structures such as spot patterns.

For the periodic phenomena it would be interesting to investigate the possibility of a Hopf bifurcation (Marsden and McCracken, 1976; Nicolis and Prigogine, 1977). The periodic states would emerge as solutions of the problem (III.1–6). For these phenomena there is an average advancement speed $U$ such that in one period $T$ the pattern would repeat itself and advance a distance $UT$. Thus the $B$ deposit layer thickness, $\tau(r, t)$ would have the periodicity property:

$$\tau(r + UT, t + T) = \tau(r, t)$$  \hspace{1cm} (VI.1)

This appears as a “shutter” of a single continuous deposition band, with a single maximum or as the periodic development of a single continuous band with multiple maxima such that new maxima appear at the leading edge and dissolve out at the tail. Alternatively discrete new bands may appear and disappear at the leading and tailing ends of the deposition zone, respectively. These various possibilities all seem likely in different domains of parameter space. Thus further analytical and numerical work on this problem seems promising.
One simplifying feature of porous-medium, flow-driven Liesegang phenomena is the existence of a steady solution of the problem that serves as a reference state for further analysis. This is in contrast to the purely diffusive problem where the dynamics is continuously slowing down and the band spacing and shape is continuously changing. Note that band regularization can also occur in Liesegang systems subject to an electric field even though both coprecipitate reactants are mobile (Feeney, 1985).

REFERENCES


Hedges, E.S. and Myers, J.E., 1926. The Problem of Physico-Chemical Periodicity. Longmans-Green, New York, N.Y.


