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Nichtgleichgewichtsprozesse und dissipative Strukturen in den Geowissenschaften
Non-Equilibrium Processes and Dissipative Structures in Geoscience

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I. Introduction

Self-organization is a family of processes and phenomena whereby a far-from-equilibrium system, through its own dynamics, adopts repetitive spatial structures in its evolution.\(^1\)\(^2\) The parallel low-oxide cement bands that cut across the bedding of some sandstones (Figure 1D), and the ripples that form in wind-blown sand, are both good examples of self-organization, geochemical and hydrodynamic respectively. No outside or preexisting factors determine the repetitive arrangement of iron atoms or sand grains; the repetitive pattern is constructed through the internal dynamics of each local system.

Necessary conditions for self-organization are disequilibrium and feedbacks.\(^3\) Both are so common in all geological environments that it is not surprising that many examples of inorganic, geochemical self-patterning have been identified so far in rocks of all types — weathering-made, sedimentary, metamorphic and igneous. These patterns consist of repetitive spatial variations in texture, mineralogy, and/or chemical composition on scales ranging from microscopic zoning (\(\text{mm}\)) to sets of sink boles in carbonates (hundreds of meters). Not all observed repetitive patterns, such as varved lake sediments, are self-organizational. Covar-

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\(^5\) E. Merino, Textures of low-temperature self-organization, in: R. Rodriguez-Clemente / Y. Tardy (Eds.), Geochemistry of the Earth’s Surface, Consejo Superior Investigaciones Científicas (Spain) and Centre Natl. Recherche Scientifique (France), Madrid 1987, p. 597 – 610.
self, oscillatory zoning in crystals was first thought to be produced by system-wide changes in physico-chemical conditions or composition but is now held to be self-organizational (see article by L’Héruex and Fowler in this volume).

Identifying a repetitive mineral or textural pattern in rocks as truly self-organizational is not easy or obvious, because information about initial and boundary conditions may have been erased or is hidden from view. Petrographic description may be imperfect or incomplete, and controlled laboratory experimentation may be out of the question. The identification of an occurrence in rocks as self-organizational should rest on a combination of field, petrographic, chemical, and isotopic observations making it clear that the pattern of interest is not inherited. In each case, the task should be to use geological evidence to select the probable mechanisms involved, to imagine which feedbacks could have operated between them, to model this interaction mathematically, and critically to compare model predictions to evidence (as much of it as possible), especially evidence not used in constructing the model in the first place. Because different feedbacks may produce superficially similar spatial predictions, the geochemical modeler should try to test model predictions rigorously enough. We devote below considerable space to self-organization in agates and to our previous model of it to show an example of stringent model testing.

Aside from the case of agate crystallization, we briefly discuss self-organization occurrences probably produced by oscillatory crystallization of minerals at a moving reaction front and occurrences where the self organization probably took place pervasively and simultaneously throughout the system. Among the first group we discuss banded fibrous textures in agates (Figure 2), mineral layering in igneous rocks (Figure 1D), oscillatory concentric zoning in crystals of many minerals, dissolution fingering and sets of sink holes in karst regions, and globular and pisolithic textures in laterites (Figure G). Among occurrences whose self-organization is pervasive in space we discuss below the formation of stylolites in carbonate rocks (Figure 1A-C), and repetitive layering in metamorphic rocks due

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Fig. 1: A. View of the “Pancake” Rocks at Panukaiki, western South Island, New Zealand. The rock “pancakes” are defined not by bedding planes but by regularly spaced stylolites. The spacing visible in this photograph is a few tens of centimeters. Between the major stylolites minor stunted ones can be seen in the field but not in this photograph. See text. – B. Stylolites (running up and down in a black limestone table top at the Indiana Memorial Union, Indiana University, crossed by white calcite veins (running right and left). When the calcium carbonate released by pressure solution at the stylolites no longer had available porosity to precipitate in, then it crystallized as veins (white) that wedged themselves in the rock and, by the force of crystallization, deformed it and expanded it in the up-down direction (see FN 127, 130). The length of the photograph is 30 cm. – C. A jog (at the arrow) joining the ends of separate stylolites in Paleozoic carbonate steps of the Indianapolis Symphony Orchestra. The spacing between two nearby stylolites is about 5 cm. This and the other jogs are micro-transform faults that allow the slow pressure-solution creep of rock toward each stylolite, on both sides. See text. – D. Repetitive iron-oxide cement bands in several sandstone plates lining the walls of the Malpensa International Airport, Milan (see FN 130). The height of the photograph is about 60 cm. The cement bands can be occasionally seen cutting across bedding. See Introduction. – E. Orbicules in a granite boulder found in a stream near Karuizawa on the west coast of South Island, New Zealand. Auckland Museum. The size of orbicules is about 15 cm across. See text. – F. Cores of goethite needles in an amethyst crystal pointing into the center of a Brazilian agate. The goethite needles coprecipitated with the quartz only toward the end of the crystallization, indicating the increase in ferric iron concentration through about by closed-system crystallization and by progressive oxidation of ferrous iron by water. The length of the photograph is about 1.5 cm. The progressive increase in ferric iron concentration also produced the increasingly dark purple color of the amethyst crystals (whose bases are colorless). See text. G. Calcium carbonate pisoliths in a calcite from Almeria, Spain. Some pisoliths (not in this photograph) include smaller ones. The pisoliths, up to 10 cm in diameter, are concentrically banded. Many of them include unrelieved remnants of the original rock that was replaced by the calcite. – H. This beautiful Aboriginal painting (almost 2 meters wide; in red and white) could be regarded – except for the scale – as an idealized proxy for a pisolitic texture developed in weathering (like the one in frame G). Reproduced with permission from the Publisher from a color photograph of Anuqurri Tjampitjinpa’s Ceremonial ground at Kulturra [Australia], 1981, published by Wally Casazza on p. 116 of “Aboriginal Art,” Thames and Hudson, 1993.
to stress-mediated chemical processes\textsuperscript{12, 13, 14}. We also cite below the interesting phenomena involving the local stress generated by crystal growth in rocks – phenomena involving new feedbacks. For each case discussed we give pertinent field petrographic, and analytical observations, and specify which feedback we hypothesize.

We first give a general modeling approach.

\section{Modeling Approaches}

\subsection{Positive Feedbacks}

Self-organization requires a chemical system both to be far from equilibrium and to have a positive feedback among the processes involved. A positive feedback consists of two or more processes in a system that can enhance each other\textsuperscript{15}. In practice, identification of a plausible self-organization mechanism usually boils down to finding a positive feedback consistent with the geological context for the rock in question. Generally, a positive feedback in a geochemical system can be formed among chemical reactions, transport processes, and stress.

\subsection{Modeling a Moving Reaction Front}

For a rigorous test of the plausibility of a particular hypothetical feedback, a mathematical model is required. For the first group of self-organization phenomena, mineral precipitation or dissolution happens only within a narrow region called a reaction front, \( F(x,y,z,t) = 0 \). The front sweeps across the system leaving precipitated solid phases on one side \((F < 0)\) and a reacting fluid on the other \((F > 0)\). Assume that \( p \) minerals crystallize from \( q \) chemical species \( A_i \) \((i = 1, 2, \ldots, q)\) at the reaction front:

\begin{equation}
\sum_{i=1}^{q} n_i A_i + n_R B = \text{Mineral} \quad i = 1, 2, \ldots, p
\end{equation}

where \( n_i \) and \( n_R \) are the stoichiometric coefficients. \$ \text{in the above equation represents a "solvent" species, e.g., H}_2\text{O in an aqueous solution or SiO}_2 \text{ in a silicate}\text{.}$

\textsuperscript{15} P. Ortlof\textsc{en} et al. (IN 3).
pelt. “Solvent” species B plays a dual role in mass transfer: it is the supporting medium through which other species diffuse, and it can transport those other species by advection
10. The mass transfer and chemical reactions at a moving reaction front can be described by:

\[ \frac{\partial C}{\partial t} = D \nabla^2 C \]

at \( t = 0 \):

\[ N^T R = D (\nabla C \cdot n) + \frac{C}{c_B} (M R) \]

where \( C = [c_1, c_2, \ldots, c_n] \) and \( c_j \) is the concentration of species \( j \); \( D \) is diagonal \([D_1, D_1, \ldots, D_n] \) and \( D_j \) is the diffusivity of species \( j \); \( R = [r_1, r_2, \ldots, r_n] \) and \( r_j \) is the rate of reaction \( j \) in moles per unit of area per unit of time; \( n \) is the unit vector normal to the front pointing out to the fluid region; \( N = [n_{x}, n_{y}, n_{z}] \); and \( c_B \) is the concentration of “solvent” species B and can be treated as a constant in the worst cases of interest.

The last term describes the segregation effect of a moving reaction front, i.e., the effect of species \( j \) “piggyback” on “solvent” B. In aqueous geochemical systems, except for those involving water freezing, the consumption of water by mineral crystallization is usually very small, if not zero, and the relative motion of bulk water to the crystallization front is thus negligible; as a result, the last term in Equation (3) vanishes, as shown for calcite growth from an aqueous solution
11. In contrast, for magma crystallization, since \( \text{SiO}_2 \) both accounts for a major part of total melt volume and is a major component taken up by mineral crystallization, the advection of bulk melt toward the crystallization front has a significant contribution to mass balance at the front, and consequently the last term in Equation (3) cannot be ignored, as demonstrated for igneous layering and orbicular formation
12.

The normal advancement velocity of the front (\( V_f \)) is determined by:

\[ V_f = v R \]

where \( v = [v_1, v_2, \ldots, v_n] \) and \( v_i \) is the molar volume of mineral \( i \). The evolution of a reaction front is described by the following kinematic equation
13:

\[ \frac{\partial C}{\partial t} + V_f (\nabla C) = 0 \]

10. Wang/Merino (FN 9).
11. Wang/Merino (FN 8).
13. Ohtake et al. (FN 6); Wang/Merino (FN 10).
The morphological instability of a reaction front can be induced if:

\[
\frac{\partial}{\partial n} (v^T \mathbf{R}) \bigg|_{r=0} > 0
\]

As shown below, a moving reaction front can display rich self-organization behaviors in geochemical systems.

3. Boundary Layer

As a reaction front advances, a boundary layer can be created, the chemistry of which could significantly deviate from that of the bulk fluid far away from the front. Let’s consider a planar reaction front with a boundary layer of thickness \( L \). Integrating Equation (2) over the boundary layer and using linear approximations for \( \mathbf{C}^0 \), we obtain:

\[
\frac{d\mathbf{C}^0}{dt} = \frac{2D}{L^2} (\mathbf{C}^e - \mathbf{C}^0) + \frac{2}{L} \left( \mathbf{M}^0 \mathbf{R}^e \mathbf{C}^0 \right) - \frac{2}{L} \left( \mathbf{N}^0 \mathbf{R}^0 \mathbf{C}^0 \right)
\]

Here superscripts \( ^{d,0} \) and \( ^{b,0} \) indicate the variables evaluated outside the boundary and at the reaction front, respectively, and the former are usually set to be constant; overbars “\( ^d \)” indicate that all variables in Equations (7) are referred to a planar reaction front. The conversion of partial differential equations (2, 3) to the ordinary differential equation (7) greatly simplifies the effort on modeling oscillatory crystallization at a moving reaction front.

4. Modeling Stress-Mediated Mineral Precipitation and Dissolution

For self-organization phenomena taking place pervasively throughout the whole spatial domain of interest, mass transfers and chemical reactions can be modeled by a set of mass continuity equations:\(^{21}\)

\[
\frac{\partial (\rho \mathbf{C})}{\partial t} = \nabla \cdot [\mathbf{D}(\rho) \nabla \mathbf{C}] + \mathbf{N}^T \mathbf{R}
\]

\[
\frac{\partial \mathbf{Q}}{\partial t} = \mathbf{R}
\]

\[
\phi + \mathbf{v}^T \mathbf{Q} = 1
\]

\(^{21}\) Wang/Merino (FN 8).

\(^{21}\) Nicolis (FN 1).
where \( Q = \{Q_1, Q_2, \ldots, Q_n\} \) and \( Q \) is the concentration of mineral \( i \) (mole per unit volume); \( \phi \) is the porosity of rock. Here the diffusivity \( D \) depends on rock porosity and tortuosity, and \( R \) is generally a nonlinear function of not only aqueous-solution chemistry (C) but also rock textures (e.g. \( \phi, Q \)) and the local stress (\( \sigma \)) to which individual mineral grains are subjected.

Stress usually increases both the solubility and the dissolution rate of a mineral grain in aqueous solution. This is called pressure solution. The increase in solubility comes from the increased strain of the atomic bonds of the mineral grain (reflected in a change in the mineral’s internal energy, thus in its equilibrium constant), so that, to the extent the grain (or a volume element) is rigid, the pressure solution does not happen only at the point where the stress is applied but nearby as well. Based on Kamb’s theory, the coupling of chemical reaction with stress can be described by:

\[
\frac{K_i(\sigma)}{K_0(\sigma)} = \left(\frac{K_i(\sigma)}{K_0(\sigma)}\right) \exp \left(\frac{-E_i}{RT}\right)
\]

where \( K_i \) is the equilibrium constant of reaction \( i \); \( k_i \) and \( t_i \) are constants; and \( \sigma \) is the stress to which mineral \( i \) is subjected. The reaction rate \( r_i \) can then be calculated by a simplified kinetic expression \( r_i = k_i[1 - \Omega_i/K_i(\sigma)] \), where \( \Omega_i \) is the ion-activity product for mineral \( i \) and \( k_i \) is the reaction rate constant.

To model stress-mediated mineral reactions requires appropriately partitioning a macroscopic stress to which the bulk rock is subjected into microscopic stressors to which individual mineral grains are subjected. This partitioning is generally difficult, because it depends on the detailed description of rock textures. Several partitioning feedbacks have been suggested:

\[
\frac{d\phi}{dt} \approx H \phi \sigma^\beta
\]

5. Linear Stability Analysis

Linear stability analysis is a useful tool for studying the behavior of a dynamic system around its steady state(s) and thus helps to construct a phase diagram that delineates the different behaviors of the system in a model parameter space. To illustrate this, let’s take Equation (7) as an example. Let’s first linearize the equation around its steady state by introducing a small perturbation \( \delta C^0 \):

\[
\frac{d\delta C^0}{dt} = H \kappa \phi \sigma^\beta
\]


\[ H = \frac{\partial}{\partial t} \left( \frac{2}{\epsilon} \right) + \frac{\partial}{\partial x} \left( \frac{\partial}{\partial y} \right) + \frac{\partial}{\partial y} \left( \frac{\partial}{\partial x} \right) + \frac{\partial}{\partial z} \left( \frac{\partial}{\partial z} \right) \]

where \( \frac{\partial}{\partial t} \) is the time derivative, \( \frac{\partial}{\partial x} \) is the spatial derivative, and \( H \) is evaluated using the steady state concentrations. We then assume that the perturbation has the form:

\[ \delta C = \rho C_{0} \]

where \( \delta C \) is the initial perturbation amplitude; \( \zeta \) is the growth rate of the perturbation. Solving Equation (12), we obtain:

\[ \rho C_{0} \]

That is, \( \zeta \) takes the eigenvalues of \( H \). If one or more eigenvalues of \( H \) are positive, the perturbation \( \rho C_{0} \) grows with time; the system becomes unstable at the steady state; and Equation (7) may then have oscillatory solutions.

In many cases, we may be interested in whether spatial fluctuations in a system would grow or not. The linear stability analysis summarized above is still applicable. But the growth rate \( \rho \) is then expressed as a function of the wavelength of the perturbations. The preferred wavelength the system selects is the one corresponding to the maximum growth rate.\(^4\)

III. Self-Organization in Agates

By "agates," we refer only to the rounded quartz bodies, up to several decimeters across, occasionally found in many basaltic on all continents. We exclude occurrences/objects such as chert nodules common in many sedimentary rocks. We believe that genetically lumping agates together with sedimentary chert nodules (whether replacement, or "push-agate") just because the two occurrences are subspherical and quartz-rich, or with igneous orbicules or weathering pods that (see Figs 1E-G) just because these two are, like agates, also concentrically layered and subspherical, is a temptation that should be avoided. Although all these spherical nodules involve in situ crystallization and one or another kind of ion transport, and although these are obvious similarities among them, it is also true that they exhibit a host of differences - textural, mineralogical, chemical, isotopic, and matrix-related - that make each of those occurrence types geologically unique, and that warrant modeling them independently.

\(^4\) Wang/Morino (PN 10).
We summarize here our self-organizational model, together with evidence confirming many predictions of the model. The associated repetitive textures that warrant considering agates a case of self-organization were described by Merino and Wang and Merino, and are summarized below too.

1. Origin of Agates in Basalts

The general problem of the genesis of agates appeared to be solved long ago by the idea that agates are infillings of vesicles in basalt. Through repetition, this hypothesis has become unquestioned truth. The infilling of cavities implies open-system, large-scale, post-basalt hydrothermal or burial alteration. Four arguments against this traditional alteration hypothesis are:

1. Some agates occur in texturally, mineralogically, and isotopically fresh basalt.
2. No direct field or petrographic evidence exists (to our knowledge) of the silica conduit(s) or the transport that the traditional hydrothermal-alteration view requires.
3. It is difficult for the hydrothermal-alteration hypothesis of agate origin to account for the occurrence in agate quartz of the magmatic trace element, nickel, which we have detected in a Brazilian agate, along with Al, Fe, Mn, Na, and K.
4. In a large quarry at Rio Jucu, Rio Grande do Sul, Brazil, all agates occur near the bottom of a 14-meter thick basalt flow of the Paranhó Basalt, and did not grow in vesicles, all of which occur near the flow top, and are all still empty.

Our new theory, summarized below, for the genesis of the striking self-organizational textures often found in agates did not start from the traditional vesicle-filling idea. It consists of a quantitative growth-transport model that incorporates two physico-chemical instabilities and that correctly predicts several associated self-organizational textures and compositional features typical of some agates — as well as the lack of such textures in other agates. The theory, together with excellent evidence...

26 FN 4.
27 FN 5.
29 Merino/Wang/Deloule (FN 25).
ence for it, has been published in three papers\(^{31}\) and three progress summaries.\(^ {32,33,34}\) More evidence, especially isotopic, is forthcoming.

A crucial result obtained from the quantitative texture model summarized below is that, for the differential equations representing agate growth to be able to oscillate (and thus correctly predict the self-organizational textures typical of agates), the growth must take place not from aqueous solutions but from lumps of very silica-rich media—such as silica gels. This model-derived requirement of course poses a new problem—how to form and emplace such lumps of gel in a basalt. For this new problem we have proposed a novel reaction and scenario\(^ {35}\) (see below).


The new theory started with the realization\(^ {36}\) that many agates display several associated repetitive quartz textures (layers of alternating fiber size, alternating degree of fiber-twisting, and alternating trace element content—see Figure 2 and below) that could not be produced by chance, even in one agate, let alone in many, through the traditional theory of successive, presumably unrelated precipitation of quartz in voids during hydrothermal alteration of basalt. Merino\(^ {37}\) concluded that agate growth must result from some kind of geochemical self-organization.

In their 3-part theoretical-analytical study, Wang and Merino\(^ {38}\) proposed a crystal growth-transport theory that beautifully accounts for the self-organizational quartz textures in agates. The quantitative model works through two hypothesized feedbacks—a “self-catalytic” feedback, which produces the repeatedly alternating layers typical of agate; and a morphological instability of the crystallization front\(^ {39}\), which produces the characteristic fibrous texture of agate quartz (Figure 3).

\(^{31}\) Wang/Meirino (FN 7, FN 10); Meirino/Wang/Delaloye (FC 25).

\(^{32}\) Meirino/Wang/Delaloye (FC 30).


\(^{36}\) Merino (FN 4).

\(^{37}\) FN 4.

\(^{38}\) Wang/Meirino (FN 7, FN 10); Merino/Wang/Delaloye (FC 25).

\(^{39}\) Wang/Meirino (FN 10).
Reading Formation: The supposed "self-catalytic" reaction is:

$$\text{Hydrous silica w/trace Elements} \rightarrow \text{quartz + cations + H}_2\text{O}$$

where the cations (or one of them) released by each increment of quartz that crystallizes further accelerate the growth of the next increment of quartz. Quartz growth rate increases fast until silica diffusion becomes unable to keep up with it, at which point the growth greatly slows down, until it "catches" again following the recovery of the silica concentration at the front. Each cycle of growth acceleration and slowing-down is predicted to produce a couplet of bands, one made of thick, untwisted fibers, the other of very-thin, twisted fibers — exactly as observed.

From Equation (7) and with a choice of appropriate scaling factors, an oscillatory agate crystallization front can be described by the following set of equations:

$$\frac{d\theta}{dt} = 1 - \theta^2 - \alpha(1 + \beta_1 \theta^2 + \beta_2 \theta^4)\theta$$  \hspace{1cm} (17)

$$\frac{d\theta}{dr} = -\theta - \lambda \alpha(1 + \beta_1 \theta^2 + \beta_2 \theta^4)\theta$$

with

$$\frac{\theta - D_1}{D_2} = \frac{D_2 c_i}{D_1 c_i} \eta$$  \hspace{1cm} (18)

where $c_i$ and $c_e$ are the concentrations of silica and cations (or "catalysts"), respectively; $\alpha$ and $\lambda$ are the scaled $c_i$ and $c_e$, respectively; $\beta_1$ and $\beta_2$ are adjustable constants; $\tau$ is the scaled time; $\eta$ is moles of cations carried by one mole of silica species. In Equations (17), the agate crystallization rate is assumed to be a linear function of silica concentration and a quadratic function of cation concentration, which can be viewed as a truncated Taylor's series of an unknown function describing the catalytic effect of cations on quartz growth.

A linear stability analysis of Equations (17) shows the different behaviors of the system around different steady states and provides fields of parameter values for the equations to have one or another behavior, labeled in Figure 4. For example, for an agate with many repeated chalcedony bands to be represented by the equations, the system would have to be in the field of oscillatory solutions with coagulant amplitude, which requires a ratio of silica to cation diffusivities $\theta = D_1/D_2 > 0.2$, i.e., the silica species must have very low diffusivity. This internal requirement of the model suggests therefore that the initial medium from which an agate with many repeated bands grows should be dense and polymerized (so as to have very low diffusivity), a requirement consistent with experiments that produced chalced-
Fig. 2: A – B
Fig. 3: Schematic diagram showing agate fibrous textures arising from morphological instability of crystallization front. Each quartz fiber grows by addition of conical sleeves. As each sleeve pierces through a decreasing trace-element concentration profile, its rim is forced to take up a higher trace-element content than its tip, thus creating an Al\(^{3+}\) gradient across fiber’s radii, which makes each fiber grow twisted because Al-O bonds are longer than Si-O bonds.

Fig. 2: A. Photomicrograph of a portion of a Devonian agate from Scotland displaying a typical repetitive fibrous texture. The fibers that make up the ribbons are coarser than those making up the broad layers between the ribbons, and have constant birefringence along their length, indicating they are not twisted. In contrast, fibers making up the broad layers between the ribbons have continuously variable birefringence along their length, indicating they are twisted, and form a well-developed chevron interference pattern. The thickness of finer fiber layers is about 0.3 mm. B. Same agate showing the transition of a layer of fine, twisted fibers to a layer of coarse, untwisted fibers, and finally to a layer of non-fibrous crystals. The thickness of untwisted fiber layers is about 0.2 mm. In some agates, layers of fibrous crystals alternate with layers of non-fibrous (microcrystalline) crystals (FN 10).
any aggregates from silica gels\textsuperscript{41,42}. Two sets of oscillatory solutions of Equations (17) are shown in Figure 5.

Fig. 4: Behavior diagram for agate banding in model parameter space (PN 10, with parameter values $\alpha = 0.01$, $\beta = 50$, $\gamma = 80$). Agates with more than several consecutive bands fall in the field of “oscillations with constant amplitude,” a behavior that requires a ratio of silica diffusivity to cation diffusivity $\ll 0.2$. Such low relative silica diffusivity implies, the silica must be polymerized. Thus, it is likely that the quantitative model that leads to the idea that agates, in order to be layered, must grow from polymerized silica gels.

Interestingly, Eqs (17) may apply also in the case of calcite’s oscillatory incorporation of trace elements\textsuperscript{43–45}. Bryant and Sheplev\textsuperscript{44,45} have studied Eqs (17) by Lyapunov coefficients and have better defined fields of behavior of their solutions. Hoitun and others\textsuperscript{46} have studied the effect of noise in boundary conditions on self-organizational behavior in Equation (17).

\textsuperscript{43} Brint/Merino (PN 8).
Fig. 5: Model predictions of agate oscillatory crystallization (FN 10). The model simulations predict (A) layers of fine and twisted fibers alternating with layers of coarse and non-twisted fibers, and (B) layers of fine twisted fibers with layers of non-fibrous microcrystalline. Note that fine fiber layers correspond to high CaSi concentrations at the crystallization front. By the mass action law, the fine fiber layers are predicted to have higher trace element contents than the coarse fiber layers, as confirmed by microanalyses (FN 25). L - the thickness of agate crystallization boundary layer, T - twisted, NT - non-twisted, MC - microcrystalline.
Genesis of Fibrous Texture. Many agates consist of layers of finely fibrous length-fast quartz. Why is the quartz fibrous? Why are the fibers related crystallographically (as shown by their common orientation and interference patterns under crossed polars)? Wang and Merino\textsuperscript{47} attributed the fibrous texture to a new mechanism—morphologically unstable crystallization fronts—of which they established a quantitative model. The predictions of this fibrosity model are so well confirmed by observations that the theory is probably general and applies to the genesis of other fibrous textures of other minerals in rocks of all types.

By introducing a morphological perturbation to a planar front at $s = 0$ (Figure 3),

$$\Delta s = \delta S \cos(n \eta)$$

Wang and Merino\textsuperscript{48} obtained the following dispersion equation giving the perturbation growth rate ($\zeta$), or fibrosity growth rate, as a function of the wave number of the perturbation ($m$), which is the reciprocal of the fiber spacing:

$$\zeta = \frac{d\Delta \zeta}{d\xi} = \frac{\alpha_0 R}{n (1 - \alpha_0^2) \gamma} \frac{\partial \gamma}{\partial \xi} = \frac{\alpha_0 R}{n (1 - \alpha_0^2) \gamma} \frac{d\gamma}{d\xi}$$

A plot of $\zeta$ versus $m$ is shown in Figure 6. For an unstable crystallization front, there is a preferred wave number ($m_0$) corresponding to which $\zeta$ achieves its maximum value. Of all the possible perturbation wave-lengths, the one with wave number $m_0$ is expected to establish itself the fastest. Thus, the fiber spacing adopted by the system should be $2\pi \xi_0 / m_0$.

It is shown that all derivatives in Equation (20) can be expressed in terms of scaled silica and cation concentrations ($\delta^s$, $\delta^c$)\textsuperscript{51}. As $\delta^s$ and $\delta^c$ oscillate, the fiber size may also oscillate (Figure 5). In some cases, the oscillations of $\delta^s$ and $\delta^c$ can even repeatedly bring the crystallization front into or out of morphological instability, and as a result the alternation of layers with fibers with non-fibrous layers is predicted, as observed in some agates (Figure 2B). Furthermore, the model simulation shows that high cation concentration correspond to the layers with thinner fibers (Figure 5). It thus follows that the finer fibers should contain high trace-element contents; the prediction has been confirmed by cathodoluminescence\textsuperscript{50} and micromorphology\textsuperscript{51}.

Twisting of Fibers. Not only are agates routinely layered and fibrous. In many agates the fibers turn out to be as twisted as corkscrews (around the directions

\textsuperscript{47} Wang/ Merino (FN 10).
\textsuperscript{48} Wang/ Merino (FN 7).
\textsuperscript{50} Merino/ Wang/ Delours (FN 25).
fibrous ystallos-
s under a new key ex-
so well i to the

Fig. 6: Growth rate of morphological perturbations of the crystallization front versus their wave number \( m \), from Equation (20) using labeled parameter values. For the parameters chosen, \( \gamma \) is positive (which means the front is morphologically unstable thus becoming fibrous) and maximizes at \( m = m_p \). The fiber spacing "preferred" and adopted by the system is \( 2\pi L/m_p \), where \( L \) is the thickness of the boundary layer.

The front is max-

Fig. 2: (111) or (100), but only in every other layer. How does this happen? We attributed the twisting of fibers to differential solid solution of \( \text{Al}^{\text{II}} \) or \( \text{Fe}^{\text{III}} \) between the center and the periphery of each fiber, a difference imposed at the moment of fiber growth (Figure 3). With this hypothesis, fiber twisting becomes a natural outcome of the morphological instability of a cation-catalyzed crystallization front. As shown in Figure 3, at a morphologically unstable crystallization front, small random bumps on the front grow longer and generate other bumps next to them. Each bump becomes a fiber. Competition for silica among neighboring fibers and surface tension determine their thickness and spacing. Each fiber grows by accretion of conical sleeves. As each sleeve pierces through a decreasing trace-element profile (generated by the autocatalytic growth reaction), its base is forced to incorporate (in substitution for Si) a higher trace-element content than its apex, and the ensemble of successive such sleeves yields a fiber with higher trace-element content along its periphery than along its center. Since Al (or Fe or any other substituting cation) is larger than Si; the lattice dilatation caused by the substitution is greater in the outer unit cells of a fiber than in those along its axis, and as a result the fiber has no geometric freedom but to grow twisted to make room for the high-

(1) Merino/Wang/Dehade (FN 25).
(2) Merino/Wang/Dehade (FN 25).
(3) Merino/Wang/Dehade (FN 25).
Annealing of Twisted Fibers. After growing twisted in the manner described, fibers are predicted to undergo annealing. This annealing is what must have produced the high defect density detected in agate by Henney and Cady et al. Since the twisted-fiber layers alternate, so should the high defect density—and indeed Gröz et al. and Xu et al. have reported alternating defect density in a few agates. The annealing converts each fiber into an aggregate of distinct submicroscopic scale subcrystals, but the fiber outline is still preserved and its optical-scale birefringence still reveals both the fibrous morphology and the twinning, as clearly shown by Lu and Sunagawa. In the layers with the highest fiber twinning, the annealing could be expected to produce the highest twinning/dislocation density possible, and thus to form "wogonite," which is simply highly-twinned quartz with twin planes one unit cell apart.

The idea that the fibrous texture or the fiber twist of agate quartz might be produced by screw dislocations does not withstand quantitative analysis carried out by Wang and Merino even for single fibers, let alone for the fibrous textures typical of agate quartz, and even though it is true that a screw dislocation can "pull" a single growing crystal into a fiber or whisker, and cause it to twist as well. To produce a fibrous texture through screw dislocations, a full-proof mechanism would be needed in order to always generate thousands of screw dislocations in the first place, one screw for each fiber, in each agate. No such mechanism exists, and no screw dislocations have been actually detected in agate fibers anyway, to our knowledge.

Original Silica Medium. Again, one fundamental requirement of the quantitative growth-transport model is that agate growth, in order for the model's differential...
equations to oscillate (and thus be able to model the self-organizational repetitve textures and trace element compositions) must take place from a medium (a) having very low silica diffusivity, and (b) from a medium whose kinetic units must be able to bring the catalyst cations to the growth front. That is, the internal qualitative requirements of the kinetic model — for it to successfully model agate self-organization — point to growth not from aqueous solutions but directly from a hydrous-silica gel. This is the conclusion that led us to seek a way of making and emplacing silica-gel lumps in a basalt. (Merino et al. thought of the erroneous possibility that these lumps might be produced by liquid immiscibility in basalt.)

Formation and Emplacement of Gel Lumps in Basalts. Our new hypothesis for the formation of these gel lumps is as follows: If a basalt flow trapped a puddle of water, the trapped water would instantly go supercritical and, in trying to escape from the flow, would instead react with silica polymers in the melt to form lumps of hydrous silica gel. The sudden addition of hydrogen ions to the melt could not but instantly break the —Si-O-Si-O— chains to form many silanol-ended chains. —Si-O-Si—OH. Each silanol H would attach via a long hydrogen bond to an O in another chain, quickly forming a scaffolding of chains just like those that make up any low-temperature silica gel made from a supersaturated aqueous solution. The basalt flow continues moving, with the gel lump in it. As the flow comes to rest and cools down, both flow and gel lump crystallize simultaneously — the flow to basalt rock, the lump of silica gel to an agate with self-organizational textures and with 

Closed-system Agate Crystalization. During the agate’s growth from the hydrous silica gel and especially towards its end, the residual trace-element-rich water is segregated to the agate center. This water is made basic by the redox reaction, Fe$^{3+}$ + H$_2$O = Fe$^{2+}$ + 0.5H$_2$ + OH$^-$, which is inexorably driven to the right by the increasing concentration of both reactant cations and H$_2$O caused by the removal of silica from the gel to build the agate layers. This reaction is crucial. The ferric iron produced accounts for the common formation of late amethyst (which is increasingly darker towards each crystal’s tip — this alone is excellent evidence of closed-system crystallization) and geothite needles (Figure 1F). If the water escapes or flashes out of the agate, it should alter a shell of surrounding

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60 Merino, Wang / Debode (SN 25).
61 Self-organization, Bd. 11
basalt to zeolites (thanks to its high pH) and/or to phyllostites (including nickel-bearing garnierite, which we have detected), and should increase the basalt's δ^{18}O in the shell. These predictions are all evidently borne out by old and new evidence. Preliminary results by E. M. Ripley\textsuperscript{68} show clearly that the isotopic alteration of the basalt around a Deccan Traps agate decays over 2 cm of the basalt around the agate, down to the regular fresh-basalt value of 5.5–6.0‰.

<table>
<thead>
<tr>
<th></th>
<th>δ^{18}O (‰)</th>
<th>distance from agate edge (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>16.0</td>
<td>–1</td>
</tr>
<tr>
<td>Agate Edge</td>
<td>9.4</td>
<td>0</td>
</tr>
<tr>
<td>Basalt: Point 1</td>
<td>9.2</td>
<td>2</td>
</tr>
<tr>
<td>Point 2</td>
<td>6.7</td>
<td>20</td>
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<tr>
<td>Point 3</td>
<td>5.5–6.0</td>
<td>Beyond 25</td>
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In our theory, agate genesis is thus syn-basalt, closed-system, and small-scale—a local phenomenon unrelated to possible late hydrothermal (and/or burial) alteration of the basalt. It contrasts sharply with the traditional view of agate genesis by which agates are post-basalt, open-system infillings of vesicles that are part and parcel of the (supposed) alteration. This is why we do not discuss here other hypotheses of agate genesis such as Lundmesner's\textsuperscript{69}, Heaney's\textsuperscript{70}, and others\textsuperscript{71}, which try to accommodate evidence in the assumed but unproven framework of open-system infilling of vesicles.

Since our theory involves crystallization at a moving reaction front in a closed system, it predicts that the crystallization of agates is fundamentally "directional". Closed system crystallization and directionality are confirmed by independent evidence: increasingly darker purple megaphanite crystals; generally inward-locating δ^{18}O; the systematic switch of length-fast to length-slow quartz in every agate; radial orientation of elongated quartz fibers; and even the production of zeolites just outside some agates (which needs the accumulated final aqueous hostivity generated by the relax reaction of ferric to ferric iron) or the production of green nickel garnierite altering the basalt shell around the agate. Ideas of agate genesis

\textsuperscript{68} E. M. Ripley, Indiana University (2000), unpublished.
Geochemical Self-Organization in Rocks

based on Ostwald ripening (such as Landmesser)\textsuperscript{12} and Ontoleva et al.\textsuperscript{21} – according to which agate textures are acquired after the first crystallization, via size/surface energy competition among early crystals, a competition that takes place all over the system simultaneously – are incompatible with the directionality indicated by the evidence cited. Furthermore, the Ostwald ripening theory necessarily would make the process enormously long, even geologically, which fails to account for the fact that there are very young agates.

1. Model Testing

A good model should have few assumptions and the most predictable ability. With four assumptions (autocatalysis, fibroform arising from morphological instability, solid solution, and accidental trapping of bubbles by a basalt flow), our model produces many predictions – geochemical, mineralogical, textural, morphological, microstructural, compositional, isotopic – all of which are confirmed by quantitative and qualitative observations. Most significant are the observations that had not been known or taken into account in building the model in the first place. The list below summarizes the major predictions: \textsuperscript{14}

1. Agates consist of concentric repeated banding. Layers consisting of twisted, very thin chalcedony fibers should alternate with layers consisting of untwisted, less thin fibers (see photomicrographs in Figure 2).

2. Not all agates should display the self-organizational textures. (This follows from the map of behaviors in phase space deduced from the model, Figure 4.)

3. The layers consisting of fine fibers have higher trace-element contents than the layers consisting of less fine fibers. This is confirmed by electron and ion probe analyses\textsuperscript{15}.

4. Twisted chalcedony fibers should contain higher density of dislocations and twins and untwisted fibers should contain lower dislocation density. Evidence of alternating defect density is reported by Götz et al.\textsuperscript{16} and Xu et al.\textsuperscript{17} The defects and twins are attributed to annealing of twisted fibers after they grow twisted.

5. Oscillatory crystallization requires an agate to form from a dense, very-low-silica diffusivity medium – such as a silica-rich gel lump, Figure 4.\textsuperscript{18}

\textsuperscript{12} FN 69.


\textsuperscript{14} Wang/Merino (FN 7, FN 10); Merino/Wang/Deloule (FN 25); Merino (FN 66).

\textsuperscript{15} Merino/Wang/Deloule (FN 25).

\textsuperscript{16} FN 57.

\textsuperscript{17} FN 58.
6. The relative size of an agate's central void reflects the density difference between the initial silica gel and the final quartz. Agates with relatively large central voids should have few concentric chalcedony bands, and should be vertically elongate too.

7. As crystallization proceeds and silica is consumed, a directional (toward or, rarely, outward) sequence consisting of a) concentric layers of length-fast fibers, b) a layer of length-slow coarse quartz, and c) a central void should form—just as observed.

8. Also as crystallization proceeds, original trace elements in the gel lump become enriched (and, in the case of Fe$^{2+}$ and Ni$^{2+}$, oxidized by water as well) in the late aqueous solution of the central void. Thus, the last quartz to form is a) often darker and darker purple amethyst (this color is produced by ferric iron), and/or b) often contains goethite fibers, FeOOH; see Figure 1E.

9. Similarly, δ$^{18}$O values in the agate quartz should generally decrease inward 79, and the trace elements should oscillate from band to band 80.

10. If forming from polymerized silica species, the fine fibers should grow length-fast, based on Folk and Pitman's reasonable guess that c-parallel chain polymers of SiO$_2$, tetrahedra tend to stick flat on the fiber's tip, at right angles to the direction of fiber growth 81. The switch from length-fast to length-slow quartz happens usually when the residual gel loses sufficient silica and depolymerizes.

11. The fibrous texture is produced by fingering of an unstable reaction front. This mechanism ensures that fibers grow not independently but forming a texture.

12. A basalt shell around each agate may be altered to zeolites and/or nickel-bearing phyllosilicates. This prediction also follows from the intra-agate oxidation of Fe$^{2+}$ and Ni$^{2+}$ by water cited in item 8, which produces Fe$^{3+}$ and Ni$^{3+}$ at high pH; this redox reaction is automatically driven by the crystallization of agate.

13. δ$^{18}$O values in the basalt shell around each agate should generally decrease away from the agate, even in fresh basalt 82.

80 S. M. Savin, Case Western Reserve Univ. (1996), unpublished results.
82 Ripley (PN-68).
4. Geochemical Self-organization in Rocks

Fibrous textures have been found for many authigenic minerals in various geological environments. Besides in agates, fibrous silica crystals commonly occur in sedimentary rocks. Similar fibrous textures have been found for calcites, magnesian clay minerals, pyrite, sphalerite, and galene. It is worthwhile to mention that organic materials are known to form fibrous spherulites. As a matter of fact, our idea about the formation of twisted quartz fibers was inspired by Keith and Padden's work on the twisting of fibricular organic crystals. The theory summarized above for the formation of fibrous textures and fiber twisting in agates is general and applicable to other authigenic minerals. Many authigenic minerals, such as calcite and quartz, can occur in fibrous or in equant-microcrystalline aggregates in rocks. What factors account for the genesis of one or the other texture in those cases? What is the geochemical interpretation of a fibrous texture versus an equant-microcrystalline texture? Equation (20), by directly giving the factors that promote fibromorphism (those to the left of the minus sign in the numerator) and the factors that inhibit fibromorphism (those after the minus sign, logically including the surface energy), has great significance in establishing a fundamental connection between geochemistry, reproduced by concentrations and
concentration gradients, and fibrous "geometry" of a crystalline aggregate\textsuperscript{94,95}. According to our work, a fibrous texture indicates that growth was rapid enough to create a steep enough concentration gradient ahead of the front to overcome the front's surface tension and thus to render it morphologically unstable. Fiber twisting is then a natural outcome of the morphological instability and the differential substitution of trace elements.

IV. Other Cases of Mineral Self-Organisation
at a Moving Reaction Front

1. Igneous Orbicules

Gribicules are subhedral, up to 50\textmu m in diameter and consisting of repeated, light and dark mineral layers, that occasionally occur in plutonic igneous rocks (Figure 1E). We proposed a novel positive feedback that can generate banding, flat or spherical, in igneous rocks\textsuperscript{97}. If some species currently forming minerals are more abundant, relative to Si, in the melt than in the minerals, then the species become necessarily more concentrated in the reaction zone as crystallization proceeds. Depending on the rate law for a particular mineral, that enrichment may cause the mineral's growth rate to increase further, thereby accelerating the advection of silica and again increasing the species concentrations. A transport-reaction model based on this feedback does indeed predict a) oscillatory crystallization, b) its occasional occurrence in igneous rocks, c) its common occurrence in alkaline rocks, d) paired layering, and e) that the oscillatory modes for two minerals are spatially staggered. All these predictions are confirmed by observation, but more confirmation is needed. No details are included here.

Earlier, a model of igneous layering had been proposed based on Ostwald ripening\textsuperscript{98}, one of whose consequences (that increases in the local mode of a mineral should be produced by increases in crystal size, not in the number of crystals of that mineral per unit rock volume) was contradicted by the observations of McBirney and Noyes\textsuperscript{99}, who found that an increase in plagoclase mode exactly corresponded to the smallest plagioclase crystal sizes. Ostwald ripening models

\textsuperscript{94} E. Merino. The geochemistry of habits and textures of authigenic quartz, in: Chemical Geology 84 (1990), p. 233–234.
\textsuperscript{96} Wang/Meckel (EN 9).
\textsuperscript{97} A. E. Boussiba, Pattern formation during crystallization and the formation of fine-scale layering, in: S. Parsons (Ed.), Origins of Igneous Layering, Boston (MA) 1987, p. 453 – 471.
have been hypothesized to apply to several self-organizational occurrence types all lumped genetically together in spite of obvious fundamental differences among them (for example, to concretions, geodes, agates, and orbicules\(^{105}\), but these models have not been well or independently tested. The fact that Ostwald ripening works on a previously formed set of crystals means that it should be easy to find cases where the ripening has not completely obscured the early set of crystals. No petrographic evidence of this has been adduced or sought in support of those models for concretions, geodes, agates, and orbicules, in the light of the diagnostic crystal size distributions described by Eberl et al.\(^{101}\).

2. Oscillatory Zoning of Trace or Major Elements in Single Crystals

This phenomenon has been the object of many modeling studies by L'Heureux and Fowler (see their chapter elsewhere in this volume), Cartwright and Garcia-Ruiz\(^{102}\), Haase et al.\(^{103}\), Wang and Merino\(^{103}\), Bryxina and Sheplev\(^{104}\), Holten et al.\(^{105}\), Hoskin\(^{106}\), and many others. There are also the excellent experimental studies by Reeder, who has produced oscillatory zoned calcite from a fixed aqueous solution in the laboratory, and several studies characterizing natural examples geochemically and analytically -- these latter are referenced by Wang and Merino\(^{107}\).

3. Dissolution Fingering

A planar dissolution front traveling through a porous rock is morphologically unstable, and spontaneously tends to become fingered\(^{108}\). The instability arises because higher infiltration promotes dissolution and dissolution (through local increase in permeability) promotes further infiltration -- at the expense of lower infiltration through a neighbor volume element, where lower infiltration promotes less

\(^{101}\) Lambeuer (FN 68); Orotolava (Chem. Chern (FN 73).


\(^{103}\) Personal communication.


\(^{105}\) FN 8.

\(^{106}\) FN 44, 45.


\(^{109}\) FN 8.

\(^{106}\) Orotolava / Chudam / Merino / Sen (FN 6).
disolution and lesser increase in permeability. A model based on this feedback yielded the dependence of the finger spacing. This was named reactive infiltration, it has great relevance for the problem of petroleum migration, for the genesis of karst sink holes, and for the dynamics of diagenesis of sedimentary basins. The concept was studied further by Steefel and Lasaga, and also has been applied to crystallization in magma chambers.

4. Spatial Self-Organizational Patterns Produced in Weathering

Ascending fresh rock and descending rainwater react the world over to form a weathering profile at the earth's surface. The profile is the reaction front. The dynamic possibilities for self-organization within weathering profiles are endless, (excluding autocatalytic reactions, morphological instability, coupled reaction-transport) and there are in fact at least the following self-organizational features in search of quantitative modeling and understanding: (a) the well-known but little-understood large-scale zones typical of profiles everywhere, each zone being a particular reaction front, (b) the deceiving front fingering discovered by Lwaxina, in bauxite laterites near Maruns; and (c) the systematic genesis of glabules in weathering profiles of all types.

Glabules are authigenic subspherical mineral accumulations up to a few centimeters across, often much smaller. A glabule starts by being a diffused spot in the middle of the saprolite zone and passes higher in the profile to a nodule with an increasingly sharp boundary and increasing sphericity, and, still higher, to a pisolith with concentric banding (Figure 10). Glabules consist of whatever elements and authigenic minerals the profile "keeps": iron oxides in iron-rich laterites and...

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terrestrial crust\(^{117}\), aluminum oxides in basaltic manganese oxides in Mn-rich laterites\(^{118}\), calcite in calcrites. Obviously, the crucial (but unknown) feedbacks that generate glauconites and pisoliths have little to do with the specific chemistry and mineralogy of the system but a lot to do with geometry. Toward the bottom of profiles, authigenic precipitation may be in horizontal bands rather than in spherical glauconites.

**V. Stress-Mediated Self-Organizational Reactions**

There is the large-scale stress applied on a large rock volume – tectonically or by weight of overlying rock – and there is the local stress applied on each rock volume element (containing, say, 100–200 grains). This local stress may be greater than the tectonic stress if grains in the rock of interest have small contact areas with coordinating grains. Pressure dissolution of grains may increase average intergranular porosity – thus lowering average contact area itself – in at least some rock volume elements. The lower average contact area further increases the local stress, which further increases pressure solution. This is the basic feedback invoked by Merino et al.\(^{119}\) in accounting for the instability that leads to stylolitization of rocks – see below, V.1.

But there is also a local stress generated by mineral growth in rocks. Identification and calculation of this growth-driven local stress and its possible consequences at once provide new insights into a number of striking phenomena and rock textures\(^{20}\) heretofore well understood – such as replacemnet, local deformation, microbrecciation, earthquake triggering, and ore-body self-localization\(^{120}\), 121, 122, 123, 124, 125. See below, V.2.

119 Merino/Otchusa/Strickland (FN 13).
120 Merino/Nahon/Wong (FN 112).
122 Nahon/Merino (FN 23).
I. Stylolitization

Many carbonate (and other nonmetallic) sedimentary rocks the world over are stylolitized. Stylolites are large, planar, regularly parallel partings between blocks of rock which exhibit complete mutual column-and-socket interdigita-
tions.170 (Figure 1A,B,C). The stylolites, incidentally viewed by Fletcher and Poll-
ard171 as anticracks, usually occur in sets of several or many parallel ones, and are produced by mutual pressure solution of the two blocks on each side of each sty-
lolite. The planar regions between partings are, not pressure-dissolved, but cemen-
ted. Many sets of stylolites can be seen in cut across bedding, or, if parallel to bed-
ding, can be seen to have developed within beds, not at the bedding planes. In these cases, it is clear that the bedding could not have caused or guided the stylolitization on the other strikingly regular spacing between stylolites (as in the Panahkaii car-
bonates in South Island, New Zealand, see Figure 1A), and that a feedback must have operated to account for the spontaneous sorting-out of the rock into regions of pressure solution interfaced with regions of cementation. Merino et al. thought of the feedback, described in section V, and their quantitative model checked it out, even to the extent of correctly predicting the order of magnitude of the spacing between adjacent stylolites in carbonates and quartzitic rocks.128, Dewers and Orito-
level129, using the same basic feedback, gave a sophisticated quantization of the stress and texture dependence of the free energy, Merino,130 described the competi-
tion between stylolites that come to be too close to each other, a condition that leads to "triage" or "weeding" through stylolitization in the "weed" stylolites become stoned, fossilized, and can be seen in many rocks as small stylolites with smaller "teeth" and less lateral extension than their adjacent "predators." Bat-
ward129 adopted Merino et al.'s self-organizational pressure-solution model, but Raisbuck131, focusing too hard on the semantic question of how regular is "regu-
lar," argued that the model is erroneous because actual stylolites are, according to his statistics of measured spacings, not as regularly spaced as he thought Merino et al. had implied they should be. Raisbuck's objection not only is based on the wrong kind of statistics (it should have consisted of autocorrelation functions but does not) but ignores the physicochemical dynamics of the phenomenon, which by
stylolites become more and more regularly spaced as more intermediate stylolites become weeded out.

Our current (but unpublished) working model for stylolitization involves feedback, "trigging", and transform faulting: (a) pressure solution starts at a myriad point-like sites within a large volume of rock, according to the texture- (or porosity-) mediated feedback described above; (b) these points extend laterally with respect to the main stress, at the same time that they release solute which starts to cement the pores of the region between any two adjacent sites; (c) stylolites that find themselves flooded by solutes coming from adjacent stylolites become "weed out", stunned; (d) lateral extension and inter-stylolite cementation continue; (e) weeding or triage continues too, by jumps leading to an increasing, and an increasingly regular, spacing between the stylolites left active; (f) micro-transform-faulting (of which we have found petrographic evidence, unpublished) takes place to link the end of nearby stylolites that have extended laterally towards each other, producing typical jogs (Fig. 1C) and leading to enormous composite stylolites; (g) throughout all these overlapping or simultaneous steps, a morphological instability perhaps generates the typical column-and-socket morphology of stylolites (and where the instability cannot work, then the pressure solution seams that form are gently wavy, and are not called stylolites)\textsuperscript{133}, and (h) when all the pores between stylolites become cemented, the solutes released by further pressure solution at the stylolites start to precipitate in the form of sets of veins, oriented across the stylolites, that make room for themselves by forcing the whole rock to creep laterally\textsuperscript{134}; these veins can in turn be dissolved by the stylolites at the points of intersection.

2. Growth-Driven Stress in Rocks: Consequences, Models

A large euhedral pyrite crystal in a shale, or a garnet in a schist, occupy space which cannot have been empty to begin with. They occupy space that they have made for themselves by removing the earlier occupier either physically (through creep) or chemically (through replacement). The growth in the rigid, constrained medium necessarily generates a local self-stress, and the stress drives creep or pressure solution. This fact was not clearly recognized until recently — independently by Carmichael\textsuperscript{135} and by Maliva and Siever\textsuperscript{136}. The old concept of force of

\textsuperscript{133} D. Gol/A. Nar/E. Ababnov, Stability analysis of a pressure-solution surface, in: Geo-

\textsuperscript{134} Merino (FN 130); Fletcher/Pollard (FN 127).


crystallization probably refers to this self-stress too, but the very term, "force of crystallization," may have obscured that it is not just any crystallization, but crystallization in a solid medium in which there was no room to grow initially, which produces the self-stress. Dows and Ortinejo \cite{13} and Merino et al. \cite{14} modeled the case where the medium is composed of local stress-pressure differences adjacent grains, producing replacement. Merino \cite{15} predicted that the growth-driven stress varies pressure-dissolve, displace, or fracture the adjacent rock. Nahm and Merino \cite{16} showed how the new stress self-adjusts so as to make the rates of growth of the new mineral and of dissolution of the old mineral automatically equal to each other; this is why replacement is characteristically constant-volume in all sorts of rocks. Minino and Dows \cite{17} have given many references to observations on replacement.

Fletcher and Merino \cite{18} have modeled the dependence among the driving supersaturation, growth and dissolution kinetics, local stress, creep, and even shape of the growing aggregate. In the case of growth of one spherical crystal accommodated by both dissolution and deformation of a viscous-elastic host under isostropic applied stress, the viscosity-dependent grain/grain normal stress and the crystal growth rate become

\begin{align}
\sigma_r(\infty) - \sigma_r(\Delta) &= \frac{K_v \Delta \rho}{K_v V_r + K_V V_r + (\rho/a)}
\end{align}

\begin{align}
\frac{d\Delta}{dt} &= \frac{K_v \Delta \rho}{K_v V_r + K_V V_r + (\rho/a)}
\end{align}

where \(a\) is the radius of the growing spherical grain; \(\sigma_r(\infty)\) is the far-field normal stress; the \(K_v\)'s and \(V_v\)'s are rate constants and specific volumes of minerals A, B; \(\Delta\rho\) is the supersaturation that drives the growth of A; and \(\eta\) is the local rock viscosity. (Transport is assumed sufficiently fast to be ignored.) The case of dissolution-only follows simply by letting \(\eta \to \infty\). The deformation-only case is obtained by letting \(\eta \to 0\) (which is the same as dropping the \(K_v\) terms against \(\rho/a\)). The ratio of the accommodation by deformation so that by pressure solution (see last bracket in Eq. 22) is a new dimensionless number, \(F = (\rho/a) / K_V V_r\). (We here call this the Fletcher number.) The case of growth of many dispersed spheres in a rock matrix has also been studied \cite{19, 20}. The effects of the feedback between non-

\textsuperscript{13} T. Dows, P. Ortinejo, Force of crystallization during the growth of siliceous concretions, in: Geology 18 (1990), p. 204 - 207.
\textsuperscript{14} FN 121.
\textsuperscript{15} FN 123.
\textsuperscript{16} FN 125.
\textsuperscript{17} FN 123, FN 124.
neutronian rheology (hardening or softening) and mineral kinetics could be studied by substituting for the viscosity χ appropriate functions of the strain rate – which equals the crystal growth rate itself.

As pointed out above, aside from accommodation by dissolution or creep, there is a third possible response of the host rock to crystal growth: overlap of stress halos around several growing grains may cause rock failure, an alternative with potential significance for tectonics and seismology. The fractures could, for example, cooperatively coalesce into one fracture that might trigger an earthquake (if sufficient elastic energy was stored in the rock to begin with). Also, growing crystals that microfracture the surrounding rock could create a halo of improved permeability; if supply of aqueous mineralizing solutions is occurring (by infiltration), the improved permeability attracts greater local supply, which leads to further precipitation, which leads to a further increase in local permeability, and so on. This feedback could explain the extraordinary fact of the self-localization of scarce ore minerals into large ore bodies.

Veins can be viewed as penny-shaped concretions that both propagate as cracks and make room for themselves143 (see last item in the working model of stylitization above). This view contrasts with veins as passive fillings of previously opened fractures – the traditional view of vein genesis. This is a large subject in structural geology.

145 Fletcher/Metson (FN 143).
Buchbesprechungen

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