Self-Organization and Nonlinear Dynamics in Sedimentary Basins [and Discussion]

Peter J. Ortoleva, J. T. Parrish and M. L. Coleman

Phil. Trans. R. Soc. Lond. A 1993 **344**, 171-179
doi: 10.1098/rsta.1993.0085

Self-organization and nonlinear dynamics in sedimentary basins

By Peter J. Ortoleva

Departments of Chemistry and of Geological Sciences, Indiana University,
Bloomington, Indiana 47405, U.S.A.

Patterns of mineralization may develop during diagenesis that are not a direct reflection of sedimentary features or stresses and fluids imposed on the boundaries of a basin. These patterns occur through the amplification of omnipresent non-uniformities of textural or compositional variables. Amplification occurs through feedback involving the coupling of diagenetic processes.

The spatial scale of these patterns varies from microns to kilometres. Examples to be discussed include intracrystalline oscillatory zoning, millimetre- to metre-scale differentiated layering and stylolites, Liesegang bands, reaction front fingering, pulsatile fluid release from overpressurized zones in deep basins, and kilometre-scale basin compartmentation.

---

1. Self-organization and reaction-transport feedback

The predominant view of repetitive mineralogic patterns in sedimentary rocks, such as marl/limestone alternations, is that they are depositional in origin. Researchers as far back as Liesegang (1913) have suggested, however, that banded or other patterns can result from the interplay of mineral reactions and solute transport. We suggest that such phenomena are widespread during diagenesis.

Advances in our understanding of self-organized repetitive compositional patterns in reaction-transport systems (Nicolis & Prigogine 1977) have greatly aided in the modelling of geochemical systems, which may develop repetitive patterns in the absence of a precursor pattern such as sedimentary bedding (Ortoleva *et al.* 1987, 1990; Ortoleva 1993*a*,*b*). As this type of pattern can organize itself from an initially undifferentiated or weakly differentiated medium, and because they evolve through grain growth/dissolution and other reactions, we suggest that they are examples of 'geochemical self-organization' as follows.

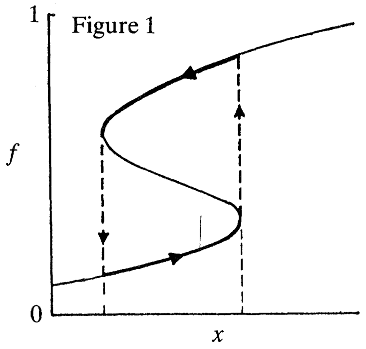
2. Oscillatory intracrystal zoning

Calcite grown from aqueous solution under diagenetic conditions may incorporate impurities in a zoning pattern consisting of concentric alternations of contrasting composition. Such oscillatory zoning in the case of Mn impurity has been demonstrated in the laboratory by Reeder *et al.* (1990) to involve a role for diffusion in the aqueous medium from which the crystals grow.

The growth of solid solution crystals involving complex end-member units may proceed via the rate limiting construction of end-member units at the crystal surface. Consider the growth of a binary crystal composed of A and B endmember units from an aqueous solution involving solutes X and Y such that $X \rightleftharpoons A$ and $Y \rightleftharpoons B$. For the

Phil. Trans. R. Soc. Lond. A (1993) **344**, 171–179

Printed in Great Britain



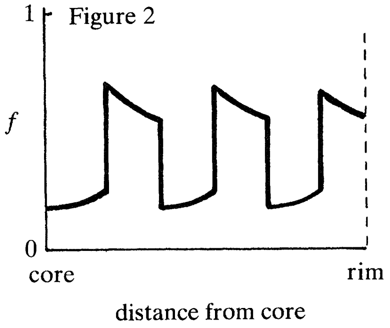


Figure 1. Folded non-equilibrium fractionation curve showing mole fraction f of one end member of a binary solid solution as a function of the concentration x of a pore fluid at the grain-melt interface, from which that end member is constructed. The indicated cycle suggests the possibility of periodic zoning when the non-equilibrium fractionation curve is multiple valued.

Figure 2. Profile of periodic zoning that would result from the cycle indicated in figure 1.

'autocatalytic' case where the rate of creation of A units increases with f, the fraction of A units at the surface, a cyclic growth can occur as suggested in figure 1. Suppose the crystal starts with an A-rich nucleus. Then f is large at the surface. Because the rate coefficient for the A production process $X \rightarrow A$ increases with f, A-rich growth can persist even after the concentration of X in the growth medium near the crystal rim is significantly depleted in X. As Y is not being consumed rapidly during this phase, it builds up near the crystal surface.

Ultimately X is so depleted that B growth tends to dominate with the resulting drop in f. Then X can build up in the growth medium near the crystal surface until A-rich growth again commences and A-autocatalysis can again take place. This process would produce a periodic zoning from core to rim, with a profile indicated in figure 2.

The above oscillatory scenario requires the essential A-autocatalytic feedback coupled to diffusion in the growth medium. Therefore, stirring the fluid from which the crystal grows would repress oscillation. Also, growth must be sufficiently rapid, i.e. the system must be sufficiently far from equilibrium; otherwise equilibrium fractionation between the growth medium and the crystal would be obtained. Under near-equilibrium conditions, gradients cannot build up in the growth medium and hence oscillation is prevented. Discussion of other mechanisms and geological examples of oscillatory zoning are cited in Ortoleva (1990, 1993*a*, ch. 3).

3. Patterning through nucleation and ripening processes

Banding arising from the interdiffusion of coprecipitates was suggested by Liesegang (1913) as a mechanism for the generation of certain types of banded mineralization patterns. The Ostwald–Prager model of Liesegang banding has been discussed extensively in the chemical and geologic literature. The O–P model is based on a repetitive cycle of supersaturation, nucleation and depletion. It is perhaps most easily understood in terms of a flow problem analogous to the situation of a redox front (Sultan & Ortoleva 1990), involving aqueous species X and Y and minerals A and B in the reactions

$$X + A \rightarrow Y, \quad X + Y \rightleftharpoons B.$$

Here X and Y play roles analogous to O_2 and Fe^{2+} while A and B are analogs of pyrite and an iron oxide mineral. The overall situation is the replacement of A by B. However, nucleation and growth of B tends to lower the concentration product XY in solution. This then tends to repress further B nucleation until the A-dissolution front advances sufficiently far downflow that upstream diffusion of Y to the region of B growth is no longer effective. The X, Y concentration product resulting from incoming X and upstream diffusion of Y can again reach the threshold for B-nucleation and a second B band is created, completing an O–P cycle.

To continue to operate, the O–P mechanism requires an ongoing influx of reactant X. Furthermore, B growth kinetics must be sufficiently fast so that downstream B nucleation can be periodically repressed. The combination of continuous maintenance out of equilibrium and the B-nucleation inhibition effect are requisites for O–P Liesegang banding.

Banded precipitation patterns may also develop via a spatial instability of the Ostwald coarsening process (Ortoleva 1993*a*, ch. 8; Feeney *et al.* 1983). Consider a spatially uniform distribution of spherical precipitate particles whose radius is greater than that of the critical nucleus. The solubility of such particles decreases with increasing radius. Thus if the particles in one region of space are slightly larger than those in its surroundings, the former will grow at the expense of the latter, increasing the amplitude of the original non-uniformity. This self-enhancing process makes the uniform precipitate unstable to the formation of patterning as suggested in figure 3. In order for the feedback leading to patterning to operate, the initial sol must be very fine and hence far from the equilibrium state (a single large crystal).

4. Mechano-chemical feedback

At sufficient depth feedbacks exist that involve the effective dependence of a grain's solubility on textural variables via the variation of grain free energy with stress. This can lead to the generation of sub-metre-scale diagenetically differentiated bedding and other patterns. Examples may include (see Ortoleva 1993*a*, *b*) roughly evenly spaced arrays of stylolites in limestones and sandstones, small-scale (micro-stylolite) laminations in chalk, diagenetic bedding in marl/limestone sequences, layers of enhanced intergranular pressure solution alternating with domains of cementation in sandstones, bands of authigenic muscovite in very fine grained sandstones, spaced cleavage in argillaceous rocks, and pressure seals of metre-scale (or greater) thickness composed of layered cements and/or arrays of stylolites.

To illustrate mechano-chemical feedback, first consider a grain in a volume element of low-porosity rock. The stress experienced by the grain depends on the mechanical properties of the grains in that volume as well as the stress $\boldsymbol{\sigma}^{\mathrm{m}}$ applied at the boundaries of that volume. The mechanical properties of the surrounding medium depend on the mineral identity, grain size, number of grains per unit volume, and grain shape and crystallographic orientation, i.e. on the 'texture' of the surrounding medium. In a sense, the stress on the selected grain depends on local texture. The stress applied to the selected grain will modify its free energy and hence its solubility. As grain dissolution affects texture and texture affects solubility, there is the potential for a mechano-chemical feedback capable of destabilizing the state of uniform texture and generating diagenetic differentiated structure.

Consider the case of a rock whose mechanical response is elastic. Then the selected grain, if roughly spherical, can be considered as an inclusion (in the sense of Eshelby

Figure 3

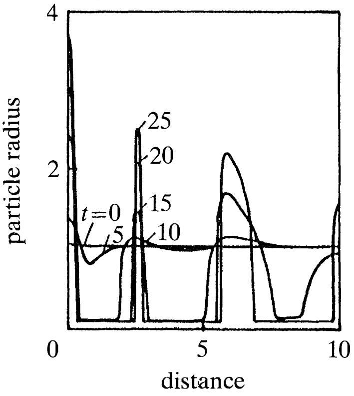


Figure 4

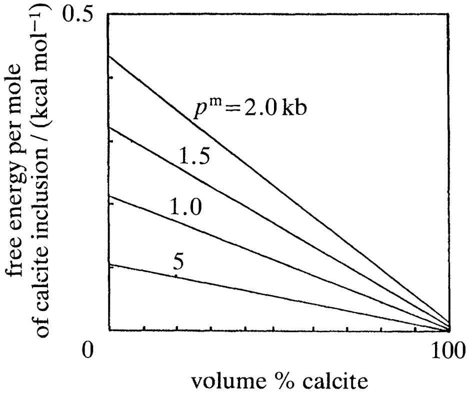


Figure 3. Simulation of a coarsening instability driven by the dependence of particle solubility on particle radius. Note the induction of a number of satellite bands by the initial ($t = 0$) small amplitude disturbance at the left.

Figure 4. Deviation in calcite molar free energy, from its value in the state of hydrostatic pressure p^m, as a function of calcite volume fraction in the surrounding macrovolume element of an argillaceous, low porosity rock. The free-energy deviation increases with decreasing calcite amount, demonstrating a driving force for segregation of calcite from clay.

(1957)) in a matrix whose mechanical properties are the statistical average of the mechanical properties of all grain types as weighted consistently with the local texture (in the simplest case, via a volume fraction average, for example). Using the results of Eshelby's matrix-inclusion calculations, the properties of the statistically weighted average medium and Kamb's (1959) formulae for the free energy of stressed solids, one can develop explicit formulae for the dependence of the free energy of the selected grain on the texture within and the stress applied to the volume element containing the grain of interest (Dewers & Ortoleva 1990*a*; Ortoleva 1993*a*, ch. 10). A result of such a MFEK (mean field Eshelby–Kamb) model is seen in figure 4; a deviatoric free energy of a calcite grain is shown as a function of calcite volume fraction in a calcite-illite rock. As the calcite free energy decreases with increasing calcite content, one can see the potential for the segregation of calcite from illite. This relationship between calcite-free energy and surrounding texture is a mechanism for differentiation between calcite and clay.

If mechano-chemical coupling can lead to self-organization in low-porosity rocks due to contrasting mechanical properties between minerals, it seems likely that contrasts between the mechanical properties of matrix and pore fluid can also lead to self-organization. The difference of normal stress at grain–grain and grain–pore fluid contacts necessitates a more detailed description of grain geometry. Furthermore, porous rocks at depth tend to compact, so that any potential feedback must operate over a background of ambient compaction.

The notion of a pattern forming feedback in porous rocks is quite straightforwardly understood (Dewers & Ortoleva 1990*b*; Ortoleva 1993*a*, ch. 12). Our original (Merino *et al.* 1983) formulation of such a simple reaction-transport model was based on the assumption that the average stress on a grain increased with porosity. Thus, dissolution would occur in higher porosity domains and grain growth would occur in lower porosity domains, thereby intensifying the initial textural contrast. Ricken (1986) suggested that a feedback could exist wherein increased local grain contact area relieves stress which in turn induced overgrowth and hence larger contact area, completing a feedback loop. To obtain a quantitative reaction-transport model that accounts for grain reaction at contacts and at free faces, compaction and the temporal evolution of the supra-grain scale distribution of stresses, a model was constructed based on Weyl's (1959) simple grain packing geometry, Kamb's (1959) expression for the free energy of a stressed grain and effective stress theory for elastic, fluid-pressured porous media (Dewers & Ortoleva 1990*b*, 1993). The result is a quantitative model of stylolites, layered compaction/overgrowth alternations, marl/limestone differentiated layering and a host of related sub-metre-scale structures as mentioned above.

5. Reaction front morphological instability

Consider the imposition of a fluid into a rock that is undersaturated with respect to at least one mineral in that rock. Reaction fronts are created across which at least one mineral in the rock is dissolved. If permeability increases as a result of the passage of a reaction front, a planar front can be destabilized through flow self-focusing as suggested in figure 5. A small bump in the reaction front focuses the flow to its tip because of the increase in permeability there. The increased flow-through raises the rate of dissolution at the pit and therefore tends to speed up the local velocity of front advancement and thereby elongate the bump. Ultimately the bump becomes long enough that the fluid reaching its tip becomes saturated due to solute diffusion from the sides. In this way, any further bump elongation becomes arrested, and the bump can reach a steady-state amplitude. Flow self-focusing can lead to the creation of scalloped or fingered reaction fronts of a variety of morphologies (Chen & Ortoleva 1990, 1993).

Natural examples of such patterned reaction fronts are reviewed in Ortoleva *et al.* (1987). Reaction fronts play an important role in diagenesis. Notable examples are redox fronts (such as those leading to roll-type uranium deposits), dissolution of carbonate cements from sandstones, dolomitization fronts in limestones (Potdevin *et al.* 1992) and feldspar dissolution fronts in sandstone (often leading to the creation of clay minerals). In the latter case, the clay may actually cause a decrease in permeability and hence the stabilization of the planar front. In extreme cases where the matrix is completely dissolved out, dissolution holes may be created leading to karst terrains. The above-cited studies also show that reaction front morphologies may take on branching tree and other complex forms as well as develop states of oscillatory finger creation and annihilation (see also Ortoleva 1993*a*, ch. 6).

6. Basin compartments and their nonlinear dynamics

According to Bradley (1975) and Powley (1990) sedimentary basins are typically divided into km-scale compartments. These compartments are defined by vertical and horizontal bounding 'seals' consisting of very low permeability rock of roughly 10–100 m thickness. Across the seals, relatively large pore fluid pressure differences can be sustained. Pressures within the compartments may be abnormal, in that they differ from their hydrostatic value, being either over- or under-pressured. A number of properties of compartments suggest that they may be an example of km-scale geochemical self-organization (Dewers & Ortoleva 1988; Ortoleva 1993*a*, ch. 15, 16; Ortoleva & Al-Shaieb 1993).

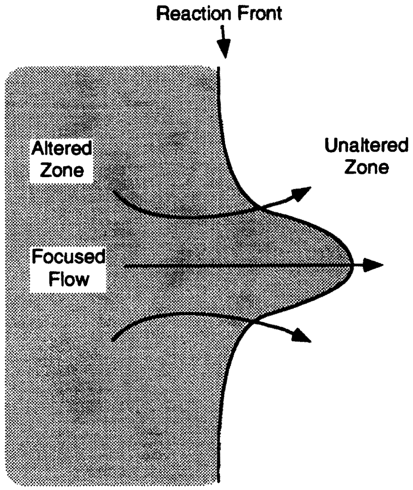


Figure 5. Flow self-focusing results when the altered zone upstream from a reaction front has higher porosity/permeability than that in the unaltered zone. This can lead to the instability of a planar reaction front to the formation of bumps or scallops.

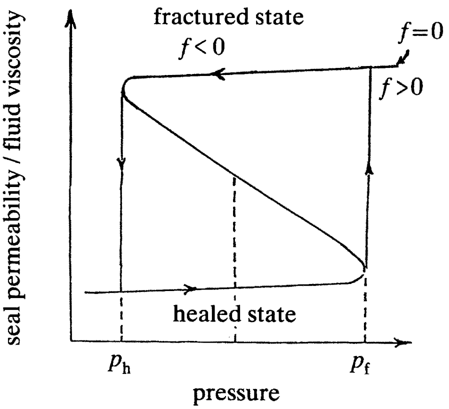


Figure 6. Plane of seal permeability and compartment pressure illustrating oscillatory fluid release. The S-shaped curve, similar in form to that seen in figure 1, suggests a repetitive cycle of fracturing, depressurizing, healing and pressurizing.

Consider the phenomenon of oscillatory fluid release from overpressured compartments via a mechanism of seal puncture and healing as suggested by Bradley (1975) and Powley (1990) and formulated as a quantitative reaction-transport problem by Ghaith *et al.* (1990) and Dewers & Ortoleva (1993). An interaction of fluid pressurizing effects and rock fracturing can lead to oscillatory fluid release from overpressured compartments as follows. Let κ be the permeability of the seal and p_c be the compartment fluid pressure (assumed spatially constant here for simplicity). The basic oscillation is illustrated in figure 6. When the seal is in the healed state, its permeability is low and a pressurization mechanism can raise p_c. If p_c exceeds the value p_f, the seal fractures and, as fracturing is relatively fast, seal permeability jumps to its value in the fractured state. In this state fluid loss dominates the overpressurization mechanism and p_c drops. If it drops below a value denoted p_h, the seal heals and seal permeability decreases. Once in the healed state, p_c can again rise due to the pressurizing mechanisms.

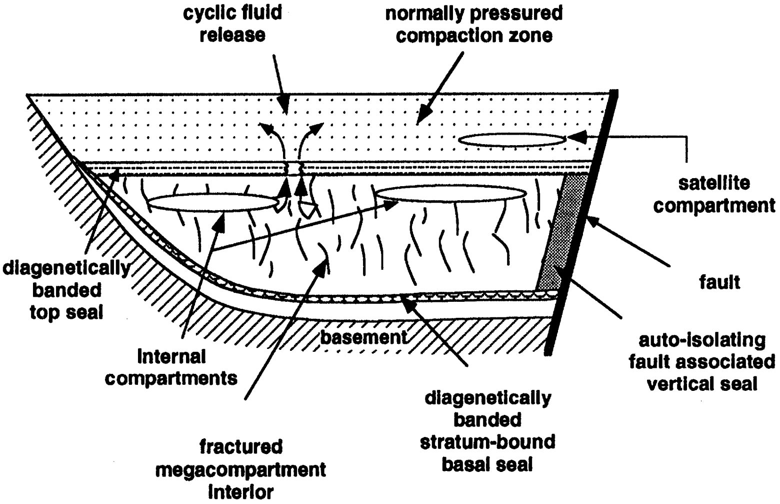


Figure 7. The compartmenting basin is a complex dynamical system evolving via a number of strongly coupled chemical, transport and mechanical processes.

7. Conclusions

All of the above mechanisms may be understood in the more general context of non-equilibrium phenomena in reaction-transport systems (Nicolis & Prigogine 1977; Ortoleva 1993). In that view there are two necessary conditions for self-organization, temporal oscillation and other nonlinear phenomena: (1) the system must be displaced sufficiently far from equilibrium, and (2) the dynamics must be nonlinear.

By definition, diagenesis is a process of rock chemical transformation and hence the first criterion may be satisfied under some conditions. Furthermore, the rates of the active diagenetic processes are often quadratic or other nonlinear functions of solute concentrations, texture, fluid pressure and other descriptive variables.

While the above necessary conditions may often be satisfied, self-organization, oscillatory or other complex temporal dynamics do not necessarily occur. Rather one can observe from the examples of the previous sections that some type of feedback arising from the active processes must be imbedded in the overall reaction-transport-mechanical network. With this, we conclude that in principle, self-organization and other nonlinear phenomena could be expected in a wide range of diagenetic contexts. Delineating quantitative criteria for their realization requires the more detailed examination of active processes.

In conclusion, we suggest that self-organization and other nonlinear phenomena can play key roles in basin diagenesis. Our object is to set forth these ideas to compliment more classical approaches – i.e. presenting them as alternatives when classical explanations do not seem to be adequate. As this field of research in diagenesis develops, new insights into heretofore perplexing occurrences will emerge. We expect that the evolution of a sedimentary basin will be viewed to have an important component of self-organization and nonlinear dynamics similar to that illustrated in figure 7.

This research was supported by grants from the Basic Energy Sciences Program of the U.S. Department of Energy, the Gas Research Institute, and the National Science Foundation.

References

Bradley, J. S. 1975 Abnormal formation pressure. *Bull. AAPG* **59**, 957–973.

Chen, W. & Ortoleva, P. 1990 Reaction front fingering in carbonate cemented sandstones. *Earth Sci. Rev.* **29**, 183–198.

Chen, W., Ghaith, A. & Ortoleva, P. 1990 Diagenesis through coupled processes: modeling approach, self-organization and implications for exploration. *AAPG Mem.* **49**, 103–130.

Chen, W. & Ortoleva, P. 1993 Development of complex reaction front morphologies through nonlinear fluid–rock interaction. In *Modeling and analysis of diffusive and advective processes in geosciences* (ed. W. E. Fitzgibbon & M. F. Wheeler), pp. 52–70. SIAM.

Dewers, T. & Ortoleva, P. 1988 The role of geochemical self-organization in the migration and trapping of hydrocarbons. *Appl. Geoch.* **3**, 287–316.

Dewers, T. & Ortoleva, P. 1990*a* Geochemical self-organization III: a mean field, pressure solution model of spaced cleavage and metamorphic segregational layering. *Am. J. Sci.* **290**, 473–521.

Dewers, T. & Ortoleva, P. 1990*b* A coupled reaction/transport/mechanical model for intergranular pressure solution, stylolites, and differentiated compaction and cementation in clean sandstones. *Geochim. cosmochim. Acta* **54**, 1609–1625.

Dewers, T. & Ortoleva, P. 1993 Nonlinear dynamical aspects of deep basin hydrology: fluid compartment formation and episodic fluid release. *Am. J. Sci.* (In the press.)

Eshelby, J. D. 1957 The determination of the elastic field of an ellipsoidal inclusion and related problems. *Proc. R. Soc. Lond.* A **241**, 376–396.

Feeney, R., Schmidt, S. L., Strickholm, P., Chadam, J. & Ortoleva, P. 1983 Periodic precipitation and coarsening waves: applications of the competitive particle growth model. *J. chem. Phys.* **78**, 1293.

Ghaith, A. Y., Chen, W. & Ortoleva, P. 1990 Oscillatory methane release from shale source rocks. *Earth Sci. Rev.* **29**, 241–248.

Kamb, W. B. 1959 The theory of preferred crystal orientation developed by crystallization under stress. *J. Geol.* **67**, 153–60.

Liesegang, R. E. 1913 *Geologische Diffusionen*. Dresden: Steinkopff.

Merino, E., Strickholm, P. & Ortoleva, P. 1983 Generation of evenly spaced pressure-solution seems during late diagenesis: a kinetic theory *Contrib. Mineralogy Petrology* **82**, 360–370.

Nicolis, G. & Prigogine, I. 1977 *Self-organization in non-equilibrium systems*. New York: Wiley.

Ortoleva, P. 1990 Role of attachment kinetic feedback in the oscillatory zoning of crystals grown from melts. *Earth Sci. Rev.* **29**, 3–8.

Ortoleva, P. 1993*a* *Geochemical self-organization*. New York: Oxford University Press.

Ortoleva, P. 1993*b* Development of diagenetic differentiated structure through reaction-transport feedback. In *Diagenesis* (ed. K. H. Wolf & G. V. Chilingarian), vol. IV. Amsterdam: Elsevier.

Ortoleva, P. & Al-Shaieb, Z. 1993 Genesis and dynamics of basin compartments and seals. *Am. J. Sci.* (In the press.)

Ortoleva, P., Merino, E., Chadam, J. & Moore, C. H. 1987 Geochemical self-organization. I. Reaction-transport feedbacks and modeling approach. *Am. J. Sci.* **287**, 979–1007.

Ortoleva, P., Hallet, B., McBirney, A., Meshri, I., Reeder, R. & Williams, P. (eds) 1990 *Self-Organization in Geological Systems. Proc. of a Workshop held 26–30 June 1988, University of California Santa Barbara. Earth Sci. Rev.* **29**. Amsterdam: Elsevier.

Park, A., Dewers, T. & Ortoleva, P. 1990 Cellular and oscillatory self-induced methane migration. *Earth Sci. Rev.* **29**, 249–265.

Potdevin, J. L., Chen, W., Chen, Y. & Ortoleva, P. 1992 CIRF, a general reaction-transport code: mineralization fronts due to the infiltration of reactive fluids. In *Water–rock interaction* (ed. Y. K. Kharaka & A. S. Maest), pp. 1047–1054.

Powley, D. E. 1990 Pressures and hydrogeology in petroleum basins. *Earth Sci. Rev.* **29**, 215–226.

Reeder, R. J., Fagioli, R. O. & Meyers, W. J. 1990 Oscillatory zoning of Mn in solution-grown calcite crystals. *Earth Sci. Rev.* **29**, 39–46.

Ricken, W. 1986 *Diagenetic bedding*. Berlin: Springer Verlag.

Sultan, R. & Ortoleva, P. 1990 Bifurcation of the Ostwald–Liesegang supersaturation-nucleation-depletion cycle. *Earth Sci. Rev.* **29**, 163–173.

Weyl, P. K. 1959 Pressure solution and the force of crystallization. *J. geophys. Res.* **64**, 2001–2025.

Discussion

J. T. Parrish. Some people argue that limestone–shale cycles are entirely diagenetic; does Professor Ortoleva agree? A counter argument is that some heterogeneities are needed to start it off (Milankovitch). My impression is that you can get something like Milankovitch features but is this not in fact a reaction front-related feature?

P. J. Ortoleva. On the larger scale, depositional processes are responsible, on a shorter scale, diagenetic. Something is needed to trigger things off: only a slight non-uniformity is required therefore there is an inherent instability.

M. L. Coleman. Will a reaction front where there is precipitation (say calcite or silica) lead to patterns of self-organization similar to those caused by dissolution?

P. J. Ortoleva. No, it will produce no pattern.