

ISOTHERMAL CONSTITUTIVE UNDERCOOLING AS A MODEL FOR OSCILLATORY ZONING IN PLAGIOCLASE

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ABSTRACT

We present a recently developed nonlinear model based on the constitutive undercooling mechanism to explain oscillatory zoning in plagioclase. It uses diffusion-controlled growth kinetics coupled with a nonlinear partition relation. Regular oscillatory zoning, period doubling sequence and chaotic zoning are possible for realistic choices of parameters. This model captures the essential features observed in actual crystals.

Keywords: oscillatory zoning, plagioclase, self-organization, nonlinear dynamics, pattern formation, diffusion-controlled growth kinetics, constitutive undercooling, period-doubling, chaos.

SOMMAIRE

Nous présentons un récent modèle non linéaire de zonation oscillatoire dans les cristaux de plagioclase. Le modèle est fondé sur un mécanisme de sous-refroidissement constitutionnel. Il utilise une cinétique de croissance contrôlée par la diffusion, ainsi qu'une relation de partage non linéaire. Les zonation oscillatoires régulières, les séquences de dédoublement de période, ainsi que les zonation chaotiques, sont possibles pour des valeurs réalistes des paramètres. Ce modèle semble bien reproduire les caractéristiques essentielles de la zonation observée dans les cristaux naturels.

Mots-clés: zonation oscillatoire, plagioclase, auto-organisation, dynamique non linéaire, formation de motifs, cinétique de croissance contrôlée par diffusion, sous-refroidissement constitutionnel, dédoublement de période, chaos.

INTRODUCTION

Many crystals of geological importance show oscillatory compositional zoning from core to rim. Examples may be found in over 70 different minerals (Shore & Fowler 1996). The classic example is plagioclase, particularly that of many intermediate volcanic rocks. Typically, the plagioclase zoning consists of a more or less regular oscillation in the anorthite content from core to rim (Pearce *et al.* 1987, Pearce & Kolisnik 1990) on a scale of approximately 10 μm . The amplitude of the zoning is generally of several mol.% anorthite (An) superposed on a baseline of decreasing An content toward the crystal's

periphery, *i.e.*, "normal" zoning. Trace elements also show an oscillatory distribution in the crystal.

The oldest models to explain the oscillatory zoning of plagioclase, as mentioned by Klein & Hurlbut (1993), were based on changes in the magma flow's parameters on a large scale (*e.g.*, inception of mixing of magma). However, as a typical growth-velocity is of the order of $\mu\text{m/s}$, the time needed to form one zone is very short in comparison to the time-scale of mixing in the magma system. More appropriate models are based on modern ideas of self-organization in nonlinear systems. Haase *et al.* (1980) and Ortoleva (1990) proposed a model based upon a diffusion mechanism and an *ad hoc* autocatalytic scheme of reaction. Brandeis *et al.* (1984) modeled oscillatory zoning as due to nucleation-induced oscillations in temperature. Allègre *et al.* (1981) considered a model with diffusion and a retarded growth-rate. They found transient solutions exhibiting a damped oscillatory character, but no sustained oscillations. Lasaga (1982) modeled

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the growth process by coupling diffusion to realistic expressions of growth velocity, but did not find self-oscillating solutions. Pearce (1994) offered a review of these models.

Another recent model has been proposed by Wang & Wu (1995). Assuming that the concentration of a species in the solid is proportional to its growth velocity, these authors obtained a nonlinear relation between concentration of the species in the solid to concentration in the melt adjacent to the growing surface, thus defining effectively a partition relation. They obtained a regime of parameters for which two stable solution branches coexist. They then related the phenomenon of oscillatory zoning to the fact that the growth dynamics may move the system from one branch to the other. No realistic dynamics are discussed, as they treated only the no-diffusion and the infinite-diffusion cases. No mechanism for more complex dynamic behavior was proposed.

Our model (L'Heureux 1993, L'Heureux & Fowler 1994, 1996) is based on a diffusion-controlled process coupled with realistic growth-kinetics appropriate for the plagioclase system. It differs from previous quantitative models in that constitutive undercooling (Tiller *et al.* 1953) and nonequilibrium partition provide the basic mechanism for the generation of oscillatory zoning. In this paper, we review the features of this nonlinear growth model, and we complement the findings of L'Heureux & Fowler (1996).

This mechanism was first applied to plagioclase in a qualitative manner by Sibley *et al.* (1976). Generally, under isothermal conditions in multiply-saturated systems, the concentration of species at the growing front of a crystal may be different from the bulk value owing to diffusion. This induces an effective undercooling near the front.

The potential for the generation of significantly heterogeneous compositional patterns can be seen from the following argument. As we will see, the growth velocity is a rapidly increasing function of the An-concentration in the melt. When the partition relation is such that the An-concentration in the crystal at the growing front is larger than in the liquid (*e.g.*, near-equilibrium growth), the crystal grows uniformly without oscillatory zoning. Indeed, consider a small random perturbation that increases the melt's An-concentration at the interface from the steady state. This will result in enhanced growth and in further consumption of the An-species in the melt, thus reducing the effect of the perturbation. The system exhibits in this case a stabilizing feedback loop. This instability mechanism is general and can be applied to other systems as long as 1) the growth velocity increases with the concentration of the species under consideration, and 2) the partition relation favors a higher concentration of a species in the crystal than in the melt.

In contrast, for a partition relation such that the

An-concentration in the crystal is less than in the melt, the system exhibits a destabilizing feedback loop that has the potential to generate nontrivial compositional zonations. Indeed, as before, a small random perturbation from the steady state that increases the melt's An-concentration results in enhanced growth. However, the crystal now rejects more An in the melt. This results in a further increase of the perturbation. This effect self-propagates until the concentration gradient is sufficiently large for the diffusion processes to stabilize the growth, resulting in the crystallization of a relatively An-rich layer. The cycle can then repeat itself.

Our model is consistent with these arguments. Here, the nonlinearities stem from the coupling between the An-concentration field and growth velocity, as well as from the boundary condition through a nonlinear partition relation. In this paper, we first review the features of the model. A linear stability analysis for the dynamics of perturbations off the steady state is then summarized. This analysis allows for the determination of ranges of parameters for which the system may develop oscillatory zoning. We next present numerical solutions that indeed demonstrate a regular oscillatory zoning as well as a chaotic zoning stemming from a period-doubling scenario. Finally, a discussion of the results and possible generalizations of the model are presented.

THE MODEL

We introduce the model in three stages. We first discuss the chemical diffusion process responsible for the growth of plagioclase crystals. We then present the parameters defining the growth velocity. The nonlinear partition relation is then introduced.

Diffusion

The plagioclase system is a solid-solution series between a Ca-rich end member (anorthite) and a Na-rich one (albite). In the model, we use a frame of reference that moves with the growing front of the crystal, so that $x = 0$ corresponds to the interface, and $x > 0$ denotes the position in the melt. Let $c(x, t)$ be the anorthite concentration in the melt at position x and time t , and D , the diffusion coefficient of An. The diffusion process in the melt can be described by the following relation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + V_T \frac{\partial c}{\partial x} \quad (1)$$

Here, $V_T(t) \equiv V_T[c(0, t)]$ is the velocity of the growing front at a fixed temperature T . In general, this velocity depends on the concentration of species at the growing front. The corresponding term in Eq. (1) describes an effective advection of material incoming toward the

crystal and constitutes a source of nonlinearity.

The initial condition for the model is given by

$$c(x, 0) = c_i \quad (2)$$

Boundary conditions also need to be specified. Very far from the crystal–liquid interface, we set the concentration field equal to the given concentration $\hat{c}$ in the bulk magma:

$$c(\infty, t) = \hat{c} \quad (3)$$

Continuity of the material flux (mass balance) at the growing front provides another boundary condition:

$$D \frac{\partial c}{\partial x} \Big|_{x=0} + [c(0, t) - c_s(t)] V_T = 0, \quad (4)$$

where $c_s(t)$ is the species concentration in the crystal at the interface. We neglect diffusion in the solid phase.

Growth velocity

As growth is typically slow ($\mu\text{m/s}$), we can assume that the growth velocity adjusts instantaneously to a value close to that described by near-equilibrium kinetics. In contrast, some previous models (Allègre *et al.* 1981, Brandeis *et al.* 1984) introduced a relaxation-time relation between the actual growth-rate and its kinetic value. Such a feature is not essential for the generation of self-organized patterns, although it could be straightforwardly incorporated in our model (L'Heureux 1993).

A realistic expression for the growth velocity was derived (L'Heureux 1993) from the Calvert–Uhlmann model for the growth of large crystals (Calvert & Uhlmann 1972).

$$V_T = U(R_s R_c^2)^{1/3}. \quad (5)$$

Here, the growth is interpreted as a geometric average of two mechanisms, a longitudinal growth R_s by surface nucleation and a continuous growth R_c along the surface. U denotes a velocity scale. Expressions for the partial mechanisms of growth R_s and R_c are given by:

$$R_s = \exp\left(-\frac{3a}{T\Delta T}\right) \exp\left(-\frac{b}{T-T_g}\right) \quad (6)$$

$$R_c = [1 - \exp\left(-\frac{\Delta G}{RT}\right)] \exp\left(-\frac{b}{T-T_g}\right). \quad (7)$$

Here, a is related to the surface tension of the critical nucleus, b is related to the viscosity of the melt, and $\Delta T = T_L - T$ is the undercooling, with T_L the liquidus temperature. T_g , the glass-transition temperature, relates to the fact that the melt's viscosity follows the Vogel – Tammann – Fulcher empirical law (Bottinga & Weill 1972). Finally, ΔG is the difference in molar Gibbs free energy between the crystal and the melt. This quantity is related to the undercooling, to the molar enthalpy of fusion ΔH_f (L'Heureux & Fowler 1994), and to the molar enthalpy of mixing ΔH_m (L'Heureux 1993).

The dependence of the growth velocity on An concentration comes from the dependence of T_L , T_g ,

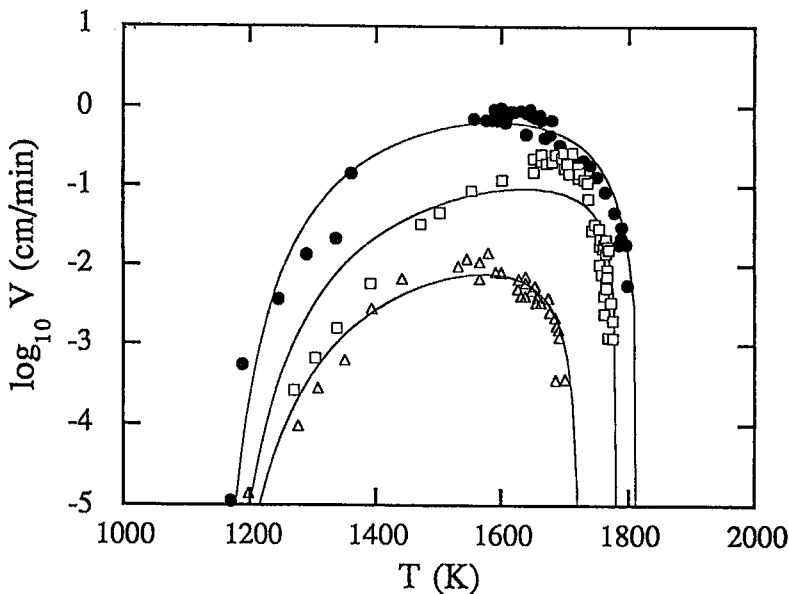


FIG. 1. Measurements of growth velocity in the synthetic Ab–An system (from Kirkpatrick *et al.* 1979) and calculated growth-velocity as a function of temperature for various An-concentrations: 100 mol.% (circles), 75 mol.% (squares), 50 mol.% (triangles).

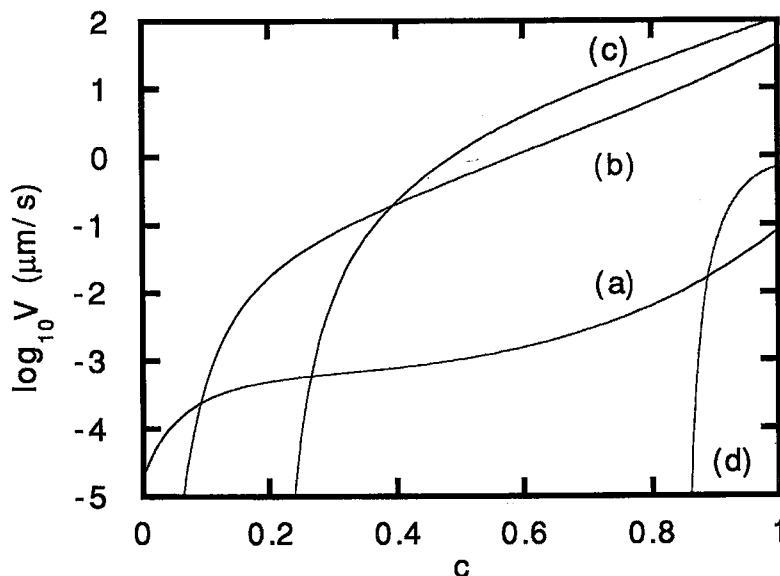


FIG. 2. Concentration dependence of the growth velocity for various temperatures: (a) $T = 1200$ K; (b) $T = 1400$ K; (c) $T = 1600$ K; (d) $T = 1800$ K.

ΔH_f , ΔH_m , U , a and b on An concentration. The first four quantities are known, whereas U , a and b are determined by fitting the expression for the growth velocity to the experimental measurements on plagioclase by Kirkpatrick *et al.* (1979). Figure 1 shows the data and the resulting fits. The important compositional dependence is due to U and T_L only. Figure 2 shows the resulting dependence of An-concentration on the growth velocity for various temperatures. Note that growth velocity is a rapidly increasing function of the melt's An-concentration at the crystal-liquid interface.

Partition relation

In order to obtain a closed set of equations, we need a relation (the partition relation) between the species concentration in the solid and in the melt at the interface. Lasaga (1982) has obtained a reasonable partition relation for two-component systems (*e.g.*, albite-anorthite):

$$c_s(t) = \frac{K_D B c(0,t)}{A + (K_D - 1)c(0,t)}. \quad (8)$$

If the superscript ' refers to the second solid-solution component, here Ab, then $K_D = c_s(t) c'(0,t)/[c(0,t) c'_s(t)]$ is an effective exchange-equilibrium constant, whereas $A = c(0,t) + c'(0,t)$ and $B = c_s(t) + c'_s(t)$ are approximately constants. Substituting the partition relation [Eq. (8)] in the boundary condition at the

interface [Eq. (4)], we see that the boundary condition introduces another source of nonlinearity.

Since the molar volume of albite and that of anorthite are approximately equal, we can express the concentration in units of molar volume so that the concentration becomes identical to the composition. We can thus choose $A = B = 1$. In summary, the model is defined by Eqs. (1–8). The control parameters consist of D , T , $\hat{\epsilon}$ and K_D .

LINEAR STABILITY ANALYSIS

The first step in analyzing the nonlinear model is to find the possible steady-state solutions. We then test for the stability of these solutions by examining the relaxation of a small perturbation about the corresponding steady-state solution (as described in the Introduction). This results in a set of linearized equations that can be solved, so that the nature of the stability can be mapped onto a phase diagram in parameter space.

To solve for the steady-state concentration c_0 at the growing front in the melt, we set the left-hand side of the diffusion equation [Eq. (1)] equal to 0. The solution is unique and is given by

$$c_0 = \hat{\epsilon} / [K_D - (K_D - 1)\hat{\epsilon}]. \quad (9)$$

The corresponding steady-state growth velocity is denoted $V_0 \equiv V_T(c_0)$. The linear stability of this steady-state solution can now be investigated. We first obtain

an integral representation of the melt concentration at the interface $c(0,t)$ involving its value at previous times. From Eq. (1), we solve for the spatial Laplace transform of $c(x,t)$, we invert and take the limit as $x \rightarrow 0$. The result generalizes Eq. (4.11) of L'Heureux (1993) and reads

$$\begin{aligned} c(0,t) = & \hat{c} - \int_0^\infty \hat{c}_{t,t'} \left[\frac{f(t')}{t-t'} - 2V_T(t') \right] dt' \\ & + \int_0^\infty \hat{c}(0,t') g_{t,t'} \frac{f(t')}{t-t'} dt' - 2 \int_0^\infty V_T(t') c_s(t') g_{t,t'} dt' \\ & + (c_i - \hat{c}) [1 + \text{erf}[f(0)/2\sqrt{D\tau}]]. \end{aligned} \quad (10)$$

Here, erf denotes the error function,

$$f(t') = \int_{t'}^t V_T(t'') dt''$$

is the length of the crystal grown between t' and t , and the propagator is

$$g_{t,t'} = \exp[-f(t')^2 / 4D(t-t')] / \sqrt{4\pi D(t-t')}.$$

We now consider the time-dependence of a small perturbation in concentration of amplitude ε about the steady state. The system can then be linearized about the steady state, so that we expect the solution to have the following exponential behavior:

$$c(0,t) = c_o + \varepsilon e^{2\omega t/\tau}, \quad (11)$$

$$V_T(t) = V_o + \frac{dV_o}{dc} \varepsilon e^{2\omega t/\tau}. \quad (12)$$

Here, $\tau \equiv 8D/V_o^2$ is a characteristic time-scale, and ω represents dimensionless eigenvalues to be found. We find by straightforward analysis (L'Heureux & Fowler 1996) that ω is a solution of:

$$\sqrt{\omega+1} = \frac{\omega Q - P}{\omega - P} \quad (13)$$

where

$$P = -4\theta \frac{1 - K_D + (K_D - 1)\hat{c}}{K_D - (K_D - 1)\hat{c}} \quad (14)$$

$$\begin{aligned} Q = & 1 - \frac{2}{K_D} (K_D - (K_D - 1)\hat{c})^2 \\ & + 2\theta \frac{1 - K_D + (K_D - 1)\hat{c}}{K_D - (K_D - 1)\hat{c}} \end{aligned} \quad (15)$$

with

$$\theta = \frac{\hat{c}}{V_o} \frac{dV_o}{dc} \quad (16)$$

being the dimensionless slope of the growth-velocity curve at the steady state.

We find from Eq. (13) that if K_D is larger than

one, the steady state is stable and overdamped, corresponding to an unzoned crystal. However, if K_D is less than 1, the situation is more interesting. Figure 3 shows the stability phase-diagram in (θ, K_D) space for two sets of $\hat{c}$ and T values. The dotted lines separate regions for which the eigenvalues have common characteristics. In the field labeled S, we find two complex conjugate eigenvalues with a negative real part. This means that the steady state is stable, but supports damped oscillations, corresponding to a crystal exhibiting a few zones of decreasing amplitude from the core. In the region U, the eigenvalues are again complex conjugate, but have positive real parts. Here, the steady state is unstable, but has the potential to exhibit nontrivial oscillatory behavior. Generally, as the nonlinear system parameters are varied, we may find circumstances for which a steady state loses its stability, in such a way that the eigenvalue with the largest real part becomes purely imaginary. In this case, the system is said to undergo a Hopf bifurcation (Hilborn 1994). The transition from region S to U thus defines a Hopf bifurcation for the plagioclase system. In the field labeled R, the eigenvalues are real and positive, corresponding to a linearly unstable steady-state. Since this region is already surrounded by an unstable area, this result is not relevant for the behavior of the actual solution. Finally, the region labeled N corresponds to a regime where no solution to Eq. (13) is found.

If we use a realistic expression for growth velocity, the path in (θ, K_D) space is given by the solid line in Figure 3. Note that for higher temperatures, the Hopf bifurcation is shifted to higher values of K_D , thus enlarging the range of parameter values for which oscillatory behavior is possible. Moreover, as $\hat{c}$ increases, the Hopf bifurcation point is shifted upward, so that there exists a maximum value of $\hat{c}$ (e.g., 0.4 for a T of 1400 K) for the onset of oscillations.

NUMERICAL ANALYSIS

The model has been solved numerically using a semi-implicit method on staggered grids in position and time. The nonlinearities were treated by an iteration scheme over successive approximations until convergence to a given tolerance was obtained. The numerical scheme was successfully tested for convergence and stability. The resulting time-series were then transformed to a dimensionless space variable L by using the relation

$$L = V_o \int_0^t V_T(t') dt' / D. \quad (17)$$

This format corresponds to that typical of a traverse across the crystal during chemical analysis.

Figure 4a shows a typical solution of Eq. (1) for a point corresponding to region S in the stability diagram. As expected from the linear stability analysis,

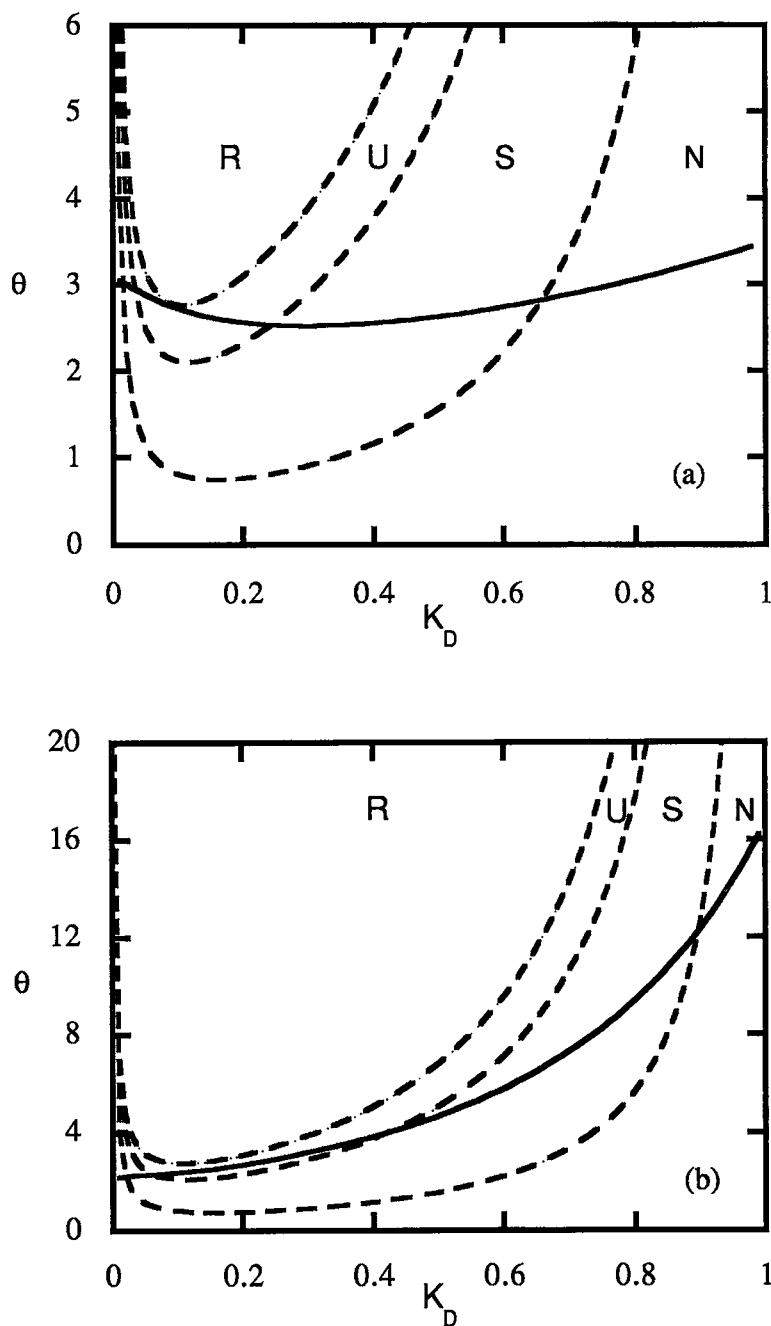


FIG. 3. Stability phase-diagram in (θ, K_D) for $\hat{c} = 0.3$. See text for an explanation of the stability fields bounded by dashed lines. The continuous curve gives the path obtained with a realistic expression for growth velocity: (a) $T = 1400$ K; (b) $T = 1600$ K.

the solution exhibits damped oscillations to a steady state. Numerical analysis also indicated that the steady state is stable in the region N of the phase diagram and does not support oscillations. The behavior of the steady state thus connects smoothly

with the one for $K_D > 1$. Figure 4b uses a smaller value of K_D and corresponds to a point in the region U of the phase diagram that is close to the Hopf bifurcation boundary. As expected from our discussion, a regular oscillatory solution is obtained. Figure 5 shows the

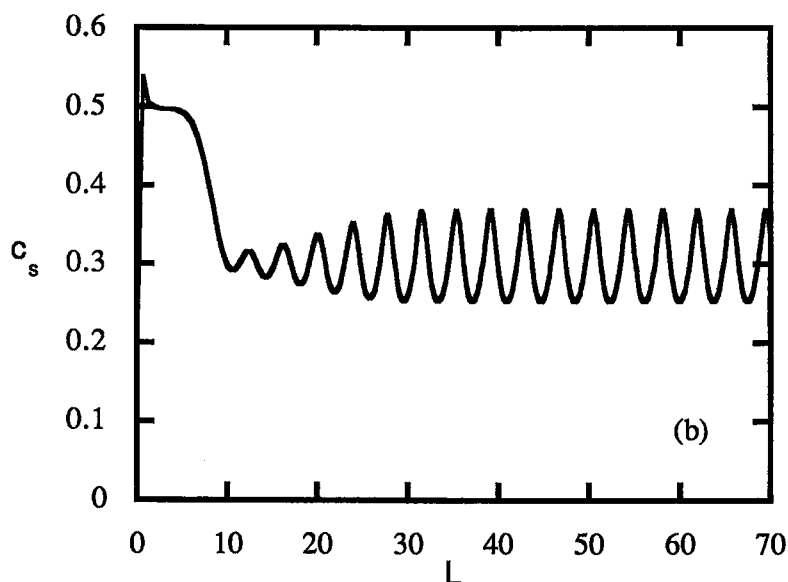
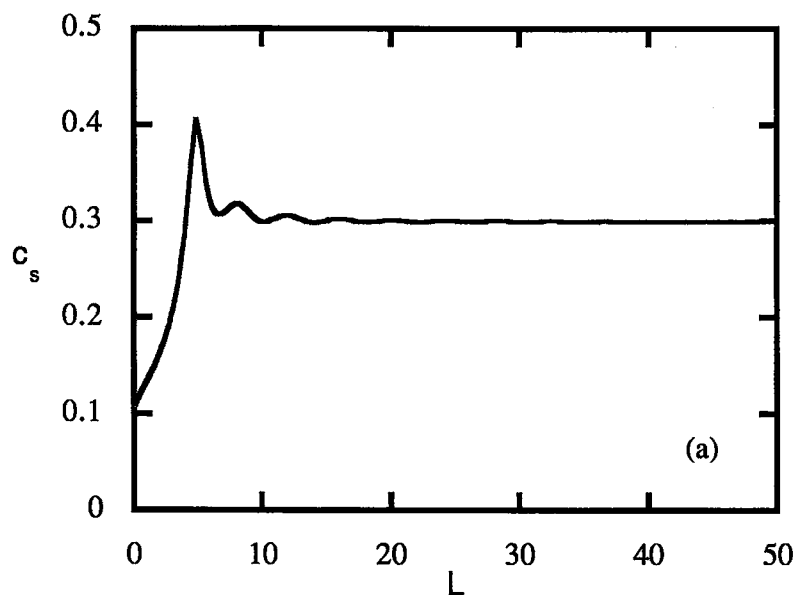
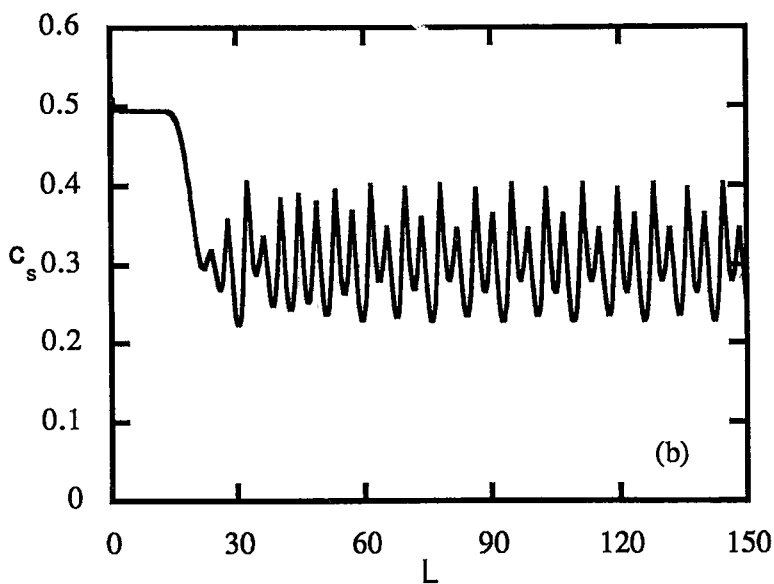
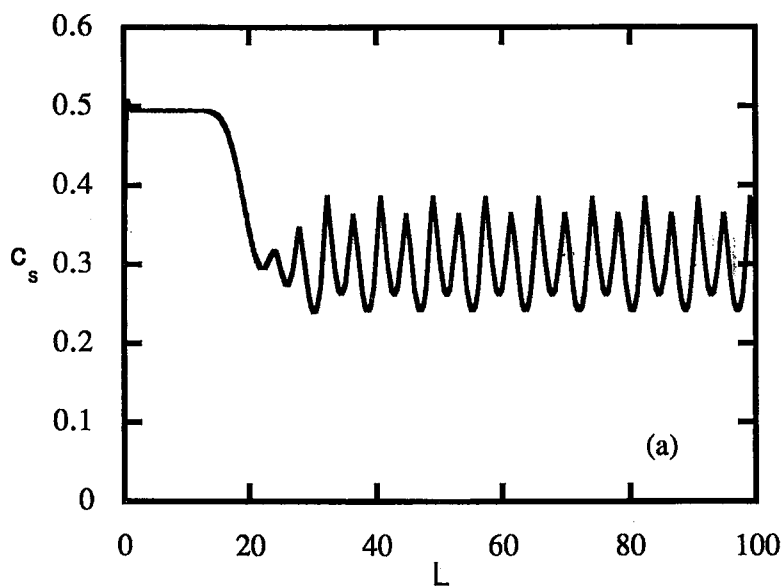


FIG. 4. Numerical solution for the An concentration in the crystal $c_s(t)$ at the growing front as a function of the dimensionless distance from the core. $L = V_0 \int_0^t V_T(t') dt'/D$, $\hat{c} = c_i = 0.3$, and $T = 1400$ K. (a) $K_D = 0.26$ ($V_o = 1.3979$ $\mu\text{m/s}$); (b) $K_D = 0.23$ ($V_o = 1.7755$ $\mu\text{m/s}$).

results when K_D takes a sequence of smaller values at a higher temperature. This corresponds to points further inside the region U of the phase diagram. Note the sequence of period-doubling leading to chaos with decreasing K_D .

DISCUSSION

With an appropriate diffusion-coefficient ($D = 10^{-7}$ cm^2/s), the zone thicknesses obtained from the numerical solutions (e.g., 21.4 μm for Fig. 4b)



correspond to those observed in natural oscillatory zoned plagioclase. Also, the amplitude of the concentration variations (e.g., 11.6 mol% An for Fig. 4b) is consistent with the observations. The parameter regime for which oscillatory zoning is obtained also is

reasonable. For instance, oscillatory zoning in plagioclase is commonly found in intermediate rocks, which corresponds well with the fact that oscillatory and chaotic solutions are found for $\hat{c} < 40\%$ An at $T = 1400$ K.

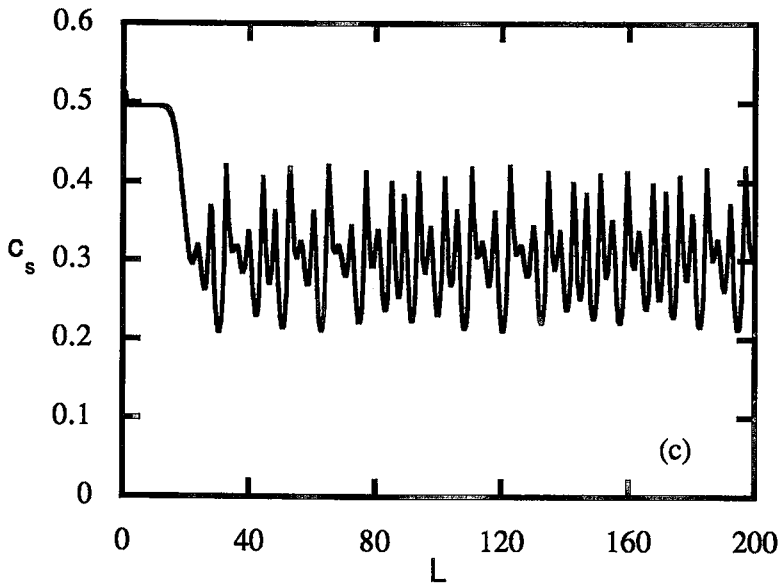


FIG. 5. Numerical solution for the An concentration in the crystal $c_s(t)$ at the growing front as a function of the dimensionless distance from the core. $L = V_o \int_0^t V_T(t') dt'/D$, $\hat{c} = 0.3$, $T = 1600$ K, and $c_i = 0.5$. (a) $K_D = 0.34$ ($V_o = 2.4721$ $\mu\text{m/s}$); (b) $K_D = 0.324$ ($V_o = 2.826$ $\mu\text{m/s}$); (c) $K_D = 0.31$ ($V_o = 3.1816$ $\mu\text{m/s}$).

In the chaotic region, the zone thickness varies irregularly. Figure 6 shows a return map corresponding to the chaotic solution of Figure 5c. Here, we plot the thickness of the n th zone (defined as the dimensionalized distance between successive maxima) as a function of the thickness of the previous one. The points are distributed on a pattern with a well-defined single maximum. This pattern is reminiscent of the logistic map, a well-studied model in nonlinear dynamics that exhibits period-doubling sequences to chaos (Hilborn 1994). The similarity between the first return map in our model and the logistic map suggests that both these models belong to the same universality class, thus explaining the presence of the period-doubling sequence. Moreover, the pattern obtained is strikingly similar to that found by Higman & Pearce (1993) in real crystals of plagioclase. In addition, they showed evidence of the existence of a Hopf bifurcation in the plagioclase data.

In the model proposed by Wang & Wu (1995), oscillatory zoning was linked to the possibility of motion between the two coexisting branches of their partition relation. This is not necessary for oscillatory zoning. Indeed, in contrast to their model, our partition relation defines uniquely the concentration of An in the solid as a function of its concentration in the melt. In our model, oscillatory zoning stems from the diffusion-controlled growth dynamics.

The concentration profiles obtained from the numerical solutions are basically symmetrical, as opposed to the sawtooth pattern characteristically observed in natural crystals (Pearce & Kolisnik 1990, Pearce 1994). Generalizations of our simple model that could lead to a closer match to natural profiles are currently under investigation. For instance, coupling of the concentration field to a temperature field could be achieved through consideration of the heat diffusion with the production of latent heat, together with a temperature-dependent diffusion coefficient. An explicit cooling rate can also easily be considered. However, consideration of the temperature variations shows that the corrections on the large-scale features of the An-concentration profile are small (of the order of 1%) because the thermal diffusivity of the melt is typically much larger than the diffusion coefficient. The isothermal assumption is therefore a reasonable one.

Another possible generalization is to consider a lag between the actual growth-velocity and its kinetic value (Allègre *et al.* 1981, Brandeis *et al.* 1984). This lag represents the possible sluggishness in the response of the system and may have an effect on the shape of the profile.

The one-dimensional model used here implies that the calculated patterns of zoning consist of growth planes of varying composition. Sufficiently far from the crystal's core, this is the type of pattern observed.

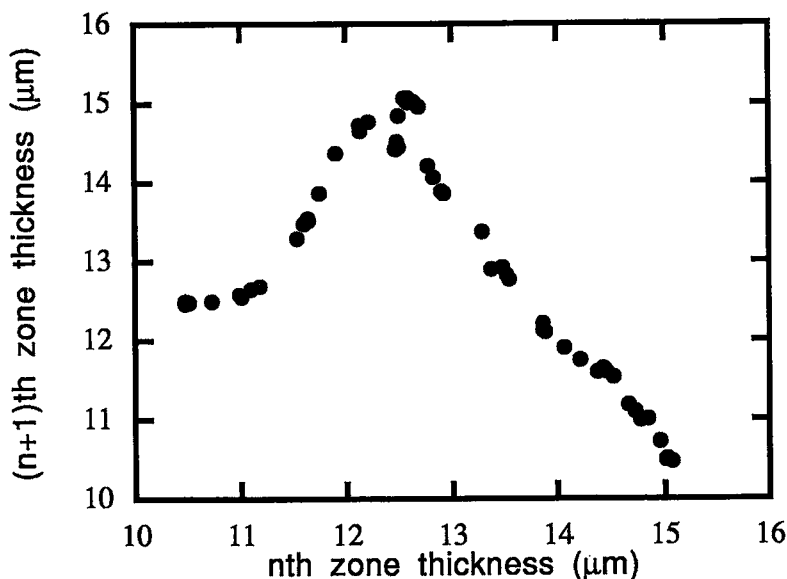


FIG. 6. First return map for the chaotic motion corresponding to the conditions of Figure 5c. The thickness of the $(n + 1)$ th zone is plotted as a function of the thickness of the n th zone. The first nine peaks were not considered, as they are transients. A value of $D = 10^{-7}$ cm²/s has been used to convert to dimensionalized lengths.

However, an interesting but difficult generalization of the model would consist in an extension to 2 and 3-dimensional patterns. Such a model could be applied to a non-equilibrium growth regime intermediate between oscillatory zoning and dendrites.

Finally, the natural system is submitted to random environmental fluctuations. The effect of such noise on values of the parameters can be investigated. In many instances, this noise may lead to nontrivial behavior, such as creation of noise-induced patterns without deterministic counterpart (Hörsthemke & Lefever 1984). In conclusion, our simple model seems to capture the essential dynamics of oscillatory zoning in the plagioclase system in a way that has not been possible with established models.

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REFERENCES

- ALLÈGRE, C.J., PROVOST, A. & JAUPART, C. (1981): Oscillatory zoning: a pathological case of crystal growth. *Nature* **294**, 223-228.
- BOTTINGA, Y. & WEILL, D.F. (1972): The viscosity of magmatic silicate liquids: a model for calculation. *Am. J. Sci.* **272**, 438-475.
- BRANDEIS, G., JAUPART, C. & ALLÈGRE, C.J. (1984): Nucleation, crystal growth and the thermal regime of cooling magmas. *J. Geophys. Res.* **89**, 10161-10177.
- CALVERT, P.D. & UHLMANN, D.R. (1972): Surface nucleation growth theory for the large and small crystal cases and the significance of transient nucleation. *J. Crystal Growth* **12**, 291-296.
- HAASE, C.S., CHADAM, J., FEINN, D. & ORTOLEVA, P. (1980): Oscillatory zoning in plagioclase feldspar. *Science* **209**, 272-274.
- HIGMAN, S.L. & PEARCE, T.H. (1993): Spatiotemporal dynamics in oscillatory zoned magmatic plagioclase. *Geophys. Res. Lett.* **20**, 1935-1938.
- HILBORN, R.C. (1994): *Chaos and Nonlinear Dynamics*. Oxford University Press, New York, N.Y.
- HÖRSTHEMKE, W. & LEFEVER, R. (1984): *Noise-Induced Transitions. Theory and Applications in Physics, Chemistry and Biology*. Springer-Verlag, Berlin, Germany.

- KIRKPATRICK, R.J., KLEIN L., UHLMANN, D.R. & HAYS, J.F. (1979): Rates and processes of crystal growth in the system anorthite-albite. *J. Geophys. Res.* **84**, 3671-3676.
- KLEIN, C. & HURLBUT, C.S. (1993): *Manual of Mineralogy*. John Wiley & Sons, New York, N.Y.
- LASAGA, A.C. (1982): Toward a master equation in crystal growth. *Am. J. Sci.* **282**, 1264-1288.
- L'HEUREUX, I. (1993): Oscillatory zoning in crystal growth: a constitutional under-cooling mechanism. *Phys. Rev. E* **48**, 4460-4469.
- & FOWLER, A.D. (1994): A nonlinear dynamical model of oscillatory zoning in plagioclase. *Am. Mineral.* **79**, 885-891.
- & ——— (1996): Dynamical model of oscillatory zoning in plagioclase with nonlinear partition relation. *Geophys. Res. Lett.* **23**, 17-20.
- ORTOLEVA, P. (1990): Role of attachment kinetic feedback in the oscillatory zoning of crystals grown from melts. *Earth Sci. Rev.* **29**, 3-8.
- PEARCE, T.H. (1994): Recent work on oscillatory zoning in plagioclase. In *Feldspars and their Reactions* (I. Parsons, ed.). NATO ASI, Kluwer Acad. Publ., Dordrecht, The Netherlands (313-346).
- & KOLISNIK, A.M. (1990): Observations of plagioclase zoning using interference imaging. *Earth-Sci. Rev.* **29**, 9-26.
- , RUSSELL, J.K. & WOLFSON, I. (1987): Laser-interference and Nomarski interference imaging of zoning profiles in plagioclase phenocrysts from the May 18, 1980, eruption of Mount St. Helens, Washington. *Am. Mineral.* **72**, 1131-1143.
- SHORE, M. & FOWLER, A.D. (1996): Oscillatory zoning in minerals, a common phenomenon. *Can. Mineral.*
- SIBLEY, D.F., VOGEL, T.A., WALKER, B.M. & BYERLY, G. (1976): The origin of oscillatory zoning in plagioclase: a diffusion and growth controlled model. *Am. J. Sci.* **276**, 275-284.
- TILLER, W.A., JACKSON, K.A., RUTTER, J.W. & CHALMERS, B. (1953): The redistribution of solute atoms during the solidification of metals. *Acta Metallurgica* **1**, 428-437.
- WANG, JIANG-HAI & WU, JIN-PING (1995): Oscillatory zonation of minerals and self-organization in silicate solid-solution systems: a new nonlinear dynamic model. *Eur. J. Mineral.* **7**, 1089-1100.

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