

A model and simulation of branching mineral growth from cooling contacts and glasses

ANTHONY D. FOWLER AND DANIEL E. ROACH

Ottawa Carleton Geoscience Centre, and Department of Geology, University of Ottawa, 770 King Edward Ave.
Ottawa, ON, K1N 6N5, Canada

Abstract

Silicate minerals grown from glasses, and rapidly cooled melts, often have non-compact branching or 'spherulitic' morphology. The branching patterns are observed in volcanic rocks, glasses, meteorites, slags and sometimes in shallow level intrusive rocks. Experiments, observations, theory and simulations all support the concept that the crystal morphology is the result of growth under diffusion limited conditions. We show that in a silicate melt under appropriate conditions the equations for heat transfer and chemical-diffusion reduce to the Laplace equation. This means that the temperature or chemical gradient is a steady state field. Interaction between this field and a random variable (Brownian motion of growth species) is modelled and yields complex branching objects. The growing cluster affects the field such that an in-filled structure cannot be formed. The branching structures of the model crystal are remarkably similar to those formed in nature, and to those produced in laboratory experiments, implying that the model captures the essence of the branching-growth process.

KEYWORDS: branching mineral growth, glass, cooling, diffusion-limited aggregation.

Introduction

BRANCHING-TEXTURED silicate minerals (and more rarely carbonates and oxides) are formed in environments where the kinetics of crystallization are rapid with respect to rates of chemical diffusion (Keith and Padden, 1963). Usually the environments are characterized by sharp thermal gradients and, sluggish diffusion or both (i.e. glassy cooling contacts of silicate melts). Natural examples are the branching plagioclase and olivines of volcanic rocks (Bryan, 1972; Fowler *et al.*, 1987 and 1989). The textures are characterized by tip splitting wherein branches bifurcate during propagation. Figure 1 exhibits an example from the quenched rim of an Archaean pillow basalt. Similar textures have been synthesized in the laboratory under conditions of very high supercooling (e.g. Lofgren, 1974; Donaldson, 1974) and simulated using a variation of the simple growth algorithm, Diffusion Limited Aggregation (Fowler *et al.*, 1989). Although at first glance the textures apparently have a random branching structure, in general they possess a dilation symmetry, or scale invariance. That is, small

segments when suitably expanded look like the whole. Fowler *et al.* (1989) show that these scale-invariant branching structures can be measured using fractal geometry which allows us to quantify irregular objects. The knowledge that these branching crystals have a fractal dimension of ~ 1.7 was the original motivation for this work, because other similar fractal objects have been modelled by related techniques (see discussion).

Theoretical work on crystal growth in silicate magmas and other systems, e.g. snowflakes (Nittman and Stanley, 1986) and plastics (Keith and Padden, 1963) demonstrates that the branching is the result of growth under chemical diffusion limited conditions. The unpredictable or random nature of the diffusion process, coupled with rapid crystal growth, leads to a texture that is not random but organized on many length scales (i.e. scale invariant).

Here we relate Fourier's heat equation and Fick's diffusion law to conditions present during non-equilibrium crystal growth, and demonstrate how they reduce to the Laplace equation (a steady state) under the imposed conditions. We then use the discrete form of the Laplace equation, suitable for

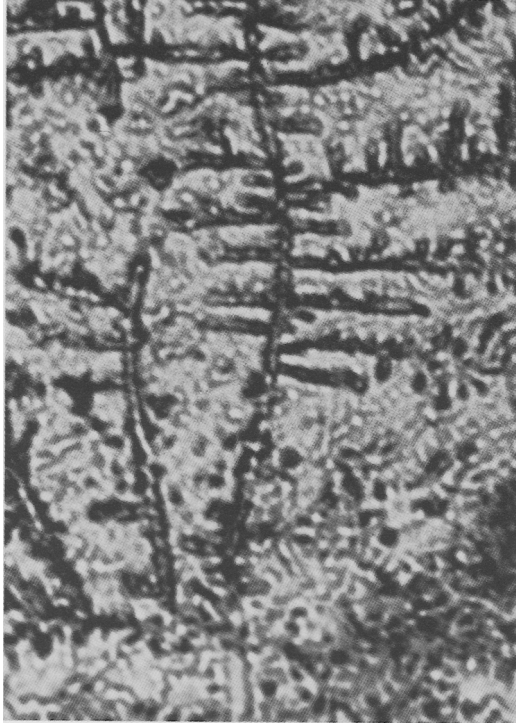


FIG. 1. Photograph of branching-textured olivine from the quenched margin of an Archaean pillow basalt, Holloway Township Abitibi Ontario. Length of main branch approximately 0.1 mm.

digital computers, in a simulation to produce a steady state field imitating temperature or concentration. With the addition of an appropriate rule for selecting growth sites on the model crystal, the field is then allowed to interact with a random component that mimics the Brownian motion of real growth species. The resulting patterns are strikingly similar to textures of branching minerals.

Theoretical considerations

First we introduce some terminology. The terms equilibrium growth and disequilibrium growth are often used to distinguish crystal growth that takes place slowly (e.g. deep within a slowly cooled pluton) from rapid crystal growth (e.g. a quickly cooled margin of a volcanic rock). By definition, at equilibrium there is no macroscopic change within the system, hence no growth, so the concept of equilibrium crystallization is incorrect. Crystals form in disequilibrium, or better, crystallization is an attempt to reach equilibrium. Thus all crystal growth and dissolution require a departure from equilibrium

which in the case of temperature driven growth can be measured by the amount of undercooling. Because heat transfer is not the only driving mechanism for crystallization, we use where appropriate, the qualitative terms near equilibrium growth and, far from equilibrium growth.

Near equilibrium silicate mineral growth is characterized by the formation of well-faceted crystals. The growth rate is slow and largely controlled by interface attachment kinetics at defects on the crystal face. The probability that an individual species in the liquid will migrate to, strike, and adhere to a crystal growth site is low; crystals develop slowly and are well-faceted. Under far from equilibrium growth conditions the growth kinetics are dominated by the transfer rate of material to the crystal, not interface attachment kinetics. Branching minerals formed in quickly cooled environments are typically found in a glassy matrix within a few mm of cooling contacts, where thermal gradients are sharp (e.g. $\sim 1,200^{\circ}\text{C}$ basalt against $\sim 0^{\circ}\text{C}$ sea water, or host rocks). Further from the cooling contact these textures are replaced by a series of other morphologies in a reasonably systematic progression that depends upon the degree of undercooling (e.g. Lofgren, 1974; Fowler *et al.*, 1987).

We consider the case of an unstirred magma of uniform composition undergoing quenching (e.g. margin of a pillow basalt, or high level intrusion) wherein the thickness of the margin is negligible (mm–cm) in comparison to the thickness of the magma body (m–10 m). We expect the heat loss from the magma to be dominated by conduction across a horizontal interface (Carlsaw and Jaeger, 1959). Thus the relevant equation for cooling is Fourier's:

$$\partial T/\partial t = k (\partial^2 T/\partial z^2) \quad (1)$$

where T = temperature, t = time, k = thermal diffusivity, and heat loss is in the vertical direction z . Under these conditions the maximum in the temperature gradient ($\partial T/\partial z$) occurs at the cooling contact (see Fig. 2). Here then, the RHS of Equation 1 is zero implying that $\partial T/\partial t$ is also zero, which holds as long as the far field initial magma temperature remains constant. This is a reasonable constraint over the short time and small scale that the quench takes place relative to the cooling of the main body of lava (e.g. pillow, tube or sill). In other words under the stated conditions, the second derivative of the temperature at the contact is given by:

$$(\partial^2 T/\partial z^2) = 0, \quad (2)$$

or

$$\nabla^2 T \approx 0 \quad (3)$$

Thus in the immediate vicinity of the cooling

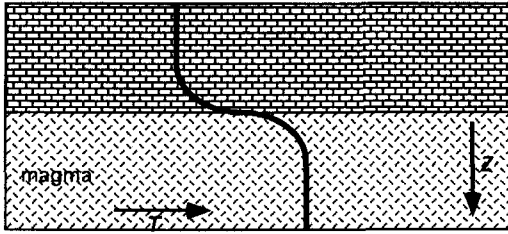


FIG. 2. Schematic diagram depicting temperature distribution across a horizontal cooling contact under conditions dominated by conduction. In nature the vertical extent of the cooling contact in which these crystals grow corresponds to only a few millimeters at the top of the cooling magma. The cooling body envisaged (e.g. a lava flow, tube or pillows, or high level intrusion) has thicknesses of the order of a metre to several 10s of metres and in general very much larger horizontal dimensions. Because of these characteristic dimensions one can assume that the far field temperature of the magma remains constant at its initial value during the time the cooling contact is formed. The maximum change in temperature is at the contact. According to Fourier's equation the maximum in the derivative dT/dz occurs at the contact. Thus the second derivative d^2T/dz^2 is zero here.

contact the temperature is a scalar field obeying the Laplace equation Equation 3. In other words close to the contact the gradient in temperature is unchanging, or a steady state condition exists.

We also consider the growth of branching textures in glass at a constant temperature. Devitrification textures are common in silica-rich glasses, such as rhyolites. They are distinguished from those grown directly from the liquid in that they are often nucleated on fractures, are distributed long distances (metres) from any evident cooling contacts, and do not have an associated progression of morphologies away from cooling contacts. The growth in these low temperature silica-rich systems is clearly diffusion limited. The relevant equation for mass transfer is Fick's second law:

$$\partial C/\partial t = D\nabla^2 C \quad (4)$$

where C is concentration and D is chemical diffusivity.

Assuming isothermal conditions, and knowing that under diffusion-limited conditions a steady state exists such that there is no change in concentration with respect to time:

$$\nabla^2 C \approx 0 \quad (5)$$

that is the Laplace equation.

Therefore a rudimentary model for growth of branching crystals in high temperature gradients or highly viscous systems incorporates conditions where the growth is largely governed by fields obeying the Laplace equation.

Method

The branching growth is modelled on a digital computer. First we set up a potential field to simulate temperature or composition that obeys the Laplace equation. In nature this could be a steady state temperature variation across a cooling contact. Next we choose a nucleus for the model crystal. Because the movement of atoms is Brownian, we simulate the crystal growth process by coupling a random component with the field governed by the Laplace equation. The algorithm is similar to that used in physics to model other branching processes (e.g. Gould and Tobochnik, 1987, pp 472–474, and discussion below). In order to simulate the field of equations 3 and 5 on a digital computer we use the Laplace equation in discrete form, and in two dimensions (i,j):

$$\mu_{i,j} = 1/4[(\mu_{i,j-1}) + (\mu_{i,j+1}) + (\mu_{i-1,j}) + (\mu_{i+1,j})] \quad (6)$$

where μ represents discrete elements of the field (C or T) at all nodes (i,j) within a 100 by 100 grid.

To mimic vertical cooling conditions (equation 1) we have imposed horizontal boundary conditions. This was done by assigning boundary values of the field variable at the grid top of $\mu = 0$, and the grid bottom $\mu = 1$, and none along the sides, and iterating equation 6 for all (i,j). The result (Fig. 3a) shows that the remaining 9,800 nodes have been assigned values in accordance with equations 3 and 5. Note the smoothly varying shades of grey from pure black ($\mu = 0$) at the grid top, to pure white ($\mu = 1$) at the grid bottom, visual confirmation that the conditions of the Laplace equation are obeyed. For thermally driven growth one can envisage that black relates to the coolest temperature and white to the hottest. Experimentation showed that sufficient convergence of the field values at each node was achieved after 50 iterations of equation 6 over the entire grid, a boundary used subsequently (see also Niemeyer *et al.*, 1984).

The crystal growth simulation starts by assigning a value of $\mu = 0$ to a node in the centre of the second row from the grid top. For clarity this nucleus node and the resulting growth structure are assigned a light grey colour (Fig. 3). Because this new value $\mu = 0$ in the second row perturbs the field (in the sense that the new value is not consistent with smooth variation the required by equation 6), the entire grid at each node must be recalculated (e.g. a further 50 iterations of equation 6).

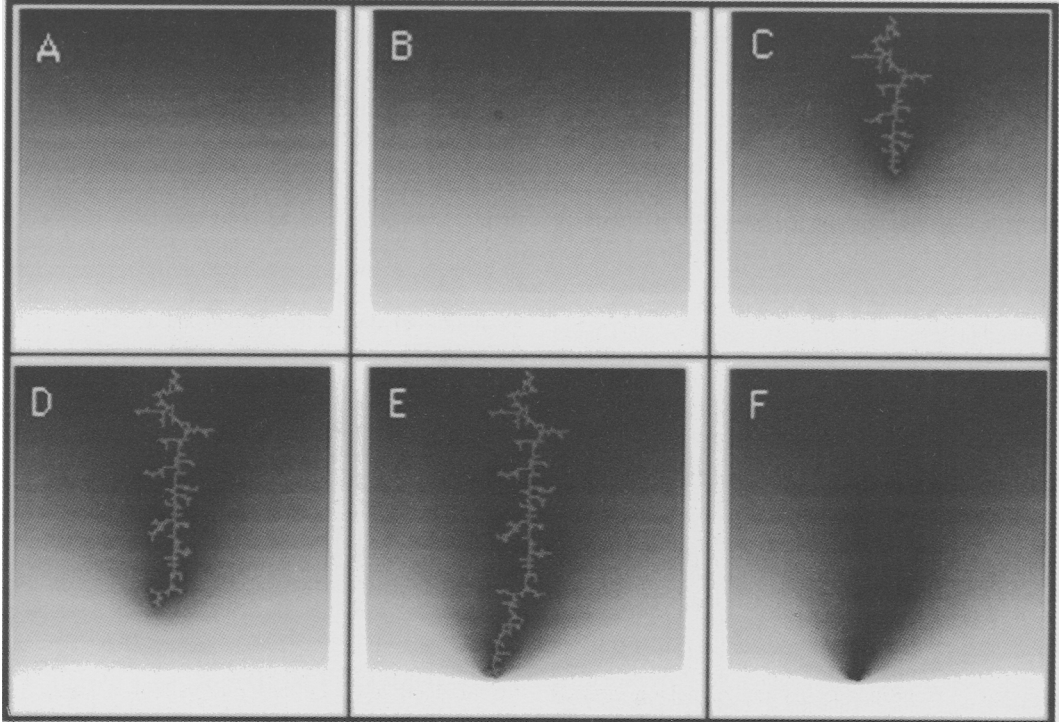


FIG. 3. (A) Potential field of a grid (100×100) constructed by iterating the discrete form of the Laplace equation (equation 6) with $\mu = 0$ (pure black) at the top boundary, $\mu = 1$ (pure white) at the lower boundary. For the case of thermally driven crystallization the black corresponds to low temperature and the white to high temperature. (B,C,D,E) Sequential images of the crystal growth simulation after many iterations (see text for details). The simulated crystal is light grey. (F) The potential field after the termination of growth. Note that in common with the real crystal of Fig. 1 the simulated pattern exhibits tip-splitting (branches grow off the main trunk) and that the branches never re-join.

Next, a new node is chosen for growth. For attachment, it must be a nearest-neighbour node to the nucleus. Actual far from equilibrium crystal growth occurs when a random-walking-growth-unit collides and adheres to a growth site of the crystal. Therefore we use a random process to choose among the nodes that are possible growth sites on the model crystal. This is accomplished by assigning a growth probability P_i , (e.g. Niemeyer *et al.*, 1984) to each possible growth node (i.e. all nearest neighbour nodes to the light grey growth array). The P_i values are calculated for each possible growth site from the field value of all their nearest neighbour nodes N , where α relates μ to the growth probabilities

$$P_i = \mu_i^\alpha * 1 / \sum_{i=1}^N \mu_i^\alpha. \quad (7)$$

Thus each possible growth site has a probability P_i of being selected. A random number generator is then

used to select one growth site among the various P_i 's. The selected node is assigned the value 0 and its pixel is illuminated light grey. The field is recalculated, new P_i 's determined, and a new nearest neighbour node is selected for growth, and so on.

Results

Figure 3*b,c,d,e* and *f* show the evolution of the simulated crystal (light grey) and the field (black, grey, and white) during growth. Note that the overall pattern produced in Fig. 3*e* is very similar to the morphology of the natural crystal documented in Fig. 1. The pattern of Fig. 3 is an un-filled structure characterized by three orders of branching (tip splitting). Note that in common with the crystal of Fig. 1 the pattern has dilation symmetry and the branches never intersect. The area within the branches remains un-filled because the gradient in the field between branches quickly becomes uniformly low in

accordance with equation 6 (Fig. 3c–e) making growth highly improbable. This occurs because interbranch areas are sandwiched between branches whose nodes have $\mu = 0$, thus the smoothing operation of equation 6 quickly reduces all node values between branches to near zero values. Therefore the interbranch nodes have only a small range in P_i and are not selected often by the random number generator. In contrast, nodes near the tips have a large range in P_i , and consequently are often selected. Branches shield their embayments from further growth. In real branching growth, the shielding occurs because the probability of a random walking growth species migrating deep within an embayment to cause infilling growth, without first colliding and sticking to a branch, is small. It is most probable that random walking growth species will collide and adhere to the structure near branch tips. Thus in the model the tips are associated with the highest range of field values and probabilities for growth. Model tip splitting occurs when a growth site is chosen that happens to be on the side of the tip of the main branch.

The imposed vertical gradient and the choice of exponent α in equation 7 of the simulation results in early arrest of horizontal branches. This is consistent with our observations of natural branching crystals wherein the prominent growth direction is normal to the cooling contact and side branching is of lesser extent. For instance, the two branches that protrude the most to the left in Fig. 3c are only slightly changed by the time-step of Fig. 3d and not at all between the steps of Figs. 3d and 3e. Figure 3f shows the final gradient after growth. Note how the field has been modified with respect to the initial conditions of Fig. 3a.

Discussion

Although the theoretical considerations and simulation presented are a simplification of physical reality, the analysis captures the essence of the far from equilibrium branching crystal growth and demonstrates that the interaction of thermal or concentration fields obeying the Laplace equation with a random selection rule results in branching growth. In effect we equate the temperature change directly to concentration change. We recognize that this is highly idealized and that the physics of the process must be complex. However we are encouraged by the results and believe that they support the approach.

The random selection rule is appropriate for both the simulation and a model of supercooled mineral growth. In the liquid, the motion of species is Brownian in the immediate vicinity of the cooling contact hence the selection of landing positions at the interface must involve a random process. Once initiated, branch propagation occurs through an

interplay of the field (that is itself modified by the growth) and the random motion of growth species. For real crystal growth the multiplicity of possible choices over the entire time of crystal growth is truly enormous. Presumably in the case of snowflakes, this leads to the old adage that no two are alike!

The choice of the exponent α in equation 7 was based on the results of Niemeyer *et al.*, (1984) who studied dielectric breakdown, a physical process that results in branching patterns (e.g. lightning) and can also be approximated by the Laplace equation. They demonstrated that dielectric breakdown in a gas is linearly related to the pattern growth probabilities, hence they used an exponent value = 1. Furthermore they suggest that a non-linear exponent is more likely relevant for solids, liquids and polymers. We have no knowledge of the microscopic relationships between the growth probability and the local field in a silicate melt. Therefore, based upon results of Niemeyer *et al.* (1984) (i.e. the suggested non-linear exponent for polymers) and because the image of Fig. 1 is strongly anisotropic we decided to use an exponent value of two for its simulation. Unlike dielectric breakdown real mineral growth incorporates anisotropy. The anisotropy of growth rate is related to the tendency for production of faceted morphologies which in itself is related to the entropy of fusion of the material (Kirkpatrick *et al.*, 1979; Jackson, 1958). Clearly we do not mean to suggest that *ad hoc* tuning of the probabilities is a rigorous way to account for mineral growth anisotropy. More work is required in order to gain a complete understanding of the effect of the interaction between crystal anisotropy and the growth probabilities on the morphology of branching crystals.

In the model the field is modified by the growth (cf. Fig. 3a and f). In the case of real far from equilibrium thermally driven growth the model predicts that the crystal must cool the environment, a counter-intuitive idea. The process whereby a crystal cools the environment from which it grows is termed constrained crystallization (Tiller, 1991). Constrained crystallization occurs during crystallization in sharp thermal gradients, or from stoichiometric melts wherein the thermal conductivity of the crystal is greater than the liquid and hence cooler. In contrast, crystals that grow freely from a high temperature multiply saturated silicate liquid having low thermal gradients will be very slightly hotter than their surroundings due to the release of latent heat, so called un-constrained crystallization. Constrained crystallization is a well known process in engineering, used to grow very pure crystals (Tiller, 1991). Moreover, Shore (1996) has demonstrated that the platy and branching olivine crystals (spinfex-texture) of Archaean ultramafic lavas (komatiites) developed because of this process. His calculations

show that the rate of heat transfer was faster through the olivine than the melt.

The fact that concentration must be a scalar quantity, i.e. an unstirred system, accords well with formation of the texture during devitrification and with the silicate melt experimental results of Kouchi *et al.* (1986). They showed that mineral textures formed in quickly cooled *and* stirred experimental charges are characterized as being more faceted than their identically cooled non-stirred counterparts. One expects stirring to destroy the steady state conditions (e.g. the relationship $\nabla^2 C \approx 0$) hence material is advected to the growing crystal and fuller crystals with faceted crystal morphologies would result. In our simulation this condition can be modelled and results in more compact morphologies although no facets arise because there are no rules in this simple model to account for surface effects.

Mixing environments are another place where one might expect similar branching growth to occur due to concentration gradients that obey the Laplace equation. Mixing of compositionally and hence thermally different viscous lavas, providing they are not vigorously stirred (i.e. turbulent), is a suitable environment, as is the juxtaposition of chemically different beds in a metamorphic environment. Also, according to Ben-Jacob and Garik (1990) the 'decorated' and irregular shape of snowflakes is due to the limited diffusion of water molecules from the gas phase into the crystal. This leads to the intriguing possibility that the solution given for Fick's second law may be more general for processes in the earth sciences, in that it may govern formation of branching mineral textures from sparse vapour and liquid phases.

In common with other branching phenomena, e.g. dielectric breakdown (Niemeyer *et al.*, 1984), lightning (Tsonis, 1991), viscous fingering during secondary recovery of petroleum, snowflake formation (Nittmann and Stanley, 1986), electrodeposition (Brady and Ball, 1984) and dissolution (Daccord and Lenormand, 1987) growth of branching minerals can also be due to the interaction of a steady-state gradient obeying the Laplace equation and the interaction of a random component. Thus the remarkable branching textures of minerals owe their organization to the interplay of the random landings of growth species on a crystal growing in an invariant gradient of chemical potential. Accordingly the growth must occur from solutions that are not vigorously agitated.

Acknowledgements

We are grateful for the support from the Natural Science and Engineering Research Council of Canada. Ivan L'Heureux of the Department of

Physics is thanked for his numerous useful comments and help. Mark Shore is thanked for introducing us to, and sharing his work on, the subject of constrained crystallization. The final version benefited greatly from the comments of an anonymous reviewer.

References

- Ben-Jacob, E. and Garik, P. (1990) The formation of patterns in non-equilibrium growth. *Nature*, **343**, 523–30.
- Brady, R.M. and Ball, R.C. (1984) Fractal growth of copper electrodeposits. *Nature*, **309**, 225–9.
- Bryan, W.B. (1972) Morphology of quench crystals in submarine basalts. *J. Geophys. Res.*, **77**, 5812–9.
- Carslaw, H.S. and Jaeger, J.C. (1959) *Conduction of Heat in Solids*, second edition. Oxford University Press, New York. 510 pp.
- Daccord, G. and Lenormand, R. (1987) Fractal patterns from chemical dissolution. *Nature*, **325**, 41–43.
- Donaldson, C.H. (1974) Olivine crystal types in Harrisitic Rocks of the Rhum Pluton and in Archean Spinifex Rocks. *Geol. Soc. Amer. Bull.*, **85**, 1721–6.
- Fowler, A.D., Jensen, L.S. and Péloquin, A.S. (1987) Varioles in Archean basalts: Products of spherulitic crystallization. *Can. Mineral.*, **25**, 275–89.
- Fowler, A.D., Stanley, H.E. and Daccord, G. (1989): Disequilibrium silicate mineral textures: fractal and non-fractal features. *Nature*, **341**, 134–8.
- Gould, H. and Tobochnik, J. (1987) *An Introduction to Computer Simulation Methods, Applications to Physical Systems Part 2*. Addison-Wesley, New York, 695 pp.
- Jackson, K.A. (1958) *Mechanisms of Growth, in Liquids, Metals and Solidification*. American Society of Metals, Cleveland, Ohio. 180 pp.
- Keith, H.D. and Padden F.J. Jr. (1963) A phenomenological theory of spherulite crystallization. *J. Appl. Phys.*, **34**, 2409–21.
- Kirkpatrick, R.J., Klein, L., Uhlmann, D.R. and Hays, J.F. (1979) Rates and processes of crystal growth in the system anorthite-albite. *J. Geophys. Res.*, **84**, 3671–6.
- Kouchi, A., Tsuchiyama, A. and Sunagawa, I. (1986) Effect of stirring on crystallization kinetics of basalt: texture and element partitioning. *Contrib. Mineral. Petrol.*, **93**, 429–38.
- Lofgren, G. (1974) An experimental study of plagioclase morphology: isothermal crystallization. *Amer. J. Sci.*, **274**, 243–73.
- Niemeyer, L., Pietronero, L. and Wiesmann, H.J. (1984) Fractal dimension of dielectric breakdown. *Phys. Rev. Lett.*, **52**, 1033–6.
- Nittmann, J. and Stanley, H.E. (1986) Tip splitting without interfacial tension and dendritic growth

- patterns arising from molecular anisotropy. *Nature*, **321**, 663–8.
- Shore, M. (1996) *Cooling and Crystallization of Komatiites*. Unpublished Ph.D. thesis, University of Ottawa.
- Tiller, W.A. (1991) *The Science of Crystallization: Macroscopic Phenomena and Defect Generation*. Cambridge University Press.
- Tsonis, A.A. (1991) A fractal study of dielectric breakdown in the atmosphere. In *Non-linear Variability in Geophysics Scaling and Fractals* (D. Schertzer and S. Lovejoy, eds.) Kluwer Academic Publishers, Dordrecht. 318 pp.

[Manuscript received 19 May 1995;
revised 20 July 1995]