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DETERMINATION OF LYAPOUNOV EXPONENTS TO CHARACTERIZE THE OSCILLATORY DISTRIBUTION OF TRACE ELEMENTS IN MINERALS

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ABSTRACT

Lyapounov exponents have been determined for patterns of oscillatory zoning as revealed by cathodoluminescence in zircon and apatite; values for the exponent range from +0.0011 to +0.0149. These positive values indicate that the zoning patterns are weakly chaotic, and that the development of the zoning was sensitive to the initial conditions of crystal growth. The Lyapounov exponent can be used as a quantitative measure of the zoning character and in comparisons of various patterns of zoning.

Keywords: attractors, oscillatory zoning, image analysis, Lyapounov exponent, trace element, chaos.

SOMMAIRE

Les exposants de Lyapounov ont été déterminés pour décrire la zonation oscillatoire du zircon et de l'apatite, telle que révélée par cathodoluminescence. L'exposant montre un intervalle de valeurs allant de +0.0011 à +0.0149. Ces valeurs positives montrent que le tracé de zonation est faiblement chaotique, et que son développement était sensible aux conditions initiales de croissance cristalline. L'utilisation des exposants de Lyapounov peut servir pour la mesure quantitative de la zonation et pour fins de comparaison des différents tracés de zonation.

(Traduit par la Rédaction)

Mots-clés: attracteurs, zonation oscillatoire, analyse d'image, exposant de Lyapounov, élément trace, chaos.

INTRODUCTION

Zoning, in one form or another, is a common characteristic of many minerals. From a purely aesthetic point of view, oscillatory zoning can in many cases be spectacular and colorful, and we are drawn to it because we intuitively believe that patterns of oscillatory zoning contain information about the growth history of minerals. Oscillatory zoning may be related to the distribution of major elements in minerals (Pearce *et al.* 1987, Jamtveit 1991, Yardley *et al.* 1991, Singer *et al.* 1993). Major-element oscillatory zoning can also be seen in synthetic minerals; a striking example of oscillatory zoning in $(Ba,Sr)SO_4$ was described by Putnis *et al.*(1992).

Oscillatory zoning can be related also to trace-element variations; although usually cryptic in nature, these patterns can be made visible using cathodoluminescence, differential interference or back-scattered electron microscopy. Figure 1 shows oscillatory variation in the intensity and color of cathodoluminescence; here, the zoning is related to the distribution of rare-earth elements (*REE*), Y and Sc in the crystal; it is distinct from any major-element variation, suggesting that the substitution of trace elements can be decoupled from major-element variation (*cf.* Halden *et al.* 1993).

Microbeam analytical techniques provide the spatial resolution necessary to detect small-scale differences in the major- *and* trace-element composition of individual zones in minerals (*cf.* Shimizu 1990, Halden *et al.* 1993, Fryer *et al.* 1995). Mineral growth takes time, and zones of differing chemistry provide us with an internal "stratigraphy" from the crystal's core to the rim, reflecting changes that occurred as the mineral grew. Other technical advances contributing to the analysis of zoning patterns include image analysis, which provides a convenient means of digitizing 2-D optical information and allowing systematic quantitative measurements of zone thickness, optical density, brightness and shape (Halden & Hawthorne 1993). These types of measurement were largely ignored, if not impractical, in the past.

Another approach in interpreting patterns of zoning is to model the physics of the growth process (*cf.* Allègre *et al.* 1981, Lasaga 1982, Wang & Merino

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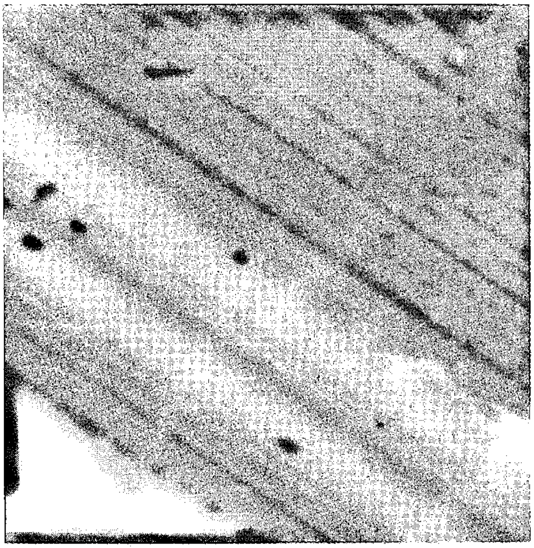

FIG. 1. Oscillatory zoning in zircon from the Silinjarvi carbonatite, Finland, as seen using cathodoluminescence. Zones tend to have sharp boundaries and are typically 20 – 50 μm wide; zones approaching the optical resolution of the microscope (*ca.* 1 μm) are just visible. Bright zones show yellow cathodoluminescence, which is probably the product of Y, Sc or rare-earth element incorporation in the zircon crystal.

1992, L'Heureux & Fowler 1996a, b). Using such models, the development of oscillatory patterns requires the coupling of at least two time-dependent variables through some sort of feedback mechanism. Models developed for major-element variation in feldspar (L'Heureux & Fowler 1996a, b) and trace-element variation in calcite (Wang & Merino 1992) can be made to show fairly regular periodic, aperiodic, damped and even chaotic patterns of zoning.

Attempts to describe zoning patterns usually resort to a qualitative descriptive terminology using such terms as "oscillatory" or "gradational". Oscillatory or gradational are terms that may refer to the general optical character of the pattern. On the other hand, "random" and "chaotic", while also conveying a qualitative feel for the complexity of the pattern, have quite precise quantitative meanings (*cf.* L'Heureux & Fowler 1996a, b, Halden & Hawthorne 1993). Previous work on the fractal character of oscillatory zoning in zircon suggests compositional repetition and zone-width-reflected repetition or periodicity in the processes contributing to mineral growth (Halden & Hawthorne 1993). The fractal character also suggests that the underlying mechanism for producing such patterns may be chaotic. If such were to be the case, then the dynamics of the crystal-growth mechanism could be represented in *phase space* as a *strange attractor*, and the growth history (or trajectory in phase space) could be quantified and characterized by the *Lyapounov exponent* for the pattern of oscillatory zoning (*cf.* Wolf *et al.* 1985). It is the objective of this paper to analyze patterns of oscillatory zoning in natural minerals made apparent by trace-element compositional variation and to provide a quantitative framework for describing and comparing of patterns of oscillatory zoning. A key consideration is that the method must facilitate comparison of model patterns of zoning and natural patterns; furthermore, the model should be accessible to petrologists in a general way.

MINERALS AS DYNAMICAL SYSTEMS

The relationship between a mineral and its surrounding environment can be described as a dynamical system where there is feedback between the mineral surface and its environment. As elements diffuse to a growing crystal, there should be a relationship between the concentration of an element in the liquid as a function of time $f(c,t)$ and concentration of the element in the mineral as a function of distance $f^*(c,x,)$; c, t and x denote concentration of an element, time and position, respectively, f is a function used to describe changing concentrations within the liquid, and f^* is a function used to describe changing concentrations within the crystal. If $f(c,t)$ is oscillatory, it is reasonable to expect $f^*(c,x)$ to be oscillatory (Halden & Hawthorne 1993). Moreover, if $f(c,t)$ is periodic or aperiodic, it is possible that $f^*(c,x)$ also can be periodic or aperiodic, and this relationship might also be extended to include random or chaotic behavior. If the growth rate of the crystal is constant (or is assumed to be constant) then the pattern of oscillatory zoning can be used in the form of a time series for subsequent analysis. If the growth rate changes, then it is necessary to understand the nature of the transformation between the space and time domains. L'Heureux & Fowler (1996a) have shown the effect of varying growth-rates on the development of zoning patterns; however, in the absence of experimental data on growth rates for many minerals, it is impossible at the moment to assess this (in any practical way) in natural samples.

A particularly useful description of dynamical systems with regard to attractors, phase space and Lyapounov exponents is given by Scott (1991) for oscillating chemical reactions. The trajectory of oscillatory chemical reactions in phase space may be used to characterize oscillatory patterns. If zoning patterns can be viewed as "orbits" in the chemical system describing a mineral's growth, then the time taken for one oscillation would be t, and the distance advanced in the crystal would be x. Any structure in the orbits of the chemical system would be seen potentially as serial correlations in the pattern of

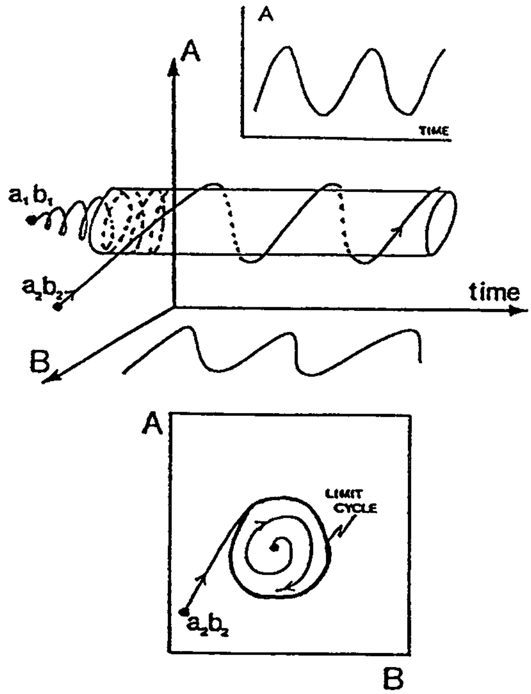

FIG. 2. Schematic phase space for two hypothetical compositional variables A and B. Two trajectories showing the evolution of a_1b_1 and a_2b_2 wind onto the surface of a cylinder. In an A *versus* B section, the cylinder defines a limit cycle. The oscillatory evolution of A or B can be seen in the projections onto the A *versus* time or B *versus* time planes (*cf.* Scott 1991, Fig. 1.5).

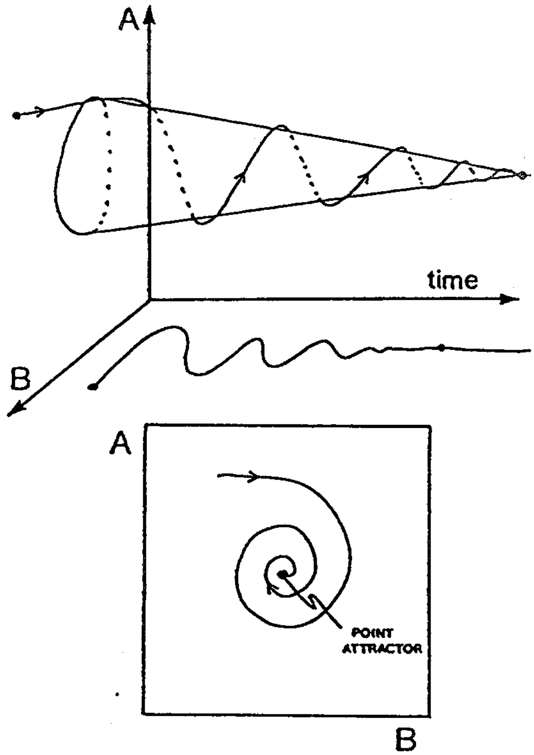

FIG. 3. Schematic phase space showing a dissipative system for two hypothetical compositional variables A and B. The trajectory winds onto the surface of a cone and evolves to a single point in the A *versus* B section; this point is called a point attractor.

oscillatory zoning. It is in this regard that the terms random, aperiodic, periodic or chaotic are subsequently of use in quantifying zoning patterns.

Using a three-dimensional phase space, a section containing time or distance can show oscillations. Figure 2 shows trajectories starting at points a_1b_1 and a_2b_2; a and b may represent the concentrations of two reacting species. The trajectories wind onto the surface of a cylinder from inside and outside the cylinder, respectively. In both cases, the concentrations evolve to the surface of the cylinder, which, when projected back onto the concentration (or phase) plane, describes a shape (in this example, a circle) called a limit cycle. The concentrations of a and b lie within the limit cycle, and as such the compositional trajectories describe a conservative system, *i.e.*, the system occupies a constant volume in phase space. Projections onto the A *versus* time and B *versus* time plane show the oscillatory character of the evolution of A and B.

A dissipative system is the other type of system of interest here. In such a system, the concentrations of A and B can still oscillate, but the amplitude of the oscillations will decrease. The concentrations of A or B will settle down to a constant value called a point attractor (Fig. 3). An attractor is "a point in phase space toward which a time history evolves as transients die out" (Turcotte 1992). Figure 4 is a cathodoluminescence image of oscillatory zoning in a zircon; although the underlying mechanism of crystal growth has not been described, oscillatory variations in the cathodoluminescence can be seen to settle down toward a more constant color. This may represent a point attractor in a system that could be used to describe this crystal's growth. Dissipative systems are characterized by having decreasing volumes in phase space. Such systems can have attractors including point attractors, but can also have chaotic and strange attractors that are associated with chaotic systems. A strange attractor is a fixed point in phase space about which orbits are chaotic; a system may be said to be chaotic if adjacent solutions to deterministic equations (that might describe crystal growth) diverge exponentially in phase space; as such, the system would have a positive Lyapounov exponent (*cf.* Turcotte 1992).

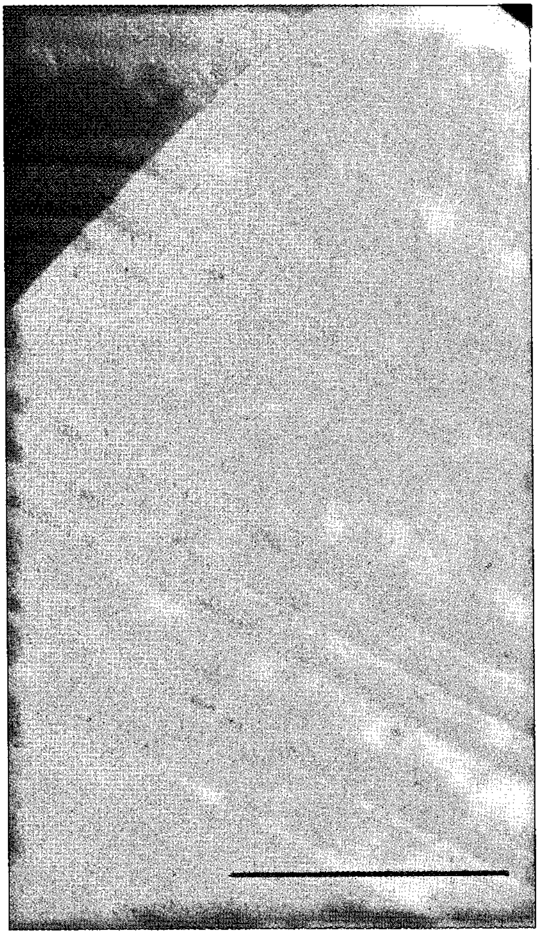

FIG. 4. Oscillatory zoning in a zircon crystal from Thailand, showing variations in cathodoluminescence (Royal Ontario Museum sample M 14788; scale bar is 1 mm). Oscillatory zones range in thickness down to a few µm. Toward the outside of the crystal (the edge is visible at the top right hand corner), there is a wide region (*ca.* 500 µm) where zoning appears to be dying out, which might be consistent with an interpretation that the system causing the zoning is dissipating.

IMAGE ANALYSIS

Minerals were viewed using a high-resolution black and white television camera connected to a Nikon microscope with a Technosyn cold-cathodoluminescence stage. A 20 kV, *ca.* 200 µA electron beam was used for sample bombardment. Images of oscillatory zoning were captured by a Kontron image-analysis system and then digitized. Intensity of light in the image is assigned a grey-level on a linear scale of 0 to 255, with 0 representing black and 255 white. To ensure even illumination in the images, some prior editing was usually required, particularly where the field of view included bright flaring connected with fractures in the mineral or black regions typical of the mounting medium. Such regions were selected and assigned a median grey-level from a grey-level histogram of the image and then the whole image was normalized to use the entire dynamic range of the grey-levels available. A traverse across the image, at right angles to the zoning, was then selected, and the grey-level in each pixel was written to an ascii file. The ascii file containing the data was then imported to DYNAMICAL SYSTEMS software (Schaffer *et al.* 1988).

CALCULATION OF THE LYAPOUNOV EXPONENT

A chaotic system is very sensitive to initial conditions. The important point here is that one set of initial conditions (expressed, for example, in terms of composition) may give rise to an oscillatory pattern that looks *very* different from a pattern derived from a set of initial conditions that is only *slightly* different. In such cases, the tendency might be to infer very different geological histories. Rather than doing this, an alternative is to examine and quantify the character of the zoning pattern, with the conception of it as a compositional trajectory in phase space. Here, the rate at which two trajectories (oscillatory patterns) evolve in phase space, or diverge from only slightly different initial conditions, is measured by the Lyapounov exponent. This is a quantitative measure of chaos.

To assess the character of an oscillatory pattern generated from coupled equations used to describe the growth of a mineral, the data series may be represented by $x_{i+1} = f(x_i)$; in this case the *Lyapounov exponent,* λ, is given by:

$$\lambda = \lim_{n\to\infty} (1/n)\sum \log_2|df/dx|$$

For a system to be chaotic, it must have a positive Lyapounov exponent, λ, measured in "bits per iteration": Scott (1991) provided a useful description of this unit. If the starting point in a data series is x_o, predicting future values $[f(x_o)]$ using a 16-bit analogue-to-digital converter with λ set to +0.5 would result in the loss of a ½ bit of information per iteration. After 8 iterations, 4 bits are lost, after 16 iterations, 8 bits are lost, such that only half of the predicted value for x_{16} later in the series will be significant. Attempting to predict x_{32} is where things break down, as with 16 bits lost, this value has zero significance. In the context of oscillatory zoning, this would correspond to an inability to predict the character of the 32nd zone on the basis of knowledge of the character of the zone at x_0, the first zone.

Considering a trajectory or zoning pattern in n-dimensional space, the first step is to choose a

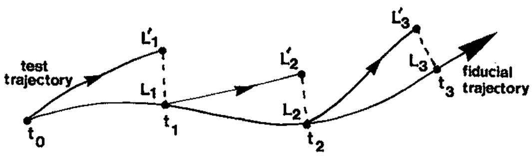

FIG. 5. Schematic illustration of how a Lyapounov exponent is determined. The distance between points on a test trajectory and the sample trajectory are measured and summed (*cf.* Scott 1991, Fig. 7.5).

starting point in the data set. Following this, the Euclidian distance between it and the closest point in the next orbit or zone is measured (Scott 1991, p. 190). This process is repeated by stepping through the trajectory or zoning profile and measuring the distance between pairs of evolving points, resulting in M pairs of points (L_i', L_i). If the distance between successive points is increasing, then the resulting exponent will be positive, and the Lyapounov exponent will be given by:

$$\lambda_1 = l/\Delta t \sum_0^{M-1} \log_2 \left(\frac{L'_k}{L_k}\right)$$

If λ is greater than 0, the pattern may be described as chaotic. If λ is less than 0, the pattern is not chaotic, *i.e.*, there is no divergence of trajectories in phase space. In the case where λ is less than 0, the pattern may still be oscillatory, showing regular or homogeneous oscillations. In this study, Δt, representing time-units, has been replaced by units of equal distance measured in pixels or micrometers. The length of the data series representing the oscillatory trajectory of the system is constant, but the length of the test trajectory can be varied (as long as one ensures that it exceeds the distance corresponding to one orbit or oscillation of the system). This method is used by Schaffer *et al.* (1988) to calculate Lyapounov exponents, and it is shown schematically in Figure 5.

SAMPLE PATTERNS FROM MINERALS

Figure 6 shows a grey-level pattern constructed from oscillatory cathodoluminescence in a zircon crystal from the Silinjarvi carbonatite, Finland. The pattern varies between two limiting grey-levels, which may represent attractors. There are also smaller-scale orbits in the system that do not reach the limits, and these contribute to the overall aperiodicity of the pattern. Lyapounov exponents for this pattern were calculated to be between +0.0085 and +0.0123, depending on the length of the test trajectory chosen. This pattern has positive values, which would indicate that the pattern is chaotic (Table 1). Table 1 also shows λ values obtained from artificially shortened data-series, in order to assess the effect that data series of different length (but the same underlying character) have on the calculation. These values are larger than

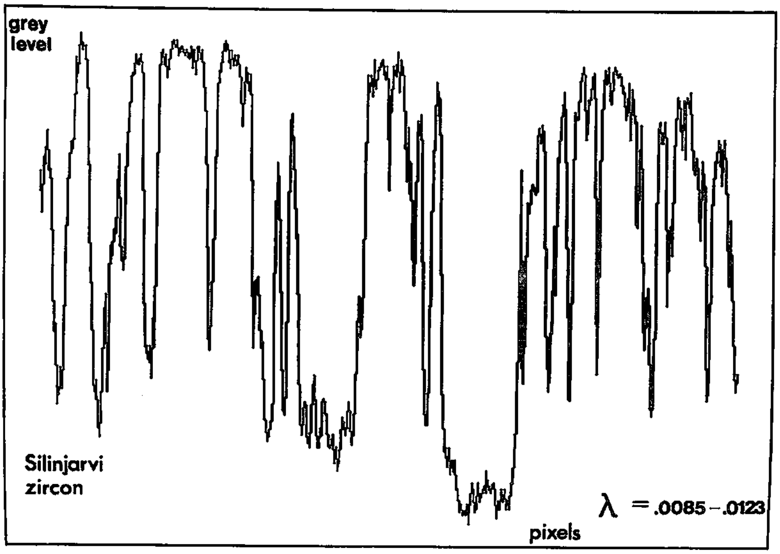

FIG. 6. Grey-level data collected along a traverse at right angles to zoning in a crystal of Silinjarvi zircon. The pattern is aperiodic, with values of λ between 0.0085 and 0.0123, depending upon the length of the test trajectory. These positive values indicate that this is a chaotic pattern.

TABLE 1. SUMMARY OF LYAPOUNOV EXPONENTS CALCULATED FOR THE ZONING PATTERN OBTAINED FROM THE SILINJARVI ZIRCON USING TEST TRAJECTORIES OF VARYING LENGTH

Length of test trajectory[1]	λ value for entire data series[2]	λ value for half data series[3]
30	0.0085	0.0270
20	0.0085	0.0211
15	0.0123	0.0220
10	0.0123	0.0220

[1] The length of the test trajectory is measured in pixel units. The lengths all exceed the minimum size for one orbit, *ca.* 5 pixels.
[2] The entire series is made up of 488 pixels (or data points); each pixel corresponds to approximately 1.6 micrometers, making a total length of about 780 micrometers.
[3] The data series was edited to contain 244 pixels.

for the full data-series, reflecting a slightly greater rate of divergence of the test and sample trajectories for the shorter data-series.

Oscillatory zoning can be seen in many mineral sections irrespective of orientation. The patterns shown in Figure 7 were collected from three different regions of a crystal of zircon from Thailand (Royal Museum of Ontario, sample #M14788). The crystal was cut perpendicular to the *c* axis, and the patterns were collected from the center of the crystal at right angles to the zoning and crystal faces, The patterns all have positive Lyapounov exponents, ranging from +0.0111 to +0.0149, indicating that the zoning is chaotic.

Figure 8 shows patterns collected from two crystals of apatite from Panasqueira, Portugal. Cathodoluminescence emissions occur in various intensities of yellow light. Semiquantitative μ-PIXE analysis showed differences in the Sr and rare-earth element content of the dark and light zones. Qualitatively, the patterns are slightly different from that seen in the zircon crystals; both patterns show regions where there is a general rise in the grey-level from one part of the traverse to another. Oscillatory peaks are superimposed on these sloping regions. If the slope were removed from the patterns, they would still show aperiodic oscillations between dark and light regions, suggesting either the presence of two attractors or constraint by a limit cycle. The values for the Lyapounov exponent obtained from these patterns range from +0.0011 to +0.0137.

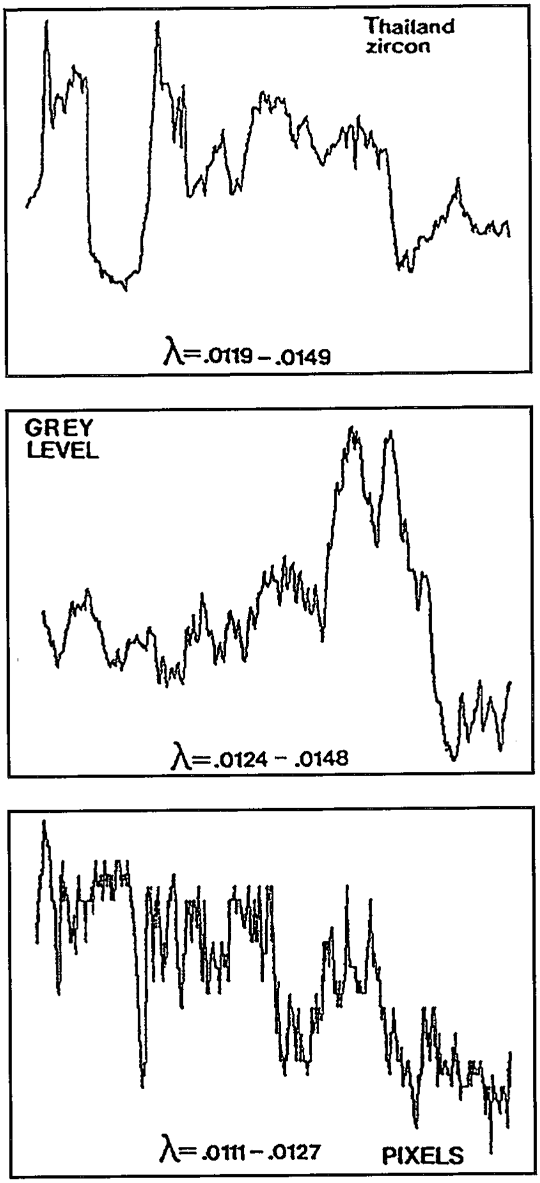

FIG. 7. Grey-level data collected along three traverses at right angles to zoning in a crystal of zircon from Thailand (ROM specimen #M 14788). The section from which these traverses were taken was cut at right angles to the *c* axis of the zircon crystal. The patterns all show similar positive values of λ, indicating that they are chaotic. The range shown for each pattern reflects the range of lengths used for the test trajectory.

DISCUSSION

A number of processes have been suggested to be responsible for the production of zoning in minerals. In igneous rocks, periodic changes in magma composition, pressure or temperature have been considered responsible. These might adequately explain some major-element variations in crystals of plagioclase, but they cannot reasonably explain the small-scale repeated aperiodic nature of trace-element variations in

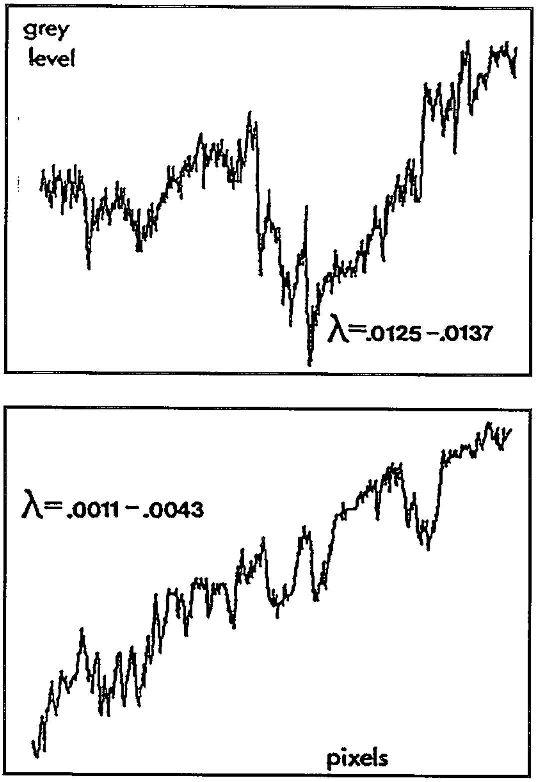

FIG. 8. Grey-level data collected along traverses from two crystals of Panasqueira apatite at right angles to the oscillatory zoning. Values of λ range between 0.0011 and 0.0053 and between 0.0125 and 0.0137 in the two patterns.

minerals like zircon and apatite. The magnitude of trace-element partitioning that is possible between two adjacent zones [in some cases the concentration difference can be orders of magnitude in a range of a few micrometers: *cf.* Halden *et al.* (1993), Shimizu (1990)] suggests that a process (or processes) other than large-scale changes within a magma chamber is responsible for trace-element zoning.

The zircon from Silinjarvi used in this study shows reaction embayments between distinct growth-regions, and all these regions are themselves zoned on a fine scale. It is possible that major-element variations in minerals (seen in association with new growth-regions separated by surfaces with reaction embayments or cross-cutting zones) provide a record of larger-scale variations in magma chemistry, whereas fine-scale oscillatory zoning reflects local feedback between the mineral's surface and the adjacent growth-medium (*cf.* Wang & Merino 1993).

In sedimentary rocks, zoned carbonate minerals are common in diagenetic cements. Complicated patterns of oscillatory zoning (as seen by cathodoluminescence microscopy) may be seen in sparry calcite in closely spaced vugs, where the general character of the zoning history is common, but the details of the zoning pattern appear different. In such cases, Emery & Marshall (1989) suggested that even though chemical analyses of such zones have improved, the mechanism that produces such zoning patterns is poorly understood. The proximity of the vugs in many limestones would argue for a similar diagenetic history, for example, the same history of fluid percolation, whereas differences in the patterns of zoning have to be explained by some other mechanism. It is possible that the development of the zoning pattern is sensitive to local conditions within a particular vug. In metamorphic and hydrothermally modified rocks, there is a similar problem where zoning is linked to fluid migration, but closely spaced minerals have subtly different patterns of zoning.

During mineral growth, the various elements making up a mineral will have to be transported to the mineral surface. It is possible that the surface of the mineral behaves as an autocatalytic environment, promoting certain reactions at the phase boundary while inhibiting others. Reactions would be coupled to the local environment, and oscillatory variations in the concentration of species might be expected (*cf.* Merkin *et al.* 1986). Considering the range of possible trace-element substitutions in minerals such as zircon and apatite, the problem might seem intractable. However, a large number of compositional variables (or dimensions within which the growth dynamics can be analyzed) is likely to more closely define the system or environment of mineral growth.

There are still a number of general questions that have to be addressed. How does one define the initial conditions of a system, particularly with regard to initial concentrations? Because chaos is associated with sensitivity to initial conditions, different patterns of chaotic zoning can be produced with only slight changes in initial conditions. This issue is addressed by L'Heureux & Fowler (1996a), where they describe the conditions that would necessary to produce chaotic zoning in plagioclase. The petrological problem is now how to look for, and recognize, chaos in natural minerals. In addition, it would be useful to consider what conditions might produce chaotic zoning in one mineral species and ask whether these conditions would produce similar zoning in other minerals.

In this study, based on the Lyapounov exponents estimated for the various patterns of zoning, it would appear that the patterns of oscillatory zoning seen by cathodoluminescence in zircon and apatite are chaotic. The values obtained, though positive, are only just slightly greater than zero, and one might ask if such values are significant. Considering that few patterns have been analyzed in this way, this situation is difficult to assess. However, in comparing values, it is worth noting that values for the Lyapounov exponent for the Belousov–Zhabotinskii reaction [a bromate-ion-driven oscillatory chemical reaction involving the oxidation of Ce^{3+} to Ce^{4+}; Field (1985)] are of a similar magnitude (0.0054 ± 0.005; Wolf *et al.* 1985) and are described by Scott (1991) to be possibly typical of "weakly" chaotic data. The Belousov–Zhabotinskii reaction can be explained in a stepwise mechanistic fashion. It involves ten reaction steps, each with a different rate-constant (*cf.* Scott 1991). If, in the case of the zircon, the coupled substitution of $P^{5+} + REE^{3+} \rightleftharpoons Zr^{4+} + Si^{4+}$ explains the cathodoluminescence, then there are at least four reacting or diffusing species to consider. This is in addition to any intermediate reaction-complexes or larger-scale geological variables. A similar situation may exist for the incorporation of rare-earth elements in apatite. The underlying similarity in the mechanism of substitution is reflected in the Lyapounov exponents.

Clearly, the solution to the mechanism of trace-element-induced oscillatory zoning in minerals such as zircon and apatite is likely to be complicated. Viewed only from a numerical and modeling perspective, any system of two coupled variables can be made to produce an oscillatory signal. From a mineralogical perspective, it is necessary to understand the underlying dynamics of trace-element incorporation in a growing mineral, which numerical parameters in an equation have physical or chemical meaning in a geological context, and what information the quantitative character of patterns of oscillatory zoning from natural minerals tells about their environment of growth. Here, measurement of the Lyapounov coefficient provides a quantitative measure with which to compare and contrast the chaotic character of patterns of oscillatory zoning. Furthermore, the positive values suggest that the patterns are sensitive to initial conditions of mineral growth. The next step is to determine the physical and chemical character of the initial conditions.

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