*American Mineralogist, Volume 78, pages 1113–1116, 1993*

# LETTER

# The fractal geometry of oscillatory zoning in crystals: Application to zircon

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## Abstract

Spectral analysis provides a quantitative method for describing oscillatory zoning patterns (OZP) in crystals in terms of self-affine fractals. An OZP may be characterized by its fractal dimension, a quantitative measure of the nonrandom nature of the pattern. Any model of oscillatory crystallization must reproduce the quantitative characteristics (fractal dimension, compositional variations) of the observed OZP.

## Introduction

Oscillatory zoning patterns (OZP) are common in many rock-forming and accessory minerals, and yet we understand very little about the mechanisms by which such zoning develops. Indeed, we cannot yet adequately describe oscillatory zoning in crystals; we can analyze the chemical compositions of the various zones, but we have no general method for describing the pattern of zones that we observe. Various causes of oscillatory zoning have been suggested: (1) temporal variations in the composition of melt and conditions of growth; (2) variations in growth rate; (3) diffusion-controlled chemical feedback between the mineral and its environment. However, we cannot adequately test any specific model because we currently have no quantitative representation of the character of oscillatory zoning in crystals. This problem is addressed here.

## Experimental

Figure 1 shows a cathodoluminescence image of a zircon crystal from the Silinjarvi carbonatite, Finland (Puustinen, 1971). There are extensive oscillatory variations in green and yellow luminescence; the crystal is optically continuous in reflected, plane- and cross-polarized light. The thickness of the zones varies between ~5 and 400 μm, and contacts between zones are sharp. Preliminary spectroscopy on the yellow zones shows a broad band of intrinsic cathodoluminescence centered at ~560 nm, but there are no bands that can be associated with activator elements. Micro-PIXE (proton induced X-ray emission) analyses show (1) the yellow and green bands to have scandium contents of ~60 and ~100 ppm, respectively, and (2) there is no correlation between the scandium abundance and the Zr and Hf content of the zircon, suggesting that spatial variation of the scandium (and possibly other trace elements as well) is decoupled from any variation in the Zr and Hf content of the mineral (Halden et al., 1993).

Images of the zoning patterns were recorded using a high-resolution black and white T.V. camera and were processed with a Kontron IAS (image analysis system). To provide maximum resolution of the patterns, the total recorded variation in gray level (determined by the initial color variation) was normalized to take advantage of the full 256 gray levels available. The variation in gray level as a function of position is then a quantitative representation of the zoning pattern. Figure 1 shows the variation in gray level as a function of position along the traverse indicated. The distance units are equal sampling units along the traverse (measured in pixels, where 1 pixel ≈ 1.6 μm). It is possible to change either the magnification or the number of pixels used in sampling the image.

## Discussion

The OZP is complicated and might be described as chaotic or random. However, in a technical sense, these terms have different meanings, and it is not possible at an intuitive level to distinguish between them. It becomes necessary, therefore, to determine if there is any structure to the pattern. At time $t$, a composition $c$ will have crystallized at position $x$; at time $t + \delta t$, a composition $c + \delta c$ will have crystallized at position $x + \delta x$. If we can write an equation (or set of equations) relating $t$, $c$, and $x$, the behavior of $c$ as a function of $x$ should be related to the behavior of $c$ as a function of $t$ (without, at this time, specifying the Laplacian relating the two functions).

### Description of OZP in fractal terms

We usually describe geometrical objects (e.g., patterns) by their symmetry properties. Most familiar to us is the example of morphological forms of crystals, whereby a form is characterized by the distance- and angle-preserving spatial transformations that leave the form un-

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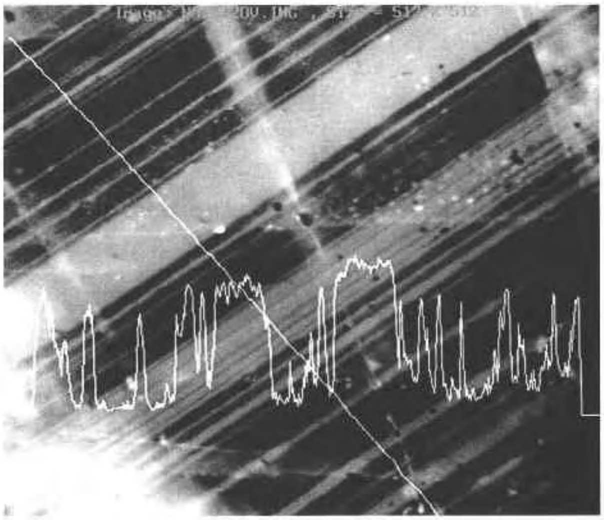

Fig. 1. Cathodoluminescence image of oscillatory zoning in a zircon crystal from Silinjarvi, Finland; dark regions show green luminescence, and light regions show pale yellow luminescence. The field of view is 1000 $\mu$m, and the zones vary in width from 5 to 150 $\mu$m. The overlay (white lines) shows (1) the traverse over which the information was collected (from top left to bottom right); (2) the gray-level variation with respect to position over the length of the traverse. The irregular bright region in the lower left of the picture is light scattered from a fracture outside the field of view.

changed. However, other sorts of transformations are possible, and these may be used to describe complex patterns such as that shown in Figure 1. It is here that the idea of fractal dimension is useful.

The term fractal is used to describe the power-law relationship between the number of objects and their linear size, where the fractal dimension is the value of the power in the fractal relationship. There are two kinds of fractal that are of interest: self-similar fractals and self-affine fractals. Self-similar fractals are those whose geometrical structure is isotropic and independent of scale; percolation clusters and diffusion aggregates would be typical examples. Self-affine fractals are nonisotropic, and different coordinates are scaled differently; in this case distance is something we can measure (e.g., zone width in pixels), but the relationship between distance and either time or crystal growth rate is unknown. Time and distance are different quantities, and they need not be scaled by the same factor (cf. Feder, 1988); rhythmic sediments and igneous layers are other examples of temporally and spatially variable geological layering (Fowler and Roach, 1993).

There are many natural examples of self-affine fractals (Turcotte, 1992; Stanley, 1991). Self-affine fractals may be described in the context of a random walk. If $N_1$ is the number of boxes with dimensions ($x_1$, $y_1$) and $N_2$ is the number of boxes with dimensions ($x_2 = rx_1$, $y_2 = r^H y_1$) that are needed to cover the walk, the walk is a fractal if $N_2/N_1 = r^{-D}$, where $D$ is the fractal dimension, and $r$ is a scaling factor. Mandelbrot and van Ness (1968) introduced $H$ as an exponent term, varying between 0 and 1, to characterize fractional Brownian motion (when $H$ = 0.5, we have the unique case of Brownian motion); $D = 2 - H$ for self-affine fractals (Feder, 1988; Turcotte, 1992). A self-affine fractal in two-D space satisfies the condition that $f(rx, r^H y)$ is statistically similar to $f(x, y)$ (Turcotte, 1992). Our interest here is the scaling relationship between distance and gray level, and we now deal with the problem of determining the fractal dimension by means of spectral analysis.

#### Spectral analysis of the pattern

The gray-level variation with respect to distance is amenable to spectral analysis (cf. Turcotte, 1992, chapter 7), a method of analyzing a single-variable function with respect to time; in this particular case, we are analyzing a single variable (gray level) with respect to distance, but the basic mathematics is the same. The problem is to determine if there is a relationship between the gray level at position $x$ and the gray level at position $x + \delta x$. Thus, as $\delta x$ increases, we have to assess the relationship (or serial correlation) between the gray levels of successive zones. A power dependence between gray level and distance would allow us to describe the pattern as fractal. Where the width, gray level, and recurrence of zones are totally unrelated, we would expect to see a Gaussian distribution of gray levels about the mean value; such a pattern could then be described as white noise.

A histogram of gray levels from Figure 1 shows that the distribution is bimodal (Fig. 2a). The next step in the spectral analysis is to take the Fourier transform of the original data. The resulting power spectrum (Fig. 2b) is not flat, indicating that the pattern is not Gaussian white noise. On the $f$ axis, peaks occur at approximately 2, 8, 12, and 24, with other possible peaks at 17, 33, and 40; the quantity $f$ is the length scale at specific values for which there is information in the spectrum. The log of spectral density (log $S_f$) for each value of $f$ is plotted against log $f$ in Figure 2c. A characteristic of self-affine fractals is a decreasing linear dependence between the log of the length scale used to measure the pattern and the log of the statistical average of a property of interest (in this case, gray level). The slope ($-\beta$) of a linear regression for this data is $-1.68$, and the fractal dimension ($D$, where $\beta = 5 - 2D$) is 1.66; thus $H = 0.34$. This process was repeated for a number of patterns, some at different magnifications, some from different areas on the crystal, and others where two images were combined to give a longer pattern; the resulting fractal dimensions ranged from 1.58 to 1.66. This value of $D$ falls within the range characteristic of fractional Brownian motion ($1 < D < 2$; Turcotte, 1992); this value shows that the zoning pattern is nonrandom.

#### Minerals as dynamic systems

The diffusion of elements to a growing crystal results in a relationship between $f(c, t)$ and $f(c, x)$; neither needs to be linear functions, and, as such, the mineral and its environment may be viewed as a dynamic system (e.g., Ortoleva, 1990). The limiting cases for such a system are (1) where $\delta c/\delta t$ and $\delta c/\delta x$ are constants, and (2) where they are nonlinear functions. Where element diffusion and crystal growth can be linked to coupled chemical reactions or metastable reaction products, the character of a zoning pattern is a function of $\delta c/\delta t$ and $\delta c/\delta x$; if $f(c, t)$ is nonrandom, $f(c, x)$ is likely to be nonrandom.

Feder (1988) and Mandelbrot and van Ness (1968) describe Brownian processes as having $H = 0.5$. Fractional Brownian process may have values of $H$ in the range 0 to 1 where $H \neq 0.5$. Where values of $H$ are in the range 0.5 to 1, a system is said to show persistent behavior. Feder (1988) described persistence in the context of ocean wave height, where if the wave height has been increasing for a period of time $t$, it will have a tendency to increase for a similar period. Antipersistent behavior (where $0 < H < 0.5$) may be characterized as a tendency to show decreasing values following previously increasing values. With reference to the zoning pattern, $H = 2 - D$ so $H = 0.34$, this is indicative of antipersistent behavior. Therefore the zoning pattern has a tendency to show bright luminescent zones occurring after zones of darker luminescence on similar length scales. A consequence of describing this particular zoning pattern as being antipersistent is that during crystal growth, after the surface has incorporated the trace elements connected with the bright luminescence, there is a tendency for the surface to reject the elements responsible for the bright luminescence; the tendency to accept a particular element followed by a tendency to reject it is occurring over similar length scales or perhaps growth increments.

The fractal dimension of the pattern is a quantitative measure of the nonrandomness of the zoning pattern and emphasizes the need to develop a model for crystal growth with the requirement that the model predict an oscillatory zoning pattern with the same fractal characteristics as the observed pattern. A component of such a model, for a case like the one described here, is that it should incorporate antipersistent behavior or a tendency to reject certain elements at the crystal surface after having accepted them.

## Conclusions

The fractal dimension of an oscillatory zoning pattern (OZP) provides a quantitative description of oscillatory zoning in a crystal. Any quantitative (or mechanistic) model of crystallization for an oscillatory-zoned mineral must produce a zoning pattern with the same fractal dimension as that of the observed pattern.

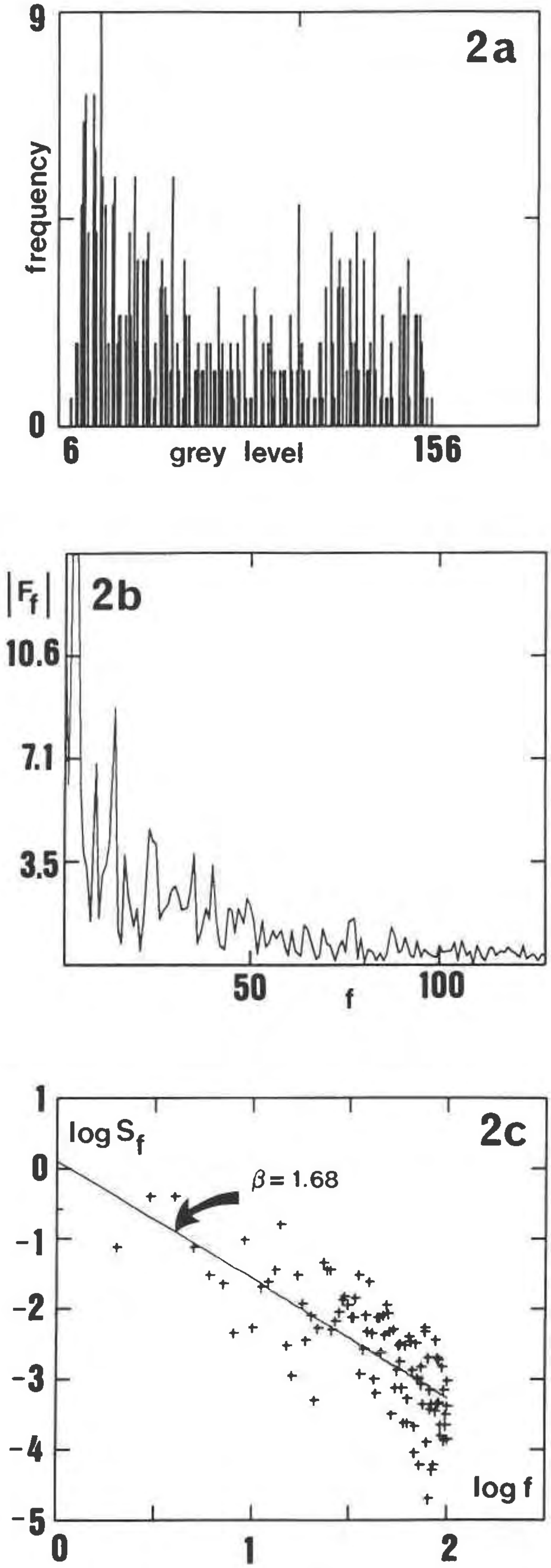


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Fig. 2. (**a**) Histogram of gray levels showing bimodal distribution; (**b**) power spectrum of gray-level variation; on the $f$(length scale) axis, peaks occur at approximately 2, 8, 12, and 24, with other possible peaks at 17, 33, and 40; (**c**) log spectral density ($S_f$) vs. log $f$; a regression line through the data has a slope ($\beta$) of 1.68.

## Acknowledgments

This work was supported by NSERC grants to N.M.H. and F.C.H. We thank Roger Mason for providing us with preliminary results of cathodoluminescence spectroscopy on this zircon sample. We also thank Tony Fowler, Herb Shaw, and an anonymous reviewer for their constructive criticism of an earlier version of this manuscript.

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Manuscript received June 14, 1993
Manuscript Accepted August 18, 1993