PERIODICO di MINERALOGIA established in 1930 An International Journal of MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY, ORE DEPOSITS, PETROLOGY, VOLCANOLOGY and applied topics on Environment, Archaeometry and Cultural Heritage

## Time series to petrogenesis: analysis of oscillatory zoning patterns in plagioclase crystals from lava flows

DIEGO PERUGINI<sup>1\*</sup>, MAX LITTLE<sup>2</sup> and GIAMPIERO POLI<sup>1</sup>

 <sup>1</sup> Dipartimento di Scienze della Terra, Università degli Studi di Perugia, Piazza Università, 06100, Perugia, Italy
<sup>2</sup> Systems Analysis, Modelling and Prediction Group, Department of Engineering Science, Oxford University, United Kingdom

ABSTRACT. — In this contribution we present preliminary results of analyses of plagioclase oscillatory zoning from three different lava flows cropping out on the island of Capraia (Tuscan Archipelago, Italy) with the aim of understanding the causes of the oscillatory zoning. Analysis are performed using a new method that combines microanalysis with image analysis and allows us to extract compositional time series with high spatial resolution along the zoning profiles. Compositional time series are analysed by the Detrended Fluctuation Analysis (DFA) method and results indicate that most zoning profiles in the studied lava flows can be regarded as having the property of 1/f-noise. By using a simple dynamical system, the logistic map, it is shown that this property can be attributed to selforganized criticality, i.e. a feature typical of systems lying at the boundary between stability and chaos. It is suggested that the statistical properties of plagioclase oscillatory zoning may be explained by continuous restructuring of flow fields in the magmatic system due to variations of the geometrical configuration in which the magmatic processes occurred at different times. It is suggested that analyses of compositional time series extracted from plagioclase crystals may be used as an additional petrological tool to better

understand the complex processes occurring in magmatic systems.

KEY WORDS: Lava Flow, Plagioclase Crystals, Oscillatory Zoning, Concentration Patterns, Time Series, Detrended Fluctuation Analysis (DFA), Nonlinear Dynamics.

RIASSUNTO. — In questo lavoro vengono presentati i dati ottenuti dall'analisi di zonature oscillanti in cristalli di plagioclasio provenienti da tre diverse colate laviche eruttate sull'isola di Capraia (Arcipelago Toscano, Italia) con lo scopo di capire le cause che hanno portato alla formazione di tali zonature. Le analisi sono state condotte utilizzando un nuovo metodo che combina microanalisi e analisi d'immagine al fine di estrarre serie composizionali attraverso le zonature oscillanti con elevata risoluzione spaziale. Le serie composizionali sono state analizzate utilizzando una tecnica nota come 'Detrended Fluctuation Analysis' (DFA) e i risultati hanno mostrato che la maggior parte delle zonature hanno caratteristiche tipiche di '1/f-noise'. Attraverso l'utilizzo di un semplice sistema dinamico, la mappa logistica, viene mostrato che queste caratteristiche possono essere attribuite all'azione di 'self-organized criticality', una caratteristica tipica di sistemi dinamici che giacciono al confine fra stabilità e caos. Viene ipotizzato che le caratteristiche di '1/f-noise'

<sup>\*</sup> Corresponding author, Tel.: 075 585 2652 Fax: 075 585 2603 e-mail: diegop@unipg.it

nei plagioclasi studiati possono essere spiegate considerando una ristrutturazione continua dei campi di flusso nel sistema magmatico associata a variazioni geometriche dell'ambiente in cui avviene il processo magmatico. I risultati presentati in questo lavoro mostrano che l'analisi di serie composizionali estratte dalle zonature oscillanti in cristalli di plagioclasio può essere utilizzata come uno strumento petrologico aggiuntivo per meglio comprendere i complessi processi che avvengono all'interno delle masse magmatiche.

KEY WORDS: Flussi Lavici, Plagioclasi, Zonature Oscillanti, Serie Composizionali, Detrended Fluctuation Analysis (DFA), Dinamiche non Lineari.

### **1. INTRODUCTION**

Mineral phases record the processes occurring in the environment during their growth as compositional zones and, hence, they offer the opportunity to reconstruct the history of the petrogenetic system by monitoring compositional variations across crystals. For instance, some authors have shown that oscillatory zoning in zircons displays all the typical properties of deterministic chaos, thus allowing the acquisition of information about the processes operating during mineral growth that would otherwise be inaccessible to conventional petrological techniques (e.g. Halden and Hawthorne 1993; Halden 1996; Holten *et al.* 1997; Hoskin 2000).

Oscillatory zoning is also shown magnificently by plagioclase crystals in both plutonic and volcanic rocks (e.g. Anderson 1984; Pearce and Kolisnik 1990; Ginibre *et al.* 2002; Wallace and Bergantz 2002). The fact that plagioclase is a common mineralogical phase in most magmas attracted the attention of many researchers whose efforts have been focused on deciphering the information contained in the oscillatory zoning to understand both the volcanological and petrological evolution of magmatic systems (e.g. Blundy and Shimizu 1991; Davidson and Tepley 1997; Stewart and Fowler 2001; Couch *et al.* 2001).

Oscillatory zoning in plagioclase crystals has been studied by a variety of methods including optical analysis, Nomarski interference imaging, Back-Scattered Electron images, and microanalysis (e.g. Pearce and Kolisnik 1990; Higman and Pearce 1993; Ginibre *et al.* 2002), and results of these studies indicate that oscillatory zoning is the result of the development of complex kinetics at the crystal/melt interface (e.g. Haase *et al.* 1980; Ortoleva et al. 1987). Higman and Pearce (1993) extracted time series by measuring the variation of zone thickness along the oscillatory pattern and suggested that thickness sequences exhibited chaotic behaviour. In addition, numerical simulations based on chaotic dynamical systems (e.g. Higman and Pearce 1993; L'Heureux and Fowler 1996; Perugini *et al.*, 2005) have shown striking agreement between natural and simulated plagioclases.

In this contribution we present preliminary results of analyses of plagioclase oscillatory zoning from three different lava flows cropping out on the island of Capraia (Italy) with the aim of understanding the processes leading to the oscillatory zoning. In particular, compositional time series have been extracted from the oscillatory zoning and have been quantitatively analyzed by using the Detrended Fluctuation Analysis method. It is suggested that analyses of compositional time series extracted from plagioclase crystals may be used as an additional petrological tool to better understand the complex processes occurring in magmatic systems.

### 2. OSCILLATORY ZONING IN PLAGIOCLASE CRYSTALS FROM CAPRAIA (ITALY)

The island of Capraia is the westernmost of the seven islands that constitute the Tuscan Archipelago. The geo-volcanological history of Capraia is related to that of the Sardinia-Corsica massif and its rotation, that led to the continental collision and the Apeninic orogenesis. The genesis of Capraia occurred during Upper Miocene-Pliocene over three main magmatic cycles at 6.9, 4.5, and 3.5 Ma (e.g. Barberi *et al.* 1986). The island resulted from the subsequent extension of the area after the collisional event and the eruption of magmas along several fractures. Capraia volcano consists of lava flows and scarce pyroclastic deposits with high-potassium (HK)-calc-alkaline affinity (e.g. Prosperini 1993; Poli and Perugini 2003). A few

lava flows having shoshonitic affinities are also present.

In this contribution we study oscillatory zoning of plagioclase crystals occurring in three lava flows with (HK)-calc-alkaline affinity belonging to Monte Campanile and Porto (CPS), San Rocco and Piano (SR), and Laghetto (LG) volcanites. CPS lava flow is a dacite with a seriate holocrystalline porphyritic texture with high phenocrysts contents (33-50%) composed of plagioclase, K-feldspar, clinopyroxene, rare orthopyroxene, biotite, Fe-Ti oxides, and apatite. SR is a porphyritc andesite with 17-28 % phenocryst content, made up of plagioclase, clinopyroxene, olivine and biotite; apatite, titanite, zircon, ilmenite, magnetite, and chromite are present as accessory minerals. LG lava flow is a dacite and shows a holocrystalline porphyritic texture with 22-57% phenocryst contents constituted by plagioclase, K-feldspar, clinopyroxene, biotite; accessory minerals are apatite, zircon, titanite, and Fe-Ti oxide.

Petrological models for these rocks are based on petrographic, geochemical, and isotope data (Prosperini 1993; Poli and Perugini 2003) and suggest evolutionary processes starting from an HK-calc-alkaline magma evolving by mixing plus fractional crystallization with mafic magmas having different geochemical affinity in a shallow magma chamber before eruption. More details about geological setting, geochemical features, and petrogenetic hypothesis for Capraia rocks can be found in Poli & Perugini (2003).

In all the studied lava flows plagioclase crystals display very well developed zoning patterns. Shown in Figure 1 are some examples of zoned plagioclases, constituting a large number of zones recognizable under both optical (Fig. 1A) and scanning electron microscope (Fig. 1B). These different zones are characterized by variable enrichment in the An/Ab ratio as evidenced by back-scattered electron micrographs (Fig. 1B) where zones enriched in the An component are light grey, whereas, dark colored zones correspond to enrichments in the Ab component.

Thin sections of a number of rock samples from each lava flow were analyzed under both optical and scanning electron microscope to study the oscillatory zoning of plagioclase. According to suggestions of Pearce and Kolisnik (1990), only properly oriented crystals, euhedral, nearly centercut with zoning perpendicular to the plane of section were analyzed.

### 3. ANALYSIS OF PLAGIOCLASES

### 3.1 Extraction of compositional time series from plagioclase oscillatory zoning

Ginibre *et al.* (2002) have shown that it is possible to calibrate the grey intensity of plagioclase zones on back-scattered electron (BSE) micrographs with their *An* content; in particular, there is a linear relationship between grey intensity and *An* content. This gives the opportunity to extract mol.% *An* compositional time series with high spatial



Fig. 1 – Examples of oscillatory zoning in plagioclase crystals from the studied lava flows: A) cross polarized optical micrographs of a crystal from the CPS lava flow; B) back-scattered electron micrograph of a crystal from the SR lava flow.

resolution and offers the possibility of studying oscillatory zoning in great detail (Ginibre et al. 2002; Wallace and Bergantz 2002). The technique developed by Ginibre et al. (2002) was used to extract compositional sequences from oscillatory zoning of plagioclase crystals occurring in the three studied lava flows. Throughout this work the terms *compositional time series* or simply time series will be used to indicate compositional sequences representing plagioclase oscillatory zonings. A Philips X1-30 scanning electron microscope and integrated XI-30 software has been utilized to acquire BSE images with an acceleration voltage of 15kV and a focused beam current of 20nA. To reduce the signal/background ratio, 10-15 images of the same crystal have been accumulated. Extraction of compositional series has been performed along a single line in order to avoid averaging different compositions. One compositional time series consisting of ca. 300 data points has been extracted for each plagioclase crystal. Determination of anorthite content has been performed by wavelength-dispersive analysis by using a JEOL JXA-8600 electron microprobe equipped with four WDS spectrometers. Accelerating voltage and beam current were 15kV and 10*nA*, respectively, with variable counting times. More details on analytical conditions can be found in Vaggelli *et al.* (1999).

Figure 2A shows an example of a crystal in which electron microprobe analysis as been performed, whereas Figure 2B displays the value of grey intensity of the image plotted against the corresponding measured concentration of *An*. As first shown by Ginibre *et al.* (2002), a good linear correlation between these two parameters is found. The equation of best fit line was used to extract compositional time series representing the variation of An along the oscillatory zoning (Fig. 3A and B).

Some representative time series from the three lava flows are reported in Figure 4. Although at first sight each time series appears different, it is worth noting that most time series from the three lava flows share a common feature: segments of zoning in which small variation of the observed *An* content are followed by sharp increments of *An*. This kind of fluctuation is repeated continuously along each time series suggesting that a common process may have acted to generate the observed compositional patterns. However, qualitative observations cannot give us detailed information



Fig. 2 – A) Example of back-scattered electron micrograph of a plagioclase crystal analyzed by electron microprobe (analyzed points indicated by white stars); B) linear correlation between grey intensity of analyzed points and mol.% An content. In the graph the equation of the linear fitting is also reported.



Fig. 3 – A) back-scattered electron micrograph of a plagioclase crystal from which the concentration profile is extracted (white line); B) concentration series along the transect  $\alpha$ - $\beta$  in A. In the graph are reported both the grey intensity and the mol. % An variation.

about the possible processes responsible for the formation oscillatory zoning and quantitative analysis needs to be performed.

# 3.2 Detrended Fluctuation Analysis (DFA) of compositional time series

In order to perform quantitative analyses of the variability of oscillatory zoning exhibited by studied plagioclase crystals the so-called Detrended Fluctuation Analysis (DFA) method has been utilised (e.g. Kantelhardt *et al.*, 2001; Hu *et al.*, 2001). In general, DFA is a statistical technique commonly used for detecting correlations in nonstationary sequences and it will be used here to explore its applicability to quantify the oscillatory zoning patterns of plagioclase crystals. In this section we describe the standard DFA method which involves the following steps:

For a given sequence (i.e. a compositional time series extracted from the oscillatory zoning; Fig. 5A) y(i), i = 1, ..., N, where *N* is the length of the time series, compute the sequence mean  $\bar{y} = \frac{1}{N} \sum_{j=1}^{n} y(i)$ . Then, an integrated sequence x(i) = 1, ..., N is obtained (Fig. 5B) as follows:

$$x(i) = \sum_{j=1}^{l} [y(i) - \bar{y}], i = 1, ..., N$$

Divide the integrated sequence x(i) into intervals of equal size *n* (Fig. 5C). A function is used to interpolate the sequence in each interval. Commonly, a linear function is utilised in the fitting procedure and, accordingly, in this paper a linear function, denoted as  $x_{lin}$  (*i*,*n*), is used. The interpolating curve  $x_{lin}$  (*i*,*n*) represents the local trend in each interval (Fig. 5C).

Compute the fluctuation sequence (Fig. 5D) as

$$z(i,n) = x(i) - x_{lin} (i;n), i = 1, ..., N$$

The fluctuation function F(n) is computed as the root-mean squared value of the sequence z(i,n):

$$F(n) = \sqrt{\frac{1}{N} \sum_{j=1}^{n} z(i,n)^2}$$

Repeat the above procedure for a broad range of interval lengths *n*. According to the recommendations made by Peng *et al.* (1994), the following range  $n_{min} = 4$  and  $n_{max} = n / 4$  has been selected.

When the sequence follows a scaling law, a power-law behaviour for the fluctuation function F(n) is observed:

$$F(n) = n^{\alpha}$$

where  $\alpha$  is called the scaling exponent, which is calculated as the slope of a plot of log[F(n)] versus log(n) (Fig. 6).

The value of parameter  $\alpha$  can be related to the type of time-delayed autocorrelation exhibited by



Fig. 4 – Representative compositional time series extracted from plagioclase oscillatory zoning from the three studied lava flows. A-B) San Rocco and Piano lava flow; C-D) Campanile and Porto lava flow; E-F) Laghetto lava flow.



Fig. 5 – Main steps of the Detrended Fluctuation Analysis used to quantify the oscillatory zoning in plagioclase crystals applied to the compositional time series shown in Figure 3B. See text for details.



Fig. 6 – Graph showing the variation of  $\log[F(n)]$  versus  $\log(n)$  for the time series reported in Figure 5A. Scaling exponent  $\alpha$  is calculated as the slope of linear fitting of data.

analysed time series. In the case of a time series having zero autocorrelations for time delays greater than zero, the detrended fluctuation analysis displays properties of standard white noise with  $\alpha = 0.5$ . On the other hand, if  $\alpha < 0.5$ the autocorrelations in the time series are antipersistent (i.e. an increment is very likely to be followed by a decrement, and vice versa), and if  $\alpha > 0.5$  the autocorrelations in the time series are persistent (i.e. an increment is very likely to be followed by and increment, and vice versa). The values  $\alpha = 1.5$  and 1.0 correspond to Brownian motion and 1/f-noise, respectively. A value  $\alpha >$ 0.5 corresponds to long-range autocorrelations. More detailed discussions about the meaning of parameter  $\alpha$  is beyond the scope of this paper, and can be found in several articles (e.g. Kantelhardt et al., 2001; Hu et al., 2001; Peng et al., 1994). Here it suffices to say that the value of  $\alpha$  quantifies the type of autocorrelation in the compositional time series and, thus, the DFA may help to identify the growth history of plagioclase crystals.

### 4. RESULTS AND DISCUSSION

The value of the scaling exponent  $\alpha$  has been estimated for all compositional time series extracted from plagioclase oscillatory zoning from the three studied lava flows. Results are summarized in the graph of Figure 7 where the ranges of  $\alpha$  values are plotted against the average SiO<sub>2</sub> content of each lava flow. Note that using any other major element as horizontal axis does not influence presented results. The graph shows that scaling exponents  $\alpha$ for plagioclases from all lava flows display a quite restricted variability with average values around  $\alpha$ ~ 1.0. It is noteworthy that no oscillatory zoning was found to be compatible with white noise ( $\alpha$ = 0.5) or Brownian motion ( $\alpha = 1.5$ ). On the contrary, most  $\alpha$  values are close to one indicating that oscillatory zoning can be regarded as having properties of 1/f-noise. As suggested above, and as indicated by DFA, the fact that plagioclase crystals from all three lava flow display this common feature argues in favour of the hypothesis



Fig. 7 – Graph showing the variability of scaling exponents  $\alpha$  estimated for plagioclase oscillatory zonings from the three lava flows plotted against the average SiO<sub>2</sub> composition of each lava flow. For each lava flow a box containing maximum (max), minimum (min) and average value (white line in the box) of  $\alpha$  is reported. For reference, lines for  $\alpha$  values representing random walk ( $\alpha$ =1.5), white noise ( $\alpha$ =0.5), and 1/*f* noise ( $\alpha$ =1.0) are also reported.

that similar processes may have acted in the three magmatic systems in generating similar features in the oscillatory zoning.

In the attempt to offer an explanation to obtained results it is worth recalling that 1/fnoise is considered by several authors to be representative of Self-Organized Criticality (SOC; Bak et al., 1987, 1988) and that several natural processes have been shown to exhibit this kind of behaviour (e.g. Bak and Tang, 1989; Hergarten, 2002). Briefly, a *critical* point is, in physics, a point at which a system changes its' behaviour or structure radically, for instance, from solid to liquid. In standard critical phenomena, there is a control parameter which can be varied to obtain this radical change in behaviour. In the case of melting, for instance, the control parameter is temperature. Self-organized critical phenomena, by contrast, are exhibited by those systems which reach a critical state by their intrinsic dynamics. The archetype of a self-organized critical system is a sand pile. Sand is slowly dropped onto a surface, forming a pile. As the pile grows, avalanches occur which carry sand from the top to the bottom of the pile. As introduced above, Bak (1990) has argued that 1/f-noise is symptomatic of SOC, i.e. of a system operating near a threshold of instability. In particular, SOC can be considered as a characteristic state of criticality which occurs by self-organization at the border between stability and chaos. Changes in such a system occur through catastrophic events rather than gradual variations. As we have earlier discussed in the paper, studied compositional time series (Fig. 4) are constituted by segments of zoning exhibiting small variation of An content followed by sudden increments of An and this fluctuation is continuously repeated along the zoning profile (Fig. 4); this property of compositional time series and the fact that most time series have scaling exponents  $\alpha$  close to 1.0 may be consistent with SOC.

In order to illustrate how SOC might be able to explain plagioclase oscillatory zoning we can use a simple non-linear dynamical system widely used in the literature: the logistic map (e.g. May, 1976; Turcotte, 1992). Note that we are not claiming that this simple system incorporates all the complex variables that may play a role in the magmatic system during plagioclase growth, but it may represent a suitable dynamic template capturing the basic properties leading to the development of observed zoning patterns.

The map is given by the following non-linear iterative map (e.g. May, 1976):

$$X_{t+1} = rX_t (1 - X_t) \quad (0 < X_t < 1, 0 < r \le 4)$$

where  $X_{t}$  and  $X_{t+1}$  represent the state of the system at time t and t + 1, respectively, and r is a control parameter. Given an initial condition  $0 < X_0 < 1$ , and by varying the parameter r, many different behaviours of the system can be obtained. A more complete and rigorous discussion of the behaviour of the map for the different r values can be found in May (1976) and Turcotte (1992). Here, for sake of simplicity, discussion about the influence of ron the dynamical output of the system is made graphically by using the bifurcation diagram shown Figure 8. The horizontal axis of the graph shows the values of the parameter r while the vertical axis shows the possible values of  $X_{i}$  once the iteration has settled down to a non-transient pattern. The graph represents two main regions characterized by stable dynamics (continuous lines in Fig. 8) and chaotic dynamics (dotted areas in Fig. 8). These two regions are largely inseparable. For instance, in the middle of the chaotic region on the right, are seen regions of stability, the most prominent



Fig. 8 – Part of bifurcation diagram of the logistic map for r ranging from 3.4 to 4. Stable regions and chaotic regions are constituted by continuous lines and dotted areas, respectively.

being located at for  $r \sim 3.83$ . There are an infinity of stable regions immersed in chaotic regions. Since we are interested in the system behaviour corresponding to a critical threshold we selected a value of r on the edge of the beginning of one chaotic region (i.e. r = 3.9601; see May, 1976 for details) and iterated the map. The time series of X values obtained by using the logistic map is shown in Figure 9A. The series shows segments characterised by periodic oscillation interrupted by segments in which X, values vary more erratically. Detrending fluctuation analysis was performed on the time series generated by the logistic map and results are displayed in the graph of Figure 9B, where log[F(n)] is plotted versus log(n). The graph shows a scaling region (from ca. 4.0 to ca. 6.5 in log units) having a slope  $\alpha = 1.005$ , indicating that the signal obtained by the iteration of the logistic map has components of 1/f-noise, as in the studied plagioclase oscillatory zonings.

From the above discussion it emerges that a dynamical system at the edge of stability may explain the major part of the dynamics of plagioclase oscillatory zoning. We now attempt to advance an hypothesis about the possible magmatic conditions that may have induced the development of these features in the zoning of studied plagioclases.

Recent research on magmatic systems and, in particular, magma mixing systems has shown that flow fields within a magmatic mass constitute two main kind of regions coexisting in the same system in space and time (e.g. Perugini *et al.*, 2002; 2003). The first kind of regions, named Active Mixing Regions (AMR; Perugini *et al.*, 2003), are characterized by apparently chaotic dynamics and in these magma volumes mass transfer processes can be greatly enhanced leading to sudden changes in the compositional fields. The second kind of regions, named (Coherent Regions, CR; Perugini *et al.*, 2003), are characterized by stable



Fig. 9 – A) Time series of X values obtained by using the logistic map with r=3.9601; B) Graph showing the variation of  $\log[F(n)]$  versus  $\log(n)$  for the time series in A. Scaling exponent is calculated as the slope of linear fitting of data in the scaling region from ca. 4.0 to ca. 6.5.

dynamics, and in these magma volumes mass transfer processes are subjected only to smooth changes. This structural configuration of a magma mixing system shares two important features with the logistic map discussed above. In both cases periodic and chaotic regions coexist in the same system. Given that a magma mixing origin was suggested for the three studied lava flows it is worth discussing the possible influence of AMR and CR in the development of oscillatory zoning in plagioclase crystals.

In this respect it is important to note that if both AMR and CR were present in a magma mixing system in which plagioclase crystals were growing, and if the structure of flow fields did not change in time (i.e. AMR and CR persisted in the same magma volumes as time progressed), we would have observed two populations of crystals, one grown in AMR and the other in CR, having different zoning profiles. This feature has been observed, for instance, in pyroxene crystals from the Santa Venera basaltic lava flow cropping out on Mt. Etna (Perugini et al., 2003). However, as shown by results presented in this paper, studied plagioclases are not discriminated into two populations - they all share the same feature, i.e. the 1/f-noise fingerprint  $(\alpha \sim 1.0)$ . A possible hypothesis to explain this lack of a double population of crystals may reside in the fact that AMR and CR were not invariant in time and space in the studied systems. On this aspect Bresler et al. (1997) have shown that flow fields in mixing systems can completely change as soon as the geometrical configuration of the system is changed (e.g. by varying the aspect ratio of the reservoir in which the mixing process occurs). Under such conditions, the system reacts to the imposed geometrical change by restructuring the flow fields and it is likely that in those regions previously characterized by AMR, CR develops, and vice versa.

In the studied magmatic systems geometrical changes can be originated by the variation of both internal and external factors. Regarding changes that may occur in response to the variation of internal factors, the crystallization of mineral phases is one of the most important; this process produces increasing amount of solids which may perturb the flow fields in the magmatic system and, thus, can induce a restructuring of dynamical regions throughout the magmatic mass. Being

the crystallization a continuous process it can be expected that the restructuring of flow fields is also continuous leading the development of a pulsating magmatic mass in the which AMR and CR are continuously generated and destroyed in time. Regarding changes that may occur in response to the variation of external factors, it has to be considered that the studied rocks are volcanic in origin and, thus, that magmatic processes occurred in different geometrical configurations. For instance, it could be supposed that the magma mixing process first occurred in a magma chamber (first geometrical configuration), then magmas migrated through fracture networks towards the Earth surface (second geometrical configuration) and, finally, magmas were erupted through a volcanic conduit (third geometrical configuration). Of course, there are many other possible geometrical configurations that a magmatic system may experience during its evolution.

It is to note that variation of internal and external factors can act synchronously, thus strongly amplifying the restructuring of flow fields in the magmatic mass. It appears, then, that flow fields may be restructured several times in the same system and that plagioclase crystals crystallized during such a complex evolution may be trapped in different regions (AMR and CR) at different times. For instance, keeping as reference the compositional zoning in Figure 4A, it could be said that that at the beginning the crystal crystallized in a CR (0-25  $\mu$ m) where there was a nearly constant amount of An component, then it was brought into an AMR where it encountered a higher amount of An component (first peak at around 45  $\mu$ m), then it was trapped in a CR where it was subjected again to a constant amount of An component (up to around 100  $\mu$ m), and so on. Similar considerations could be made for all other crystals.

According to these considerations, plagioclase crystals may be considered as recorders of the dynamical history of a magmatic system and, as such, they become a fundamental tracer of the magmatic process. Of course, further research needs to be carried out possibly by coupling the approach proposed here with trace element microanalysis and with numerical models of plagioclase oscillatory zoning formation in order to check the validity of the arguments presented in this paper.

### 5. SUMMARY AND CONCLUSIONS

In this contribution we studied the oscillatory zoning of plagioclase crystals in three different lava flows cropping out on the Island of Capraia (Tuscan Archipelago, Italy) with the aim of understanding the basic process leading to the development of oscillatory zoning. Analysis has been performed using a new method that combines microanalysis and image analysis and allows us to extract compositional time series with high spatial resolution along the zoning profiles. Compositional time series have been analysed by the Detrended Fluctuation Analysis (DFA) method and results have shown that most zoning profiles in the studied lava flows can be regarded as having properties of 1/f-noise. By using a simple dynamical system, the logistic map, it was shown that this feature might be attributed to self-organized criticality, i.e. a feature typical of systems lying at the border between stability and chaos. It was suggested that the statistical properties of plagioclase oscillatory zonings may be explained by continuous restructuring of flow fields in the magmatic system due to variations of the geometrical configuration in which the magmatic processes occurred at different times.

#### ACKNOWLEDGMENT

This work is dedicated to the memory of Dr. Filippo Olmi. He assisted D.P. during EMPA analysis of plagioclase crystals used in this work. His untimely death leaves a large hole in the Petrological and Mineralogical Italian community that will be very difficult to fill. This work was founded by MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca) and Università degli Studi di Perugia grants. Constructive comments by two anonymous referees are gratefully acknowledged.

### REFERENCES

- ANDERSON A.T. (1984) Probable relations between plagioclase zoning and magma dynamics Fuego Volcano, Guatemala. Am. Mineral., 69, 660-676.
- BAK P. (1990) *Self-organized criticality*. Physica A, **163**, 403-409.
- BAK P. and TANG C. (1989) Earthquakes as a selforganized critical phenomenon. J. Geophys. Res., 94, 15.635-15.637.

- BAK P., TANG C. and WIESENFELD K. (1988) Selforganized criticality. Phys. Rev. A, **38**, 364-374.
- BAK P., TANG, C. and WIESENFELD K. (1987) *Self-organized criticality: an explanation of 1/f noise*. Phys. Rev. Lett., **59**, 381-384.
- BARBERI F., FERRARA G., FRANCHI F., SERRI G., TONARINI S. and TREUIL M. (1986) – Geochemistry and geochronology of the Capraia island volcanic complex (North Tyrrhenian Sea, Italy). Terra Cognita, 6, 185.
- BLUNDY J.D. and SHIMIZU N. (1991) Trace element evidence for plagioclase recycling in calc-alkaline magmas. Earth Planet. Sci. Lett., 102, 178-197.
- BRESLER L., SHINBROT T., METCALFE G. and OTTINO J.M. (1997) – Isolated mixing regions: origin, robustness and control. Chem. Eng. Sci., 52, 1623-1636.
- COUCH S., SPARKS R.S.J. and CARROLL M.R. (2001) – Mineral disequilibrium in lavas explained by convective self-mixing in open magma chambers. Nature, **411**, 1037-1039
- DAVIDSON J.P. and III TEPLEY F. (1997) Recharge in volcanic systems; evidence from isotope profiles of phenocrysts. Science 275, 826-829
- GINIBRE C., KRONZ A. and WORNER G. (2002) Highresolution quantitative imaging of plagioclase composition using accumulated back-scattered electron images: New constraints on oscillatory zoning. Contrib. Mineral. Petrol., **142**, 436-448.
- HAASE C.S., CHADAM J., FEINN D. and ORTOLEVA P. (1980) Oscillatory zoning in plagioclase feldspar: Science, **209**, 272-274.
- HALDEN N.M. (1996) Determination of Lyapounov exponents to characterize the oscillatory distribution of trace elements in minerals. Can. Min., 34, 1127-1135.
- HALDEN N.M. and HAWTHORNE F.C. (1993) The fractal geometry of oscillatory zoning in crystals: Application to zircon. Am. Mineral., 78, 1113-1116.
- HERGARTEN S. (2002) Self-Organized Criticality in Earth Systems. Springer-Verlag, Berlin Heidelberg, 272 pp.
- HIGMAN S.L. and PEARCE T.H. (1993) Spatiotemporal dynamics in oscillatory zoned magmatic plagioclase. Geophys. Res. Lett., 20, 1935-1938.
- HOLTEN T., JAMTVEIT B., MEAKIN P., CORTINI M., BLUNDY J.D. and AUSTRHEIM H. (1997) – Statistical characteristics and origin of oscillatory zoning in crystals. Am. Mineral., **82**, 596-606.

- HOSKIN P.W.O. (2000) Patterns of chaos: fractal statistics and the oscillatory chemistry of zircon. Geochim. Cosmochim. Acta, 64, 1905-1923
- HU K., IVANOV P.C., CHEN Z., CARPENA P. and STANLEY H.E. (2001) – *Effect of Trends on Detrended Fluctuation Analysis.* Phys. Rev. E, 64, 1-19.
- KANTELHARDT J.W., KOSCIELNY-BUNDE E., REGO H.H.A., HAVLIN S. and BUNDE A. (2001) – Detecting long-range correlations with detrended fluctuation analysis. Physica A, **295**, 441-454.
- L'HEUREUX I. and FOWLER A.D. (1996) Dynamical model of oscillatory zoning in plagioclase with nonlinear partition relation. Geophys. Res. Lett., 23, 17-20.
- MAY R.M. (1976) Simple mathematical models with very complicated dynamics. Nature, **261**, 459-467.
- Ortoleva P., Merino E., Moore C. and Chadam J. (1987)-Geochemical self-organization I: Reactiontransport feedbacks and modeling approach. Am. J. Sci., 287, 979-1007.
- PEARCE T.H. and KOLISNIKA.M. (1990)–*Observations* of plagioclase zoning using interference imaging. Earth Sci. Rev., **29**, 9-26
- PENG C.K., BULDYREV S.V., HAVLIN S., SIMONS M., STANLEY H.E. and GOLDBERGER A.L. (1994) – Mosaic Organization of DNA Sequences. Phys. Rev. E, 49, 1685-1689.
- PERUGINI D., BUSÀ T., POLI G., NAZZARENI S. (2003) – The Role of Chaotic Dynamics and Flow Fields in the Development of Disequilibrium Textures in Volcanic Rocks. J. Petrol., 44, 733-756.

- PERUGINI D., POLI G. and GATTA G. (2002) Analysis and Simulation of Magma Mixing Processes in 3D. Lithos, **65**, 313-330.
- PERUGINI D., POLI G. and VALENTINI L. (2005) – Strange Attractors in Plagioclase Oscillatory Zoning: Petrological Implications. Contrib. Mineral. Petrol., 149, 482-497.
- POLI G. and PERUGINI D. (2003) The Island of Capraia. In: Poli G. Perugini D. Rocchi S. Dini A (Eds.) Miocene to Recent Plutonism and Volcanism in the Tuscan Magmatic Province (Central Italy). Per. Mineral., 72, 195-210.
- PROSPERINI N. (1993) Petrologia e geochimica delle rocce dell'isola di Capraia (Arcipelago Toscano, Italia): un vulcano calcalcalino di origine complessa, M. S. Thesis, University of Perugia, Italy, 223 pp.
- STEWART M.L. and FOWLER A.D. (2001) The nature and occurrence of discrete zoning in plagioclase from recently erupted andesitic volcanic rocks, Montserrat. J. Volcanol. Geotherm. Res., 106, 243-253.
- TURCOTTE D.L. (1992) Fractals and chaos in geology and geophysics. Cambridge University Press, Cambridge, U.K.
- VAGGELLI G., OLMI F. and CONTICELLI S. (1999) – Quantitative electron microprobe analysis of reference silicate mineral and glass samples. Acta Vulcanol., 11, 297-304.
- Wallace G. and Bergantz G. (2002) Wavelet-based correlation (WBC) of crystal populations and magma mixing. Earth Planet. Sci. Lett. 202, 133-145.