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# Weathering reactions and isometric log-ratio coordinates: Do they speak to each other?

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A B S T R A C T

The aim of this contribution is to explore the relationship among some concepts, often considered to be unrelated, such as weathering reactions, compositional data and fractals by means of distribution analysis.

Weathering reactions represent the necessary transfer of heat and entropy to the environment in geochemical cycles. Compositional data express the relative abundance of chemical elements/species in a given total (i.e. volume or weight). Fractals are temporal or spatial objects with self-similarity and scale-invariance, so that internal structures repeat themselves over multiple levels of magnification or scales of measurement.

Gibbs's free energy and the application of the Law Mass Action can be used to model weathering reactions, under the hypothesis of chemical equilibrium. Compositional data are obtained in the analytical phase after the determination of the concentrations of chemicals in sampled solid, liquid or gaseous materials. Fractals can be measured by using their fractal dimensions.

In this paper, the presence of fractal structures is observed when the frequency distribution of isometric log-ratio coordinates is investigated, showing the logarithm of the cumulative number of samples exceeding a certain coordinate value plotted against the coordinate value itself. Isometric log-ratio coordinates (or balances) were constructed by using the sequential binary partition (SBP) method. The balances were identified to maintain, as far as possible, the similarity with a corresponding weathering reaction affecting the Arno river catchment (Tuscany, central Italy) as described by the Law of Mass Action. The emergence of fractal structures indicates the presence of dissipative systems, which require complexity, large numbers of inter-connected elements and stochasticity.

## 1. Introduction

### 1.1. Investigating the frequency distribution shape

Weathering reactions contribute to mobility of the elements among different natural reservoirs, generating variability in complex geochemical systems at different scales (Berner et al., 1983; Oelkers et al., 2011; Bouchez et al., 2012; Hartmann et al., 2013; Weyer et al., 2014; Sun et al., 2016). A way to investigate the variability characterising different reservoirs is to analyse the shape of the frequency distribution of the abundance of chemical element/species determining their composition. The histogram is the basic plot where linearly scaled concentration intervals are reported on the abscissa, while the frequency of individual values, which fall in a particular class interval, is reported on the ordinate (Gaillardet et al., 1999; Allègre and Lewin, 1995). In a histogram the density (i.e., the relative frequency divided by the amplitude of the class) should be represented, so that the area of each bar is the relative frequency. The graphical analysis of the histogram shape may give some indications about the probability density function able to model data variability. Often this information is relegated only to check the presence of normality, as required by several inferential methods of statistical analysis (Mateu-Figueras and Pawlowsky-Glahn, 2008). However, this analysis may give more information about how the geochemical system under investigation is working

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(Allen et al., 2001; Buccianti, 2011a; Bowers et al., 2012).

First investigations on frequency distribution are historically attributed to Ahrens (1954a, b; 1957). He pointed out that the frequency distribution of chemical components in natural material are often positively skewed and satisfactorily described by the log-normal law. However, subsequent investigations have revealed that the positive skewness cannot be considered only a property of the log-normal law and that other statistical relationships with long Pareto tails can also be adopted (Oertel, 1969; Link and Koch, 1975). In this context, several authors have pointed out that the power-law (fractal) distributions can be used to describe many different positively skewed natural data (e.g. Mandelbrot, 1983; Monecke et al., 2001; Agterberg, 2007).

Revealing the presence of a power law distribution in a histogram requires the log-scaling of the abscissa and the ordinate, yielding an approximately straight line fitting the frequencies (Sornette, 2006). From this point of view a more satisfying graphical representation is given by the display of the logarithm of the cumulative number of samples equal or exceeding a certain element concentration, plotted against the logarithm of the element concentration. In these plots power law relationships yield straight lines (Mandelbrot, 1983; Sornette, 2006) while log-normal distribution form strongly curved graphs with significant deviations from linearity (Monecke et al., 2001).

However, sometimes the graph is characterised by different portions where linearity and curvature are either maintained or difficult to clearly discriminate (Ma et al., 2013). For example, the distinction between a log-normal distribution and a power-law relationship may be difficult when the shape factor of the log-normal is large (Mitzenmacher, 2004; Sornette, 2006; Seuront, 2010). Monecke et al. (2005) have shown that processes of metasomatic element enrichment can result in a fractal distribution of element abundance data only in the low concentration region with a smooth truncation at higher concentration values. The existence of physical upper concentration limits imposed by the mineralogical nature of the ore appears to be determinant in governing this behaviour. Similarly, Allègre and Lewin (1995) have previously shown that different processes of element enrichment are able to generate different frequency distributions of element concentration. They concluded that differentiation (geochemical) operators resulted in fractal distributions and mixing processes in Gaussian distributions. However, if the final distribution is due to a repetitive series of enrichment/depletion episodes, occurring over a long geological time, it tends to be log-normal (Allègre and Lewin, 1995). In this framework, simple multiplicative cascade phenomena can result in discrete log-binomial distributions that closely approximate the log-normal (Agterberg, 2007; Gao et al., 2007). Moreover, many natural phenomena do not have perfect homogenous scale-invariant characteristics described by a single fractal dimension. Fractal sets having multiscaling are heterogeneous fractal sets and are called multifractals. Multifractals consists of infinitely many intertwined subfractal sets of different dimensions (Cheng, 1999; Halsey et al., 1986). Multifractal models can be related to specific probability distributions and statistics, e.g. combined normal, log-normal and power-law distributions. Many geochemical processes, including geochemical dispersion patterns, exhibit high variations and strong non-linearites over a wide range of spatial scales. Scaling approaches and multifractal models are thus used for their statistical analysis (Panahi and Cheng, 2004). A wide review about the use of fractal/multifractal modelling in geochemistry can be found in Agterberg (2014) and Zuo and Wang (2015).

### 1.2. Investigating the link between chemical reactions and fractals

The Second Law of Thermodynamics states that entropy always increases and that order spontaneously tends to disorder while energy gradients spontaneously disperse. However, following Kondepudi and Prigogine (1998) irreversible processes act as destroyers of order near equilibrium and as creators of order far from equilibrium. Equilibrium systems evolve to a state that minimizes free energy; non-equilibrium systems can evolve unpredictably. In the latter condition, as a result of random fluctuations or other random factors such as minor inhomogeneity, the system evolves to one of many possible states, often “ordered states” that possess spatial-temporal organisation (Sornette, 2006; Seuront, 2010). Since the creation and maintenance of organised non-equilibrium states are due to dissipative processes, these non-equilibrium systems are called *dissipative structures* (Prigogine, 1980; Prigogine and Stengers, 1984).

Several investigations indicate that in this context fractal structures are spontaneously created because they enable the optimal dissipation of energy gradients. Seely and Macklem (2012) demonstrated that fractal structures optimize entropy production when dissipative structure systems are present. Circumstantial evidence to support this hypothesis includes the ubiquitous association between energy gradient dissipation and fractal structures that appear in nature, including both spatial (e.g. river deltas, lightning, coastline, mountain ranges) and temporal (e.g. avalanches, earthquakes and solar flare dynamics) phenomena.

Is there a link between weathering processes (and reactions used to describe them), and the presence of dissipative structures and fractals? Shvartsev (2009) discusses the role of self-organising abiogenic dissipative structures in the geologic history of the Earth. The author focuses his attention on the evolution of water-rock systems. Kleidon (2010a, b) discusses why the Earth system is maintained in a state so far away from thermodynamical equilibrium despite the natural direction towards mixing matter (geochemical cycles) and depleting sources of energy. Consequently, the trend away from equilibrium is related to the proposed thermodynamic principle of maximum entropy production (Dewar, 2003, 2005a, b; Kleidon and Lorenz, 2005). It states that thermodynamic processes in non-equilibrium systems assume steady states at which their rates of entropy production are maximized.

The coupled biosphere–atmosphere system includes a vast range of processes at different scales, from ecosystem exchange fluxes of energy to the processes that drive global biogeochemical cycles, atmospheric composition and, ultimately, the planetary energy balance. These processes are generally complex with numerous interactions and feedbacks, and they are irreversible in their nature, thereby dissipating energy and producing entropy at the maximum possible rate (Kleidon, 2010a, b).

Kirchner et al. (2001) report that fractal scaling can be observed in stream tracer concentrations due to catchment-scale advection and dispersion mechanisms, all factors also able to influence water chemistry. Xu and Du (2014) report that groundwater flow systems appear to be typical dissipative structure systems, and that the scaling behaviour affects water chemistry. Hunt et al. (2015) indicated that reactions within porous media exhibit non-trivial dependencies on time and space. These authors found that solute velocity is not based on diffusion but it is rather generated by the flow of fluids in the medium and is nearly a power law in both space and time, thus generating a scaling behaviour.

### 1.3. Compositional data: how to manage their relative nature?

When the frequency distribution of compositional data represents the core of the investigation it is not possible to avoid the problems presented by this type of numerical information.

A (row) vector, $x = [x_1, x_2, \ldots, x_D]$, is a $D$-part composition when all its components are strictly positive real numbers and carry only