

Determination of Poly Morphological Transitions of Dendrites on Natural Magnesite Surfaces

Mehmet Bayirli(Corresponding author)
Science & Literature Faculty, Balikesir University
PO box 10145, Balikesir, Turkey
E-mail: mbayirli@balikesir.edu.tr

Tugba Ozbey
Science & Literature Faculty, Balikesir University
PO Box 10145, Balikesir, Turkey
E-mail: mbayirli@balikesir.edu.tr

Ilhan Gulgonul
Balikesir Mining Department, Balikesir University
PO box 10145, Balikesir, Turkey
E-mail: igulgonul@balikesir.edu.tr

Abstract
Manganese dendrites on the magnesite ore are natural solid phase and poly morphological structures of manganese oxides ($MnO^{2+, 3+- 4+}$). They are a wide variety of structures.In this study, radial particle distribution and growth critical exponents are investigated by using the scaling method for natural manganese dendrites.For this purpose, the samples are grouped according to the superficial heterogeneity of the deposits and the calculations are made**.** The results of radial particle distributions are similar to the Gaussian distribution approach**.** We have performed the radial growth distribution function to test this hypothesis.The obtained data are fitted to thenon-regression method as the Gaussian function and determined their both median and the median diameter for the manganese dendrites that have various solid morphological transitions. Also, growth critical exponent values vary between $0.424 \leq \alpha \leq 0.732$ and $2.153 \leq \beta \leq 10.457$ by using linear regression method. The results were compared with the real and simulated representation values in the literature.

Keywords: Mineral structure, Fractals in geophysics, Numerical methods, Scaling method

1. Introduction

In recent years, very successful studies have been in field of no-equilibrium physics on naturally growing patterns (Meakin, 1998). It is known that there are often self-similar patterns or fractal in nature. One of them is manganese dendrites which are formed on natural surface, subsurface and interface at the rocks, quartz and magnesite ore typically results in the different rich growing patterns (Vicsek, 1991; García-Ruiz et al., 1994).

Structures of dendrites on the magnesite ores may consist of birnesite, coronadite, cryptomelane, hollandite, romanechite, todorokite, and other species. These dendrite structures have heterogeneous growth and a universal distribution for the particles. A many number of experiment (Potter and Rossman, 1979; Chopard et al., 1991), theoretic analyses (Bayirli and Ozbey, 2013), and the computer simulations (Chopard et al., 1991) have been carried out to investigate the relationship between the geometrical structure and the formation mechanism. Chopard et al. (1991) proposed that the reaction-diffusion process deposits them when super saturated Mn-rich solutions are exposed to air on the rock surfaces. Garcia Ruiz et al. (1994) obtained three-like manganese patterns for experimental studies and presented data supporting the ideais that the manganese dendrites are the mineral record of flow in

stabilities. Potter et al. (1979) reported that many samples have similar strong x-ray lines or line broadening can make x-ray diffraction identification ineffectual. They have also determined that infrared spectroscopy has been helpful in verifying some dendrite mineralogy. Meanwhile, it is proposed that the formation of some manganese dendrites geometrically can be explained by the diffusion limited aggregation (DLA) model (Witten and Sander, 1981). Several researchers showed that manganese dendrites can be identified with eight or ten basic groups according to their geometrical parameters (Potter and Rossman, 1979). Dorn and Dickinson (1981) also, indicated that the presence of dendrite formation would be a strong evidence for the biological contribution (Dorn and Dickinson, 1981) .The mineralogy of the Iron Mountain dendrites due to todorokite and birnessite offers the possibility of a role for microorganisms in their formation. Their researchers have argued that rock varnish, a close relative to dendrites, was formed through bacterial precipitation Mn-fixing bacteria precipitate Mn from solution by oxidizing Mn^{2+} and Mn^{3+} to Mn^{4+}. Therefore, they were performed deoxy ribonucleic acid (DNA) extractions on dendrite samples in order to determine whether Mn-fixing bacteria are presented (Dorr et al, 1981).
In this study, the radial particle distribution was determined by using scaling and image processing method for natural manganese dendrites. For this purpose, the number of sites in the radius r range from the seed to the periphery was calculated. The nonlinear regression method was used to determine the probability distribution function. In addition, growth-critical exponent values were calculated using the linear regression method. The results were compared with the similar samples in the literature.

1. Material and method

The samples used in this study were collected from KUMAŞ magnesite production area in Kutahya, Turkey. The samples generally are in small rock blocks. The manganese dendrites on the rocks have a very distinct geometric and random distribution in brown form. Some of them have a fractal structure. It is observed that each of them grows outwardly around a nucleus by separating the branches from the lower branches. In addition, since the branch thicknesses are different from each other, the heterogeneity is also different morphologically.
The sample surfaces were displayed with a camera and then transferred to ~~a~~ computer. A typical magnesite ore surface image is shown in Fig. 1. Five different samples belonging to two groups were constructed for calculations in view of heterogeneity and branch thicknesses. These samples were named G1-A, B, C, D, E and G2-A, B, C, D and presented in Fig. 2. Radial structures were observed on the surface of selected manganese dendrites samples. Then, we scaled the homogeneous patterns using the special software (imageJ) numerically with BMP formats that images are transformed into binary images (Schneider et al., 2012). We computed with the number of the dark square pixels by dividing the pattern into boxes of size ϵ=1 pixel. Each pixel is redistricted in the memory in a such a way that the local density $\rho(r)$ of a pixel is 1, in which *r* is radius from the seed to the pattern perimeter, if any part of manganese dendrite patterns is on pixel, and 0 if otherwise is 0. Then, we determined that the black pixels containing occupied pixels in image map as a radial function of interval r (Δr) and the number of sites from the seed to perimeter, in the usual way. The systematic solution application was geometrically shown in Fig. 3.

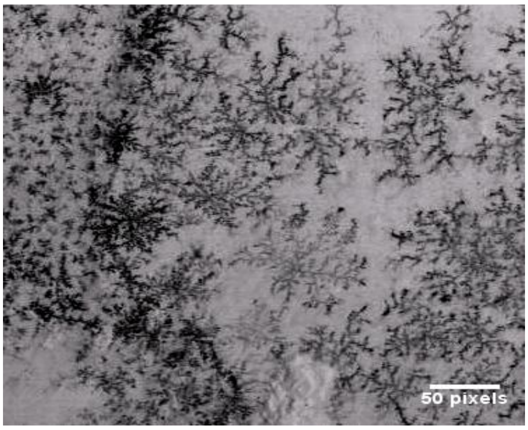

Fig. 1.Typical image of the natural magnesite ore surface.

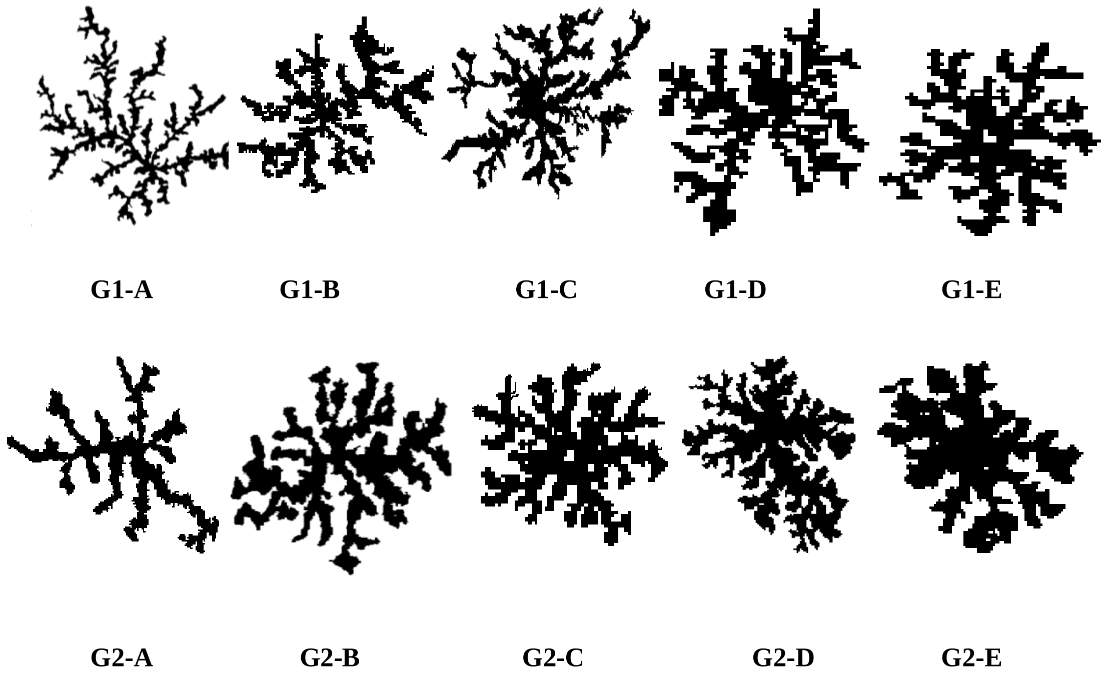

Fig. 2.Selected manganese dendrites on the surface of natural magnesite (particle density, branch thickness and, heterogeneity were preferred as a selection rule).

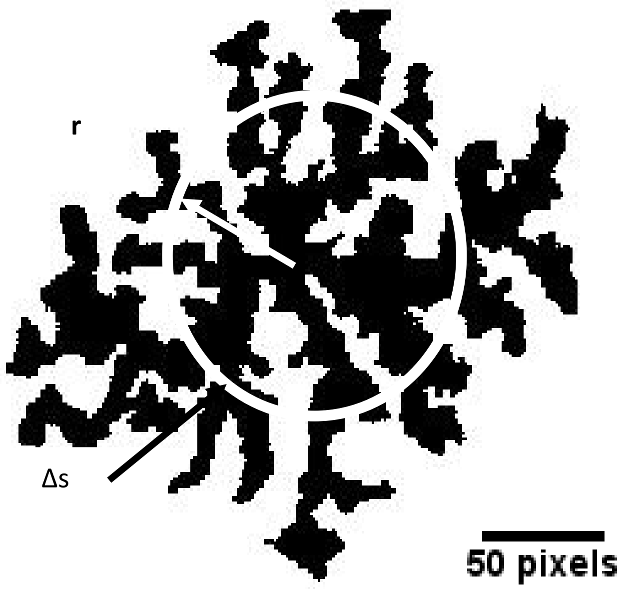

Fig. 3.Algorithm for calculating particle numbers around the seed on the selected manganese dendrite. The unit radial surface in the each steep, Δs, for the counting particles from the seed to pattern perimeter are shown the white ring line on the pattern surface shown in Fig. 3.

4. Results and discussion

Numerical computations were performed on a finite-size square lattice with linear dimension L by using the image processing method. The length of the manganese particle was chosen as linear dimension of $\varepsilon = 1$ lattice unit black pixel and surface size $s_i = \varepsilon^2$. The particle density on the magnesite surface of the square lattice is given by

$$\rho = N / L^2 \quad (1)$$

where N is the total number of particle in the square lattice. The number of the particle, which is proportional to coverage, is on the lattice surface. Some manganese patterns have a radial fractal structure. Especially, there is a seed at the center of the generic pattern and grows by adding new particles around the seed. Geometrically, since the patterns of the DLA model were similar to the structure, we calculated the particle density for each sample and summarized in Table 1.Firstly, to determine the radial particle distribution, the number of particles is computed from the seed to the cluster perimeters. The number of particles in the radius of pattern Δr interval can be defined by the relationship defined below:

$$\Delta n_i = p(s)\Delta s_i \quad (2)$$

And the function of probability distribution can be defined as:

$$p(s) = \Delta n_i / \Delta s_i \quad (3)$$

Where Δs_i is the interval size of sites.p(s) is positive and independent random variables that each with the some probability distribution in Eq. 3, and it is follows from the central limit theorem of mathematical statistics that this quantity is asymptotically a Gaussian distribution (Charmer, 1962). Hence, at last of much diffusion limit events the particles surfaces can be growth as the Gaussian distribution function. Accordingly, the relationship between the number of particles and the radial radius can be determined by a Gaussian distribution. The distribution function of particles Δn per surface interval Δs can be written with:

$$f(s) = p(s_0) + \frac{a}{\sqrt{2\pi\sigma}} \exp\left\{-0.5\left[\frac{s - s_0}{\sigma}\right]^2\right\} \quad (4)$$

Where σ, s_0 are the statistical median of the surface, their geometrical standard derivation, respectively. For special case of function, one is normalized distribution function

$$N(r,n) = f(r_0, n_0) + \frac{a}{\sqrt{2\pi\sigma}} \exp\left\{-0.5\left[\frac{r - \overline{r_0}}{\sigma}\right]^2\right\} \quad (5)$$

Here R, r_0 and σ are diameter, donates the median diameters, and is the gyration diameter for the patters, respectively.

The site distribution of samples is proportional to the particles distributions in the scaling manganese patterns. To compute the scaling function N(r, n) for sites distribution in each steps numerically we obtained patterns from the real samples. We compute to describe the distribution as radial that the next in coming particles touch the mass of cluster, M, at a distance r which is diameter from the seed to pattern perimeter. The typical dependence of the pattern site distribution on interval Δr at fixed values of interval Δn is shown in Fig. 4. It is possible to define each with Gaussian function approximate. Non-linear regression calculation is shown in the graph as a line (Charmer, 1962). The total number sites of the pattern are N. In Fig. 4, we plotted the asymptotic sites distribution, N (r, n) against the r. Particles distributions approximately showed the Gaussian distribution for site distribution as redial. The data spectrums of some manganese particle have one or two, and multi picks. Nevertheless, the approaches to the initial Gaussian parameters estimate functions N(r, n) taken form Eq. 5 using non-linear regression method. The regression coefficients vary interval from 0.64555 to 0.96793. The site distributions as the radial function are identified with the good agreement of the data spectrums for the real manganese patterns with the Gaussian function. In addition, the median values and diameters change from 3.518 to 22.169 and from 6.252 to 20.321, respectively. As the manganese structures change from the dendrite to compact, the median values decrease. However, the values of the median diameters approximately are constant. The one of the reason of that, it can be the number of particles not constants for the real manganese groups. The results of the Gaussian fit parameters for the sample groups are presented in Table 1.On other hand, it is numerically detected that a Gaussian is not a good description for the particles distribution near the seed of patterns, for small r the tail behaves like power law. Furthermore, one has to realize that N(r, n) drops to zero for large r simply because of the finite size of the patterns.

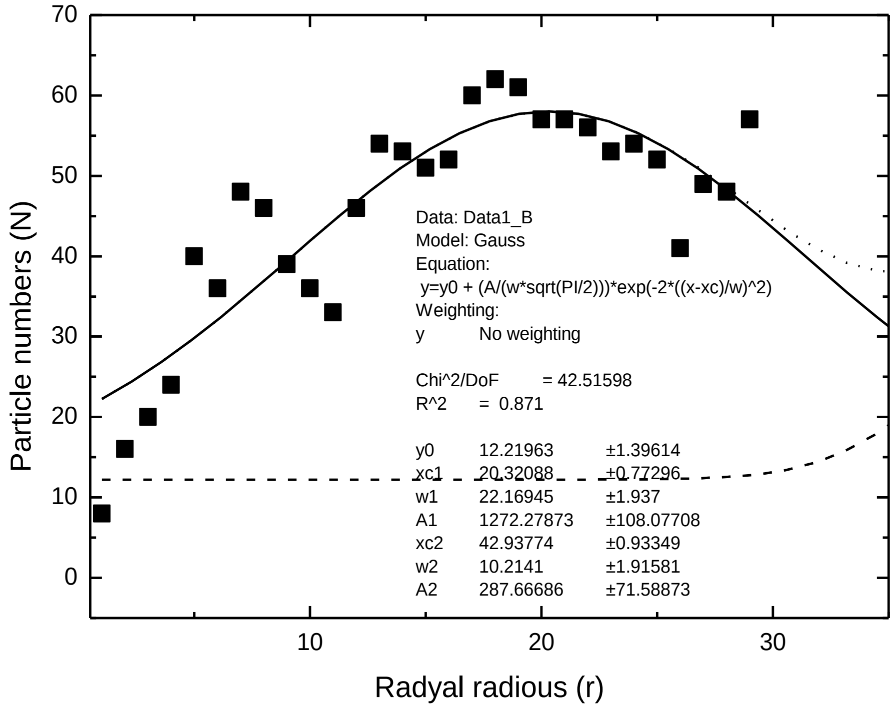

Fig. 4.Typical graphs of radial particle distributions from the core to the periphery of the manganese dendrite groups.

Secondly, the particle distribution function can be defined as the first region where the number of particles is the greatest from the core toward the periphery and the other region as the second region. The first zone is the dead zone; the second region is the active and clustering region.

Both regions can be defined by the power-law relations. Accordingly, the following equation for r $<r_{max}$, N < Nmax 1. region and for r > r_{min} and N > N_{max}2. region, respectively, can be written as:

$$r \sim N^{\alpha}. \qquad (6)$$

and

$$r \sim N^{-\beta} \quad (7)$$

where α and β are critical exponents. They are the growth exponents according to the scaling theory.

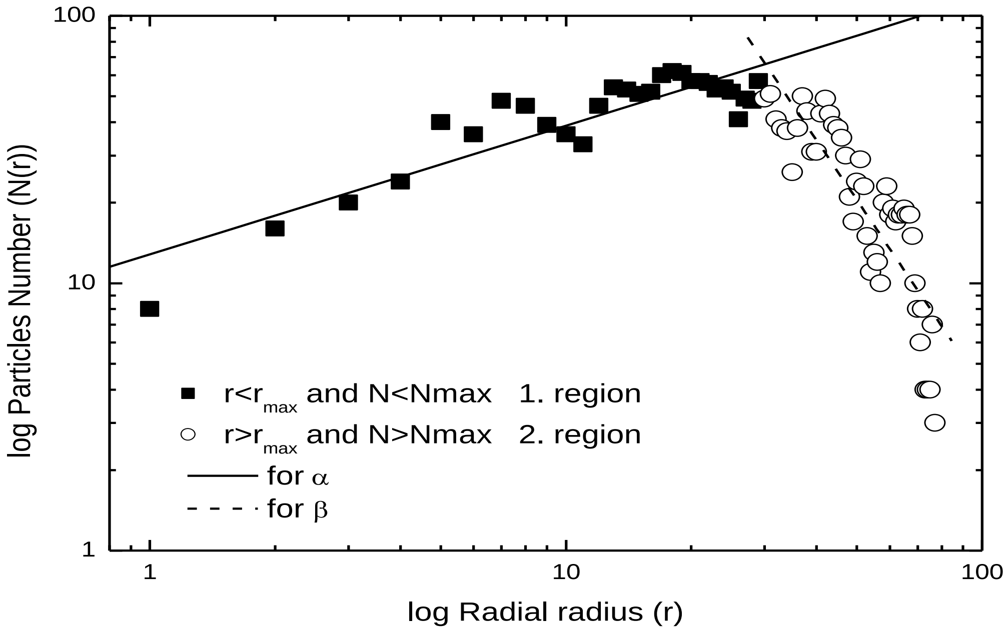

Fig. 5.Typical graphs of radial particle distributions from the core to the periphery of the manganese dendrite groups.

Growth along the boundary of manganese cluster is concentrated at the outer tips as Fig 5. The particle number during to growth increases the values of the gyration diameter, r_{max}, and it decreases towards from gyration diameter. The active region moves out-wards leaving behind "dead zones" which are shielded by outer tips of the center of seed during to growth process. To calculate growth critical exponents, the logarithms of the maximum values of particle radius have been taken for both axes. We did the same for the next half-maximum of the data. Then, critical exponents were calculated using the linear regression method and the obtained results were compared with the values of structures generated by the DLA (Ossadnikand lee, 1993). It is possible to obtain natural manganese dendrites by the DLA algorithm. To characterize the particle distribution and the growth process; we consider the particles distribution affect that occurs during the growth.

Table 1.The calculated parameters of manganese dendrite groups as particle count, particle density, growth critical exponents and regression constants.

Samples	Particle numbers (N)	Particle density (%ρ)	median (σ)	Median diameter (r)	Regression constant (R^2)	Critical exponents 1 region (α)	Critical exponents 2 region(β)	Regression constant (R^2)
G1-A	14592	16.226	3.518±0.573	5.252±1.463	0.64555	1.964±1.376	1.250±0250	0.89528
G1-B	14976	21.267	5.056±0.636	6.252±2.027	0.92711	0.424±0.067	3.826±0.497	0.80981
G1-C	15576	26.236	8.827±0.568	8.775±1.047	0.94484	0.548±0.050	4.502±0.281	0.93977
G1-D	20286	26.624	11.483±3.226	10.857±0.757	0.81389	0.551±0.049	3.619±0.518	0.78686
G1-E	71820	26.034	18.927±2.405	10.889±1.527	0.87532	0.066±0.054	4.018±0.378	0.88277
G2-A	13312	15.737	4.478±0.506	12.294±0.214	0.87079	0.430±0.107	2.153±0.351	0.74633
G2-B	14692	30.325	14.884±1.472	13.294±0.214	0.84076	0.562±0.035	5.904±1.355	0.72625
G2-C	14080	30.675	22.169±1.937	15.419±0.842	0.90811	0.732±0.0687	6.701±0.930	0.84955
G2-D	13696	36.427	18.735±±1.021	17.632±0.501	0.871	0.482±0.047	2.312±0.211	0.8499
G2-E	14976	40.475	33.746±3.544	20.321±0.772	0.96793	0.548±0.036	10.457±0.801	0.9315

The approach of Mulheran et al. (Mulheran and Harding, 1992) is interesting to describe a manganese dendrites-like formation and have given gave some interesting insights into why such a universal function should exist, at least for the case of heterogeneous growth. At the beginning of the growth, nucleation centers form for the manganese dendrites. Then each centre grows by catching the monomer falling inside it, being “active zone”, roughly identified with its Voronoï polyhedron. Therefore its size is proportional to the surface of Voronoï polyhedron during to growth process which does not change with time if nucleation of new islands in the case of homogenous nucleation is neglected (Mulheran, 1992). Nevertheless, while the poly morphological structures of the manganese are changed from the dendrite to the compact structures in macroscopic scale, the polyhedron structures in them are nearby lasted. The result is that at any coverage the site size distribution of the islands reproduces that of the Voronï cells, which explains the rescaling for different coverage for the manganese groups. Therefore, manganese particles growth seems natural that the character of a growing patterns must be represented by a hierarchy structure reflecting whole growth properties of the subtract surface.

4. Conclusion

In this paper, the irregular particles distributions having from the DLA-likeform to compact crystal growth of the real manganese groups are investigated by using scaling method. Radial manganese particle distribution and probability distribution function were determined using nonlinear regression method. Also, it is clarified that the numerical data spectrums only consistent with a Gaussian behavior around maximum numbers but this description indeed fails in the small r tail. In addition, growth critical exponents were calculated using a linear regression method. Critical base values were shown to consistent with the values calculated for the DLA model representations. As a result, while it is possible to explain the formation of manganese dendrites geometrically, the crystal structure of branches is not possible to define. Therefore, this study is very important for statistical physics.

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