Quantitative characterization of individual particle surfaces by fractal analysis of scanning electron microscope images

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Abstract. Morphological characterization of individual particle surfaces was explored by off-line image processing of data obtained by scanning electron microscope – microanalyzer. The fractal geometry was studied by two methods, the power spectrum and the variogram approach. Both methods were evaluated, theoretically by a series of numerically simulated surface profiles and experimentally on a set of pre-recorded secondary electron images of particle surfaces exposing characteristic textures. It was shown that the fractal approach could stand as a base of the methods enlarging the application of electron probe X-ray microanalyzers for individual particle characterization.

Introduction

Electron probe X-ray microanalysis (EPXMA) has for long been extensively used for quantitative measurements of the elemental composition of individual particles. Scanning electron microscopy (SEM) has been used for their visual morphological examination. Quantitative interpretation of surface textures has also been applied for various purpose (see, e.g. [1]). However several facets of texture ougth to be mastered quantitatively, a discipline in which so far little progress has been made [2]. Texture quantification would not only lead to reliable surface characterization, it would also extend the knowledge on relating structure with surface properties (i.a. adsorption) and with shaping processes (i.a. physical and chemical weathering). In this respect, direct measurements are becoming increasingly important through the availability of sophisticated image analysis systems and associated software. The recent introduction of fractal analysis as a refinement on the conventional roughness parameters provides a powerful tool capable of revealing systematic differences in texture.

The surface characteristic of particles are important since they are really their 'fingerprints'. Indeed, the particle surface texture itself results from a combination of alternating chemical and physical processes, leaving markings that reflect more or less the origin of the particles. So far, SEM exoscopic studies [3] allowed, to a certain extent, the reconstruction of the history of individual suspended particles based on their surface texture. An example can be found in the study of suspended quartz grains in the Loire river [4]. This method is however very time consuming which makes the need of an automated direct method through a quantitative description of texture even more necessary. Therefore an attempt was made to extract information on surface morphology of individual microscopic particles by mathematical processing of SEM images. The interpretation of SEM images is clearly of paramount importance if conclusions are to be drawn about the morphological nature of individual particles. A quantitative description of surface texture, based on digital images of surfaces, could eventually contribute to the classification of particles of different morphology, origin or history. In the first instance, this can be done by incorporating the surface descriptors in a form suitable for computer processing off-line. In a later stage on-line processing may become possible.

Up till now the problem of texture quantification essentially lay in the fact that it is very difficult to grasp a concept such as texture and evaluate it by a single parameter, as we intuitively view texture as a measure of several properties such as smoothness, coarseness, heterogeneity and regularity. However, the introduction of a fractal geometry provided a tool to tackle the problem of describing the concept texture. Theoretically a fractal can be defined as a set for which the only consistent illustration of its metric properties requires a dimension value D (called fractal dimension) larger than the standard topological dimension (T):

$$D = T + (1 - H)$$

where the parameter H is commonly referred to as the codimension. This practically means that curves can have their ruggedness described by allocating a fractal number between one and two establishing the space filling ability of the curves. Similarly, the concept of fractal dimension can be extended to higher dimensions, e.g. a rugged surface can be given a number between 2 and 3. Assigning fractal dimension values to rugged surfaces therefore allows the texture to be mastered quanitatively rather than qualitatively. Several methods may be applied to obtain the codimension H and thus the fractal dimension D.

In a first method the fractal dimension of the function z(x) may be defined in terms of the Fourier power spectrum $P(\omega)$ of the function, as the Fourier power spectrum falls off with increasing frequency ω [5], proportional to:

$$P(\omega) \approx \omega^{-(2H+1)}$$

By using a linear regression on the log-log plot of the observed power spectrum (PWS) as a function of frequency, the codimension H and the fractal dimension D can be determined. This method of surface analysis in terms of the power spectrum appears to be so far little explored in the microscopic domain [6] in comparison with the Fourier approach of macroscopic surfaces such as landscapes and environmental topographies [7].

Another method for fractal dimension calculation that was implemented is the so-called variogram method. This method can be defined in terms of how the variance of interpixel differences changes with distance. The fractal dimension of the function z(x) may then be estimated from a log-log plot of the variance of increments versus increments:

$$Var(x) \approx x^{2H}$$

The resulting graph is called a variogram, from which the name variogram method of this fractal dimension calculation procedure originates. The variogram method has been extensively adapted to analyze a number of environmental data (from anemones to rainfall). A review of the applications has been given by Burrough [8].

Other experimental methods for fractal-based characterization of surface texture exist, but are more complicated being mainly based on the different sectional approaches and are beyond the intention of this paper. The vertical section method comprehends for example the structured walk technique [9] or the box dimension approach [10] on vertical sections to the fracture plane, whereas the slit island technique [6] makes use of sequentially prepared sections parallel to the fracture plane and is based on the perimeter-area relation.

Experimental

Image acquisition

The images are recorded and stored with the Tracor Northern TN 2000 and TN 1310 automating system of a JEOL 733 electron microprobe. The images collected for our purposes were 256 analysis pixels in both x and y directions. All images were collected in the secondary electron mode because the secondary electron images generally show very low noise level and a sharp contrast with high spatial resolution [11]. The absolute signal intensity at each analysis pixel was converted from an analogue to a digital signal by an 8 bit resolution analogue to a digital converter (ADC). The system is thus capable of coding the images in as much as 256 brightness levels. Since the system does not offer adequate bulk storage and processing facilities, the images are stored on floppy disk or on tape and transferred to VAX/VMS minicomputer for further processing.

Image processing

To constraint the processing time and to simplify the interpretation for the power spectrum method, the one-dimensional version of the fast Fourier transform (FFT) was preferentially applied. In this one-dimensional approach, the FFT was run consecutively on the 256 transsect lines composing the image. The PWS was calculated by recombining the imaginary and real part of the transform to establish real data. Subsequently the 256 power spectra, taken from serial sections, were averaged to reduce the influence of microstructure and statistical artefacts. This average PWS was finally transformed into a log-log plot before exercising a linear regression fit routine. The fractal dimension was estimated from the slope, considering the following equation:

$$P(\omega) \approx \omega^{-(5-2D)}$$

The variogram method of measuring the fractal dimension has the advantage that it is an easy method in application, which does not involve too difficult mathematics and which does not require any preceding data adaptation. Additionally, it was based on good statistics since the method was applied in its two-dimensional version, i.e. on the whole data matrix simultaneously. Hence the occurrence of possible problems due to directionality of the surface is also excluded. Since it is more convenient, the standard deviation was calculated and used instead of the variance. Nevertheless, the term variogram will be maintained because it is commonly used in the literature. For this method, it was sufficient to scan the whole 256×256 matrix, to calculate the differences in image intensity, in the horizontal and the vertical direction. Starting with a pixel step size equal to 1, the procedure was repeated for successively increasing pixel step increments (up to 200). The distributions of the intensity differences were approximately Gaussian, with zero mean, for all increment settings. The standard deviation $\sigma(k)$ value corresponding with a certain pixel step k was calculated by recombining the individual sums of squared differences respectively for the x and y directions. The whole procedure was repeated for a limited number of pixel distance up to 200, because for higher pixel distances the statistics readily deteriorate. Also at higher pixel steps, only differences in the boundaries will be measured. Subsequently the standard deviation was plotted as a function of the pixel step in a log-log graph. From the linear least-

squares fit of the data the fractal dimension could be calculated as:

$$\sigma(k) \approx k^{2(3-D)}$$

with T = 2.

Results and discussion

Fractal Brownian function simulation

First the fractal dimension calculation methods based on power spectrum and variogram were tested on fractal Brownian motions (FBM) with controlled fractal dimensions. For this purpose, a set of FBM's were generated by the successive random addition algorithm [12]. These fractal Brownian functions have the same properties as the conventional fractal Brownian function, namely a power spectrum $P(\omega)$ that varies with $\omega^{-(5-2D)}$ and a variogram that varies with $(x)^{2H}$.

In Figs. 1–4, four fractal Brownian functions with theoretical fractal dimensions varying from 1.2 to 1.8 with increments of 0.2 (A) together with the PWS (B) and variogram (C) evaluation of the fractal dimensions are shown. This set of functions covers nearly the whole possible range of fractal dimensions. The functions were generated with 4096 points. A comparison between the theoretical and the experimental dimension values shows that both methods provide fair estimates of the fractal dimension values in the relatively broad range.

Observations on natural surfaces

Images of real particle surfaces were collected with SEM in view of an evaluation of their dimensionality by both fractal dimension calculation procedures. However before engaging ourselves with the fractal calculations, we acknowledged the necessity to verify the applicability of the methods on the intensity images of these surfaces rather than on the surfaces themselves. Pentland [13] proved, in this respect, that the fractal dimension methods can be used on particular image data as a representative of the actual three dimensional fractal surface. Moreover the obtained fractal dimension for the intensity surface agrees with that of the real three dimensional surface.

The two naturally occurring particle surfaces that will be represented were chosen so that they clearly demonstrate which information their PWS or variograms provide. In addition they also allow a simple and illustrative interpretation of this information. Two silicon dioxide particles were chosen for this purpose. The first particle was a radiolaria particle, one out of two possible SiO_2 (opal) forms of biogenic origin, the round shaped radiolaria and the oblong shaped diatoms. The second particle was a quartz particle of lithogenic origin, selected from a suspended matter sample from the Scheldt estuary (Belgium). These two surfaces were processed with both PWS and variogram methods. The 3 d representations of the morphology of these particles (at the magnification 3000×) are shown in Fig. 5 A and 6 A.
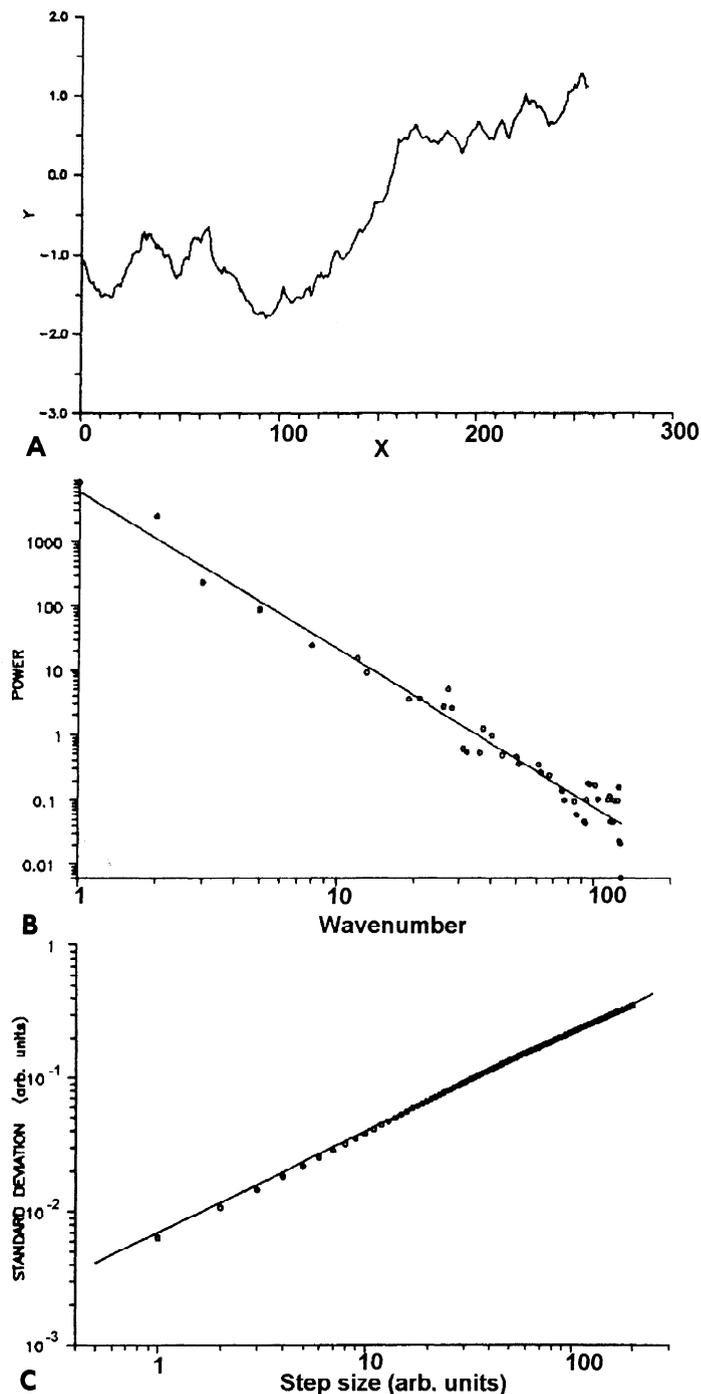
Fig. 1 A–C. Fractal Brownian function, generated by the successive random addition algorithm, with theoretical fractal dimension 1.2 (A) together with the PWS (B) and variogram (C) evaluation of fractal diameter

Biogenic silicon dioxide particles

Since all radiolaria (and diatoms) reveal a regular surface pattern and overall structure, it is apparent that any attempt to differentiate biogenic from lithogenic SiO_2 particles has primarily to be based on differences in morphology rather than on differences in composition. Many studies tried to use morphology based parameters such as the shape factor. But no exclusive selection can be estab-
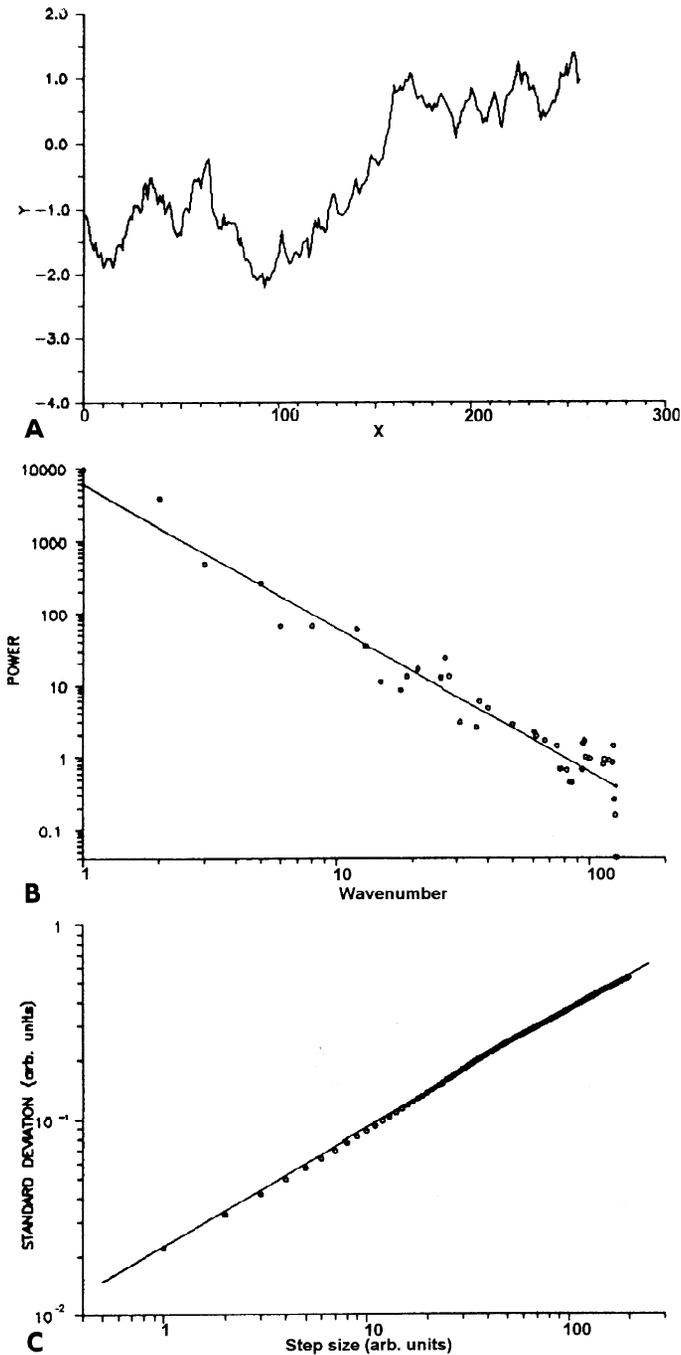
Fig. 2 A – C. Fractal Brownian function, generated by the successive random addition algorithm, with theoretical fractal dimension 1.4 (A) together with the PWS (B) and variogram (C) evaluation of fractal diameter

Fig. 3 A – C. Fractal Brownian function, generated by the successive random addition algorithm, with theoretical fractal dimension 1.6 (A) together with the PWS (B) and variogram (C) evaluation of fractal diameter

lished because the shape factor is generally not sensitive enough. Obviously an alternative solution may be found in the application of the technique which picks up and reflects periodicity. In this respect Fourier transform based methods have proven their applicability. The FFT is ideally suited for describing the periodicity, as the fundamental spatial period of the pattern will appear as distinguishable prominent peaks in the PWS at locations corresponding with the frequency of the pattern.

The PWS for the radiolaria exhibits a broad peak at an average wavelength of 1.2 μm as it is an average of 256 line scans with mutually slight different periodicity (see Fig. 5 B). The practical meaning of this dominant wavelength of 1.2 μm is that the average distance between the middle points of two neighbour holes on the surface of radiolaria is 1.2 μm. The same perception can be made from the variogram where the distance between the middlepoints of the holes corresponds with a minimum in the
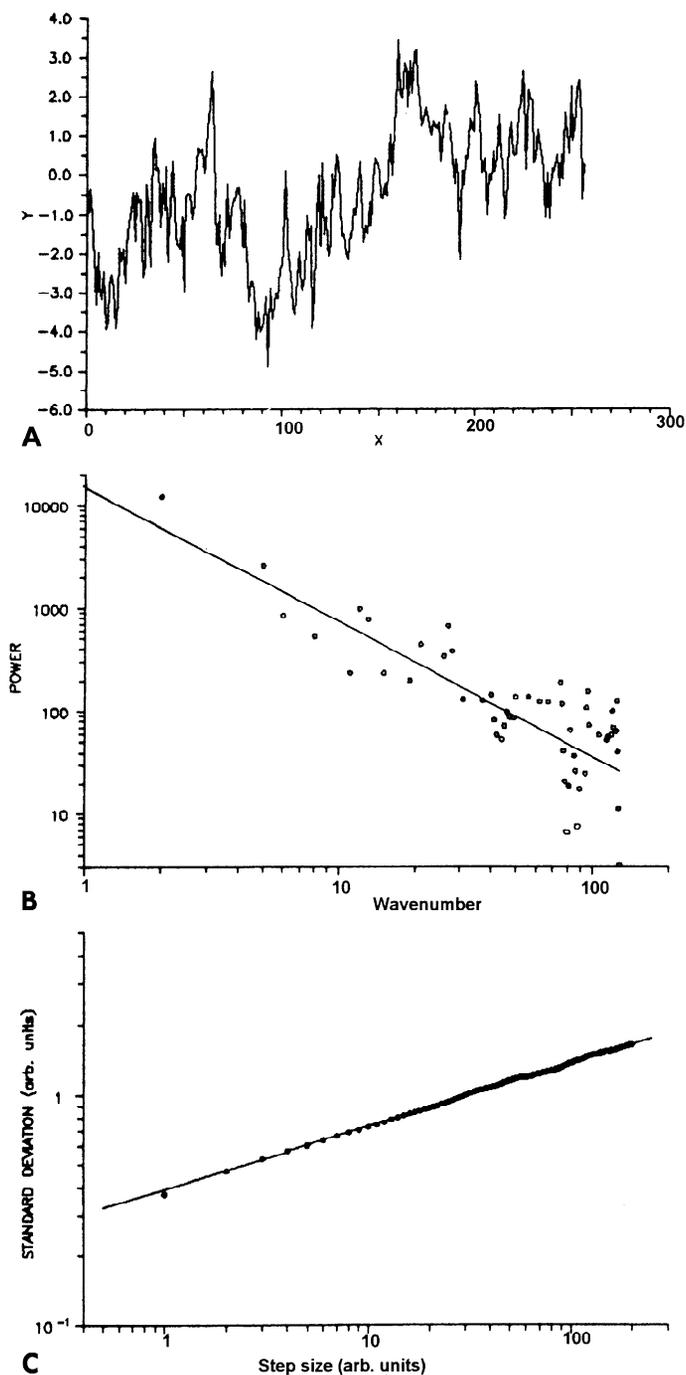
Fig. 4A–C. Fractal Brownian function, generated by the successive random addition algorithm, with theoretical fractal dimension 1.8 (A) together with the PWS (B) and variogram (C) evaluation of fractal diameter

plot (see Fig. 5C). This minimum reflects the narrow variance for the distribution for the step size equal to 1.2 μm.

It must however be stated that the correspondence between the PWS and the variogram for the scaling of the microstructure is not so straightforward as suggested. The variogram scales the surface structure in increments whereas the FFT expresses the same surface morphology in wavelengths. To relate the pixel size increments with the

PWS wavelengths a factor of two should be incorporated. Therefore, to avoid any confusion, it would have been better to relate the maximum power peak with the maximum in the variogram (at 0.6 μm) taking into consideration that the scaling of the microstructure by the two methods differs by a factor of 2.

So surface structures with periodic structure can have their pattern characteristics extracted and differentiated by both the PWS and variogram methods. Not only will, for example, the appearance of a peak in the PWS and variogram allow the recognition of biogenic particles, the position of peak maxima may also be characteristic for the radiolaria/diatom type. In case that the positions differ significantly, it may be sufficient to perform a single line scan over the surface of the biogenic particle in the automatic routine (at a specified constant magnification) to specify the radiolaria/diatom types by performing FFT (or variogram) routine. The problem associated with the directionality of the periodicity − the diatoms have their periodicity directed along their longest axis, whereas radiolaria do not expose any directionality of their surface pattern − can be solved by letting the line scans coincide with the direction of the maximum diameter. One major drawback is that not all opal particles have their periodicity aligned along a length axis; some radiolaria have a rotational symmetry. In these cases a more complicated rotational PWS routine can provide a solution. Nevertheless, this solution would implicate a compilation of adaptations, making it practically unattractive.

It should be emphasized that the problem of differentiating and characterizing biogenic particles is not restricted to silicon dioxide particles only. It is equally hard to differentiate, based on composition solely, between calcite/aragonite particles and coccolith/foraminifera organisms.

Lithogenic quartz particle

Careful analysis of the PWS plot (Fig. 6B) for the quartz particles indicates that the spectrum splits up into 3 distinct subregions, each characterized by a different fractal value. The short distance part is sensitive to the discrete approach imposed for the computation of the PWS as it is subjected to large statistical noise. This is manifested by the fractal dimension value for this range, which exceeds 2. Such a value has neither a physical nor a fractal meaning as it depicts the unnatural case of increasing amplitudes with increasing frequency. Such a noise event can impossibly be accounted for by fractal Brownian functions, as such a situation cannot be caused by Brownian processes. This range is also far too short and no lower limit distance could be determined. To determine, as yet, the lower limit distance, higher magnification examination of the sample has to be performed [14].

The intermediate range between approximately 9.3 and 0.82 μm is characterized by a fractal dimension equal to 1.29. The question is now, over how many orders of magnitude a power law should hold in order to give rise to an effective surface dimension greater than 1. Normally it is believed that reliable estimates of the dimen-
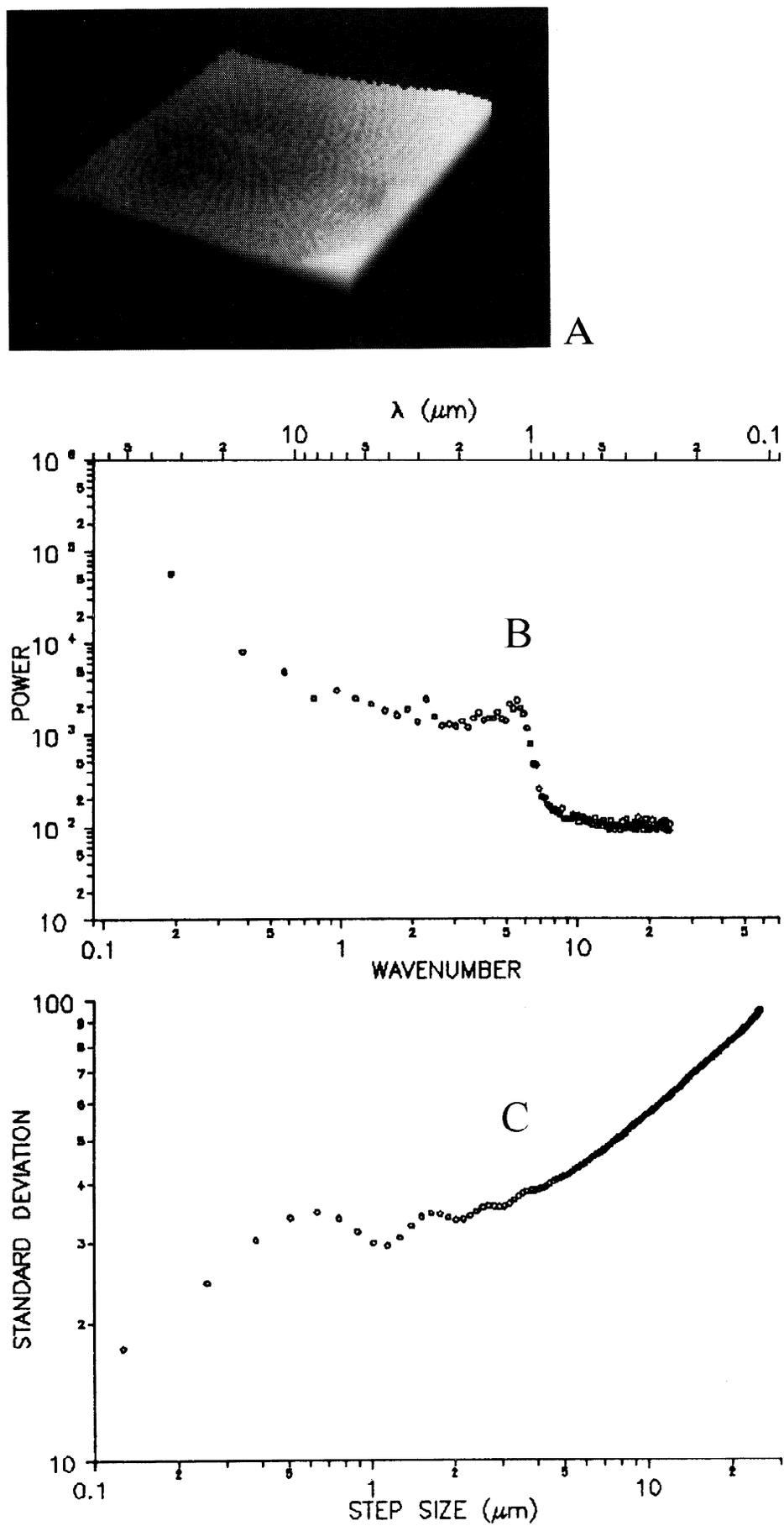
Fig. 5 A–C. Three dimensional representation (A) of the secondary electron image of a biogenic SiO_2 particle (radiolaria) at magnification 3000× along with PWS (B) and variogram (C)
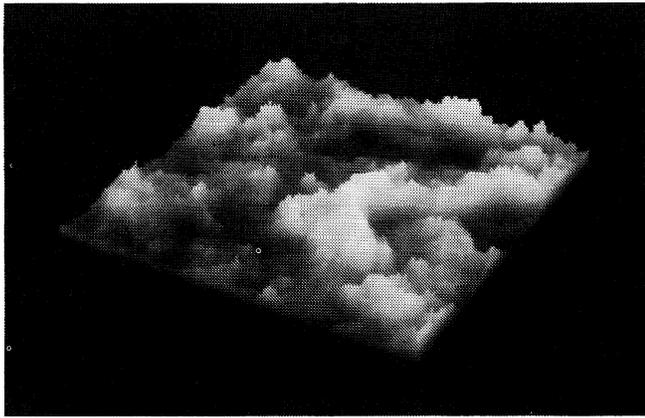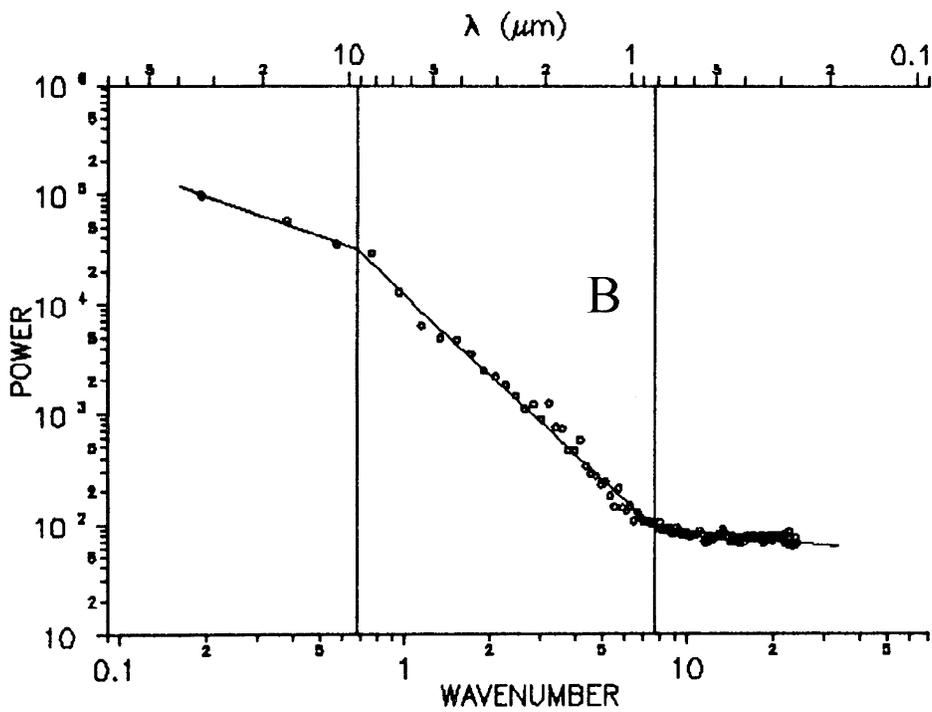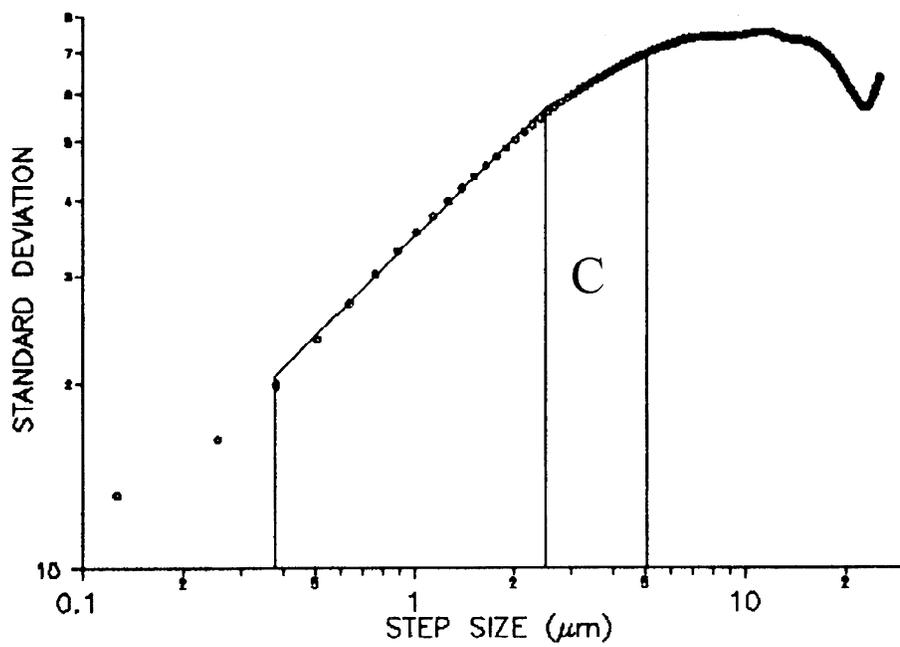
Fig. 6 A – C. Three dimensional representation (A) of the secondary electron image of a lithogenic quartz particle, originating from the Scheldt estuary, at magnification 3000× along with PWS (B) and variogram (C)

sion can only be obtained when the power law extends over at least two decades [15]. This stringent criterion, however, has not been met so far in the discussion of fractal surfaces or in environmental data. Mandelbrot himself [6], for instance, has focused his fractal dimension evaluation of fractured surfaces of metals on the central straight portion of the PWS which hardly stretched over a range of approximately 1.5 decades. Besides, real images cannot be true mathematical fractals, defined to exist at all scales [16]. Therefore, with necessary caution, it can be specified that the fractal dimension of the particle surface shows fractal properties over a range of 1 decade. The long distance range is built on an insufficient amount of data to reveal any relevant fractal property.

The results for the variogram method are shown in Fig. 6C. The dimension for the variogram has been estimated through a value between 2 and 3 as the method was applied to the whole surface rather than to transsect lines. The standard deviation in the variogram does not increase without limit, but attains a more or less constant value from a certain step size on. This range corresponds most likely with the spatial structure of the surface. The short distance range (first 5−6 points approximately) should also be excluded from the fractal evaluation as it is not relevant to the fractal determination [17]. Besides the long and the short distance region, the variogram was characterized by two additional ranges covering a transition zone, which was as such preferentially approached by a multiple fit. These two central ranges jointly coincide remarkably well with the fractal range in the PWS, as they together cover 1 decade of the microstructure, between approximately 0.76 and 10.2 μm. There is, however, slight inconsistency with average values obtained by PWS and variogram results. In the variogram method the values of fractal dimensions were 2.47 for the range from 0.38 to 2.52 μm and 2.69 for the range 2.52 to 5.08 μm. This difference is explained by the different grounds of the both methods; still it is not essential.

Burrough [8] interpreted the sets of dimensions for restricted ranges in his variograms as the result of the variety of natural phenomena having their levels of variability clustered at particular scales and to a certain degree displayed over multiple spatial scales. Therefore, the subdivision of the central region for the suspended particle surface may be interpreted in the same way, namely as a compilation of two fractal impacts.

Conclusions

The fractal based characterization of texture by means of SEM reveals systematic differences in texture and is more detailed than the conventional roughness parameters. Both the PWS and variogram method are sensitive enough for surface roughness evaluation and moreover they coincide with the human concept of roughness. Gen-erally we can decide that the central region satisfying the fractal power law for about one decade in scale is the most appropriate zone for fractal characterization. The contribution of noise can than be considered to be minimal. Moreover, this region is well defined both by the PWS and variogram method. Herewith it should be recognized that the fractal description will not only allow to characterize the microstructure of a surface. It may also be possible that the fractal dimension in combination with the range over which a certain process (e. g. weathering) operates is sensitive to the type of processes and to the extent they had an impact on the surface. As such the fractal description may prove its value for future quantitative approaches of the impact of a variety of processes on the surface structure and in any research field concerned with physical and chemical properties related with surface structure. Final dimension calculation methods may also be very useful tools to be incorporated in routine procedures for individual particle analysis when the automation system is extended with a powerful image processing system. It could complement the particle classification procedure, based generally on composition only, and it could contribute to the differentiation of the particles, which cannot be differentiated on the basis of their composition alone.

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