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Multifractal characterization of microbially induced magnesian calcite formation in Recent tidal flat sediments

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Abstract

Structures resulting from biogenic carbonate cementation of microbial mats in Recent siliciclastic tidal flat sediments of the North Sea are analyzed quantitatively by a novel combination of scanning electron microscopy and energy-dispersive X-ray spectrometry (SEM/EDX) imaging and subsequent multifractal analysis. Evaluation of calcium distribution patterns and their links to sediment-intrinsic mineralization processes show that the applied geometrical technique is an efficient tool for detecting microscopic variations in elemental distributions and related minerals within sedimentary matrices. Two main conclusions can be drawn: (i) magnesian calcite is a rapidly formed product of the early diagenesis of organic matter in Recent bioactive marine sediments; and (ii) multifractal spectra are measures for the spatial inhomogeneity of authigenic calcification processes acting on the sedimentary structure. This implies that elemental distribution patterns in a sedimentary system are scale-independent phenomena. Processes causing such patterns have occurred over certain periods with varying rates and on different scales. The detection of multifractal measures also opens a way towards a systematic survey of dynamic processes occurring in sedimentary structures.

Keywords: Early diagenesis; Carbonate cements; Microbial mats; Fractals; SEM/EDX

1. Introduction

Calcium carbonate, (i) as a product of microbial and geochemical processes in marine and terrestrial systems and (ii) as a global carbon dioxide reservoir in the course of geophysiological or climatic processes, has been studied in many contexts. Geochemical investigations are focussed on formation mechanisms and dissolution rates (see, e.g. Boudreau and Canfield, 1993). In geological studies, occurrence, envi-

ronment of formation, and mineralogy and petrography (Moore, 1989; Gaillard et al., 1989) are examined. Biological investigations deal with the biogenic influence on formation mechanisms, biological significance, and ecophysiological aspects of carbonate minerals (Krumbein, 1986; Krumbein and Schellnhuber, 1990; Riege et al., 1991; Gerdes et al., 1993).

While these studies are mainly based on the analysis of integrated geophysical, chemical and biological data, the exploration of the internal geometrical properties of the different sedimentary geosystems, as the arena for calcium carbonate formation, may yield deeper insights into the formation mechanisms.

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This conjecture is based upon two general findings. The first is that, by using modern image-analysis techniques and the concept of fractality as a quantitative framework for the description and classification of spatial features of complex geometries, much progress in the characterization of the internal surface and pore space properties has been achieved (Krohn, 1988a; Hansen and Skjeltorp, 1988; Huang and Turcotte, 1988; Bølviken et al., 1989; Keller et al., 1989). The key observation is that these structures, grown and modified by mainly stochastic processes, are often not simply disordered, but exhibit non-trivial statistical scale invariance over several orders of magnitude. The second finding is the observation that diffusion and chemical-reaction rates in these kinds of disordered systems do not follow the classical laws which describe these processes in ordered media (see, e.g. Havlin, 1989; Avnir and Farin, 1989). Anomalous diffusion properties with diffusion-limited reaction rates lead to different mineralization intensities, and thus to different distribution patterns of diagenetically formed minerals like carbonates. By using a recently proposed method consisting of a combination of scanning electron microscopy, and energy-dispersive X-ray spectrometry (SEM/EDX) elemental mapping and multifractal analysis of tracer distribution patterns, fingerprints of these fundamental processes can be extracted for a more comprehensive understanding of early diagenetic mineralization in complex media (Block et al., 1991; Kropp et al., 1994).

The aim of this paper is to demonstrate the application of this novel technique for determination of complex geometries and of sedimentary processes. This strategy and the resulting possibilities of application are still quite unusual for geophysicists (see e.g. Mandelbrot, 1989) and geologists as well as for geochemists. Therefore, discussions between the related disciplines are especially important in order to explore the possibilities and limits of the new procedures.

More specifically, we report on the formation of calcite coupled with the microbial mineralization of organic matter in microbial mats in Recent tidal flat sediments of the North Sea. The identification of particular processes and rates of calcite formation in those sediments remains an interesting question, since carbonates have been found to be mineralog-

ical contributors to early diagenetic cementation in organic-rich siliciclastic sediments even in temperate shallow marine and tidal sediments (Jorgensen, 1976; Pye et al., 1990; Moore et al., 1992). To address this question we detected and visualized calcite in microbial mats of different diagenetical stages by Ca-images obtained from SEM/EDX-elemental mapping. We used image-processed SEM/EDX elemental dot maps to separate the original sedimentary matrix from the primary pore space of detrital components, which has been filled by the formation of calcite. By quantifying the scaling characteristics of these different spatial distributions it was found that the microbially induced formation of magnesian calcium carbonate is a significant, locally dominant, and rapid early diagenetic process in Recent tidal sediments. The intensity of cementation and the distribution of carbonates exhibit microscopic variations and are connected with the structural features of the sedimentary substructure under investigation. Thus, multifractal analysis is a geometrical method which can provide further information on sedimentary systems and intrinsic processes.

First, the concept of multifractal analysis is briefly reviewed (see also Feder, 1988; Scholz and Mandelbrot, 1989; Korvin, 1992). Geochemical implications are then discussed and summarized.

2. Fractal geometry and multifractal measures

Disordered structures, such as sedimentary systems, can be characterized by their invariance under contractions or dilations. This kind of self-similarity is often realized in a subtle and seemingly random way. It can be quantified by calculating the fractal dimension (see, e.g. Feder, 1988; Mandelbrot, 1983), defined as:

$$D_B = \lim_{\varepsilon \rightarrow 0} \frac{\ln N(\varepsilon)}{\ln(1/\varepsilon)}$$

where ε is the lattice constant of d -cubic and non-overlapping covers of the structure under investigation, and $N(\varepsilon)$ is the number of the cubes contained in the minimal cover (Fig. 1).

Careful fractal investigations on the microstructure of sandstones indicate that pore volume distribution can be divided into two domains: a short-range regime with fractal behaviour and a long-range

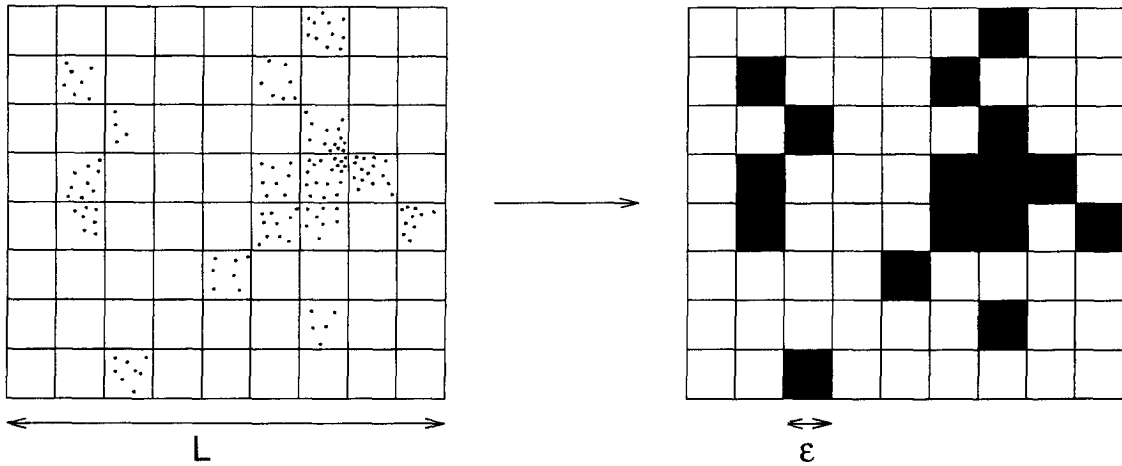


Fig. 1. Determination of a minimal non-overlapping cover (black boxes) of a point set embedded in 2-dimensional Euclidean space. ϵ denotes the lattice constant of the covering d-cubes and L is the diameter of the set.

regime where fractal characteristics are negligible. The fractal part appears to be strongly governed by the growth of minerals and cements in the pore space (Krohn, 1988b).

Factors that control sediment-intrinsic growth and cementation are the geometry of the pore structure itself and the interaction between solid matrix components and the components transported by the percolating fluids. As a consequence, one has to consider a complex spatial distribution of sorption and cementation intensities defining a distribution measure on the sedimentary microstructure, which is itself a self-similar object. As a consequence, such a pattern shows a more complicated behaviour than a distribution on objects which are homogeneous and translationally invariant. One single number, namely the ‘ordinary’ fractal dimension, is sufficient for the scaling characterization of the sedimentary matrix, but physical, chemical or biological processes, or probability and weight distributions that take place on a fractal structure, have to be described by multifractal measures (see, e.g. Tél, 1988). Such a measure describes the ‘probability’ of a functional value on these fractals. Here, the functional value is expressed by the mineralization of organic material coupled with the growth of carbonate, traced by calcium.

In practice, the measure under investigation is encoded as a finite ensemble of points in Euclidean space (in our case it is given by the 2-dimensional

coordinates of the elemental dots). Within this approximation it can be calculated by:

$$p_\nu(\epsilon) = \frac{N_\nu(\epsilon)}{N}$$

where $N_\nu(\epsilon)$ is the number of points falling into the ν -th box and N is the total number of dots. Instead of considering only the existence of calcium at a point (x,y) , new structural information is received by investigating the scaling of this density distribution.

One concept for quantifying the density distribution is based on the work of Hentschel and Procaccia (1983). This scaling index $D_B(q)$, the so-called ‘generalized (box-counting) fractal dimensions’, describes the scaling behaviour of a distribution measure on a fractal, *not* the fractal itself. It is defined by the following equation:

$$D_B(q) = \lim_{\epsilon \rightarrow 0} \frac{1}{q-1} \frac{\ln \sum_{\nu=1}^{N(\epsilon)} [p_\nu(\epsilon)]^q}{\ln \epsilon}$$

Here, the index ν labels the individual boxes of the ϵ -cover and $p_\nu(\epsilon)$ denotes the relative weight of the ν -th box. Another approach to treat multifractals is provided by Halsey and Jensen (1986), which resolves these measures into scaling components located on subsets of the individual ordinary box-counting dimension $f(\alpha)$. The entire range from $f(\alpha)$ of dimensions can be constructed easily via Legendre transformation once the $D_B(q)$ are known.

In our work we use the concept of Hentschel and Procaccia (1983).

It should be emphasized here that such a spectrum of generalized fractal dimensions $D_B(q)$ quantifies the non-uniformity of the density distribution of calcium found in the sedimentary pore space. If the generalized fractal dimensions $D_B(q)$ depend on the moment q , then this density distribution scales multifractally with respect to the chosen measure and the evaluated $D_B(q)$ quantify the nonuniformity.

A simple example of the non-isotropic elemental distribution in a geosystem illustrates this mathematical formalism. Normally, calcium enrichments (cumulated points) occur only in a few subregions of a sedimentary structure. Such a distribution of dots has to be described by a smaller fractal dimension. On the other hand, lower concentrations of calcium are more widespread. Such a set is characterized by a higher fractal dimension. A full description of the distribution with both higher- and lower-graded calcium domains succeeds only by calculating the fractal dimensions corresponding to each calcium concentration (dot density) as documented by multifractal spectra.

3. Study site

Investigations were carried out on lower supratidal sandy tidal flat sediments of Mellum Island in the East Frisian Wadden Sea of the southern part of the German Bight/North Sea (53°42.8'N, 8°8.1'E). Sandy and sandy/microbial mat supratidal flat sediments near Mellum Island have been studied with respect to their sedimentological conditions (Gerdes et al., 1985) as well as to their biology and to their microbiology (Stal, 1987; Wachendörfer, 1991).

The investigated cores of the upper sedimentary layers consist of (i) microbial mats and (ii) sand layers (Fig. 2). Microbial mats exhibit variable thickness due to the duration and rates of primary productivity and the activity of decomposer communities. The inorganic mineral components of the mats are quartz, feldspars and clay minerals (illite, chlorite, kaolinite and mixed layer minerals). Authigenic iron sulphides are common. The porosity is about 50–75% of the total volume. By contrast, sand layers consist nearly exclusively of quartz and have larger grain sizes and porosity of 40–55%.

Primary producers within the sedimentary system are cyanobacteria, e.g. *Microcoleus chthonoplastes* and *Oscillatoria limosa*, in the upper layers of the surface mat. In the lower parts of this mat and in the buried mats the organic substrate is progressively degraded by sulphate-reducing heterotrophic microbial communities.

The buried microbial mats are strongly anoxic. However, in the upper 85 mm of the profile the sediment is not permanently waterlogged, and oxygen ingressions can create oxic conditions in the sandy layers, causing precipitation of iron(III)oxyhydroxides in the sandy intercalations. In the deeper waterlogged zone, the sediments become oxygen-deficient as a whole.

In the upper aerated part of the profile horizontal stratification is dominant, whereas in the lower waterlogged part, vertical features (traces of bioturbation or wash-out features) and diffuse patches of varied geochemical condition and less vertical stratified petrographic features are visible. Typically, the wash-out features indicate preferential vertical interstitial water percolation.

4. Methods

4.1. Sampling and preparation

Samples were taken in April 1989 and in October 1990. At the sampling location a REINECK-box corer was carefully inserted. The microbial mats (Fig. 2) were subsampled in the field and prepared for optical/analytical SEM/EDX investigation.

Small parts of the sediment cores were cut off and fixed in 4% 1,5-pentanedial in seawater overnight. The specimens were washed several times to remove salt from the samples, before dehydration in a graded series of ethanol/aqua bidestillata mixtures (concentration series from 10 to 100% ethanol). The unconsolidated sediment was embedded in epoxy resin prior to polishing. Special care was taken to achieve a smooth polished surface. Finally, the specimens were sputtered with a thin gold or graphite coating.

4.2. Image analysis

Specimens were examined under a ZEISS DSM 940 scanning electron microscope (SEM) equipped

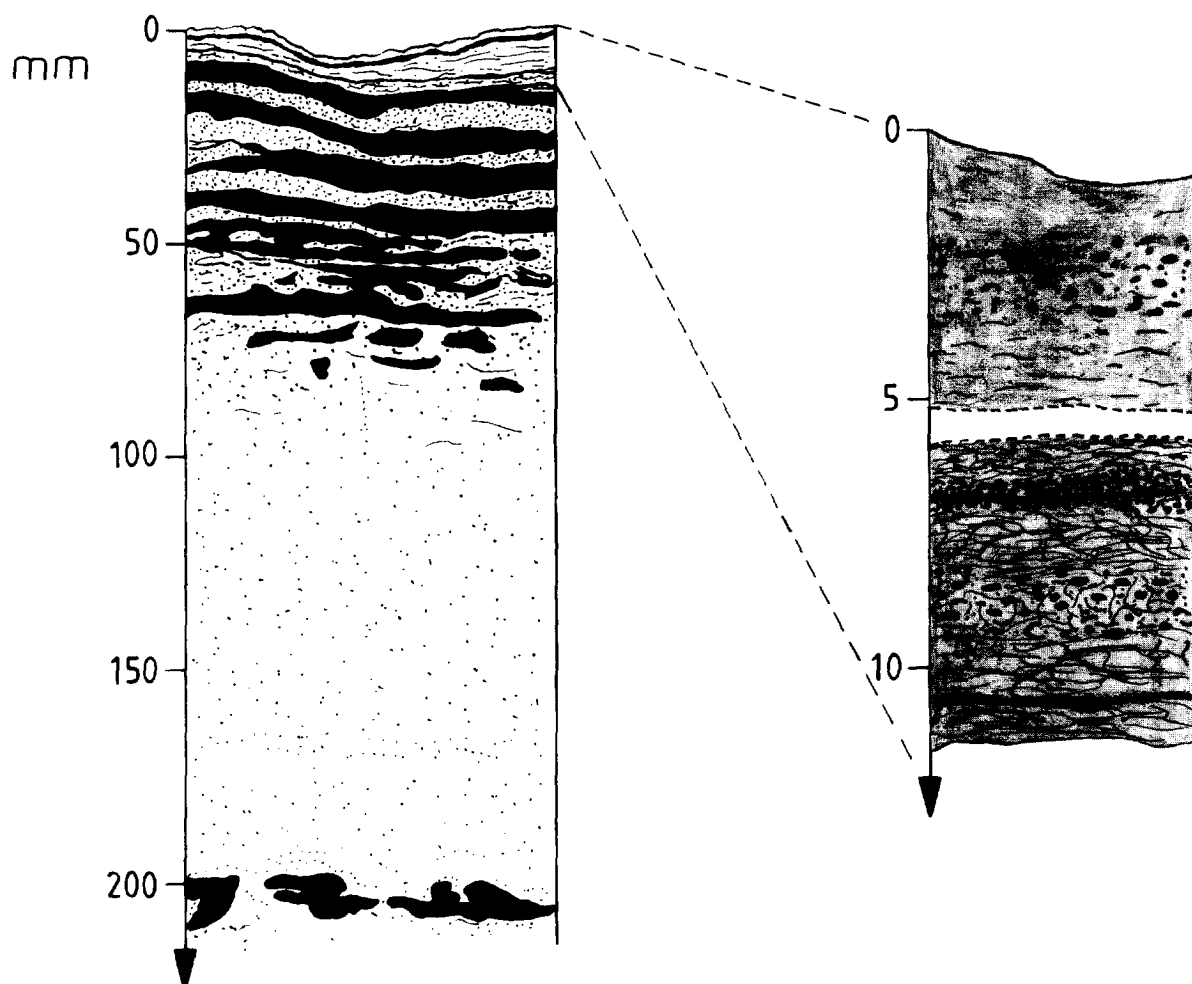


Fig. 2. Profile of a versicoloured sandy tidal flat sedimentary column. The first few millimetres represent the Recent microbial mat system, followed by an alternating bedding of sand layers and subrecent mats (black) of variable thickness. The Recent microbial mat system is characterized by different textural properties like smoothly shaped or partly degraded organic matter.

with a LINK QX 2000 energy-dispersive X-ray spectrometer (EDX). Elemental dot maps were obtained and digitized with a resolution of 412×512 pixels in 256 grayscales using an image processing unit (Series 151 image processor by Imaging Technology Inc.).

The elemental dots in the images mark the occurrence of calcium in the sedimentary sample. Obviously, this spatial distribution corresponds to the pore distribution. In order to get a coordinate list, which is the appropriate data structure for the used box-counting algorithm (Block et al., 1990), the image data were reduced to binary information by performing threshold filtering and extracting the coordinates

of the elementary distribution from the digital picture. The box-counting algorithm directly calculates the generalized fractal dimensions $D_B(q)$ by using the coordinate list of elemental dots. The algorithm is implemented on a parallel computer consisting of four transputers from INMOS (T800 + 1 MB RAM), which are installed in an ordinary AT personal computer controlling the image-processing unit and allowing fast processing of SEM/EDX images.

To estimate the effects of the X-ray background signal on our results we produced random maps and dot maps of the embedding material (blind values) for various acceleration voltages and background

compensations. Analysis of these maps shows in every case a uniformly distributed scaling characteristic ($D_B(q) \propto 1.85$, $0 \leq q \leq 10$). We suppressed these overall effects extensively by choosing suitable numbers for both the acceleration voltage and the background compensation.

The accuracy of the D_B -values was improved by applying a classwise linear regression method for minimizing the mean square deviation. This method also gives an estimate of the scaling region, which is always limited by finite size effects, i.e. by the limited resolution of the images. For details and further tests, see Block et al. (1991).

4.3. Mineralogical characterization

The analysis was carried out in the following steps. (i) A visual SEM-examination of the sedimentological situation with respect to both the mineralogical composition and the biological phenomena was performed. (ii) Elemental dot maps from different horizons and distinct domains of the observed structure were prepared. It was important during this stage to suppress the influence of detrital compounds, such as mussel shells, etc. Only those horizons were analyzed, which were originally exclusively composed of organic matter. (iii) If higher concentrations of authigenic mineral phases were detectable, these layers were prepared for mineralogical identification by X-ray diffractometry (XRD).

The identification of mineralized calcium compounds was performed by XRD (Philips PW 1410) after completion of all optical and analytical investigations. Horizons containing authigenic calcium minerals were located visually by comparison with the electron photomicrograph. Subsequently, the specimens in question were sliced into thin layers under a light microscope. After this procedure the sub-specimens with a higher content of carbonates were separated, pulverized and examined by common powder spectrometry methods.

5. Results

For the structure under investigation the following main observations can be made.

(i) With respect to the scaling behaviour, the density distributions of calcium dot maps show large

differences and non-uniform characteristics, depending on the observed sedimentary layer. In certain realms (thickness approximately 100–300 μm) a higher content of calcium was found. Other horizons exhibit a quite low or negligible concentration.

(ii) In Ca-rich horizons syndepositional and early diagenetic high-magnesium calcite ($\text{Ca}_{1-x}\text{Mg}_x$) CO_3 , $x \simeq 0.13$; the value of x is determined after Goldsmith et al. (1961)) is present. This authigenic calcite can be located by calcium dots during SEM/EDX analysis. The distribution and formation of this mineral is coupled to the breakdown and replacement of organic matter due to the activity of heterotrophic microbial communities.

6. Discussion

6.1. Elemental maps

Each elemental dot map is described by a fractal dimension $D_B = D_B(0) \simeq 1.85$ (see Table 1). That quantifies the scaling behaviour of the underlying sedimentary structure, namely the organic matrix. Consequently, all samples exhibit the *same* morphological and geometrical characteristics. Further information and a definite description of the differences in the calcium density distributions are provided by the generalized fractal dimensions $D_B(q)$, $q > 0$. Different classes of scaling behaviour are observed relative to these spectra.

Fig. 3 shows a sequence of dot maps and their associated multifractal $D_B(q)$ -spectra obtained from different horizons of the site investigated. The layer at a depth of 6 mm (Fig. 3c) exhibits a strong decline

Table 1
Values of $D_B(q)$ belonging to the dot maps of Fig. 3

Depth (mm)	Generalized box-counting dimension of subsets (weighted by q)		
	0	3	10
0.50	1.82 ± 0.04	1.16 ± 0.11	0.94 ± 0.14
2.75	1.85 ± 0.05	1.78 ± 0.04	1.77 ± 0.05
6.00	1.84 ± 0.06	1.23 ± 0.14	1.12 ± 0.23
6.25	1.87 ± 0.05	1.63 ± 0.03	1.54 ± 0.13
6.50	1.86 ± 0.05	1.83 ± 0.04	1.85 ± 0.06
8.00	1.84 ± 0.05	1.40 ± 0.11	1.14 ± 0.15
8.50	1.85 ± 0.05	1.50 ± 0.07	1.37 ± 0.09
9.25	1.87 ± 0.05	1.75 ± 0.03	1.76 ± 0.07

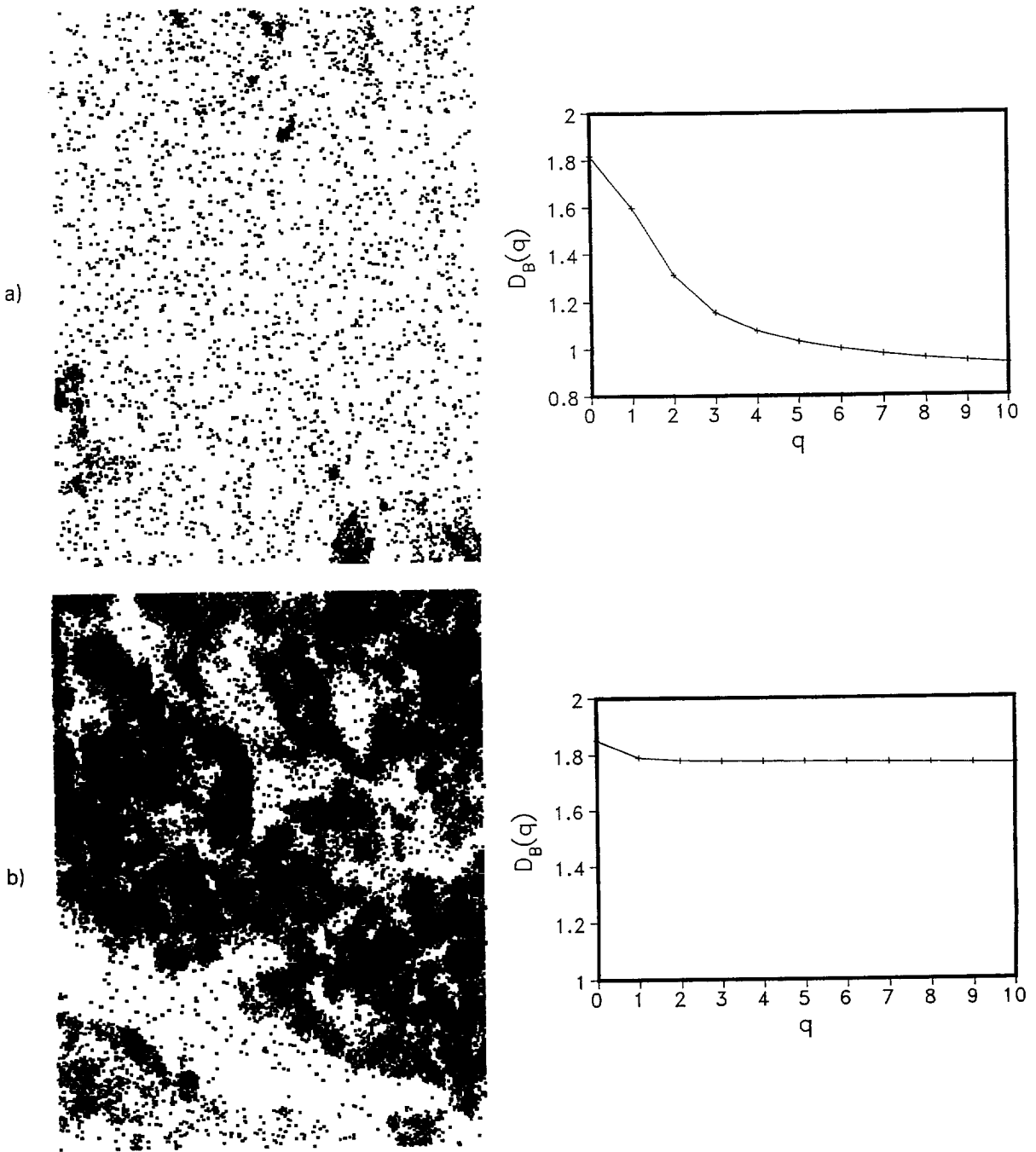
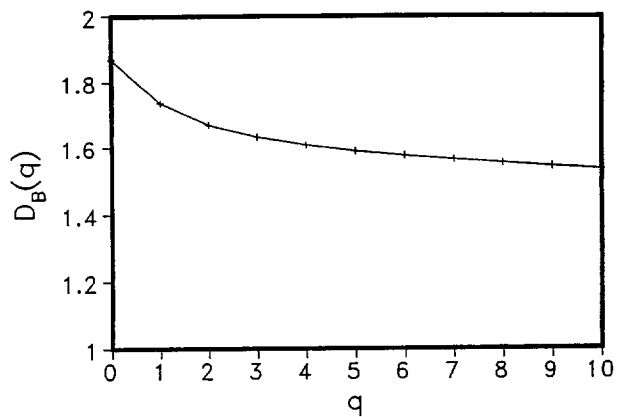
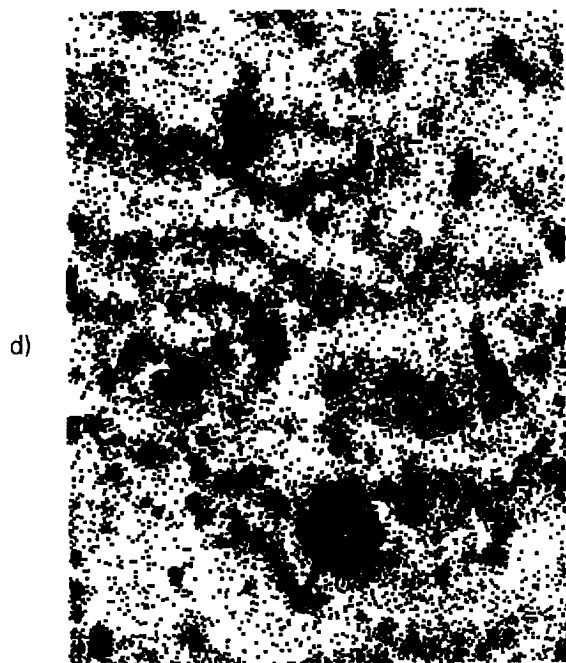
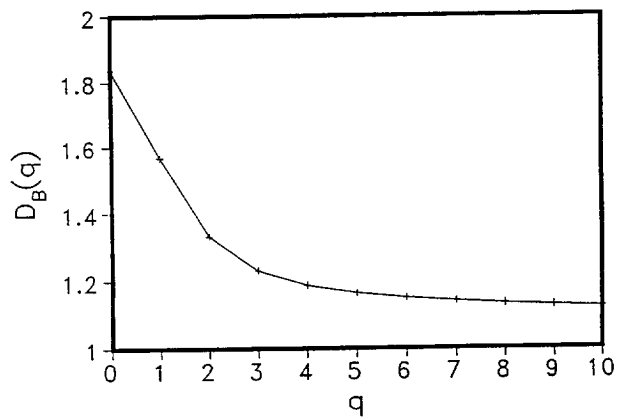
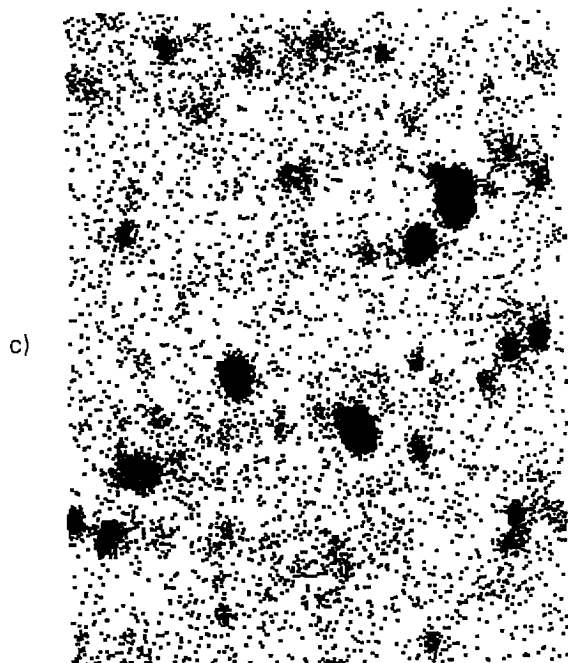


Fig. 3. Digitized calcium distribution maps (412×512 pixel) obtained from different horizons of a Recent microbial mat and their associated multifractal spectra: (a) 0.5 mm, 5253 points; (b) 2.75 mm, 60,261 points.

of $D_B(q)$: from $D_B(0) \simeq 1.84$ to $D_B(3) \simeq 1.23$, and finally to $\simeq 1.12$, at $q = 10$. The calcite concentration in this layer is quite low and is characterized by

inhomogeneously distributed single dots or by small and sharply bordered clusters of points. The next layer (Fig. 3d) exhibits an increase in the number of calcite



scale:  20 μm

Fig. 3 (continued). (c) 6.0 mm, 10,794 points; (d) 6.25 mm, 34,019 points.

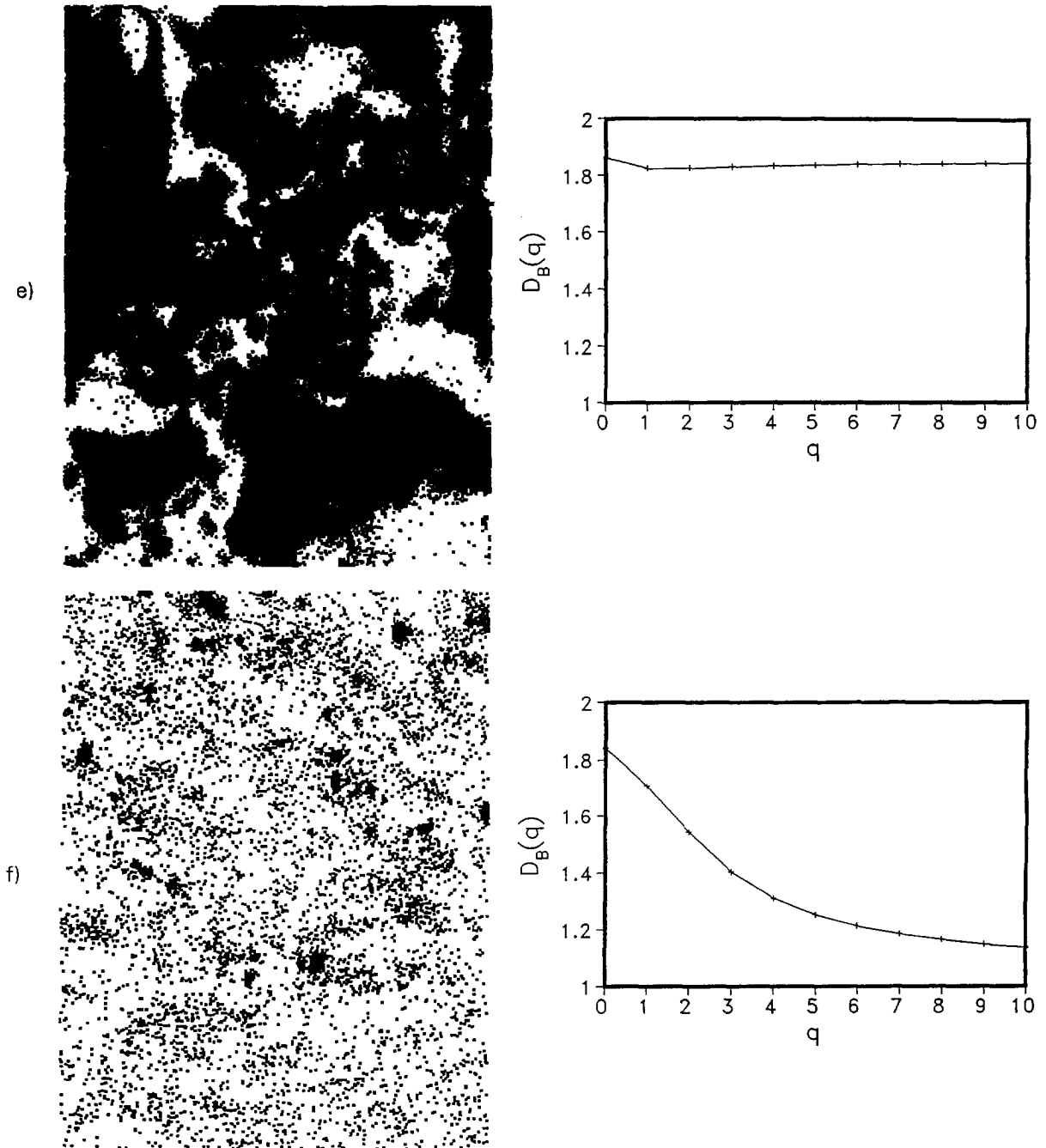


Fig. 3 (continued). (e) 6.5 mm, 110,487 points; (f) 8.0 mm, 9057 points.

clusters and shows less inhomogeneous behaviour. This distribution is characterized by the dimensions $D_B(3) \simeq 1.63$ and $D_B(10) \simeq 1.54$, respectively. In

some other cases the small residue of organic matter is completely calcified (Fig. 3e). These space filling distributions scale almost homogeneously and, in

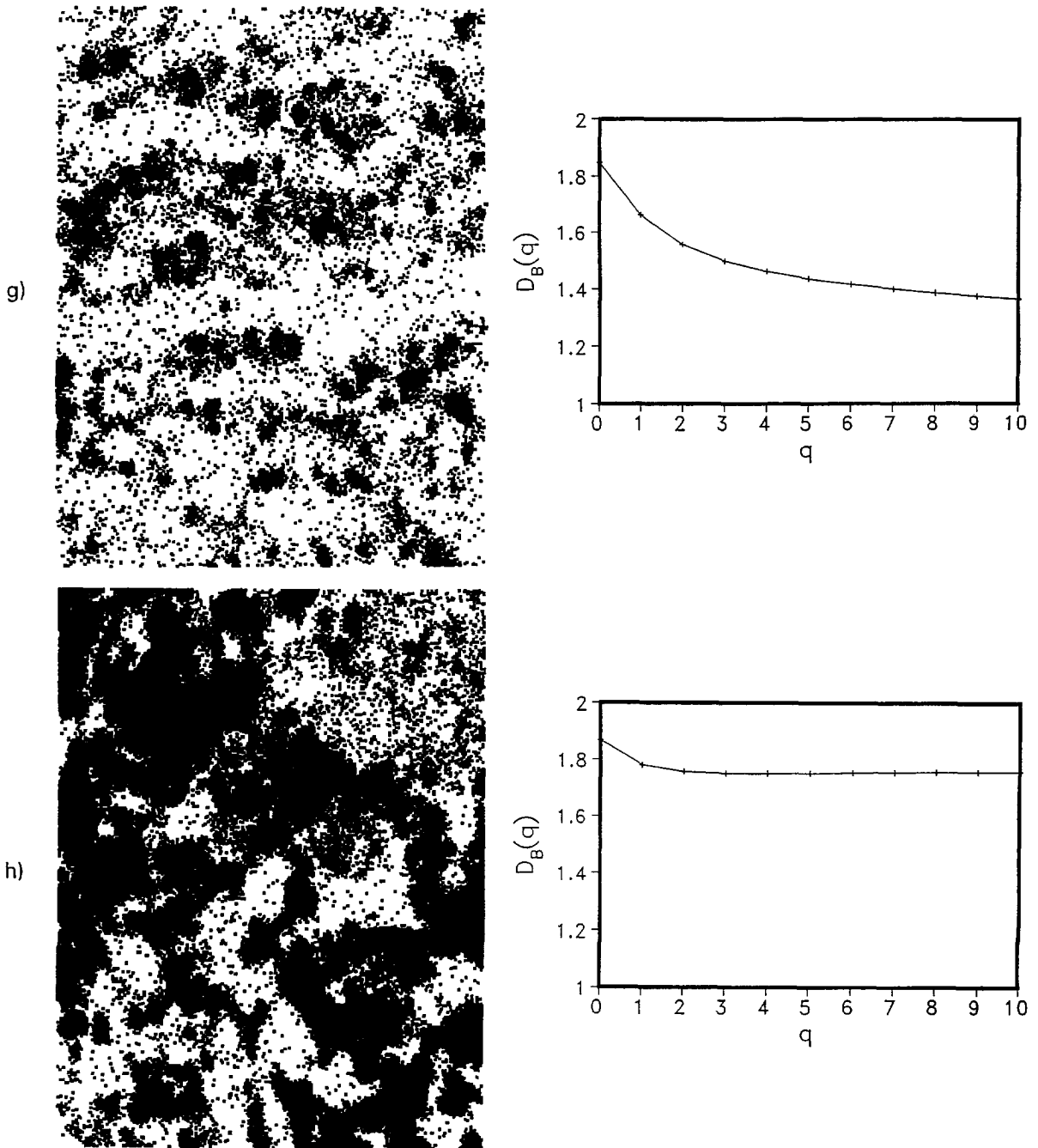


Fig. 3 (continued). (g) 8.5 mm, 21,677 points; (h) 9.25 mm, 74,258 points.

consequence, a distinct change in the behaviour of the multifractal spectra appears: there is no decline of $D_B(q)$ (e.g., $D_B(3) \simeq 1.83$, $D_B(10) \simeq 1.85$).

Such a homogeneous distribution corresponds to an increase in the intensity of the mineralization process. In this sense, the emerging spectra can simply

be conceived as a measure of the significance of the authigenic calcite formation on a microscopic scale.

One probable reason for such differences in distribution may be seen in the activities of various decomposer communities. Their metabolism is a fundamental precondition for a suitable environment for calcium carbonate formation (see Berner, 1971). But their distribution itself is not homogeneous and is influenced by environmental factors, such as absence of oxygen, salinity, and availability of different organic nutrients etc. (see, e.g. Stal et al., 1985). Diagenetic calcite formation is a complex interlinking of processes that often are locally separated from each other. Calcite precipitation and calcification usually occur in layers below regions of maximal heterotrophic activity. Within microbial mats, however, microbial degradation of organic matter and calcification proceed simultaneously, as documented by the structural and geochemical data. Assuming that conditions of calcite formation are a function of microbial activity, quantification of such activities during certain periods of time seems to be possible by using multifractal measures.

6.2. Calcite

The syndepositional and early diagenetic formation of high-magnesian calcite ($(\text{Ca}_{1-x}\text{Mg}_x)\text{CO}_3$, $x \approx 0.13$) is linked with the simultaneous degradation of organic matter (Fig. 4). This replacement of organic matter by authigenic carbonates is directly or indirectly related to the activity of heterotrophic microbial communities. This has already been studied in artificial systems. It has been found, in particular, that marine heterotrophic bacteria precipitate aragonite and other carbonates (magnesium calcite and mono-hydrocalcite) from seawater under anaerobic and aerobic conditions at pH 6.9 to 8.7 directly on the cell surface (Krumbein, 1974). In addition, autotrophic as well as heterotrophic bacteria shift the fugacity of CO_2 of their environment and induce carbonate formation. Magnesian calcite rather than pure calcite will precipitate from seawater solutions (Mucci and Morse, 1984). Precipitates of other minerals of the characteristic assemblage of authigenic minerals, such as sulphides, phosphates and amorphous silica, that also indicate microbial activities (Suess, 1979), were not identified in our study.

As indicated by Figs. 3 and 4, calcite formation depends on the sedimentary organic material. Thus, the organic structure rules the transport properties of the substances involved in the formation as well as in the metabolic activity of the sedimentary bacteria. The microbes of the microbial mats produce large amounts of extracellular polymeric substances. These exopolymers, mainly polysaccharides, are interlinked by ionic and covalent bridges (Decho, 1994) involving exchangeable Ca- and Mg-cations. In the course of the mineralization of the exopolymers, Ca- and Mg-cations are mobilized and available for calcite formation. In natural aphotic sediments this formation requires the presence of active heterotrophic bacteria (Chafetz, 1994). Direct or indirect formation of calcite only takes place on the surface of cells, organic material, and pore surfaces. During early diagenesis pore space increases and simultaneously calcifies, while the primary organic matter is progressively degraded. Chafetz (1994) gives examples of the different morphologies of carbonates formed during the lithification of cyanobacteria in environments where, in general, calcite precipitation is thermodynamically favoured or prevented. In both cases, he identified aggregates composed by a myriad of monomineralic micro-sized carbonate crystals. The aggregate morphologies do not show the habits of the different minerals observed, namely calcite, aragonite, and high-magnesian calcite. In our microscopical investigations we did not find crystals either. Thus, it can be concluded that calcite formation starts in a sediment where the local biologically controlled geochemical conditions favour precipitation of calcite. Therefore, the calcite density distribution indicates the state of this biogenic morphogenetic process.

In bioactive sediments, calcite formation is common, prominently in warmer and especially in hypersaline environments (Riege et al., 1991; Gerdes et al., 1993; Chafetz, 1994). Carbonate precipitation is a normal phenomenon in tidal flats under tropical and subtropical conditions. Even under temperate climatic conditions, the formation of carbonate cementations in siliciclastic coastal sediments can be observed. However, one precondition for carbonate formation is a reducing interstitial environment plus a high content of organic material. Pye et al. (1990) and Al-Agha et al. (1995) have shown that

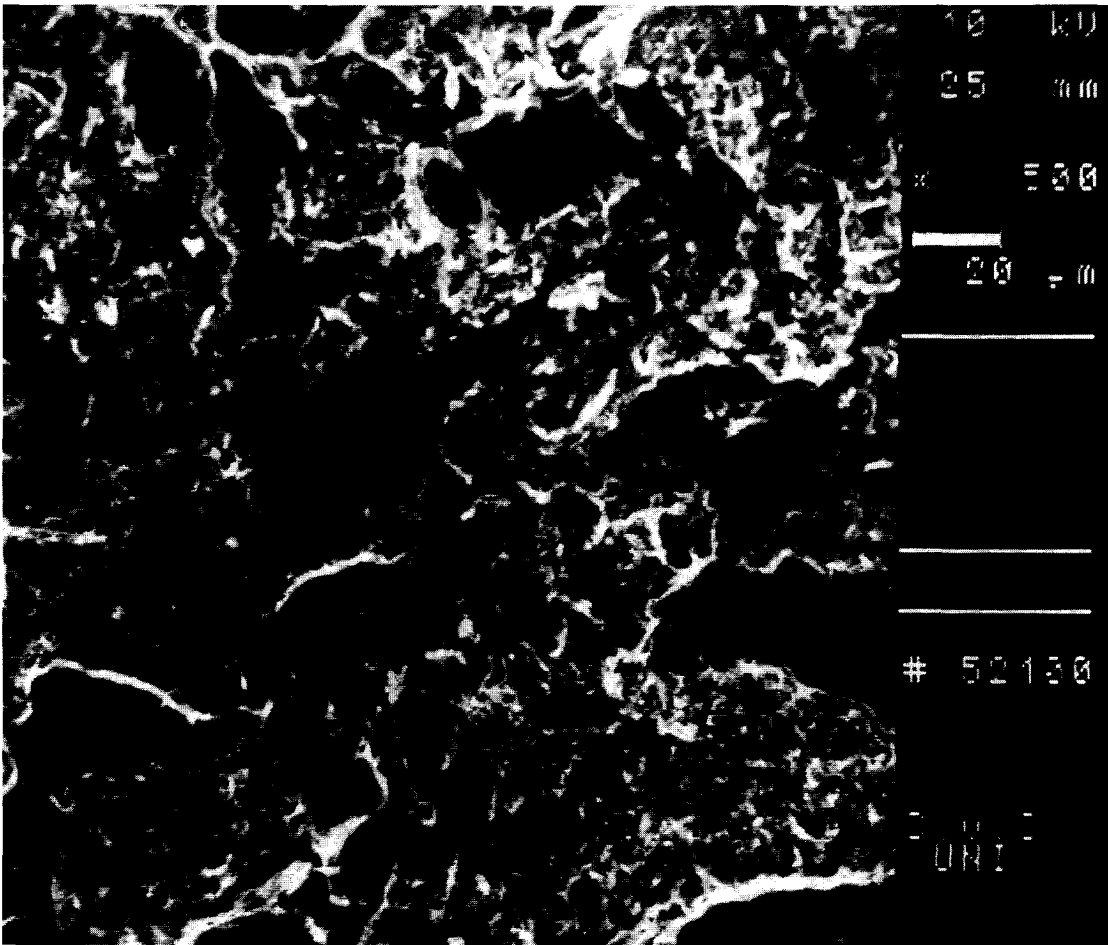


Fig. 4. Scanning electron photomicrograph of a Recent microbial mat (the same detail as Fig. 3e). The black zones represent organic matter, the grey zones authigenically formed calcite.

carbonates based on several nuclei can be formed sequentially with different early diagenetic minerals. This carbonate formation only occurs several centimetres or more below the surface of the sediment. According to Pye et al. (1990), the formation of carbonate cementation takes 6 months. However, as documented by this study, magnesian calcite formation occurs: (i) even in the uppermost layers of siliciclastic tidal sediments in humid climate and at generally moderate temperatures; and (ii) these carbonates are rapidly formed within a time space of some days or less. Riege and Villbrandt (1994) have shown that this is a common phenomenon in siliciclastic sediments containing microbial mats in the southern North Sea. This can be attributed

to situations where there are high overall levels of microbiological activity in the sediment and when temperatures within the upper sedimentary layers are unusually high during the summer.

6.3. Wider implications

Even though the definition of the fractal calculus is derived from geological objects, the identification and quantitative investigation even of geologically significant processes by means of multifractal analysis raises special difficulties, in contrast to corresponding investigations of chemical and biological processes. Very often, this is the consequence of the superposition of many, sometimes opposed, pro-

cesses that influence the formation and modification of materials, as, for example, for the sediments studied. There is, however, a suitable basis for geometric quantification via multifractal analysis. This means that the calcification of organic substance is the dominant process of the early diagenesis in this sediment.

It must be emphasized that, by means of multifractal analysis of distribution geometries, exemplified by still unfamiliar characteristic values, sediment structures can be used for the investigation of dynamic processes. Thus, multifractal data are a direct basis for quantitative comparisons between different rocks and are potentially as important as geochemical, microbiological and mineralogical data. It seems reasonable to relate distribution geometry and the intensity of processes effective during the first phase of early diagenesis. In the example documented here, although variations in calcification rate cannot be determined, the overall calcification rate can be calculated.

Calcite formation in temperate water intertidal siliciclastic sediments seems to be an evident phenomenon. However, formation processes and occurrence in the geological record are not well documented. The example of Recent North Sea sediments is relevant to the stabilization of tidal sandy sediments by carbonates and even to the development of siliciclastic stromatolites (Martin et al., 1993).

7. Conclusions

Imaging of calcium by combination of scanning electron microscopy, X-ray energy-dispersive analysis, and X-ray diffraction methods allows clear detection of early diagenetic magnesian calcite in Recent microbial mats. Moreover, the SEM/EDX images show the spatial distribution of calcium in the sedimentary layer. The major advantage of the applied SEM/EDX method is the non-destructive character of the analysis: even sensitive organic sedimentary structures are not damaged and can be examined. By applying multifractal box-counting analysis to such elemental dot maps, a *quantitative* description of the distribution can be obtained.

The microscopic variations in calcium distribution measured in the specimens exhibit an unambiguous multifractal behaviour. These spectra describe the state of calcification and seem to be connected to the

local activity of microbial decomposer communities. The observed periodic structure of the calcification intensity has not yet been explained. It requires further examination.

The method presented is not limited to the analysis of microbial mats; it can be applied to other sedimentary substructures, e.g. sand layers. Preliminary results of calcium distribution behaviour in sand layers show different multifractal characteristics when compared to microbial mats. These distributions are governed by abiotic processes, mainly diffusive flux and other transport mechanisms. Virtual structures evolved by 2-D-computer simulations (cellular automaton technique) of such mechanisms show structures similar to those found in Recent sediments (Kropp and Klenke, 1994).

Future work will focus on a better understanding of the connection of multifractal spectra with chemical and biological processes and the investigation of other authigenic mineralization processes, e.g. formation of pyrite.

Summing up, we feel that the results obtained open a promising new road towards quantitative description of diagenetic processes and the microstructure of the underlying sedimentary system. Further insights into intrinsic dynamic events recorded in these ordered and disordered structures can be expected.

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References

- Al-Agha, M.R., Burley, S.D., Curtis, C.D. and Esson, J., 1995. Complex cementation textures and authigenic mineral assemblages in Recent concretions from the Lincolnshire Wash (East coast, UK) driven by Fe(0) and Fe(II) oxidation. *J. Geol. Soc.*, 152: 157–171.
- Avnir, D. and Farin, D., 1989. The fractal nature of molecule-surface interactions on reactions. In: D. Avnir (Editor), *The Fractal Approach to Heterogeneous Chemistry*. Wiley and Sons, Chichester, pp. 271–294.
- Berner, R.A., 1971. *Principles in Chemical Sedimentology*. McGraw Hill, New York, pp. 114–137.
- Block, A., Von Bloh, W. and Schellnhuber, H.J., 1990. Efficient

- box-counting determination of generalized fractal dimensions. *Phys. Rev. A.*, 42: 1869–1874.
- Block, A., Von Bloh, W., Klenke, T. and Schellnhuber, H.J., 1991. Multifractal analysis of the microdistribution of elements in sedimentary structures using images from scanning electron microscopy and energy dispersive X-ray spectrometry. *J. Geophys. Res.*, 96: 16223–16230.
- Bölviken, B., Stokke, P.R., Feder, J. and Jössang, T., 1992. The fractal nature of geochemical landscapes. *J. Geochem. Explor.*, 43: 91–109.
- Boudreau, P.B. and Canfield, D.E., 1993. A comparison of closed- and open-system models for porewater pH and calcite-saturation state. *Geochim. Cosmochim. Acta*, 57: 317–334.
- Chafetz, M.S., 1994. Bacterially induced precipitates of calcium carbonate and lithification of microbial mats. In: W.E. Krumbein et al. (Editors), *Biostabilization of Sediments*. BIS, Oldenburg, pp. 149–163.
- Decho, A.W., 1994. Molecular-scale events influencing the macroscale cohesiveness of exopolymers. In: W.E. Krumbein et al. (Editors), *Biostabilization of Sediments*. BIS, Oldenburg, pp. 135–148.
- Feder, J., 1992. *Fractals*. Plenum Press, New York, 283 pp.
- Gaillard, J.F., Pauwels, H. and Michard, G., 1989. Chemical diagenesis in coastal marine sediments. *Oceanol. Acta*, 12(3): 175–187.
- Gerdes, G., Krumbein, W.E. and Reineck, H.E., 1985. The depositional record of sandy, versicolored tidal flats (Mellum Island, Southern North Sea). *J. Sediment. Petrol.*, 55: 265–278.
- Gerdes, G., Claes, M., Dunaitshik-Piewak, K., Riege, H., Krumbein, W.E. and Reineck, H.E., 1993. Contribution of Microbial Mats to Sedimentary Surface Structures. *Facies*, 29: 61–74.
- Goldsmith, J.R., Graf, D.L. and Eard, H.C., 1961. Lattice constants of the calcium–magnesium carbonates. *Am. Mineral.*, 46: 453–457.
- Halsey, T.C. and Jensen, M.H., 1986. Spectra of scaling indices for fractal measures: theory and experiment. *Physica D*, 23: 112–117.
- Hansen, J.P. and Skjeltorp, A.T., 1988. Fractal pore space and rock permeability implications. *Phys. Rev. B*, 38: 2635–2638.
- Havlin, S., 1989. Molecular diffusion and reactions. In: D. Avnir (Editor), *The Fractal Approach to Heterogeneous Chemistry*. Wiley and Sons, Chichester, pp. 251–270.
- Hentschel, H.G.E. and Procaccia, I., 1983. The infinite number of generalized dimensions of fractals and strange attractors. *Physica D*, 8: 4435–4444.
- Huang, J. and Turcotte, D.L., 1989. Fractal mapping of digitized images: Application to the topography of Arizona and comparison with synthetic images. *J. Geophys. Res.*, 94: 7491–7497.
- Jorgensen, N.O., 1976. Recent high magnesian calcite/aragonite cementation of beach and submarine sediments of Denmark. *J. Sediment. Petrol.*, 46: 940–951.
- Keller, J.M., Chen, S. and Crownover, R.M., 1989. Texture description and segmentation through fractal geometry. *Comput. Graphics Image Process.*, 45: 150–166.
- Korvin, G., 1992. *Fractal Models in the Earth Sciences*. Elsevier Science Publ., Amsterdam, 396 pp.
- Krohn, C.E., 1988a. Sandstone fractal and Euclidean pore volume distributions. *J. Geophys. Res.*, 93: 3286–3296.
- Krohn, C.E., 1988b. Fractal measurements of sandstones, shales and carbonates. *J. Geophys. Res.*, 93: 3297–3305.
- Kropp, J. and Klenke, T., 1994. Fraktalgeometrische Analyse und Modellierung von Mineralisationsprozessen in porösen Medien. In: J. Matschullat and G. Müller (Editors), *Umwelt und Geowissenschaften*. Springer Verlag, Berlin, pp. 341–345.
- Kropp, J., Block, A., Von Bloh, W., Klenke, T. and Schellnhuber, H.J., 1994. Characteristic multifractal element distributions in recent bioactive marine sediments. In: J.H. Kruhl (Editor), *Fractals and Dynamic Systems in Geosciences*. Springer Verlag, Berlin, pp. 369–375.
- Krumbein, W.E., 1974. On precipitation of aragonite on the surface of marine bacteria. *Naturwissenschaften*, 61: 167.
- Krumbein, W.E., 1986. Biotransfer of minerals by microbes and microbial mats. In: B.S.C. Leadbeater et al. (Editors), *Biomining in Lower Plants and Animals*. Blackwell, Oxford, pp. 55–72.
- Krumbein, W.E. and Schellnhuber, H.J., 1990. Geophysiology of carbonates as a function of bioplanets. In: V. Ittekkot et al. (Editors), *Facets of Modern Biogeochemistry*. Springer, Berlin, pp. 5–22.
- Mandelbrot, B.B., 1983. *The Fractal Geometry of Nature*. Freeman and Co., New York, 468 pp.
- Mandelbrot, B.B., 1989. Multifractal measures, especially for the Geophysicists. *PAGEOPH*, 131: 1–42.
- Martin, J.M., Braga, J.C. and Riding, R., 1993. Siliciclastic stromatolites and thrombolites. Late Miocene, S.E. Spain. *J. Sediment. Petrol.*, 63: 131–139.
- Moore, C.H., 1989. *Carbonate Diagenesis and Porosity*. Elsevier, Amsterdam, 338 pp.
- Moore, S.E., Ferrell, J.R. and Aharon, P., 1992. Diagenetic siderite and other ferroan carbonates in an modern subsiding marsh sequence. *Sedimentology*, 62: 357–366.
- Mucci, A. and Morse, J.W., 1984. The solubility of calcite in seawater solutions of various magnesium concentration, $I_1 = 0.697$ m at 25°C and one atmosphere total pressure. *Geochim. Cosmochim. Acta*, 48: 815–822.
- Pye, K., Dickson, J.A.D., Schiavon, N., Coleman, M.L. and Cox, M., 1990. Formation of siderite–Mg–calcite–iron sulphide concretions in intertidal marsh and sandflat sediments, north Norfolk, England. *Sedimentology*, 37: 325–343.
- Riege, H. and Villbrandt, M., 1994. Microbially mediated processes in tide influenced deposits and their importance in stabilization and diagenesis of sediments—Seasonal field studies, Norderney survey. In: W.E. Krumbein et al. (Editors), *Biostabilization of Sediments*. BIS, Oldenburg, pp. 339–360.
- Riege, H., Gerdes, G. and Krumbein, W.E., 1991. On the contribution of heterotrophic bacteria in the formation of CaCO₃-aggregates in hypersaline microbial mats. *Kieler Meeresforsch., Sonderh.*, 8: 168–172.
- Scholz, C.H. and Mandelbrot, B.B., 1989. Fractals in Geophysics. *Spec. Iss., Pure Appl. Geophys.*, 131(1/2), 313 pp.
- Stal, L.J., 1987. Ökologie der Bakterien des Farbstreifensandwattes. In: G. Gerdes et al. (Editors), *Mellum Portrait einer Insel*. Kramer, Frankfurt, pp. 188–202.

- Stal, L.J., Van Gemerden, H., and Krumbein, W.E., 1985. Structure and development of a benthic marine microbial mat. *FEMS Microbiol. Ecol.*, 31: 111–125.
- Suess, E., 1979. Mineral phases formed in anoxic sediments by microbial decomposition of organic matter. *Geochim. Cosmochim. Acta*, 43: 339–352.
- Tél, T., 1988. Fractals, multifractals and thermodynamics. An introductory review. *Z. Naturforsch.*, 43a: 1154–1174.
- Wachendörfer, V., 1991. Parahistologische und sediment-mikrobiologische Untersuchungen an einem potentiellen silikolastischen Stromatolithen. PhD dissertation, University of Oldenburg.