

LIFE ON AND IN STONE – AN ENDLESS STORY?

Wolfgang E. Krumbein

Biogema-Consulting, Edeweicht, Germany

E-Mail: wek@biogema.de Internet: <http://www.biogema.de>

Abstract

Concern with rock decay started early in the history of the mankind. However, the last two centuries yielded a large wealth of information on the manifold aspects of rock decay and rock protection related to the physical cultural heritage. The most important branches of scientific endeavour in this field were air pollution related studies and the increasing awareness of biodeterioration. In this overview the evolution of trends and techniques in the study of rock biology is described. The main lines of the presentation are the changes in search for the most detrimental organisms and the causes for their deteriorating activity. An attempt is made to quantify the influence of organisms within the general frame of rock decay mechanisms. Another focus of the contribution is on protective biofilms or products of biofilms. Within this context the role of lichen, algae, cyanobacteria and fungi in the formation of rock films usually described as patina is elaborated. A brief summary is given on modern molecular techniques of analysis and novel combined or multi-technical approaches to eliminate or avoid detrimental growth on and in rock.

Keywords: Biodeterioration, biofilm, heterotrophy, micromycetes, patina, subaerial biofilms,

1. Introduction

The history of general restoration and conservation ideas goes far back. Goetz (1999) has recently published the history of conservation ideas in Europe. Early European attempts were summarised by Brimblecombe (1986) The history of biological attack and damage was summarised by Koestler and Vedral (1991), Krumbein (1973, 1986) and Saiz-Jimenez (1995, 1999). Yearbooks and symposium publications are useful sources (Baer and Snethlage, 1997; Besch, 2002; Krumbein et al., 1994; Snethlage 1989-1996). Noteworthy activities in Germany originated in 1972 with the Archeometry Programme of the Volkswagenstiftung. These activities were re-activated and continued by the DFG through the SFB 315, "Erhalten historisch bedeutsamer Bauwerke" (Wenzel, ed., 1985-1996) and by the Ministry of Science and Technology through the Programme "Steinzerfall und Steinkonservierung" (Snethlage, ed., 1986-1999). This contribution deals mainly with the problems and the status of the art of biogenic damage and diagnosis of rock materials. The importance of bioreceptivity of rocks, biofilms and bio-networks (Biodyction) and, obviously biodeterioration and techniques to avoid biological attack are in the centre. Two books have been devoted to the topic in the frame of the „Dahlem Conferences“ (e.g. Viles et al., 1997; Krumbein et al., 1994; Baer and Snethlage, 1997). Recently biodeterioration of cultural heritage expanded that far that a special Symposium Series was created, namely "Of Microbes and Art, The Role of Microbial Communities in the Degradation and Protection of Cultural Heritage". The first Symposium was held in Firenze (Ciferri et al., 2000) the second one took place at the Metropolitan Museum in New York and the third one is announced for the United Kingdom (Portsmouth Polytechnic, Eric May). Thus the impact of microbes on the deterioration and also the invasion of surfaces by biofilms as well as the protection of monument surfaces through similar communities evolved into the central focus of a still growing scientific community

(Saiz-Jimenez, 2003; Krumbein et al., 2003). In this contribution the major qualitative and quantitative issues will be discussed and gaps of our knowledge as well as future fields of research will be defined.

2. Damage Functions – Biodeterioration

The main factors ruling damage and decay on and in rock materials are the decay resistance and cohesivity of minerals and rocks. The main building rocks are either magmatic and metamorphic rocks such as basalt, granite, diorite, marble, quartzite, schist (slates) to name a few, or sedimentary rocks consisting mainly of a large variety of sandstones (calcareous and siliceous) and limestones. The resistance to wear down of the most common minerals decreases in the following sequence: Quartz, Mica, K-Plagioclase, Na-Plagioclase, Amphibole, Oxalates, Dolomite, Pyroxene, Apatite, Calcite, Feldspatoids, Olivine. The listing gives an idea about the resistance of minerals to dissolution and destruction. In general these resistance factors are related to the solubility of certain minerals. However, some exceptions do occur. Calcium oxalate for example is a very insoluble mineral, which is created in large amounts in biofilm generated patina layers on many rocks and monuments. Despite the relatively low solubility (by several orders lower than that of calcium carbonate, including calcite and dolomite) it is, however quite rapidly transformed into calcite, and even gypsum in the course of biodeterioration and biotransformation of rock surfaces (Verrecchia et al., 2003). Calcium oxalate stained by organic pigments causes coatings of anaesthetic appearance. In this case the oxalate seems not to be transformed into calcite. Krumbein (1966, 1972, 1988, 1993, 1998, 2003) as well as Saiz-Jimenez (1999, 2003) have indicated the catalytic power of rock biota in the general process of rock decay. Under relatively low air and material humidity regime rock is even biodeteriorated faster than wood. Wood rot is typically occurring only or at least is only accelerated when humidity exceeds the values critical for rock decay. Rock biodeterioration starts at humidities as low as 55- 60%, while wood decay is accelerated only above 70-75% and drastically increases at 80-90%, whereas the biodecay of rock may even decrease at very high humidity because of the protective role of rock biofilms. The main processes of biodeterioration have gone through interesting cycles in terms of the theories related to the biogenic attack. Literature summarized by Krumbein (1972, 1986) and Koestler and Vedral (1991) for the ICOMOS stone Committee and other groups gives an idea about the early phases and the later opinions changing with new findings. At first (1860-1890) attention was directed towards nitric acid forming bacteria (ferments), later (1890-1920) to lichens, fungi and algae, while heterotroph bacteria initiating solution by organic chelating acid compounds and the bacteria of the sulphur cycle initiating sulphuric acid related damage and gypsum crust formation dominated the research period between 1920 and 1965. Krumbein (1966) already hinted to the fact that heterotrophic microcolonial fungi (micromycetes) may perhaps be the major damage factors not unlike the effect of micromycetes and basidiomycete types in wood rot and destruction. Table 1 summarizes the damage potential of the most common microorganisms involved in rock decay as elaborated by doctorate students and collaborators of geomicrobiology at ICBM, Oldenburg.

3. Patina

The formation of patina bases on complex processes, in which material and energy is exchanged between two open and heterogeneous systems. These may be rocks like marble, a solid melt like glass, artificial rocks as mortar, stucco, fresco; or biominerals such as ivory and bone; organic materials such as parchment, paper, wax and other substances. The second

system is the immediate surrounding which, in general will be gaseous. Also neighbouring materials and liquids as e.g. the liquids into which wooden artefacts are submersed for protection and restoration need to be included into examinations. Both systems are defined by (a) their physical characteristics (mass, particle size and shape, volume, density, cohesion,

Table 1 Some main processes and results of microbial rock wear down

Organisms	Mechanisms	Results
Epilithic lichens (Dornieden et al., 1997, 2000, Gehrmann et al. 1988; Krumbein, 2003)	Physical (e.g. rhizines penetration) and chemical (lichen acids, organic acids) Crustose cover undergoes differential expansion by thallus wetting and drying, as well as by differential heating and heat transfer	Detachment of grains and particles Detachment by fractional heating Chemical etching around penetration structures Partial protection from environmental impact by the formation of a mechanically stable protective crust
Epilithic free living algae, fungi and cyanobacteria (Gorbushina and Krumbein 1999, 2000)	Mainly chemical Photosynthesis induced alkalinisation of rock surfaces with the dissolution and even fragmentation of smaller grains Creation of a diffusion decelerating layer of extracellular polymeric substances (EPS)	Solution of rocks, even of quartz and silicates Protective surface biofilm, hereby slowed down chemical transfers of weathering agents (e.g. salts) into the rock
Chasmolithic and endolithic cyanobacteria, algae, chemoorganotrophic bacteria and fungi (Krumbein, 1966, 1988; Sterflinger and Krumbein 1995, 1997; Warscheid et al. 1991)	Physical (e.g. swelling movements) and chemical action (acid polysaccharides) through (EPS) Differential heating and heat transfer mainly through protective pigments (melanins)	Exfoliation, chipping, pitting, increase in porosity; Surface parallel cracking and access of water and chemicals through cracks; hereby deeper penetration and separation of large portions of rock surface material.
Endolithic lichens, fungi, bacteria (rarely algae) (Dornieden et al. 1997, 2000; Krumbein and Diakumaku, 1996; Sterflinger and Krumbein 1997)	Penetration of rhizines, hyphae, microcolony propagation through satellite colonies Chemical action by excretion of organic acids (oxalic and others). Physical action by turgor pressure and EPS Physical and chemical action by turgor pressure and EPS	Deep penetration (several centimetres are recorded) Enlargement of pores and cracks, pitting Reactive surface area increase; Paving the way to the deeper penetration of surface water and chemicals Deep grain detachment and disintegration of several mm of rock material

pressure, humidity, diffusion constants), (b) their chemical, crystallographic/mineralogical and petrographic composition and characteristics, (c) biological components, or inhabitants including their metabolic and physical/chemical activities, and (d) the energies and energy

flows participating in the exchanges between these two systems. The natural limit to the interactions is the local dimension of the gradients characterising the border zone between the solid and gaseous/liquid system (in exceptional but important cases also the neighbouring solid system such as wood/mortar or wood/brick etc.) and the depth of penetration of the individual components. In the case of monuments and objects of art the environmental conditions and thus the exchange zone can be limited from a few mm to a maximum of several meters. Substrate participation in the exchange process can be limited to a range of a few micrometers to several cm (Krumbein 1966, 1993, 2003; Wolf and Krumbein, 1996). At the borderline of the substrate and the (gaseous) environment a patina may frequently form and indicate a slow-down or still stand of the exchange processes, when almost all dynamic exchange processes are compensating each other and gradients are near zero at the immediate material /environment interface. New patina or new decay processes may, however be initiated if only one of the interacting materials, substances or parameters changes. Intermediate stabilisation of a “status quo” is characterised usually by a typical characteristic patina. In this case patina is a static and surface stabilising phase in the process of material ageing and decay. If the patina formation leads to a considerable mass increase of the substrate (deposits, subaerial biofilms, microbial mats, microstromatolites, sinter, silica skins, crusts, black crusts, internal consolidation, cementation etc.) the mechanical and chemical influence of the mass increase may produce fissures and cracking, exfoliation, desquamation and other alteration processes (Gorbushina et al., 1996, 1998; Sterflinger et al., 1996). This way an intermediate stabilisation may lead to even more critical damage. In cases where the rock substrate is very soft and the atmospheric and biological deterioration processes can act rapidly a patina (colour change, crust etc.) cannot form. In these cases biological (and physical-chemical) attack leads to serious biopitting, exfoliation, sanding and general backward losses of surface material. Much attention was given to the atmospheric attack of especially architectural surfaces and mural paintings exposed to open air or in cave environments. The attack by freeze-thaw cycles, by sulphuric acid and nitrous and nitric compounds including ammonia, however, is much less important than the direct or indirect biological attack. On the other hand air pollution by organic substances drastically increases the growth of detrimental biofilms in city centres worldwide. While inorganic pollutants (including particle pollution) have been banned in many countries and are eliminated in filter systems and car catalysators organic pollution was and still is silently increasing (Krumbein and Gorbushina, 1996). This leads to deposition of many organic energy sources and nutrients for mainly fungi and heterotrophic bacteria. These may be detrimental for the aesthetic outlook by ugly dark biofilms as well as by physical and chemical penetration through biodeteriorative agents. In special cases massive biofilms may protect the rock surface better than no growth and this factor may be increased occasionally through increased organic pollution (Krumbein and Gorbushina, 1996; Dornieden et al., 2000).

4. Spectral characteristics of patina

Since mediaeval time a special aesthetic quality has been attributed to patina. Hard contours get softer; a kind of a protective veil is covering the object. There is even reference to the golden shine of Paestum and the Greek monuments in Sicily and Greece being created by organismal protective coatings. Changes of the spectral characteristics lead to individual colour impressions. These may be caused by pigments absorbed to the rock surface and particles (Gorbushina et al., 1993; Krumbein and Urzi, 1996; Sterflinger et al., 1999) but may also be caused by a physical change in the surface roughness and reflectivity. Also fly ashes and industrial dust and soot may contribute to these phenomena to some extent. However, recently microbial pigments, freshly deposited stained biogenic minerals and metal ion

oxidation and reduction by microbes have been identified as the most conspicuous sources of problems and a stained patina layer on rock surfaces (Gorbushina et al., 196, 2003; Krumbein, 1966, 2003; Saiz-Jimenez, 1999; Sterflinger et al., 1999).

5. Conservation/Restoration

Thus the conservation of monuments with respect to biological causes of change and decay will always have to take into account, that some of the biologically produced changes will rather improve the object and may even have a protective character. Also patina is a witness of the time passed and should not be invariably eliminated in the context of conservation. In the case restoration is really needed and must be applied, many additional problems occur with the materials in question. If new rock has to be added like it is the case in many monuments and especially those valuable buildings of the Greek and Roman periods the new rock will look totally different. In this case the patina of the old surfaces needs to be carefully cleaned away or the new surfaces need to get artificially patinated. Both processes are possible by chemical and also by biological means. In the microbiological laboratories several techniques of artificial patination have been recently developed and tested. Also biocide treatment has been tried and in cases successfully applied (Dornieden et al., 1997; Heyn et al., 1995; Machill et al., 1997). Other suggestions have been made for the maintenance of building surfaces and on the ways to inhibit or to eliminate microbial biofilm activities at any surface exposed to subaerial impact (Gorbushina et al., 1996, 2003; Krumbein, 1988, 1998, 2003; Krumbein et al., 1999, 2003; Warscheid and Krumbein, 1996).

6. Conclusions/Outlook

Physical and chemical impact of rock biofilms leads to stains and soiling in the cases of mild damage functions and to visible lesions (without serious change of the spectroscopic characteristics of the surfaces) exhibiting freshly exposed rock surfaces at the place of serious damage. Many problems have been detected in relation to biogenic patina and other biological changes of material surfaces. The main points of interest are summarised below:

- (1) The survival of the physical heritage in the form of monuments and mural paintings depends on the type of environmental conditions the monuments have been submitted to since their production and how, over the course of time, they directly interacted with the environment.
- (2) Although microorganisms usually exist and grow permanently in and on such structures of the physical heritage, they exhibit only brief but sometimes very harmful outbursts of damaging activity.
- (3) Damage is invariably related to (i) humidity conditions, (ii) biological supply of nutrients for growth and physiology, (iii) type of organisms present, and (iv) persistence and periods of activity of the microflora dwelling on in and beneath the artefacts.
- (4) Mechanical damage through microorganisms, especially poikilotroph microcolonial micromycetes (PMM), may be more important for the conservation status in time and space, than environmental and biochemical induced damage.
- (5) The main reason of damage on building surfaces in big cities is the establishment of dense and fast developing multicoloured biofilms dominated by fungi deriving their organic nutrition from the atmosphere.
- (6) These biofilms are often misinterpreted as depositions of soot and dust or oxidation products of the original rock material.
- (7) Many of the biofilms are invisible to the naked eye except for heavy growth of mosses

and lichens.

- (8) The pigments created by the biofilms firmly adsorb to the monument surfaces and polymerise into large molecule complexes changing the spectroscopic characteristics from a multitude of colours into the mixed colours grey and black.
- (9) Some pigmentation is occasionally created by soot and rubber particles attaching to the surfaces via the flypaper effect of biofilms growing on the surfaces.
- (10) Damage factors through acid or alkaline air pollution need to be studied very carefully before taking far ranging conclusions relating air pollution with building decay.
- (11) The chemical and physical (mechanical) factors of microbial biofilms growing on most building surfaces need to be further studied in detail in order to better understand the sources and causes of building damage.
- (12) Esthetical damage seems to be more important in most cases than true loss of material.
- (13) The combined effects of atmospheric influence, dense microbial growth on and below the surface and the strength of the rock material itself often cause the actual damage.
- (14) Frequent and careful but very cautious cleaning by experts (restorers) is the best remedy against biogenic changes and decay. The comparison with the regular use of a toothbrush and intensive but irregular cleaning by a specialised dentist may be most appropriate.

Acknowledgements

The author acknowledges financial support by the EC by grants EVK- CT-1999-200001, EVK-CT-2002-00098. Also BMFT, DBU, DFG and INTAS have supported the work.

References

- Baer, N.S. and Snethlage, R. eds., 1997. Saving our architectural heritage – The Conservation of Historic Stone Structures. Wiley, Chichester, 425p.
- Besch, U., ed., 2002. Restauratorenaschenbuch 2002. Callwey, München, 368p.
- Brimblecombe, P., 1987. The Big Smoke. Methuen, London, 185p.
- Ciferri, O., Tiano, P., Mostromei, G., 2000. Of Microbes and Art. The role of microbial communities in the degradation and protection of cultural heritage. Kluwer, Dordrecht, 250p.
- Dornieden, Th., Gorbushina, A., Krumbein, W.E., 1997. Änderungen der physikalischen Eigenschaften von Marmor durch Pilzbewuchs. Int. Journal for Restoration of Buildings and Monuments, 3, 441-456.
- Dornieden, Th., Gorbushina, A. A., Krumbein, W. E., 2000. Biodecay of mural paintings and stone monuments as a space/time related ecological situation – an evaluation of a series of studies. Int. Biodeterioration & Biodegradation 46, 261-270.
- Goetz, W., 1999. Beiträge zur Vorgeschichte der Denkmalpflege. Vdf Hochschulverlag AG an der ETH Zürich, 189p.
- Gehrmann, C. K., Petersen, K. and Krumbein, W. E., 1988. Silicole and calcicole lichens on jewish tombstones - interactions with the environment and biocorrosion. In VIth International Congress on Deterioration and Conservation of Stone, p. 33-38, edited by Nicholas Copernicus University, Torun, 350 p.
- Gorbushina, A. A., Diakumaku, E., Müller, L. and Krumbein, W. E., 2003. Biocide Treatment of Rock and Mural Paintings: Problems of Application, Molecular Techniques of Control and Environmental Hazards. P. 61-72 in: Saiz-Jimenez, C., ed., Molecular Biology and Cultural Heritage. Balkema, Lisse, Netherlands, 287p.
- Gorbushina, A., Krumbein, W.E., Panina, L., Soukharjevsky, S., Wollenzien, U., 1993. On the role of black fungi in colour change and biodeterioration of antique marbles. Geomicrobiology Journal 11, 205-221.

- Gorbushina, A. A., Krumbein, W. E., 1999. Poikilotroph response of micro-organisms to shifting alkalinity, salinity, temperature and water potential. p. 75-86 in Oren, A., ed., *Microbiology and Biogeochemistry of Hypersaline Environments*, CRC Press, LLC, Boca Raton.
- Gorbushina, A., A. and Krumbein, W. E., 2000. Subaerial Microbial Mats and Their Effects on Soil and Rock. p. 161-170 in Riding, R. and Awramik, S. M., eds., *Microbial Sediments*, Springer, Heidelberg.
- Gorbushina, A., Krumbein, W. E., Vlasov, D., 1996. Bioclast cycles on monument surfaces. pp. 319-332 in: Pancella R., ed., *Preservation and restoration of cultural heritage. Proceedings of the 1995 LPC Congress*. EPFL, Lausanne, 773p.
- Gorbushina, A. A., Palinska, K. A., Sterflinger, K. and Krumbein, W. E., 1998. Biotechnologische Verfahren zum Schutz von Kulturgütern. *BioForum, Forschung und Entwicklung* 21, 274-277.
- Gorbushina, A., Panina, L. K., Vlasov, D., Krumbein, W.E., 1996. Fungi deteriorating marble in Chersonesus. *Mykology and Phytopathology*, 30, 23 - 30.
- Heyn, C., Petersen, K., Krumbein, W.E., 1995, Investigations on the microbial degradation of synthetic polymers used in the conservation and restoration of art objects, pp. 73-79 in A. Bousher, M. Chandra, R. Edyvean, eds., *Biodeterioration and Biodegradation* 9, Inst. Chem. Rugby, U.K., 663 p.
- Koestler, R. J. and Vedral, J., 1991. Biodeterioration of cultural property: A bibliography. In *Biodeterioration of Cultural Property*, ed. R. J. Koestler, Elsevier, New York, pp. 233-344.
- Krumbein, W. E., 1966. Zur Frage der Gesteinsverwitterung. Ph. D. Thesis, Würzburg 106p.
- Krumbein, W. E., 1972. Rôle des microorganismes dans la g n se, la diag n se et la d gradation des roches en place: *Rev. Ecol. Biol. Sol* 9, 283-319.
- Krumbein, W. E., 1986. ICOMOS-Stone-Committee - Group Biology -Literature List. Universit t, Oldenburg, 121 p.
- Krumbein, W. E., 1988. Biotransfer in Monuments - a sociobiological study: *Durability of Building Materials* 5, 359-382.
- Krumbein, W. E., 1993. Zum Begriff Patina, seiner Beziehung zu Krusten und Verf rbungen und deren Auswirkungen auf den Zustand von Monumenten. In *Jahresberichte aus dem Forschungsprogramm Steinzerfall – Steinkonservierung*, ed. R. Snethlage, Ernst und Sohn, Berlin, pp. 215-229.
- Krumbein, W. E., 1998. Mikробenbefall und Steinzerst rung: autotroph oder heterotroph? chemisch oder physikalisch? Strategien der Verhinderung und Behebung - Eine Bilanz pp 173-205 in Snethlage, R., ed., *Denkmalpflege und Naturwissenschaft. Natursteinkonservierung II*. Fraunhofer IRB Verlag, Stuttgart, 365p.
- Krumbein, W. E., 2003. Patina and Cultural Heritage – a geomicrobiologist’s Perspective. p. 39-47 in Kozlowski, R., ed., *Proceedings of the Vth EC Conference Cultural Heritage Research: A Pan-European Challenge*. EC and ISC, Krakow, 415p.
- Krumbein, W. E., Brimblecombe, P., Cosgrove, D. E. and Staniforth, S., 1994. *Durability and Change, The Science, Responsibility and Cost of Sustaining Cultural Heritage*. Wiley, Chichester, 307p.
- Krumbein, W. E., and Diakumaku, E., 1996. The role of fungi in the deterioration of stones. pp. 140-170 in: M. deCleeve, ed., *Interactive physical weathering and bioreceptivity study on building stones, monitored by computerized X-Ray tomography (CT) as a potential non-destructive research tool. Protection and Conservation of the European Cultural Heritage Research report Nr.2*. Science Information Office, Gent, 286p.
- Krumbein, W. E., Dornieden, Th. and Gorbushina, A. A., 1999. Patina - physical and chemical interactions of sub-aerial biofilms with objects of art. p. 120-126 in Ciferri, O., Mastromei, G. and Tiano, P. eds., *Of Microbes and Art. Proceedings of the Int.Conference on microbiology and conservation (IMC)*. FEMS; CNR, Firenze, 279p.
- Krumbein, W. E. and Gorbushina, A. A., 1996. Organic pollution and rock decay. p. 277-284 in: Pancella, R., ed., *Preservation and restoration of cultural heritage. Proceedings of the 1995 LPC Congress*. EPFL, Lausanne, 773p.
- Krumbein, W. E., Paterson, D. W., Zavarzin, G. A., 2003. *Fossil and Recent Biofilms – A Natural History of Life on Earth*. Kluwer, Dordrecht, 482p.

- Krumbein, W. E., Urzì, C. 1996. Microbiological impacts on the cultural heritage with special reference to rock materials, p. 151-178, In: *La Pietra Dei Monumenti Nel Suo Ambiente Fisico*, Eds., Roger-A. Lefèvre, Verlag: Istituto Poligrafico Roma
- Machill, S., Althaus, K., Krumbein, W.E., Steger, W. E., 1997. Identification of organic compounds extracted from black weathered surfaces of Saxonean sandstones, correlation with atmospheric input and rock inhabiting microflora. *Organic Geochemistry*, 27, 79-97.
- Petersen, K. Neugebauer, D., Krumbein, W.E., 1995. Aspects of biocide application on objects of art, pp. 81-86, A. Bousher, M. Chandra, R. Edyvean, eds., *Biodeterioration and Biodegradation 9*, Inst. Chem. Rugby, U.K., 663 p.
- Saiz-Jimenez, C., ed., 1995. *The Deterioration of Monuments. Special Issue, Sci. Total Environ.* vol. 167, 400 p.
- Saiz-Jimenez, C., 1999. Biogeochemistry of weathering processes in monuments. *Geomic. Jour.* 16, 27-37.
- Saiz-Jimenez, C., ed., 2003. *Molecular Biology and Cultural Heritage*. Balkema, Lisse, Netherlands, 287p.
- Snethlage R., ed., 1995, 1997. *Denkmalpflege und Naturwissenschaft I, II*. Ernst und Sohn, Berlin, 362, 425p.
- Snethlage, R. ed., 1990-1996. *Jahresberichte Steinzerfall, Steinkonservierung 1989-1995*. Ernst und Sohn, Berlin.
- Sterflinger, K., Blazquez, F., Garcia-Valles, M., Krumbein, W.E., Vendrell-Saz, M., 1996. Patina, Microstromatolites and black Spots as related to biodeterioration Processes of Granite, p. 391 – 398 in M.A. Vicente, J. Delgado-Rodrigues, J. Acevedo, eds., *Degradation and conservation of granitic rocks in monuments*. Brüssel.
- Sterflinger, K., Krumbein, W.E., 1995. Multiple Stress Factors affecting Growth of Rock inhabiting Black Fungi. *Botanica Acta* 108, 490-496.
- Sterflinger, K., Krumbein, W.E., 1997. Dematiaceous fungi as the main agent of biopitting on mediterranean marbles and limestones. *Geomicrobiology Journal*, 22, 219-231.
- Sterflinger, K., Krumbein, W. E. and Rullkötter, J., 1999. Patination of marbles, sandstone and granite by microbial communities. *Z. Dtsch. Geol. Ges.*, 150, 299-311.
- Verrecchia, E. P., Loisy, C., Braissant, O., Gorbushina, A. A., 2003. The role of fungal biofilms and networks in the terrestrial calcium carbonate cycle. P. 363-369 in Krumbein, W. E., Paterson, D. M., Zavarzin, G. A., eds., *Fossil and Recent Biofilms - A Natural History of Life on Earth*. Kluwer, Dordrecht, 482p.
- Viles, H. A., Camuffo, D., Fitzner, B., Lindquist, O., Livingston, P., Maravelaki, N. V., Sabbioni, C. and Warscheid, T., 1997. What is the state of our knowledge of the mechanisms of deterioration and how good are our estimates of rates of deterioration. In: N. S. Baer and R. Snethlage, eds., *Saving our architectural heritage – The conservation of historic stone structures*. Wiley, Chichester, pp.95-112.
- Warscheid, Th. , Krumbein, W. E., 1996. General Aspects and selected Cases p. 274-295 in Heitz et al. eds, *Microbially induced Corrosion of Materials*, Springer Berlin.
- Wenzel, F., ed., 1986-1996. *Erhalten Historisch bedeutender Bauwerke, SFB 315, Jahrbücher*. Ernst und Sohn, Berlin.
- Wolf, B., Krumbein, W.E., 1996. Tiefenbesiedlung und Biodeterioration an Marmorkapiteln des Freundschaftstempels im Park von Sanssouci (Potsdam), *Internationale Zeitschrift für Bauinstandsetzen*, 2, 15-32.