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Biodeterioration of stone: a review

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Abstract

The alteration and weathering of stone is basically determined by natural and anthropogenic impacts influencing various physical, chemical and biological damage factors at the object site. Whether as direct or catalytically enhancing factor, the biodeterioration of stone is coupled with nearly all environmentally induced degradation processes: the presence of the one makes deterioration by the other all the more effective. The bioreceptivity of stone is described by its structure and chemical composition, while the intensity of the microbial contamination is determined by the referring climatic conditions and the anthropogenic euthrophication of the atmosphere. The microflora improves the nutrient and moisture-restricted growth conditions on building stones by the formation of surface-covering biofilms. Besides the aesthetical impairment caused by the coloured biopatina, the biofouling effect promotes even "abiotic" deterioration processes due to the alteration of the material structure as well as their thermo-hygric properties; in addition, mechanical pressure due to the shrinking and swelling of the colloidal biofilms might cause a further weakening of the mineral lattice. Acidolytic and oxido-reductive biocorrosion processes complete the biodeteriorating attack of stone acting as a preliminary precursor for the latter formation of detrimental crusts. Suitable and reliable methods for the detection of biodeterioration processes are available, but only the interdisciplinary diagnosis and evaluation of the entire decay process of stone allows the formulation of adaequate countermeasure strategies. In case the significance of biodeterioration impacts is proven, the possible effects of the microbial contamination on cleaning procedures, protective treatments as well as biocidal applications has to be considered. This paper will give a comprehensive overview to the biodeterioration of stone and stresses the practical relevance for the conservation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Biodeterioration; Stone; Bioreceptivity; Biofilm; Biofouling; Biocorrosion; Prevention; Conservation; Biocide

1. Introduction

The use of stone as a medium for artistic expression has ranged from the construction of ancient monuments and historic buildings to small-scale statues. While the weathering of rocks to soil formation is unquestionably essential for the evolution of life on earth, the decay of culturally significant stone artifacts represents an irretrievable loss of our heritage and history (Fig. 1).

Moving rocks from the quarry to the stonemasons' yard, to be transformed into a final or nearly final object, and from there to its final location, starts the deterioration of the stone which then continues as it is exposed to weathering agents. Among these are wind, sunlight and temperature, as well as rain, snow and moisture. These agents will induce both physical and chemical weathering processes. The first affect the stability of the rock matrix, while the second act through chemical corrosion of the stone-forming minerals, such as oxidation and hydration reactions as well as dissolution of carbonates and solubilization of some elements from silicate bearing minerals (Keller, 1957).

Mankind, as part of the natural environment, contributes to the decay of exposed stone materials. Air pollution resulting from anthropogenic sources such as electric utilities, domestic heating, car and airplane transportation have increased the atmospheric concentration of inorganic and organic compounds in the form of gases, aerosols or particulate matter and their deposition on stone surfaces. The complex physical and chemical interactions of these agents with the mineral material has dramatically accelerated the decay of stones (Arnold, 1981, 1993; Winkler, 1973, 1987; Johanson et al., 1988; Rodrigues, 1991; Furlan and Girardet, 1992; Baedecker and Reddy, 1993). In addition, the

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Fig. 1. Influence of biodeterioration processes on an angel statue at the "Peters"-Portal on the cathedral of Cologne (Germany); documented by the original object in 1880 ((a) photograph by Anselm Schmitz, Cologne) and the respective weathered statue in 1993 ((b) photograph by Dombaumeister Prof. Dr. A. Wolff, Cologne).

neglect of historic sites and its consequent deterioration, and/or improper restoration and conservation treatments have aggravated the preservation of cultural properties world-wide (Charola, 1993).

A considerable number of investigations have begun to elucidate the essential role biological agents play in the deterioration of stone (Paine et al., 1933; Pochon and Jaton, 1968; Strzelczyk, 1981; Caneva and Salvadori, 1989; Griffin et al., 1991; May et al., 1993; Bock and Sand, 1993; Urzi and Krumbein, 1994; Warscheid and Krumbein, 1996; Koestler et al., 1997). What is becoming clear is that many factors affect the durability of stone. Physical, chemical, and biological agents act in co-association, ranging from synergistic to antagonistic, to deteriorate stone (Valentin, 1993; Koestler, 1994).

Biodeterioration has usually been considered to be a degradation process following the initial deteriorating effects of inorganic agents. These agents were thought to condition stone surfaces for microbial contamination due to structural changes and the enrichment of inorganic and organic nutrient substrates. However, recent investigations on the biodeterioration of stones, especially regarding the surface-covering biofilms formed by microorganisms to protect themselves against harmful environmental factors, have found that biodeteriorating effects can be clearly detected in the early stages of stone exposure (Warscheid, 1990, 1996a; de la Torre et al., 1991, 1993a, b; Gaylarde and Morton, 1999).

These effects include, in the first place, the well-known aesthetically unacceptable appearance of staining of the stone surfaces by biogenic pigments (Urzi et al., 1992, 1993). Secondly, but far more important, is the presence of extracellular polymeric substances (EPS) that result in mechanical stresses to the mineral structure due to shrinking and swelling cycles of the colloidal biogenic slimes inside the pore system (Warscheid, 1996a; Dornieden et al., 2000). This can lead to the alteration of the stone's pore size distribution and resulting in changes of moisture circulation patterns and temperature response (Krumbein, 1988; Garty, 1991; Warscheid and Krumbein, 1996; Warscheid, 1996b). Last, but not least, it has been shown that the early presence of biofilms on exposed stone surfaces accelerates the accumulation of atmospheric pollutants (Steiger et al., 1993; Wittenburg, 1994). Thus, the microbial contamination acts as a preliminary precursor for the formation of detrimental crusts on rock surfaces caused by the acidolytic and oxido-reductive (bio-) corrosion on the mineral structures (Blaschke, 1987; Krumbein and Petersen, 1987; Ortega-Calvo et al., 1994).

Biological infections and the intensity of the biodeterioration processes are strongly influenced by water availability. This is determined by both, material-specific parameters, like porosity and permeability, as well as environmental conditions of the site and exposure of the object (Berthelin, 1983; Hopton, 1988). Furthermore, the natural biomass accumulated by photosynthetic microorganisms (Eckhardt, 1978; Curri and Paleni, 1981; Jaton et al., 1985; Palmer and Hirsch, 1991), anthropogenic pollutants (e.g. nitrogen compounds, hydrocarbons) from agricultural and industrial sources can serve solely the nutrient demand of the stone-colonizing microorganisms (Warscheid et al., 1988b, 1991; Bock and Sand, 1993; Cadot-Leroux, 1996; Ortega-Calvo and Saiz-Jimenez, 1996; Mitchell and Gu, 1999; Zanardini et al., 2000).

Evaluation of the biological contribution to stone decay starts with the description of the type of stone material and exposure conditions for the entire object/building, including water presence (e.g., rising dampness, damaged water drainage, condensational moisture) and nutrients (e.g., inorganic and organic compounds from natural or anthropogenic sources). The diagnosis should also provide detailed information on the form, intensity, and extent of weathering damages as well as its distribution on the monument (Fitzner et al., 1992). This information, together with the historical anamnesis is essential for a successful conservation procedures. Restorators and conservators should consider biodeterioration processes as part of a complete and careful diagnosis of stone decay in cultural objects (Warscheid, 1996b).

Once the evaluation has been completed and analyzed, practical and adequate countermeasures can be initiated (Kumar and Kumar, 1999; Warscheid, 2000). Remedial steps may include in the first instance an effective control of the water and nutrient availability by and in the material. Only in the last instance is the use of biocides, directly or additives to stone-protective treatments, to be considered. The latter, however, requires preliminary testing for the compatibility of the biocide compounds with the materials in question (Richardson, 1988; Tudor et al., 1990; Martin and Johnson, 1992; Lisi et al., 1992; Krumbein et al., 1993; Nugari et al., 1993a, b; Tiano et al., 1993; Young et al., 1995; Cameron et al., 1997). Finally, the nutritive function of organic biocides and ecotoxicological considerations demand a careful use of the chemicals in the conservation practice (Krumbein and Gross, 1992; Leznicka, 1992; Kumar and Kumar, 1999; Warscheid, 2000).

Certain physiological capabilities of microbial consortia can even be useful and might be applied in the restoration and conservation practice. The feasibility of microbiotechnological applications has been proved for the biogenic formation of protective carbonate coatings (Castanier et al., 2000; Perito et al., 2000) and for the biogenic removal of salts, such as sulfate (Atlas et al., 1988) and nitrate (Ranalli et al., 2000). Further developments in this approach are to be expected in the future.

This paper will try to give a comprehensive and practical overview to the biodeterioration of stone.

2. Bioreceptivity of building stones

The weathering characteristics of stones, including their bioreceptivity (Guillitte, 1995), is obviously influenced by their chemical nature, physical structure and geological origin, such as from igneous, sedimentary, or metamorphic rocks. As previously mentioned, microbial colonization of stones depends on environmental factors, such as water availability, pH, climatic exposure, nutrient sources, and on petrologic parameters, such as mineral composition, type of cement as well as porosity and permeability of the rock material (Warscheid et al., 1989a, 1993; Braams, 1992; Arino and Saiz-Jimenez, 1996).

The presence of an extensive inner pore surface ($> 5\,\mathrm{m}^2/\mathrm{g}$ as determined by BET, a method that determines specific surface by nitrogen adsorption) resulting from a high porosity or the presence of clay minerals, facilitates the spreading of microflora within the pore system. High-porosity values (from around 14 vol % with an average pore radius between 1 and 10 μm), allow deep penetration of moisture into the material preparing the way for a microbial contamination to a depth of up to 3–5 cm. While large-pore sandstones, due to their short water retention, promote microbial contamination only temporarily, small-pore stones, with longer water retention time, offer more suitable conditions for the settlement of stone-colonizing microorganisms (Warscheid et al., 1989a, 1993).

The microbial contamination and the resulting deterioration processes on fine-grained stones, having maximal pore radii of 1–2 μm, can only occur under the protection of surface stone scales resulting from the preceding corrosion processes. Under the influence of strong solar radiation and consequently high temperatures, stone scales and crusts provide suitable protection for colonizing microflora from detrimental UV-light and desiccation (Warscheid et al., 1996).

The presence of significant amounts of carbonate compounds (e.g., $> 3\%$ w/v $CaCO_3$) in the stone, as in the case of calcareous sandstones, concrete or lime mortars, results in the buffering of biogenic metabolic products producing a constant suitable pH-milieu for the growth of bacteria (Warscheid, 1989a). For example, mortar or cement repairs in masonry structures made of silicate-based stones favor microbial contamination of the previously unaffected rock material (Willimzig and Bock, 1995; Arino and Saiz-Jimenez, 1996). Limestone and marble commonly consist of a dense calcareous matrix allowing mainly a superficial microbial contamination. Nevertheless the material seems to be subject to lichens and fungal attack (Giacobini et al., 1985; Seaward et al., 1989; Saiz-Jimenez and Garcia-Rowe, 1992; Nimis et al., 1992; Gorbushina et al., 1993; Gehrmann and Krumbein, 1994; Urzi et al., 1994).

Stones containing significant amounts of weathering-prone minerals (i.e., feldspars, clays and ferruginous minerals, $> 5\%$ w/v) are particularly susceptible to the development of microorganisms (Warscheid et al., 1993). Even diagenetic organic residues in sedimentary stones can be considered as possible nutrient sources for the stone-inhabiting microflora (Hunt, 1961; Degens, 1968; Pettijohn, 1975).

Man-made stones, such as brick, mortar or concrete, are also susceptible to microbial attack. The degree of contamination will depend on the pore size distribution as well as on the alkalinity of the artificial stones (Arino and Saiz-Jimenez, 1996; McCormack et al., 1996; Gu et al., 1998). They are particularly evident at interfaces between

Table 1
Patina types on building stones as references to the physical manifestation of biodeterioration impacts on rocks (I)

Patina Type 1	Film-formation synonyms: patina, deposit, coating, staining, chromatic alteration
Type of rock	Dense or fine-grained stones: siliceous sandstones, granite, basalt, slate, limestone and metamorphic rocks (gneiss, quartzite, marble)
Petrophysical characteristics (appr. values)	Most abundant grain size: < 0.1 mm porosity (Hg-porosimetry): $< 14\%$ vol inner surface (BET): $3.5\,\mathrm{m}^2/\mathrm{g}$ major pore size: $< 3\,\mu\mathrm{m}$
Moisture balance	Poor penetration (max. up to 1 mm); short-time of wetness
Distribution and type of microflora	Superficial or along natural cracks and fissures, mostly unilamellar biofilm; mainly dominated by a phototrophic microflora and fungi
Typical biodeterioration processes	(i) Discolorations by biogenic pigments and biogenic oxidation of mineralic iron or manganese (ii) Biofilm formation (EPS) leading to the enrichment of atmospheric particles and causing subsequently the development of thin-skinned scales (iii) Local biocorrosion (“biopitting”) due to the microbial excretion of organic acids

Table 2
Patina types on building stones as references to the physical manifestation of biodeterioration impacts on rocks (II)

Patina type 2	Surface-corrosion synonyms: granular disintegration, sanding, pulverization, erosion
Type of rock	Coarse-grained, porous stones: tuff, clay-cemented or siliceous sandstones, man-made stones (brick, mortar, concrete)
Petrophysical characteristics (appr. values)	Most abundant grain size: > 0.5 mm porosity (Hg-porosimetry): $> 18\%$ vol inner surface (BET): $< 3\ \mathrm{m}^2/\mathrm{g}$ major pore size: 3–8 μm
Moisture balance	Deep penetration (up to 10 cm); frequent changes between wetness and desiccation
Distribution and type of microflora	Microbial contamination up to 5 cm deep; mainly dominated by bacteria
Typical biodeterioration processes:	(i) Biofilm formation (EPS) narrowing rock pores, possibly leading to an increase in capillary water uptake (ii) Biocorrosion due to the microbial excretion of inorganic and organic acids

Table 3
Patina types on building stones as references to physical manifestations of biodeterioration impacts on rocks (III)

Patina type 3	Crust-formation synonyms: exfoliation, chipping, shales, flakes, scales
Type of rock	Middle-grained sandstones, clay-cemented and calcareous types of rock, respectively, binding material
Petrophysical characteristics (appr. values)	Most abundant grain size: 0.1–0.5 mm porosity (Hg-porosimetry): 14–18% vol inner surface (BET): $5–7\,\mathrm{m}^2/\mathrm{g}$ pore size: $> 8\,\mu\mathrm{m}$
Moisture balance	In the uppermost layers of the stone (max. 0.5–2 cm deep); longlasting dampness
Distribution and type of microflora	In the uppermost layers of the stone deep) (max. up to 1 cm and/or behind the rock shales; complex and stable microflora (“microbial mat”)
Typical biodeterioration processes	(i) Discolorations by biogenic pigments and biogenic oxidation of mineralic iron or manganese (ii) Biofilm formation (EPS) sealing rock pores causing a reduced diffusion of humidity and enrichment of atmospheric particles with a subsequent crust formation (iii) biocorrosion due to the microbial excretion of inorganic and organic acids

alkaline mortar and acidic siliceous stone material, or in cement repairs of stone, due to the pH-gradients developed there (Willimzig and Bock, 1995). Historical brick and mortar often contain organic adhesives, such as sawdust, hair, and glue, which increase the susceptibility of the mineral substrate to microbial attack (Palmer et al., 1991).

In the course of the microbial contamination the physico-chemical properties of the mineral substrate itself are altered significantly improving their later bioreceptivity. Microbial biofilms in conjunction with physical and chemical weathering may develop into surface decay forms called *patina* ranging from the formation of films to crusts (Tables 1–3 and Figs. 2–4; Warscheid, 1996a).

Biofilm formation is first manifested as a discoloration of the stone surface due to organic pigments (e.g., chlorophylls, carotenoids, and melanins). Depending on the type of stone, the uppermost layers are later preconditioned by the enrichment of adhesive epilithic biofilms resulting from fungal and bacterial growth. Here, precipitating salts get encrusted together with airborne particles and chemical compounds serving as an additional nutrient source for the stone microflora (Nord and Ericsson, 1993; Steiger et al., 1993; Wittenburg, 1994; Viles and Moses, 1996). Subsequent physical stresses induced by freeze-thaw changes and salt recrystallizations as well as (bio-) corrosive and (bio-) oxidative processes continue the weakening and leaching of the mineral material under the superficial crust (Eckhardt, 1985; Arnold, 1993). Finally, the decomposition of the stone-cementing binders results in the weakening of the mineral structure manifested by sanding or granular disintegration of the stone's uppermost layers thus opening the space for further microbial contamination (Krumbein, 1988; Urzi et al., 1992; de la Torre et al., 1993a). The process is enhanced by repeated

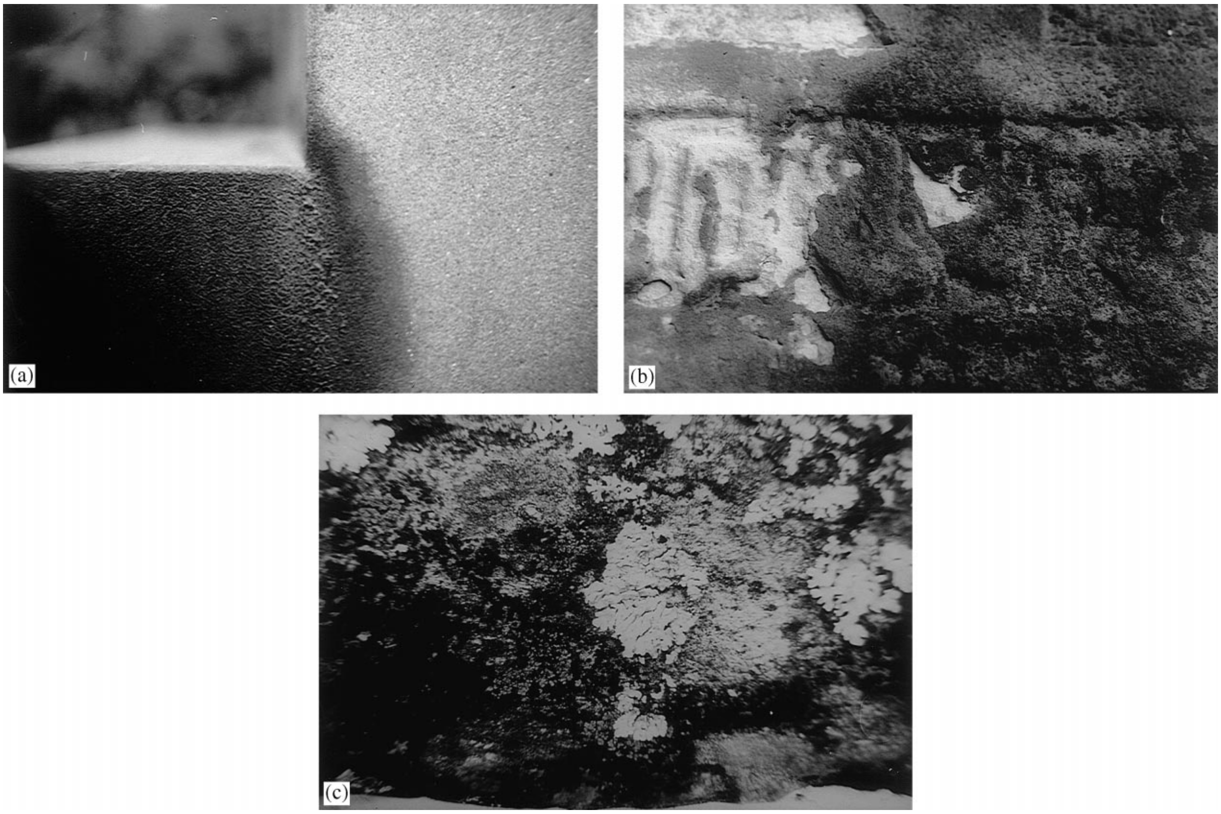

Fig. 2. (a) Fresh algal mat on a siliceous sandstone, in the design of an "Asterix"-testblock, on an exposure field in Duisburg (Germany) two years after exposure (Warscheid et al., 1993). (b) Alive and resting algal contamination on a siliceous sandstone in a moisture changing object area leading to the blackening of the respective rock surface and thermo-hygric material deterioration (Church of the monastery of Obernkirchen, Germany). (c) Surface-covering multicolored lichens and blackening melanin-producing fungi growing on a soapstone at the sanctuary of senhor Bom Jesus de Matosinhos in Congonhas (Brazil) (Becker et al., 1994).

wet–dry cycling and leads to enhanced moisture condensation in the stone's pore system favoring microbial growth. Consequently, secondary diffusion barriers for humidity and gases inside the mineral structure will be established (Kiessl, 1989). Ultimately, scales will detach exposing a fresh surface to continue the cycle of biodeterioration (Krumbein and Petersen, 1987; Krumbein, 1988).

In the course of biocorrosion of marble the formation of a biogenic "protective" calcium oxalate monohydrate (whewellite) and calcium dihydrate (weddelite) layer, called "scialbatura" (brownish, reddish or yellowish patina), has been reported, but its origin is still controversial discussed (Monte and Sabbioni, 1987; Monte et al., 1987; Lazzarini and Salvadori, 1989; Caneva, 1993; Pinna, 1993). Mechanical action of black fungi (*Dematiaceae*) contributes to structural alteration ("chipping") of the metamorphic material (Badalyan et al., 1996; Dornieden et al., 2000).

3. The micro-ecology of building stones

3.1. *Organisms involved in the deterioration of stone*

The microflora on building stones represents a complex ecosystem which develops in various ways depending on environmental conditions and the physico-chemical properties of the material in question. Microorganisms can be divided into the following groups (Brock et al., 1994):

Photolithoautotrophic organisms, such as algae, cyanobacteria, mosses and higher plants, which use sunlight as energy source, and release oxygen during photosynthesis. Their carbon requirements are met by fixing CO_2 from the atmosphere.

Chemolithoautotrophic bacteria use inorganic compounds (e.g., ammonia, nitrites, hydrogen sulfide, thiosulfates or elementary sulfur) to obtain energy from their oxidation and fix CO_2 from the atmosphere. This results in the release of nitrous acids (e.g., *Nitrosomonas* spp.), nitric acid (e.g., *Nitrobacter* spp.) or sulfuric acid (e.g., *Thiobacillus* spp.). A few bacteria of this group are also capable of growing mixotrophically, using organic nutrients for the synthesis of cell components (chemolithomixotroph).

Chemoorganotrophic bacteria and fungi use organic substrates as hydrogen, carbon, and energy source. They commonly release complexing biocorrosive organic acids or weaken the mineral lattice by the oxidation of metal cations such as Fe^{2+} or Mn^{2+}.

Lichens are a symbiotic association, between a fungus (called the mycobiont) and an alga or cyanobacteria (either

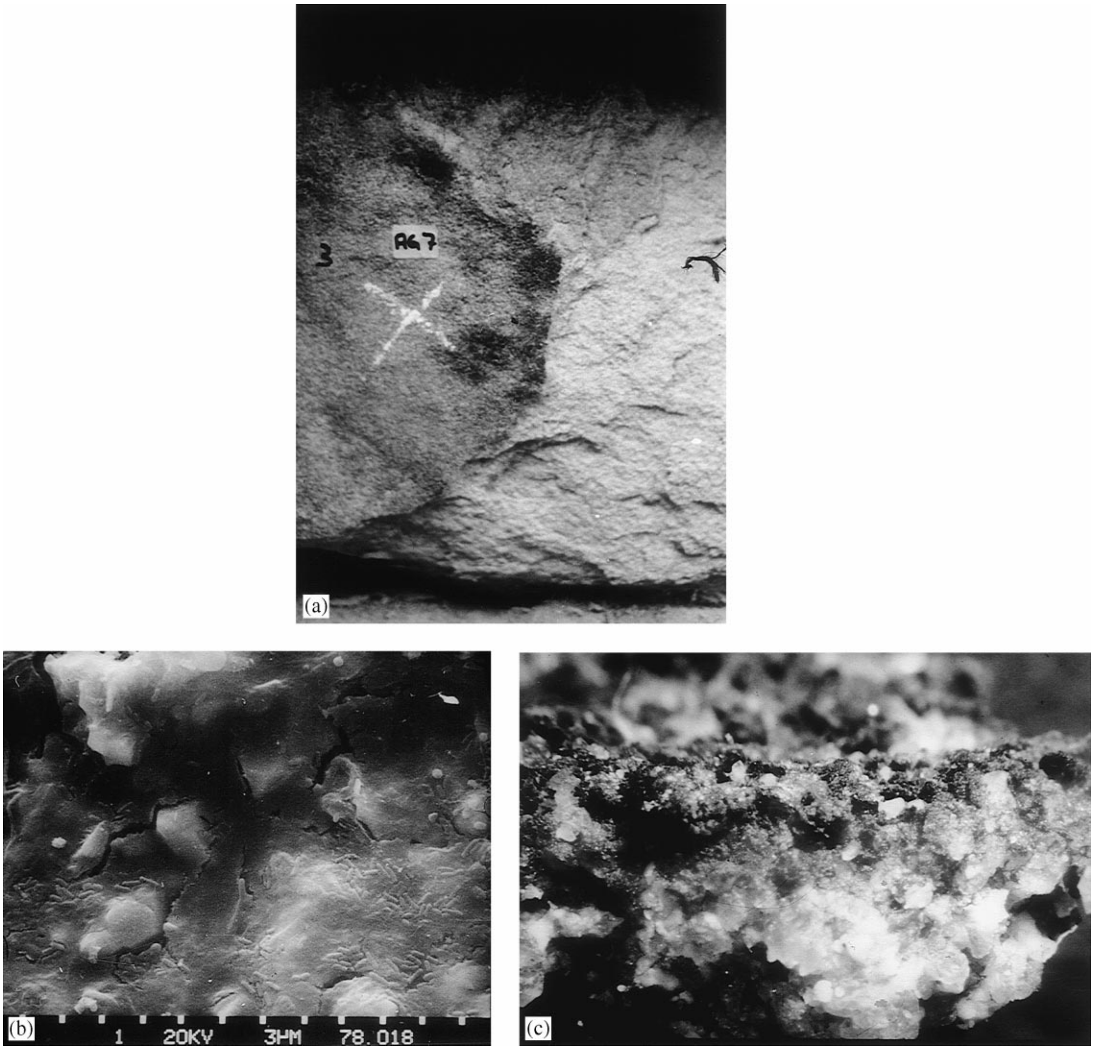

Fig. 3. (a) Granular disintegration on the surface of a coarse-grained quartzitic sandstone at the Castle of Pommersfelden (Germany) (Warscheid, 1990). (b) SEM-micrograph of rod-shaped bacteria embedded in a surface-covering biofilm on the respective stone material shown in (a) (Warscheid, 1990). (c) Visualization of the distribution of the microbial contamination in the rock profile of the respective stone material, shown in (a), by a red colored PAS-staining (Warscheid, 1990).

is termed the phycobiont). The fungus is believe to utilize organic nutrients produced by the algae through photosynthesis; in return, the algae is believed to gain minerals leached from the stone by fungal acids secreted by the hyphae of the lichen. The fungus also protects the alga from harmful environmental conditions, such as dessication or toxic chemicals.

While chemolithotrophic microorganisms have often been described in association with damaged inorganic materials (Barcellona-Vero and Mont-Sila, 1976; Milde et al., 1983; Meincke et al., 1988; Wolters et al., 1988; Bock and Sand, 1993), more recent studies have emphasized the significance of chemoorganotrophic bacteria and fungi, together with photoautotrophs, as the primary microbial colonizers of building stones (Lewis et al., 1986; Eckhardt, 1988; Lyalikova and Petushkova, 1991; May et al., 1993; Gorbushina et al., 1993; Krumbein et al., 1996). The respective microorganisms, especially coryneform actinomycetes (Warscheid, 1990; Lyalikova and Petushkova, 1991; Groth et al., 1999) and dematiaceous fungi (Braams, 1992; Wollenzien et al., 1995), are often present in surface biofilms on stones, which allow them to withstand abrupt changes in environmental conditions (e.g., temperature, humidity, and osmotic pressure), as well as food shortages. The activity of the primary colonizers preconditions the building for the chemolithoautotrophs and gives rise to the biological succession (Warscheid et al., 1993).

3.2. Biological succession on building stones

The microbial colonization of stones commonly starts with phototrophic organisms which build up a visible protective biofilm enriched with inorganic and organic biomass on the nutrient-depleted stone surface (Jaag, 1945; Darlington, 1981).

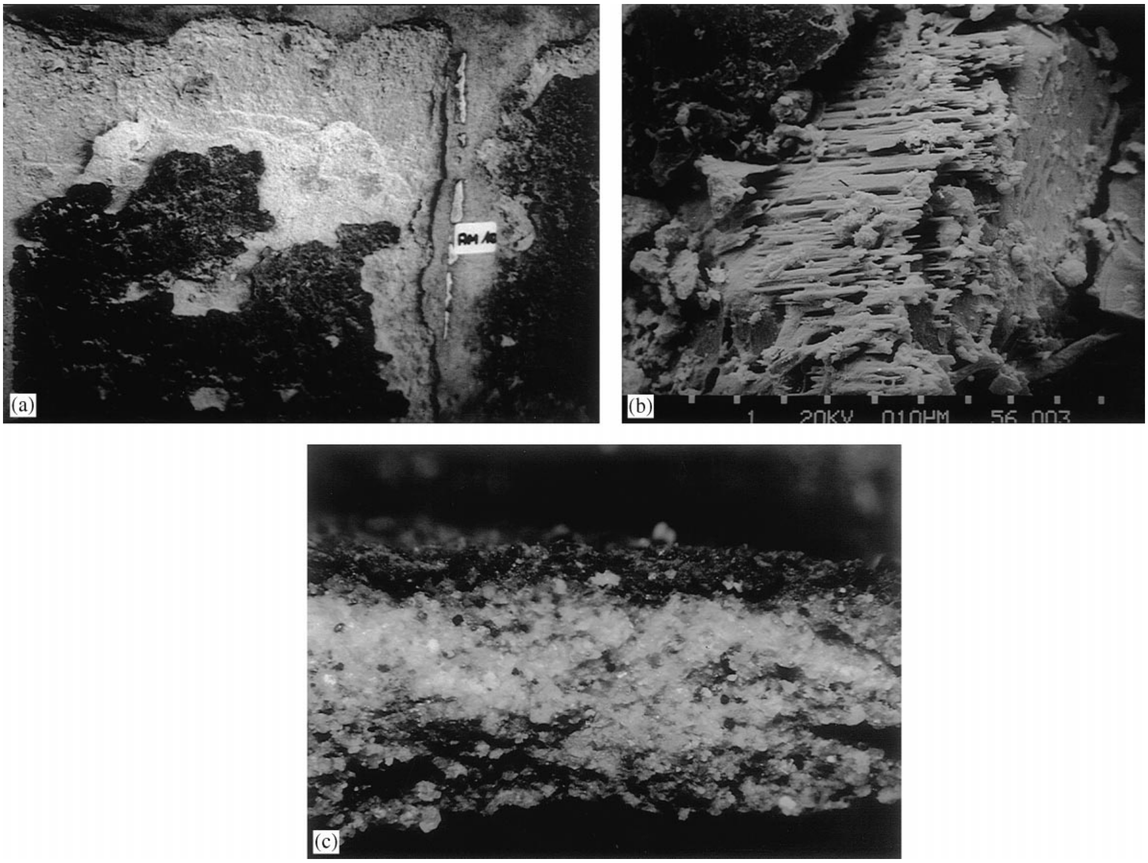

Fig. 4. (a) Scaling on the surface of a fine-grained calcareous sandstone at the Cathedral of Regensburg (Germany) (Warscheid, 1990). (b) SEM-micrograph of a biocorroded carbonate mineral, characterized by biofilm embedded carbonaceous needles, within the respective stone material shown in (a) (Warscheid, 1990). (c) Visualization of the distribution of biocorrosion activity in the rock profile of the respective stone material, shown in (a), by a red-colored DHA-redox indicator (Warscheid et al., 1990).

The growth and metabolic activity of algae, cyanobacteria, and lichens, as well as mosses and higher plants, is regulated by natural parameters such as light and moisture (Monte, 1993; Ortega-Calvo et al., 1995). In rural areas, their growth is enhanced by nitrogen-rich air from fertilizers (Thiebaud and Lajudie, 1963; Krumbein, 1972; Arino and Saiz-Jimenez, 1996; Cadot-Leroux, 1996; Young, 1997).

Phototrophic microorganisms may grow on the stone surface (called epilithicphototrophs) or may penetrate some millimeters into the rock pore system (called endolithicphototrophs) (Golubic et al., 1981; Friedmann and Ocampo-Friedmann, 1984). They do not seem to grow under thin stone scales (Garg et al., 1988; Caneva and Salvadori, 1989), however recent investigations revealed the presence of phototrophs even under rock scales a few millimeters thick providing shelter against dessication and intense UV-radiation from sunlight (Warscheid et al., 1996).

It was believed that the phototrophic microorganisms had no direct effect on the deterioration of stones, except for the aesthetically detrimental effect due to their pigments (Pietrini et al., 1985; Urzi et al., 1992), and that under certain climatic conditions (e.g., tropical environments) they provided a protective film on the stone surface regulating humidity and temperature (Delvert, 1962; Wendler and Prasartset, 1999; Warscheid, 2000). However, other investigations have stressed the importance of phototrophs in the physical and chemical deterioration of stones, especially when fed by anthropogenic pollution under moderate climates. These biodeterioration processes are characterized by the excretion of corrosive organic acids especially on limestone and marble (Jones and Wilson, 1985; Seaward et al., 1989; Caneva et al., 1992; Gehrmann and Krumbein, 1994; Arino et al., 1997), the uptake and accumulation of sulfur and calcium into their cells (Bech-Andersen, 1985; Caneva and Salvadori, 1989; Ortega-Calvo et al., 1994; Viles and Moses, 1996), the alteration of stone-forming minerals (Jones et al., 1988; Prieto et al., 1994) and the enlargement of pores due to the penetration of hyphae and roots, thus loosening stone particles from the parent rock material mainly on granitic rocks (Jaton et al., 1985; Arino and Saiz-Jimenez, 1996; Romao and Rattazzi, 1996; Galsomies, 1995; Ascaso et al., 1998). This attack is intensified by the growth of biofilms weakening the mineral lattice by repeated wetting and drying cycles (Ortega-Calvo et al., 1991). A comprehensive model for the possible interactions between lichens and mineral as an example for a biological impact on mineral dissolution by phototrophic microorganisms is given by Banfield et al. (1999).

While the impact of lichens weathering of rocks, like any biodeterioration of mineral-containing materials, has to be considered on a global scale in terms of climatic consequences and the habitability of our planet (Schatz, 1962; Lovelock, 1979; Ehrlich, 1981; Krumbein and Dyer, 1985; Schwartzman and Volk, 1989; Seaward, 1997), the biodeteriorating effects of lichens on historical stones and their consequent removal has to be critically evaluated from case to case. In addition, the possible protective properties of the symbiotic biopatina on some materials under certain environmental conditions has to be considered (Lallement and Deruelle, 1987; Wendler and Prasartset, 1999; Warscheid, 2000).

The accumulation of photosynthetic biomass provides an excellent organic nutrient base for subsequent heterotrophic microflora and their biodeterioration activities (Caneva and Salvadori, 1989). Phototrophs may excrete carbohydrates, growth factors, and antibiotics, thus facilitating the establishment of a complex microbial community on the rock (Strzelczyk, 1981). The associations formed by phototrophic organisms on stone can be used as bioindicators of the physico-chemical parameters of the environment surrounding them (Caneva et al., 1993; Piervittori and Laccisaglia, 1993; Seaward, 1997).

The establishment of a heterotrophic microflora on rocks is possible even without the pioneering participation of phototrophic organisms (Krasilnikov, 1949). In this case, the microorganisms use organic substrates derived from the rock material (Nooner et al., 1972; Benassi et al., 1976) or from deposits introduced by dust and rain (Fennelly, 1975; Karavaiko, 1978). Deposition of various particulate and gaseous organic compounds on stone surfaces from air-pollution as well as organic biomass contributes to the nutrient supply (Palmer et al., 1991). The studies of Simoneit (1984) showed that most of the organic compounds found in atmospheric aerosols derive from automobile exhausts (especially diesel engines), and/or industrial and domestic oil combustion. The biogenic hydrocarbon emissions from forests also contribute to the organic load in the atmosphere (Lamb et al., 1987). In consequence, the compounds found on stone surfaces include aliphatic and aromatic hydrocarbons, short-chain mono- and di-carboxy acids, and long-chained fatty acids and alcohols (Oelting et al., 1988; Saiz-Jimenez, 1993; Steiger et al., 1993).

Chemoorganotrophic fungi are especially concentrated in stone crusts. They are able to penetrate into the rock material by hyphal growth and by biocorrosive activity, due to the excretion of organic acids or by oxidation of mineral-forming cations, preferably iron and manganese. Predominately strains of *Exophiala, Penicillium, Aspergillus, Cladosporium, Alternaria, Aureobasidium, Ulocladium* and *Phoma* have been isolated (Eckhardt, 1978, 1985, 1988; Koestler et al., 1985; Kuroczkin et al., 1988; Lyalikova and Petushkova, 1991; de la Torre et al., 1991, 1993a, b; Braams, 1992; de la Torre and Gomez-Alarcon, 1994; Krumbein et al., 1996).

Their deteriorating activity includes discoloration of stone surfaces, due to the excretion of melanins by dematiaceous fungi (Braams, 1992; Gorbushina et al., 1993; Urzi et al., 1992, 1993; Becker et al., 1994; Wollenzien et al., 1995; Warscheid et al., 1996), and mechanical stress to stone structures (Badalyan et al., 1996; Dornieden et al., 2000). Furthermore, their ability to attack a wide range of polymeric substances, including those added to stone for protective reasons, means that their presence has to be considered during conservation treatments (Koestler and Santoro, 1988; Salvadori and Nugari, 1988; Leznicka et al., 1991; Koestler, 2000; Tiano et al., 2000).

Chemoorganotrophic bacteria could be seen as a mediating factor in the stone microflora (Tayler and May, 1991; Warscheid et al., 1993; Krumbein et al., 1996; May et al. 2000). Gram-positive, coryneform actinomycetes, such as *Arthrobacter*, *Clavibacter*, *Aureobacterium*, *Rhodococcus*, *Brevibacterium*, *Micrococcus* and *Streptomyces*, are able to withstand the severe conditions on stone surfaces (Warscheid, 1990; Lyalikova and Petushkova, 1991; Groth et al., 1999), and predominate over the more sensitive gram-negative bacteria (Wolf, 1997), commonly found as biodeteriogens in soils. However, the presence of heterotrophic bacteria has been shown to correlate with the state of decay of stones and their biocorrosion activity has been evaluated as low (Lewis et al., 1985, 1986, 1988a,b). Nevertheless, they are extensively involved in biofilm formation on stones and they cause considerable changes in the physico-chemical properties of the mineral structure (Warscheid et al., 1991; Warscheid, 1996a) and interfere in salt crystallization processes (Papida et al., 2000). Due to their wide range of nutrient utilization they are able to serve the entire microflora by the breakdown of low degradable compounds, like aliphatic and aromatic hydrocarbons (Warscheid et al., 1988b, 1991; Ortega-Calvo and Saiz-Jimenez, 1996; Zanardini et al., 2000) contributing to the stabilization of the stone microflora. The porosity of stones as well as the nature of their binding material determines their stability against bacterial attack (Warscheid et al., 1989a; May et al., 2000).

Colonization of building stones by sulfur-oxidizing or nitrifying bacteria (chemolithoautotrophic microorganisms) is dependent on the presence of reduced sulfur and nitrogen compounds (e.g., H_2S, S, SO_3^{2-}, NH_3 or NO_2^-).

The biodeterioration of sulfur-oxidizing bacteria *Thiobacillus* sp. was first described on sandstones in France and Cambodia (Pochon et al., 1960; Pochon and Jaton 1967, 1968; Jaton, 1973). The colonization of marble by sulfur-oxidizing bacteria was later documented by several Italian groups (Lepidi and Schippa, 1973; Barcellona-Vero and Mont-Sila, 1976; Sila and Tarantino, 1981). However, the presence of these bacteria has not been established on historical monuments in northern Europe to date (Sand and Bock, 1991). It is unclear if, in fact, sulfur-oxidizing bacteria were isolated from the respective building stone rather than heterotrophic microorganisms capable of metabolizing reduced sulfur compounds (Lewis et al., 1988b). Current microbiological techniques should be able to answer this question.

The role of nitrifying bacteria on the deterioration of building stones was first studied by Kauffmann (1952, 1960). Nitrifying bacteria have been associated with the accumulation of nitrate in stones (Bock et al., 1988; Wolters et al., 1988; Bock and Sand, 1993) and new taxonomical strains have been isolated and characterized (Meincke et al., 1988). The biodeterioration of stone by nitrifying bacteria has been impressively documented in simulation chambers to occur at eight times the rate of a purely chemical corrosion process (Mansch and Bock, 1993).

However, the deteriorating effect of chemolithotrophic bacteria will be probably be minimal under severe building conditions, since they are very sensitive to desiccation and grow slowly in moderate temperatures. However, they may have a major role to play in the decay of stones under warm and wet conditions, such as (sub-)-tropical climates, waterlogged excavations or within complex “mature” biofilms, when reduced sulfur and nitrogen compounds are present (Pochon et al., 1960; Delvert, 1962; Sand and Bock, 1991; Bock and Sand, 1993). It is important to stress that biodeterioration processes on a given site are rarely caused by only one distinct group of microorganisms. Many groups of microorganisms co-exist at the same time in the same place. Any biodeterioration occurring is probably the result of complex microbial interactions. This complexity has to be taken into account during the evaluation of conditions and the control of biodeterioration phase for each historic stone (Warscheid, 1996b).

4. Biodeterioration mechanisms on building stones

The detrimental effects of stone-colonizing microflora on cultural property range from the impairment of the aesthetic appearance to changes in the physical and/or chemical characteristics of the stone. In nature, it is difficult, if not impossible to separate the biological influences on stones from physical and chemical impacts (Schneider, 1976; Ehrlich, 1981) but on the basis of the actual knowledge in biodeterioration of stone we have to eliminate the purely abiotic approach in the analysis and evaluation of the stone deterioration process (Arnold, 1981, 1993; Winkler, 1973, 1987; Johanson et al., 1988; Rodrigues, 1991; Brüggerhoff and Mirwald, 1992; Furlan and Girardet, 1992; Baedecker and Reddy, 1993). It has to be recognized that microbes are involved directly and/or indirectly in the weathering of stones and constituent minerals (Gomez-Alarcon and de la Torre, 1994; Warscheid, 1996b; Koestler et al., 1997).

While the effects and extent of biogeochemical deterioration processes are controlled and determined by the chemistry of minerals and the binding cement of each rock, biogeophysical influences are mostly regulated by the porosity or shape of the interior surface.

Table 4
Biodeterioration mechanisms on stones (I)

Biogeochemical Influences
Acidolysis: chemolithotrophic processes (sulfuric acid, nitric acid)
Complexation chemoorganotrophic processes (organic acids)
Redoxprocesses on cations and anions (e.g., iron- and manganese oxidation) and selective cellular enrichment
Phototrophic processes (accumulation of organic nutrients, supply of oxygen)

4.1. Biogeochemical deterioration mechanisms

Berthelin (1983) divided the microbial deterioration processes of stones into soluble and insoluble mechanisms. Soluble ones include acid reactions, basic or complexation, as well as other enzymatic and non-enzymatic processes. Microbial insoluble mechanisms are caused by oxidation (e.g., iron, manganese), reduction of sulfur complexes, degradation of metal organic complexes and metal organic chelates (Table 4).

The biogenic release of corrosive acids is probably the best known and most commonly investigated biogeochemical damage mechanism in inorganic materials. The process, known as biocorrosion, is caused by the microbial secretion of inorganic and organic acids (acidolyisis and complexation). These agents dissolve and etch the mineral matrix with subsequent weakening of the binding-system (Mandl et al., 1953; Keller, 1957; Schatz et al., 1957; Duff et al., 1963; Henderson and Duff, 1963; Boyle et al., 1967; Schalscha et al., 1967; Huang and Keller, 1970, 1971, 1972; Silverman and Munoz, 1970; Razzaghe-Karimi and Robert, 1975, 1979; Eckhardt, 1979; Silverman, 1979; Robert et al., 1980; Manley and Evans, 1986; Schenk et al., 1989). Depending on petrological, morphological and physico-chemical parameters of the stone, biocorrosion results in local “pitting” (e.g., distinct blind holes, generally of cylindrical shape) and, on a larger scale, in sanding and flaking of the surface, leaving the stone surface eroded and exposed to freeze-thaw deterioration (Hueck-van der Plas, 1968; Jaton, 1973; Lepidi and Schippa, 1973; Bech-Andersen, 1985; Eckhardt, 1978, 1985, 1988; Lewis et al., 1986; Garg et al., 1988; Kuroczkin et al., 1988; Jain et al., 1989; Saxena et al., 1989; Sand and Bock, 1991; de la Torre et al., 1991, 1993a; Caneva et al., 1992; Danin, 1993; Gehrmann and Krumbein, 1994; Becker et al., 1994; Willimzig and Bock, 1995; Resende et al., 1996). Figs. 5a–c illustrate the biocorrosion impact on stones.

Acidolysis is the reaction of non- or weakly complexing acids (e.g., carbonic, nitric, sulfuric, formic, acetic, lactic, gluconic) following the formula (Keller, 1957):

$$(\text{mineral})^{-}\text{M}^{+} + \text{H}^{+}\text{R}^{-} \rightleftharpoons \text{H}^{+}\,(\text{mineral})^{-} + \text{M}^{+}\text{R}^{-},$$

where $\text{R}^{-} = \text{NO}_3^{-}, \text{R}_1\text{COO}^{-},\ \text{HCO}_3^{-},\ \text{SO}_4^{-2}$.

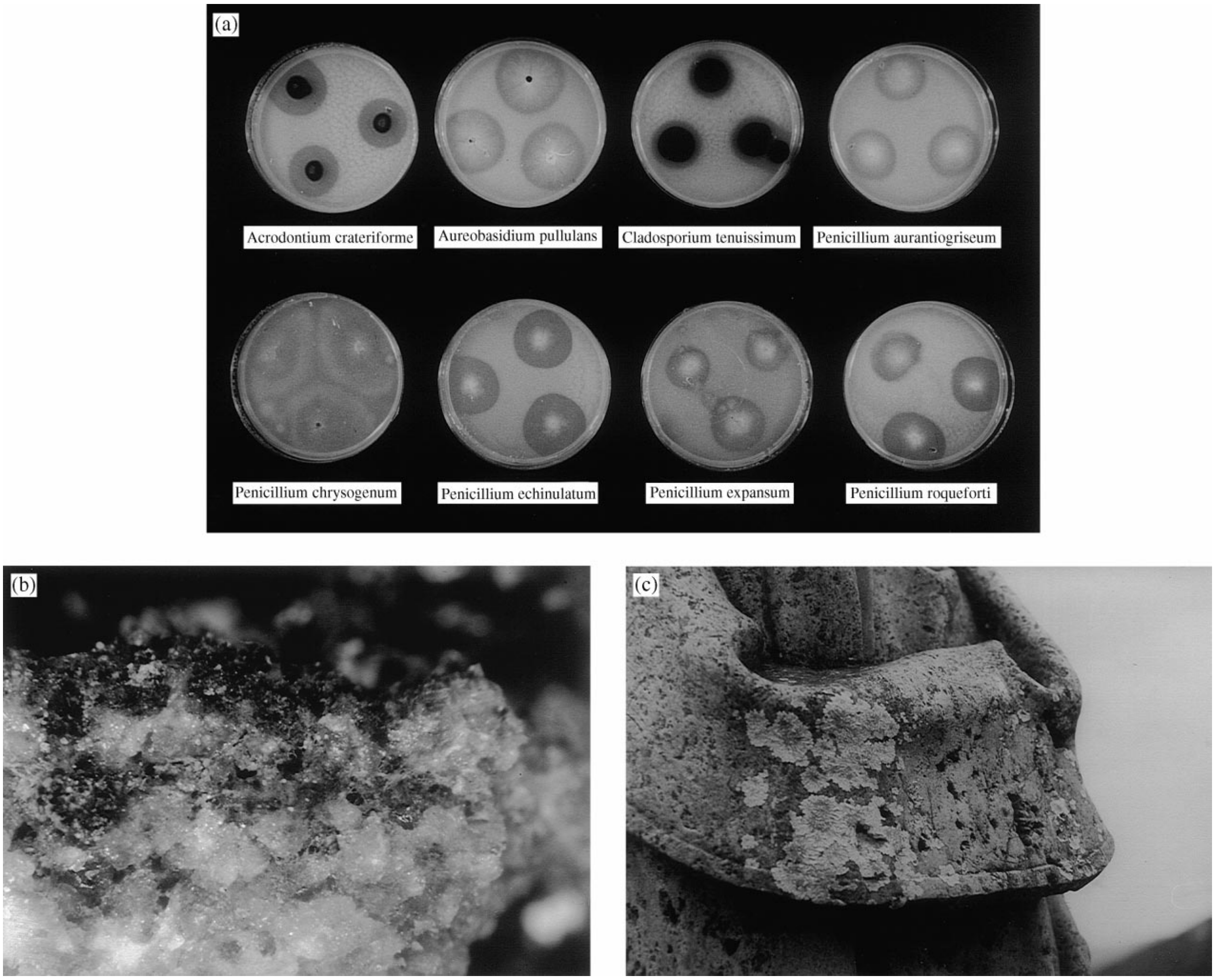

Fig. 5. (a) Screening of fungal strains isolated from sandstones on their capability to release biocorrosive organic acids indicated by clearing zones on chalky testagar (Braams, 1992). (b) Iron-oxide crust due to the interaction of algal photosynthesis and oxygen supply supporting later fungal biooxidation on Schlaitdorfer Sandstone at the Cathedral of Cologne (Warscheid et al., 1990). (c) "Pitting" formation due to lichen attack on dolomitic inclusions of a soapstone of prophet Obadiah at the sanctuary of senhor Bom Jesus de Matosinhos in Congonhas (Brazil) (Becker et al., 1994).

The proton–cation exchange can result mainly from the activity of chemolithotrophic microorganisms, in particular nitric and sulfuric acid-forming bacteria. The nitrifying bacteria cause oxidation of not readily dissolved (not washable) ammonia (mainly from agricultural fertilizers) and nitrite (deriving from atmospheric pollution) into the dissolvable (washable) nitrous and nitric acids. Their reaction with calcium carbonate and other minerals results in the formation of nitrates and nitrites, which are more soluble than the original mineral phases (Bock et al., 1988). Sulfur-oxidizing bacteria excrete sulfuric acid during their metabolism that reacts with calcium carbonate to form calcium sulfate (gypsum) (Sand and Bock, 1991).

The biocorrosive activity of chemoorganotrophic microorganisms, including lichens, is mainly characterized by the excretion of organic acids complexation. They include a variety of acids, such as oxalic, citric, gluconic, 2-oxogluconic, 2-oxoglutaric, glyoxalic, oxalacetic and fumaric, as well as inorganic carbonic acid formed during respiration (Eckhardt, 1978, 1985, 1988; Lewis et al., 1986, 1988a, b; Garg et al., 1988; Kuroczkin et al., 1988; Warscheid et al., 1988b; de la Torre et al., 1991, 1993a; Caneva et al., 1992; Becker et al., 1994; Willimzig and Bock, 1995; Resende et al., 1996). These acids are also capable of chelating cations such as Ca, Al, Si, Fe, Mn and Mg from minerals forming stable complexes (Keller, 1957; Schatz et al., 1957; Schalscha et al., 1967). It has been shown that biogenic organic acids are considerably more effective in mineral mobilization than inorganic acids and are considered as one of the major damaging agents affecting stone deterioration (Eckhardt, 1979; Razzaghe-Karimi and Robert, 1975, 1979; Manley and Evans, 1986). Many microbes are capable of producing these acids, but fungi (also as mycobiont in lichens) are considered to be the most significant organisms in nature to biocorrode rocks and minerals (Henderson and Duff, 1963; Webley et al., 1963; Silverman and Munoz, 1970; Eckhardt, 1979; Bech-Andersen, 1985; Kuroczkin et al., 1988; de la Torre et al., 1991, 1993a; Caneva et al., 1992; Danin, 1993; Gehrmann and Krumbein, 1994; Becker et al., 1994).

Biocorrosion processes on stones can also be established by alkaline reactions. The ability to degrade nitrogen complexes and sodium salts of organic acids is widespread among microorganisms. The compounds resulting from this process (ammonia or sodium salts) raise the pH of the solution in the stone pores and induce, above pH 9, a subsequent solubilization of silica, as reported from specific mycobacterial strains (Keller, 1957; Berthelin, 1983; Krumbein and Werner, 1983; Eckhardt, 1985). Trapping of CO_2 by photosynthetic activity also leads to a slight alkalinization of the microbial environment (up to pH 8.3) and buffering of biogenic respiration exudates (Berthelin, 1983).

A further important biogeochemical deterioration mechanism, which can frequently be observed in the biodeterioration of natural rocks and building stones, is caused by various chemoorganotrophic bacteria and fungi capable of removing iron and manganese cations from the mineral lattice by oxidation (Eckhardt, 1985; Braams, 1992; de la Torre et al., 1994).

The cation transfer from mineral to microbial cells can be affected by specific protein compounds called "siderophores" (Callot et al., 1987), or by active ion-uptake and subsequent accumulation in the bacterial cell walls (Beveridge and Murray, 1976). The final immobilization of the leached cations is caused by the degradation of metal organic transport complexes and metal organic chelates and subsequent redox reactions favored by the release of oxygen by cohabitant photosynthetic algae and cyanobacteria (Iskandar and Syers, 1972). Biochemical redox processes of cations, especially iron and manganese, can take place through indirect (metabolic products) or direct (enzymatic) activities of heterotrophic microorganisms (Arrieta and Grez, 1971; Lundgren, 1989). The resulting oxides are preferentially deposited on the outer cell-surface of the active microorganisms (Silverman, 1979; Berthelin, 1983; Braams, 1992). The biochemical immobilization of the metal cations causes a permanent concentration gradient that maintains the solubilization process within the crystal lattice and results in the decreasing strength of the material.

Iron and manganese serve as essential elements for stone dwelling microflora (Boyle et al., 1967; Krumbein and Jens, 1981; Grote and Krumbein, 1986; de la Torre et al., 1994). Many of the filamentous fungi isolated from weathered stone were found to oxidize both elements, by both direct (enzymatic) and indirect paths. However, oxidation by fungi is primarily an enzymatic process. Secondary metabolic products indirectly promote Mn(II) oxidation to a certain degree. Investigations by de la Torre and Gomez-Alarcon (1994) clearly showed that the oxidation by filamentous fungi was caused by extracellular and hydrophylic enzymes. The authors reported that the ability to oxidize manganese was related to that of oxidizing iron. However, the metabolic energy advantage gained by the microorganism through this oxidation remains uncertain (Ehrlich, 1981; de la Torre and Gomez-Alarcon, 1994).

Table 5
Biodeterioration Mechanisms on Stones (II)

Biogeophysical Influences
Alteration of the porosity/pore size distribution caused by the biofilm formation linked with
Changes in the vapor diffusion inside the material caused by extracellular polymeric substances
(EPS) and surface tension reducing compounds
Discoloration by biogenic pigments (e.g., melanin, chlorophyll) and thermal-hygric alterations
Biofilms in the function as "pollutant-absorber" and precursor for crust formation
Enhancement of salt migration
Alteration of the aerobic/anaerobic environment

4.2. Biogeophysical deterioration mechanisms

Depending on the environment and the resulting exposure, the surface of stones can be susceptible to structural and material changes over time. These are caused by the attack of acidic gases in the atmosphere and deposition of particles that may form various "patinas". The formation of different strata, due to the chemical changes in the material and structure of the upper material surface, leads to the development of crusts (crystalline) and incrustations (micro-crystalline or amorphous) (Künzel, 1988; Krumbein and Warscheid, 1996).

The formation of "black crusts" was thought to be mainly related to the deposition of gases such as SO_2, NO_x, and CO_2, organic components, iron oxides and hydroxides, as well as particles originating from dust, soot, metal and rubber (Nord and Ericsson, 1993; Steiger et al., 1993). Its development is influenced by the climatic conditions (out- and indoor climate) around the structure (object geometry) and can affect the physical properties (damp absorption, damp diffusion, capillary action and heat/moisture expansion) of the structural material (Kiessl, 1989).

Recent investigations have shown that microorganisms contribute to the formation of crusts by accelerating and/or catalyzing the reactions (Warscheid, 1996a, b; Table 5). The biogenic influences are closely related to the formation of microbial biofilms in the surface layers of stones on historical monuments. Depending on the type of rock, exposure and environmental conditions different biofilms may occur (Gaylarde and Morton, 1999).

While the basic parameters for the development of microbial contamination are given by the nature of the material and the environment, the development of a biofilm further facilitates the succession of mixed microbial communities as already addressed in previous chapters. Even severe, nutrient- and humidity-restricted living conditions on different kinds of materials are improved by the successive buildup from unilayer to complex biofilms. Biofilms

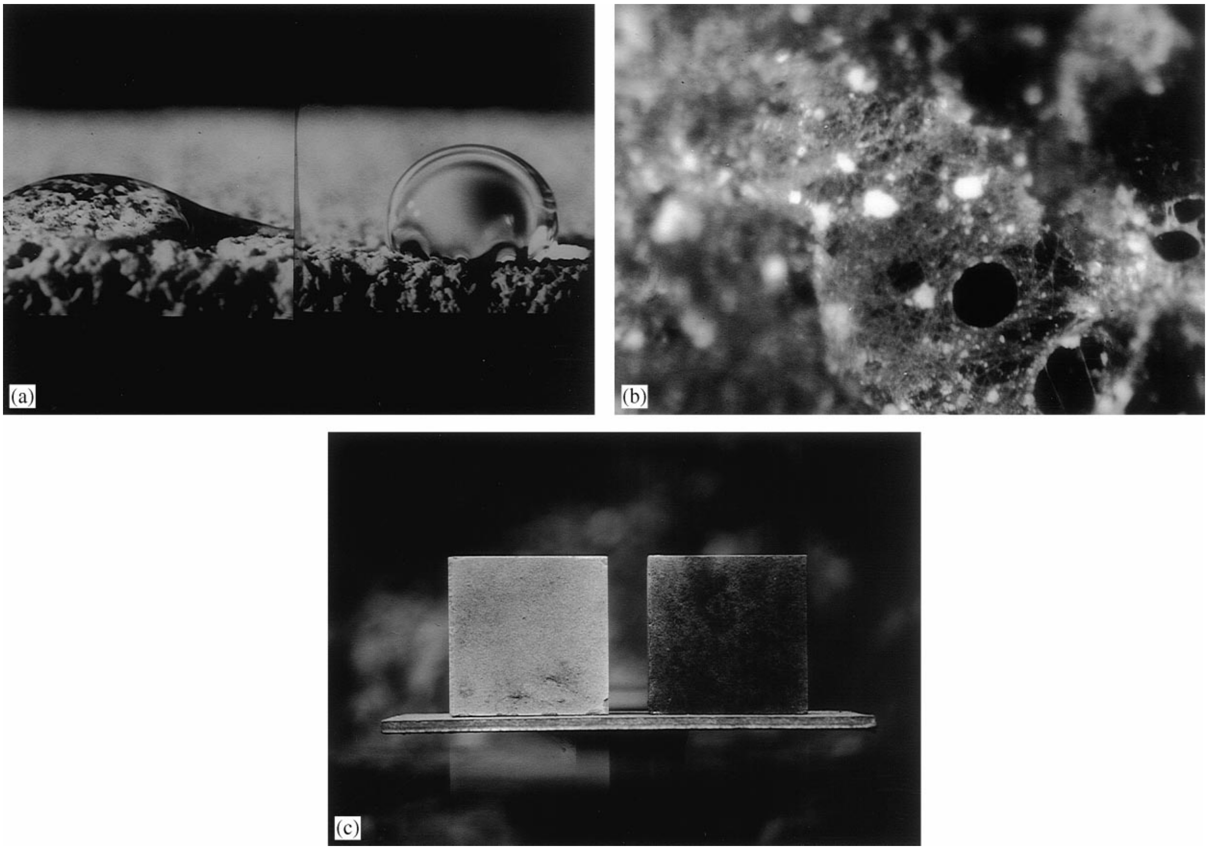

Fig. 6. (a) Loss of hydrophobic properties on an impregnated rock surface due to the presence of hydrated fungal biofilms indicated by an altered water contact angle (left: fungal contaminated rock surface; right: original and microbial unaffected hydrophobic control) (Leznicka et al., 1991). (b) Fungal hyphae network covering rock pores of a tuffa rock on the "St. Pauli-Landungsbrücken" in Hamburg (Germany), leading to an decrease in water-vapour diffusion of the porous material (Warscheid et al., 1991). (c) Deposition of airborne particles and consequent crust-formation on biofilm contaminated quartzitic fine-grained "Obernkirchener"-sandstone on an exposure testfield in Duisburg after three years of exposition (left: biocidal poisoned test cube; right: untreated biofilm infected test cube).

consist of microbial cells immobilized on the stone surface (substrate) and frequently embedded in an organic polymer matrix of microbial origin. The matrix is formed from extracellular polymeric substances (EPS), such as polysaccharides, lipopolysaccharides, proteins, glycoproteins, lipids, glycolipids, fatty acids and enzymes. It is responsible for binding cells and other particulate matter together (cohesion) and to the substratum (adhesion) (Characklis and Marshall, 1990; Beech and Gaylarde, 1991). Within the complex biofilm not all inhabiting microorganisms that can affect the stone surface need to be in direct contact with the substrate as shown in Fig. 6a (Warscheid, 1996a; Gaylarde and Morton, 1999).

The microbial discoloration of stone and rock surfaces has to be considered as a primary biogeophysical impact on the mineral surfaces. It acts as an important precursor for the formation of rock crusts. For monuments this can mean the loss of aesthetic value (Krumbein and Petersen, 1987; Urzi et al., 1993; Agrawal et al., 1987). Furthermore the coloration of stone surfaces can change their thermal-hygric properties (Garty, 1991; Badalyan et al., 1996; Dornieden et al., 2000) leading to significant damages especially on stones with high proportions of quartz (thermal impact) or clay-containing minerals (hygric impact) (Yatsu, 1988; Warscheid, 2000).

The first mention of a biogenic black pigmentation on stones, caused by partly mineralized chlorophyll, was by Jaag (1945). The color changes on the exposed stone surfaces were attributed to the enrichment of chlorophyll by cyanobacteria and green algae. Their brown-black mineralized by-products, such as phaeophytin, as well as other biogenic pigments such as phycobiliproteins, carotenoids and bacterial pigments also contributed to the discoloration. This was complemented by inorganic products such as iron and manganese oxides from heterotrophic fungi found in desert "rock varnish" (Krumbein and Jens, 1981; Grote and Krumbein, 1992).

The discoloration of stone surfaces by biogenic pigments can further be subdivided into (i) black stains (melanin and melanoidins, products of chlorophyll degradation, iron and manganese minerals), (ii) green and greenish stains (photosynthetic pigments from algae and cyanobacteria), (iii) yellow–orange–brownish stains (carotenes and carotenoids and degradation products of chlorophyll such as phycobiliproteins) as well as (iv) bright orange, pink and red stains deriving from pigments of chemoorganotrophic (halophilic) bacteria and degradation products of cyanobacteria and algae with iron enrichment (Pietrini et al., 1985; Realini et al., 1985; Urzi et al., 1992; Schostak, 1993).

During the studies on biogenic stone discoloration the origin and function of brownish-black melanins received special attention. Willimzig et al. (1993) attributed the blackening of stone crusts to enzymatic activities of many microbial groups found on exposed rock surfaces. They postulated that tyrosinase, a wide spread enzyme in nature, was released by dead microbial cells during mineralization and gave rise to melanin. This product is reported to protect microorganisms against UV-irradiation, desiccation, temperature changes as well as hydrolytic enzymes (Zhdanova and Pokhodenko, 1973; Zhdanova and Melezhik, 1980; Bell and Wheeler, 1986; Hudson, 1986; Berry, 1989). Melanins and melanin-related pigments are secondary metabolite products of numerous fungi, actinomycetes as well as some bacteria including pseudomonads, gram-positive coryneform- and methylotrophic bacteria (Urzi et al., 1993; Willimzig et al., 1993). In recent investigations special attention has been given to the excretion of melanins by dematiaceous fungi (Braams, 1992; Gorbushina et al., 1993; Urzi et al., 1992, 1994; Becker et al., 1994; Wollenzien et al., 1995; Warscheid et al., 1996).

Microbial biofilms modify the capillary water uptake of the porous stone material causing measurable alterations in the water-vapor diffusion (Fig. 6b). Surface-active compounds (e.g. fatty acids, glycolipids or enzymes) in the biofilm cause a decrease of the pore water tension changing the specific moisture relationship of stone and protecting the microorganisms against water loss and desiccation and favoring subsequent microbial contamination and their biocorrosive activity (Warscheid et al., 1991). Besides balancing humidity changes, the biofilm protects the stone microflora from extreme temperatures as well as toxic impacts by salt and heavy metal accumulation. This may explain the resistance of bacteria to biocidal treatments, where the biofilm hinders the penetration of biocides through the colloidal biogenic slime (Kinniment and Wimpenny, 1990; Koestler et al., 1997; Gaylarde and Morton, 1999).

The adhesive biofilm can be compared to “fly-paper” as it collects airborne particles like soot and dust as well as absorbing corrosive atmospheric pollutants thus contributing to an increase of the reaction rate of chemical induced corrosion processes (Wittenburg, 1994; Viles and Moses, 1994; Fig. 6c). The additional enrichment in oxalates, phosphates, sulfates and carbonates (Urzi et al., 1992) and melanins (Willimzig et al., 1993) from microbial origin enhances the process of crust formation (Krumbein and Petersen, 1987; Urzi et al., 1993).

Mechanical pressure is introduced to the mineral lattice of sandstones due to the contraction and swelling of slimy biofilms containing colloidal carbohydrate and protein molecules (Warscheid, 1996a). Penetration of hyphae from fungi and lichens also induce stresses in calcareous rocks (Koestler et al., 1985; Nimis et al., 1992; Gehrmann and Krumbein, 1994; Dornieden et al., 2000) or granite (Jones et al., 1988; Ortega-Calvo et al., 1991; de la Torre et al., 1993b; Arino and Saiz-Jimenez, 1994; Prieto et al., 1994; Galsomies, 1995). Biogeophysical influences reinforce any mechanical processes caused by freeze-thaw cycles or from crystallization pressure by accumulated salts and accelerate further abiotic deterioration processes (Arnold, 1993; Winkler, 1987; Rodrigues, 1991; Warscheid, 1996b).

5. Identification of biodeterioration on stones

Biodeterioration processes on stones are one of several damage functions influencing the disintegration and destruction of historical monuments and sculptures. The impact of physical and chemical factors determined by exposure conditions such as moisture, atmospheric and anthropogenic influences, and the nature of the stone itself needs to be considered during any preliminary data elaboration and object anamnesis.

As pointed out above, microbial contamination and their deteriorating activities contribute significantly to the acceleration of weathering processes. Even though its importance in stone decay may not be as obvious and significant as for “sensitive” materials like paper, leather, textile, or wood, a timely recognition of any biodeterioration process will help to prevent further damage. Moreover, it is critical in the development of suitable steps for conservation and restoration measures that require an interdisciplinary evaluation.

For this purpose, suitable and reliable methods for the detection and evaluation of biodeterioration processes on stones, such as biochemical and microbiological analyses, are needed. As previously mentioned, it should begin with an extensive object anamnesis including preliminary microscopical and analytical field studies that will determine the necessary microbiological investigations in the laboratory.

5.1. Field studies on microbial influenced stone decay

Scientific investigations on historical objects are often faced with the problem of avoiding or minimizing the removal of sample material for analysis. In some cases, where no stone material can be taken from the object in question, microbiological studies are restricted, apart from the above-mentioned preliminary anamnesis studies, to non-destructive analytical methods. These techniques include the application of contact-less CCD-video-microscopy (up to 1000-fold magnification), reflectance spectroscopy for the characterization of biogenic pigments and exudates (e.g., oxalates, melanins, chlorophylls, carotinoids, etc.) on stone surfaces, the Rodac impression plate-technique or Gauze-technique for the microbiological cultivation of the surface microflora and the respiration bell-jar measurement as well as ATP-analysis to assess the microbial metabolic activity in situ and under various environmental impacts (Salvadori et al., 1994; Becker et al., 1994; Sterflinger et al., 1994; Hirsch et al., 1995; Warscheid, 2000).

If scrapings from the surface or removing fragments of the stone are a possibility, the non-destructive field studies should be supplemented by microscopy and enrichment cultures for isolation and identification purposes.

The first comprehensive analysis of common histological staining methods for visualization of biofilms on natural stones was compiled by Kallass (1995). This comparative study included the application of various staining methods for polysaccharides, proteins, lipids and fluorochromes to visualize microbial biofilms. The best results for visualizing biofilm contamination in the uppermost stone layers were obtained by using the PAS — periodic-acid-schiff — staining procedure for polysaccharides (Whitlatch and Johnson, 1974) in conjunction with light-microscopy analysis as shown in Fig. 3c (Warscheid, 1990). The biogeophysical impact of the biofilm on the stone surface could be assessed by measuring the capillary water uptake using the Karsten tube test (Wendler and Snethlage, 1989). The distribution of the microflora in the rock profile and their actual metabolic activity can be assessed by using the DHA — dehydrogenase activity determination — assay (Warscheid et al., 1990, Fig. 4c) or high-resolution fluorescence staining techniques (e.g. CTC, calco-fluor-white), which allow the detection of microbial infections right on an early stage (Rodriguez et al., 1992; Mcfeters et al., 1995). The presence of specific enzymatic activity can be detected by fluorescence dyes based on 4-methylumbelliferone (MUF)-labelled substrate analogues (Hirsch et al., 1995).

5.2. *Microbiological investigations in the laboratory*

The current methods consist of quantification of microbial biomass in the stone and identification of the main types of microbes present as well as their metabolic activity. These types of investigations might be expanded by chemical analysis of specific microbial cell and biofilm compounds (fatty acids, carbohydrate content) and the biocorrosive properties of the stone-colonizing microflora (acid production, metal oxidation). Finally, if conservation treatments are required, supplementary testing of the microbial susceptibility of the potential stone consolidants, resins, and biocidal additives is needed (Barcellona-Vero et al., 1976; Vero et al., 1976; Benassi et al., 1976; May and Lewis, 1988; Warscheid et al., 1989b; Santoro and Koestler, 1991; Nugari et al., 1993a, b; Becker et al., 1994; Hirsch et al., 1995; Koestler, 2000).

The number of different enrichment media for stone microorganisms is legion and cannot be listed here (references are given in the last paragraph). Nevertheless, there is one important point to consider to achieve a representation of the microbial infection by cultural techniques. Eckhardt (1988) showed that, with respect to the nutrient-limited situation on buildings, a higher number and more representative species of microorganisms will be isolated preferentially by the use of “oligotrophic” (low organic content) media; moreover the addition of stone extracts to the nutrient solution will improve the cultivation results (Warscheid et al., 1988b). Modern molecular approaches (e.g., PCR) allow higher resolution in microbial community analysis and a further identification of non-culturable microorganisms (Rölleke et al., 2000); even the presence of genes involved in aromatic hydrocarbon biodegradation can be detected by these methods (Daffonchio et al., 2000).

The determination of biomass (e.g., protein, phospholipids) and numbers of microorganisms only allows an estimate of the presence and composition of the microbiological contamination on stone surfaces (Hirsch et al., 1995). Further quantitative data about metabolic status have to be obtained by photometric enzyme tests, such as the determination of the dehydrogenase activity (DHA) or the concentration of the adenylate energy-charge ATP in the stone samples, which relate to the biodeteriorating activity (Warscheid et al., 1990; Salvadori et al., 1994). These studies can also be correlated to the determination of CO_2 release as an index of microbial respiration in the stone material under investigation (Becker et al., 1994; Sterflinger et al., 1994; Hirsch et al., 1995).

The results of the light microscopy examination can be supplemented with a detailed and high-resolution study of the microbial contamination by scanning electron microscopy (Bassi and Giacobini, 1973; Koestler et al., 1985), for example after cryofixation in liquid nitrogen to avoid artifacts (Blaschke, 1987). Other techniques such as confocal laser microscopy may give detailed information about the distribution of specific microorganisms in rock biofilms (Lawrence et al., 1991; Quader and Bock, 1995, Tobin et al., 1999) and FTIR spectroscopy may detect microbial cell compounds or residues on material surfaces (de la Torre et al., 1993b). The meaningfulness, in practical terms, of these techniques needs to be carefully considered.

Evaluation of the microbiological results always has to be critically reviewed with respect to purely climatic, material-related and physico-chemical damage functions in order to quantify and state more precisely the real role biodeterioration processes can play on a specific object to ensure appropriate countermeasures such as described in the following section.

6. Preventive methods for biodeterioration processes on stone

Biodeterioration of exposed stone is primarily dependent on the availability of water and nutrients. Thus, material specific parameters, like porosity and permeability, architectural conditions, which determine exposure and environmental factors at the site will determine the intensity and rate of biocorrosive attacks. Only a comprehensive analysis of all these individual functions, their causes and functional relationships can provide the basis for evaluation and control of biodeterioration processes. Biocides should only be applied, where the environmental damage factors favoring biodeterioration cannot be controlled and chemical interventions are unavoidable (Warscheid, 2000).

The application of water repellants or consolidants to the stone has to be planned and carried out with regard to the prevailing exposure conditions of the monument (Wendler, 1997) and the possibility of future retreatment of the monument should be considered (Sasse and Snethlage, 1997; Teutonico et al., 1997). When biodeterioration processes are suspected of playing an important role, the development and selection of microbiologically resistant stone treatments is advised. Otherwise the effect of the conservation measures might be of very short-term or even lead to an increase in the microbial contamination and subsequent biodeterioration activity (Warscheid and Krumbein, 1996).

6.1. Cleaning

Conservation practice has to choose between many different techniques when addressing the cleaning of stone surfaces on historical buildings from dust, soot, biofilms or surface crusts. The analysis and characterization of the chemical and structural nature of the “dirt” by mineralogical, chemical and microbiological laboratory analysis is essential (Nord and Ericsson, 1993; Steiger et al., 1993).

Water cleaning helps to remove efflorescent and soluble salts and gives temporarily relief from biological infections, but in the long run it leads to a much greater microbial spreading due to increased dampness and humidity (Warscheid et al., 1988a). Mechanical and chemical cleaning occasionally show a restricted efficiency and can cause discolorations and severe damages to the stone work (Ashurst and Ashurst, 1990; De Witte and Dupas, 1992).

The removal of fungal stains with bleaching agents is best carried out by the use of calcium hypochlorite (Barov, 1987; Leznicka et al., 1988). Nevertheless, frequent application of highly concentrated bleaching agents, such as hypochlorite, on natural stones may aggravate the salt burden of the building material and leaves behind residuals of very hygroscopic calcium chloride. Other bleaching agents, like hydrogen peroxide, chlorine and chloramine, are also unsuitable in conservation practice because they may oxidize iron inclusions in the mineral material (Kumar and Kumar, 1999). Some of these may present health hazards during application and/or may be ineffective in removing discoloring stains. Barov (1987) suggests a mild and effective treatment with a mixture of low toxic bleaching compounds, called “OSC”, based on the reducing action of hydrogen sulfite, in the presence of bicarbonate, either as a sodium or ammonia salt, using a carboxymethylcellulose support material and quaternary ammonia compounds as the active biocidal ingredient. It has proved efficient in the removal of the more resistant organic discolorations and it has a relative low toxic effect.

6.2. Stone treatments and microbiological impacts

If stone treatments for the conservation of historical objects are planned, supplementary investigations on the microbial, especially fungal, susceptibility of the consolidants and water-repellents considered for use should be carried out.

The resistance of stone treatments can be tested and evaluated, besides long-term test fields at object sites, in laboratory tests by exposing respective specimens inoculated with object-related microbial flora in climate-controlled chambers or in vermiculite beds as proposed by Grant and Bravery (1985), where the specimens are kept under saturated humidity (Koestler et al., 1988; Leznicka et al., 1991). Some parameters that can easily be assessed are: fungal sporulation scale, percent coverage, weight loss measurements, and FTIR-analysis of the changes in polymer or resin composition (Santoro and Koestler, 1991; Koestler, 2000). Another technique that has been shown to be useful is respiration measurement techniques (Koestler, 1993; Petersen et al., 1993; Tiano et al., 2000).

Consolidants, like silanes, acrylics or epoxy resins are resistant to biodeterioration (Pankhurst et al., 1972; Charola et al., 1984, 1985; Charola and Koestler, 1986). However, epoxy-treated specimens showed increased fungal growth compared to the untreated controls; these phenomena might be explained by the presence of non-polymerized or partially polymerized monomers serving as nutrient substrates for the inoculated microflora (Domaslowski and Strzelczyk, 1986). Polyurethanes have been shown to be subject to direct biodeterioration. The microbial attack depends on their molecular structure and the type of chemical links; polyester-based polyurethanes are more susceptible to biodeterioration than polyether-based polyurethanes (Seal, 1985; Wales and Sagar, 1988, 1991; Kay et al., 1991a, b).

Water-repellents based on polysiloxanes applied to exposed stone surfaces might cause, under favorable environmental conditions, a considerable increase in the microbial contamination by serving as additional energy and carbon source (Leznicka et al., 1991; Krumbein et al., 1993). Especially, fungi have been shown to grow on treated stone specimens causing them to lose their hydrophobic properties; this phenomena might also be attributed to the superficial accumulation of hydrated biofilms (Leznicka et al., 1991). The fungal degradation may be related to the degree of substitutions and the type of organic side groups attached to the resin back-bone, in particular the abundance of silanol molecules (Si–OH) for silicone-based products and C–H bonds for carbon-containing products, or the presence of “inert” material used as bulking agents (Koestler and Santoro, 1988; Koestler, 2000).

Polyvinyl alcohol, polyvinyl acetate and hydroxypropylcellulose turned out to be the polymers most susceptible to biodeterioration (Petersen et al., 1993). Acrylic polymers, like Paraloid B72 and Primal AC33, do not tend to serve easily as carbon source for fungi (Nugari and Priori, 1985; Tiano et al., 2000), but their microbial resistance depends a lot on their respective product formulation (Koestler and Santoro, 1988; Koestler, 2000). Fungal growth might even interfere with the structural properties of the polymers tested due to the release of microbial catabolytes and/or exoenzymes. Some of the agents used to remove graffiti art are based on natural plant polymers, waxes or silicones, which are also suspected to be susceptible to microbial attack (Krumbein et al., 1993).

The use of coatings during the restoration of historical monuments and sculptures has seen a revival of historic recipes, based on linseed oil, lime or casein, and an increased use of modern paints, based on acrylic, silicone resin and silicate dispersion formulations. The chemical nature of the binder medium and the organic additives are generally the most vulnerable components for biodeterioration attack; especially when the media of the paints is water based (Bravery, 1988). Besides their chemical impact, paints tend to alter the moisture exchange and migration inside the mineral substrate, providing potentially favorable growth conditions for the infecting microflora. Microbiological studies on the suitability of paints for the application on calcareous sandstone have confirmed that organic-based paints (e.g., linseed oil, casein and acrylic resin), due to their nutritive value, promote the growth of the existing microbial contamination. In some cases (e.g., linseed oil) they intensified the microbial infection by sealing the pore structure of the sandstone. Lime paints favored microbial contamination due to their buffering properties, while added pigments had no significant influence on the microbial processes. Only silicone resin and silicate dispersion paints could be recommended as suitable for conservation, providing they have sufficient resistance to microbial attack and they do not affect the water exchange properties of the mineral substrate (Herm and Warscheid, 1995).

The evaluation of the life expectancy of a conservation treatment requires that the microbial susceptibility of the polymer or resin in question be assessed together with the material specific, architectural and environmental conditions around the object in question. The resistance of microbiologically sensitive products can be improved by biocidal additives or, possibly by the careful use of biocides applied directly to the substrate. This is discussed in the following section.

6.3. Measures against biodeterioration of stone

The control of biodeterioration processes should start with the adoption of measures that will prevent favorable growth conditions for the contaminating microflora. This objective might be achieved by the reduction of moisture within the stone material, e.g., by optimizing drainage systems, correcting faulty architectural details or by the application of stone protective treatments, but from case to case these measures may be insufficient or practically impossible. Here the application of effective, sound and environmentally friendly inorganic and organic biocides is advised. The choice of a particular commercial product must be done after considering a number of parameters (Richardson, 1988; Martin and Johnson, 1991; Kumar and Kumar, 1999).

The stability and effectiveness of any biocidal additives has to be analyzed with reference to the infecting microflora. The effectiveness of biocides is normally tested by the agar diffusion method (Krumbein and Gross, 1992) or via antibiogram (Curri, 1978) using isolated strains of microorganisms. Considering the complexity of stone-colonizing microflora which is mostly embedded in a protective biofilm, more confident results concerning the evaluation of biocidal additives for the conservation practice will be obtained by the treatment of microbial consortia on infected material samples from the respective object or reinoculated specimen of the referring stone material incubated in vermiculite beds (Grant and Bravery, 1985; Becker et al., 1994). During the evaluation of biocides, any detrimental effects to the stone material, such as color changes or salt impact, have to be tested before application (Tiano and Caneva, 1987; Richardson, 1988; Tudor et al., 1990; Schnabel, 1991; Krumbein and Gross, 1992; May et al., 1993; Nugari, 1993a, b). Furthermore, it should be considered that the effectiveness of biocides in interaction with the stone-matrix, especially charged clay-minerals, can be reduced significantly (Young, 1997; Cameron et al., 1997; Warscheid, 2000).

Commercial biocides and antimicrobially active substances can be commonly classified as alcohols, aldehydes, organic acids, carbon acid esters, phenols and their derivatives, halogenated compounds, metals and metal-organic substances, oxidizing compounds, enzymes, surface-active compounds or various synthetic organic products (Allsopp and Allsopp, 1983; Wallhäußer, 1988). Compounds such as surface-active quarternary ammonium salts, metals and metal organic substances, oxidizing compounds and heterocyclic organic products, have been widely applied for the control of microbial growth on stones (Richardson, 1988; Kumar and Kumar, 1999).

The antimicrobial effect of quaternary ammonia compounds ("quats") is probably based on the inactivation of proteins and enzymes and the detrimental impact on the microbial cell membrane. The effectiveness is dependent on their chemical structure, such as the presence of an aromatic ring structure and the respective length of the four radicals. The quaternary ammonia compounds affect a broad microbial spectrum ranging from bacteria, fungi to algae and lichens. The presence of proteins, ferrous iron and sodium chloride ($> 3\%$) as well as acids in the pore solution or mineral structure inhibit their activity, while their effectiveness increases under alkaline conditions and high temperatures during application. In some cases one has to be aware of corrosion processes on mineral iron inclusions. Further properties depend on the particular product in question and should be considered with regard to the intended application (Wallhäußer, 1988).

The susceptibility of stone colonizing microorganisms to quaternary ammonium compounds has been reported by many authors in laboratory tests and field studies (Sharma et al., 1985; Krumbein and Gross, 1992; Lisi et al., 1992). Applied to frescoes the surface active compounds led to a proportional decrease of the contamination by cyanobacteria and algae (Pietrini and Ricci, 1989). Nevertheless, it has to be emphasized that the nitrogen-containing "quats" after successive mineralization might serve as a nutrient source for surviving or newly attaching microorganisms aggravating the biodeterioration status of the treated object. Also, the surface active properties of quaternary ammonia compounds should be considered when sensitive historical paints or coatings are to be treated. In studies of surface-active compounds, Bettini and Villa (1981) reported the successful application of a neutral detergent (Lito 7) combined with a successive application of an unfortunately not clearly indicated biocide (Lito 3) for the cleaning of an algal contaminated tombstone. This product was also claimed by Tiano and Caneva (1987) to have good herbicidal effects, but it leaves white deposits after the subsequent water evaporation.

Tin organic compounds (TOC) were among the most used metal-organic substances for protection against bioinfestation. The biocidal effect is based on the inhibition of the energy metabolism of microbial cells, affecting bacteria, fungi and algae as well. The effectiveness depends on the type and number of organic substitutes in the compound in question. The activity of tin organic compounds remains unaffected in a pH-range between 4.6 and 7.8 and temperature conditions between 22 and 37°C. In contrast to "quats", TOC do not absorb onto material surfaces and keep thus their effectiveness over a long period of time. Nevertheless, due to their instability to UV-light and from environmental concerns, the application of TOC to open, exposed, stone surfaces seems to be very questionable, especially since less toxic biocidal treatments are available for the conservation practice as discussed later (Wallhäußer, 1988).

Apart from the biocides mentioned above, other organic-based compounds have been tested for application to stone surfaces. Curri (1978) studied the applicability of isothiazolinone chloride for inhibiting the growth of bacteria, fungi and yeasts; nevertheless, it is not recommended for long-term treatments due to its instability at higher temperatures and oxidizing conditions, and its short-term effect (Wallhäußer, 1988). *p*-chloro-*m*-cresol, commonly suggested for biodeterioration control, showed no inhibiting effect on the microflora of stones (Strzelczyk, 1981), while in combination with PCP it seemed to be effective (Dhawan et al., 1989), but these chemical mixtures should be, and are in many areas, strictly banned for ecotoxicological reasons. Thymol is capable of reducing lichens contamination on soapstones for some years, but the inhibiting effect on the entire stone colonizing microflora remained weak (Becker et al., 1994).

In order to evaluate the effectiveness of biocidal treatments on stones not only the short-term effects on the microbial contamination has to be addressed, but also the stability and long-term influence of the agents need to be critically analyzed. Organic-based biocides bear the risk of becoming, after natural or microbiological enhanced mineralization, nutrient sources for the stone-colonizing microflora, as already mentioned for the application of quaternary ammonia compounds. Furthermore, the inhibition of specific groups of microorganisms will favor the blooming and spreading of other hidden microbial species (Agarossi et al., 1988). Inorganic biocides will tend to build up additional deposits of soluble salts or form detrimental hardened stone surface films affecting secondary damage processes, such as salt crystallization stress, or impeding the access of further applied stones protectives (Ashurst and Ashurst, 1990; Schnabel, 1991; Brown and Martin, 1993).

The most important objection to the use of biocides in the conservation of exposed and often highly frequented historical stonework, is the ecotoxicological impact of the biocidal agents. The toxic nature of tin organic compounds makes them an unlikely candidate for the treatment of contaminated stone. The allergenic and synergistic effects of biocides on human health are not completely understood. These potential effects should be seriously considered by restorers and conservators when selecting a biocide and application method. The synergistic combination of biocidal agents, while reducing their concentration, may be the key to an environmental sense of responsibility in an effective struggle against biodeterioration of stones (Nugari et al., 1993a; Warscheid, 2000).

In the search for environmentally friendly treatments, Leznicka (1992) demonstrated the long-lasting effectiveness of *p*-hydroxybenzoic acid ethyl ester (PHB, Aseptine A) in combination with silicone resins to control biodeterioration processes caused by fungal and algal infections. The result achieved was more satisfying than with commonly used biocides, such as *o*-phenylphenol, triazine- and organotin derivatives, since the PHB-ester is not toxic for humans (it is commonly used for preservation of cosmetic and food, Wallhäußer, 1988).

For centuries it has been known that traces of heavy metals affect the growth and viability of microorganisms. This "oligodynamic" effect is mostly expressed by cadmium and, to a lesser degree by silver, tin, copper and mercury. Gold, platinum, iron, aluminum and zinc do not show any comparable properties. A high microbial contamination and considerable amount of organic residue causes a decrease in the biocidal effectiveness of heavy metals, whereas their inhibitory effect increases with higher (ionization) temperatures. At low concentrations heavy metals tend to have a bacteriostatic action, while at high levels they have been proven bactericides.

Copper is known to bind proteins and DNA, inactivating them. Based on this knowledge and translating those observations on buildings and sculptures into conservation practice, Ashurst and Ashurst (1990) suggested the application of brass strips on object sites exposed to run-off rainwater for a long-term control of microbial contamination. The slow and constant leaching of copper ions by water would result in the generation of a solution toxic enough to combat microbial contamination on stones. Nevertheless, the measure can lead to the appearance of unaesthetic green stains, depending on the reactivity of depositing air pollutants at the object site; thus, the proposed treatment requires careful consideration before the strips are installed, especially on light colored stones. Commercial biocides containing copper as an active ingredient (e.g., cupric ethanolamine or cupric sulfate) proved to have a significant influence in the long-term removal of lichens growth on historical monuments (Brown and Martin, 1993; Warscheid et al., 1996).

Other alternative treatment are ionizing radiation (Ley, 1988), UV-irradiation (van der Molen et al., 1980) and gas fumigation using computer controlled chambers (Elmer et al., 1993) and have been proved to be effective against microbial contamination on stones, however their application in the stone conservation practice is limited to movable and small-scaled objects.

7. Conclusions

The long-term preservation of stone objects, sculptures and monuments requires a holistic approach. To begin with, anamnesis comprising the assessment of the historical background of the building, which should include any previous treatments, is of fundamental importance to understand any changes in deterioration patterns over time. The stone type and the climatic conditions to which it is exposed will determine the predominant weathering phenomena and deterioration patterns. Any possible pathways for moisture within the stonework caused by architectural factors or structural damages will enhance the distribution of salts and air-pollutants and their concentration over time as well as contributing significantly to its biological colonization. The careful recording of the existing deterioration patterns will allow a preliminary evaluation of biodeterioration activity as a function of the environmental parameters thus helping in the selection of sampling sites required for the microbiological investigations. These should follow a practical approach. Finally, any conservation intervention has to consider the possibility of the effect any method or new compound to be applied to the stone may have on the general biosusceptibility of the object.

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