Patina and cultural heritage – a geomicrobiologist's perspective

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Summary

The following is a summary of 40 years of patina research conducted by the author, BIOGEMA Consulting (Inc.), and the Geomicrobiology Group of the Carl von Ossietzky University in Oldenburg. The author also acknowledges the generous support provided by numerous grants from the Environment Programme of the European Union, especially under the heading 'City of Tomorrow and Cultural Heritage'. Art history and the history of science are intimately entwined in this report. The main goal was to analyse changes in the surfaces of historical stone objects (sculptures, buildings and rock art surfaces). These changes are often summarised as 'patina', and have usually been attributed to chemical redox processes and to soot deposits or soiling. A second type of patina (bio-patina) was initially attributed to phototrophic micro-organisms. It has turned out, however, that chemo-organotrophic fungal microbiota are widespread and often the most important inhabitants of rock surfaces. The latter contribute many stable and lasting organic pigments to the rock surfaces. This is mainly caused by heavy and ever silently increasing loads of natural and anthropogenic organic materials in the atmosphere, deposited on and in rocks over time. This organic pollution leads to the colonisation of rock surfaces by chemo-organotrophic bacteria and fungi, which form multicoloured and often aggressive biofilms. The latter can destroy the rock surface (biodeterioration) or, in milder cases, cover the original architectural or sculptural surface with a densely coloured layer, called 'patina'. Several poikilotrophic micro-organisms that have been isolated from monument surfaces have been found to form stable pigments that cause these effects. It has been demonstrated that these organisms can rapidly create coloured patinas on rocks, and that natural rock samples from patinated quarries and stone monuments contain the same pigments when extracted and measured. Thus, a major source of coloured patinas on rocks are microbially produced stable pigments such as chlorophylls, carotenoids, melanins and possibly mycosporines and Maillard reaction products. The interpretation of these coloured biofilm products as air-borne soot and dust deposits has often misled research and the application of restoration/conservation techniques. The data presented here were gained thanks to generous support from the EU Environmental Programme.

Introduction

The term 'patina' usually brings to mind the inimitable and sometimes nostalgic traces of the ageing processes of art objects. 'Patina' was originally defined by Filippo Baldinucci, in his 1681 dictionary of art, as the time-dependent darkening of frescos and oil paintings. In the 18th century, the term was commonly applied to the colour changes that occur on bronze – *verde di bronzo* – and copper, caused by oxidation of the metals. Today, the term 'patina' is used in a broad sense, denoting all processes connected with the ageing of surfaces of works of art. Brachert (BRACHERT, 1985) has defined all surface transformations of (and crust formation on) all types of materials used in the production of artistic objects as 'patina'. In this paper, the term 'patina' is used in reference to two types of aesthetic changes of rock surfaces: the development of brightly pigmented crusts covering rock surfaces, and a pigmentation that is directly incorporated into the fabric of the uppermost layer of rock crystals. Chemical alterations, such as the dissolution of the rock material itself, are not necessarily connected with these phenomena.

The black, orange or brown crust-forming deposits causing colour changes on rock surfaces – especially marble and limestone – were for a long time believed to be the result of physico-chemical reactions caused by climatic factors and inorganic pollution, or remnants of ancient paint or conservation activity (JENKINS, 1988; BORSELLI, 1990; GRATZIU, 1989; KOUZELI, 1988; TAYLOR, 1989). Within the last few years it has been widely accepted that rock surfaces and other inorganic materials are common habitats for a wide variety of micro-organisms, such as chemo-organotrophic, chemolithotrophic and phototrophic bacteria, actinomycetes, and especially fungi and lichens. The interactions of these epi- and endolithic micro-organisms with the rock material have been studied more intensively, and it has been discovered that micro-organisms play an important and substantial role in all alteration processes that occur in rock, including physical and chemical alteration of the material components, material loss, the alarming deterioration of historical buildings and works of art, as well as the formation of brightly coloured patinas on material surfaces (MAY, 1993; URZI, 1991; KRUMBEIN, 1993; GORBUSHINA, 1993; STERFLINGER, 1997).

The processes of patina formation

The phenomenon of multiple changes occurring upon surfaces exposed to the environment has been known since antiquity, and has been appreciated or disliked according to the taste and fashion of the period in question. Also, the term 'patina' sometimes combined with or replaced by 'lacquer', 'crust', 'hue', has a long tradition. The term initially appeared in upper Italian dialects as a deliberately produced hue or a change generated by exposure over time on easel paintings. The first classical description comes from a Venetian poet (M. Boschini, 1660):

Tute le cose el tempo descoverzè;/Questa xe cosa chiara e la savemo;/Ma la pittura, contra lu medemo,/ D'un velo trasparente el la coverze,//Come una verzenela Veneziana/ Che se sconde col velo de l'onor/ Per covrir de modestia un bel rossor,/Che la rende pudica, e sora humana//Così intravien à la pittura/ ***La Patina*** *del tempo fà do efeti,/I colori vien sempre più perfeti,/ E in mazor stima l'istessa fatura.*

Later, the term 'patina' was used primarily to denote the colour change and ageing of copper roofs and bronze objects. In the 16th and 17th centuries, the yellow and orange patina on ancient marble monuments was also described, painted and cherished. In 1853, Justus von Liebig attempted to chemically analyse the surface transformations of the Acropolis monuments in Athens, after receiving some samples from Professor Thiersch. He identified the oxalates and gave the name 'thierschite' to the mineral. However, priority was later given to the names 'weddelite' and 'whewellite' for these calcium oxalates appearing in the surface layers of marble, the formation of which is a result of biological activity as Liebig (LIEBIG, 1853) had already claimed. Only very recently have modern scientists, dealing with physical heritage, adapted all former explanations of the term to an all-embracing definition: 'Patina is the sum of material and textural changes that occur in the surface zone of all materials, especially in objects of physical cultural heritage. These changes are caused by ageing, material decay and environmental impact, including the biological environment.' (KRUMBEIN, 1992 and 1993). Since 'patina' is obviously the oldest term for surface changes of any material that is exposed to the environment (atmosphere), all other terms related to surface changes may be subordinated to this general term. Such terms are oxalate film (*pellicole ossalati*), lacquer, crust, deposit, karst, rock varnish, micro-stromatolite, efflorescence, carbonate, gypsum, iron, manganese, oxalate and silica skins, as well as many other descriptions of environmentally induced surface changes.

The formation of patina certainly is a very complex process. Since it develops over a very long period of time, the patina itself is often seen as an object of historical interest. Not unlike the individual archaeological layers of Troia or Jericho, a patina's onion peel-like layering, often described as micro-stromatolitic in geological terms, documents the individual changes of climate and exposure, as well as any past human intervention. The main process can be described as an exchange of matter and energy between two open systems: the usually solid substrate, and the surrounding environment. These may be the indoor or outdoor atmosphere, water, soil, an intermediate cover of plaster or paint, or various other materials such as protective coatings or packaging. Both systems are defined by:

- Their physical characteristics (mass, particle size and shape, volume, density, cohesion, pressure, humidity, diffusion constants, etc).
- Chemical, crystallographic/mineralogic/petrographic characteristics.
- Biological components and activities.
- The associated energies (thermodynamics).

The natural limits of the process of patina formation are the local extension of the gradients and the mutual penetration depth of the components. In general, the environmental conditions can be related to a scale of several metres, while the material conditions to a scale of micrometers, up to a centimetre.

The formation of patina can come to a standstill under conditions wherein the mutual characteristics and influences compensate each other. However, this process of ageing or patina formation can be revived even if one parameter of the interacting systems is changed or changing. An intermediate standstill of the material and energy exchange, however, is noticed by the human observer (owner, conservator, architect, restorer) as a characteristic patina. In this case, patina truly is a static or stabilising component of the ageing process. In cases in which patina formation becomes a historic evolution of the surface area of a monument, the real danger is in the addition of new layers or historical deposits on top of the original material. These deposits, crusts, skins, sinters, gypsum crusts, etc., may represent an increasingly dangerous hazard for the original material they cover since the mass increase may lead to fissures, exfoliation, or desquamation and loss of the original surface material. Figures 1–10 document the biological impact on rock surfaces over time. The chemical analytical work has already been presented (KRUMBEIN, 1993; STERFLINGER, 1999).

The most interesting and intriguing questions related to these processes are the following:

- Is the orange-brown or black patina of selected rock samples directly related to the production of organic pigments by micro-organisms inhabiting the rock surfaces?
- Can patination of freshly prepared, unaltered rock surfaces be produced by micro-organisms under laboratory conditions?
- How long does such a process take under natural environmental conditions?

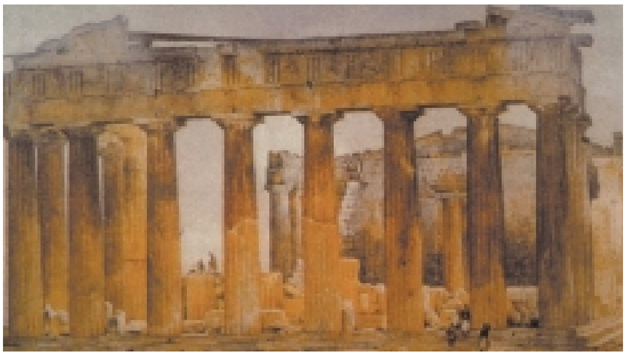

Figure 1. An early 19th century painting of the Parthenon, Athens. The Parthenon is depicted in the original colours of about 1840. At that time, biogenic patina covered the entire monument in yellow to brown pigments produced by microbial biofilms thriving at that time.

Figure 2. A fragment of the restored Acropolis (Athens), with original marble blocks as well as the Pentelic marble recently inserted to restore the architectural structure. The ancient marble pieces are bio-patinated, while the replacements still possess the colour of freshly quarried marble.

Figure 3. A limestone (oolithic) statue in the Market Square of Piazza Armerina in Sicily, a city which was destroyed by an earthquake and rebuilt in the Baroque period using materials from the quarry in Figure 4. All colours are biologically generated and represent organic pigments produced by bacteria and fungi.

Organisms involved

Organisms isolated from natural samples were screened, and those the colour of which resembled the colour of the patinas under analysis were selected for pigment analysis. Certain fungal strains with bright, orange-brown mycelium as well as bacteria forming orange colonies were isolated, purified and maintained in culture for further experiments.

The bacteria was characterised as gram-negative, non-motile and non-sporulating cocci, single cells of which were adhered to each other in irregular clusters. The colonies were extremely slow-growing. They were round with a smooth margin and glistening surfaces. After isolation and during the first purification steps, the bacteria usually formed large amounts of extra cellular polymeric substances, excreted to the medium as loose slime or biofilm material. The characteristic orange pigmentation was produced under all of incubational conditions.

Many of the fungi isolated from different monuments, natural quarries and outcrop surfaces around the Mediterranean and in Central Europe were identified as microcolonial fungi (MCF), also known as black yeast or yeast-like meristematically growing fungi. The first of these types of fungi was isolated by Gorbushina (GORBUSHINA, 1993) and Wollenzien (WOLLENZIEN, 1995) during work on marble monuments in Athens, the Crimea, Rome (including Carrara), Didymae (Turkey) and Caesarea (Israel). This important work of the ICBM Geomicrobiology Group at Oldenburg University began in 1989 and has been extended

Figure 4. A quarry near Piazza Armerina in Sicily with typical (humidity-related) organic pigments produced by bacteria and fungi biofilms, which have colonised the abandoned quarry rock surfaces for about the past 50 years. The pigmentation thus represents an evolutionary history of no more than half a century.

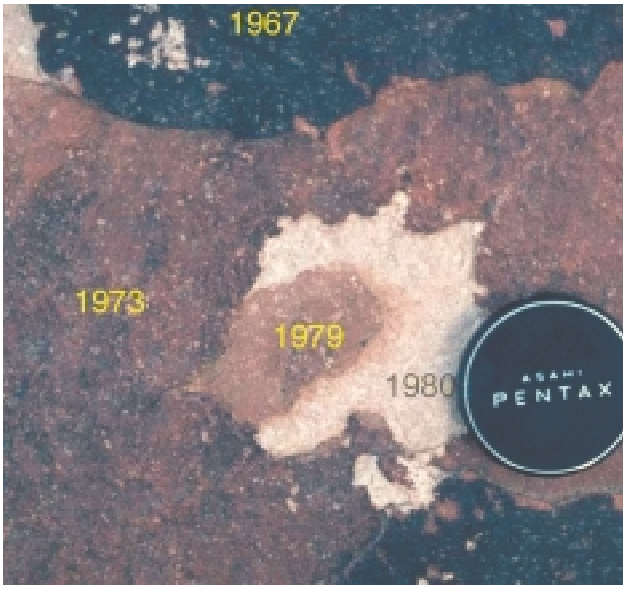

Figure 5. A petroglyph site in the Negev Desert in Israel monitored for the past 40 years by the Oldenburg Geomicrobiology Group. Subsequent petroglyph-like carvings and incisions were made at different time intervals to follow the development of organic biogenic patinas under natural environmental conditions.

since 1992 to incorporate comparative research activities on poikilophilic subaerial black fungi from European monuments, as well as natural rock outcrops in Russia, the Ukraine, the Negev Desert (Israel), the Mohave Desert (USA), the Namib Desert (Africa), and the Gobi Desert (Mongolia) (GORBUSHINA, 2000).

These meristematically growing, yeast-like black fungi, the colour of which can vary from yellow, orange, rust-red and brown to totally black, seem to be the most predominant rock-dwellers worldwide, according to present research (Gorbushina 1993 and 2000). The typical surface changes, usually referred to as 'soiling' (e.g. in monuments in Scotland, England and Germany) always seem to be related to fungal growth resulting from heavy organic pollution of the atmosphere, especially in major cities (KRUMBEIN, 1966; KRUMBEIN, 1995 and 1996). A case of rapid patination caused by black fungi was observed at the monastery of St. Trophime (Arles, France). Only three months after cleaning the surfaces of the sculptures, new black spots occurred. The fresh spots were easily identified as fungal colonies of *Nigrospora sp.* by the author along with a microbiologist from the LRMH research group at Champs-sur-Marne (G. Orial) and C. Urzì, Messina. Another case was reported in the 'Neue Pinakothek' (Munich), where serious black stains developed within a year or two after the erection of the building complex (BRAAMS, 1992). In this case, the black patina was not caused by black yeast, but rather by a close relative (*Exophiala jeanselmii*).

Patination of rock in the geomicrobiology laboratory

Carrara marble cubes were cut and incubated with bacteria and black yeast for 8 weeks in a laboratory. The bacterial growth on the marble caused a bright orange colour to appear that resembled the colour of the microstromatolitic patina of many Mediterranean monuments. A SEM analysis has shown that the bacteria and fungi invariably formed a thick biofilm on the marble cubes, accompanied by small orthorhombic crystals that were mostly identified as whewellite and weddelite (calcium oxalates deposited as a by-product of microbial metabolism).

The patination of the marble developed in several stages. First, the fungus formed a thick, fluffy mycelia layer on the liquid medium surface. The colour of this layer was initially white, but after a period of two weeks became pigmented exactly where it was in contact with the edges of the marble cubes. After three months of incubation, the mycelium became completely reddish-orange and orange-brown. The later stages of these experiments invariably produced black layers (multilayered, as in stromatolites) of several generations of pigment deposition on the rock surfaces.

Results of UV-VIS analysis and mass spectroscopy demonstrate that the pigments extracted from original samples and from the bacteria isolated from the samples are alike, and that the pigments of *Giberella intricans* are the same pigments as those extracted from the rock samples. This correspondence leads to the conclusion that the orange patination of rock samples is a product of microbial activity. In many cases, the bacteria form yellow to orange patinations (sometimes also pink to purple red). In other cases, fungi stain the rock surfaces with intense yellow, brown, and black pigmentation, easily related to melanin formation in different intensities. Of course, many other organic pigments that have not yet been detected with the methods that we have used may play a role in the complex composition of the patinas. However, it is safe to assume that the organisms isolated and analysed by the Oldenburg Geomicrobiology Group, as well as other groups (URZÌ, 1991), dominate the patination of ancient monuments. These findings are supported by our inoculation experiments and subsequent chemical analysis (STERFLINGER, 1999). The colours that emerged on the inoculated marble cubes strongly resembled the appearance of the original patinas. It was interesting to observe that only 8 weeks of bacterial or fungal growth are needed to create a patina of the same tint and intensity as that which can be observed on mediaeval buildings. Laboratory data strongly support the hypothesis forwarded by Krumbein (KRUMBEIN, 1993) that the patination of buildings may change with time, as a result of climate-related changes in the biodiversity of the flora inhabiting the rock. In 1969, Krumbein observed such patina formations in natural desert environments and attributed the changes to bacteria and fungi. Subsequently, a field site in the Negev Desert (KRUMBEIN, 1981) was visited many times, and new surfaces were exposed to biodeterioration processes and bio-patination.

On the basis of absorption spectra and mass spectroscopy, the carotenes isolated from the samples and the organisms could clearly be identified through comparison with previously gathered data. The pigments β-carotene, γ-carotene, eschscholzxanthene and rhodoxanthene isolated from the rock samples, as well as pigments from fungi isolated from the same rocks, were identified according to data provided previously, mostly on plant pigments by Davis (DAVIS, 1976), Karmakar (KARMAKAR, 1954), Karrer (KARRER, 1951) and by Gribanovski-Sassu & Foppen (GRIBANOVSKI-SASSU, 1967 and 1968). The latter isolated and identified pigments from the soil fungus *Epicoccum nigrum*, which occurs also on rock surfaces (BRAAMS, 1992). The pigment composition of *G. intricans* has never been described, but γ-carotene, lycopene and rhodoxanthene have been described as common fungal pigments occurring in the anamorph genus *Fusarium*, which is closely related to *Gibberella* (DOMSCH, 1993). The pigment composition (an important chemotaxonomical feature in mycology) and the relative amounts of pigment resemble those of the genus *Epicoccum*, with the exception that *Epicoccum* additionally produces small amounts of torularhodine, which has not been found in *G. intricans*.

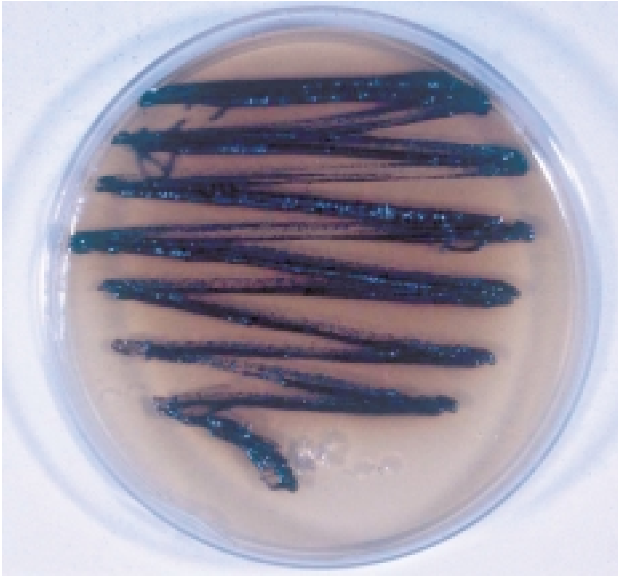

Figure 6. A colony of a melanin-producing fungus isolated from a rock surface and transferred to the laboratory in order to imitate natural bio-patination processes.

For the assessment of the patinas created in the laboratory, it must be taken into account that these patinas are a result of a maximum of three months of incubation, while natural patinas develop over a much longer time period. In both the laboratory experiments and the samples taken from field sites, small orthorhombic crystals were observed within the biofilms. This strongly suggests that bacteria and fungi are involved in the process of whewellite and weddellite formation, and that a microstromatolitic patina would develop even in a laboratory, given enough time for a longer incubation. This is supported by data of Blazquez (BLAZQUEZ, 1997), who found bacteria-like structures as the crystallisation nuclei in the patina of rock samples and proposed a biogenic origin of the mineral component of the patina. They, however, did not offer an explanation of the orange colour of the patina.

We would like to stress that the bacteria and fungi that we have found and isolated, as well as their characteristics and pigments, do not belong to the classical rock-dwellers isolated so far, namely gram-positive, chemo-organotrophic bacteria including coryneforms, red and orange pigmented micrococci, members of the genus bacillus and actinomycetes (WARSCHEID, 1990; URZÍ, 1996). The bacteria responsible for the bright orange colour on our rock samples have been clearly determined as gram-negative by gram-stain and fatty acid analysis.

Interestingly, on the basis of microbiological isolation experiments and cell counts the orange colour

Figure 7. The skull of a horse at the Colonna Traiana in Rome. The horse skull (and especially the eye) exhibit (1) surface loss resulting from pollution and acid rain, and (2) different stages of bio-patina formation and bio-pitting of the patina as well as the original rock.

Figure 8. Prehistoric paintings in the cave in Lascaux (France, Magdalénien). Artists in prehistoric times used organic and inorganic pigments to make the beautiful mural paintings. On the unpainted sections of the rock surfaces, microbial growth has created bio-patina. The similarity of human paint (or treatment) to biological causes is clearly visible when analysed by microbiological work (POCHON, 1964).

of Mediterranean rocks has often been assumed to be due to mere bacterial activity, since 'no significant fungal growth' was reported (URZÍ, 1996). The authors even state that mainly chemo-organotrophic bacteria, cyanobacteria and algae are responsible for red, yellow and orange colour changes, while fungi are only responsible for dark brown to black patination, although it is generally agreed that carotene production is a feature of both the bacterial and the fungal kingdom.

The physiological production, the chemical analysis of pigments and the artificial patination of white rock presented in this review disprove a mere algal or bacterial origin of orange stains and clearly demonstrate that an orange patination can well originate from fungal growth. Dark brown or black stains, on the other hand, have been reported to be caused by fungal and/or bacterial oxidation of iron and manganese (KRUMBEIN, 1981; STALEY, 1992) or by melanised microcolonial fungi and bacteria (actinomycetes) growing on and in the rock material (GORBUSHINA, 1993 and 2000; EPPARD, 1996; STERFLINGER, 1997). All of this, together with the fact that hyphomycetes such as G. intricans – till now only known as a cosmopolitan species with a special affinity to a wide variety of plants (DOMSCH, 1993) – are also active agents of bio-patina formation, leads to the conclusion that the origin of a stained patina must be analysed individually in each case. Furthermore, it seems that our understanding of patinas and colorations on natural and artificial rock surfaces is only in its beginning stages.

Conclusions

In many publications and reports, the ICBM Geomicrobiology Group in Oldenburg has shown that patina is very often a clearly microbiogenic formation derived from the bioreceptivity of the rock surface, organic pollution and environmental conditions that encourage the growth of subaerial rock biofilms.

Most patinas on works of art, especially those that have been transferred from their outdoor environment to museums, are ancient and the organisms are no longer detectable and cultivable.

Patina-related organisms are often not cultivable due to their special living conditions. Among other things, this may explain why most patinas on the surfaces of monuments are still interpreted as ancient paint or as the result of mere environmental pollution. However, the isolation of several gram-negative, stain-forming bacteria, and of black yeast from rock surfaces, formerly interpreted as stains caused by soot and soiling, clearly reveals that rock patina has been misinterpreted in previous work.

In spite of the difficulties that arise during microbiological analysis, it should be possible to clarify the biogenic origin of a patina, since:

- Biogenic pigments are preserved in crystalline structures for long time periods and with little change in their chemical composition, and thus the biochemical analysis of the pigment composition is also possible for ancient patinas.
- Carotenes have even been analysed in the shells of brachiopods from the Jurassic period – thus more than 138 million years old (CURRY, 1991). On the basis of chemo-taxonomic data, the authors have proposed a fungal origin for this pink or orange pigmentation (PROWSE, 1991).

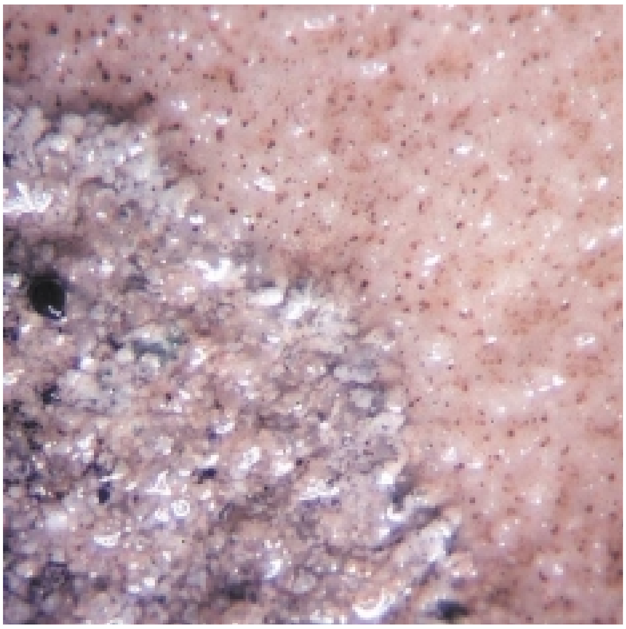

Figure 9. A rock specimen from the Negev Desert carrying a lichen cover. The part of the rock not covered by the easily identified lichen is covered by small microcolony remains of black fungi, which create an orange to brown patina (see Figure 10).

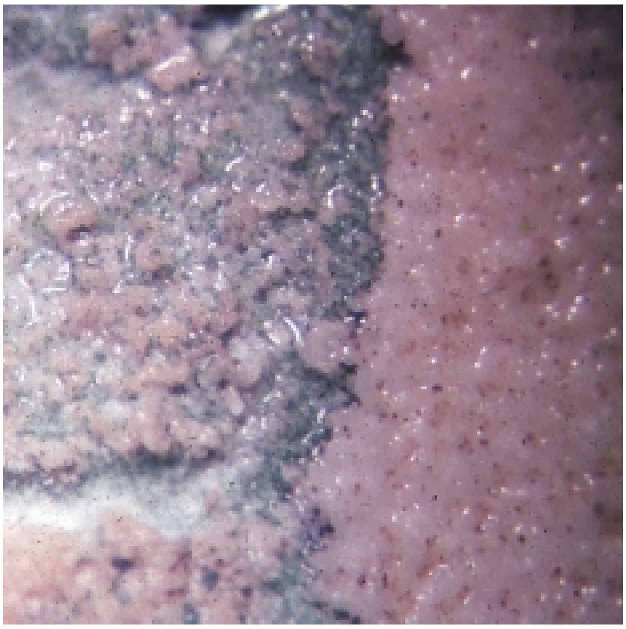

Figure 10. A rock specimen from which a lichen similar to that in Figure 9 was removed with a steel brush. The subsurface area of the lichen exhibits the same pattern of biopitting and growth as the zones adjacent to it and to the lichen in Figure 7. It can thus be concluded that a lichen cover, including pigment-producing, free-living black fungi, can produce uniform yellow, orange, brown and even black patina (see also Figure 5).

– Although the organisms might no longer be viable, their structures are frequently preserved in mineral components and can be visualised through electron microscopy combined with casting-embedding techniques and petrographic thin-sectioning, especially if the organisms have been involved in bio-mineralisation processes (TAYLOR, 1989; GARCIA-VALLES, 1996).
– Literature on biogenic pigments (e.g. DAVIS, 1976; STRAUB, 1987) combined with chemo-taxonomical approaches (AULING, 1992) and pigment analysis of common epi- and endolithic organisms (e.g. from the culture collection of the Geomicrobiology Division of the Carl von Ossietzky University in Oldenburg) may allow conclusions to be drawn in the future about the origin of biogenic pigments in ancient patinas.

Detailed knowledge of biogenic patina (*biopatina sensu lato*), along with laboratory experiments involving rock patination, could also lead to improvements in restoration treatments in which rock material is needed either for the replacement of monument components or for re-building purposes. Fresh rock material can be pre-patinated in a laboratory and would thus be adapted to the aesthetic appearance of an old monument. Such 'natural' patinas would be subject to the same time-dependent changes as the original material of the monument under restoration. Living subaerial biofilms on rocks may be the best way to adapt the new material used in restoration to the natural process of ageing and on the other to protect it from further damage (DORNIEDEN, 2000; GORBUSHINA, 2003; STERFLINGER, 1999). This would allow inappropriate conservation and restoration techniques to be replaced by the dignity of a biological (or normal) ageing process, which in turn can be controlled by a second protective treatment.

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