ARE PATINAS OF MEDITERRANEAN MONUMENTS REALLY RELATED TO THE ROCK SUBSTRATE?

VENDRELL-SAZ,M.

Dep. Cristallografia i Mineralogia. Universitat de Barcelona. c/ Martí i Franquès, s/n, 08028 Barcelona, Spain.

KRUMBEIN,W.E.

Geomicrobiology, ICBM, Carl von Ossietzky Universitaet Oldenburg.POB 2503, D-26111 Oldenburg, Germany.

URZÌ,C.

Istituto Policatedra di Microbiologia, Università di Messina,Salita Sperone, 31, 98166 Villa S. Agata-Messina Italy.

GARCIA-VALLÈS,M.

Dep. Cristal.lografia i Mineralogia. Universitat de Barcelona. c/ Martí i Franquès, s/n, 08028 Barcelona, Spain.

SUMMARY

Patinas of different mineralogies and colours occur on most monuments of the Mediterranean area. The origin(s) of the latter have often been related to previous painting and/or protective treatment(s). Microbial and biogeochemical pathways of formation, however, have as well been proposed and discussed. Paintings and photographs make it clear that coatings of changing colours have covered famous monuments in the past 200 years. Also the presence of microbiota has been recorded already 150 years ago. The work recorded here was done on several buildings in the Mediterranean area. A wide variety of localities and rock substrates and the patinas on them have been studied. Among the rocks were marbles, limestones calcarenites, granites and sandstones. In all cases studied patinas, their thickness and colour as well as their mineralogical composition were related to the exposure type. The patinas usually are multi-layered, the individual layers characterized by different crystal size, texture, mineralogy, and colour. Orange to grey layers are characterized by calcium carbonates and oxalates with some phosphates admixed, while the dark grey to black layers are rather characterized by gypsum with some trapped air-borne particles in cases. The petrology and mineralogy of the patinas is practically identical in all cases. Many of the patinas are inhabited by a variated microflora causing pitting and exfoliation in cases of the patina. Sometimes the pitting is only seen in the patina, and it reaches also the bedrock. A relationship between patina formation, preservation, destruction and climatic changes over the past 200 years is derived from these findings.

1. INTRODUCTION

Most of the objects exposed to the open air exhibit a patina on their surface which consists in a change of the colour and, sometimes, the texture of the object. This is often considered a positive value by adding lustre and dignity of age to a particular object of art. But in the case of monuments and statues made of stone it is mainly regarded as a dirty coat and as the result of a damaging action on the rock surface which must be eliminated by cleaning the surface in order to "see" the stone. This way many monuments have been cleaned by the mechanical or chemical removal of the patina causing serious damage to the stone itself. This fashion has been progressively abandoned and nowadays the old value of the patina increasing the aesthetic look of the monuments is re-established and most of the cleaning interventions are preceded by accurate studies of the stone and the patinas in order to avoid unnecessary cleaning actions (Verges-Belmin *et al.*, 1993, Garcia-Vallès *et al.*, 1996a).

The origin of individual patinas was widely discussed and two specific meetings on this topic (Alessandrini, 1989; Realini and Toniolo, 1996) served as a forum to show and discuss the main points reached by the scientific community in the study of origin, features and evolution of patinas with special reference to the case of oxalate patinas. From the communications to these two congresses and from previous literature two different points of view and opposite ways to consider patinas emerged:

Some authors (Gratziu *et al.*, 1989; Jenkins *et al.*, 1988; Lazzarini and Salvadori, 1989; Borselli *et al.*, 1990; Kouzeli *et al.*, 1988; Taylor and Simkiss, 1989; Franzini, 1984) claim that patinas are the result of man-made treatments applied to the stone to protect it against environment or to adjust the colour of the monument after environmental changes or replacements of stones caused unconformities of appearance. There are some facts supporting this idea: i) there are several cases in which patinas form an uniform film; ii) there are ancient photos of monuments showing a very uniform film from which only few remains are presently visible, this is explained as the normal erosive process of the paint that need to be renewed from time to time; iii) in some ancient documents there are drawings of people painting building surfaces; iv) the organic matter content of patinas may be interpreted as the body of a paint based on organic pigments; and v) the oxalate content is considered as the evolutive product of the organic components of the oginal paint. It was even mentioned that one of the recepees of former restorators includes plant derived oxalates ("Kleesalz" or "clover salt").

There are some other authors (Del Monte and Sabbioni, 1983, 1987; Del Monte, 1990; Krumbein *et al.*, 1989; Watchman, 1991; Ciccarone and Pinna, 1992; Krumbein, 1992; Krumbein and Warscheid, 1992; Krumbein and Urzì, 1993) who support the hypothesis of a biogenic origin of patinas and their ideas are based on the following points (among others): i) Ca oxalate present in the patina may be seen as a reaction between oxalic acid produced by the metabolim of certain rock dwelling microflores and the underlying stone or the components in the atmosphere; ii) organic matter may be the result of the diagenesis of organisms after their decomposition; iii) the laminated structure of such deposits (sometimes typically stromatolithic) is clearly related to a biogenic process; iv) the different levels of the patina may be regarded as a consequence of the climatc shifts during deposition; v) it is difficult to explain why patinas of the whole Mediterranean basin show the same colour, independently of the chronology of the monument (it is too uniform to be a man-made painting); vi) also different colours of patinas may have different biological explanations, while these individual colours occur all around the Mediterranean.

Further studies of the macroscopical features, morphological characteristics, composition, petrology and geochemistry as well as the biological history of the patinas will lead to a better understanding of origin and evolution of such coatings. Recent research on patinas and coatings of monuments and natural outcrops indicates different possibilities of origin of patinas, such as from urban pollution in the last half Century or a mixture of both, pollution and pollution enhanced microbial growth (Krumbein, 1966; Alaimo and Montana, 1993; Alaimo *et al.*, 1996).

On the basis of a study of patinas developed under different conditions on several monuments in the Mediterranean some common trends may be established, which suggest that a common origin may exist in all the cases analyzed.

2. OBJECTIVES

The aim of this work is to compare the characterization of patinas from different monuments and to show which are common characteristics and which are local and specific. Also the present state of dynamics (decay and/or deposition) of the patinas will be discussed. On the basis of these results a discussion about the origin (environmental, biological or man-made) will conclude the report.

3. MONUMENTS AND MATERIALS STUDIED

Several monuments have been studied and the patinas developed on their surfaces analyzed from the mineralogical, petrographical, biological and geochemical points of view. The monuments studied have been choosen using the following criteria: i) different types of rocks as a substrate; ii) only rural environment or areas with low level pollution, in order to avoid heavy sulphatation. The sampling of each monument has been done as extensively as possible in order to get samples from different orientations and sheltering conditions. Our approach was mainly concerned with patinas as deposits of minerals and organic matter but not with biofilms or microbial mats as a living deposit or "biopatina" occuring frequently e.g. on permanently wetted fountain sculptures in parks and public places. For this reason evident biological patinas and thick biofilms developed on areas of the monuments where running water or water accumulation was frequent have not been considered here.

The monuments from which the data of this paper have been obtained are as follows (Figure 1):

3.1. Cathedral of Tarragona.

The Cathedral of Tarragona is located in a city with a recent industrial development and affected by the marine spray (Vendrell-Saz *et al.*, 1992, 1996). The facade of the cathedral was built with imported limestones and marbles of different varieties chosen for their better quality and to guarantee a better durability of the sculptural works such as archs, reliefs, scuptures, etc. The lower part of the facade, the main door and some of the sculptures were made of marble from different origins, some of them most probably re-used from the Roman buildings of the city. Almost all samples were taken from the material of the facade because there is a great variety of rocks and a very well preserved patina. Additionally, some samples from the calcarenites used for the bulk of the building were included, however. The different limestones and marbles used in this building may be described as follows: i) Compact limestone, with many skeletal fragments of shells whose cavities and fissures are often filled by sparite, and a micritic matrix. ii) Dolostone formed by abundant skeletal remains; cavities filled by sparite, stylolites, and partially dolomitized. iii) Calcarenite (a bioclastic rock with detrital components e.g.quartz grains and clays) in a micritic matrix and cemented by sparite. In this rock inter- and intra-particle porosity was observed (the most important being moldic), and iv) marbles (formed by uniform interlocked calcite crystals) which can be further differentiated by the degree of cohesion among crystals and the crystal size (Garcia-Vallès *et al.*, 1996b).

3.2. Santa Maria de Montblanc (Tarragona).

The Church of Santa Maria de Montblanc was built with limestones and dolostones, it is located near Tarragona in a rural Mediterranean environment influenced by continental climate. This church is a notable Gothic building and there is a Barroc facade with Renaissance influences (1673 to 1688). Sampling was done exclusively on the facade. The latter consists of different varieties of sandstone mainly composed of quartz, calcite, biotite and rock fragments as detrital phases in a matrix with different clay mineral content (illite and kaolinite) and cemented by sparite. The differences among the varieties range are based on the clay content and the intergranular porosity leading to different durability of the types (Garcia-Vallès *et al.*, 1996a).

3.3. Cathedral of Seu d'Urgell (Lleida).

The Romanesque Cathedral of Seu d'Urgell is at 700 m of altitude in the Pyrenees, thus in a rural environment. The monument was built exclusively with granite in the 12th Century. Only minor changes were later added. Sampling was done on the whole building. Particular attention was given to capitals and columns of the cloister and of the apse because they are coated by a quite uniform orange to black film. This granite is a coarse-grained rock containing quartz, alkali-feldspar, plagioclase, biotite and some muscovite as essential minerals. The most common weathering products are chlorite and kaolinite, associated to the hydrolysis of biotite and feldspars, respectively (Sterflinger et al., 1995; Blázquez *et al.*, 1996).

3.4. Monastery of Sant Cugat (Barcelona).

The Romanesque Monastery of Sant Cugat (finished in Gothic style) near Barcelona (15 Km). Sant Cugat is a small town with moderate traffic and low levels of pollution. Most of this monument was built with limestones with abundant skeletal remains only partially cemented by sparite and with clay minerals in the matrix, but for the sculptural elements different rocks of better durability were chosen. The facade, the small rosettas of the lateral walls of the church and some elements of the cloister were made with a siliceous sandstone cemented by criptocrystalline quartz (chalcedony). The capitals of the cloister were made of bioclastic limestone cemented by sparite and, sometimes, with interparticular porosity. The column fusts consist of bioclastic limestone with different cementation grade.

3.5. Reials Col.legis (Tortosa).

The Reials Col.legis (Tortosa) is a Renaissance building placed in a small city in the lower part of the Ebro valley. The environment is rural with slight influence of winds from the sea. The stones used to built the cloister are different varieties of a dolostone with a variable content of detritical phases in a micritic matrix and different clay content from one variety to another. Dolomitization produced intercrystalline porosity which in some samples has been filled by calciticcement (Garcia-Vallès *et al.*, 1996d).

4. METHODS

For all samples petrographic thin sections were prepared and optically analyzed. Scanning electron microscopy (SEM), Energy dispersive X-ray (EDS) and X-ray diffraction analyses were routinely done. Several samples were analyzed microbiologically using routine techniques (Commissione Normal, 1989, Krumbein *et al.*, 1996). In exceptional cases isolates were taken using needles and transferring directly on agar plates. The selection of samples for microbial examinations was usually decided on the basis of careful examinations using dissecting microscopy. Colour and staining characteristics were measured using diffusive reflectance spectroscopy or directly on the building with a Minolta colorimeter. In exceptional cases pigment analyses were done using Gas Chromatography (GC) and pyrolysis mass spectroscopy.

5. RESULTS

5.1. Description of the patinas.

Most of the monuments studied are more or less uniformly coated by a patina, which colours ranged from yellow over orange, (dark) brown, (dark) grey to almost black in many cases. As a general trend, surfaces sheltered from run-off water and never affected by washing, even during strong torrential rains, (e.g. inner parts of the portals or cloisters) show a dark patina which surficially accumulates atmospheric dust and dirt. The surfaces relatively sheltered from running water but occasionally affected by washing (e.g. walls finished in the upper part by a cornice) show an uniform orange patina of more intense colour just below the protective element. And those areas were run-off water often washes the surface or completely exposed to rain do not show any apparent patina and the surface of the stone can be seen whithout any apparent alteration in the case of durable rock materials. Coatings invariably did not occur in such cases. These general aspects of the patinas may be modified by the local conditions of each particular point of the momunent, as for instance under a cornice with loosing of the joint mortar between two constructive elements the surface of the stone does not show any patina because of the washing effect of the running water (Figure 2). Thus, washing by running water seems to be one of the factors controlling the apparent colour of the patina. If patina is regarded as the sum of all reactions of the material with the atmospheric environment (Krumbein and Warscheid, 1992) then these patinas are unstained. In general it was observed that the colour and intensity of stain decreases with decreasing shelter.

In order to determine the colour attributes of the patinas, spectral curves of the diffuse reflectance were measured on several patinas and the colour coordinates CIE (1931) were calculated. Some spectra were obtained from small samples in the laboratory by using a spectrofotometer VIS-UV with an integrating sphere of Ba sulphate as white standard but many other measurements were directly obtained from monument surfaces with a Minolta Colorimeter. In all of the cases the dominant wavelength (584 nm) is quite the same (all the patinas exhibit the same hue) and only excitation purity and luminosity vary from one case to another according to the darkness of the surface. Two main conclusions may be drawn from these results: (i) the colour of the patina is independent of the colour and composition of the rock substrate, and (ii) the colour (and probably the colourant) is the same - or at least, of the same characteristics- in all the cases. Figure 3 shows the chromaticity coodinates of some of the samples measured. Thus in conclusion the yellow to orange component is invariably the same, while the grey to black component seems also to be the same, although it more or less makes the hue darker or brighter and does not change spectral distributions.

When patinas are observed in thin section several layers may be distinguished by their colour, microstructure, fabric and mineral composition. Thus, patinas may be regarded as multilayered deposits in which each layer shows different characteristics. Not all the cases exhibit a complete sequence of layers and in some of the samples only one single layer appears under the microscope. However, when a complete sequence is visible (which occurs in those patinas from completely sheltered areas) an ideal stratigraphy of the layers may be established as common for many of the patinas studied, which is independent of the mineralogical composition and fabric of the underlying stone (Figure 4). Beginning with the original rock surface and moving from interior to exterior these individual stratigraphic layers may represent a historical sequence of up to several hundred years. This may be described as follows:

5.1.1. Calcitic layer

This layer is normally orange to light brown. The main mineralogical composition is calcite, altough some other mineral phases such as Ca-oxalate (weddellite and/or whewellite) and Ca-phosphate (hydroxyl apatite) are often found. The petrographic fabric is usually micritic but in some cases, particularly in those samples from very sheltered zones, a microstromatolithic structure is clearly visible (Figure 5). In all the cases analyzed, we observed a thin (from 30 to 70 mm) orange micritic coating in contact with the underlying rock substrate, which occasionaly interacts with the rock producing the micritization of calcite or dolomite crystals of the stone. The orange/brown colour may be interpreted as organic matter trapped between the crystals of the micritic level. This is in agreement with the fact that a more intense colour and a more intense yellow UV fluorescence occur the smaller the crystals are. Occasionaly, remains of lamination have been identified in this micritic level.

In most of the cases, there is a micro-sparitic level on the orange one. This level shows, occasionaly, a microstromatolithic structure constituted by several sublevels of different crystal size and with a typical spherulitic or pseudoparallel arrangent of the calcite crystals. The thickness ranges from 100 to 300 mm. In some of the spherulites a nucleus with a P-rich micritic fabric may be distinguished from the surrounding crystals. The intercrystalline porosity between the calcite crystals of these levels show often small crystals of calcite growing on the spherulitic crystals, which suggests at least two distinct and subsequent generations of crystals building the laminated crust (Figure 6). This process is similar to the cementation of a rock and produces some kind of diagenesis that in this particular case consolidates the fabric of the layer. However, in other cases with higher water availability or a colonization by a well developed chasmolithic microflora, the diagenetic processes may lead to the compaction of these levels and the destruction of the original fabric. In these cases only a microsparitic level is identified with only some occasional remains of lamination. In those samples with a complete microstromatolithic sequence, erosive surfaces between sub-levels may be recognized in SEM observations. This indicates several hiati (time lapse interruptions) in the depositional process and sequence leading to the erosion of the uppermost surface before a new depositional event (biofilm formation, microbial mat?) is initiated.

5.1.2 Gypsum layer

This layer generally lies above the calcite/oxalate layer and is always on the calcitic layer, when it exists. The main mineral component is gypsum. Small quantities of quartz, clay minerals and calcite have been also determined by XRD. Under SEM, occasional crystals of Ca-oxalate (weddellite, according the tetragonal morphology) are also occuring in this layer. The thickness ranges from 40 to 400 mm. The colour is dark brown, almost black, and the outer surface is formed by lenticular gypsum crystals in sheltered areas, or smoth by dissolution in zones affected, even when occasionaly, by running water. When observed in thin transversal sections it appears transparent with many black bodies (of about 10 to 15mm diameter) trapped into the layer. The concentration of black bodies is higher to the surface, giving to the outermost zone a darker aspect (Figure 7). Whether or not these black bodies were fly-ashes or soot or rather represented spores and micro-aggregates of the frequently observed black yeasts could not be decided in all cases. Diakumaku *et al.* (1994) have described some of these aspects.

The fabric is mainly formed by gypsum crystals arranged perpendicular to the surface and in some cases it shows remains of lamination that have been interpreted as remnants of the original stromatolithic

structure of the calcitic layer after the transformation into gypsum. Based on this observation, some of the gypsum layers have been interpreted as a sulphation of the underlying calcitic layer but in some other cases, remains of fungal hyphae partially coated by gypsum crystals seem to indicate a possible biological transformation (Figure 8). Both origins have to be taken into consideration in the discussion of the genesis of this layer but it needs further investigations to go deeper in the knowledge of such layers.
The relatively high solubility of gypsum allows its dissolution and circulation with the running water and, as has been observed in many cases, there are several fissures of the rock and of the calcitic layer filled with gypsum crystals, leading to the decay of the stone by the crystallization pressure exerted by the growth of these crystals.

5.1.3. Dust and crystals on the surface
In some of the samples studied, mainly in those from more or less horizontal areas, there is a surficial accumulation of atmospheric dust and some small crystals of rhombic shape the origin of which may be related to the presence of bacteria (Figure 9). Some of the minerals forming the dust are clays which facilitated the water retention and thus, the growth of flora on the dust. This is not a real layer or continuous patina. In sheltered horizontal zones, however, it cannot be neglected as a water buffer.
From the chemical point of view the major elements of each layer here described correspond to the major mineral phases determined by XRD, thus Ca is the main component of the calcitic layer and Ca and S in the gypsum one. The X-ray maps obtained from several patinas show that there is a uniform distribution of Si, K and Al in the gypsum layer, which is in agreement with the quartz and clays determined by XRD and interpreted as trapped atmospheric dust. In those monuments of urban areas (even of low pollution) elements like Hg and Pb have been also determined in small (ppm) quantities that may be related to the industrial or traffic pollution In the calcitic layer ICP-MS analyses indicate some concentration of Mn (between 200 and 400 ppm) Garcia-Vallès *et al.* 1996b) also determined through its typical CL emission at 615nm (El Ali, 1989). Astonishingly iron has not been determined in noticeable amounts in the calcitic layer. This total lack of iron oxides and hydroxides further strengthens the view that the orange colour derives from former microflores and their typical pigments. Some of them (melanins, melanoidins, carotenes etc. are refractory substances which have even been determined in Jurassic pink or yellow limestones.

5.2. Microflora of the stromatolithic patinas
Microscopical observations (both optical and SEM) indicate the presence of a chasmolithic and endolithic microflora living on the surface and inside fissures often forming a system parallel to the surface. From laboratory isolations several bacteria and fungi have been determined in many samples and only occasionally algae have been also found. Among the fungi the so-called Dematiacea are the most important group and have been devided into two morphotypes: i) strains forming hyphae with the reproductive structure visible, mainly living inside fisures under the surface, and ii) black yeast-like colonies producing micropitting on the surface of the patina and the stone which affects few microns of depth. They are often chasmolithic (Figure 10). Bacteria have been also isolated and cultured in laboratory conditions, forming slime and showing a low ability to solubilize calcite (Garcia-Vallès *et al.*, 1996c). From other localities (Urzì and Realini, 1996) and also from some of the samples of Tarragona the few actinomycetes and coryneform bacteria isolated exhibit typical yellow, orange or even pinkish to black pigmentation. These pigments are presently studied and compared to pigment extractions of the patinas.

6. DISCUSSION

There are several common characteristics among the patinas studied from different monuments made of different stones, which may be summarized as follows:

6.1. Uniformity principle of the sequences.
Whenever a complete sequence of layers is present, it is quite similar in all the cases. The contact layer with the rock itself is a thin calcitic orange often wavy lamina (with different degrees of interaction with

the rock), the next layer is also calcitic but consists of bigger crystals (microsparitic or microstromatolithic, depending of the diagenesis suffered after deposition), and on the top there is the gypsum layer which may be a sulphation of the underlying calcite and/or deposition (dry deposition as the presence of atmospheric dust indicates, or biologically induced, or both). This sequence of layers is almost totally independent of the rock substrate (limestone, marble, sandstone or granite) indicating that it is not a transformation of the underlying stone but a deposition or product of the interaction of the rock dwelling microflores with atmospheric compounds (mineral, organic nutritive or biological air borne in rare cases).

6.2. Uniformity principle of the mineralogies.

From the compositional point of view the layers forming the patina are also quite similar in all of the monuments described in this paper and in other monuments studied by us (e.g. the Acropolis monuments, the Sicilian patinas and some rock varnishes in Israel). On any type of rock (marble, limestones, sandstones, granite) the main component of the layers is calcite, except in the gypsum layer where gypsum exceeds the calcite, and also in all the cases Ca-oxalates and Ca-phosphates -these latter occasionally- are present as minor components. In few cases Ca-oxalate has been reported as main component. This fact does not exclude a possible earlier deposition of Ca-oxalate and a later transformation into calcite, as Verrecchia *et al.* (1993) suggest in some examples of biomineralization by lichens and algae forming oxalates which later would recrystallize into calcite. One has to keep in mind, however, that the solubility of Ca-oxalates is lower than that of Ca-carbonates and sulphates. Thus the mineralogies indicate that the stromatolithic layers are fed and supplied in their components from the atmosphere and that low pollution creates more calcite and oxalate, while high pollution creates more gypsum and also oxalate and phosphate.

6.3 Uniformity principle of colours.

The colours of the individual layers or laminae forming the patina range from orange to dark brown but when their attributes are calculated from the spectral reflectance, it shows that the hue is the same for all the cases studied. As Fe oxides have been excluded as a possible pigmentation source, we must consider some organic component as a pigment. Diagenetic processes like those occuring in organic sediments (coal deposits) produced changes in the organic matter leading to the enrichment in C by loosing other elements. A similar set of processes may be imaginated in these thin deposits which, except the lithostatic pressure compacting the sediment, produce a condensation, polymerisation and transformation of the organic matter that may be reflected by the different luminosity and purity of the colour and the different intensity of the yellow UV fluorescence (I.C.C.P., 1963). It has been shown and analysed in many cases that yellow to orange and brown pigmentation may derive from the melanin and stable carotene pigments formation by fungi and bacteria, mainly coryneform and actinomycetes. Thus we strongly feel and have collected evidence for a biogenic origin of the stain of the stromatolithic patinas.

6.4 Biogenicity of the patina.

Especially in those patinas with very well developed stromatolithic structures (rock or desert microstromatolites) there are some evidences of a biological origin which may be summarized in the following ways:

6.4.1. Morphotype microstromatolite.

Some of the layers here described have a typical microstromatolithic structure which, according to the definition given by Walter (1976) and later revised by Krumbein (1983), are laminated deposits of biological origin. Many desert stromatolites, rock skin stromatolites and microstromatolites of phosphatic composition are described in the geological literature (Krumbein and Giele, 1979; Krumbein, 1983) On the other hand, most of the layers studied cannot be interpreted as ancient treatments or paints because this wavy stromatolithic and partly spherulithic fabric has never been found in paint layers. Also Watchman (1996) describes many examples of stromatolithic skins into which organisms are embedded without taking conclusions on biological influences on their origins.

6.4.2. Biospherulithic (oncoidal) components.
Inside the stromatolithic structure there exist several spherulitic arrangements of crystals with a P-rich micrite in the centre (Figure 11). The only possible origin for this kind of crystal arrangement is biological. Moreover, in some cases of recent crusts in monuments the biological body has been observed as a remain in the centre of the spherulite. Several geological authors describe the same phenomena in calcareous and phosphatic stromatolites.

6.4.3. Direct evidence of microbiota.
In patinas with a fabric more or less affected by diagenetic processes and, thus, with a high compaction of the crystals, some remains of spherical or filamentous structures coated (totally or partially) by different crystals of different mineralogies have been observed (Figure 12). This has been interpreted as a mineralisation of biological bodies during life or upon death and lysis.

In some examples the presence of crystals associated to fungal hyphae or bacteria have been observed on the surface of the patina, suggesting that a process of biomineralization is still in progress. According to Pinna (1993) and Caneva (1993), the ecological behaviour of microorganisms and the environmental factors affect the biomineralisation processes and thus the formation of specific mineral phases. Thus organisms leading to crystal precipitation and to these biomineralisation processes have to be included into the mechanisms of origin of rock patinas (Figure 13). In laboratory experiments many microbiologists have stained rock samples in different very resistant colours and hues of colours ranging from yellow over orange to pink, grey and black
(Krumbein *et al.*, 1989; Urzì *et al.*, 1992).

7. PRESENT SITUATION OF THE PATINAS

Some ancient photos and paintings (Urzì *et al.*, 1992) show how most of the monumental surfaces were uniformely coated by an orange to brown patina around the beginning and middle of the 19th Century and more black or blackish around the beginning of the 20th Century, according the dates of the photos. Presently, many parts of these surfaces do not exhibit any more this patina and only those areas more or less sheltered from run-off are still coated by patinas (like portals, windows, etc.). Additionally, there are some stripes were runnig water occasionaly falls where there is a development of patina which cannot be considered as a remain of the ancient one. Thus, is seems that there is an erosive process that eliminates the patina of the areas exposed to running water and
that the deposition has stopped except in some particular points with occasional water availability and a somewhat similar climatic situation to those in the 19th and early 20th Centuries.
Furthermore, most of the organisms presently colonizing the monument surfaces are bacteria living on the surface of the patina and chasmolithic and endolithic fungi (mainly dematiaceous or black yeast colonies). The presence of bacteria produces a diffuse crystals precipitation on the surface of the patina and on the stone while the colonies of endolithic fungi produce (or at least enlarge) the fissures inside the rock and the patina itself, leading to the decay of the patina and, thus, the loss of the coatings of monuments. This fact may be related with the global climatic shift produced in the middle of this Century, which changed from very dry conditions over rather wet conditions to the now observed drastic changes between rain and dryness and in several consecutive wet and dry years as typical for the time between 1945 and the recent time (Urzì *et al.*, 1992). These conditions imposed a new microflora with a lower potential of patina formation and forced the microflora to go inside the stone to look for more convenient conditions. Thus the microflora seeks in about 2-4 mm depth for less direct sun exposition and lower UV radiation, with a better and more constant water supply within the uppermost layers of the rock or the patina.

8. CONCLUSIONS

From our detailed study of the patinas of Catalonia (Spain) with some reference to Italy, Greece and other Mediterranean areas we dare to take the following preliminary conclusions:

(1) The patinas studied here form on all rock types in the Mediterranean.

(2) They are not influenced by chemistry, mineralogy or porosity and durability of the rock substrate in the cases studied by us.

(3) They represent former environments and former processes which have probably changed with changing climatic conditions (climate oscillations).

(4) The patinas can be regarded as microstromatolites or "desert stromatolites" sensu Krumbein and Giehle (1979).

(5) The present day microflora of the patinas apparently does not reflect the microbial association initially responsible for the biogenicity of the patina.

(6) We assume that microbial films and mats in some cases also extensive and repeated cover by endolithic and epilithic lichens have biogenically created the patinas (orange and grey to black) consecutively in periods of several hundred years.

(7) The present microflora rather acts together with other environmental factors to eliminate the patinas, which formerly were much more richly and abundantly developed on monuments surfaces of the Mediterranean area.

Remaining patinas of a natural, partially biogenic origin are presently eliminated by new environmental conditions and new microbial growth on and within the patinas and/or the rock substrates in question.

9. REFERENCES

Alaimo, R. and Montana, G. (1993): Study of calcium oxalates bearing patinas of altered calcareous artifacts by sei technique. *Neues Jahrbuch Miner. Abh.*,165 (2), 143-153.

Alaimo, R.; Di Franco, L.; Giarrusso, R. and Montana, G. (1996): Presence of magnesium oxalate dihydrate on marble capitals and columns of the cloister of the Monreale cathedral (Sicily, XII century). *In The Oxalate Films in the Conservation of works of Art. ed. G. Alessandrini.* Milano, 1996. 129-146

Alessandrini, G. (ed.) (1989): International Symposium The oxalate films: origin and significance in the conservation of works of art. Centro congressi CARIPLO, Milano, 381p.

Blázquez, F.; Garcia-Vallès, M.; Krumbein W.E.; Sterflinger, K. and Vendrell-Saz, M. (1996): Microstromatolitic deposits on granitic monuments: development and decay. (in press)

Borselli, G.; Camaiiti, M.; Pasetti, A.; Maravelaki, P. and Mateoli, U. (1990): Protettivi impiegati nella conservazione dell materiali lapidei: istoria, impieghi e svilluppi. *Edilizia*, 4: 1-2.

Caneva, G. (1993): Ecological approach to the genesis of calcium oxalate patinas on stone monuments. *Aerobiologia*, 9: 149-156.

Ciccarone, C. and Pinna, D. (1992): Calcium oxalate films on stone monuments-Microbiological investigation. *Aerobiologia*, 8: 33-37.

Commissione Normal (1990): Raccomandazioni Normal 9/88 . Microflora autotrofa ad eterotrofa: tecniche di isolamento in coltura. Roma: C.N.R. - I.C.R.

Del Monte, M. (1990): Microerosions and biodeposits on stone monuments pitting and calcium oxalalate patinas. *Advanced workshop "Analytical Methodologies of the Investigation of Damaged Stones".*

Del Monte, C. and Sabbioni, C. (1983): Weddelite on limestone in the Venice environment. *Envir. Sci. Tecnol.*, 17: 518-521.

Del Monte, C. and Sabbioni, C. (1987): A study of the patina called "Scialbatura" on Imperial Roman Marbles. *Studies in Conservation.*, 32: 114-121.

Diakumaku, E., Ausset, P., Sterflinger, K., Wollenzien, U., Krumbein, W.E., Lefèfre, R. , (1994). On the problem of rock blackening by fly-ash, fungal and other biogenic articles, and their detection in Mediterranean marbles and monuments. p. 305-310 *In: Fassina, V., Otta, H. and Zezza, F. (eds.) Proc. 3rd Int. Conf. on the conservation of monuments in the Mediterranean Basin. Soperintendanza ai Beni Artistici e Storice, Venice,* 962p.

El Ali (1989): Étude des roches carbonatées de réservoirs d'hydrocarbures pae résonance paramagnétique électronique et cathodoluminescence (EPR and CL applied to the study of carbonaceous rocks). *Thesis*, Université de Paris, France.

Franzini, M.; Gratziu, C. and Wick, E. (1984): Patine ad ossalato di calcio su monumenti marmorei. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 39: 59-70

Garcia-Vallès, M.; Blázquez, F.; Molera, J. and Vendrell-Saz, M. (1996a): Studies of patinas and decay mechanisms leading to the restoration of Santa Maria de Montblanc (Catalonia, Spain) *Studies in Conservation*, 41: 1-8.

Garcia-Vallès, M.; Krumbein, W.E.; Urzì, C. and Vendrell-Saz, M. (1996b): Coloured coatings of monument surfaces: A result of biomineralisation controlled by global climate change or anthropogenic? The case of the Tarragona cathedral (Catalonia). *Applied Geochemistry* (in press).

Garcia-Vallès, M.; Krumbein, W.E.; Urzì, C.; Vendrell-Saz, M. (1996c): Biological pathways leading to the formation and transformation of oxalate-rich layers on monumental surfaces exposed to Mediterranean climate. *In The Oxalate Films in the Conservation of works of Art. ed. G. Alessandrini.* Milano, 1996. 319-334

Garcia-Vallès, M.; Molera, J. and Vendrell-Saz, M. (1996d): Patination as a constructive and destructive process: the case of "Reials Col.legis" (16th century, Catalonia, Spain). *Quaternari Science Reviews* (in press).

Gratziu, C.; Jenkins, I.D. and Middleton, A.P. (1989): Dati preliminari sulle relazioni fra patine e polycromia nei fregi del mausoleo di alicarnasso. 317-326 *In Allessandrini, G. Ed. The Oxalate films: Origin and significance in the conservation of works of art,* Milano.

I.C.C.P. (1963): International Handbook for Coal Petrology. 2 Ed. *CNRS*

Jenkins, I.D. and Middleton, A.P. (1988): Paint on the Parthenon Sculptures. *The Annual of the British School of Archeology at Athens*, 87: 183-207.

Kouzeli, K.; Beloyiannis, N.; Tolias, C. and Dogani, Y. (1988): Ancient and Byzantine conservational treatments on the Parthenon. *Proceedings 6th International Congress on Deterioration and Conservation of Stone,* Torun 12-14 september 687-694.

Krumbein, W.E. (1966): Zur Frage der Gesteinsverwitterung (åber geochemische und mikrobiologische Bereiche der exogenen Dynamik). Ph.D. thesis, W¦rzburg, 106p. and appendices.

Krumbein, W.E. (1983): Stromatolites-The Challenge of a Term in Space and Time. *Precamb. Res.*, 20: 493-531.

Krumbein, W.E. (1992): Color changes of building stones and their direct and indirect biological causes. *Proc. 7th Int. Cong. Deterioration and Conservation of stone. Ed. J. Delgado Rodrigues, Henriques, F. and F. Telmo Jeremias*. pp. 443-452.

Krumbein, W.E. and Giele, C. (1979): Calcification in a coccoid cyanobacterium associated with the formation of desert stromatolites. *Sedimentology*, 26: 593-604.

Krumbein, W.E., Petersen, K. and Schellnhuber, H.J. (1989): On the geomicrobiology of yellow, orange, red, brown and black films and crusts developing on several different types of stone and objects of art. *In International Symposium, 25-26 octobre 1989, The Oxalate films: Origin and significance in the conservation of works of art, Proceedings,* p. 337-347, edited by G. Alessandrini, Milano, 380 p

Krumbein, W. E.; Sterflinger, K.; Becker, Th. and Warscheid, Th. (1996): Four non-destructive techniques to study the degree of microbial infection and pathology of objects of the cultural heritage. in Proc. of the CEE Conference on Building materials, Leuwen (K. van Balen, ed., in press).

Krumbein, W.E. and Urzì, C. (1993): Biologically induced decay phenomena of antique marbles Some general considerations. *In The conservation of monuments in the Mediterranean Basin, Proc. 2nd Int. Symp. Ed. Decrouez, D., Chamay, J. and Zezza, F., 2: 19-235. Gèneve: Museè d'Art et d'Histoire Naturelle.* Loughnan, F.C., 1969.: Chemical weathering of the silicate minerals. Elsevier, New York.

Krumbein, W.E. and Warscheid, T. (1992): Patina-Ein schillernder Begriff-Biologisch beschleunigte Alterung mineralischer Werkstoffe und Baudenkm ler. *Geowissenschaften,* 10: 274-276.

Lazzarini, L. and Salvadori, O., 1989. Reassessment of formation of the patina called "scialbatura". *Studies in Conservation*, 34, 20-26.

Pinna, D. (1993): Fungal physiology and the formation of calcium oxalate films on stone monuments. *Aerobiologia*, 9: 157-167.

Realini, M. and Toniolo, L. (eds.) (1996): II Int. Symposium: The oxalate films in the conservation of works of art. EDITEAM, Castello d'Argile (Bo), 539p.

Saiz-Jimenez, C. (1989): Biogenic vs anthropogenic oxalic acid in the environment. pp. 207-214 *In: The Oxalate films: Origin and significance in the conservation of works of art, Proceedings*, edited by G. Alessandrini, Milano, 380 p.

Sterflinger, K; Blázquez, C.; Garcia-Vallès, M.; Krumbein, W.E. and Vendrell-Saz, M. (1994): Patina, black spots ans related biodeterioration process on granitic monuments: Delos (Greece) and Seu d'Urgell (Catalonia, Spain). *Degradation and Conservation of granitic Rock Monuments*. Santiago de Compostela (1994) (in press).

Taylor, M.G. and Simkiss, K. (1989): Structural and analytical stadies on metal ion-containing Granules. In Biomineralization. *Chemical and Biochemical Perspectives (eds. S. Mann, J. Webb and R.J.P. Williams), VCH Pub. Weinheim*, FRG, 541 pp.

Urzì, C. and Realini, M. (1996): Bioreceptivity of rock surfaces and its implications in colour changes and alterations of monuments. Study case of Noto's calcareous sandstone. *In Proceedings of the International Congress on Biodeterioration of materials, Hamburg.*

Urzì, C.; Krumbein, W.E. and Warscheid, Th. (1992): On the question of biogenic colour changes of mediterranean monuments (Coating-crust-microstromatolithe-patina-scialbatura-scin-rockvarnish). *In The conservation of monuments in the mediterranean basin, Proc. 2nd Int. Symp. Ed. D. Decrouez, J., Chamay and F. Zezza*, 397-420. Geneve, Musee d'Art et d'Histoire Naturelle.

Urzì, C.; Krumbein, W.E.; Criseo, G.; Gorbushina, A.A. and Wollenzien, U. (1993): Are colour changes of rocks caused by climate, pollution, biological growth or by interactions of the three?. *Conservation of stones and other materials, ed. M. J. Thiel*, 279-286. London, Chapman and Hall.

Verges-Belmin, V.; Pichot, C. and Orial, G. (1993): Elimination de croûtes noires sur marbre et craie: quelquel niveau arrêter le nettoyage?. pp.534-541 *in: M. J. Zhiel (ed.): Conservation of stone and other materials. E and FN Spon*, London, 892pp.

Verrechia, E.P.; Dumont, J.L. and Verrechia, K.E. (1993): Role of calcium oxalate biomineralization by fungi in the formation of calcretes: a case study from Nazareth, Israel'. *Journal of Sedimentary Petrology*, 63 (5): 1000-1006.

Vendrell-Saz, M.; Garcia-Vallès; Molera, J. y Cid, E. (1992): Estudio de la degradación de la muralla de Tarragona, sector Portal de Sant Antoni. *I Congreso International de Rehabilitación del Patrimonio Arquitectónico y Edificación (Canarias'92)*, Tenerife 1992, Vol. I: 210-214.

Vendrell-Saz, M.; Molera, J. and Garcia-Vallès, M. (1996): Environmental impact on the Roman monuments of Tarragona (Spain). *Environmental Geology* (in press)

Walter, M.R. (1976): Stromatolites. *Developments in Sedimentology*, 20, Elsevier Publishing Co., Amsterdam.

Watchman, A.L. (1991): Age and composition of oxalate-rich crusts in the northern territory, Australia. *Studies in Conservation*, 36: 24-32.

Watchman, A.L. (1996): Properties and dating of silica skins associated with rock art. Ph. D. thesis, Univ. of Canberra, 390pp.

ACKNOWLEDGEMENTS

The authors acknowledge the skilled help of the technicians Renate Kort Michael Pilzen and Sabine Willig. The collaboration of the authors was enabled by the EU grant "Atmospheric eutrophication and saecular organic pollution" (AESOP CT94-0569). Some studies here exposed have been developed in the frame of the project SEC95-114 of the CICYT (Ministerio de Educación y Ciencia, of the Spanish Government. The authors also knowledge the financial suport of the Catalan Government (Dept. of Culture) and the facilities for sampling most of the monuments. Some fungal and bacterial identifications as well as some material colour change experiments were also supported and financed by grants to one of us (Krumbein) on the conservation and restoration of sandstone and marble monuments of cemeteries (DBU 02895) and on surface changes of marble and glass (DFG Kr 333/25-1). The contribution of C.N.R. (National Council of Research) is acknowledged by C Urzì.

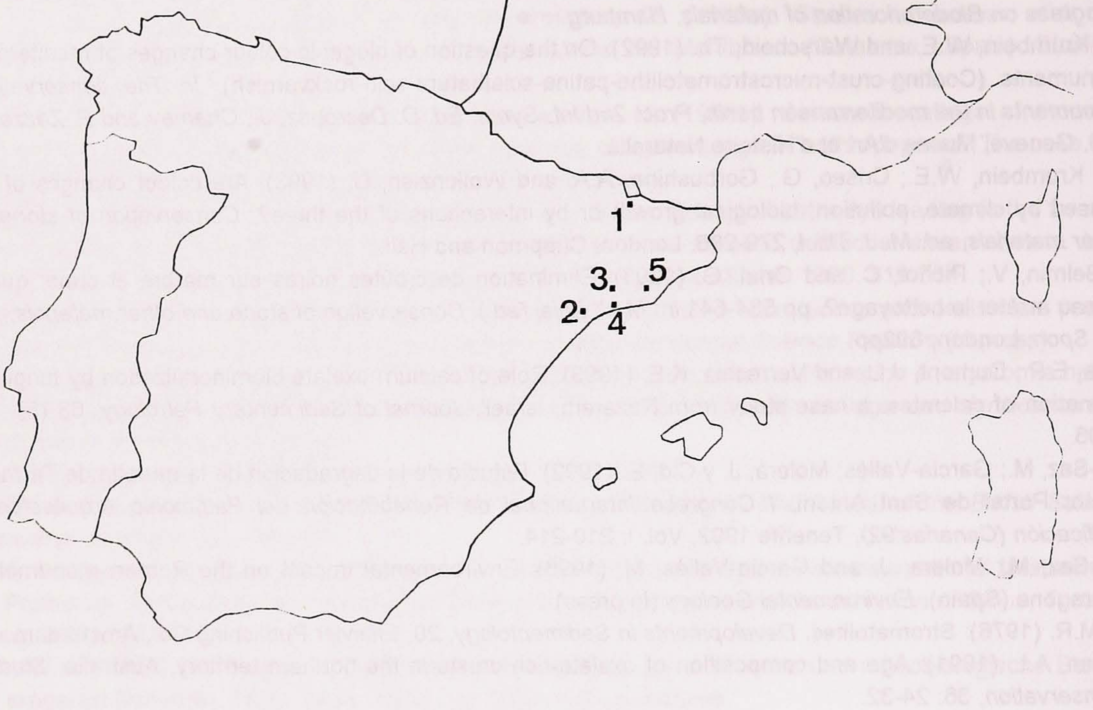

Fig. 1: Schematic map showing the situation of the monuments studied in this paper. 1: Cathedral of Seu d'Urgell; 2: Reials Col.legis de Tortosa; 3: Church of Montblanc; 4: Cathedral of Tarragona; 5: Monastery of Sant Cugat

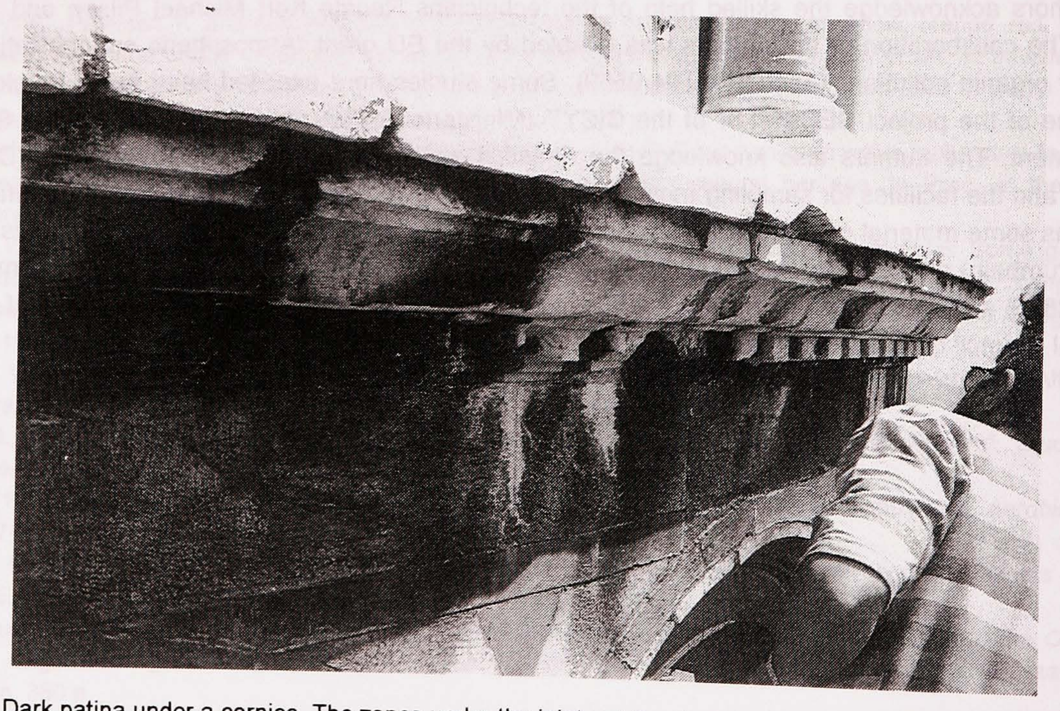

Fig. 2: Dark patina under a cornice. The zones under the joints of the elements of the cornice have been washed because the decay of the joint mortars concentrates the running water.

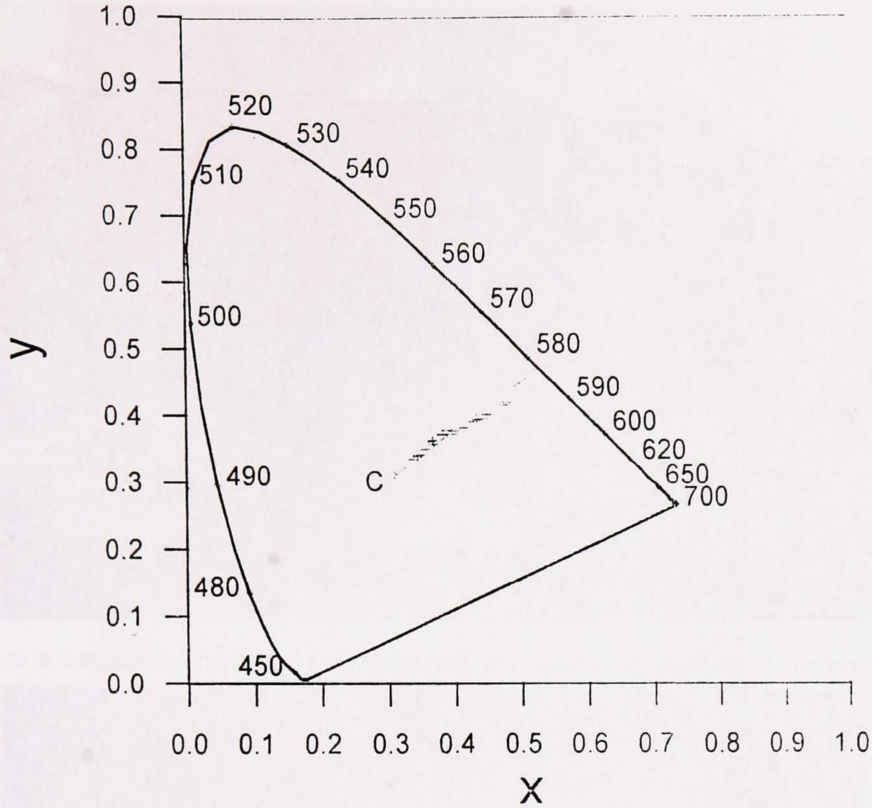

Fig. 3: CIE 1931 diagram with the chromatic points corresponding to some of the patinas studied. The line linking the achromatic point C with the spectral locus corresponds to a constant hue.

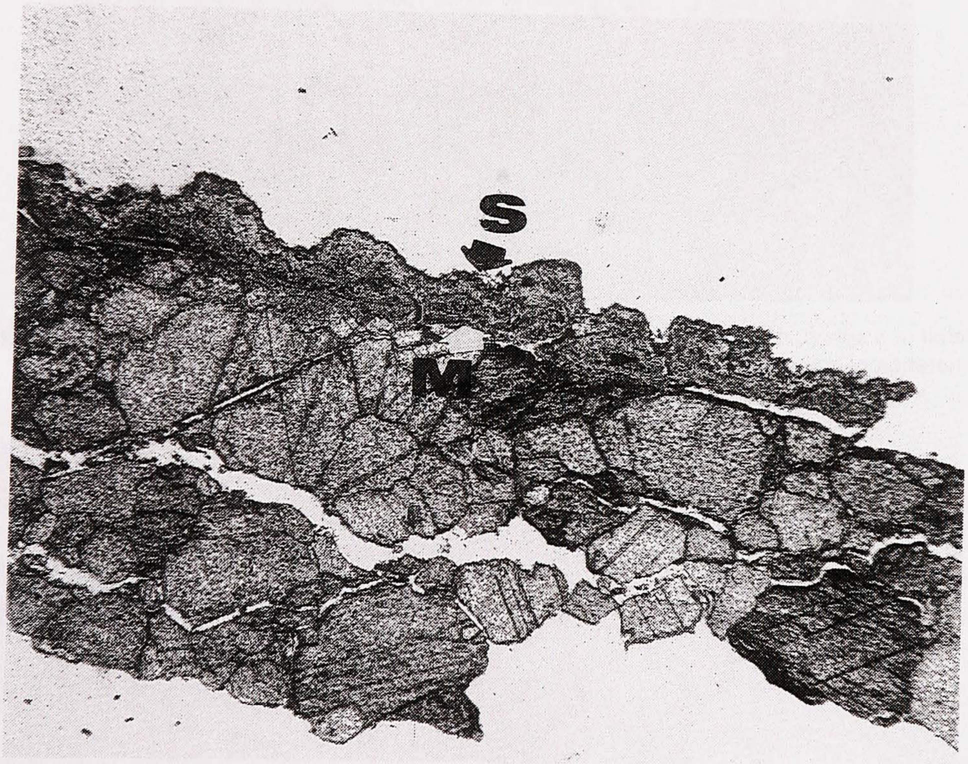

Fig. 4: Thin section of a patina developed on a marble (Cathedral of Tarragona). The two main levels of the calcitic layer are marked: i) micritic (M) with a white arrow, and ii) sparitic (S) with a black arrow.

Fig. 5: Thin section of a microstromatolithic level developed on a granitic stone (Cathedral of Seu d'Urgell).

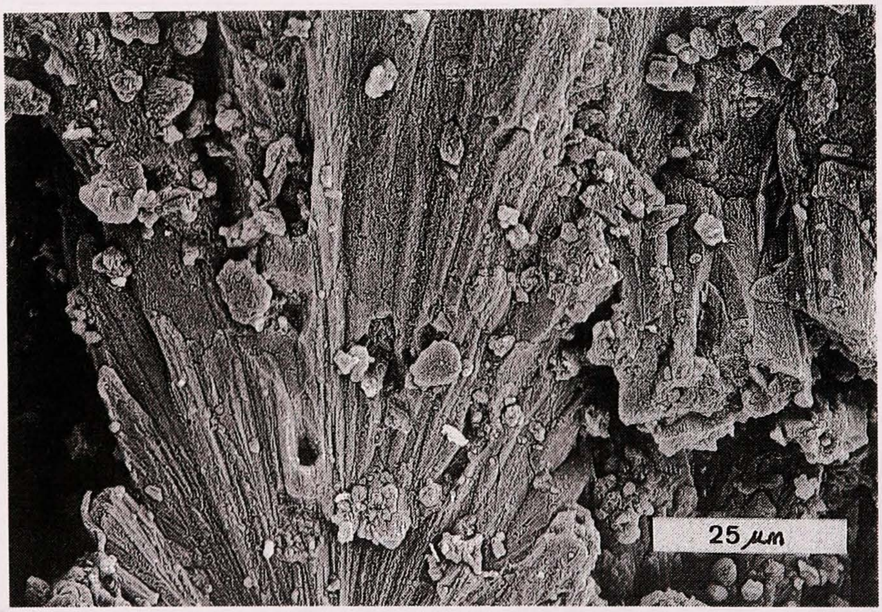

Fig. 6: Detail of a spherulitic arrangement of calcite crystals in a microstromatolithic structure in which a second generation of small crystals of calcite may be seen growing on the big ones.

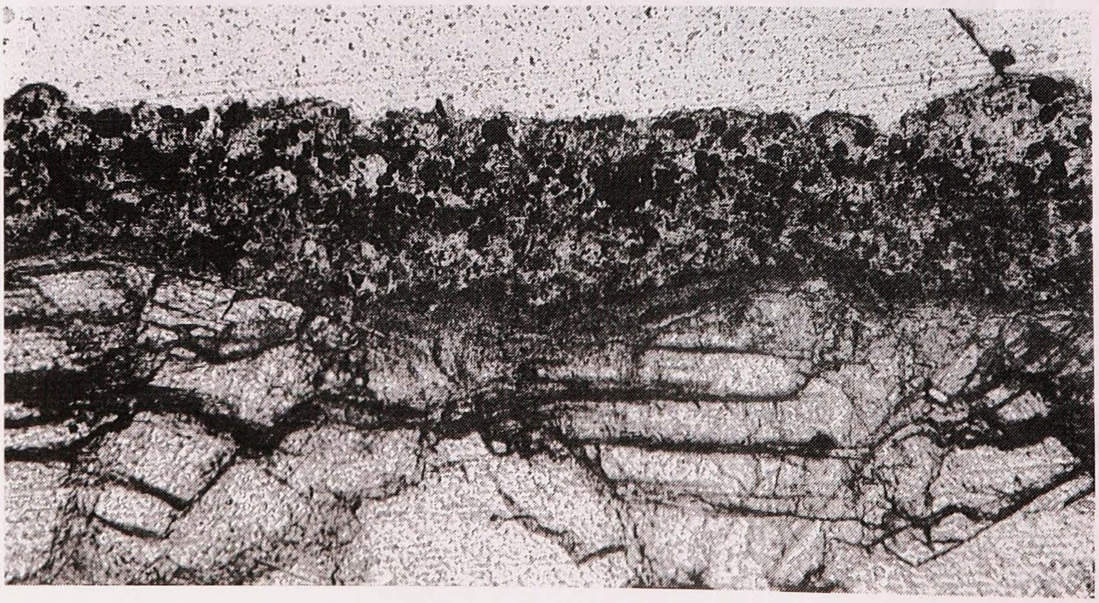

Fig. 7: Gypsum layer on a thin micritic layer. Inside the gypsum layer there are

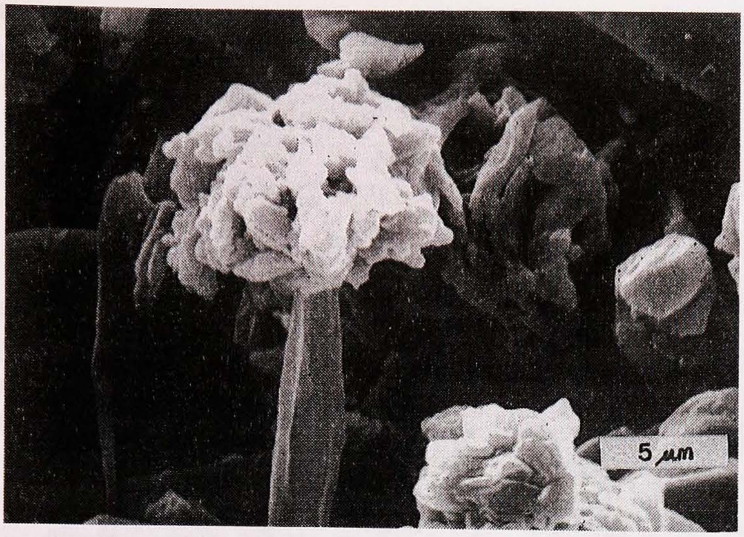

Fig. 8: Gypsum crystals associated to a filament. According to the size and shape of the crystal aggregate it seems to be developed on this filament, suggesting a biological origin for these crystals.

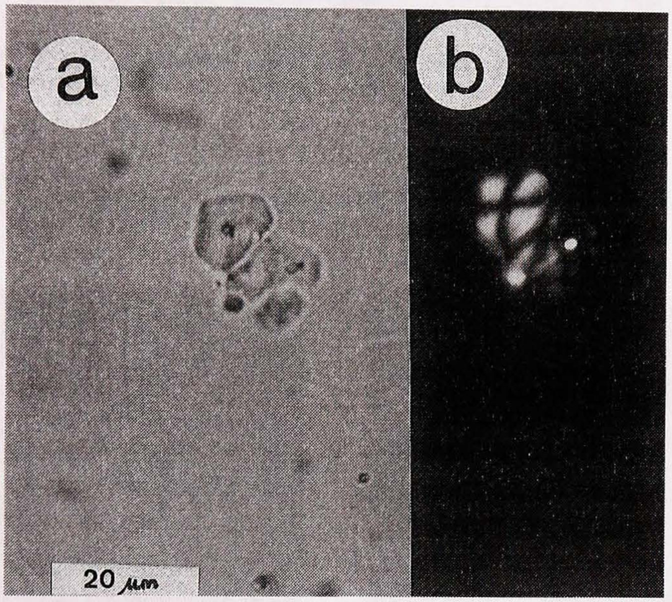

Fig. 9: Small crystals od weddellite (?) accumulated on the surface of the patina. a) polarized light, b) under crossed polars. In the center of each of the crystals a highly birefringent body (a bacteria?) causes a deformation of the crystal structure which is visible by the ondulating extinction visible under crossed polars.

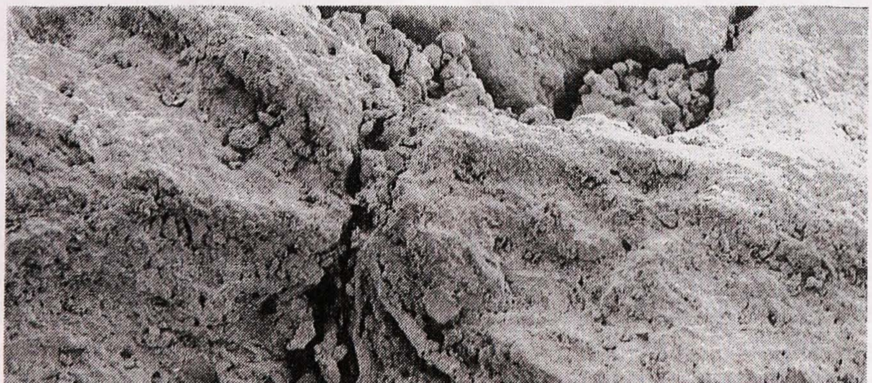

Fig. 10: Orange micritic layer developed on a siliceous sandstone. The patina itself is colonized by black yeast-like fungal colonies (upper part of the photo) which develop hifae penetrating inside the patina and leading to ist decay. The sample corresponds to the Monastery of Sant Cugat del Vallès.

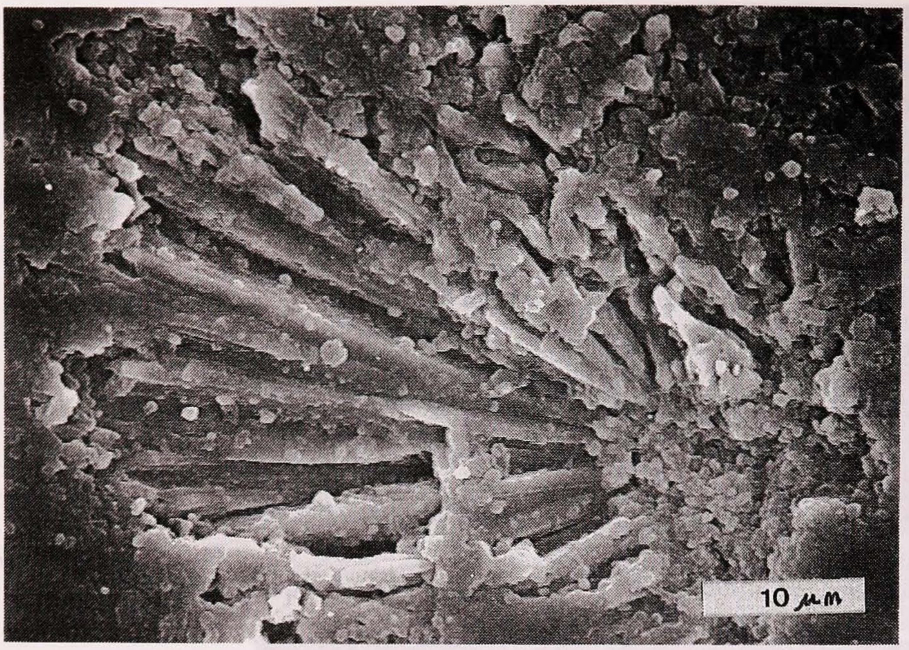

Fig. 11: SEM image of a spherulitic arrangement of calcite crystals around a central micritic nucleus which is rich in P. It corresponds to a microstromatolithic layer developed on granite. Cathedral of Seu d'Urgell.

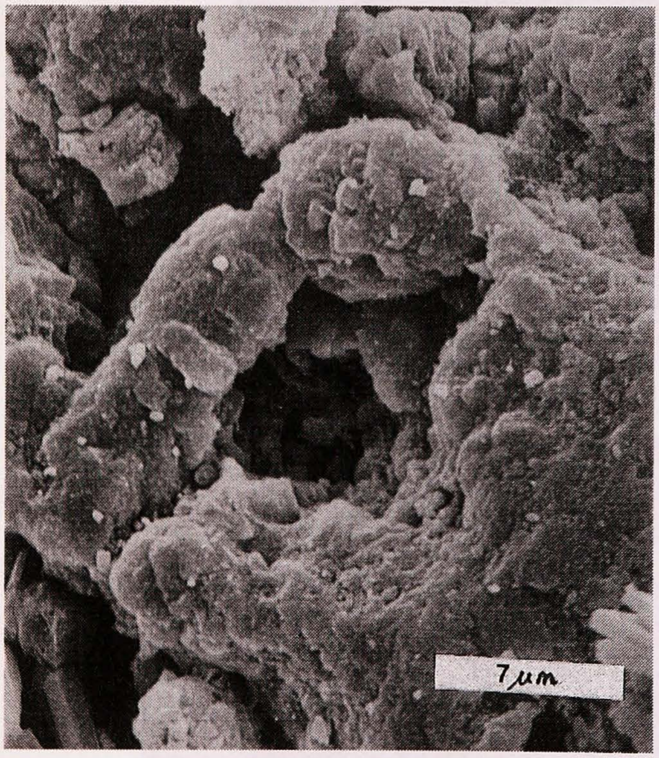

Fig. 12: Mineralization of calcite and Ca-oxalate (?) developed on a filament in the upper part of a patina developed on a calcarenite (Church of Montblanc).

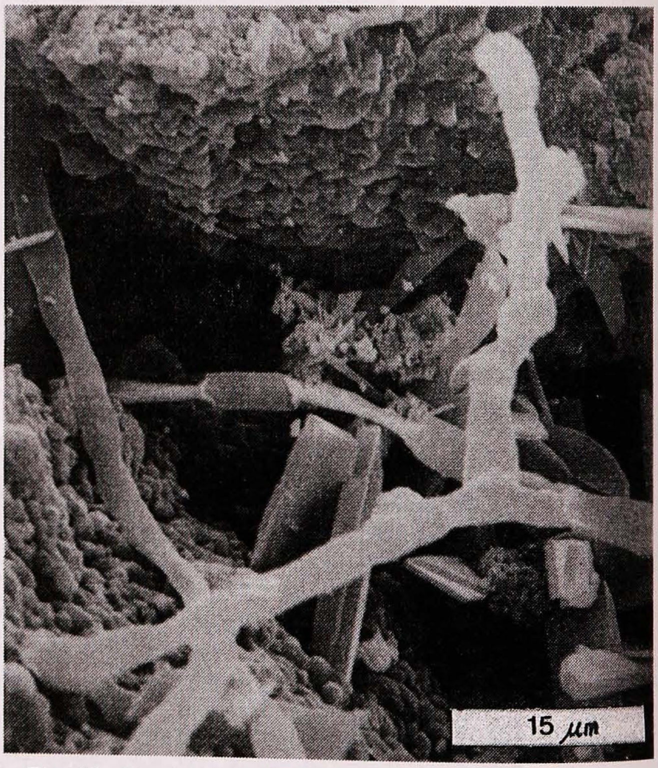

Fig. 13: Crystals associated to fungal filaments (Cathedral of Tarragona)