

Biodeterioration of calcareous and granitic building stones in urban environments

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Abstract: Scanning electron microscopy in secondary (SEM) and back-scattered (BSEM) mode associated with energy-dispersive X-ray spectroscopy has been used to investigate decay features associated with biological colonization of calcareous and granitic building stones in monuments and rock outcrops in the UK, Portugal and Spain. In combination with physical decay caused by lichen hyphae penetrating the stone substrate, this study reveals how chemical attack by organic acid exudates derived from metabolic activity of lichens and leading to the crystallization and growth of inorganic salt compounds within the stone microfabric is contributing to the destruction and weakening of the building stone surface. BSEM analysis is particularly useful in showing extensive dissolution and corrosion of mineral surfaces underneath biological patinas. Both Ca-sulphate (gypsum) and Ca-oxalate (weddelite) precipitates are clearly associated with the presence of fungal hyphae and bacterial activity particularly in the case of calcareous building stones; the Ca-oxalates present in the example examined are then the result of biomineralization processes and do not derive from past restoration treatments or from air pollution as suggested by many authors. In urban locations, lichenous cover may facilitate the deposition of particulate airborne pollutants on the stone surface. Biological patinas are by no means forming a protective layer on the biocolonized substrate; as is the case with sulphate or non-sulphate soiling patinas from urban air pollution, they act as localized sites of intense desegregation of the stone underneath. Their prompt (but careful) removal and a biocidal treatment of the infested sites in the building is then suggested to avoid permanent loss of detail, particularly harmful in the case of carved surfaces.

Air pollution has been widely recognized as the main factor responsible for decay of building stones in urban areas. High levels of SO₂ in the polluted atmosphere lead to the well-known sulphation mechanisms in a variety of lithological types used as building materials such as limestone, granite and sandstone. It is often assumed that inorganic salt precipitation such as sulphates and nitrates at the surface and/or within the stone fabric comes only as a result of dry and wet deposition processes of urban air pollutants on the stone substrate. Biological colonization by bacteria, algae, fungi and lichens is often regarded as playing a significant role in physical and chemical stone decay only in rural, unpolluted areas. The origin of oxalate patinas in urban monuments, for instance, is at the centre of a scientific debate between researchers who advocate a biologically mediated precipitation mechanism involving the reaction between metabolically produced oxalic acid by lichens and Ca-bearing building materials (DelMonte *et al.* 1987) and others who claim an anthropogenic origin for the oxalic acid either as

airborne pollutant (Saiz-Jimenez 1989) and/or as a residue from past conservation treatments applied to stone surfaces (Lazzarini & Salvadori 1989). Back-scattered electron microscopy has proved a useful tool in investigating rock biodeterioration (Wierzchos & Ascaso 1994).

This paper illustrates the use of scanning electron microscopy, both in secondary and back-scattered mode (SEM and BSEM, respectively) interfaced with energy-dispersive spectroscopy (EDS) in investigating decay features and microfabric aspects associated with extensive biological colonization of granitic and calcareous building stones from monuments and buildings across Europe (UK, Spain and Portugal). The main aims of the project were to ascertain whether biodeterioration plays a major role in urban stone decay as it does in the rural environment and to assess whether lithological parameters (mineralogy, porosity) might influence the type of biodeterioration active in monuments built in granite or limestone. The possible presence of common decay forms induced by biological attack on stones of different lithology

and in different environmental conditions was also a goal of this research.

Materials and experimental

Surface weathered samples with or without a macroscopically evident biological cover (i.e. lichen colonization; Fig.1) of calcareous and granitic building stones have been collected from the following monuments/buildings and locations.

1. Ely Cathedral, UK: micritic limestone substrate ('clunch') with lichenous cover. Urban environment, low pollution.
2. London Bridge, UK: granitic substrate. Urban environment, high pollution.
3. Monasterio S. Martin Pinario, Santiago de Compostela, Spain: granitic substrate. Urban environment, low pollution.
4. Iglesia Santiago de Vigo, Vigo, Spain: granitic substrate with reddish surficial patinas. Urban environment, medium pollution.

5. Igreja dos Carmo, Oporto, Portugal: granitic substrate with dark surficial patinas. Urban environment, medium pollution.
6. Torre dos Clerigos, Oporto, Portugal: granitic substrate with dark, thin surficial patinas. Urban environment, high pollution.
7. Dartmoor National Park, Merrivale, UK: granitic substrate with lichenous cover. Rural environment, very low pollution.

Rough specimens and thin sections spanning the patina–stone substrate contact were examined by electron microscopy. Thin sections were hand polished down to a thickness of 60–70 μm (thicker than the standard 30 μm used in routine petrographical analyses to account for differences in hardness between rock substrate and weathering patinas). After sputter coating with a thin carbon (thin sections) or gold (rough specimens) layer, samples were examined in a Jeol 820L SEM (with a Robinson back-scatter detector) interfaced with a Link 860 EDS system. Back-scattered electron imaging was used for thin-section work as it provides better image resolution when studying materials with a complex chemical/mineralogical composition such as the weathering patinas under investigation.

Electron microscopy results

Limestone substrate, urban environment

Examination of the outer surface of the weathered stone colonized by epilithic lichens shows a thick and dense network of lichen rhizines and thalluses, masking the limestone–patina interface (Fig. 2). Associated with algal filaments, amorphous and well crystallized Ca-rich precipitates can be found. Crystals have been identified by BSEM and EDS (C/O ratio and Mg content) and by X-ray diffraction (XRD) as calcite (Ca-carbonate) and weddellite (Ca-oxalate). Clusters of Ca-oxalate crystals with bipyramidal habit and tetragonal symmetry are particularly frequent on the outer portion of the lichenous patinas within the lichen medulla and in an extracellular position (Fig. 3). Ca-sulphate (gypsum) is also present as small crystalline aggregates but is not common. Spherical aluminosilicate particles typical of air pollution from fossil fuel combustion together with quartz and K-feldspar particles from soil dust are present but not abundant. The growth of calcium oxalate crystals does not seem to affect the substrate directly but the contact between the



Fig. 1. Lichen colonization of chalk building limestone. Ely Cathedral, UK.

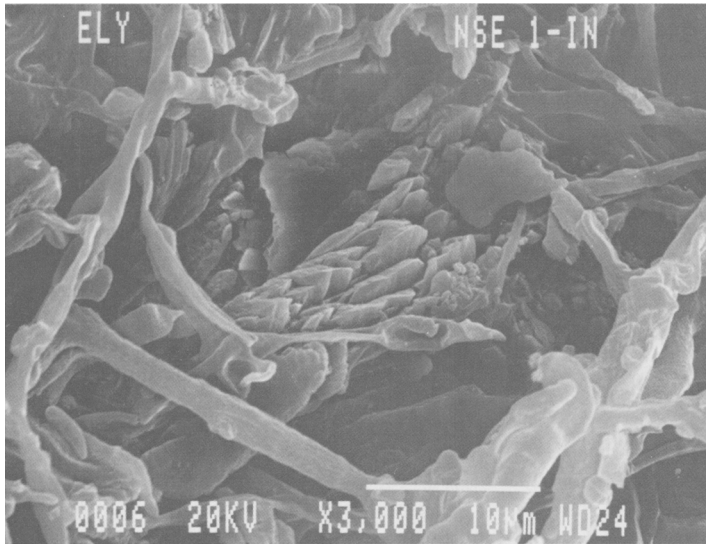


Fig. 2. SEM micrograph view of the exposed surface showing thick and dense network of lichen hyphae and rhizines on limestone. Ely Cathedral, UK.

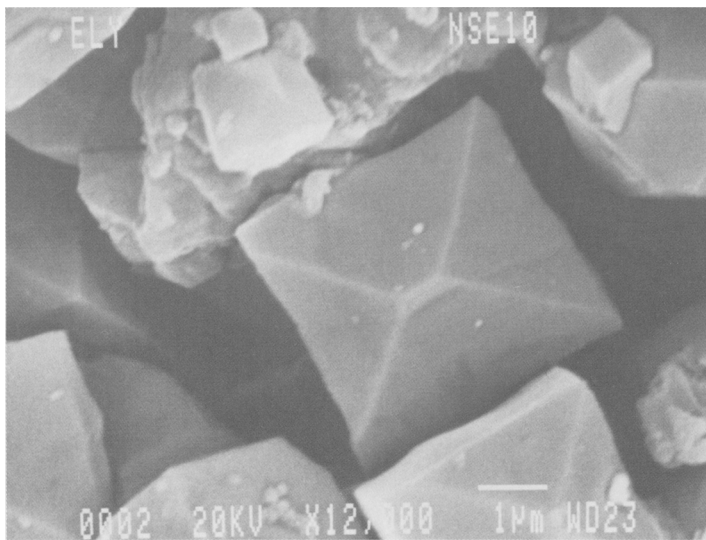


Fig. 3. SEM micrograph view of the exposed surface showing clusters of well formed authigenic Ca-oxalate crystals with bipyramidal habit within lichen biofilm on limestone. Ely Cathedral, UK.

patina and the underlying limestone shows episodes of dissolution and corrosion affecting in particular calcite grains (Fig. 4).

Granitic substrate, urban environment

Whether or not the presence of a biological cover is macroscopically evident on the samples

examined, bacterial activity, algal filaments and lichen elements are all clearly detected under SEM examination. All samples show, albeit at different degrees, extensive biocolonization. Lichen hyphae are often penetrating between mineral grains in the granitic substrate enlarging pre-existing weakness points such as cleavage planes in feldspars and micas and/or

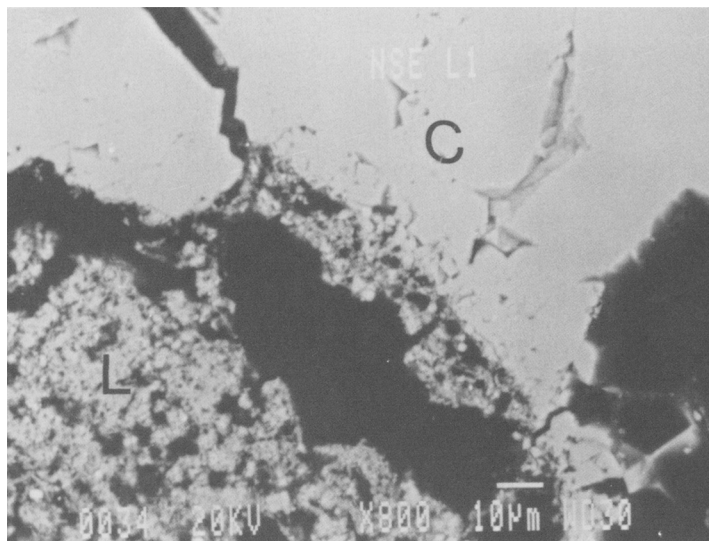


Fig. 4. BSEM micrograph of limestone–lichen patina interface. Calcite of the stone substrate (C) shows evidence of dissolution at the contact with biofilm (L). Ely Cathedral, UK.

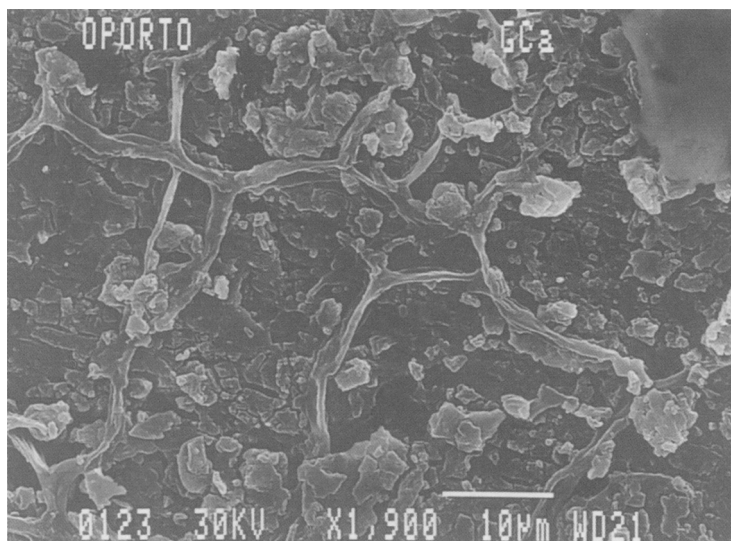


Fig. 5. SEM micrograph view of the exposed surface showing widespread colonization of K-feldspar by algal filaments leading to desegregation of granite superficial microfabric. Igresia dos Carmo, Oporto, Portugal.

intragranular cracks in quartz crystals, and resulting in intense desegregation of the stone fabric (Fig 5). Besides this decay action of a physical nature, episodes of dissolution/etching of mineral grains and precipitation of amorphous and crystalline compounds intimately associated with biological activity are evidence for biochemically derived decay. Etching pits and grooves and dissolution cavities are particu-

larly frequent on feldspars and muscovite micas (Fig. 6) but are common also in more chemically resistant quartz surfaces and on other less soluble accessory granite minerals such as apatite. Chemical weathering fronts do not proceed preferentially along pre-existing mineral weakness points and lines (such as fractures and cleavage planes) but often cut across mineral cleavage planes (Fig. 6). Dissolution

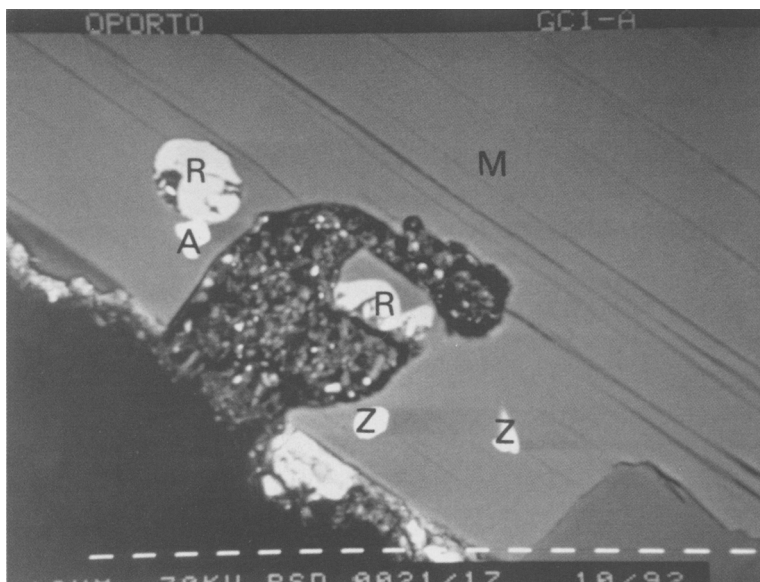


Fig. 6. BSEM micrograph of biological patina–granite interface. Weathering patina on granitic substrate shows selective dissolution of muscovite mica (M) relative to zircon (Z), allanite (A) and rutile (R) inclusions. Note how dissolution front cuts across cleavage planes in muscovite. Torre dos Clerigos, Oporto, Portugal.

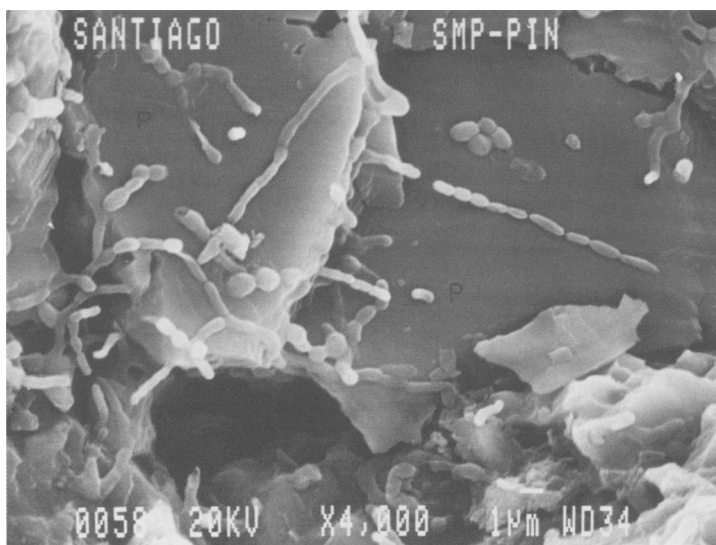


Fig. 7. SEM micrograph view of the exposed surface showing biocolonization by cyanobacteria of biotitic mineral surface leading to the precipitation of biofilm of polysaccharide nature. Monasterio de S. Pinario, Santiago de Compostela, Spain.

episodes on silicate minerals are often coupled with precipitation of amorphous deposits with an Si-rich or Al+Si-rich elemental composition.

Cyanobacterial activity is also responsible for the coating of the stone surface with amorphous

P-rich compounds, resembling polysaccharide gels (Fig. 7). The crystallization of gypsum with authigenic crystals displaying the typical monoclinic habit is often localized on algal filaments, suggesting a biologically mediated mechanism



Fig. 8. SEM micrograph view of the exposed surface showing authigenic gypsum crystals nucleating on lichen hyphae on etched albite surface. Monasterio de S. Pinario, Santiago de Compostela, Spain.

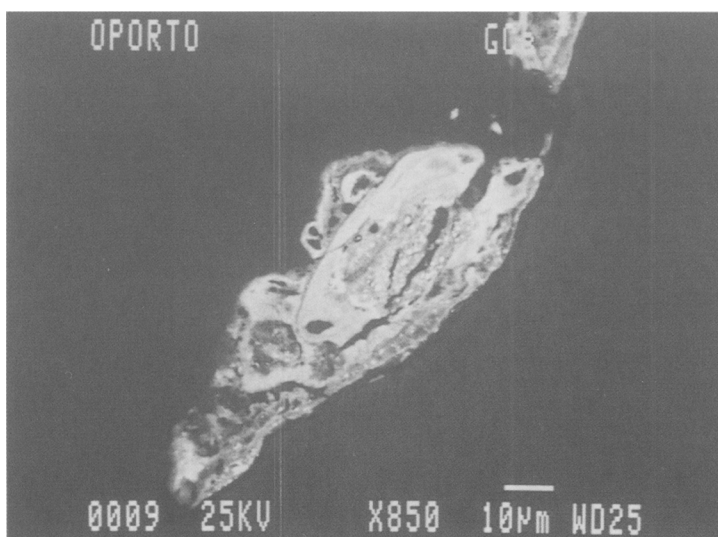


Fig. 9. BSEM micrograph of biological patina–granite interface. Dark, thin iron-rich (brighter areas) patinas on albite surface display faint lamination pattern and chemical attack of granitic substrate. Torre dos Clerigos, Oporto, Portugal.

of growth (Fig. 8). Dark patinas often displaying a reddish colour in field samples, a feature common to many sampling sites, reveal an Fe-rich composition under EDS analysis and a faintly laminated microstructure under BSEM (Fig. 9) resembling that of algal growth; underneath these thin dark patinas an area of intense decay of the granitic substrate is commonly present.

Granitic substrate, rural environment

As a reference for biological decay of granite in a rural, unpolluted location, samples of granitic rocks coated by foliose epilithic lichens in the Dartmoor National Park, UK, have been analysed. The contact between the stone substrate and the lichenous cover shows intense

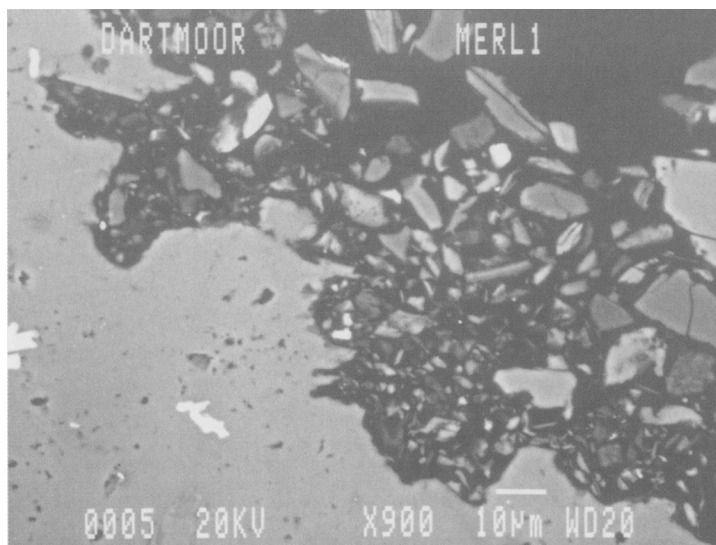


Fig. 10. BSEM micrograph of lichenous patina–granite interface. Note deep chemical corrosion of quartz with incorporation of quartz fragments in growing weathering patina. Dartmoor National Park, UK.

desegregation of the granite surface with incorporation of fragmented material clearly derived from the building stone underneath into the biological patina. In fact, the patina is largely made up of fragments of granitic minerals, i.e. micas, feldspars and quartz (Fig. 10). The depth of the weathered zone from the lichen–stone interface ranges from few micrometres up to 0.5 cm. The EDS chemical analysis of these patinas confirms an elemental composition consistent with that typical of granite apart from higher levels of Ca and Fe. Iron-oxidized outer rims are often visible on weathered granite minerals. Besides physical decay particularly active on biotite crystals where it causes the splitting of biotite flakes along cleavage planes, the electron microscopy investigation shows evidence for etching and chemical attack on quartz (Fig. 10), feldspar and biotite (Fig. 11) surfaces; etch pits are common and the examination of thin sections previously treated with concentrated H_2O_2 to remove the organic fraction, clearly shows the casts of dissolution trenches and pits on mineral surfaces (Fig. 12).

Discussion

Despite high levels of air pollution from both domestic/industrial and motor traffic activities, all the weathering patinas from urban sites display a medium to high degree of biocolonization. This is not unexpected given the

fact that cyanobacteria and some lichen species are known to be resistant to relatively high concentrations of air pollutants in the atmosphere and that bacterial activity may metabolize N and S compounds through redox reactions and may also utilize polycyclic aromatic hydrocarbons (PAH) as the sole carbon source (Saiz-Jimenez 1993). Moreover, electron microscopy investigation reveals extensive lichenous and bacterial activity on the stone surface in samples without macroscopic evidence for a biological cover. Penetration of lichen hyphae and rhizines deep within the substrate causing the destruction of the stone microfabric is common not only on ‘soft’ lithologies such as limestone but also on ‘hard’ stones such as granites (Del Monte *et al.* 1996). The mechanism of hyphae penetration is not only of a physical nature, i.e. through hyphae turgor pressures which have been shown to reach values exceeding the compressive strength of most rock substrates (Dornieden & Gorbushina 2000), but also of a chemical nature as the dissolution trenches associated with fungal hyphae on quartz mineral surfaces and the extensive evidence for biocorrosion occurring at the rock substrate–biological patina interface clearly show (Figs 4, 6, 10–12).

The chemical attack by lichens on rock substrates may be explained by the chelating action of the so-called ‘lichen substances’ (a group of weak organic acids such as oxalic acid) responsible for the formation of complexes with

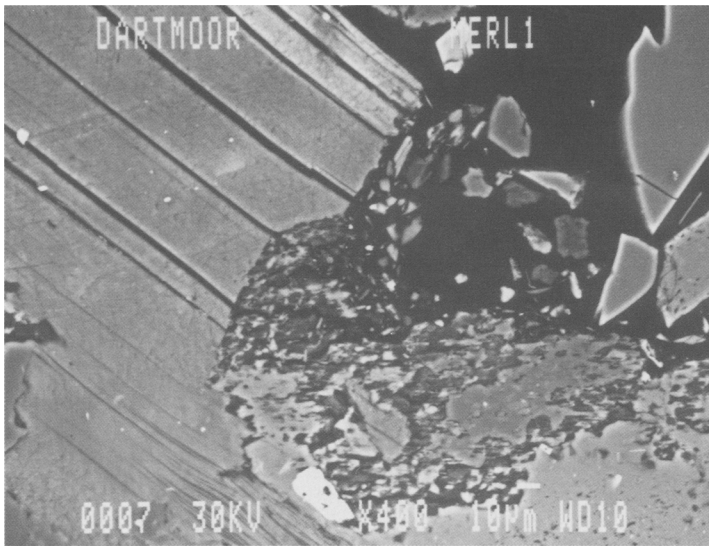


Fig. 11. BSE micrograph of lichenous patina–granite interface. Physical and chemical decay of biotitic mineral substrate underneath the biological cover leads to the desegregation of the stone fabric. Dartmoor National Park, UK.

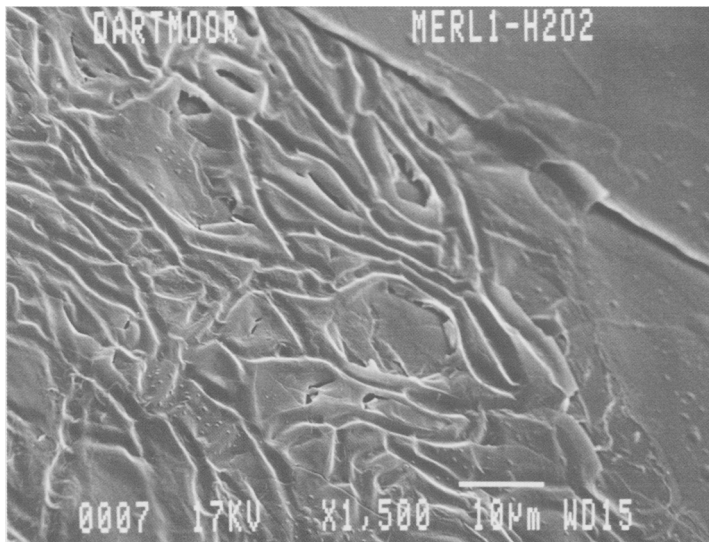


Fig. 12. SEM micrograph view of the surface of the granite after treatment with H₂O₂ to remove the biological patina. Dissolution trenches left on mica surface after removal of the organic cover are clearly visible. Dartmoor National Park, UK.

metallic cations extracted from the stone and used as nutrients (Eckhardt 1985; Robert & Berthelin 1986; Wierzechos & Ascaso 1994; DelMonte *et al.* 1996; Figueiredo & DaSilva 1996; Jones & Wakefield 2000). Bio-erosion may also be performed by cyanobacteria which have been shown to extract calcium ions from

calcareous stones and precipitate them as calcium carbonate in extracellular polymeric substances (EPS) of a mucopolysaccharide nature (Albertano *et al.* 2000). If these cations were indeed leached from the building stone and not from mineral fragments from soil dust and/or anthropogenic airborne particulate from

air pollution incorporated in the patinas as suggested by some authors (Casal-Porto *et al.* 1989), then one would expect the elemental composition of the patinas to be correlated with the mineralogical composition of the lithic substrate; the latter option seems to better explain the evidence presented in this study according to the following considerations.

Ca-rich precipitates

A Ca-rich substrate such as limestone provides Ca ions leading to the widespread precipitation of Ca-oxalate, Ca-carbonate and amorphous Ca-rich aggregates (Fig. 4). Of particular interest to stone conservators and scientists is the genesis of calcium oxalate films on works of art and monuments with the presence of Ca-oxalate being ascribed either to the degradation of past protective treatments applied to the stone (Lazzarini & Salvadori 1989), or to oxalic acid present as an air pollutant in urban areas (Saiz-Jimenez 1989), or to oxalic acid derived from metabolic activities of lichens and its reaction with Ca-bearing materials (DelMonte *et al.* 1987). The SEM evidence presented in this study showing extracellular precipitation of well formed, authigenic crystals of weddellite within lichen thalli growing on a limestone substrate supports the biological mechanism advocated by the latter authors; furthermore, the dissolution features present at the interface of lichen–Ca-bearing building stone suggests that the oxalate crystals grow at the expense of the limestone substrate. Despite the fact that biologically mediated Ca-oxalate has been found on rocks with low Ca content, the predominantly sodic plagioclasic composition of the granitic rocks investigated in this study does not seem to have favoured the precipitation of well-formed Ca-oxalate crystals which in fact have not been detected. Nevertheless, EDS analysis has shown a certain degree of Ca enrichment in amorphous deposits in the patinas; this Ca may derive from Ca-feldspars (plagioclases) in the granite (DelMonte *et al.* 1996), although, in this case, an external source such as leaching from adjacent mortar joints is more likely (Casal-Porto *et al.* 1989; Schiavon 1993).

Fe-rich patinas and other amorphous deposits

Weathering patinas growing on granitic stone in both urban and rural environments often show areas enriched in Fe relative to the rock substrate (Isherwood & Street 1976; Schiavon

1993). BSEM is particularly useful in showing how this iron enrichment is commonly associated with the presence in the substrate immediately underneath the weathered surficial layer of minerals containing Fe such as biotite. An external source for iron may be postulated for the red patinas from urban areas, i.e. from railings, road chippings or anthropogenic iron-rich airborne particulates (Nord & Ericsson 1993; Schiavon & Zhou 1996) but the ubiquitous presence of iron enrichment in lichenous layers coating outcrops of granite in the unpolluted location of Dartmoor National Park, far away from possible sources of air pollution, suggests leaching from the stone substrate by the chelation mechanism as the most likely cause of Fe enrichment. Leaching of Fe from biotite in granitic rocks by lichen-produced organic acids through the mechanism of chelation with the subsequent precipitation, for example, of Fe-oxalate crystals (humboldtite) has often been reported (Robert & Berthelin 1986; DelMonte *et al.* 1996; Figureido & DaSilva 1996).

Despite the absence of crystalline Fe-oxalate in the cases examined here, the following lines of evidence confirm a mainly biological origin for the weathered layers examined in this study, not only when an obvious lichen cover is present such as in the case of the Dartmoor patinas but also for the dark and thin Fe-rich patinas found in the Oporto and Santiago urban samples.

- (a) Back-scattered electron microscopy detailing the microfabric of the patinas shows the development of a laminated 'stromatolitic' texture (Fig. 9) reminiscent of desert varnish deposits for which a bacterially mediated mechanism of growth is widely assumed (Krumbein & Jens 1981; Nagy *et al.* 1991).
- (b) Secondary electron microscopy of rough surfaces of patinas reveals extensive biocolonization with cyanobacteria and lichen elements (hyphae, medulla, rhizines, fruiting bodies) adhering to the stone substrate (Figs 2, 5, 7).
- (c) Decay features such as desegregation of the stone microfabric underneath weathered surficial patinas in urban areas (Figs 5, 6) are very similar to the ones observed in the unpolluted reference location in Dartmoor (Figs 10, 11) where there is no contribution to decay from air pollution.
- (d) The ability of bacteria, fungi and lichens to concentrate and precipitate Fe and P (see below) compounds is

indeed well known (Robert & Berthelin 1986; Krumbein & Jens 1981; Nagy *et al.* 1991).

Moreover, iron-rich patinas investigated in this study are often associated with P-rich amorphous patinas developing preferentially where the localized presence of phosphate-rich accessory minerals such as apatite and allanite in the granitic substrate is associated with colonization by lichens and cyanobacteria. Extracellular polymeric substances (EPS) of mucopolysaccharide nature with a P-rich composition found at the surface of building stones have indeed been identified as products of lichens and of cyanobacteria metabolic activities (Gutierrez *et al.* 1995; Pinna & Salvadori 2000).

The Si-rich and Al-Si amorphous deposits are mainly associated with feldspar and quartz mineral surfaces which again show dissolution features and evidence of leaching (Figs 10, 12). Eckhardt (1985) has shown in leaching experiments using 0.1M oxalic acid, substantial extraction of K from micaceous silicate minerals. Microbially produced organic acids and complexing compounds are also known to increase the solubility of silicate and quartz minerals (Bennett & Siegel 1987). Taking into account the widespread occurrence of iron oxides in the investigated patinas, it is interesting to note that redox reactions involving iron have been reported to lead to increased solubility of quartz in laboratory experiments (Morris & Fletcher 1987), probably because of breakdown of an ultra-thin ferrous iron/silica complex formed on the quartz surface with accompanying liberation of silica. On the other hand, quartz solubility is also greatly increased under alkaline conditions (pH > 9) and studies have shown that conditions resulting from the production of alkaline compounds (ammonia and sodium carbonate) by micro-organisms and lichens can promote the solubilization of silica (Robert & Berthelin 1986; Leite-Magalhes & Sequeira-Braga 2000).

Biomineralization chemical processes also lead to the precipitation of crystalline inorganic compounds such as sulphates that are often regarded as products derived exclusively from the interaction of air pollutants (namely SO₂) with building materials (Leite-Magalhes & Sequeira-Braga 2000). SEM evidence showing authigenic gypsum crystals nucleating on algal filaments (Fig. 8) suggests that sulphate deposition may well be enhanced by biological mechanisms. Whether or not gypsum crystallization comes solely as a result of air pollution or is a biologically mediated

process, relative to a fresh building surface, biological patinas are sites of increased deposition of both gaseous (SO₂ and NO_x) and particulate (anthropogenic fly-ash and soil dust) pollutants due to their enhanced porosity (either intrinsic to the patinas open fabric or bioinduced on the stone mineral fabric) and moisture retention.

Conclusions

This SEM study confirms previous findings highlighting the important contribution of biologically mediated processes in the decay of building stones in urban as well as in rural areas. Electron microscopy reveals colonization patterns and decay features on building stone surfaces undetected under visual inspection of the building.

Biodeterioration contributes to decay in a twofold manner: (a) by a direct action either physical, i.e. penetration of hyphae within the stone substrate leading to desegregation of the stone into mineral fragments, or chemical by dissolution and precipitation of inorganic compounds within the stone fabric; (b) by an indirect action through the absorption of gaseous and particulate air pollutants (such as SO₂) leading to the sulphation of the stone and decay due to crystallization of sulphate and other salts.

The nature of authigenic mineral and amorphous deposits making up the weathered patinas and their chemical composition largely depends on the mineralogical nature of the stone substrate to which they adhere, inasmuch as the colonizing organisms (bacteria, fungi, algae, lichens) require mineral elements, i.e. Ca, Fe, Si, Al, P, as nutrients.

Biological patinas, in particular lichenous ones, do not play a protective role with respect to the building stone substrate as some authors suggest (Nimis *et al.* 1990; Ariño *et al.* 1995); on the contrary, their prompt removal followed by adequate biocidal protection is needed to avoid and stop important loss of surface material from buildings and monuments.

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